

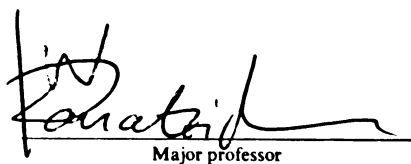
This is to certify that the

dissertation entitled
Exploratory Synthesis In The Quaternary System
Including Rare-Earth, Transition Metal, Gallium
And A Tetrelide Using Liquid Gallium As A Solvent.

presented by
Marina A. Zhuravleva

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry


Major professor

Date 12/10/02

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EXPLORATORY SYNTHESIS IN THE QUATERNARY SYSTEM INCLUDING
RARE-EARTH, TRANSITION METAL, GALLIUM AND A TETRELIDE USING
LIQUID GALLIUM AS A SOLVENT.

VOLUME I

By

Marina A. Zhuravleva

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

2002

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ABSTRACT

EXPLORATORY SYNTHESIS IN THE QUATERNARY SYSTEM INCLUDING RARE-EARTH, TRANSITION METAL, GALLIUM AND A TETRELIDE USING LIQUID GALLIUM AS A SOLVENT.

By

Marina A. Zhuravleva

A long established field of scientific excellence, the area of solid state chemistry continues to experience rapid growth and development. In past decades, the material exploration began to occupy the place of central importance in material science and solid state chemistry. Recently, we initiated investigations of new pathways for preparation of multinary intermetallic compounds and employed a synthetic technique that utilizes molten metals as solvents (fluxes). From these reactions we have reported a number of quaternary and ternary compounds obtained from molten Al solutions. Our continued investigation was further extended to probe the applicability of molten Ga to perform similar reaction chemistry. Consequently, we find molten Ga flux to be an excellent tool for exploration in the quaternary system that includes rare-earth element (RE), transition metal (M), gallium and a tetrelide (Tt = silicon or germanium).

In Chapter II, examples of non-reactive behavior of Ga as a solvent are presented. The synthesis, structure and magnetic properties of new intermetallic compounds

$\text{RE}_2\text{Ni}_{1-x}\text{Si}_x$

systems obtained

ternary compounds

included in

electronic and

The Part B reports

$\text{RE}_3\text{Ga}_2\text{Ge}_3$ and

obtained in the

with $M = \text{Fe}$.

and characterized

The system

especially interesting

structural arrangements

new families of

were discovered

compounds having

with the ratios

properties of the

and $\text{RE}_4\text{Ni}_3\text{Ga}_2$

Lastly, the

$\text{RE}_2\text{Ga}_2\text{Ge}_3$ and

together with other

$\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ and Tb_4FeGe_8 are discussed in Parts A and B, respectively. Further, the systems obtained via reactive behavior of molten Ga are considered. In Chapter III the ternary compounds of the general formulae $\text{RE}/\text{Ga}/\text{Ge}$ (where the transition metal is not included in the structure) are reported. The Part A gives the synthesis, structure, electronic and magnetic properties of new Zintl compounds $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ and $\text{Yb}_3\text{Ga}_4\text{Ge}_6$. The Part B reports on the structure and magnetic properties of new family of polygallides $\text{RE}_3\text{Ga}_9\text{Ge}$. A number of quaternary compounds of the $\text{RE}/\text{M}/\text{Ga}/\text{Tt}$ type have been also obtained in the reactions in molten Ga. In particular, Chapter IV is devoted to the systems with $\text{M} = \text{Fe}$, where novel cubic phases of the formula $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ were produced and characterized from the point of view of their structural and magnetic properties.

The systems with $\text{M} = \text{Ni}$ and Co , as presented in Chapters V and VI, are especially interesting, owing to their rich chemistry, magnetism and, most of all, unusual structural arrangements. Chapter V deals with the systems with $\text{RE} : \text{M} < 1$. Here, two new families of compounds $\text{RE}_{0.67}\text{M}_2\text{Ga}_{5+n-x}\text{Ge}_x$ of homologous series with $n = 0$ and 1 were discovered. A thorough investigation of structural and magnetic properties of these compounds has been carried out and the results are reported. In Chapter VI the reactions with the ratios $\text{RE} : \text{M} \geq 1$ are considered. The synthesis, structure and magnetic properties of three families of novel quaternary compounds REMGa_3Ge , $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ and $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ are presented.

Lastly, the preparation of the new compounds $\text{RE}_2\text{MGa}_9\text{Ge}_2$ ($\text{M} = \text{Ni}, \text{Co}$), $\text{RE}_2\text{Ga}_2\text{Ge}_5$ and $\text{La}_3\text{Ga}_2\text{Ge}$ using $\text{RE} : \text{M} \gg 1$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Co}$) is given in Chapter VII together with characterization of their structural and magnetic properties.

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LIST OF ABBREVIATIONS

RE	Rare-Earth
Tt	Tetrelide
CCD	Charge Coupled Device
EDS	Energy Dispersive Spectroscopy
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscope
SAED	Selected Area Electron Diffraction
XRD	X-Ray Diffraction
SQUID	Superconducting Quantum Interference Device
DMF	Dimethylformamide
BM	Bohr Magneton

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Chapter I

Part A

Exploratory Synthesis in quaternary systems including rare-earth metal, transition element and telluride.

1. Scientific importance of the exploratory solid state synthesis

A long established field of scientific excellence, the area of solid state chemistry continues to experience rapid growth and development¹. At its core, it is an interdisciplinary melding of chemistry, physics, engineering and materials science, as it focuses on the design, synthesis and structural characterization of new chemical compounds and investigation of their properties. In past decades, the material exploration began to occupy the place of central importance in material science and solid state chemistry. While the designed synthesis is well established in the area of organic

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chemistry and biochemistry, there is still a paucity of such examples when the field of solid state chemistry is considered. The factors contributing to the low predictability of the reaction products include limited diffusion and mobility of the reactants in the reaction media, incomplete understanding of the mechanisms of solid state reactions, of which the nucleation process is of primary importance, rudimentary perception on the relationship between the structure and properties and many more.

This inability to foresee the composition or the structure of the extended solids governs trends of the modern solid state chemistry, setting the objective of advancing and improving means and methods of the discovery and preparation of new materials. While the control over the reaction in solid state and rational design of the extended solids is beyond doubt still one of the goals of solid state chemistry, the classes of compounds with most intriguing and fascinating properties have so far been obtained as a result of the exploratory synthesis. Examples include high-temperature oxide² and molecular³ superconductors, intermetallic rare-earth transition metal borocarbides⁴, carbon fullerenes⁵ and nanotubes⁶, quadruple perovskites with giant dielectric response^{7,8,9} and many others. However serendipitous the discovery of some of these compounds and their properties may seem, the enormous amount of work performed in the direction of their synthetic exploration should not be overlooked. Bednorz and Muller², the discoverers of the high-temperature superconductivity in La-Ba-Cu-O perovskites, recognized the principal role of the new material exploration, saying: *"At the extreme forefront of research in superconductivity is the empirical search for new materials"*. In the same way, the discoverers of quaternary intermetallic borocarbides⁴, Cava and co-workers, note the lack of work that has been done in the complex chemical systems, explaining

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that “*for many desired properties, materials with optimal chemical complexity have undoubtedly not yet been found*”. This idea is widely supported among the researchers in the solid state community, as one of the leaders in this area concludes in his work¹⁰ “Solid State Chemistry” that “*the structural and electronic degrees of freedom offered by complex quaternary and quinary structures allows at least enhanced if not novel behavior and properties*”. Thus, the importance of the exploratory synthesis for the preparation of novel compounds can be hardly overestimated. As the combination of the possible coordination arrangements between the elements in the periodic table is truly innumerable, the discovery of new complex structures and novel phenomena will most certainly engage solid state chemists and material scientists for decades to come. This work, being just a minute contribution to this immense field of the exploratory research in the area of intermetallic compounds, presents part of the systematic investigation performed in the novel quaternary system rare-earth – transition metal – gallium – germanium (silicon).

2. Rationale

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2. Rationale of conducting systematic research in the RE/M/Ga/Tt system (RE = rare-earth, M = transition metal; Tt = silicon or germanium)

Similar to the famous motto “Divide and Conquer”, the main objective of the study given in this dissertation could be outlined as: “Discover and Optimize”. The first part, “discover”, incorporates all aspects of systematic study of the particular chemical system aimed in obtaining new structures (or even structure types) with potentially new properties. In the second part, optimization of the synthetic conditions is done to isolate the desired product in pure form and at the least cost. This also includes optimization of the useful properties of some type of compounds, such as obtaining various analogs of the given structure type, carrying out chemical modifications, doping, and so on. In the course of this work, we initiated research of the quaternary system RE–M–Ga–Ge(Si) by the means of exploratory synthesis. The choice of these particular elements comprising the system may be thought as originating in the related quaternary system rare-earth transition metal borocarbide^{11,12}. Compounds such as $\text{LaNi}_2\text{B}_2\text{C}^{13}$ and $\text{Y-M-B-C}^{14,15}$ and also thorium-based borocarbides¹⁶ were shown to exhibit high-temperature superconductivity and intriguing interplay of superconductivity and magnetism. Mimicking this system, we substituted boron for higher trielide and carbon for higher tetrelide, moving downward in the thirteenth and fourteenth group of the extended periodic table from boron to gallium and from carbon to silicon or germanium.

In any case, in our rationalization in the selection of the RE–M–Ga–Ge(Si) intermetallic system we, first of all, were governed by the fact that this quaternary system has not been previously investigated and presents a fundamental interest for solid state

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chemistry, material science and condensed matter physics. Secondly, the properties of the rare-earth intermetallics with a transition metal may combine localized magnetism of RE sub-lattice with itinerant magnetism of $3d$ sub-lattice^{17,18,19} thus making this class of compounds potentially promising as magnetic materials. Moreover, the rare-earth-containing intermetallics themselves are interesting with respect to their widespread magnetic and electrical properties^{20,21} such as long-range magnetic ordering at high temperatures^{22,23}, Kondo effect^{24,25}, magneto-resistive effects, magnetically mediated superconductivity^{26,27,28}, heavy-fermion behavior^{29,30} superconductivity^{31,32,33,34}, valence fluctuation phenomena^{35,36} *etc.* Thirdly, the presence of tetrelide could contribute to the refractory properties of these materials. The tetrelides of the intermetallic compounds, of those silicides in particular, are well-known for their high chemical stability, hardness, and high melting point^{37,38,39}. This property is potentially useful in the technological applications such as aero-turbine engines^{40,41} and high-temperature coating materials^{42,43} where high melting point and stability toward oxidation at elevated temperatures is desired^{44,45,46}. Lastly, the selected metals have quite different electronegativities (ranging from 1.1 to 2.0 on the Pauling electronegativity scale⁴⁷) and dissimilar valence electron configurations (p -, d - and f -block elements) that additionally tend to adopt different coordination polyhedra. The collective effect of mentioned properties promises to yield rich crystal chemistry, novel compounds of possibly new structure types and interesting physical properties.

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Chapter I

Part B.

Introduction to molten metal fluxes: a compromise between room temperature solution chemistry and high-temperature solid state synthesis.

1. Introduction

As the objectives of exploratory synthesis were outlined in the previous section, the next step is to determine the means by which these synthetic reactions can be carried out. To get an insight into the problems of this task, consider the melting points of the elements constituting the pursued chemical system RE–M–Ga–Tt (RE = rare earth, M = 3d transition metal, Tt = Si, Ge). The melting points of all the elements in the periodic table are outlined in Table 1.1. The inspection of the Table 1.1, and the elements of the 4th and 6th row in particular, shows that melting points of the rare-earth metals are typically over 800°C and up to 1656 °C.

Table I.A.1. *The long form of the periodic table emphasizing the melting points of the elements measured in degrees Celsius.*

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The transition metals of the first row usually melt at 1000° and higher, and the tetrel elements (Si and Ge) are also very high-melting species (> 1400°C). Because the diffusion and mobility of the species in the solid state is limited, very high temperatures are needed to liquidize (mobilize) the reactants. Ideally, for the reaction in solid state to take place, the temperature of the reaction should be taken above the melting point of the highest melting component in the reaction mixture. That is, in the case of RE–M–Ga–Tt, the reaction should be ideally carried out at 1500°C and higher.

The limitations of the reactions performed at such high temperatures are dual. First, due to the fact that the conventional “heat and beat” solid-state reaction is often carried out at very high temperatures (up to 2500 °C), the performance of the reaction is confined to the use of an arc-welder or inductive furnace that inevitably results in microcrystalline or even polycrystalline material. In order to obtain the crystalline product of desired quality or single crystals of large size, extended times (days and weeks) of annealing are often necessary. Even then, the size of the crystals may not be large enough for some property measurements that require the use of large single crystals. Second, owing to very high temperatures and long periods of time that are normally required for a conventional solid state reaction to take place, the system typically reaches thermodynamic equilibrium. As a result, the reaction products are often limited to the ones most thermodynamically stable; of those, simple binary and ternary compounds are most common. Additionally, the prolonged time and the performance of the reaction at high temperatures also contribute to high-energy consumption, which is undesirable especially for large-scale material production. At present, a number of ways has been devised to avoid the formation of unwanted known thermodynamically stable binary or

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ternary compounds and to promote crystal growth. The examples of these unconventional methods include use of precursors⁴⁸, soft chemistry (or “chimie douce”)⁴⁹, hydrothermal^{50,51,52}, solvothermal methods^{53,54,55}, molten salt fluxes^{56,57,58}, hydroxide fluxes^{59,60}, and molten metal⁶¹ (Al^{62,63,64}, Sn^{65,66,67}, Cu^{68,69}, Na^{70,71} etc.) fluxes. One of the methods, namely molten metal flux technique using liquid gallium, will be put in focus in this dissertation.

2. Crystal growth from molten metal solutions

One of the alternative routes to the classic methods of solid state synthesis – the molten metal flux technique – involves the use of metals or eutectic alloys as a solvent media. This approach has a number of advantages over the conventional solid state techniques such as enhanced diffusion, lower reaction temperatures and additional room for the kinetic control, to name a few. In general, the most practical metal solvents for solution growth are those which (1) are readily available and safely handled; (2) have relatively low melting point; (3) dissolve sufficient quantities of solute so it is possible to obtain crystals of usable size; (4) have low solution vapor pressures at growth temperatures to prevent unwanted loss of solvent and to eliminate the danger of high pressure; and (5) are easily separable from the solute crystals.

Molten metal solution growth in its simplest form is carried out by saturating a solution with desired solute(s) and growing crystals after spontaneous nucleation within the solution. This freely nucleated or self-seeding growth results in the production of

numerous crystals with natural growth habit*. The crystal size could hardly be controlled in this type of growth; the crystals grown from molten metal solutions, however, are normally large enough and adequate for determining crystal structures, for observing morphological characteristics, and for making physical property measurements.

The crystal growth from solutions of molten metals is conceptually similar to any other solution growth processes. It could be best illustrated using a temperature – composition equilibrium phase diagram, shown in Figure I.B.1, where the binary system consisting of metal solvent (A) and a solute substance (B) is considered.

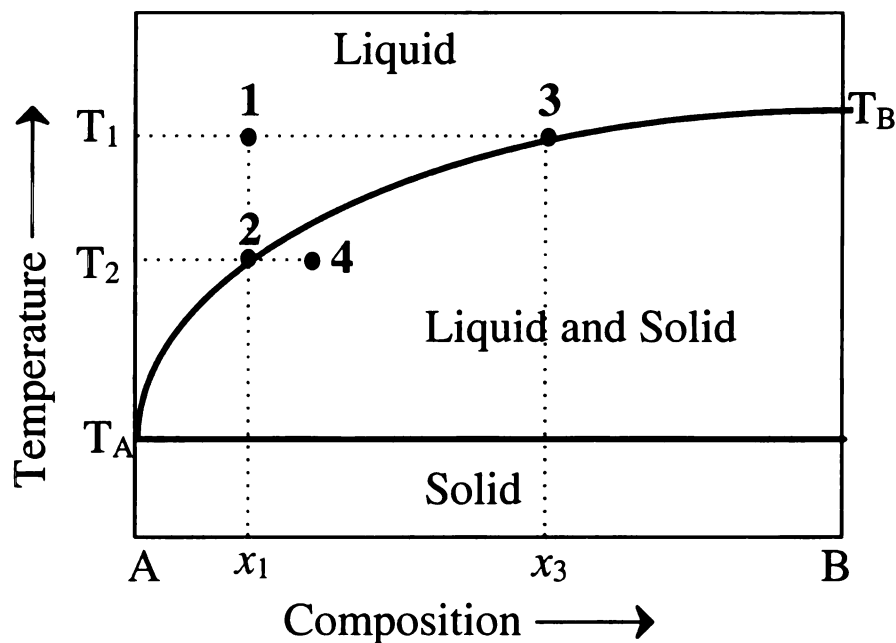


Figure I.B.1. Generalized temperature-composition equilibrium phase diagram for the binary A – B system.

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A solution of composition x_1 and temperature T_1 is represented by position **1** in the completely liquid region of the diagram. Since position **1** lies above the liquidus, solid – liquid equilibrium can be attained by movement to the liquidus line. This could be accomplished either (a) by a reduction in the temperature of the solution to T_2 which is represented by position **2**; (b) by a change in composition of the solution to correspond to x_3 at position **3** on the liquidus, or (c) by a combination of both processes. In any case, after the liquidus line is reached, further cooling under equilibrium conditions will result in precipitation of the material B. Similarly, if supersaturation occurs (position **4** below the liquidus line), the solution will adjust toward equilibrium (by moving at constant temperature to a point on the liquidus) giving rise to solute precipitation and crystal growth. The growth will continue until saturation is established for the lower temperature. Thus, the rate at which the crystal grows from solution depends on the saturation of the liquid phase at the solid-liquid interface.

When a crystal grows from solution, the concentration of solute in the liquid in contact with crystal is reduced, and a concentration gradient results, as shown in Figure I.B.2. Diffusion of the solute components down the concentration gradient supplies the additional material needed at the solid-liquid interface in order for the crystal to continue growing. This diffusion normally controls the rate of crystal growth. Additionally, if crystal growth is achieved by temperature reduction, the rate at which system is allowed to cool plays an important role. The variation of cooling rate may affect the crystal morphology or even define the crystalline structure.

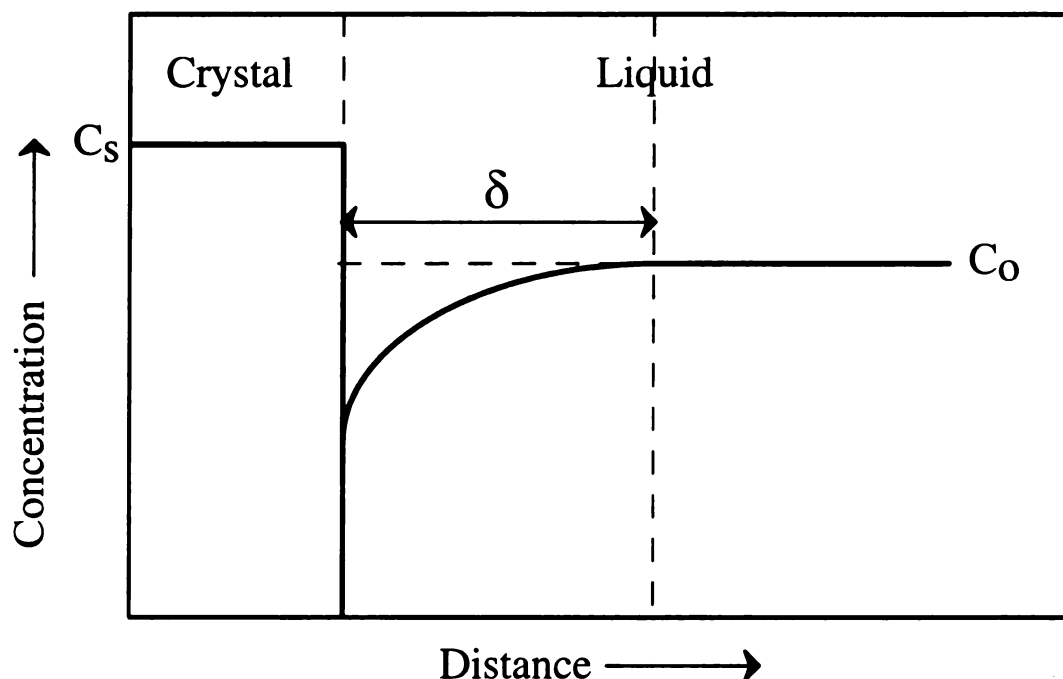


Figure I.B.2. Solute composition profile in solution just ahead of the growing interface of a solute crystal.

3. Molten gallium flux: historical background and recent developments

Among all metal fluxes, molten Ga is exceptionally attractive owing to a combination of remarkable physical properties of this element. First of all, metallic Ga is known for its extremely low melting point⁷² ($T_m = 29.78^\circ\text{C}$) and very high boiling point ($T_b = 2403^\circ\text{C}$), which makes the liquid range of this metal very large (above 2300°C). Secondly, gallium is nearly non-toxic and is characterized with very low vapor pressure even at elevated temperatures (only 1 mm of Hg at 1350°C). Another very important condition that has to be met is that the reagents should be soluble to some extent in the

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solvent melt. Fortunately, most metals have appreciable solubility in liquid Ga⁷³, and since we are particularly interested in the RE–M–Ga–Tt system, the solubility of the rare-earths, transition metals, silicon and germanium in Ga is crucial. Lastly, Ga has a rather low oxidation potential which makes the isolation of crystals from flux feasible.

The ability of the molten Ga to dissolve other metals and promote crystal growth was noticed long ago. Thus, since the 1950's, molten gallium metal along with many other metals (Sn, Bi, Pb, Al, In etc.) was used for crystal growth of simple semiconducting materials such as Si, Ge, GaAs, GaN, GaP, ZnTe, etc⁷⁴. However, since then, the reports on the use of molten Ga as flux medium for the synthesis of intermetallic compounds are rather sporadic. Thus, after 1992, only few scientific publications have been released that contain an account of molten Ga being used as a solvent. These rare examples include synthesis and crystal growth of ternary gallides RE_{2-x}Pt₄Ga_{8+y} (RE = La, Ce, Pr, Nd, Sm, Gd, Er, Yb, Y)⁷⁵ performed in liquid Ga; the large single crystals grown by this technique were then used in elaborate magnetic and transport studies. Molten Ga flux was further found to be useful for growing single crystals of gallium nitride GaN⁷⁶ or even multinary nitrides such as Ln₃T₂N₆⁷⁷ (Ln = La, Ce; T = Nb, Ta). It has been used again in recent times for the synthesis of semiconducting intermetallic compounds FeGa₃, RuGa₃⁷⁸ and Zn-, Co-, In-substituted variants of FeGa₃⁷⁹. Molten Ga solution growth was lately applied for the synthesis of clathrates of type I, as was reported for Ba₈Ga₁₆Ge₃₀⁸⁰ as well as for clathrate networks such as Eu₄Ga₈Ge₁₆⁸¹. Additionally, the use of Ga flux in the combination with another element like zinc is also known. This mixed-metal flux was successfully employed in synthesis of EuZn₂Si₂ and EuZn₂Ge₂⁸² compounds. More systematic reports on the use of metal fluxes for synthesis

of complex intermetallides come from a research group in Germany lead by Wolfgang Jeitschko. Of those, a few compounds obtained from molten Ga such as RERu_2Ga_8 ($\text{RE} = \text{La} - \text{Nd}$)⁸³ and LnOsGa_4 ($\text{Ln} = \text{La} - \text{Nd}$)⁸⁴ have been reported.

Despite the fact that a number of molten metals have been employed as solvents (mostly for crystal growth) for over the last five decades, no reports relevant to the use of these metals in the exploratory synthesis of complex intermetallic compounds have been available in the scientific literature up to this time. The lack of systematic research in complex intermetallic systems employing molten metals as solvents poses an interesting and challenging task of investigating the applicability of molten metal solvents for the exploratory synthesis of multinary intermetallic compounds. As it was discussed above, molten Ga in particular is very interesting, as it showed excellent metal solvent characteristics and suitability as a flux medium. These preliminary considerations motivated us to undertake the exploratory research in the RE-M-Ga-Ge(Si) quaternary intermetallic system employing molten Ga as a solvent.

4. Synthetic approach and experimental techniques

For the synthesis in molten Ga, the high-purity (99.99% and higher) reagents – rare earths, transition metal, telluride – are usually taken in elemental form and combined together with an approximately 5-fold excess of Ga. The reagents are handled in a Vacuum Atmospheres Dri-Lab glovebox due to air-sensitivity of rare-earths and powdered transition metals. Unlike conventional solid state synthesis, the metals could be taken in large chunks, and not necessarily in powdered form. No grinding or pressing of

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pellets is required. As-combined elements are then loaded into alumina crucibles of 10 mm in diameter. The crucible is next placed in the fused silica tubes (13 mm in diameter) and the system is evacuated up to $1 \cdot 10^{-4}$ Torr and then sealed. The use of alumina crucibles is required due to high reactivity of rare earth elements and Ga at high temperature. Without protective crucibles, these elements react with silica ampoules and cause contamination, cracking and loss of protective atmosphere and severe oxidation.

The reaction containers sealed in the silica ampoules are consequently subjected to heat treatment. Figure I.B.3 diagrammatically shows the stages involved in preparing crystals by varying the temperature.

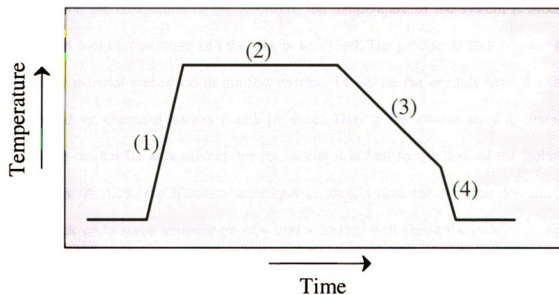


Figure I.B.3. Temperature profile used in preparing solution-grown crystals: (1) heating; (2) isothermal; (3) slow cooling; and (4) fast cooling steps.

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The simplest thermal cycle consists of (1) a heating time during which the system is brought up to desired temperature; (2) a stabilization period at prescribed constant temperature (or isothermal step) to ensure that enough of the solute components have dissolved in the solvent or, in case the crystal growth occurs at this stage, to allow crystals to develop; (3) a slow cooling period to the temperature of flux solidification during which the solution becomes continually supersaturated resulting in crystal growth; (4) the final stage of fast cooling to the room temperature. Since the precise stage at which the crystal growth occurs is not known *a priori*, it is worthwhile to conduct the experiment under the conditions that are characterized with both extended isothermal and slow cooling steps.

Upon the completion of the reactions, the temperature of the system is brought back to the room temperature and the flux is solidified. The product is then represents a crystalline material embedded in the flux matrix. To isolate the crystals from the flux, mechanical or chemical means could be used. During the course of this research employing molten Ga as a solvent, we found that it is best to use both of the isolation approaches. At first, the filtration technique is used, where the reaction container is heated back up to some temperature of $\sim 200 - 250^{\circ}\text{C}$, well above the melting point of Ga. The reactions are then taken out for hot-filtration using a specially designed silica filter with coarse frit, see Figure I.B.4.A.

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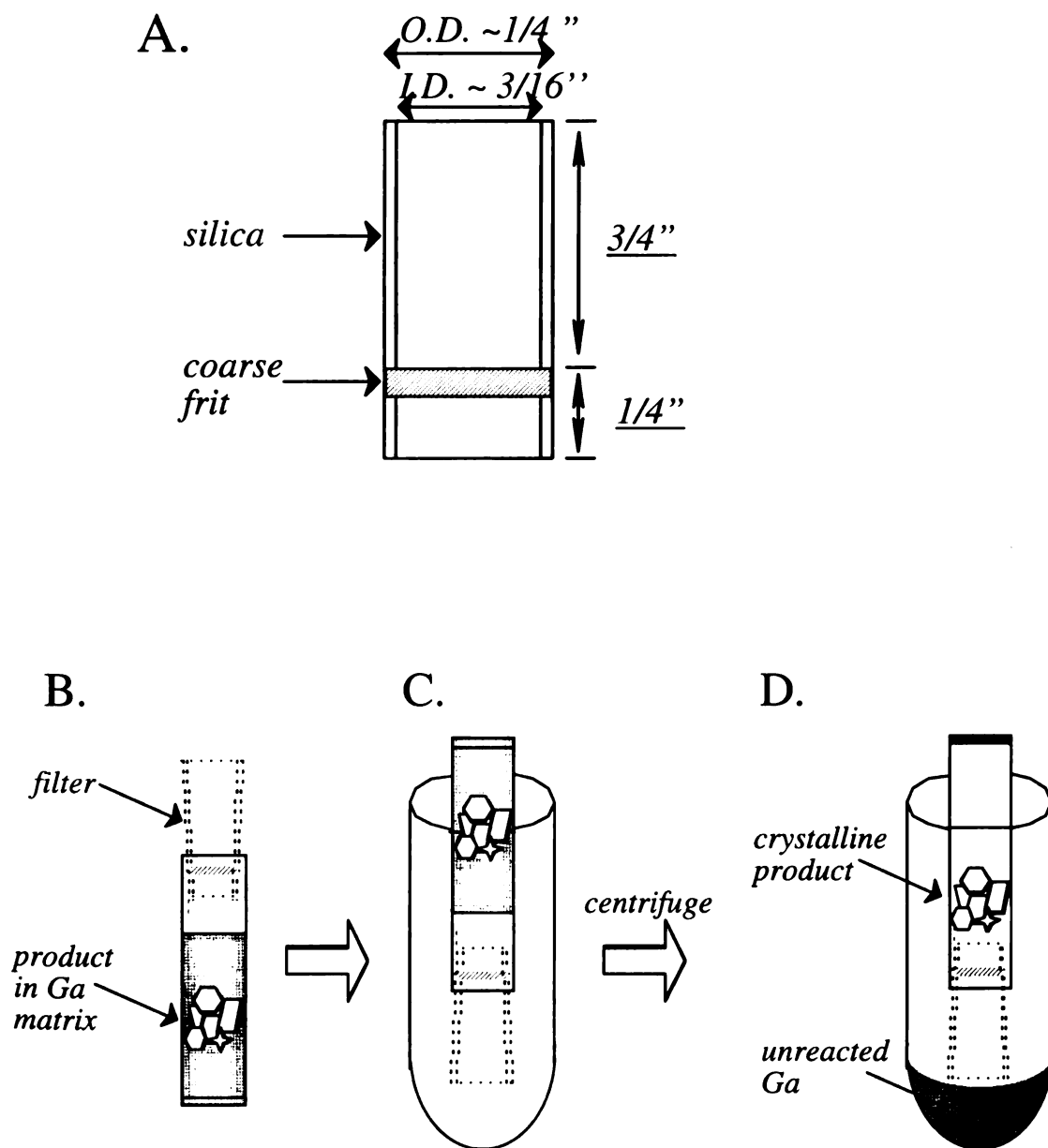


Figure I.B.4. (A) Specially designed filter for high-temperature filtration; (B)-(C) Assembly before filtration; (D) Crystalline product and excess Ga after filtration.

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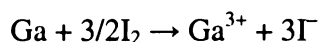
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For high-temperature filtration (HTF), the filter is first inserted in the crucible, see Figure I.B.4.B. Then, the whole assembly is inverted and placed into centrifuge cup, as shown in Figure I.B.4.C. Second, the system is positioned in the centrifuge (IEC Clinical Model) and subsequently centrifuged. The high setting of the centrifuge speed is used, producing rotation above 3000 rpm; the centripetal forces push out liquid Ga through the filter into collector leaving the crystalline product inside, see Figure I.B.4.D.

With mechanical spin-filtration, normally ~ 90% of the unused Ga flux is removed. However, the peculiar characteristic of molten Ga is its ability to wet the surface of grown crystals. Hence, further chemical etching is necessary in order to reduce the possibility of the interference with physical measurements* and avoid misreading of the elemental analysis results†. In the second part of isolation, the product is treated with the 3-6 molar solution of iodine in demethylformamide (DMF) over 12 – 48 hours at room temperature or at elevated temperatures (up to 60°C). In this process, Ga is oxidized to Ga³⁺ by the reaction:



with the standard reduction potentials at 298 K of half-reactions given below:

$$(a) E^0 (\text{Ga}^{3+}/\text{Ga}) = -0.560\text{V}$$

$$(b) E^0 (\text{I}_2/2\text{I}^-) = +0.535\text{V}$$

The difference 3/2 (b) – (a) gives + 1.363 V, meaning that the equilibrium constant $K > 1$ strongly favors the formation of products. The GaI₃, pale yellow material, is soluble and could be washed away with few aliquots of hot water. The remaining crystalline product is subsequently rinsed with DMF and acetone, sonicated in water to remove the surface

* Elemental Ga is superconductive at low temperatures with $T_c = 6.2\text{ K}$

† The elemental analysis, such as Electron Dispersive Spectroscopy (EDS) are often surface techniques

adhered impurities and, finally, dried with acetone and ether. The resultant crystalline product is then ready for structure determination and physico-chemical characterization experiments.

As one could see, the chemical means of flux dissolution may perhaps be used as the only isolation technique. However, the drawback of using chemical etching alone is that the crystals of the material under investigation may not be stable in the oxidative environment and get dissolved before ever getting discovered by the scientist. Even if this is not the case, and the reaction product is stable and possibly will endure the chemical etching, prolonged exposure to the oxidative medium is undesirable, as surface etching or alteration may eventually occur. Therefore, for the exploratory synthesis in molten Ga, the final isolation step involving both mechanical spin-filtration and chemical etching is recommended.

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5. Conclusion

A new quaternary system RE–M–Ga–Tt with rare-earth, transition metal, gallium and tetrelide (germanium or silicon) was selected for investigation in this dissertation. This novel intermetallic system presents both fundamental and practical significance, as was outlined in the Part A of Chapter I. The exploratory synthesis approach was chosen to carry out a systematic investigation. In this work we principally focus on the unconventional solid state technique that uses molten gallium as a solvent. The exceptionality of Ga metal to serve as a flux media is discussed in the Part B of Chapter I together with some theoretical aspects and practical techniques of molten metal solution growth.

It is appropriate now to move ahead and illustrate some of the results of the exploratory research performed in the quaternary intermetallic system RE–M–Ga–Tt using molten Ga growth as a synthetic technique. Three major systems will be considered in this dissertation: two ternary systems RE–M–Tt, RE–Ga–Tt and a quaternary system RE–M–Ga–Tt. For the first ternary systems, Ga is acting as a non-reactive solvent only, where rare-earth transition metal tetrelides are produced. Next, the ternary rare-earth germanides-gallides obtained via reactive action of molten Ga solvent are considered. For the quaternary RE–M–Ga–Tt, only three systems with $M = \text{Fe, Ni and Co}$ will be discussed as they are the ones exhibiting the most interesting and rich crystal chemistry and unusual structural peculiarities.

6. References

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Chapter II

Part A

Molten Ga as a Non-Reactive Solvent: Synthesis and Characterization of New Ternary Silicides $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ (RE = Sm, Gd and Tb).

1. Introduction

As in any solvent system acting as a reaction medium, the solvent may or may not be incorporated into the final product. This is also what happens with Ga. In case of solvent incorporation, the solvent is said to be reactive. Interestingly, in the course of the research presented in this dissertation, we find quite extreme examples of molten Ga serving both as a reactive solvent producing polygallides^{1,2}, and as a non-reactive solvent yielding Ga-free products³. It is yet difficult to predict the outcome of the reaction and the behavior of the molten gallium metal in it, although subtle

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indications could be found in observing the series of the reactions performed with different temperature and duration profiles or with various concentrations of the reactants in molten Ga. Thus, in the RE–Ni–Ga–Si system the reaction predominantly yields ternary rare-earth transition metal silicides at shorter reaction times, whilst for the longer reaction times the amount of the quaternary rare-earth transition metal gallide silicides becomes appreciable. However, in similar reactions with germanium RE–M–Ga–Ge, a completely different tendency is followed.

Because silicides are technologically⁴ essential for their high oxidation stability, hardness^{5,6} and refractory properties^{7,8,9}, it is important to study and further develop preparative techniques of these materials. Some of the silicides are also known to have interesting electronic and magnetic properties, such as superconductivity^{10,11,12,13} and coexistence of magnetism and superconductivity¹⁴. One of the challenges in synthesis of silicides and germanides is that high reaction temperatures are usually needed due to very high melting points of the reactants. At such high temperatures it is rather difficult to prepare complex silicide compounds, as the reaction outcome is normally drawn to its thermodynamic minimum that often includes only the most stable simple binary compounds.

Fortunately, the synthetic approach adopted in this dissertation allows lower reaction temperatures despite the high refractory properties of the starting materials. The lower reaction temperatures are achieved due to enhanced diffusion which is caused by partial solubility of the reactants in molten Ga. Preliminary results on the use of molten Ga as a non-reactive solvent for synthesis of silicides and germanides are also promising. First, it was shown that crystals of the elemental Si and Ge

themselves could be easily grown from the molten Ga solutions¹⁵. Second, our own investigations of the crystal growth of rare-earth transition metal silicides from molten metal solutions led to the synthesis of the family RENiSi_3 ³ (RE = Sm, Y). Here we report the synthesis, crystal structure and magnetic properties of rare-earth nickel silicides of the general formula $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$, (RE = Sm, Gd and Tb) obtained from molten Ga solutions.

2. Experimental

Synthesis

Elemental RE, Ni and Si of typical purity 99.9% and higher (CERAC Inc.) were combined together with a large excess of Ga in the ratio Sm : Ni : Si : Ga as 1 : 2 : 2 : 30 and placed in the alumina crucible. The metals were handled in a dry box under nitrogen atmosphere. The crucible was then sealed in a quartz ampoule under high vacuum ($\sim 1 \cdot 10^{-4}$ Torr). The reaction conditions at which first representatives of $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ phase were obtained, included very short heat treatment: (a) the reaction mixture was heated to 1000°C in 15 hours, held at 1000°C for 5 hours, then slowly cooled to 600°C in 16 hours, followed by fast cooling to 50°C in 5 hours. The heating profiles with subsequently increasing time of isothermal step were later used. In these reactions metal mixtures were (b) heated to 1000°C in 15 hours, cooled down to 850°C in 5 hours and held at 850°C for 3 to 10 days, then subsequently cooled to 200°C in 36 hours (at the rate 18°/h) and, finally, to 50°C in 2 hours.

The crystalline product obtained in these reactions was isolated from unreacted Ga flux using 1 – 2 molar solution of iodine in dimethylformamide over six hours at 60°C followed by isolation at room temperature over ~18 hours. The product was then washed with water and dried with acetone and ether. The resulting crystals of $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ with characteristic rod-like habit and metallic luster were recovered from the reaction product in high yield (~90%). Additionally, a binary $\text{Ni}_3(\text{Ga},\text{Si})_2$ phase¹⁶ was detected in minor quantities as by-products. An image of a typical crystal of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ grown under Ga flux conditions, taken on a scanning electron microscope (SEM) JEOL JSM-35C, is shown in Figure II.A.1.

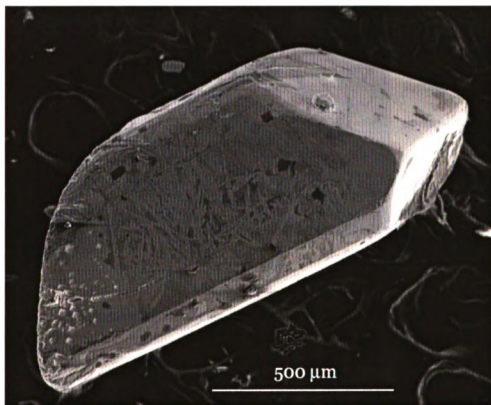


Figure II.A.1. SEM image of a typical Ga flux-grown single crystal of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$.

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The higher magnification SEM image, see Figure II.A.2, exhibits round to elliptical holes on average 5 – 10 μm in size which formed on the surface of the crystal. The observed surface imperfections are the indicative of severe chemical etching that was most likely caused by the I_2 treatment. The SEM image shown in Figure II.A.2 is a convincing example of the true importance of the combined chemical and mechanical isolation. Chemical isolation alone led to partial surface alteration of the isolated crystals.

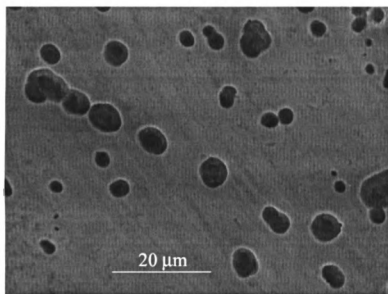


Figure II.A.2.

SEM image of a typical surface of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ crystal.

Scanning Electron Microscopy and Elemental Analysis

The elemental composition was studied by Energy Dispersive Spectroscopy (EDS) semi-quantitative analysis on the SEM equipped with the NORAN Inc. EDS detector. The routine data acquisition was done at acceleration voltage 20 kV and

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collection time 30 seconds. An extensive averaging of the results obtained on the different crystals was carried out in order to attain accurate values of the atomic ratios.

For the Sm analog of $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$, an averaged composition (normalized to the amount of Sm) was determined to be “ $\text{Sm}_2\text{Ni}_{2.79}\text{Si}_{5.27}$ ”. Although a small amount of Ga was occasionally observed in the EDS results (up to 5 at. %), it was attributed to surface impurities from incompletely removed flux. Analysis taken on freshly exposed cross-section of the crystal showed an absence of Ga. The results of elemental analysis are in agreement with single crystal X-ray refinement given by the formula $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ($x \sim 0.5$). However, for the Tb analog, the situation seems to be different, as the elemental analysis taken on both surface and the cross-section showed a substantial amount of Ga present. The composition of the Tb analog could be then formulated as “ $\text{Tb}_2\text{Ni}_{2.77}\text{Si}_{4.63}\text{Ga}_{0.64}$ ”. Nonetheless, if we were to rewrite the formula with a combined Ga and Si content, one would obtain “ $\text{Tb}_2\text{Ni}_{2.77}(\text{Si,Ga})_{5.24}$ ”, which is very close to the result found for the Sm analog. Thus, it is plausible to assume that if there is any substitution in $\text{Tb}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ with Ga, it will most probably occur on the Si site.

X-Ray Powder Diffraction

In order to probe the purity and crystallinity of the resulting product, an X-ray diffraction experiment was performed using pulverized samples*. The X-ray powder

* The reaction product was typically dry-ground with mortar and pestle to obtain polycrystalline material.

diffraction (XRD) patterns of products were taken at room temperature on a CPS 120 INEL X-ray diffractometer (Cu $K\alpha$ radiation) equipped with position-sensitive detector. Experimental XRD patterns were then compared to that calculated from single crystal data using CERIUS² software package¹⁷.

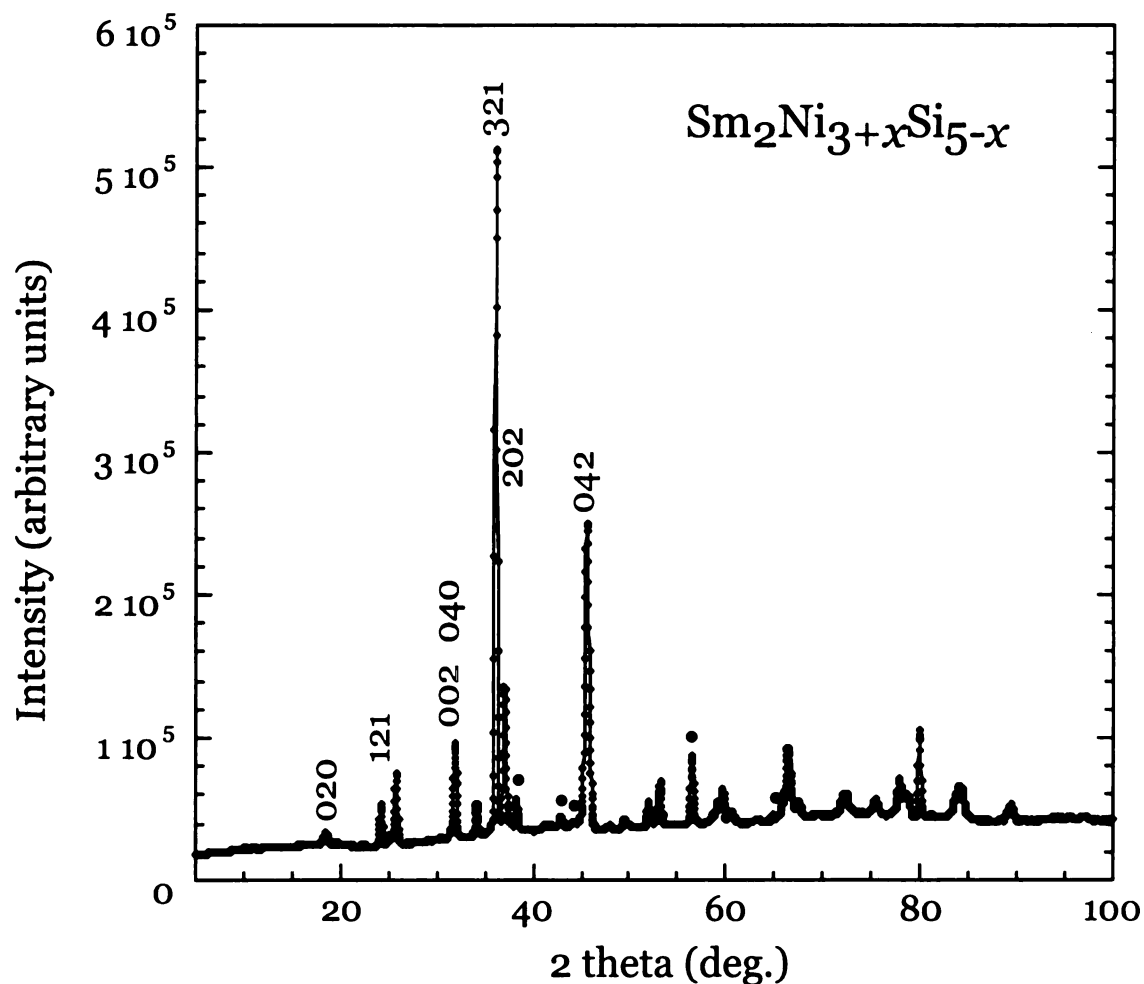


Figure II.A.3. X-ray diffraction powder pattern of the product with initial composition “ $\text{SmNi}_2\text{Si}_2\text{Ga}_{30}$ ”. Bragg peaks indicated by dots belong to impurities. The remaining peaks belong to the target phase $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$. The indexing is shown for the most intense reflections.

The example powder pattern collected on the product obtained from the reaction with the initial ratio Sm : Ni : Si : Ga 1 : 2 : 2 : 30 using heating regime (a) is shown in Figure II.A.3. The position and the intensity of the Bragg reflections corresponded for most part to the target phase $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$. All strong intensity peaks were indexed in the orthorhombic space group *Ibam* with cell and positional parameters of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$. The minor impurity peaks (marked by dots) have weak intensities. Thus, the purity of the resulting product is high, up to 90%, and was confirmed with both elemental analysis and powder X-ray diffraction.

Single Crystal X-Ray Diffraction

The intensity data was collected on a single crystal of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ at room temperature with a Siemens Platform SMART¹⁸ CCD X-ray diffractometer. The crystal of suitable size $0.04 \times 0.06 \times 0.12 \text{ mm}^3$ was mounted on glass fiber. A hemisphere of reciprocal data (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$, the X-ray radiation was generated at 50kV and 40mA) was acquired up to 56° in 2θ . The individual frames were measured using the ω -steps of 0.30° and exposure time of 30 s per frame. The data reduction and integration was performed with the SAINTPLUS¹⁹ software package. An empirical correction for absorption based on symmetry equivalent reflections was applied with the SADABS²⁰ program.

The initial unit cell reduction readily gave body-centered orthorhombic lattice with parameters $a = 9.6396(12) \text{ \AA}$, $b = 11.3219(14) \text{ \AA}$, $c = 5.6967(7) \text{ \AA}$. Following space group determination based on the systematic absences led to two possible space

groups *Iba2* and *Ibam*, of which the centrosymmetric one was found to be correct during the structure refinement. The structure solution and refinement were done by direct methods with the SHELXTL²¹ software package. All atomic positions were refined anisotropically. The setting of the cell was standardized with the STRUCTURE TIDY program²². The information relevant to the data collection and structure refinement is given in the Table II.A.1. The final atomic positions and the equivalent thermal displacement parameters are listed in Table II.A.2. The interatomic distances up to 3.5 Å and selected bond angles are presented in Table II.A.3 and Table II.A.4, respectively. The anisotropic displacement parameters for all atoms are given in Table II.A.5.

Table.II.A.1. Crystal data and structure refinement for Sm₂Ni_{3+x}Si_{5-x}.

Empirical formula	Sm ₂ Ni _{3+x} Si _{5-x}
<i>x</i>	0.47(1)
Formula weight	631.98
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Ibam</i> (#72)
Unit cell dimensions (Å)	<i>a</i> = 9.6396(12) <i>b</i> = 11.3219(14) <i>c</i> = 5.6967(7)
Volume (Å ³)	621.73(13)
<i>Z</i>	4
Density (calculated) (g/cm ³)	6.752
Absorption coefficient (mm ⁻¹)	29.662
<i>F</i> (000)	1139
Crystal size (mm ³)	0.04 × 0.06 × 0.12
Theta range for data collection	2.78 to 27.88°
Index ranges	-12 ≤ <i>h</i> ≤ 10, -14 ≤ <i>k</i> ≤ 9, -7 ≤ <i>l</i> ≤ 7
Reflections collected	1867
Independent reflections	411 [<i>R</i> _{int} = 0.0306]
Completeness to θ = 27.88°	99.8 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	411 / 0 / 33
Goodness-of-fit on <i>F</i> ²	1.001
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] [*]	<i>R</i> ₁ = 0.0206, <i>wR</i> ₂ = 0.0492
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0252, <i>wR</i> ₂ = 0.0510
Extinction coefficient	0.00080(10)
Largest diff. peak and hole (e·Å ⁻³)	1.149 and -0.928

^{*} $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table II.A.2. Atomic coordinates, equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and occupancies for $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$.

Atomic Positoin	Wykoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*	Occupnacy
Sm	8 <i>j</i>	0.2626(1)	0.3692(1)	0.0000	4(1)	1.0
Ni(1)	4 <i>b</i>	0.5000	0.0000	0.2500	6(1)	1.0
Ni(2)	8 <i>j</i>	0.1124(1)	0.1323(1)	0.0000	6(1)	1.0
Si(1)	4 <i>a</i>	0.0000	0.0000	0.2500	3(1)	1.0
Si(2)	8 <i>j</i>	0.3491(2)	0.1069(2)	0.0000	4(1)	1.0
	8 <i>g</i>	0.0000	0.2654(1)	0.2500	4(1)	0.763(7) Si
Si/Ni	8 <i>g</i>	0.0000	0.2654(1)	0.2500	4(1)	0.237(7) Ni

* U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table II.A.3. Bond lengths [$\text{\AA}$] for $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$.

Bond	Distance	Mult.	Bond	Distance	Mult.
Sm-Ni(1)	3.2599(4)	×2	Sm-Si/Ni	3.1331(7)	
Sm-Ni(2)	3.0481(9)		Ni(1)-Si(2)	2.3685(14)	×4
Sm-Ni(2)	3.2128(10)		Ni(1)-Si/Ni	2.6562(15)	×2
Sm-Ni(2)	3.3726(11)		Ni(1)-Ni(1)	2.8484(4)	×2
Sm-Ni(2)	3.0927(5)	×2	Ni(2)-Si(2)	2.299(2)	
Sm-Si(1)	3.0755(4)	×2	Ni(2)-Si(1)	2.3336(7)	×2
Sm-Si(2)	3.0568(7)	×2	Ni(2)-Si/Ni	2.3398(12)	×2
Sm-Si(2)	2.898(2)		Si(1)-Si(1)	2.8484(4)	×2
Sm-Si(2)	3.0849(19)		Si(2)-Si/Ni	2.4973(17)	×2
Sm-Si/Ni	3.0966(8)	×3	Si/Ni-Si/Ni	2.8483(4)	×2

Table II.A.4

Bond

Si(2)-Ni(1)-

Si(2)-Ni(1)-

Si(2)-Ni(1)-

Si(2)-Ni(1)-

Si-Ni-Ni

Si(2)-Ni

Si-Ni-Ni

Si(2)-Ni

Si(2)-N

Si-Ni-N

Ni(1)-N

Si(1)-N

Si(1)-

Si(1)-

Si(2)-

Si-N

Si(2)-

Ni

Ni

Ni

Table II.A.4. Selected bond angles [°] for $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$.

Bond	Angle	Bond	Angle
Si(2)-Ni(1)-Si(2)	106.07(5)	Ni(2)-Si(2)-Ni(1)	132.33(6)
Si(2)-Ni(1)-Si(2)	104.19(8)	Ni(1)-Si(2)-Ni(1)	73.93(5)
Si(2)-Ni(1)-Si(2)	118.55(9)	Ni(1)-Si(2)-Si/Ni	66.11(5)
Si(2)-Ni(1)-Si/Ni	59.28(4)	Si/Ni-Si(2)-Si/Ni	69.54(6)
Si/Ni-Ni(1)-Si/Ni	180.0	Ni(2)-Si(2)-Si/Ni	120.37(7)
Si(2)-Ni(1)-Si/Ni	120.72(4)	Ni(1)-Si(2)-Si/Ni	106.31(7)
Si/Ni-Ni(1)-Si/Ni	180.0	Ni(1)-Si(2)-Ni(1)	73.93(5)
Si(2)-Ni(1)-Ni(1)	126.96(3)	Ni(2)-Si/Ni-Ni(1)	130.10(3)
Si(2)-Ni(1)-Ni(1)	53.04(3)	Si(2)-Si/Ni-Ni(1)	54.62(5)
Si/Ni-Ni(1)-Ni(1)	90.0	Ni(2)-Si/Ni-Si/Ni	127.49(2)
Ni(1)-Ni(1)-Ni(1)	180.0	Si(2)-Si/Ni-Si/Ni	55.23(3)
Si(1)-Ni(2)-Si(1)	75.22(3)	Ni(1)-Si/Ni-Si/Ni	90.0
Si(1)-Ni(2)-Si/Ni	80.02(3)	Ni(2)-Si/Ni-Si/Ni	52.51(2)
Si(1)-Ni(2)-Si/Ni	124.73(4)	Si(2)-Si/Ni-Si/Ni	124.77(3)
Si(2)-Ni(2)-Si/Ni	122.69(4)	Si/Ni-Si/Ni-Si/Ni	180.0
Si/Ni-Ni(2)-Si/Ni	74.99(4)	Ni(2)-Si/Ni-Si(2)	107.21(3)
Si(2)-Ni(2)-Si(1)	112.37(5)	Si(2)-Si/Ni-Si(2)	109.23(9)
Ni(2)-Si(1)-Ni(2)	104.78(3)	Ni(2)-Si/Ni-Ni(2)	99.79(6)
Ni(2)-Si(1)-Ni(2)	100.15(4)	Ni(2)-Si/Ni-Si(2)	116.76(4)
Ni(2)-Si(1)-Ni(2)	124.65(4)	Si(2)-Sm-Ni(2)	43.90(4)

Table II.A.4 (continued)

Bond	Angle	Bond	Angle
Si(2)-Sm-Ni(2)	129.86(4)	Si(1)-Sm-Ni(2)	44.459(16)
Si(2)-Sm-Si(2)	77.70(4)	Si(1)-Sm-Ni(2)	98.002(19)
Ni(2)-Sm-Si(2)	84.88(4)	Si(2)-Sm-Ni(2)	83.65(2)
Si(2)-Sm-Si(1)	80.17(3)	Si(2)-Sm-Ni(2)	98.61(2)
Ni(2)-Sm-Si(1)	140.992(16)	Ni(2)-Sm-Ni(2)	134.14(3)
Si(2)-Sm-Si(1)	130.60(4)	Si(2)-Sm-Si/Ni	137.01(3)
Si(2)-Sm-Si(1)	77.75(4)	Ni(2)-Sm-Si/Ni	85.28(3)
Si(1)-Sm-Si(1)	55.170(9)	Si(2)-Sm-Si/Ni	137.08(3)
Si(2)-Sm-Si(2)	173.88(3)	Si(2)-Sm-Si/Ni	82.83(3)
Ni(2)-Sm-Si(2)	44.02(4)	Si(1)-Sm-Si/Ni	58.26(3)
Si(2)-Sm-Si(2)	100.39(4)	Si(1)-Sm-Si/Ni	84.26(2)
Si(1)-Sm-Si(2)	105.22(4)	Si(2)-Sm-Si/Ni	47.66(3)
Si(2)-Sm-Ni(2)	98.61(2)	Ni(2)-Sm-Si/Ni	44.42(2)
Ni(2)-Sm-Ni(2)	100.379(18)	Ni(2)-Sm-Si/Ni	97.640(19)
Si(2)-Sm-Ni(2)	174.74(4)	Si/Ni-Sm-Si/Ni	54.763(16)

Table II.A.5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$.

Atomic Position	U11	U22	U33	U23	U13	U12
Sm	4(1)	4(1)	4(1)	0	0	0(1)
Ni(1)	5(1)	8(1)	6(1)	0	0	0
Ni(2)	4(1)	7(1)	6(1)	0	0	0(1)
Si(1)	1(1)	4(1)	3(1)	0	0	0
Si(2)	3(1)	3(1)	6(1)	0	0	1(1)
Si/Ni	3(1)	4(1)	4(1)	0	0(1)	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Table II.A.4 (continued)

Bond	Angle	Bond	Angle
Si(2)-Sm-Ni(2)	129.86(4)	Si(1)-Sm-Ni(2)	44.459(16)
Si(2)-Sm-Si(2)	77.70(4)	Si(1)-Sm-Ni(2)	98.002(19)
Ni(2)-Sm-Si(2)	84.88(4)	Si(2)-Sm-Ni(2)	83.65(2)
Si(2)-Sm-Si(1)	80.17(3)	Si(2)-Sm-Ni(2)	98.61(2)
Ni(2)-Sm-Si(1)	140.992(16)	Ni(2)-Sm-Ni(2)	134.14(3)
Si(2)-Sm-Si(1)	130.60(4)	Si(2)-Sm-Si/Ni	137.01(3)
Si(2)-Sm-Si(1)	77.75(4)	Ni(2)-Sm-Si/Ni	85.28(3)
Si(1)-Sm-Si(1)	55.170(9)	Si(2)-Sm-Si/Ni	137.08(3)
Si(2)-Sm-Si(2)	173.88(3)	Si(2)-Sm-Si/Ni	82.83(3)
Ni(2)-Sm-Si(2)	44.02(4)	Si(1)-Sm-Si/Ni	58.26(3)
Si(2)-Sm-Si(2)	100.39(4)	Si(1)-Sm-Si/Ni	84.26(2)
Si(1)-Sm-Si(2)	105.22(4)	Si(2)-Sm-Si/Ni	47.66(3)
Si(2)-Sm-Ni(2)	98.61(2)	Ni(2)-Sm-Si/Ni	44.42(2)
Ni(2)-Sm-Ni(2)	100.379(18)	Ni(2)-Sm-Si/Ni	97.640(19)
Si(2)-Sm-Ni(2)	174.74(4)	Si/Ni-Sm-Si/Ni	54.763(16)

Table II.A.5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$.

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Sm	4(1)	4(1)	4(1)	0	0	0(1)
Ni(1)	5(1)	8(1)	6(1)	0	0	0
Ni(2)	4(1)	7(1)	6(1)	0	0	0(1)
Si(1)	1(1)	4(1)	3(1)	0	0	0
Si(2)	3(1)	3(1)	6(1)	0	0	1(1)
Si/Ni	3(1)	4(1)	4(1)	0	0(1)	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

The crystal structure of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ is related to the previously reported $\text{U}_2\text{Co}_3\text{Si}_5$ structure type²³. However, the structure of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$, refined using single crystal X-ray diffraction data, revealed severe discrepancies with that reported for $\text{U}_2\text{Co}_3\text{Si}_5$. The problem is the assignment of the atomic positions of the transition metal (Co or Ni) and Si in the two structures. Thus, in $\text{U}_2\text{Co}_3\text{Si}_5$, out of six crystallographic atomic sites two (*4a* and *8j*) were assigned to Co atoms, three (*4b*, *8g*, *8j*) to Si atoms, and one site *8j* was found to belong to U. Similarly, during the structure refinement of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$, a total of six atomic sites were identified. However, our initial refinement showed that Ni atoms were located at the *4b* and *8j* crystallographic sites, while the Si atoms were found at three sites with multiplicities *4a*, *8g* and *8j*. The Sm atoms were analogously found at *8j* site. Moreover, further structural refinement revealed appreciable population of the Si *8j* site with Ni. The introduction of the Si/Ni mixed occupancy site at *8j* led to substantial reduction in R-values from 0.043 to 0.021 in the consecutive refinement cycle. The occupancy parameters of respectively 0.763(7) and 0.237(7) were determined for Si and Ni at *8j*. The resulting convergence factor 0.0206 [for 368 reflections with $I > 2\sigma(I)$]^{*} undoubtedly evidences the correctness of the atomic assignment presented herein. The exact empirical formula and corresponding Pearson's symbol are $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ($Z = 4$) and *oI40*, respectively.

^{*} Compare to R-value of 0.122 reported for $\text{U}_2\text{Co}_3\text{Si}_5$.

3. Results and Discussions

Reaction Chemistry

A number of isotypes²⁴ of the $U_2Co_3Si_5$ family of compounds have been reported in the literature. The generalized formula could be represented as $A_2M_3Tt_5$, where A can be actinide or lanthanide, M is a transition metal (*3d*, *4d* and *5d*) and Tt is a tetrel element (Si, Ge and Sn). The above mentioned compounds were obtained in small crystalline or polycrystalline form from arc-melting reactions ($T > 2500^\circ C$) with subsequent annealing ($800 - 1000^\circ C$). Oppositely, large single crystals (up to few millimeters on the side) of the $RE_2Ni_{3+x}Si_{5-x}$ ($RE = Sm, Gd$ and Tb) family of compounds could be easily grown from molten Ga solutions at $850^\circ C$. Although the highest yield of this phase was obtained from reactions with a short isothermal step, the crystal size noticeably improves upon prolonged heating of the reaction mixture. Thus, large well-faceted crystals were isolated from the reactions with 3 and 10 days of isothermal step. Additionally, the amount of Ga flux seems to play a role in the formation of the Ga-free $RE_2Ni_{3+x}Si_{5-x}$ phase. From four sets of experiments using 8, 16, 30 and 40 equivalents of Ga under otherwise identical conditions, the ternary silicides ($RE_2Ni_{3+x}Si_{5-x}$ and $RENiSi_3$) preferably form at the extreme ends with a Ga content of 8 or 40. The medium Ga content (16 or 30) instead promotes formation of the quaternary $RE_{0.67}Ni_2Ga_{5+n-x}Si_x$ ($n = 0,1$) phases²⁵.

Interestingly, the Ge analog of the $RE_2Ni_{3+x}Si_{5-x}$ phase could not be obtained from similar reactions with Ge. In such reactions, Ga invariably gets incorporated in

the final product giving rise to quaternary phases like $\text{RE}_{0.67}\text{M}_2\text{Ga}_{5+n-x}\text{Ge}_x$ ^{25, 26} ($n = 0, 1$), REMGa_3Ge ²⁷, $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ ²⁷, $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ ²⁸ and $\text{RE}_2\text{MGa}_9\text{Ge}_2$ ²⁹, where $\text{M} = \text{Ni}$ or Co . Similarly, molten Al solutions could not be used for the synthesis of transition metal silicides such as $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ or RENiSi_3 ³, as Al always integrates into the product. The capability of molten Ga to serve as a non-reactive solvent to form rare-earth transition metal silicides is thus of great interest.

Crystal Structure

The drawing of the crystal structure of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ projected onto the *ab*-plane is depicted in Figure II.A.4. For simplicity, the bonds to Sm atoms were omitted. The structure is three-dimensional (3D), although for better understanding it is worthwhile to sub-divide it into a pair of slabs. The first one is a 2D $\{\text{Ni}_{3+x}\text{Si}_{5-x}\}$ puckered layer, and it is shown in Figure II.A.5. In this layer, the Ni and Si atoms form a distorted square net, which is outlined by the dashed contour. Above and below the hollows of the squares, the atoms of $\text{Ni}(2)$ and $\text{Si}(2)$ are situated. The capping occurs in such a manner that the hollows capped from the same side (above or below the square net) share their corners, and the squares capped from above share the edges with the squares capped from below. In such type of filling, the capping atoms are most effectively separated from each other to avoid excessively close contacts between the atoms.

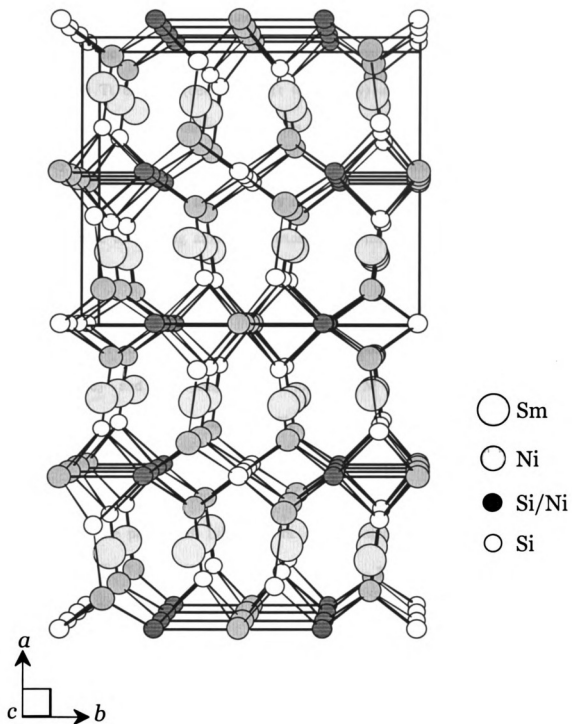


Figure II.A.4. The structure of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ viewed along the c -axis. The unit cell is drawn in bold line.

In the intermetallic compounds containing RE, transition metal (M) and tetrel element (Tt), the occurrence of the puckered layers consisting of square lattices of M capped with Tt element (denoted $M_{\square}Tt$ for brevity) and vice versa ($Tt_{\square}M$) are widespread. For instance, the representatives of the $ThCr_2Si_2$ structure type, such as YNi_2Ge_2 ³⁰, $LnNi_2Ge_2$ ³¹, ANi_2Ge_2 ³² ($A = Ca, Sr$) and $TbFeSi_2$ ³³, exhibit $M_{\square}Tt$ arrangement, where the M atoms occupy corners of the square lattice, and the Tt elements serve as capping atoms. The examples of the $Tt_{\square}M$ arrangement where hollows of Tt square lattice are capped with M-type atoms are even more common. Besides the ternary compounds like $CeNiSi_2$ ³⁴, $NdRuSi_2$ ³⁵ and $TmLi_{0.5}Ge_2$ ³⁶, it has also been observed in a number of quaternary compounds such as $REMGa_3Ge$ ²⁷, $RE_3Ni_3Ga_8Ge_3$ ²⁷ and $RE_4Ni_3Ga_6Ge_4$ ²⁸. The mixing of M with Tt on the capping site of $Tt_{\square}M$ lattice is known as well ($Ce_3Ni_2Si_8$ ³⁷, $Ce_2Rh_{1.35}Ge_{4.65}$ ³⁸). However, the M/Tt arrangement in the $\{Ni_{3+x}Si_{5-x}\}$ puckered layer is unique in one sense. In the corners of the $\{Ni_{3+x}Si_{5-x}\}$ distorted square net Si, Ni, and Si/Ni atoms (Si(1), Ni(1) and Si/Ni atomic sites) are positioned. Likewise, the capping elements are both Si and Ni (atomic sites Si(2) and Ni(2)). Thus, in $Sm_2Ni_{3+x}Si_{5-x}$, the Ni and Si elements are distributed nearly evenly throughout the puckered layer (the equal Si and Ni content would occur for $x = 1$). This particular feature differentiates $Sm_2Ni_{3+x}Si_{5-x}$ from all other compounds where M-Tt puckered layer is observed. Because the electronic properties and bonding interactions of such lattices are of continuing interest^{39,40,41}, discovery of yet another type of M-Tt lattice is invaluable for future examination in order to better understand the electronic properties and the nature of chemical bond in intermetallic compounds.

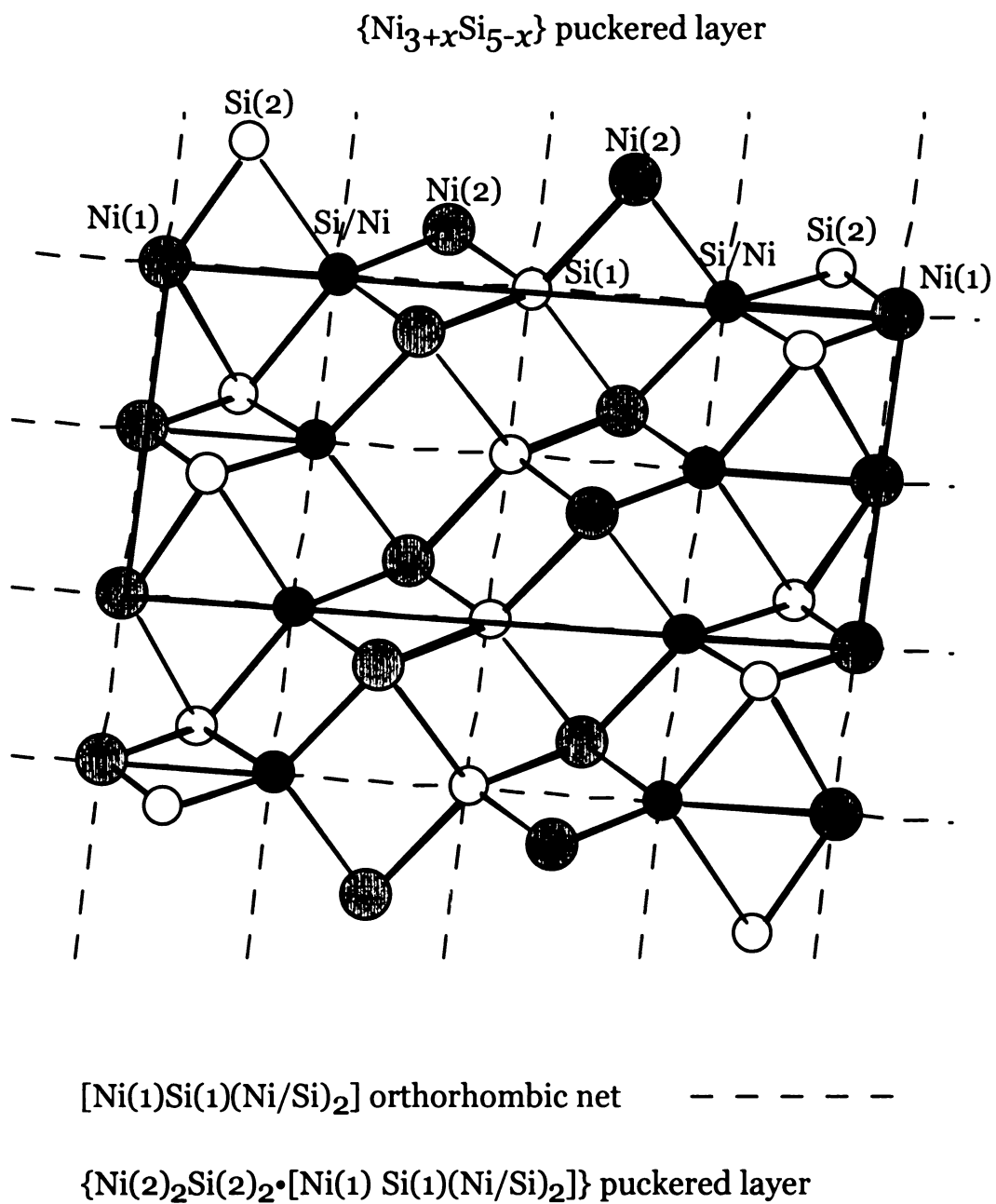


Figure II.A.5. $\{\text{Ni}_{3+x}\text{Si}_{5-x}\}$ puckered layer viewed approximately along the a -axis.

The unit cell is indicated with bold line. A distorted square net is outlined in dashed lines.

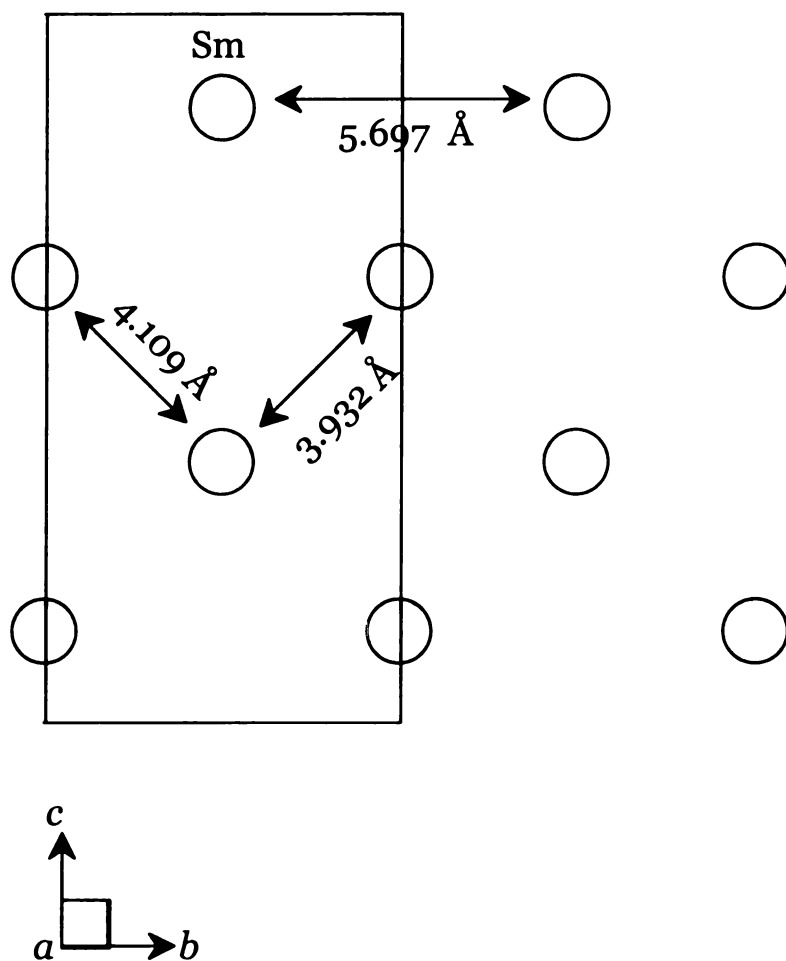


Figure II.A.6. The Sm-only structural fragment projected onto bc -plane. The closest bonding contacts are indicated by the arrows and the distance is given in Å.

The second structural motif is a distorted square lattice of Sm atoms. This Sm-only monoatomic layer viewed down the a -axis is shown in Figure II.A.6. The Sm-only plane and the $\{\text{Ni}_{3+x}\text{Si}_{5-x}\}$ puckered layer alternate along the a -axis to build the 3D structure.

The local coordination environments of the Ni and Si atoms within 3.0 Å and Sm atoms within 3.5 Å are presented in Figure II.A.7. The Ni(1) atoms have eight Si and Ni atoms in their immediate coordination environment. Four Si(2) atoms are bonded to Ni(1) in the form of a distorted tetrahedron at 2.3685(14) Å. The Si(2)-Ni(1)-Si(2) angles deviate slightly from the ideal tetrahedral (104.19(8)°, 106.07(5)° and 118.55(9)°). The remaining four atoms of the Ni(1) coordination sphere are two Si/Ni (Ni(1)-Ni/Si = 2.6562(15) Å) and two Ni(1) atoms (Ni(1)-Ni(1) = 2.8484(4) Å) arranged in-plane with a central Ni(1) atom. The Ni(2) atoms are in the distorted square pyramidal environment of Si and Ni atoms. The orthorhombic base of the pyramid consists of two Si(1) atoms (Ni(2)-Si(1) = 2.3336(7) Å) and two Si/Ni atoms (Ni(2)-Si/Ni = 2.3398(12) Å). The apex of the pyramid is a Si(2) atom, and it is linked to the central Ni(2) atom at 2.299(2) Å, which is the shortest bond distance found in the structure. The Si(1) atoms are six-coordinate, and they are bonded to four Ni(2) atoms in the shape of a slightly distorted tetrahedron (Ni(2)-Si(1)-Ni(2) angles are 100.15(4)°, 124.65(4)° and 104.78(3)°). Two additional Si(1) atoms cap the edges of the tetrahedron and are located at 2.8484(4) Å from central Si(1) atom. The Si(2) atoms have a mono-capped distorted square pyramidal environment. The pyramid is built up from a base consisting of two Si/Ni atoms connected at 2.4974(17) Å and two Ni(1) atoms at 2.8483(4) Å, with the apex of a Ni(2) atom. The capping Sm atom is located at 2.898(2) Å from Si(2). The Si/Ni atoms of the mixed occupancy site occupy the center of a tri-capped tetrahedron. The four corners of the tetrahedron consist of two Ni(2) and two Si(2) atoms. Three edges of this tetrahedron are capped with Ni(1) and two Si/Ni atoms at 2.3398(12) Å and 2.8483(4) Å, respectively.

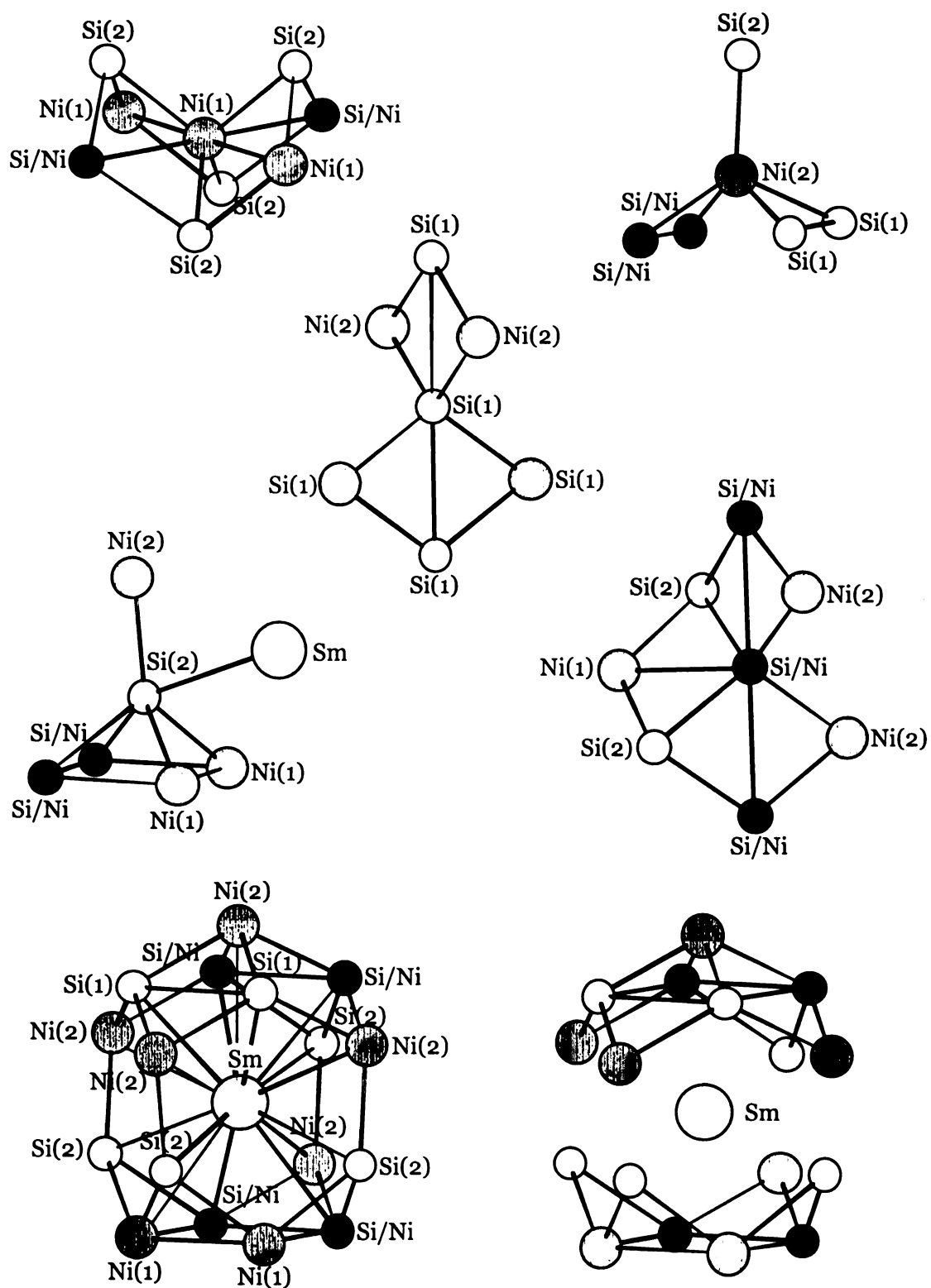


Figure II.A.7. Local coordination environment of Sm, Ni and Si atoms.

The Sm atoms are 17-coordinate, bonded within 3.5 Å to four Si(2) atoms, five Ni(2) atoms, two Si(1) atoms, four Si/Ni atoms and two Ni(1) atoms. The coordination polyhedron of Sm atom is rather complicated, see Figure II.A.7. In the pictorial representation displayed on the right, no bonds were drawn to the central Sm atom, as well as between Ni(2) and Si(2) atoms. In this view, the Sm atom is positioned in a crib of eight Si and Ni atoms (below) and capped with another nine Si and Ni atoms (above).

Crystal Chemistry and Chemical Bonding

It is difficult to judge the electron charge distribution in $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$, and intermetallic compounds in general, since simple electronegativity considerations may not always be applied in this case. However, in our case the situation is simplified by knowing that RE atoms are tri-positive, as indicated by the magnetic data (see below) and follows from electronegativity inspection (the RE atoms are least electronegative). Thus, the formal charge could be assigned only to the whole $\{\text{Ni}_{3+x}\text{Si}_{5-x}\}$ framework, giving the charge distribution $\text{Sm}_2^{6+}\{\text{Ni}_{3+x}\text{Si}_{5-x}\}^{6-}$. For a rigorous assignment of charge on Ni and Si atoms, electronic structure calculations ought to be performed. This work is currently in progress.

On the basis of connectivity arguments, it follows that the strongest bonding interaction takes place between adjacent $\{\text{Ni}_{3+x}\text{Si}_{5-x}\}$ slabs, which are linked via Ni(2)-Si(2) bonds at 2.299(2) Å. This result is consistent with the connectivity data obtained for RENiSi_3 ³, where the closest bonding contacts also occur between Ni and

Si with an average Ni-Si distance of 2.293 Å (RE = Sm). For the latter compound, the theoretical electronic band structure calculations were also carried out indicating that Ni atoms are the most reduced species in the structure. Because of the quite close relationship of these two rare-earth nickel silicides, it is plausible to assume that a similar situation also holds true for $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$, given that the magnetic data also does not reveal any measurable moment on the Ni atoms. This reduction gives rise to electron-rich configuration of Ni atoms ($3d^{10}$ or $4s^23d^{10}$), and is most likely to explain relatively short bonding contacts between Ni-Si and Ni-Sm atoms and the non-magnetic behavior of Ni atoms as well.

The bonding within the $\{\text{Ni}_{3+x}\text{Si}_{5-x}\}$ layer and between the Sm and $\{\text{Ni}_{3+x}\text{Si}_{5-x}\}$ slabs is also strong. Thus, the Si-Ni and Si-Si distances cover the range of 2.3336(7) Å–2.6561(15) Å and 2.4973(17) Å– 2.8483(4) Å, respectively. The average Ni-Si and Si-Si bond distances found in $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ are respectively 2.402 Å and 2.673 Å, and are comparable to the sum of the single-bonded metallic radii⁴² of Ni and Si (2.39 Å and 2.36 Å). Similar Si-Ni distances of 2.283(2) Å, 2.295(3) Å and 2.303(1) Å were also found in the related SmNiSi_3 compound³. The contacts between the Sm and Ni and Si atoms are likewise bonding, with the Sm-Ni and Sm-Si bond lengths of 3.191 Å and 3.067 Å on average, respectively. In contrast, the Sm-Sm distances in the Sm distorted square plane are 3.932 Å and 4.109 Å, and they could be considered only weakly bonding, taking into account that the sum of two covalent radii⁴³ of Sm (coordination number 12) is 3.608 Å. The next closest Sm-Sm contact is found at 5.697 Å.

The magnetism of the $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ family of compounds was studied on the Tb analog. The molar magnetic susceptibility (χ_m) and inverse molar magnetic susceptibility (χ_m^{-1}) plotted against temperature are shown in Figure II.A.8.

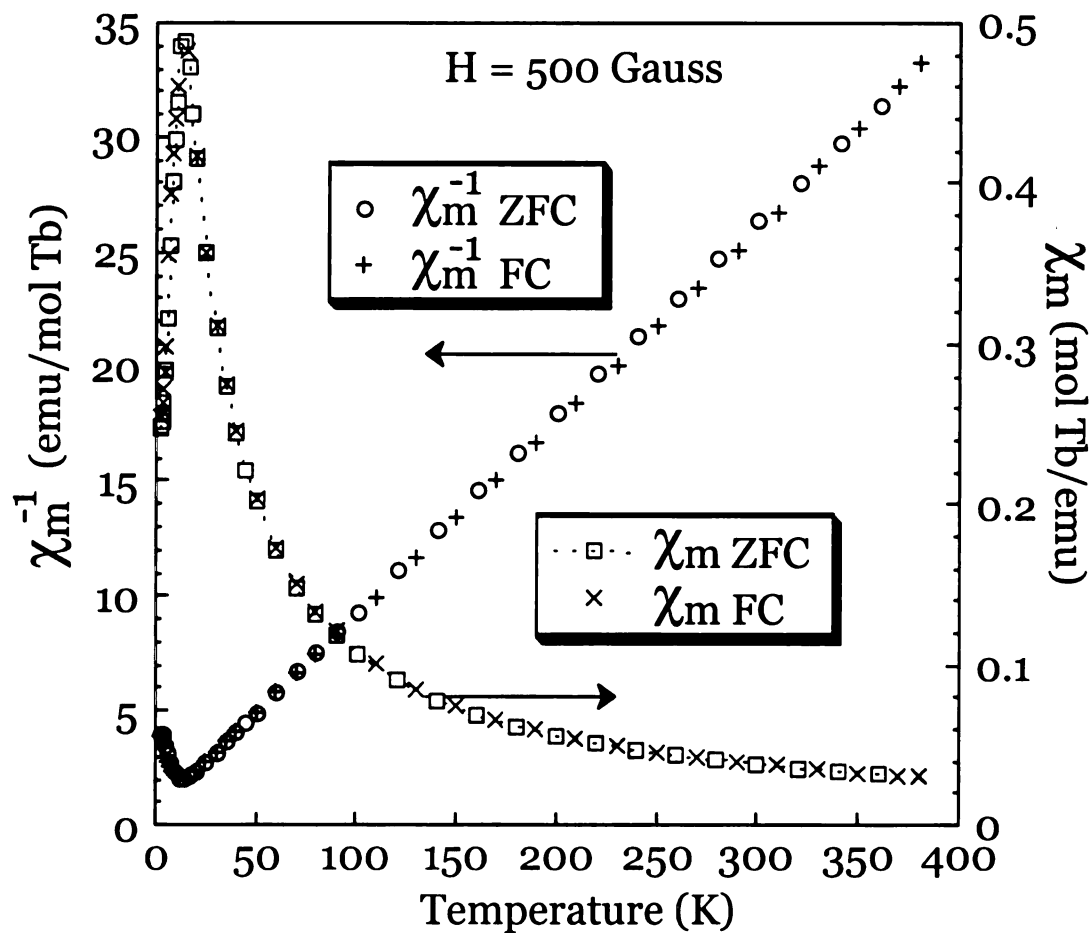


Figure II.A.8. Temperature dependence of the molar magnetic susceptibility (calculated per mole of Tb) and inverse molar susceptibility measured in a field 500 Gauss.

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The susceptibility goes through a maximum at low temperature, as can be seen in Figure II.A.9, with maximal magnetic susceptibility ($T_{\max}$) occurring at ~ 13 K. Such behavior of $\chi_m - T$ plots usually arises in magnetic systems undergoing short-range antiferromagnetic ordering below the temperature $T_{\max}$.

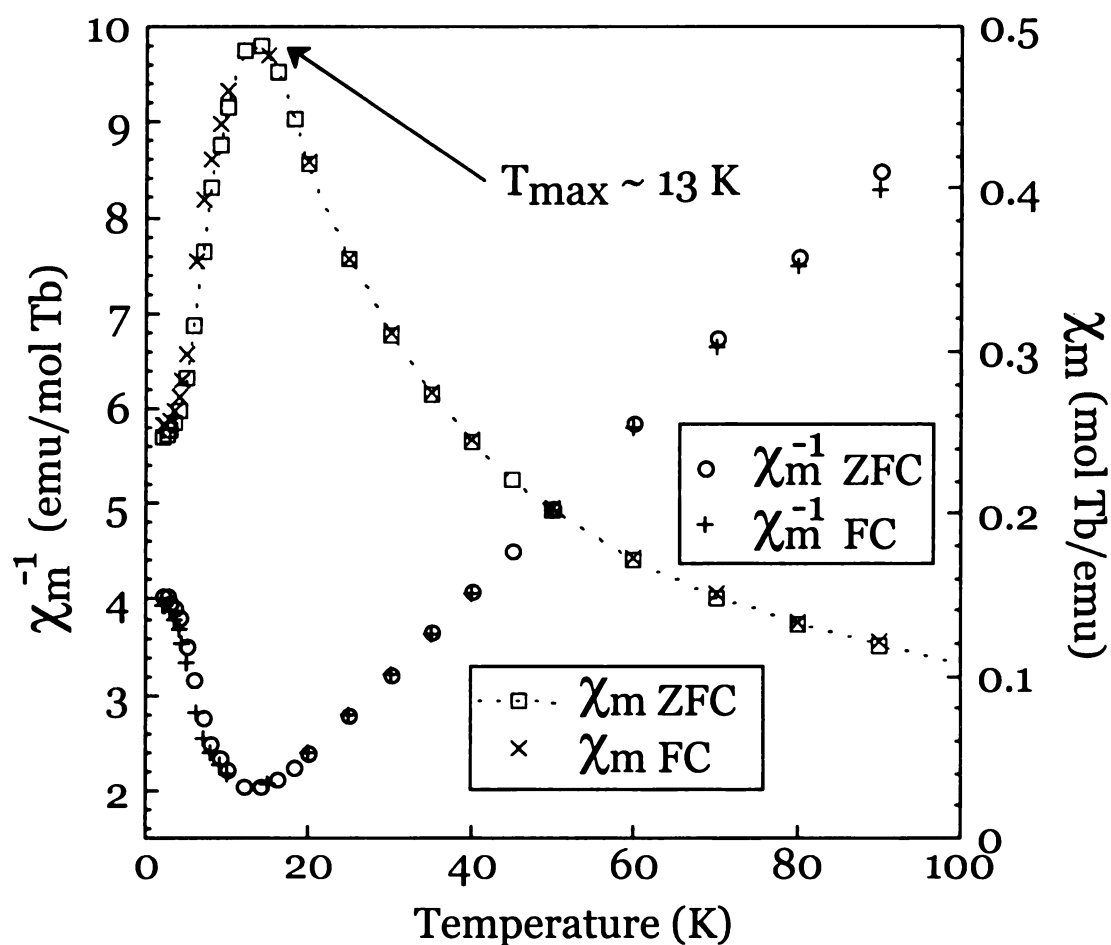


Figure II.A.9. Susceptibility data in the vicinity of the antiferromagnetic ordering transition. Zero-field-cooled (ZFC) and field-cooled (FC) parts of the susceptibility are shown.

To probe the exact value of the temperature of the antiferromagnetic transition (Néel temperature, T_N) a set of isofield χ_m - T measurements was performed, see Figure II.A.10. Consequently, the T_N was determined to be 13.25 K, very close to the value for $T_{\max}$.

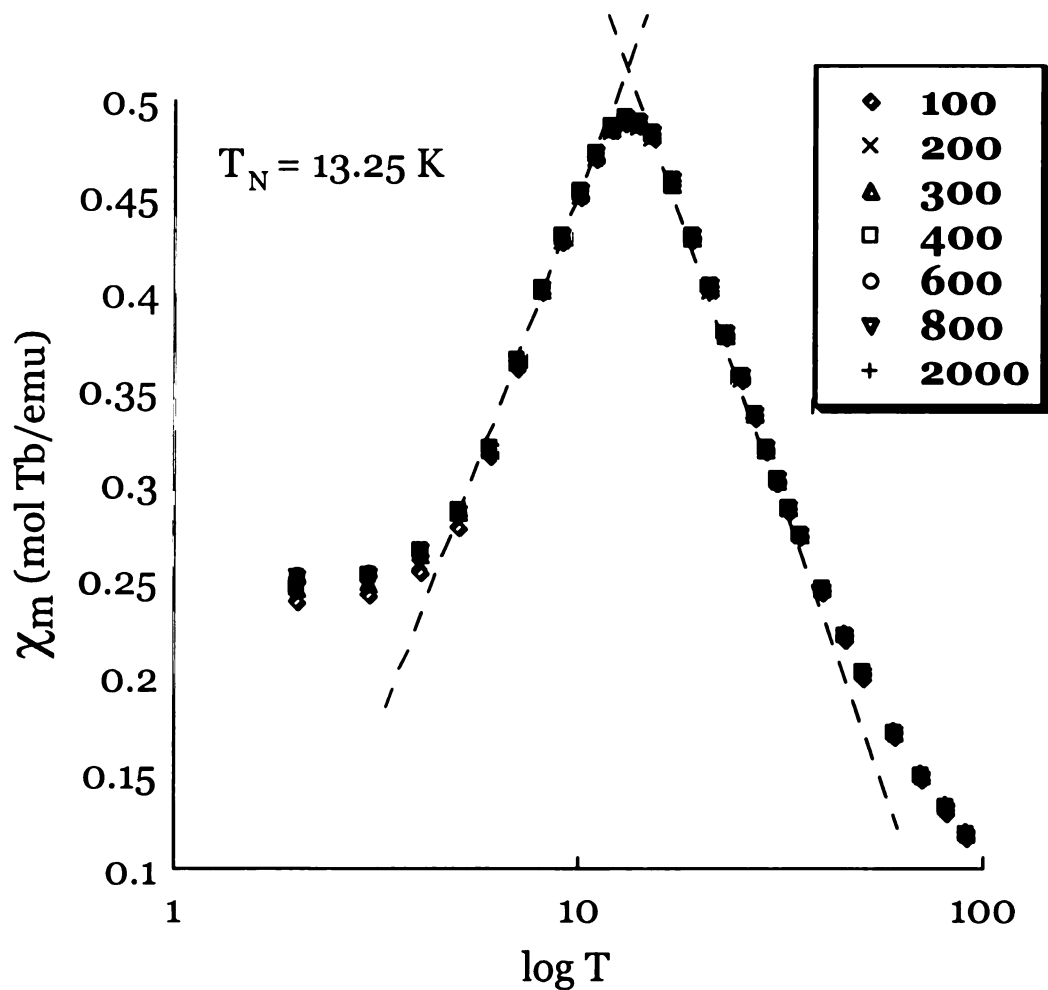


Figure II.A.10. Isofield plots of the molar magnetic susceptibility vs temperature measured on the polycrystalline sample. The applied fields were varied from 100 to 2000 Gauss.

As the temperature increases, in particular above 30 K, the reciprocal magnetic susceptibility increases linearly with temperature, following the Curie-Weiss law, see Figure II.A.11. The effective magnetic moment (μ_{eff}) and the Weiss constant (θ) obtained from the linear part of the temperature dependence of the inverse magnetic susceptibility are 9.69 BM and -8.4 K, respectively.

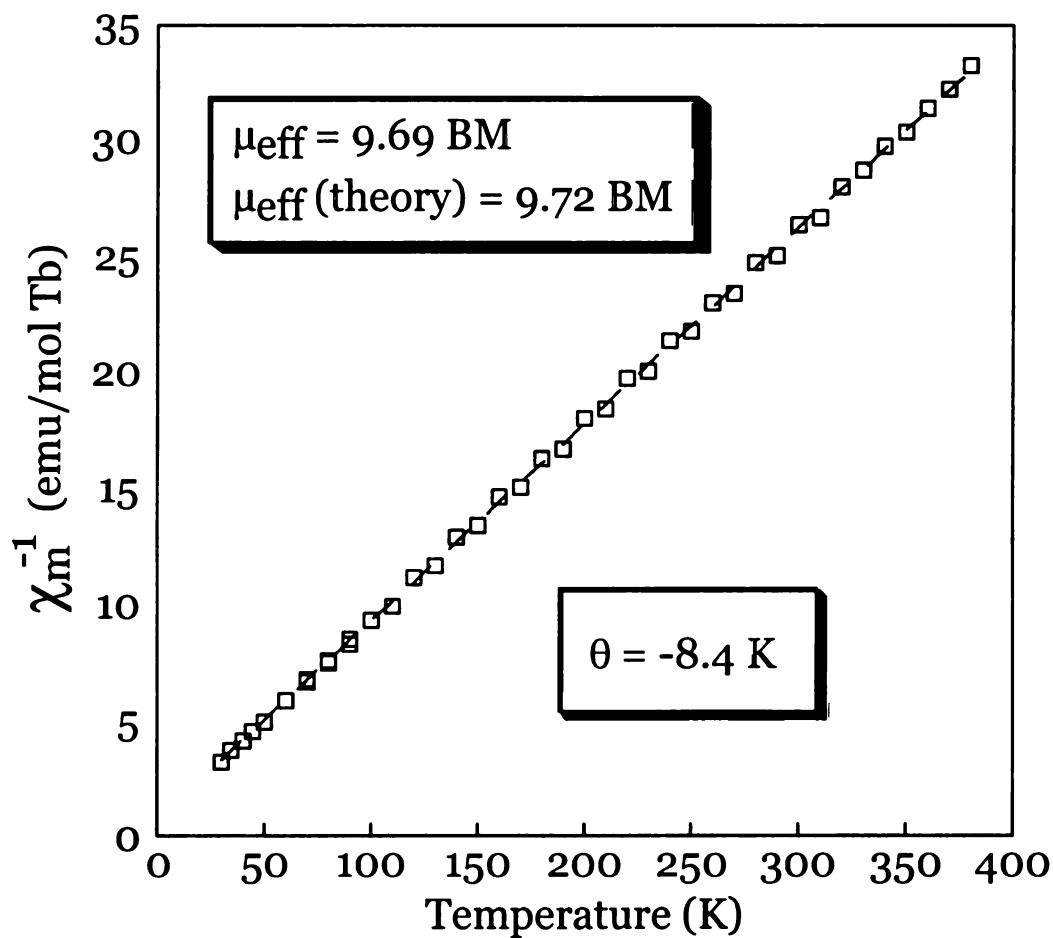


Figure II.A.11. Linear part of the reciprocal molar magnetic susceptibility.

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The negative sign of the Weiss constant is further indication of the antiferromagnetic transition taking place at the low temperatures. The experimental value of the effective magnetic moment agrees well with the theoretical value given by the formula $\mu_{\text{eff}} = g_J[J(J+1)]^{1/2}$, where g_J is a Landé factor⁴⁴, and J is a total angular momentum of the Tb^{3+} ion⁴⁵. It is now possible to conclude that magnetism in $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ is caused solely by the magnetic moments localized on the RE ions, whilst Ni atoms are in non-magnetic state. Theoretical electronic structure calculations performed for nickel-containing intermetallics such as YNiSi_3 ³ and $\text{Sm}_2\text{NiGa}_{12}$ ¹, show that Ni atoms are in a reduced state approaching a diamagnetic $4s^23d^{10}$ electron configuration. Therefore, the absence of localized magnetic moment on the Ni atoms suggests completely filled Ni 3d orbitals. A similar situation was observed in a number of intermetallic compounds containing both RE and Ni as possible magnetic centers. The examples of the non-magnetic behavior of Ni atoms include $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Si}_{1-x})\text{Al}_4\text{Si}_6$ ⁴⁶, $\text{RENiAl}_4\text{Ge}_2$ ⁴⁷, RENiSi_3 ³, $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Ge}_x$ ²⁵, RENiGa_3Ge ²⁷, $\text{La}_{5-x}\text{Ni}_{12}\text{Sn}_{24}$ ⁴⁸ and many more.

The field dependence of the magnetization for $\text{Tb}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ calculated in Bohr magnetons per mole of Tb is shown in Figure II.A.12. The observed change of the slope is probably due to impurity. The magnetization does not reach saturation, and in the highest measured field (± 5 T) a moment of only 4 BM is developed, which is less than 50% of the full saturation value ($\mu_{\text{sat}}(\text{Tb}^{3+}) = 9.0$ BM). Similar results were obtained for other Tb-containing intermetallic compounds such as TbNiGa_3Ge ²⁷, Tb_4FeGe_8 ⁴⁹ and $\text{TbAl}_{3-x}\text{Ge}_x$ ⁵⁰.

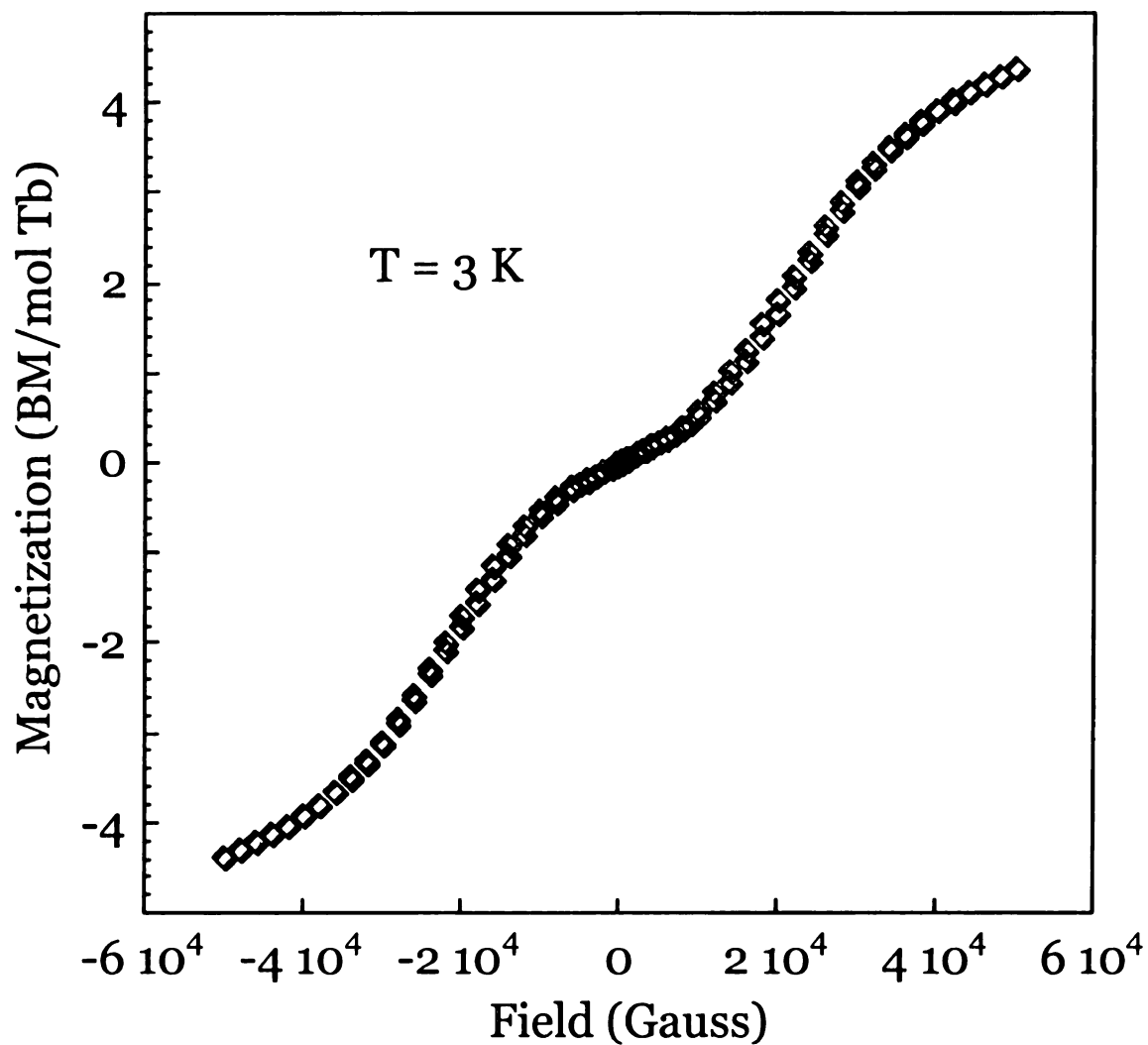


Figure II.A.12. Magnetization as a function of applied magnetic field for $\text{Tb}_2\text{Ni}_{3+x}\text{Si}_5$.
 x measured on polycrystalline sample at 3 K. Magnetization is given in Bohr magnetons per mole of Tb.

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4. Conclusions

The use of molten Ga as a non-reactive solvent for synthesis of intermetallic silicides was demonstrated on the family of new ternary compounds $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ (RE = Sm, Gd and Tb). Large single crystals could be easily grown from solutions of molten Ga for various members of this phase at moderate temperatures (850°C). The structure of $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ was solved from single crystal X-ray data in the orthorhombic space group *Ibam*, $Z = 4$, cell parameters $a = 9.6396(12)$ Å; $b = 11.3219(14)$ Å; and $c = 5.6967(13)$ Å. The refinement based on the full-matrix least-squares on F_o^2 [$I > 2\sigma(I)$] converged to final residuals $R_1/wR_2 = 0.0206/0.0492$. The structure of $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ is related to the $\text{U}_2\text{Co}_3\text{Si}_5$ structure type; however, discrepancies exist between the solution obtained for $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ and that reported for $\text{U}_2\text{Co}_3\text{Si}_5$. The better convergence factor and overall refinement parameters indicate that the atomic assignment proposed in this dissertation is accurate. The following atomic positions were identified in the structure of $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$: $4a$ and $8j$ for Ni atoms, $4b$, $8g$, $8j$ for Si atoms, and $8j$ site for RE atom. The Si at $8j$ was additionally found to contain a disorder with Ni.

The peculiar characteristic of the structure of this compound is a puckered layer, where no separation onto the Si square lattice capped with Ni (or vice versa) was observed. Instead, both Si and Ni are uniformly participating in constructing the square lattice and capping elements. This is in contrast to what has so far been observed in a large number of other intermetallic silicides^{26,27,29-37}.

The magnetic susceptibility data for Tb analogue indicate that at low temperatures antiferromagnetic ordering takes place with $T_N = 13.25$ K, while at higher temperature the Curie-Weiss law is followed for the temperature dependence of the reciprocal magnetic susceptibility. The experimental effective magnetic moment for Tb^{3+} is in excellent agreement with the theoretical value for the free Tb^{3+} ion. The Ni atoms are found to be in the reduced non-magnetic state.

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Chapter II

Part B

Crystal Growth and Characterization of Novel Ternary Rare-Earth Iron Germanide Tb_4FeGe_8 Using Molten Ga as a Non-Reactive Solvent.

1. Introduction

The examples of molten Ga serving as a non-reactive flux for synthesis of complex transition metal tetrelides (silicides, germanides, stannides) are extremely rare. Although hundreds of ternary rare-earth transition metal tetrelides have been discovered over the past decades^{1,2,3}, mostly conventional methods were applied for their synthesis. As it is often the case, classical solid state synthetic techniques do not provide sufficiently good means for single crystal growth. At the same time, the need for large

single crystals of some scientifically important intermetallics is great⁴. This fact raises an issue of improving the quality and size of grown crystals. Because molten metal solution synthesis normally promotes crystal growth^{5,6} and provides an excellent means for new material exploration, continued research in the area of complex rare-earth transition metal tetrelides employing molten Ga as a solvent is justified in every respect. However, since molten metal growth techniques have not been used a great deal in the realm of intermetallics, we are just starting to learn the potential of this method and its applicability for the synthesis of complex intermetallic compounds containing tetrel elements^{7,8,9,10,11}. The preliminary results of crystal growth of complex rare-earth nickel silicides from molten Ga solutions are encouraging. Successful crystal growth of ternary $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ compounds has been presented in preceding Chapter II, Part A. Another family of ternary silicides RENiSi_3 ¹² has been effectively synthesized from molten Ga solutions. In view of these results in the synthesis of silicides, it is worthwhile to extend the research to the systems that include Ge, and probe the usability of molten Ga flux for the crystal growth of rare-earth transition metal germanides as well. Hence, in the following sections of Chapter II, Part B the synthesis, crystal structure and magnetic properties of the novel rare-earth iron germanide Tb_4FeGe_8 grown from molten Ga are presented.

2. Experimental

Synthesis

The Tb_4FeGe_8 compound was synthesized at reasonably high yield from the reaction containing 4, 1, 30 and 4 equivalents of Tb, Fe, Ga and Ge, respectively. The metals: Tb (1 mm chips), Fe (300 mesh powder), Ga (3 mm shots) and Ge (polycrystalline, hand-ground), all of purity 99.99 and higher, CERAC Inc. were weighed in the dry box under nitrogen atmosphere and loaded into an alumina crucible. The crucible was then sealed in a quartz ampoule under high vacuum ($\sim 1 \cdot 10^{-4}$ Torr). The following heating profile has been used for growing single crystals of Tb_4FeGe_8 : the reaction mixture was heated to 1000°C , held there for just a few hours to allow proper homogenization of the melt, cooled to 850°C in 2 hours, then held isothermally at 850°C for 144 hours, and finally cooled to 200°C in 72 hours. The reactions were taken out at 200°C for hot filtration to remove unreacted liquid Ga. Afterwards, the reaction product was treated with 3 M solution of I_2 in DMF to isolate it from the remaining Ga flux. The final product was rinsed (under sonication) with water, DMF and subsequently dried with acetone and ether.

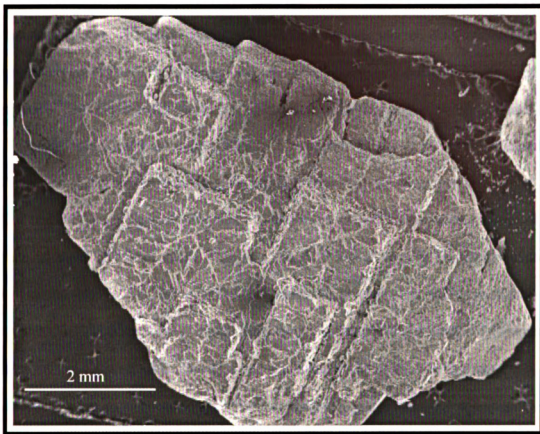


Figure II.B.1. SEM image of a typical crystal of Tb₄FeGe₈ grown from the molten Ga solution.

Scanning Electron Microscopy and Elemental Analysis

The elemental composition was studied by Energy Dispersive Spectroscopy (EDS) semi-quantitative analysis on the scanning electron microscope (SEM) equipped with the NORAN Inc. EDS detector. The routine data acquisition was done at acceleration voltage 20 kV and collection time 30 seconds. An extensive averaging of the

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results obtained on the different crystals was carried out in order to attain accurate values of the atomic ratios. A typical crystal of Tb_4FeGe_8 grown in molten Ga flux conditions is shown in Figure II.B.1. The layered character of the crystals is a distinctive feature of this compound. The crystals are normally morphologically properly developed, plate-like, well-faceted and often feature right angles. The surface of the crystals, as indicated by EDS analysis is prone to adhering the small particles of the side products. Thus, the FeGa_3 and Tb-Ga-Ge phases were found to be locally present in the selected areas of the surface of the Tb_4FeGe_8 crystal. However, the EDS analysis made on freshly exposed cross-section of the Tb_4FeGe_8 crystal produced the averaged result (normalized per amount of Tb) " $\text{Tb}_4\text{Fe}_{1.24}\text{Ge}_{8.34}$ " which is (despite the complications caused by the partial overlap of the $\text{K}\alpha$ -line of Fe (6.403 keV) and $\text{L}\alpha$ -line of Tb (6.272 keV) in the X-ray emission spectra) in very good agreement with the formula obtained from the single crystal X-ray diffraction refinement.

Powder X-ray Diffraction

The X-ray powder diffraction (XRD) patterns of pulverized products were taken at room temperature on a CPS 120 INEL X-ray diffractometer (Cu $\text{K}\alpha$ radiation) equipped with position-sensitive detector. Experimental XRD patterns were then compared to that calculated from single crystal data using CERIOUS² software package¹³. The yield of the Tb_4FeGe_8 phase was found to be maximal when the longer isothermal and cooling steps of the temperature variation profile were chosen. At the reaction conditions described above, the yield of the Tb_4FeGe_8 phase was ~ 60-70%, according to

the X-ray powder diffraction pattern. From the XRD pattern the presence of Ge and ternary $\text{Tb}_2\text{Ga}_3\text{Ge}_5$ phases was also evident. Additionally, traces of binary FeGa_3 and quaternary $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ ¹⁰ phases were observed during EDS elemental analysis, but not in the XRD pattern. The latter two phases are therefore present in the amount less than 2%, below the resolution limit of powder X-ray diffraction.

Single Crystal X-ray Diffraction

The X-ray intensity data collection was carried out at room temperature on the Siemens Platform SMART¹⁴ CCD diffractometer using a single crystal of dimensions $0.06 \times 0.04 \times 0.02$ mounted on a glass fiber. A hemisphere of reciprocal data (Mo $K\alpha$ radiation generated at 50 kV and 40 mA, $\lambda = 0.71073 \text{ \AA}$) was acquired up to 65° in 2θ . The individual frames were measured using the ω -steps of 0.30° and an exposure time of 45 s per frame. The data acquisition and cell reduction were performed using SMART¹⁴, and further data reduction and integration was done with SAINTPLUS¹⁵ software packages. The face-indexing procedure was used to analytically correct for absorption, the empirical corrections for absorption were consequently applied using SADABS¹⁶ program. The structure solution and refinement was done by direct methods on the basis of full-matrix least-squares on F^2 using SHELXTL¹⁷ software package. All atoms were refined anisotropically. The setting of the cell (substructure only) was standardized with STRUCTURE TIDY program¹⁸.

Substructure Refinement

The initial cell reduction using SMART¹⁴ readily gave an orthorhombic *C*-centered lattice with parameters: $a = 4.1118(14) \text{ \AA}$, $b = 15.844(5) \text{ \AA}$ and $c = 3.9885(13) \text{ \AA}$. The systematic absence exceptions led to three possible space groups: *Cmc2₁*, *Cmcm* and *Ama2*, of which the centrosymmetric one was proven to be correct during the substructure refinement. A total of four atomic positions (all of multiplicity $4e$) were identified in the substructure of Tb_4FeGe_8 . The site population of Fe was found to be substantially lower than full, whilst the rest of the atoms were found with ideal occupancies. Free refinement of the occupancy parameter of Fe at $4e$ showed it to be nearly 0.25, and therefore in the final refinement cycle it was constrained to exactly $\frac{1}{4}$. Slightly shortened bond distances between Fe and Ge atoms ($2.147(3) \text{ \AA}$) also validate the partial occupancy detected for Fe atoms. Additionally, the anisotropic displacement parameters U^{11} and U^{33} (directed along the a and c -axis, respectively) of Ge(2) atoms are enlarged. The U^{33} parameter for the rest of atoms is on the contrary quite low.

The details of the data collection and substructure refinement are given in Table II.B.1. The fractional atomic coordinates, isotropic thermal displacement parameters and occupancies are presented in Table II.B.2. The interatomic distances up to $3.5 \text{ \AA}$ and selected bond angles are listed in Tables II.3.B and II.4.B, respectively. The anisotropic thermal displacement parameters are given in the Table II.B.5.

Table II.B.1. Crystal data and structure refinement for the substructure of Tb₄FeGe₈.

Empirical formula	Tb ₄ FeGe ₈
Formula weight (g/mol)	1272.25
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Cmcm</i> (#63)
Unit cell dimensions, (Å)	<i>a</i> = 4.1118(14) <i>b</i> = 15.844(5) <i>c</i> = 3.9885(13)
Volume (Å ³)	259.84(15)
Z	1
Density (calculated) (g/cm ³)	8.130
Absorption coefficient (mm ⁻¹)	50.850
F(000)	542
Crystal size (mm ³)	0.06 × 0.04 × 0.02
θ range for data collection (°)	2.57 to 28.36
Index ranges	-5 ≤ <i>h</i> ≤ 3, -18 ≤ <i>k</i> ≤ 13, -3 ≤ <i>l</i> ≤ 5
Reflections collected	502
Independent reflections	181 [R(int) = 0.0338]
Completeness to θ = 28.36°	85.4 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	181 / 0 / 18
Goodness-of-fit on F ²	1.115
Final R indices [I > 2σ(I)] [*]	R ₁ = 0.0363, wR ₂ = 0.0893
R indices (all data)	R ₁ = 0.0371, wR ₂ = 0.0898
Extinction coefficient	0.0096(14)
Largest diff. peak and hole (e/Å ³)	2.953 and -2.171

^{*} R₁ = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR₂ = $[\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table II.B.2. Atomic coordinates, equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and occupancies for the substructure of Tb_4FeGe_8 .

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*	Occ.
Tb	4 <i>c</i>	0	0.3966(1)	¼	7(1)	1
Ge(1)	4 <i>c</i>	0	0.0519(1)	¼	10(1)	1
Ge(2)	4 <i>c</i>	0	0.7525(2)	¼	25(1)	1
Fe	4 <i>c</i>	0	0.1972(5)	¼	4(2)	¼

* U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table II.B.3. Bond lengths [$\text{\AA}$] for the substructure of Tb_4FeGe_8 .

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
Tb-Ge(1)	2.9778(10)	× 4	Ge(1)-Ge(1)	2.586(3)	× 2
Tb-Ge(2)	3.073(2)	× 2	Ge(1)-Tb	2.9778(10)	× 4
Tb-Ge(2)	3.092(2)	× 2	Ge(2)-Fe	2.147(3)	× 2
Tb-Fe	3.159(8)	× 1	Ge(2)-Fe	2.235(3)	× 2
Tb-Ge(1)	3.2063(19)	× 2	Ge(2)-Ge(2)	2.8653(7)	× 4
Tb-Fe	3.228(4)	× 4	Fe-Ge(2)	2.147(3)	× 2
Ge(1)-Fe	2.302(9)	× 1	Fe-Ge(2)	2.235(3)	× 2

Table II.B.4. Selected bond angles [°] for the substructure of Tb₄FeGe₈.

Bond	Angle	Ge(1)-Tb-Fe	98.75(4)
Ge(1)-Tb-Ge(1)	148.24(9)	Ge(2)-Tb-Fe	39.76(9)
Ge(1)-Tb-Ge(1)	87.32(4)	Ge(2)-Tb-Fe	94.80(12)
Ge(1)-Tb-Ge(1)	84.09(3)	Ge(2)-Tb-Fe	41.34(9)
Ge(1)-Tb-Ge(2)	131.70(5)	Ge(2)-Tb-Fe	92.65(13)
Ge(1)-Tb-Ge(2)	75.02(4)	Fe-Tb-Fe	62.55(13)
Ge(2)-Tb-Ge(2)	83.99(7)	Ge(1)-Tb-Fe	139.65(10)
Ge(1)-Tb-Ge(2)	129.87(4)	Ge(1)-Tb-Fe	86.86(12)
Ge(1)-Tb-Ge(2)	77.12(5)	Fe-Ge(1)-Ge(1)	129.53(8)
Ge(2)-Tb-Ge(2)	55.390(17)	Ge(1)-Ge(1)-Ge(1)	100.94(16)
Ge(2)-Tb-Ge(2)	80.32(7)	Fe-Ge(2)-Fe	136.5(4)
Ge(1)-Tb-Fe	105.88(5)	Fe-Ge(2)-Fe	98.35(14)
Ge(2)-Tb-Fe	41.99(3)	Fe-Ge(2)-Fe	133.9(4)
Ge(1)-Tb-Ge(1)	49.26(5)	Fe-Ge(2)-Ge(2)	50.50(8)
Ge(1)-Tb-Ge(1)	103.46(3)	Fe-Ge(2)-Ge(2)	131.04(10)
Ge(2)-Tb-Ge(1)	177.89(3)	Fe-Ge(2)-Ge(2)	130.49(11)
Ge(2)-Tb-Ge(1)	98.13(6)	Fe-Ge(2)-Ge(2)	47.86(8)
Ge(2)-Tb-Ge(1)	125.90(2)	Ge(2)-Ge(2)-Ge(2)	176.8(2)
Fe-Tb-Ge(1)	140.12(3)	Ge(2)-Ge(2)-Ge(2)	88.21(3)
Ge(1)-Tb-Ge(1)	79.76(6)	Ge(2)-Ge(2)-Ge(2)	91.70(3)
Ge(1)-Tb-Fe	168.43(14)	Ge(2)-Fe-Ge(2)	81.65(14)
Ge(1)-Tb-Fe	43.33(14)	Ge(2)-Fe-Ge(1)	111.8(2)
Ge(1)-Tb-Fe	95.75(5)	Ge(2)-Fe-Ge(1)	113.1(2)

Table II.B.5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the substructure of Tb_4FeGe_8 .

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Tb	8(1)	9(1)	2(1)	0	0	0
Ge(1)	9(1)	20(1)	1(1)	0	0	0
Ge(2)	30(1)	10(2)	34(1)	0	0	0
Fe	5(3)	7(5)	0(3)	0	0	0

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

The structure of Tb_4FeGe_8 is related to a well-known CeNiSi_2 structure type¹⁹. Although the structure of the latter does not exhibit any deficiency on the corresponding Ni site, a number of isotypic to CeNiSi_2 compounds of general formula LnM_xTt_2 ¹ ($0 \leq x \leq 1$), where Ln is a lanthanide element, M is a transition metal, and Tt is a tetrel element (Ge and Sn) were reported. Most of these compounds are non-stoichiometric and exhibit a wide homogeneity range²⁰.

Superstructure Refinement

In Tb_4FeGe_8 , the deficiency on the Fe site, as well as the shortened Fe-Ge bond distances and unusual thermal displacement parameters may indicate the existence of a superstructure. Even though the supercell could not be found during the cell reduction²¹, further search for it was done with zone photographs. Interestingly, the X-ray zone photographs finally indicated the existence of the 4-fold supercell $(a^2+c^2)^{1/2} \times 2(a^2+c^2)^{1/2}$ where a and c are the parameters of the subcell. Given that the autoindexing algorithm of the SMART¹⁴ software package was unable to carry out the indexing of the supercell (possibly due to the lack of data) the cell transformation matrix was introduced to convert the subcell to the 4-fold supercell:

$$\begin{pmatrix} \mathbf{a} & \mathbf{b} & \mathbf{c} \end{pmatrix} \begin{pmatrix} 1 & 0 & -2 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix} = \begin{pmatrix} \mathbf{a} + \mathbf{c} & \mathbf{b} & -2\mathbf{a} + \mathbf{c} \end{pmatrix}$$

The direction and the magnitude of the supercell vectors were evidently obtained from the results of the X-ray zone photographs. The resultant supercell is monoclinic ($\beta = 91.724(4)^\circ$) with primitive Bravais lattice and unit cell parameters $a = 5.7315(11) \text{ \AA}$, $b = 15.842(3) \text{ \AA}$ and $c = 11.438(2) \text{ \AA}$. Due to the insufficient data supporting the superstructure, the systematic absences conditions were ambiguous and did not point to any space group. Only after tedious manual inspection of the intensity statistics, the $P2_1/n$ space group was chosen²². Subsequent refinement of the superstructure in the monoclinic

space group $P2_1/n$ led to a reasonable convergence factor of 0.0643 for $I > 2\sigma(I)$, although the Fourier difference map featured elevated (but not alarming) residual electron density peaks 5.424 and -6.753 $\text{e}\cdot\text{\AA}^{-3}$.

A total of fourteen general positions were found in the superstructure of Tb_4FeGe_8 . Four of those were assigned to Tb, eight for Ge and two to Fe atoms. Full occupancy was observed for all Tb and Ge sites, whereas the two Fe sites were found to be partially occupied (0.80 and 0.20 for Fe(1) and Fe(2), respectively) with a combined occupancy of 1. In the superstructure, all interatomic bond distances are regular, including Fe(1) atom with the exception of Fe(2) site, which exhibits short distances of 1.989(17) $\text{\AA}$, 2.130(19) $\text{\AA}$ and 2.181(17) $\text{\AA}$ to the neighboring Ge atoms. Owing to its low occupancy, the Fe(2) site that causes unreasonably close distances could be considered as a satellite peak, arising from either poor (weak) intensity data for the superstructure, or from the fact that a higher than 4-fold supercell may exist in Tb_4FeGe_8 .

For the details of the data collection and superstructure refinement, see Table II.B.6. Final atomic positions, isotropic thermal displacement parameters and occupancies are listed in Table II.B.7. Selected bond distances up to 3.5 $\text{\AA}$ are given in Table II.B.8, and anisotropic displacement parameters are given in Table II.B.8. Further studies of the supercell in Tb_4FeGe_8 were continued by carrying out electron diffraction experiments on single crystals.

Table II.B.6. Crystal data and structure refinement for the superstructure of Tb₄FeGe₈.

Empirical formula	Tb ₄ FeGe ₈
Formula weight	1272.25
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (#14)
Unit cell dimensions (Å)	<i>a</i> = 5.7315(11) <i>b</i> = 15.842(3) <i>β</i> = 91.724(4)° <i>c</i> = 11.438(2) Å
Volume (Å ³)	1038.1(4)
Z	4
Density (calculated) (g/cm ³)	8.141
Absorption coefficient (mm ⁻¹)	50.913
F(000)	2168
Crystal size (mm ³)	0.06 x 0.04 x 0.02
θ range for data collection (deg.)	6.29 to 32.79
Index ranges	-8 ≤ <i>h</i> ≤ 7, -17 ≤ <i>k</i> ≤ 23, -17 ≤ <i>l</i> ≤ 17
Reflections collected	5694
Independent reflections	3367 [R(int) = 0.0448]
Completeness to θ = 32.79°	87.4 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3367 / 0 / 118
Goodness-of-fit on F ²	0.851
Final R indices [I > 2σ(I)] [*]	R ₁ = 0.0643, wR ₂ = 0.1735
R indices (all data)	R ₁ = 0.1457, wR ₂ = 0.2159
Extinction coefficient	0.00051(6)
Largest diff. peak and hole (e·Å ⁻³)	5.424 and -6.753

^{*} $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table II.B.7. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the superstructure of Tb_4FeGe_8 .

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*	Occupancy
Tb(1)	4 <i>e</i>	0.8756(5)	0.1029(1)	0.1884(2)	5(1)	1.0
Tb(2)	4 <i>e</i>	0.3744(4)	0.1011(1)	0.4342(1)	5(1)	1.0
Tb(3)	4 <i>e</i>	0.3757(4)	0.1025(1)	-0.0591(1)	6(1)	1.0
Tb(4)	4 <i>e</i>	0.1250(4)	-0.1069(1)	0.3140(2)	6(1)	1.0
Ge(1)	4 <i>e</i>	0.3746(10)	0.0464(2)	0.1881(4)	6(1)	1.0
Ge(2)	4 <i>e</i>	0.8758(10)	0.0543(3)	-0.0615(3)	8(1)	1.0
Ge(3)	4 <i>e</i>	0.6260(11)	-0.0572(2)	0.3134(4)	8(1)	1.0
Ge(4)	4 <i>e</i>	0.8743(10)	0.0507(3)	0.4356(3)	9(1)	1.0
Ge(5)	4 <i>e</i>	0.0946(6)	0.2487(3)	0.0532(2)	10(1)	1.0
Ge(6)	4 <i>e</i>	0.6497(6)	0.2534(3)	0.0548(3)	12(1)	1.0
Ge(7)	4 <i>e</i>	0.1082(7)	0.2541(2)	0.3221(3)	13(1)	1.0
Ge(8)	4 <i>e</i>	0.6492(7)	0.2498(2)	0.3246(3)	16(1)	1.0
Fe(1)	4 <i>e</i>	0.3753(10)	0.1977(2)	0.1872(5)	2(1)	0.8
Fe(2)	4 <i>e</i>	0.8730(30)	0.1971(10)	0.4392(15)	6(3)	0.2

* U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table II.B.8. Bond lengths [$\text{\AA}$] for the superstructure of Tb_4FeGe_8 .

Bond	Distance	Bond	Distance	Tb(4)-Fe(2)	3.163(18)
Tb(1)-Ge(4)	2.946(4)	Tb(2)-Fe(2)	3.235(18)	Tb(4)-Ge(1)	3.184(4)
Tb(1)-Ge(2)	2.961(4)	Tb(3)-Ge(1)	2.963(5)	Tb(4)-Ge(4)	3.218(4)
Tb(1)-Ge(1)	2.997(7)	Tb(3)-Ge(2)	2.964(7)	Ge(1)-Fe(1)	2.397(4)
Tb(1)-Ge(1)	3.008(7)	Tb(3)-Ge(2)	2.967(7)	Ge(1)-Ge(2)	2.564(8)
Tb(1)-Ge(5)	3.070(4)	Tb(3)-Ge(8)	2.971(4)	Ge(1)-Ge(3)	2.589(7)
Tb(1)-Ge(6)	3.095(5)	Tb(3)-Ge(7)	2.983(4)	Ge(6)-Fe(2)	2.181(17)
Tb(1)-Ge(8)	3.106(4)	Tb(3)-Ge(3)	2.996(5)	Ge(6)-Fe(1)	2.385(7)
Tb(1)-Ge(7)	3.119(4)	Tb(3)-Ge(5)	3.120(5)	Ge(6)-Ge(5)	2.552(3)
Tb(1)-Fe(2)	3.234(17)	Tb(3)-Ge(6)	3.123(5)	Ge(6)-Ge(7)	2.668(3)
Tb(1)-Fe(1)	3.234(6)	Tb(3)-Fe(2)	3.175(16)	Ge(3)-Ge(4)	2.604(8)
Tb(1)-Ge(2)	3.235(4)	Tb(3)-Fe(1)	3.195(5)	Ge(4)-Fe(2)	2.320(17)
Tb(1)-Fe(1)	3.236(6)	Tb(3)-Ge(1)	3.149(4)	Ge(4)-Ge(4)	2.587(9)
Tb(2)-Ge(1)	2.946(4)	Tb(3)-Ge(2)	3.205(4)	Ge(5)-Fe(2)	2.259(19)
Tb(2)-Ge(3)	2.969(5)	Tb(4)-Ge(3)	2.966(7)	Ge(5)-Fe(1)	2.333(6)
Tb(2)-Ge(4)	2.975(7)	Tb(4)-Ge(3)	2.978(7)	Ge(5)-Ge(8)	2.643(3)
Tb(2)-Ge(6)	2.996(5)	Tb(4)-Ge(4)	2.999(4)	Ge(2)-Ge(2)	2.616(9)
Tb(2)-Ge(5)	3.000(5)	Tb(4)-Ge(2)	3.005(4)	Ge(7)-Fe(2)	2.130(19)
Tb(2)-Ge(8)	3.117(4)	Tb(4)-Fe(1)	3.096(3)	Ge(7)-Fe(1)	2.380(7)
Tb(2)-Ge(7)	3.118(4)	Tb(4)-Ge(7)	3.123(4)	Ge(7)-Ge(8)	2.632(4)
Tb(2)-Ge(4)	3.187(4)	Tb(4)-Ge(6)	3.126(5)	Ge(8)-Fe(2)	1.989(17)
Tb(2)-Fe(1)	3.213(5)	Tb(4)-Ge(5)	3.158(4)	Ge(8)-Fe(1)	2.339(6)
Tb(2)-Ge(3)	3.226(4)	Tb(4)-Ge(8)	3.160(4)	Fe(2)-Ge(6)	2.181(17)

Table II.B.9. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for the superstructure of Tb_4FeGe_8 .

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Tb(1)	6(1)	7(1)	2(1)	0(1)	0(1)	0(1)
Tb(2)	7(1)	7(1)	2(1)	0(1)	0(1)	0(1)
Tb(3)	6(1)	8(1)	3(1)	0(1)	0(1)	-1(1)
Tb(4)	6(1)	8(1)	4(1)	1(1)	0(1)	0(1)
Ge(1)	6(1)	9(1)	3(1)	0(2)	-1(1)	1(2)
Ge(2)	7(2)	15(2)	2(2)	-1(1)	1(1)	-2(2)
Ge(3)	8(1)	13(1)	4(1)	0(2)	-1(1)	-1(3)
Ge(4)	5(2)	19(2)	4(2)	0(1)	-2(1)	0(2)
Ge(5)	6(1)	12(2)	14(1)	-2(1)	0(1)	-2(2)
Ge(6)	4(1)	14(2)	17(1)	0(2)	1(1)	1(2)
Ge(7)	18(1)	9(1)	12(1)	-2(2)	-7(1)	1(2)
Ge(8)	24(2)	13(1)	11(1)	-4(1)	13(1)	-4(2)

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Transmission Electron Microscopy and Electron Diffraction

The transmission electron microscopy (TEM) studies were performed on JEOL 100CX microscope. The electron beam was generated from the CeB₆ filament at accelerating voltage 120 kV. Both the imaging mode and the selected area electron diffraction (SAED) were used. The samples were stable under the impact of the electron beam.

Sample preparation: large, plate-like single crystals of Tb₄FeGe₈, normally over 10 mm² in area and up to 500 μ m in thickness were selected. Due to the plate-like habit of the crystals, only the [010] zone axis could be observed at zero tilt. The samples were hand-polished with sandpaper of subsequently increasing grit (1000 – 1500) to a thickness of approximately 200 – 300 μ m. A core drill was then used to cut out a circular shape specimen 3 mm in diameter suitable for use in the TEM holder. As-prepared samples were electrochemically thinned using Tenupol-3 twin-jet polishing unit equipped with an infrared detector. The electropolishing experiment was conducted at the temperature range from –35°C to –40°C with applied potential 30 – 35V using a four-component acidic electrolyte²³. During the thinning procedure, the sample is electrolytically removed from the solid phase into the solution, and the bowl-shape specimen starts to form, see Figure II.B.2A. As a result, a gradient in thickness appears. The thinning process is continues until the formation of the hole (zero thickness) in the center and a thin area around it.

Though the resultant hole is larger than usual ($800\text{ }\mu\text{m} \times 1000\text{ }\mu\text{m}$) and of irregular shape, as evident from the TEM image given in Figure II.B.2B, the thin area is perfectly suitable for TEM observation, with an electron lucent area that is extremely large (on the order of thousands of square micrometers).

A.

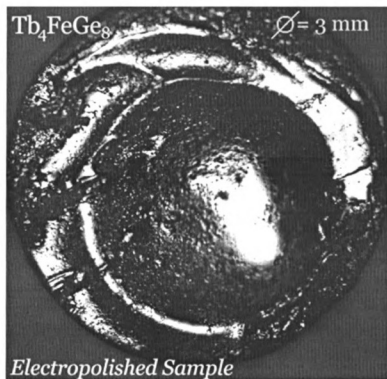


Figure II.B.2. (A) An image of the electropolished sample of Tb₄FeGe₈. The outside diameter of the pellet is 3 mm.

B.

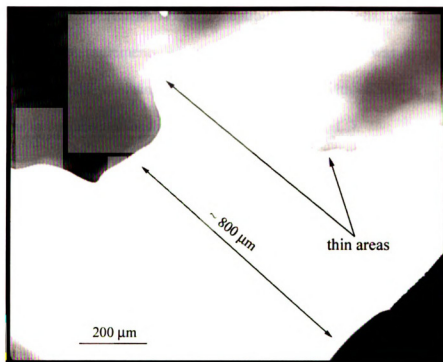


Figure II.B.2. (B) Low magnification bright-field TEM image (negative) of the hole and the thin area around it of an electropolished sample of Tb_4FeGe_8 .

Magnetic Measurements

Magnetic susceptibility studies were carried out on single crystal and polycrystalline samples of Tb_4FeGe_8 . *Sample preparation:* single crystals of Tb_4FeGe_8 were selected manually and polished with sandpaper of increasing fineness (1000 – 1500) to remove possible surface impurities.

The measurements were carried out in the temperature range 2 – 350 K with an applied magnetic field 500 Gauss. Measurements of magnetization as a function of field (up to ± 5 T) were also performed. Both susceptibility and magnetization data acquisition included isotropic measurements where the pulverized sample was used, as well as anisotropic, for which the single crystal was placed with the *b*-axis parallel or perpendicular to the direction of the external magnetic field (H_{ex}).

3. Results and Discussion

Reaction Chemistry

Large single crystals Tb_4FeGe_8 phase could be grown from molten Ga solutions, see Figure II.B.1. This ability of the Ga flux to enable crystal growth is thus quite remarkable, considering that compounds of this type (rare-earth transition metal tetrelides) are usually produced as micro- or polycrystalline materials. As a matter of fact, it has been shown for the first time for Tb_4FeGe_8 that large single crystals of a representative of $CeNiSi_2$ structure type could be grown from molten Ga melts.

It is also interesting to see the pathways of the phase formation which occur in the quaternary Tb-Fe-Ga-Ge system under flux conditions. As was mentioned above, the prolonged stages of heating and cooling give rise mainly to Tb_4FeGe_8 . At the same time, shorter temperature profiles result in the formation of the quaternary $Tb_4FeGa_{12-x}Ge_x$ ¹⁰ phase. It appears that at a certain point of the reaction time phase separation takes place,

so that at shorter periods the quaternary $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ phase is produced, while at extended times the Ga-free phase Tb_4FeGe_8 along with the Fe-free phase $\text{Tb}_2\text{Ga}_2\text{Ge}_5$ ²⁴ are found. The latter two thus could be considered as thermodynamically stable compounds in contrast to $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ that could be regarded as only kinetically stable.

Crystal Structure

(a) Substructure Description

The structure of Tb_4FeGe_8 viewed along the c -axis is shown in Figure II.B.3. No bonds were drawn to Tb atoms to emphasize an open three-dimensional $[\text{Fe}_{1/4}\text{Ge}_2]$ that features large channels. The channels stretch along the c -axis, and each of them accommodates two Tb atoms in the voids. If broken down into fragments, the $[\text{Fe}_{1/4}\text{Ge}_2]$ framework could be thought as constructed of Ge(1) zigzag chains and $[\text{Fe}_{1/4}\text{Ge}(2)]$ puckered layer. The Ge(1) zigzag chains extend infinitely along the c -axis with the plane of the chain being parallel to the bc plane, see Figure II.B.4A. In the chain, the Ge(1)-Ge(1) distance and the Ge(1)-Ge(1)-Ge(1) angle are 2.586(3) Å and 100.94(16)°, respectively, which is close to those observed, for example, in the related LaNiGe_2 ²⁷ compound (2.5630(14) Å and 111.48(9)°).

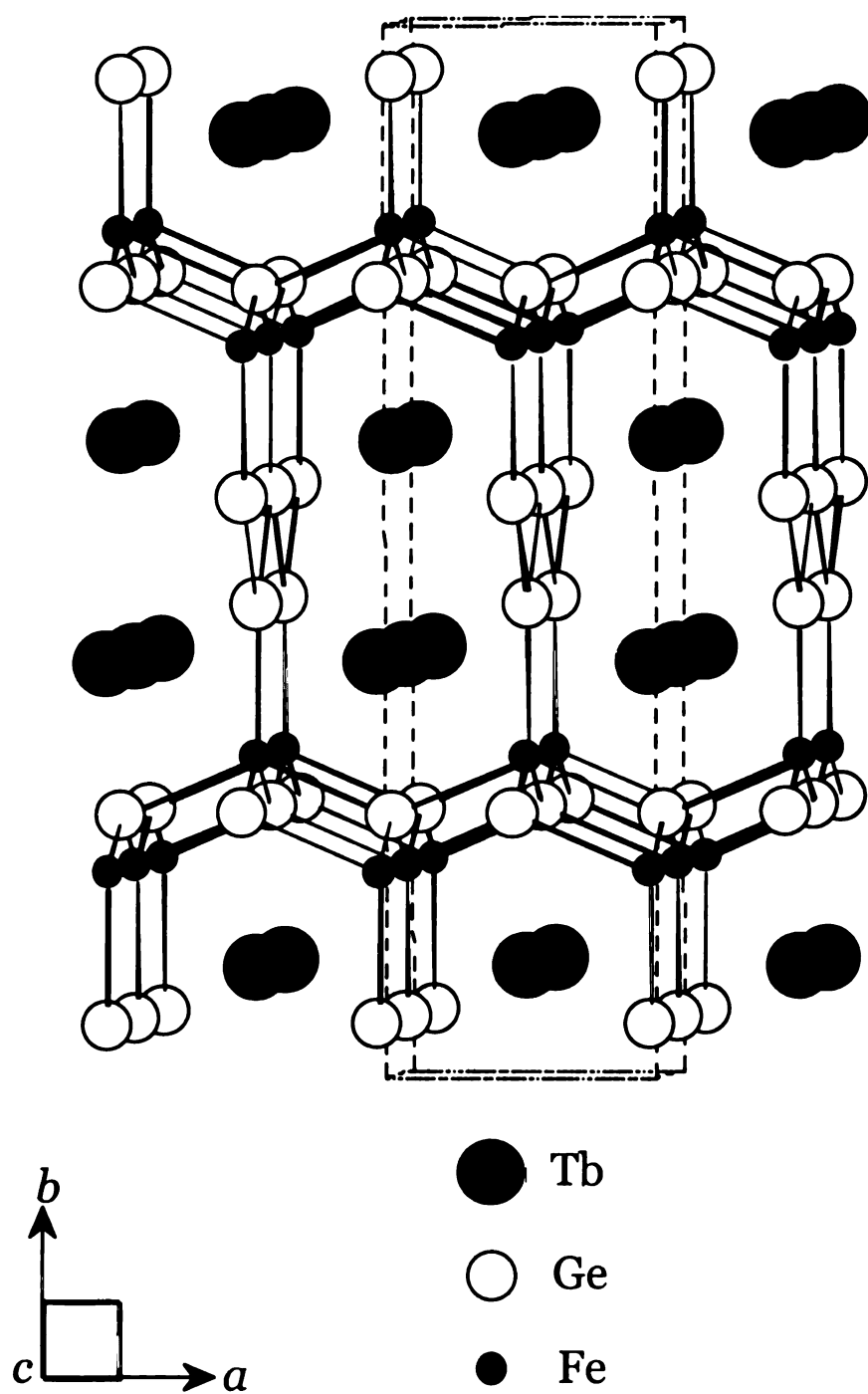


Figure II.B.3. Projection of the sub-structure (*Cmcm*) of Tb_4FeGe_8 onto *ab*-plane. Larger grey spheres represent Tb atoms, open circles correspond to Ge atoms and filled smaller black spheres are Fe atoms. For clarity, the bonds to Tb atoms are not drawn.

A.

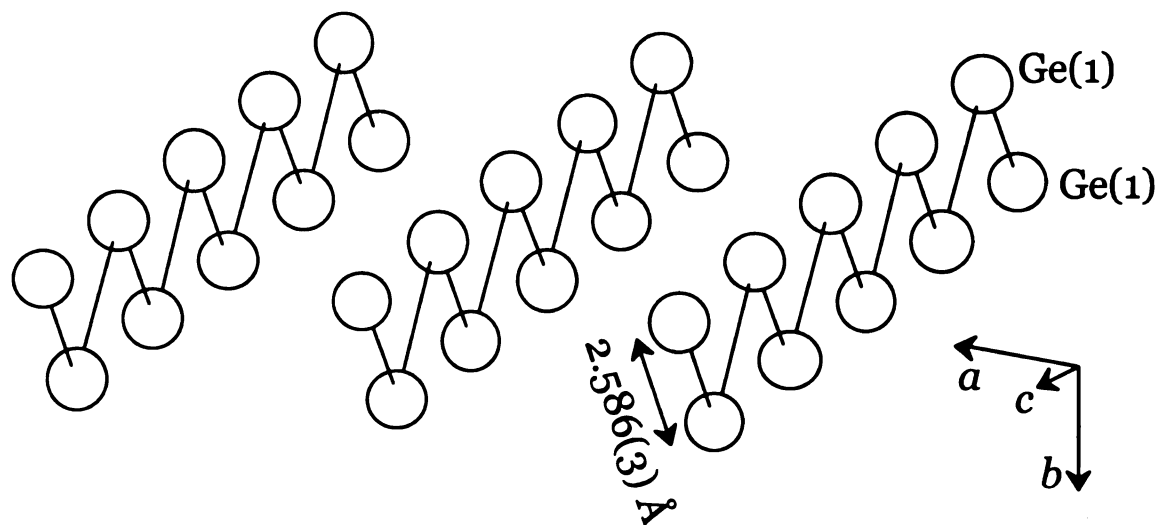
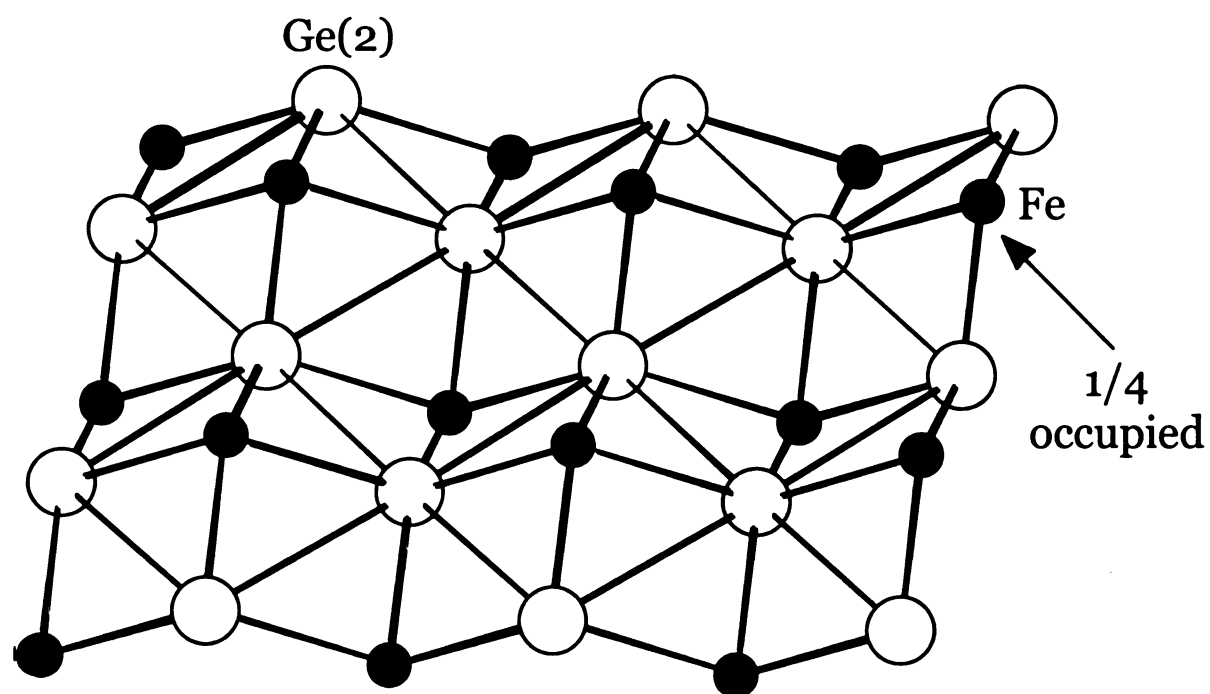


Figure II.B.4. (A) The Ge(1) zigzag chains. The direction of chain propagation coincides with the *c*-axis. The Ge(1)-Ge(1) bond length is uniform throughout the chain and equals 2.586(3) Å and the Ge(1)-Ge(1)-Ge(1) angle is 100.94(16)°.

The $[\text{Fe}_{1/4}\text{Ge}(2)_2]$ slab, shown in Figure II.B.4B, contains a monolayer of Ge(2) atoms arranged with tetragonal symmetry. The Ge(2)-Ge(2) bond distance in this layer is quite large, 2.8653(7) Å, substantially exceeding the sum of covalent radii²⁵ (2.44 Å) and the Ge-Ge distance in diamond-like Ge structure²⁶ (2.45 Å). However, when compared to similar Ge(2)-Ge(2) bonding contacts in LaNiGe_2 ²⁷ (3.020 Å), this distance is significantly shortened (~ 5%). Above and below the Ge(2) square net, in puckered manner located are the Fe atoms (just like the Si and Ni atoms in the structure of $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ²⁸ described previously in Chapter II, Part A). In Tb_4FeGe_8 , the Fe atoms are partially occupied (25%) which obviously compensates for unrealistically shortened Fe-Ge(2) bond distances of 2.147(3) Å that occur in this layer. The next closest Fe-Ge(2) contact is at 2.235(3) Å, and it is again considerably shorter than corresponding Ni-Ge(2) bonds in LaNiGe_2 ²⁷ (2.4055(9) Å and 2.4360(10) Å).

The puckered arrangement, combining the square lattice of Ge (tetrelide) atoms and capping of transition metal element, is a very common structural fragment for intermetallic tetrelides. It has been observed in a large number of compounds of CeNiSi_2 ^{19,29} structure type, for instance, as well as in quaternary gallium germanides like REMGa_3Ge ³⁰, $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ ³⁰ and $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ ³¹. It should be noted that in these three quaternary compounds, the capping M site is partially occupied (50%), similar to what is observed in Tb_4FeGe_8 .

B.



$$\text{Ge(2)}-\text{Ge(2)} = 2.8653(7) \text{ \AA}$$

Figure II.B.4. (B) A fragment of the $[\text{Fe}_{1/4}\text{Ge(2)}_2]$ puckered layer. The Ge(2) atoms form a square lattice with Ge-Ge distances of $2.8653(7) \text{ \AA}$. The hollows of the net are capped with Fe atoms. The Fe position is only $1/4$ occupied.

The local coordination of the Tb atoms within 3.5 Å, and Fe and Ge atoms within 3.0 Å is depicted in Figure II.B.5. The local environment of Fe atoms include five Ge atoms in the form of a square pyramid with the base made of four Ge(2) atoms and the apex of Ge(1) atom. The bond angles between Ge and central Fe are 81.65(14)° for Ge(2)-Fe-Ge(2), and 111.8(2)° and 113.1(2)° for Ge(2)-Fe-Ge(1). The Ge(1) is 7-coordinate, and it is bonded to four Tb atoms that form a plane (Ge(1) is located above the Tb plane). Three additional contacts of Ge(1) atoms are in the shape of the distorted triangle Ge(1)₂Fe; the plane of the triangle is perpendicular to the plane of Tb atoms. The angles within Ge(1)₂Fe triangle are 129.53(8)° and 100.94(16)° for the Fe-Ge(1)-Ge(1) and Ge(1)-Ge(1)-Ge(1) bonds, respectively. The Ge(2) atoms are 8-coordinate (if partial occupancy on Fe is not taken into account), they are bonded to four Fe atoms in the shape of a severely distorted tetrahedron (Fe-Ge(2)-Fe angles are 136.5(4)°, 98.35(14)° and 133.9(4)°) and to four additional Ge(2) atoms in form of a slightly distorted square (Ge(2)-Ge(2)-Ge(2) angles are 88.21(3)° and 91.70(3)°). The Tb atoms are in a cage of 15 Ge and Fe atoms (again, considering that all Fe atoms are present). The bonding includes four Ge(2) atoms, four Fe atoms and six Ge(1) atoms. The bond distances and angles could be found in Tables II.B.3 and II.B.4.

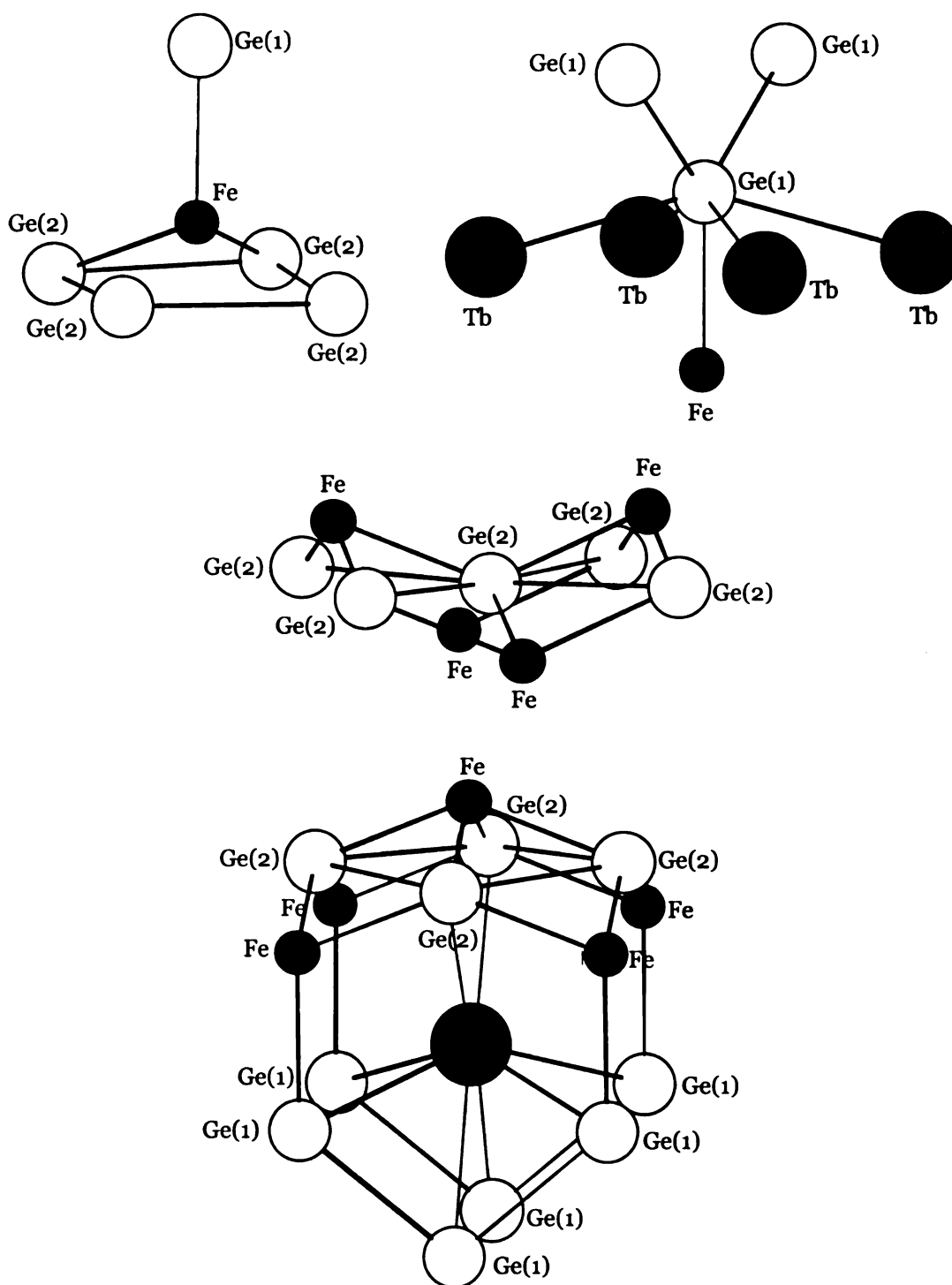
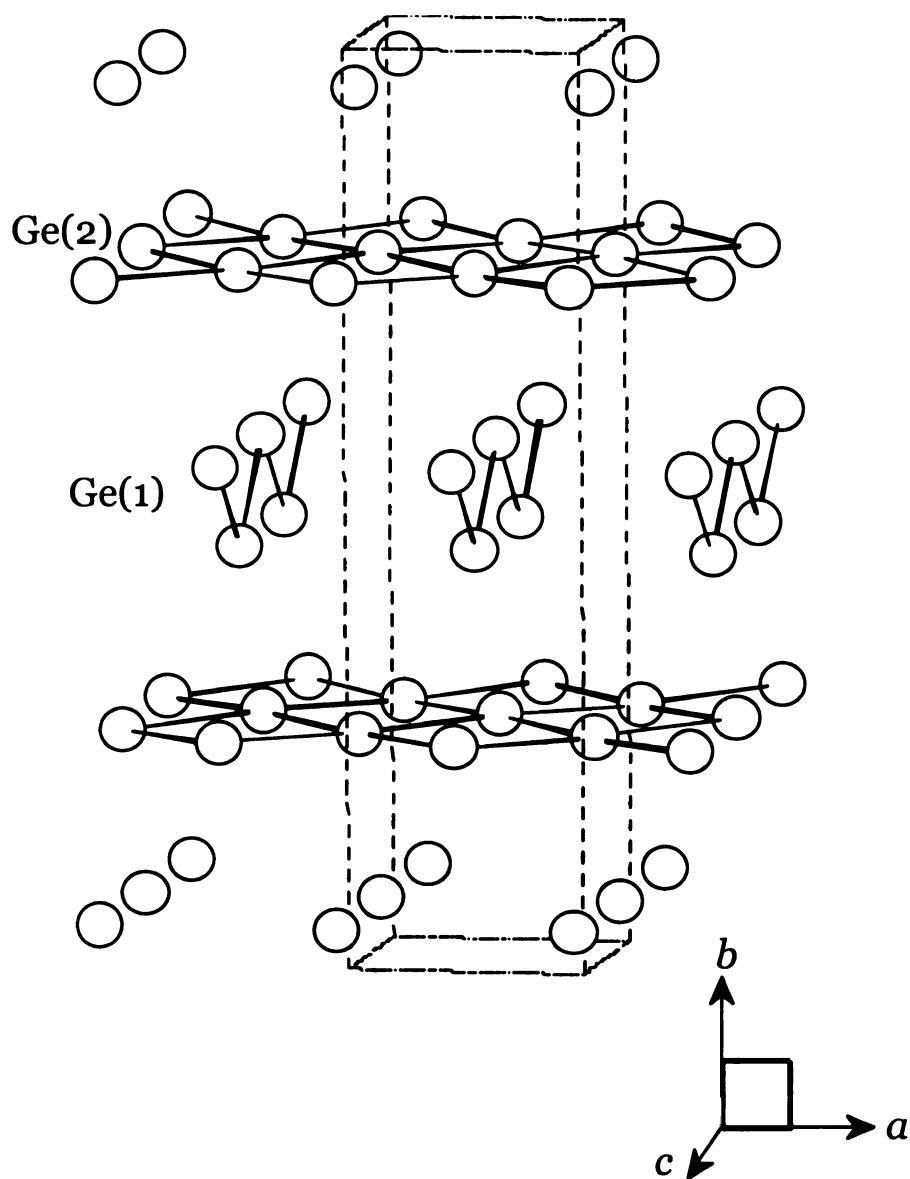


Figure II.B.5. Near-neighbor coordination environment of Fe and Ge atoms within 3.0 Å. Ge atoms are shown in open circles and Fe atoms are filled black spheres. The local coordination of Tb atom (large grey spheres) is shown up to 3.5 Å.

Because of the Fe disorder and the associated distortion in the bond distances, it is difficult to judge the connectivity between Fe and Ge in the $[\text{Fe}_{1/4}\text{Ge}_2]$ sublattice. Therefore, only bonding between ordered Ge and Tb atoms will be considered. First, consider the Ge-only substructural unit shown in Figure II.B.6. In it, two distinct motifs of two- and one-dimensional character could be easily recognized. The strongest Ge-Ge interaction ($2.586(3) \text{ \AA}$), comparable to the sum of the covalent radii of Ge ($2.44 \text{ \AA}$), takes place in the 1D chains. The bonding within the chain is thus of significant covalent character. The next closest Ge-Ge contact of $2.8653(7) \text{ \AA}$ occurs within the 2D plane and could be considered weakly bonding. The distance separating the 1D and 2D fragments is even larger, $3.685 \text{ \AA}$, which could only be thought of as weak Van-der-Waals interaction.

Second, consider the Tb-only environment within $6.0 \text{ \AA}$, shown in Figure II.B.7A. The Tb-Tb closest bond contacts occur at $3.835 \text{ \AA}$, $3.988 \text{ \AA}$ and $4.112 \text{ \AA}$. These distances are quite close to the sum of single-bonded metallic radii $3.55 \text{ \AA}$ for Tb^{32} (CN = 12) and therefore contain a certain amount of covalent character. The next nearest Tb-Tb contact is at $5.459 \text{ \AA}$, which could only be regarded as weakly bonding or even non-bonding. The Tb-only framework could also be considered as consisting of Tb_6 trigonal prisms condensed via edge-sharing into 2D layers that are infinitely extending in the *ac*-plane, see Figure II.B.7B. These Tb slabs are then alternating along the *b*-axis and separated from each other by a considerable distance of $\sim 5.5 \text{ \AA}$.



1D zig-zag chain:	$\text{Ge(1)-Ge(1)} = 2.586(3) \text{ \AA}$
2D square net:	$\text{Ge(2)-Ge(2)} = 2.8653(7) \text{ \AA}$
Between 1D and 2D:	$\text{Ge(1)-Ge(2)} > 3.685 \text{ \AA}$

Figure II.B.6. The Ge-only substructural unit. The one dimensional (1D) chains are formed by Ge(1) atoms. The planes are constructed of Ge(2) atoms arranged with tetragonal symmetry. Unit cell is drawn in dashed lines.

Oppositely, the Tb-Ge bonding is very strong. The nearest Tb-Ge contact is at 2.9778(9) Å (Ge(1), zigzag chain) which is even shorter than the sum of single-bonded metallic radii of Tb and Ge (2.993 Å). The next closest Tb-Ge distances are 3.073(2) Å and 3.092(2) Å (Ge(2), square plane) and those are also strongly bonding.

A.

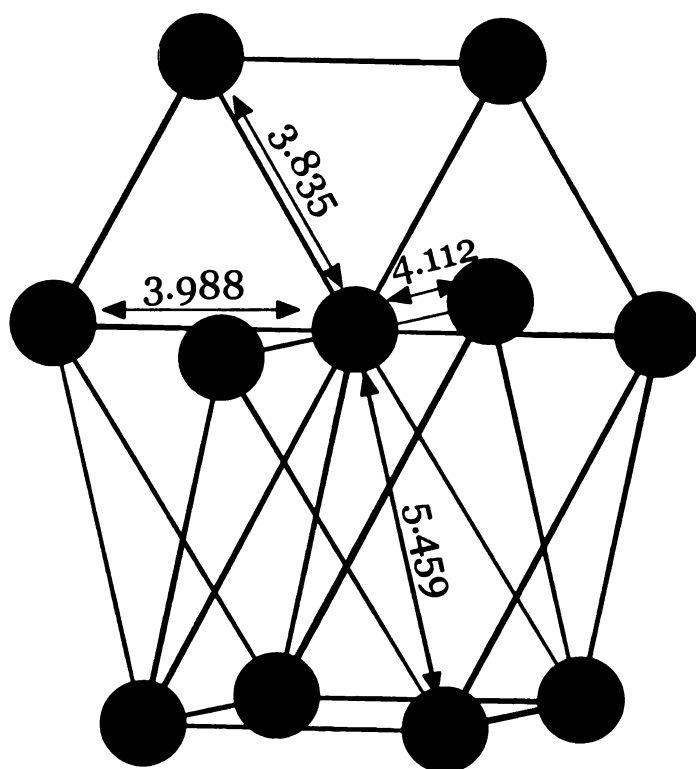


Figure II.B.7. (A) Local Tb-Tb environment. The Tb atoms are shown within 6 Å from the central Tb.

B.

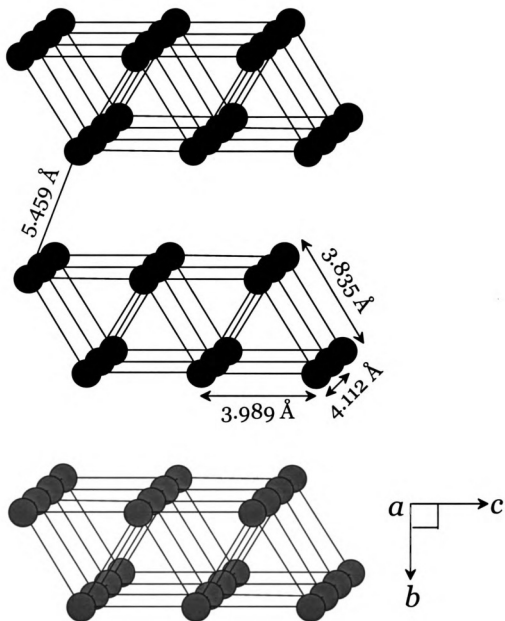


Figure II.B.7. (B) The Tb-only network. The $[\text{Tb}_6]$ trigonal prisms are condensed into 2D layer. The layers are stacked along the *b*-axis and separated from each other by the distance of $\sim 5.5 \text{ \AA}$

Due to the complexity of bonding interactions occurring in intermetallic compounds, assigning the charge distribution in Tb_4FeGe_8 may not be a trivial task. However, because Tb atoms are the most electropositive species, they are likely to donate all of their three valence electrons to the $[\text{Fe}_{1/4}\text{Ge}_2]$ framework. The results of magnetic measurements are consistent with Tb^{3+} oxidation state (discussed in the next section “*Magnetic Properties*”). The resulting charge distribution could be written as $\text{Tb}^{3+}[\text{Fe}_{1/4}\text{Ge}_2]^{3-}$. Next, it is interesting how the 3– charge is divided within the $[\text{Fe}_{1/4}\text{Ge}_2]$ network itself. On account of relative electronegativities, the Fe atoms are less electronegative than Ge (1.83 versus 2.01 on Pauling electronegativity scale) and therefore the latter could be regarded as the most reduced. The connectivity arguments seem to be consistent with these electronegativity considerations, as the closest bonding contacts in the structure involve Ge atoms. Likewise, the Fe atoms are expected to be in a reduced state with a fully filled $3d^{10}$ electron configuration; this assumption is also supported with the magnetic data.

Interestingly, among two crystallographically distinct Ge atoms Ge(1) in the zigzag chains and Ge(2) in the square lattice, the distribution of charge may not be equal. Thus, in the structures containing the Si or Ge zigzag chain such as RENiSi_3 ¹², LaNiGe_2 ²⁷ and DyGe_3 ³³, it was found that the tetrelide (Tt) atoms within the chain were found to be more reduced than other Tt species present in the structure. On the basis of both connectivity considerations and theoretical electronic structure calculations, the bonding interactions involving the Tt atoms of zigzag chain were shown to be very strong with the calculated formal charge on the $\text{Tt}_{\text{zigzag}}$ being close to 1–. The same tendency is clearly observed in Tb_4FeGe_8 , suggesting the following charge distribution scheme: the Fe and

Ge atoms are in the reduced state with Ge(1) atoms from the zigzag chain bearing more negative charge than the corresponding Ge(2) atoms from the square net, and the Tb atoms are in the oxidized state with formal charge 3+.

(b) Superstructure Description

The first indication of the existing superstructure for Tb₄FeGe₈ was found in the X-ray [010] zone photograph taken on the CCD diffractometer with the exposure time 3000 seconds, see Figure II.B.8. In this photograph, only four reflections with indices ± 2 0 ± 1 (marked by arrows) correspond to a subcell. The remaining reflections belong to a supercell and were indexed in the monoclinic primitive lattice with dimensions $(a^2+c^2)^{1/2} \times b \times 2(a^2+c^2)^{1/2}$ where a , b and c are the substructure parameters. No superstructure reflections were seen along the b^* -axis in the $hk0$ or $0kl$ zone photographs indicating that there is no modulation along the b -axis.

It is not surprising that the supercell reflections could not be observed during the data collection since their intensity is very weak even in zone photographs taken at high exposure times. Nevertheless, the attempt was made to use the information on the supercell found in zone photographs and apply it in the subsequent X-ray superstructure refinement. Evidently, due to the lack of strong intensity data for the superstructure, the overall superstructure solution and refinement was not the best. However, it is good enough to get substantial insights in understanding the substructure – superstructure relationship.

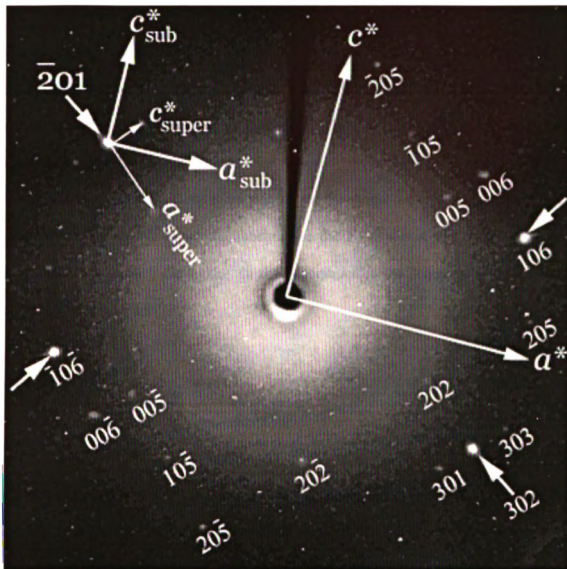


Figure 11.B.8. $[h0l]$ X-ray diffraction zone photograph for Tb_4FeGe_8 taken with the exposure time 3000 seconds. The Bragg spots are indexed in the $(a^2+c^2)^{1/2} \times b \times 2(a^2+c^2)^{1/2}$ super-cell. The reflections of the subcell $(2\ 0\ 1, -2\ 0\ -1, -2\ 0\ 1, 2\ 0\ -1)$ are pointed out with arrows. The corresponding vectors of the reciprocal subcell and supercell are denoted as a^*_{sub} , c^*_{sub} and a^*_{super} , c^*_{super} , respectively. The supercell modulation takes place along the diagonal of the subcell.

The drawing of the 4-fold superstructure is depicted in Figure II.B.9A. For the sake of consistency, all atoms are depicted in the same manner as in the substructure. In order to relate it better to the substructure, it is useful to look along the [110] diagonal and down the *bc*-plane, see Figures II.B.9A and B. The substructure drawing (viewed along the diagonal) is given for reference. It could be clearly seen from Figure II.B.9B that in the superstructure (left) a fraction of the Fe atoms are missing compare to the substructure (right). While for the substructure the Fe atoms in this projection appear above and below every Ge square, in the superstructure the sequence is different and could be represented as

++ --	++ --	++ --	
-----			<i>etc.</i>
-- ++	-- ++	-- ++	

where the dashed line represents the Ge plane, the “+” and “–” are respectively present and absent Fe atoms. At the same time, the appearance of the Ge atoms in the zigzag chain, as well as Tb atoms is the same for both sub and superstructure. Thus, the dissimilarity of the sub- and superstructures lies mainly in the Fe-Ge puckered layer. For this reason, it is worthwhile to consider the [Fe-Ge] substructural unit separately in more detail.

A.

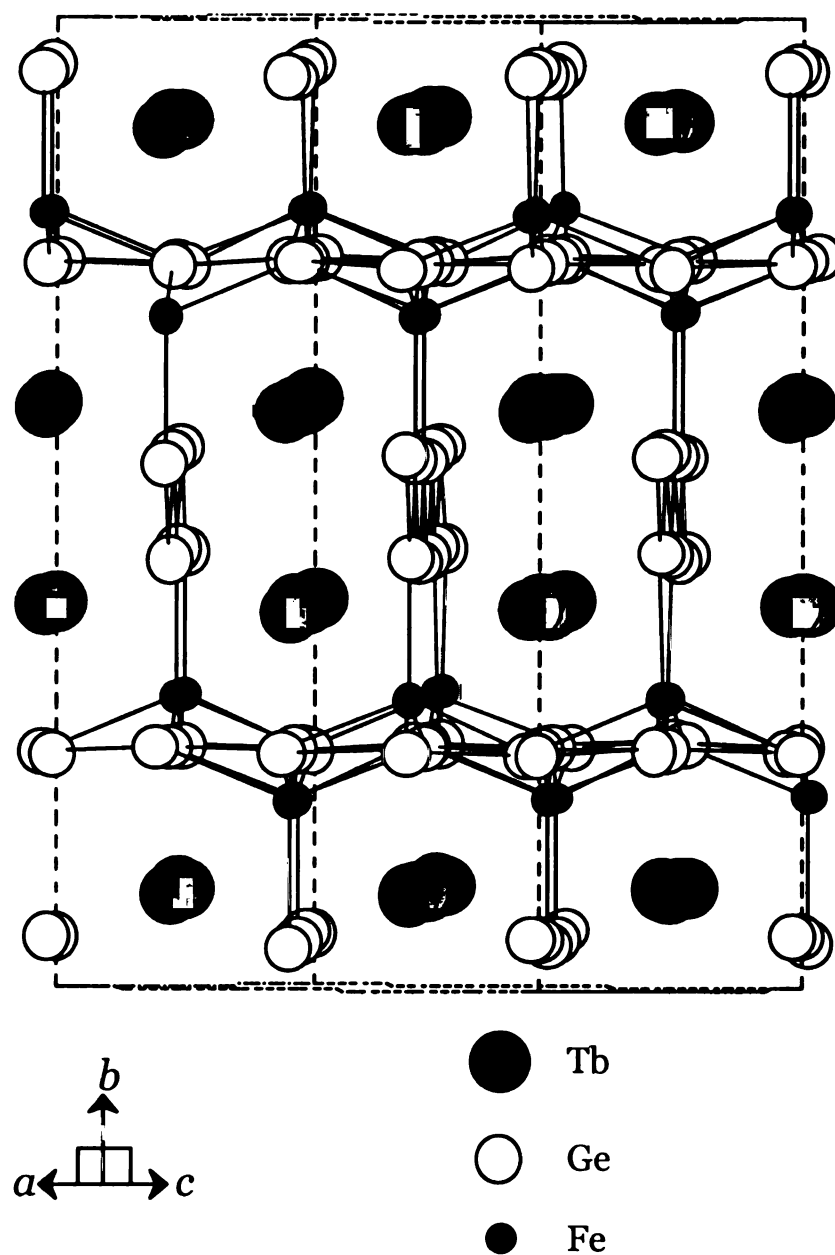


Figure II.B.9. (A) The superstructure of Tb_4FeGe_8 ($P2_1/n$) viewed along the $[101]$ direction. The atoms are depicted in the same manner as for the sub-structure.

B.

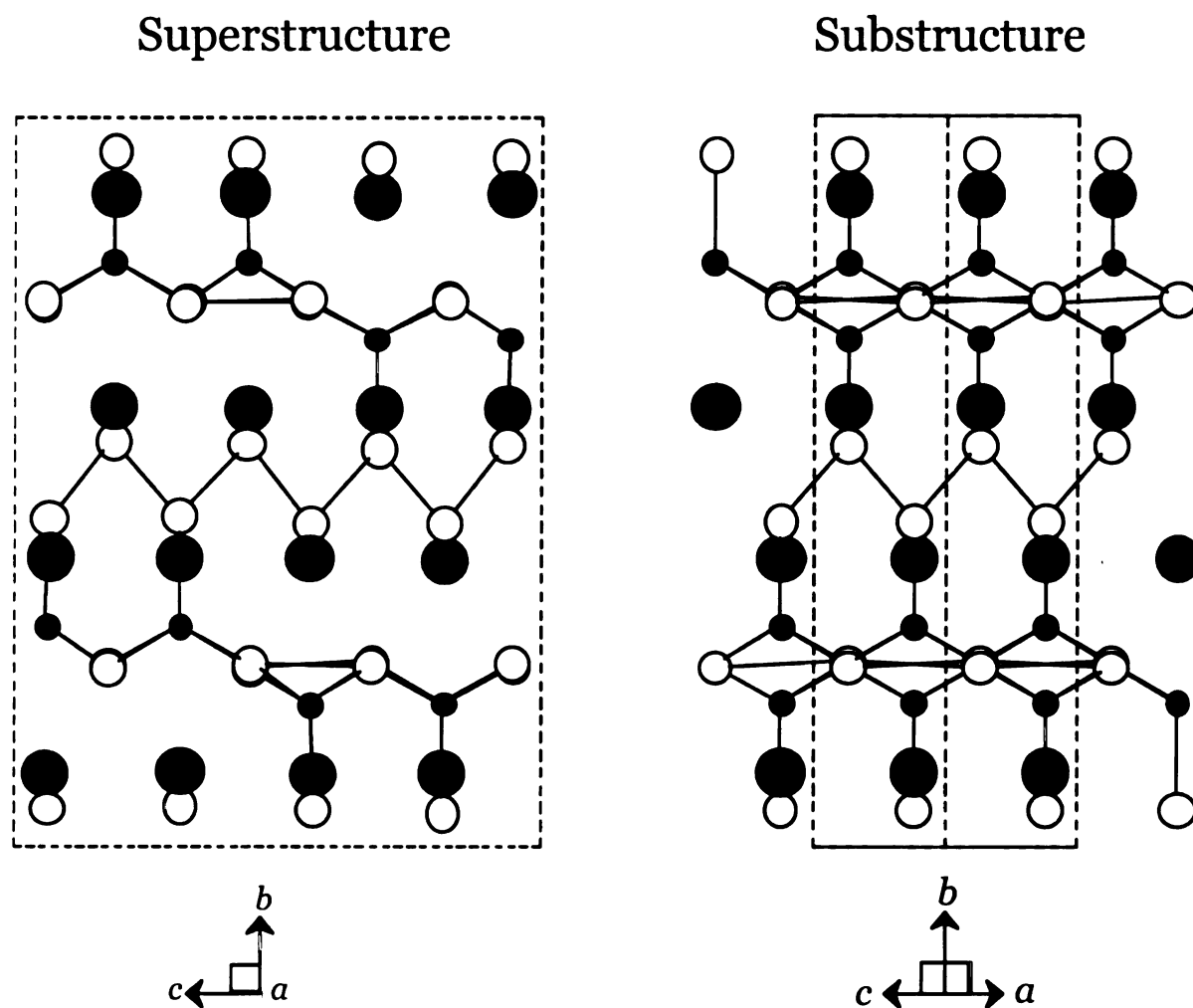


Figure II.B.9. (B) Side-by-side representation of the superstructure (left) and a substructure (right). The superstructure is viewed along the a -axis, and the substructure is depicted along the diagonal $[101]$ for comparative purposes.

The [Fe-Ge] puckered layer, viewed approximately along the *b*-axis, is depicted in Figure II.B.10. Four crystallographically distinct Ge atoms (Ge(5) – Ge(8)) participate in the construction of this layer. The first four Ge atoms (Ge(1) – Ge(4)) are, correspondingly, part of the Ge-only zigzag chains. Two additional Fe atoms (Fe(1) and Fe(2), with the numbering for Fe is given in bold) take part in the formation of the [Fe-Ge] layer. It could be clearly seen from Figure II.B.10A that the filling of the hollows of what used to be a Ge square net is less dense than that of a substructure (compare to Figure II.B.4B).

In the superstructure, two hollows capped with Fe atoms from above and below alternate with two completely uncapped hollows. Note that the total occupancy of Fe(1) and Fe(2) equals 1 (see Table II.B.7). Next, if the 2D Ge sublattice is considered alone, it can be seen that the distortion of the Ge square lattice is extremely severe. That is, if we were to connect the Ge atoms with the bond distances up to 3.0 Å, chains of the Ge atoms are produced, see for example Figure II.B.10B. The distances within chains range from 2.552(3) Å to 2.668(3) Å, shorter than that in the Ge-only square net in the substructure. The distances between the chains, however, is large and span a range of 3.076 Å to 3.182 Å. The average Ge-Ge distance in the Ge-only plane of the superstructure is 2.868 Å, which is very close to that found for the Ge(2)-Ge(2) distances in the substructure (2.8653(7) Å).

A.

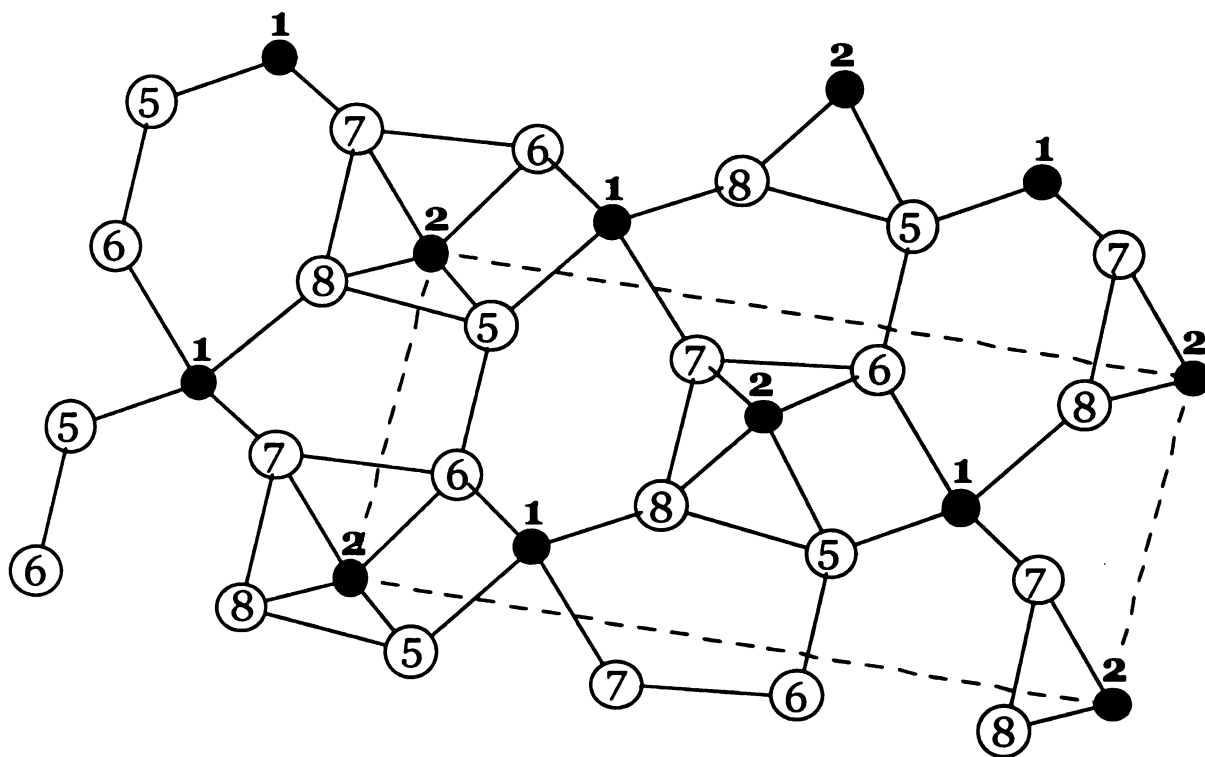


Figure II.B.10. (A) A single Fe-Ge puckered layer found in the superstructure of Tb_4FeGe_8 viewed approximately down the b -axis. For the Ge atoms the numbering of the corresponding crystallographic site is enclosed in the circle. For Fe atoms the numbering is given on the side of the atom in bold. The unit cell is shown in dashed line.

B.

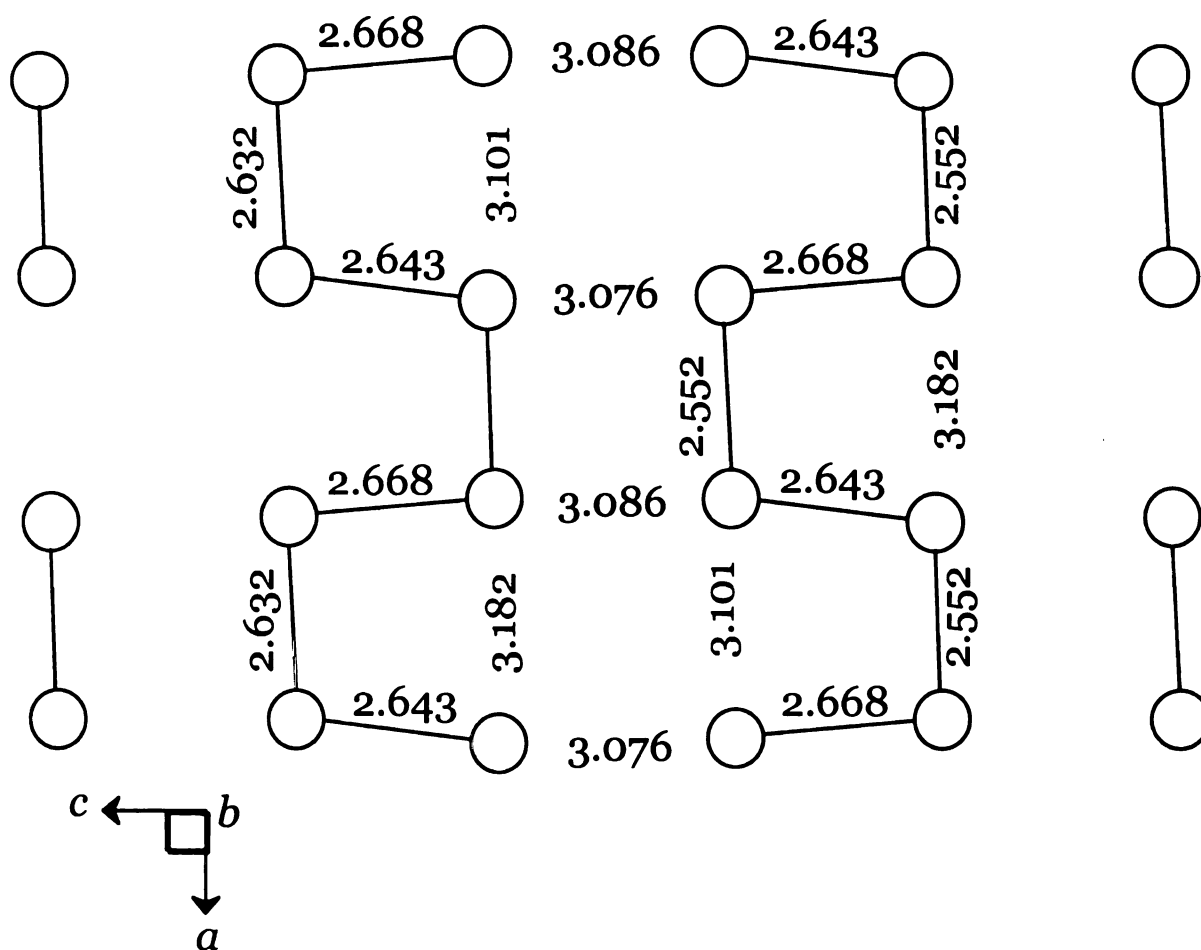


Figure II.B.10. (B) Ge-only 2D layer (square net in substructure) of the superstructure featuring bond distances between Ge atoms. The Ge-Ge bonds were drawn within the cut-off distance of 3 Å.

Second, the Ge zigzag chains are distorted from the original Ge(1) chain of the substructure conforming to the changes brought about by the distorted Fe-Ge net. In the superstructure, the Ge-Ge distances within the chain are not equal any longer. Relative shortening (Ge(1)-Ge(2) = 2.564(8) Å) and elongation of the Ge-Ge bond (up to 2.616(9) Å) occur in places where the capping Fe atom is absent or present, respectively. The average Ge-Ge distance in the 1D chain of the superstructure is 2.592(Å), and it is slightly stretched compared to that of the substructure (2.586(3) Å).

The supercell in Tb₄FeGe₈ can now be understood as follows. The superstructure is formed due to distortion of the square Ge net bringing about the differentiation between the Ge-Ge bond distances and producing the set of short Ge-Ge bonds and long non-bonding interactions. Note that the thermal displacement parameters of the Ge atoms within the 2D plane have substantially improved in the superstructure refinement (see Table II.B.9) compared to those of the substructure (see Table II.B.5). The reason for this type of distortion most likely originates in the electronic structure of this compound. Conversely, at present, the information provided by the X-ray diffraction data solely is not sufficient to draw a definitive conclusion on what the exact origin of the distortion is. To explore this further, theoretical electronic structure band structure calculations are highly desirable. This work is currently in progress.

The substructure, in its turn, demonstrates once again¹¹ only the average picture of what the real structure is. In other words, the picture given by the substructure with equally spaced Ge atoms in the Ge-only square net and disturbed thermal displacement parameters corresponds to an average representation of the Ge-only layer with short and long bonds observed in the superstructure.

The partial occupancy on the Fe(1) and Fe(2) atoms, and the short bond distances generated between the Fe(2) atoms and Ge atoms, could possibly indicate the presence of even higher order superstructure. Interestingly, electron diffraction does show a higher order superstructure for Tb_4FeGe_8 , see Figure II.B.11A. The selected area electron diffraction pattern taken along the [010] zone axis on a single crystal sample of Tb_4FeGe_8 shows the presence of an eight-fold superstructure. The modulation occurs, as in the previous case, along the diagonal of the tetragonal cell, however, a' and c' supercell parameters are equally large: $2(a^2+c^2)^{1/2} \times b \times 2(a^2+c^2)^{1/2}$. The corresponding thin area of the single crystal shown in Figure II.B.11B does not contain any irregularities. Because of the lack of reflections in the X-ray data corresponding to a supercell, it would be practically impossible to reliably refine the 8-fold superstructure from the X-ray intensity data. As was shown above, however, the 4-fold superstructure provides a lot of new information that is completely masked up in the substructure. Therefore, the refined 4-fold superstructure is a good compromise between the misleadingly averaged substructure and the correct 8-fold superstructure in Tb_4FeGe_8 .

A.

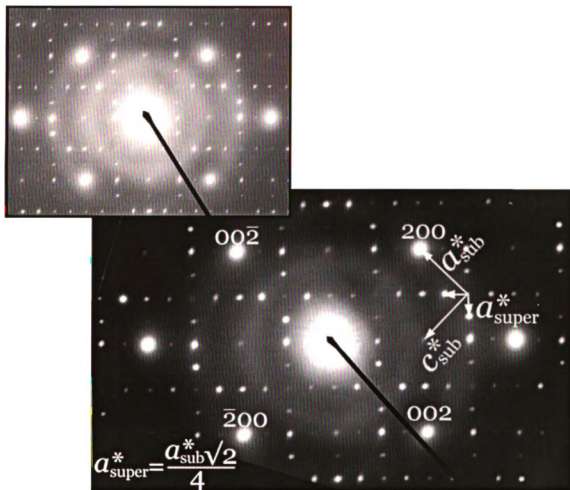


Figure II.B.11. (A) The [010] zone axis selected area electron diffraction pattern and (b) the TEM image of the corresponding thin area of the single crystal of Tb_4FeGe_8 . Selected subcell reflections are indexed. The corresponding vectors of the reciprocal subcell and supercell are denoted as a_{sub}^* , c_{sub}^* and a_{super}^* , c_{super}^* , respectively. The approximate relationship between the reciprocal supercell and subcell vectors is shown in the left lower corner.

B.

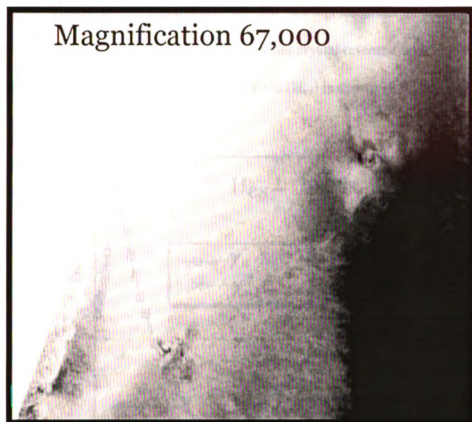


Figure II.B.11. (B) The [010] zone axis bright-field TEM image (negative) of the thin area of the single crystal of Tb₄FeGe₈. The magnification $\times 67 \cdot 10^3$ was used.

Magnetic Properties

Temperature dependence of the molar magnetic susceptibility ($\chi_m^\perp$) and reciprocal molar susceptibility ($\chi_m^\perp$)⁻¹ for the crystal oriented with crystallographic *b*-axis perpendicular to the external magnetic field (H_{ex}) is shown in Figure II.B.12A.

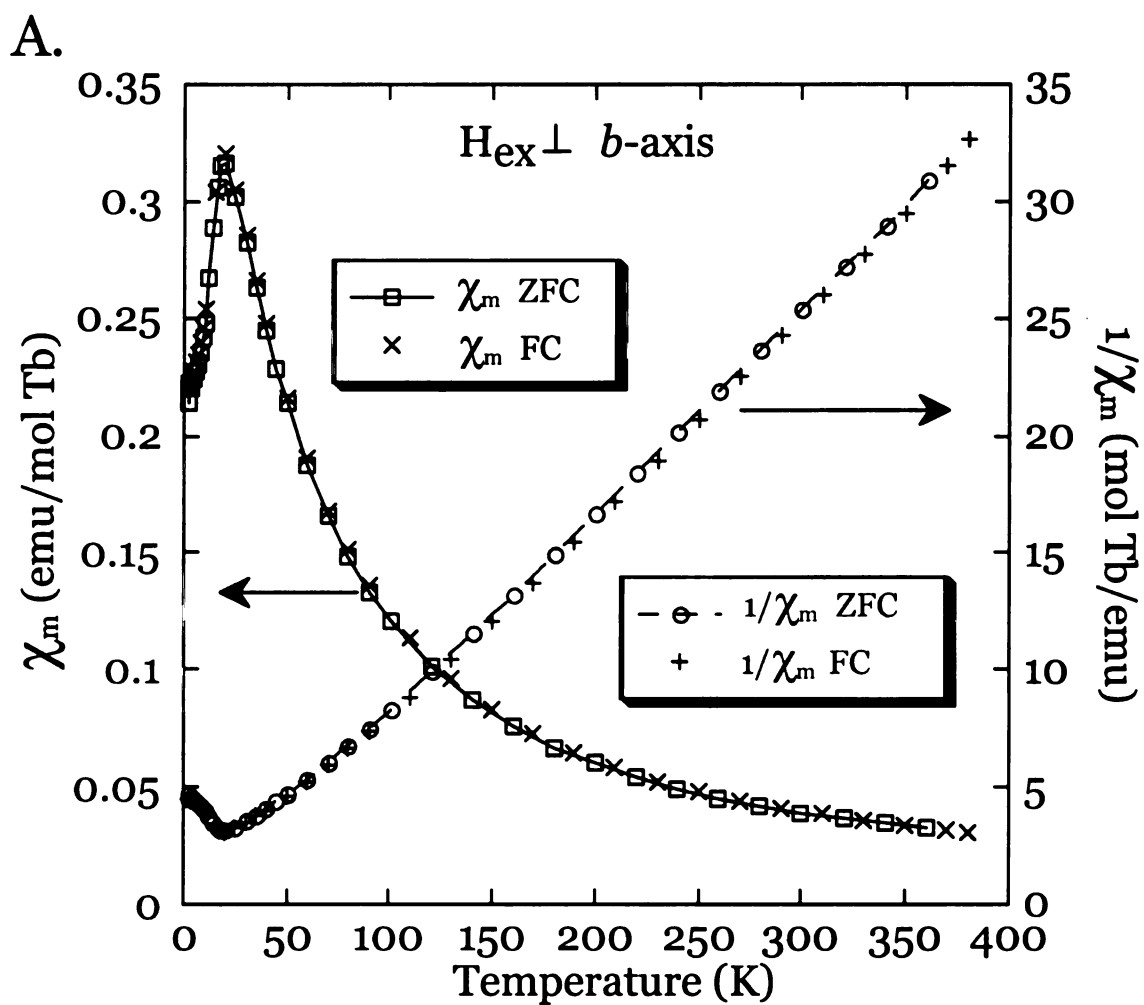


Figure II.B.12. (A) Temperature dependence of molar magnetic susceptibility and inverse susceptibility of Tb_4FeGe_8 single crystal sample oriented with *b*-axis perpendicular to the external magnetic field (H_{ex}). The susceptibility was measured with an applied magnetic field 500 Gauss and given per mole of Tb.

The low temperature region of $\chi_m^\perp$ is characterized with the maximum centered at $T_{\max}$ ~ 19 K, as can be seen in Figure II.B.12B. The system thus undergoes an antiferromagnetic transition below $T_{\max}$. For the determination of the Néel temperature (T_N), a series of susceptibility measurements were done in the fields 100 – 2000 G. The result is shown in Figure II.B.13.

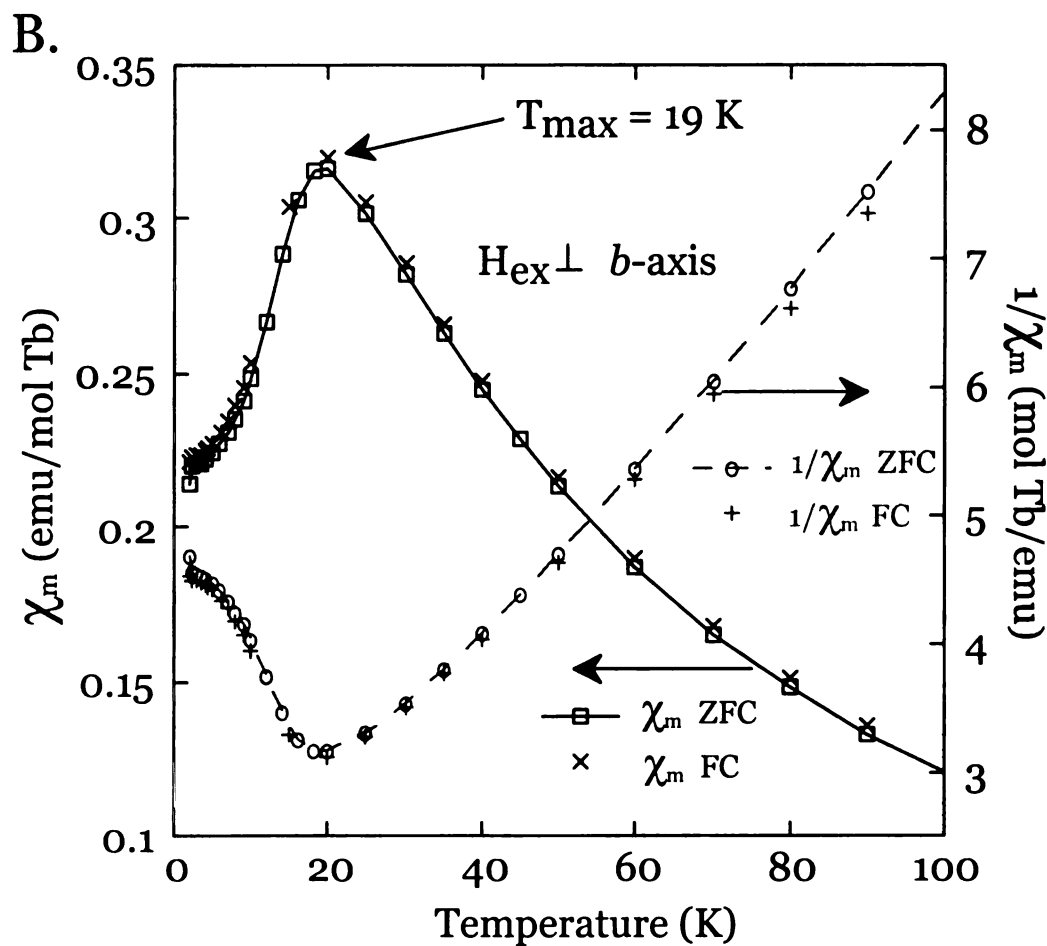


Figure II.B.12. (B) Temperature dependence of molar magnetic susceptibility and inverse susceptibility of a Tb_4FeGe_8 single crystal in the proximity of an antiferromagnetic transition temperature.

The value of $T_N = 20.4$ K was then determined by extrapolation of the line passing through $T_{\max}$ at various fields to the zero field.

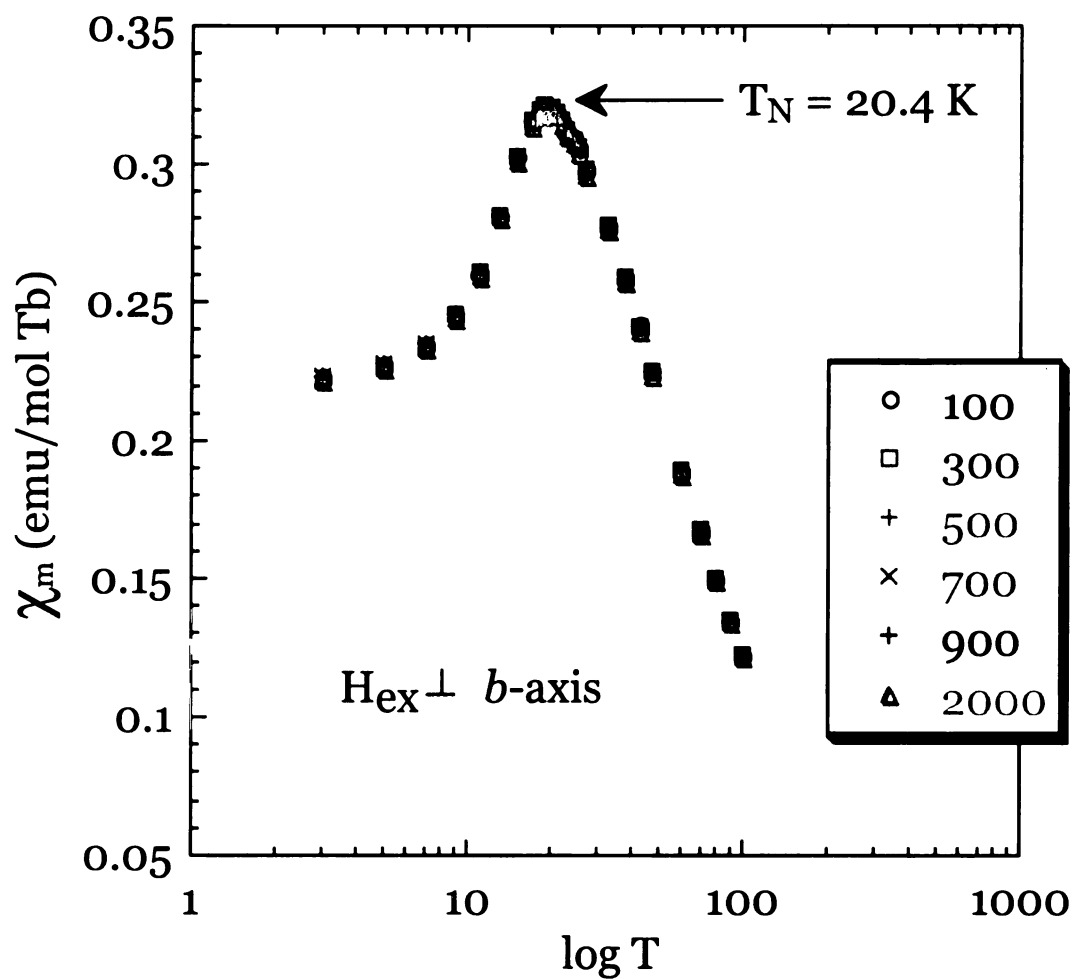


Figure II.B.13. Isofield plots of the molar magnetic susceptibility vs temperature for single crystal of Tb_4FeGe_8 measured with b -axis perpendicular to H_{ex} . The applied fields were varied from 100 to 2000 Gauss.

As the temperature increases above 50 K, the inverse magnetic susceptibility increases linearly with temperature, see Figure II.B.12C. The intercept with the temperature axis gives the value of Weiss constant ($\theta^\perp$), which has a small positive value of +3.8 K. The behavior of $(\chi_m^\perp)^{-1}$ vs T obeys the Curie law. The effective magnetic moment ($\mu_{\text{eff}}^\perp$) obtained from the slope of the line is 9.68 BM, and it is very close to the value for the free Tb^{3+} ion (9.72 BM)³⁴.

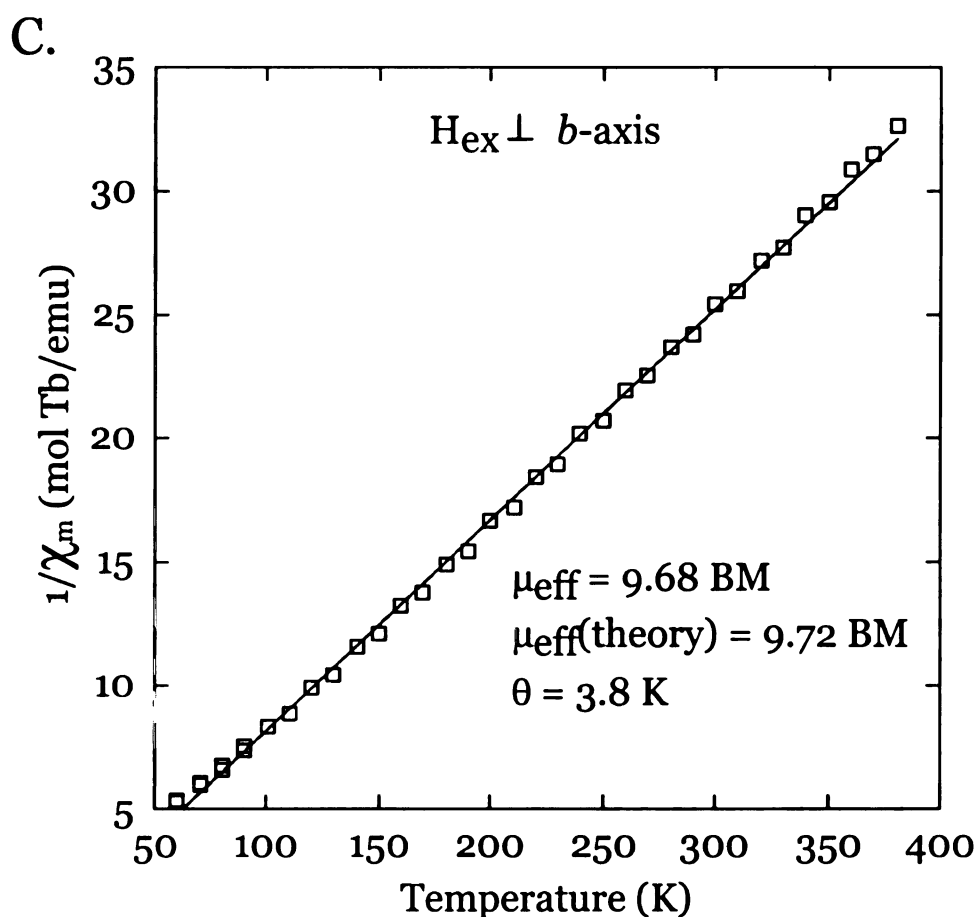


Figure II.B.12. (C) Temperature dependence of the inverse magnetic susceptibility measured on the single crystal sample of Tb_4FeGe_8 oriented with b -axis perpendicular to H_{ex} .

Interestingly, in the parallel orientation, where the b -axis is directed parallel to H_{ex} , the magnetic response is quite different, see Figure II.B.14A. First of all, no T_{max} is observed up to the temperature of 2.5 K. Instead, the $\chi_m^{\parallel}$ continues to rise, as could be seen in the expanded area of the low temperature region in Figure II.B.14B.

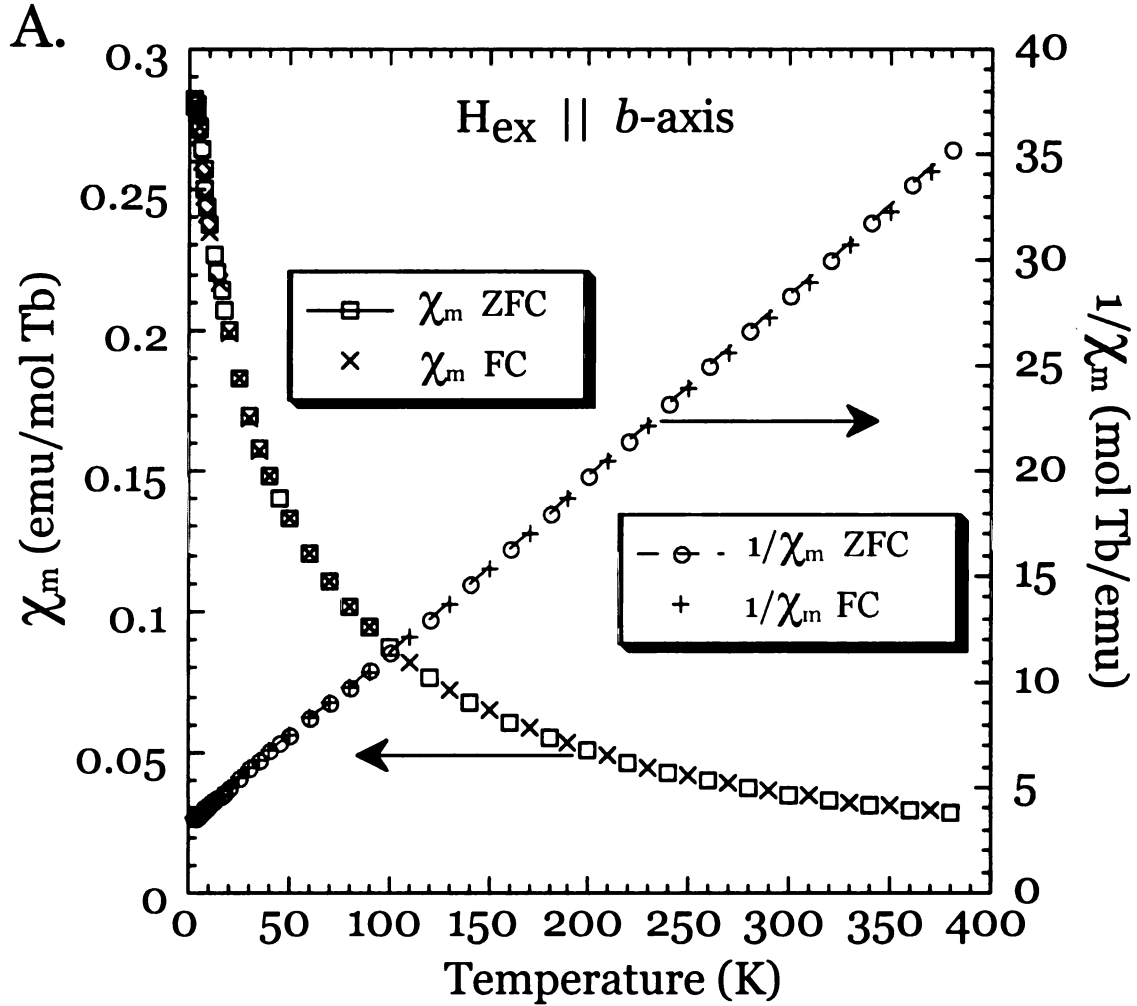


Figure II.B.14. (A) Temperature dependence of molar magnetic susceptibility and inverse susceptibility of Tb_4FeGe_8 single crystal sample oriented with b -axis parallel to the external magnetic field (H_{ex}). The susceptibility was measured with an applied magnetic field 500 Gauss and given per mole of Tb.

The pronounced maximum that was observed at ~ 20 K in the $\chi_m^\perp - T$ plot, is revealed only as a weak shoulder in the $(\chi_m^\parallel)^{-1} - T$ graph. Moreover, the onset of an additional upturn on $\chi_m - T$ plot appears at approximately 2.5 K. Thus, in the parallel orientation, possibly two types of short range ordering compete, so that the effect brought about by the antiferromagnetic ordering below 20 K (lowering of the net moment due to antiparallel pairing of magnetic moments) is compensated by another opposite interaction that tends to increase the net moment of the system. This “second type” interaction between the moments could be a ferro-, ferri- or an antiferromagnetic. The qualitative measure of the nature of moment-moment interaction could be found in the sign of the Weiss constant (θ). Conventionally, for isolated moments with no means of “communication”, θ is considered to be zero. For the interaction involving a ferromagnetic coupling, the θ is normally positive, and for an antiferromagnetic coupling it is usually negative. Thus, the “second type” interaction between the moments is, judging by the negative sign of $\theta^\parallel$ (-36 K), most likely of an antiferromagnetic nature. This antiferromagnetic ordering transition takes place at very low temperatures, below $T'_{\max} \sim 2.5$ K, indicating that the strength of this interaction is much weaker than the one that gives rise to an antiferromagnetic ordering at $T_{\max} \sim 20$ K. This is because the input of less amount of thermal energy ($k_B T_{\max}$, where k_B is a Boltzman constant) is sufficient to disorient (randomize) the magnetic moments.

The presence of two competing interactions brings an interesting issue of establishing the magnetic species on which the moments responsible for the transition at $T'_{\max}$ and $T_{\max}$ are centered. The answer to this question is very straightforward and could

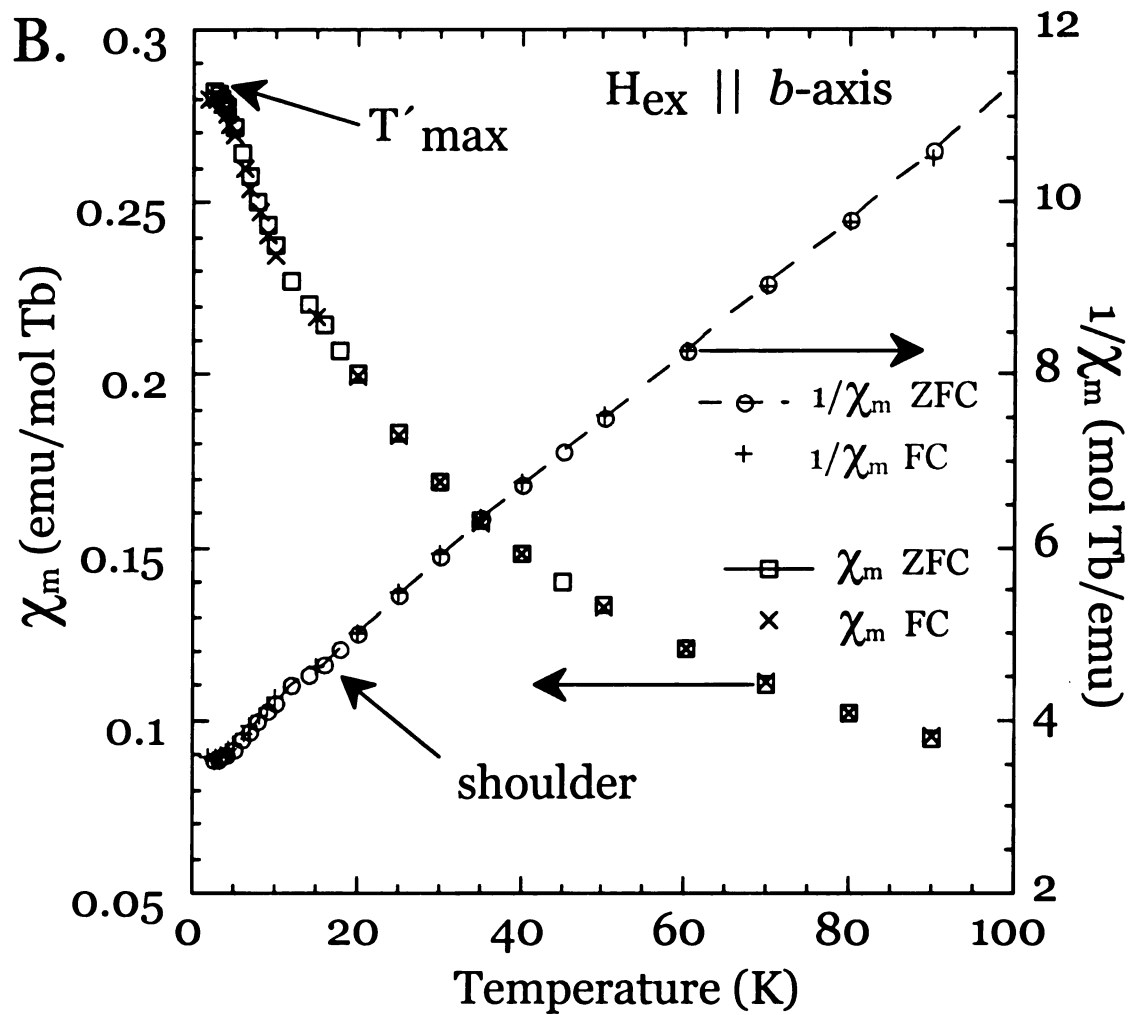


Figure II.B.14. (B) Low temperature region of the temperature dependence of molar magnetic susceptibility and inverse susceptibility of Tb_4FeGe_8 single crystal oriented with b -axis parallel to H_{ex} .

be found in the values of μ_{eff} . As it is for $\mu_{\text{eff}}^{\perp}$, the experimental values of $\mu_{\text{eff}}^{\parallel}$ calculated from the slope of $(\chi_m^{\parallel})^{-1}$, see Figure II.B.14C, is in excellent agreement with the theoretical μ_{eff} for the free Tb^{3+} ion given by the formula $\mu_{\text{eff}} = g_J[J(J+1)]^{1/2}$. Thus, in both cases the magnetic centers are the Tb^{3+} ions, whereas the Fe atoms are in a non-magnetic state. Similar non-magnetic character of the Fe atoms was observed in the intermetallic compounds $\text{RE}_4\text{Fe}_{2+x}\text{Al}_{7-x}\text{Si}_8$ ³⁵ (RE = Ce, Pr, Nd, Sm) and $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ ¹⁰.

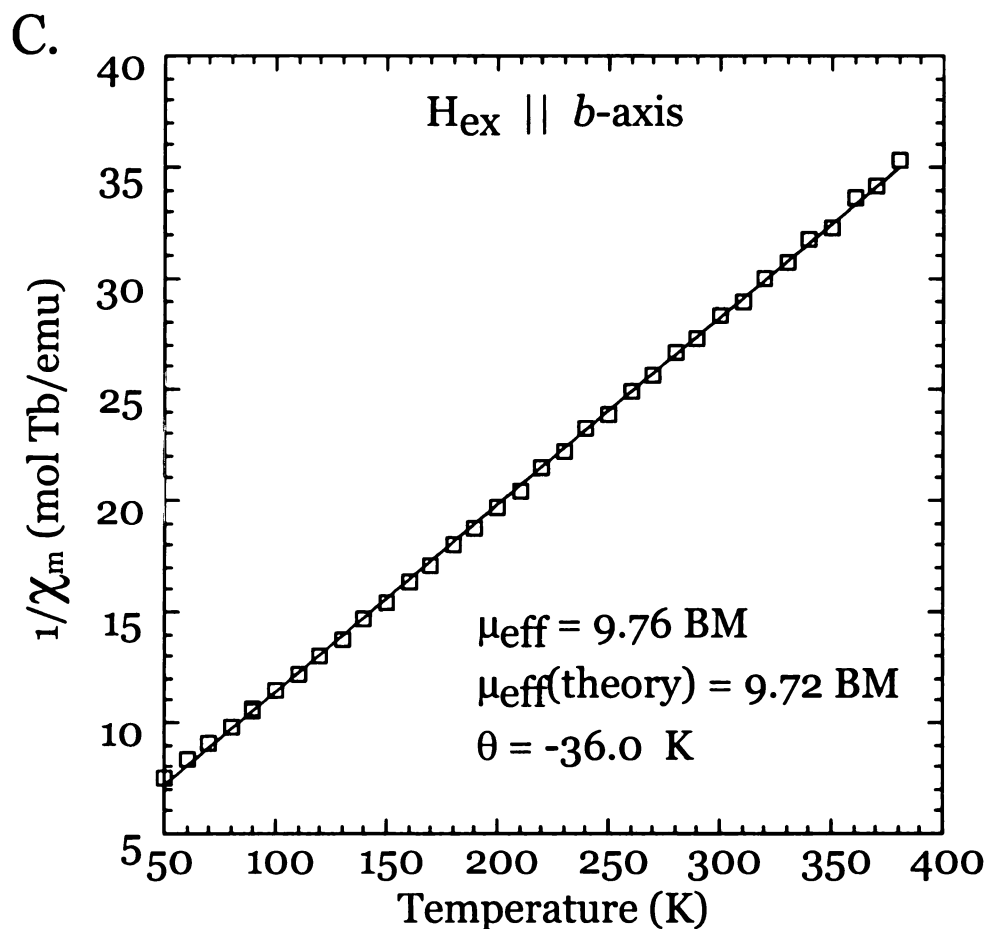


Figure II.B.14. (C) Temperature dependence of the inverse magnetic susceptibility measured on the single crystal sample of Tb_4FeGe_8 oriented with b -axis parallel to H_{ex} .

The origin of the two different kinds of ordering may lie in the packing of Tb atoms in the structure of Tb_4FeGe_8 . Thus, in the Tb-only framework, see Figure II.B.7B, the bonding interactions in $[\text{Tb}_6]$ prisms are comparable in both orthorhombic faces (ac -plane) and pseudo-trigonal faces (bc -plane). It is then possible to assume that two antiferromagnetic ordering interactions could arise from these competing bonding interactions. It could be the case that when the magnetic field is directed perpendicular to b -axis (parallel to ac -plane), the moments centered on Tb atoms tend to align along with the field and antiparallel with respect to each other, see Figure II.B.15A. Similarly, if the magnetic field is parallel to b -axis, the moments are likely to align antiferromagnetically in pseudo-trigonal plane, see Figure II.B.15B. The first interaction seems to be stronger and more favorable than the second one, as a slightly larger magnetic moment was developed in $H_{\text{ex}} \perp b$ than $H_{\text{ex}} \parallel b$ for both temperature- and field-dependent types of measurements. Regardless, neither of these two crystal orientations defines the direction of the magnetically easy axis, so that the actual arrangement of the magnetic moment is likely to be an intermediate between that shown in Figure II.B.15A and II.B.15B.

Interestingly, in the compounds with a pure trigonal (hexagonal) arrangement of Tb atoms and comparable Tb-Tb distances of $\sim 4 \text{ \AA}$, such as $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ ¹¹, the values of T_{max} ($\sim 3 \text{ K}$) are very close to $T_{\text{max}}^{\parallel b}$ ($\sim 2.5 \text{ K}$) observed in Tb_4FeGe_8 . Analogously, the Tb compounds containing only orthorhombic arrangement of Tb atoms such as $\text{Tb}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ²⁸ (and again comparable Tb-Tb distances of $\sim 4 \text{ \AA}$), are characterized with T_{max} ($\sim 15 \text{ K}$) comparable to $T_{\text{max}}^{\parallel b}$ ($\sim 20 \text{ K}$) of Tb_4FeGe_8 . This serves as an additional indication that in the latter, interplay of two magnetic interactions takes place.

A.

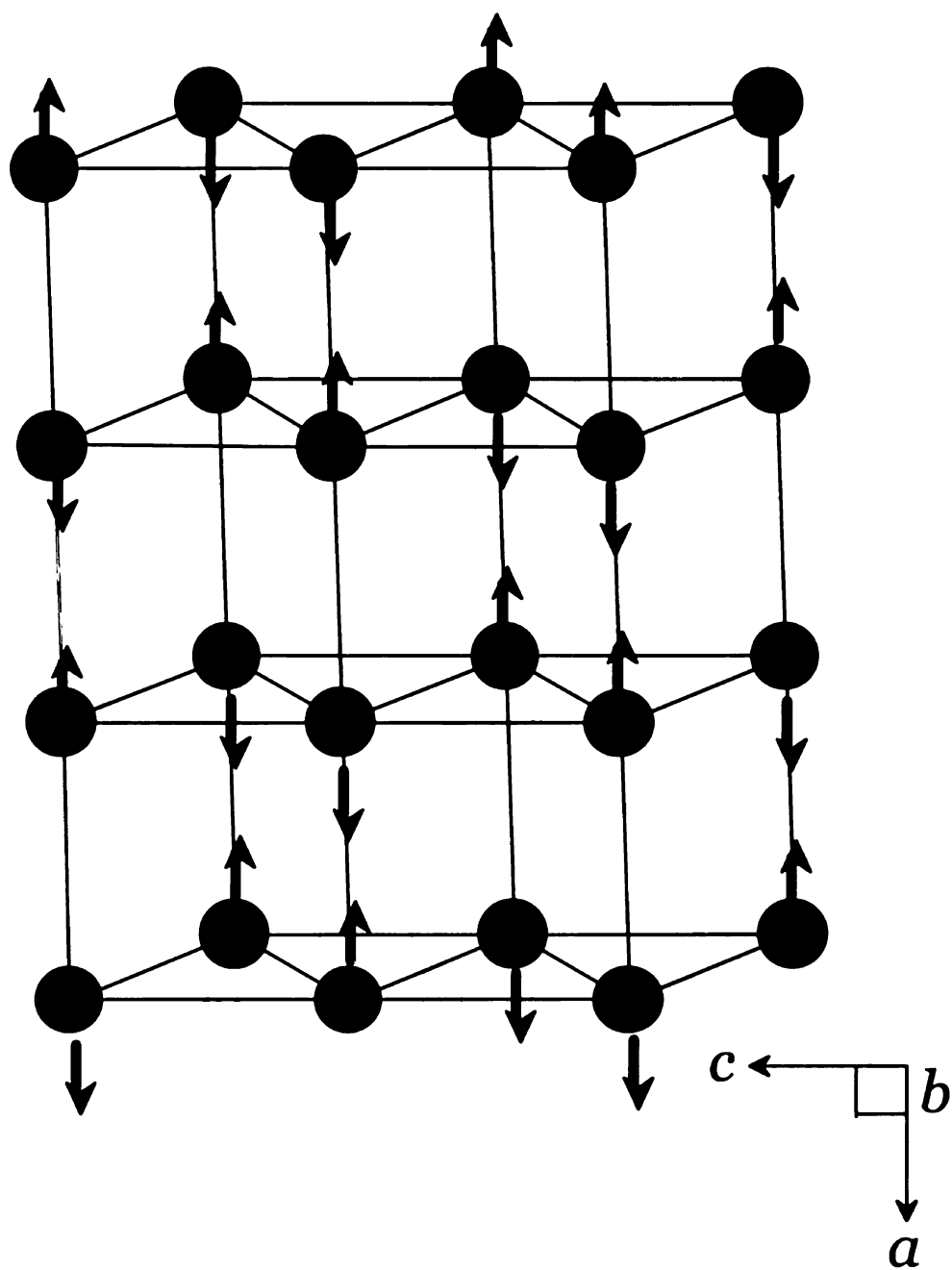


Figure II.B.15. (A) Modeled orientation of moments centered on the Tb atoms in the direction perpendicular to b -axis. The direction of the magnetic moment is shown with an arrow and the magnitude is taken arbitrary.

B.

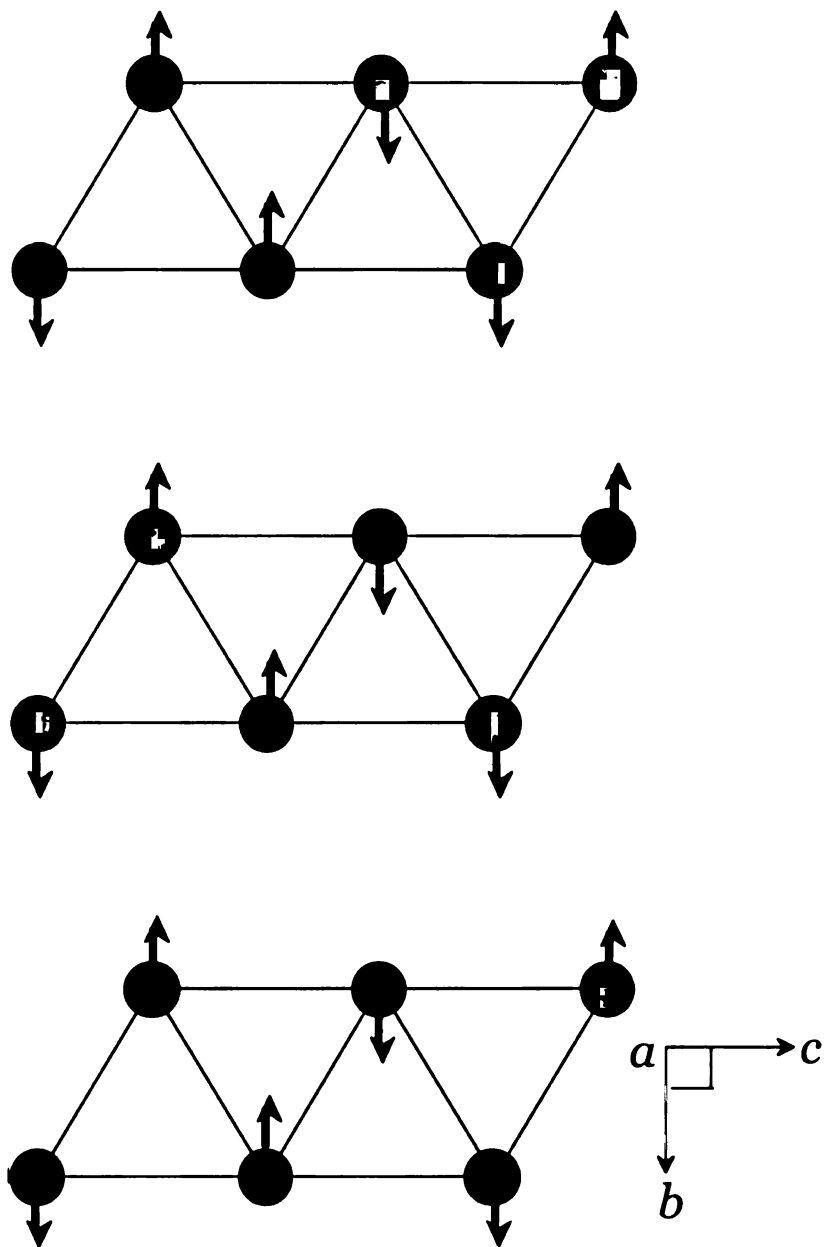
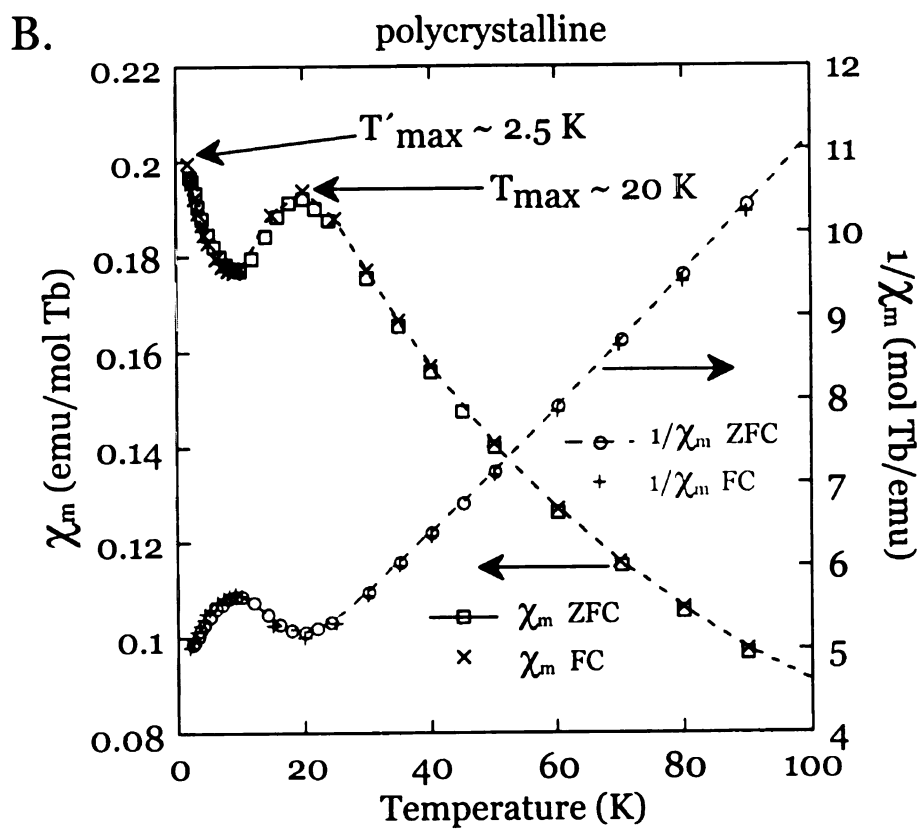
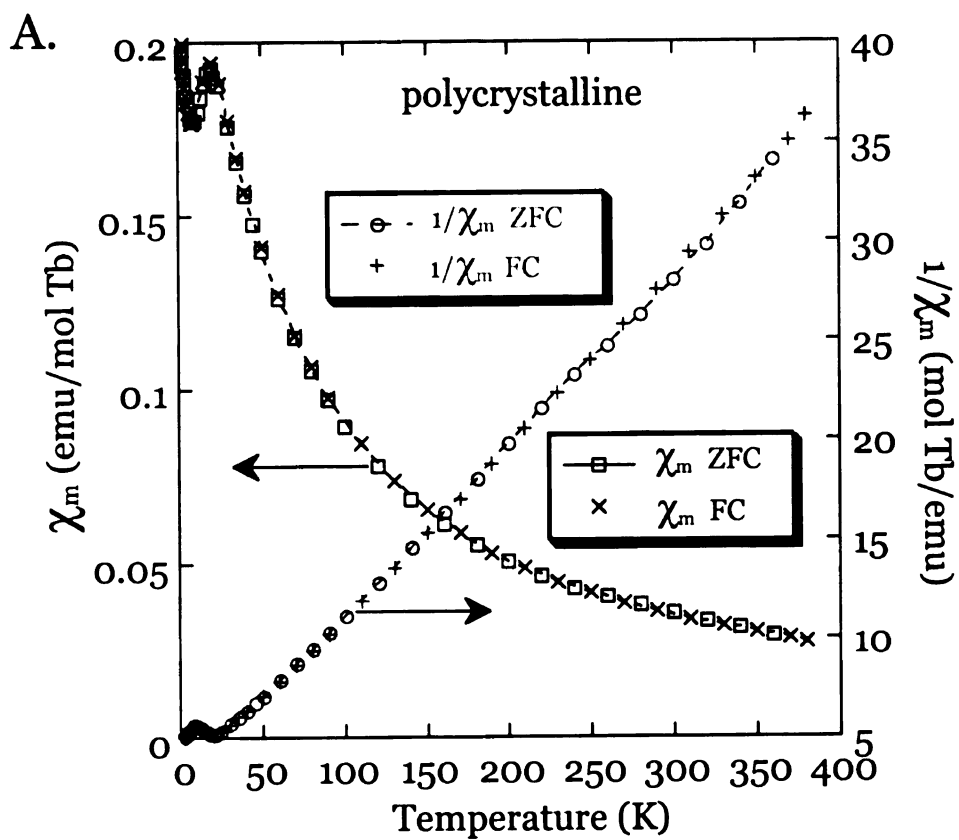


Figure II.B.15. (B) Modeled orientation of magnetic moments centered on Tb atoms in the bc -plane. The direction of the magnetic moment is shown with an arrow and the magnitude is taken arbitrary.

The isotropic susceptibility of the polycrystalline sample is expected to reflect the average contribution from both antiferromagnetic transitions. Indeed, isotropic magnetic susceptibility measurements performed on the polycrystalline samples of Tb_4FeGe_8 , see Figure II.B.16A, clearly show two ordering transitions to an antiferromagnetic state. The inspection of the expanded low-temperature region of χ_m^{iso} and $(\chi_m^{\text{iso}})^{-1}$, see Figure II.B.16B, shows that the first transition is centered at ~ 2.5 K and the next one is at ~ 20 K, just as in the case of $\chi_m^{\parallel b}$ and $\chi_m^{\perp b}$, respectively. The effective magnetic moment obtained from the slope of the $\chi_m^{\text{iso}} - T$ plot, see Figure II.B.16C, gives the value 9.61 BM, close to that calculated for the free Tb^{3+} ion (9.72 BM).

The field-dependence measurements show no saturation up to fields of 5 T, with the maximal magnetic moment ranging from 1.8 BM to 3 BM depending on the orientation, see Figure II.B.17. An analogous situation was observed in a number of Tb-containing intermetallic compounds including $\text{Tb}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ²⁸, TbNiGa_3Ge ¹¹ and $\text{TbAl}_{3-x}\text{Ge}_x$ ³⁶.



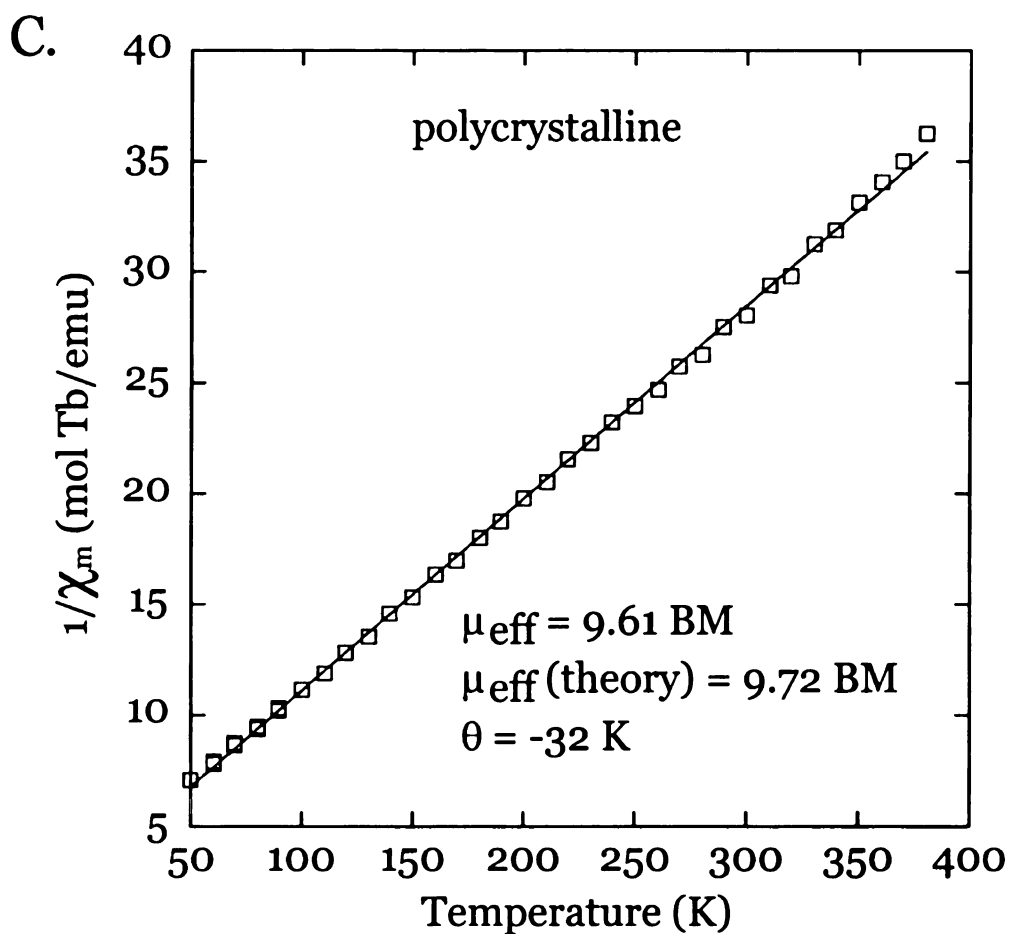


Figure II.B.16. (A) Temperature dependence of molar magnetic susceptibility and inverse susceptibility of Tb_4FeGe_8 polycrystalline sample; (B) χ_m and χ_m^{-1} in the low-temperature region; (C) Inverse magnetic susceptibility as a function of temperature. The susceptibility was measured with an applied magnetic field 500 Gauss and given per mole of Tb.

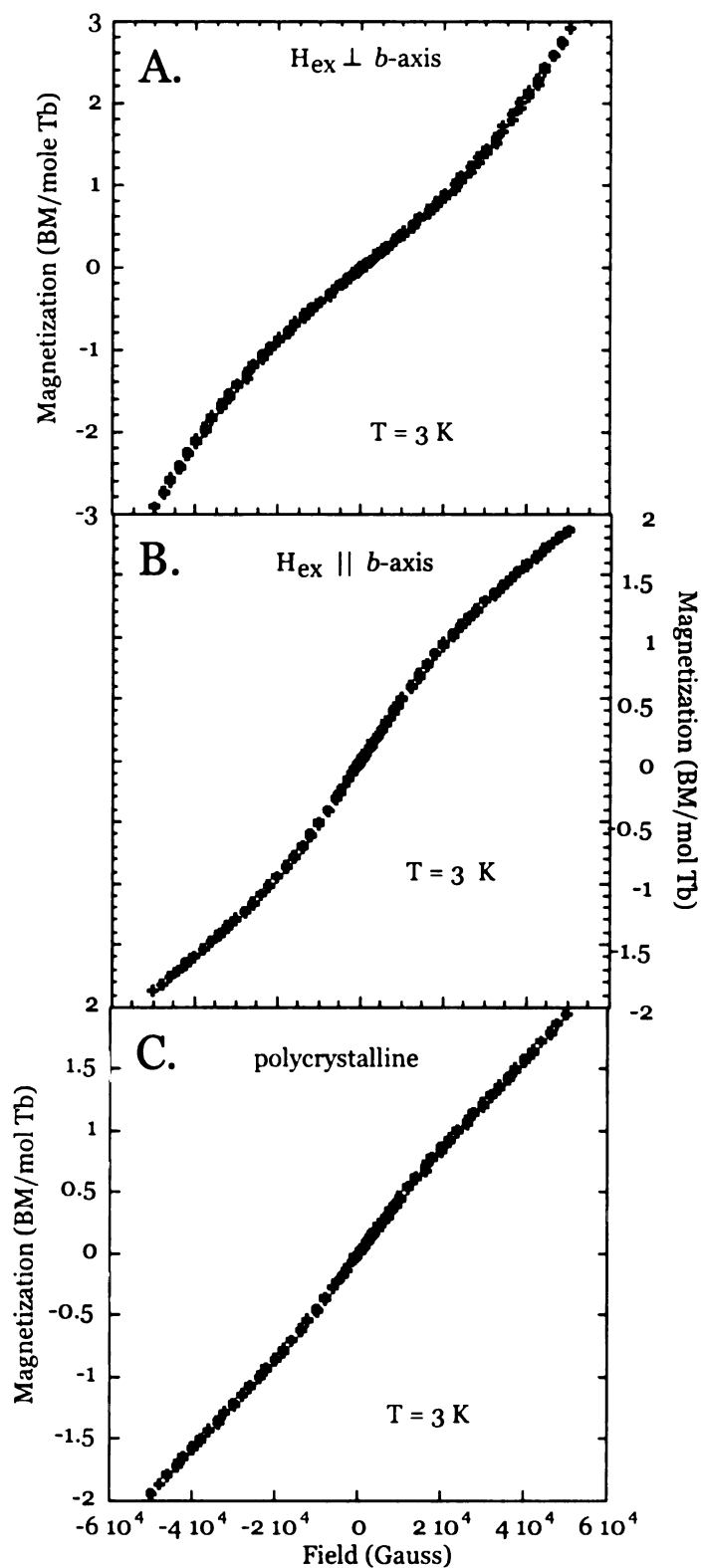


Figure II.B.17. Magnetization of the Tb_4FeGe_8 sample as a function of field with single crystal sample oriented (A) perpendicular to b -axis, (B) parallel to b -axis and (C) isotropic.

4. Concluding Remarks

A new derivative of the CeNiSi_2 structure type, Tb_4FeGe_8 , has been obtained in reactions involving excess liquid Ga. Large single crystals of Tb_4FeGe_8 phase grown from molten Ga facilitated extensive studies of the structural and magnetic properties of this new compound. An interesting structural peculiarity is a “disorder” observed in the $[\text{Fe}_{1/4}\text{Ge}]$ plane and revealed in the Fe site vacancies and the shortened Fe-Ge bond distances. X-ray and electron diffraction zonal photographs point to the existence of a 4-fold to 8-fold supercell, with the modulation propagating along the diagonal of the orthorhombic subcell. The strong modulation is due to a distortion in the square net in the structure. A model for an ordering arrangement is proposed on the basis of a refined 4-fold supercell based on single crystal X-ray data.

The magnetic measurements indicate the presence of two antiferromagnetic ordering interactions within the Tb sublattice with corresponding Néel temperatures of 2.5 K and 20 K. These ordering transitions were attributed to competing Tb-Tb interactions in the direction parallel and perpendicular to the crystallographic b -axis. The calculated effective magnetic moments agree well with the values obtained for free Tb^{3+} ion. The Fe atoms are shown to be in a non-magnetic state.

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²³ Electrolyte composition, (vol. %): 10% H_2SO_4 , 1% HF , 1.5% H_2NO_3 , 87.5% CH_3OH .

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³⁴ Effective magnetic moment could be obtained by the formula $\mu_{\text{eff}} = g_J [J(J+1)]^{1/2}$, where g_J is a Landé factor and J is a total angular momentum of the Tb^{3+} ion. For the systems with strong spin-orbit coupling the g_J differs from the spin-only value 2.0 and can be calculated using the formula $g_J = 1 + \{[S(S+1) - L(L+1) + J(J+1)]/[2J(J+1)]\}$, where S is spin momentum, L is orbital momentum and J is total angular momentum. The total angular momentum (J) of the ion with unfilled 4f shell is determined by the Hund's rules. $J = L + S$, $|L - S|$ for shells greater or less than half full, respectively.

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Chapter III

Part A

RE₃Ga₉Ge (RE = Y, Ce, Sm, Gd and Yb): New Compounds with an Open Three-Dimensional Polygallide Framework Synthesized From Liquid Gallium.

1. Introduction

In recent investigations aimed at developing new routes for the exploratory synthesis of intermetallics we have reported results in the quaternary systems RE/M/Ga/Tt (RE = rare earth; Tt = Si or Ge). We have described a number of new rare-earth transition metal tetrelides synthesized from reactions employing liquid Ga as the solvent. In the reactions above, Ga flux acted as a non-reactive solvent, *i.e.* did not get

included into the final reaction product. However, in a number of instances Ga flux not only serves as a reactive solvent, but also yields Ga-rich products, or polygallides. The examples of polygallides obtained from molten Ga solutions include the tetragonal $\text{RE}_2\text{NiGa}_{12}$ and $\text{RE}_2\text{NiGa}_{12-x}\text{Si}_x$ ¹ compounds with a three-dimensional (3D) Ga framework, and the hexagonal $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ ² ($x < 1$) compound possessing a two-dimensional (2D) Ga structure. Ga flux was also used by others in the synthesis of RERu_2Ga_8 ³, with 2D Ga-only sheets, and $\text{RE}_{1.34}\text{Pt}_4\text{Ga}_{10}$ ⁴ where Ga atoms form 2D As-type layers. Numerous ternary intermetallic polygallides with RE and transition metal such as $\text{RE}_2\text{NiGa}_{10}$ ⁵ (RE = La, Ce), $\text{RE}_3\text{NiGa}_{10}$ ⁶ (RE = Ce, Pr, Nd), $\text{Ce}_3\text{Ni}_2\text{Ga}_{15}$ ⁷, $\text{RE}_4\text{NiGa}_{18}$ ⁸ (RE = Ce, Nd), $\text{RE}_2\text{Ru}_3\text{Ga}_{10}$ ³ and $\text{RE}_2\text{Ru}_3\text{Ga}_9$ ⁹ are also known.

The variety of the geometrical configurations of Ga networks found in polygallides is both striking and unique, and the observed structures are fascinating. The diversity of the 2D Ga networks mentioned above includes square, pentagonal and triangular assemblies, as well as As-type puckered layers of Ga six-member rings. No apparent relationship exists between these phases and the much more studied Zintl phases¹⁰. This rich chemistry justifies a continued search for new structure types. Our own efforts in the systems RE/M/Ga/Ge (M = transition metal) employing Ga flux were further extended to Co, Cu and Fe. Surprisingly, we found that particular reaction stoichiometries yield products of phase separation where the transition metal is excluded, and the major components of the reaction product are Ga-rich ternary rare-earth-gallide-germanides. In this Chapter we report the synthesis, crystal structure, and magnetic properties of a new family of compounds $\text{RE}_3\text{Ga}_9\text{Ge}$ (RE = Y, Ce, Sm, Gd and Yb).

2. Experimental Section

Synthesis

Although members of this family were originally discovered in the reactions containing transition metals, the latter is not needed for their synthesis. The reactions between the rare earth (Y, Ce, Sm, Gd, Yb), Ga and Ge were carried out in the excess of molten Ga in the alumina crucibles sealed in the evacuated ($<1 \cdot 10^{-4}$ Torr) silica ampules. The elements of typical purity 99.9% and higher (Cerac Inc.): RE (2.48 mmol), Ga (37.0 mmol), Ge (2.48 mmol) were mixed in the ratio:¹¹ RE : Ga : Ge as 1 : 15 : 1 under a nitrogen atmosphere. The reaction mixtures were then slowly heated (60°/hour) up to 1000°C, shortly (5 hours) held at 1000°C to obtain proper melt, then cooled (75°/hour) to 850°C and held there isothermally for 6 days and, finally, cooled at 9°/hour to ~200°C.

The excess of Ga was removed in a two-step process: first by hot-temperature span-filtration forcing liquid Ga through specially designed filters by centrifuging at high speed (> 3000 rpm) for approximately 30 seconds, and second by treating the product with ~3 M solution of I₂ with dimethylformamide (DMF) for 12 - 24 hours. The product was subsequently washed in DMF, hot water, and dried with acetone and ether. No other products except the target phase RE₃Ga₉Ge (and recrystallized Ge) were observed. A quantitative yield of the phase was confirmed by powder X-ray diffraction (XRD) and the energy dispersive spectroscopy (EDS). The resultant crystalline product possessed needle to bar-like morphology and typical metallic luster. In some cases aggregation of needles

into bundles was observed. The micrograph of a typical crystal of $\text{Sm}_3\text{Ga}_9\text{Ge}$ is shown in Figure III.A.1.

Scanning Electron Microscopy and Elemental Analysis

Micrographs of the samples were taken with a scanning electron microscope (SEM) JEOL JSM-35C. A semi-quantitative elemental analysis by EDS was done on SEM equipped with NORAN Inc. EDS detector. The analysis was conducted at accelerating voltage 20 kV, and the collection count time was 30 seconds. The EDS analysis showed that the average elemental composition for all samples corresponded to “ $\text{RE}_3\text{Ga}_{7.8}\text{Ge}_{1.6}$ ”.

Powder X-ray Diffraction

The X-ray powder diffraction (XRD) patterns were taken at room temperature on a Rigaku-Denki/Rw400F2 (rotaflex) rotating-anode ($\text{Cu K}\alpha$) powder diffractometer and a CPS 120 INEL X-ray diffractometer ($\text{Cu K}\alpha$) equipped with position-sensitive detector. The crystalline samples were ground with mortar and pestle to achieve polycrystalline material. Experimental powder patterns were compared to that calculated from single crystal data using CERIUS² software package¹².

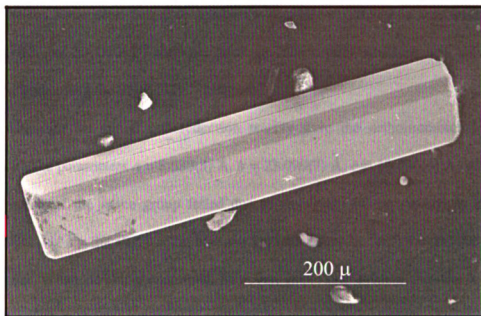


Figure III.A.1. SEM image of a typical $\text{RE}_3\text{Ga}_9\text{Ge}$ crystal (RE = Sm).

Single Crystal X-ray Crystallography

Single crystal X-ray diffraction data was collected on the Ce analog at room temperature with a Siemens Platform SMART¹³ CCD diffractometer. The needle-like crystal with the dimensions $0.12 \times 0.06 \times 0.05 \text{ mm}^3$ was mounted on glass fiber. A hemisphere of reciprocal data up to 76° in 2θ (Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, the X-ray radiation was generated at 34 kV/40 mA) was acquired using an exposure time of 90 s per frame. The data collection and acquisition was performed with the SMART¹³ software package and the SAINTPLUS¹⁴ program was used for data reduction. The analytical absorption corrections were done using a face-indexing routine, and an empirical

correction for absorption based on symmetry equivalent reflections was consequently applied with the SADABS¹⁵ software package. The crystal structure was solved with direct methods using the SHELXTL¹⁶ program.

Although the initial cell reduction readily gave the orthorhombic *C*-centered lattice with the parameters $a = 8.680(3) \text{ \AA}$, $b = 23.090(7) \text{ \AA}$, $c = 10.836(3) \text{ \AA}$, subsequent determination of the space group failed due to ambiguity of the systematic absences, namely: hkl : $h + k = 2n$, $0kl$: $k = 2n$, $h0l$: $h = 2n$; $hk0$: $h, k = 2n$; $h00$: $h = 2n$; $0k0$: $k = 2n$; $00l$: $l = 2n$. When carefully examined, however, it became evident that the reflections with somewhat stronger intensity obeyed the following limiting conditions:

$0kl$	$k = 4n + 2$ when $l = 2n + 1$, and $k = 4n + 4$ when $l = 2n$;
$h0l$	$h = 4n + 2$ when $l = 2n + 1$, and $h = 4n + 4$ when $l = 2n$;
$hk0$	$h + k = 4n + 4$;
$h00$	$h = 4n + 4$;
$0k0$	$k = 4n + 4$;
$00l$	$l = 2n$

Despite the unusual expression of the observed reflection conditions, they can be easily accounted for. The stronger reflections can be indexed if a sub-cell is assumed that is characterized with half a' , b' parameters (and therefore with doubled h' , k' indices). This transformation ($a' = a/2$, $b' = b/2$, $c' = c$ or $h' = 2h$, $k' = 2k$, $l' = l$) leads to the very clear conditions:

$0k'l'$	$k' + l' = 2n$
$h'0l'$	$h' + l' = 2n$
$h'k'0$	$h' + k' = 2n$
$h'00$	$h' = 2n$
$0k'0$	$k' = 2n$
$00l'$	$l' = 2n$

that correspond to an *I*-centered cell $a = 4.3400(12)$ Å; $b = 10.836(3)$ Å; and $c = 11.545(3)$ Å. This further leads to four possible space groups *I*222, *I*2₁2₁2₁, *Imm*2, and *Immm*, of which the highest symmetry space group *Immm* was used for the sub-structure solution.

(a) Substructure

A total of seven atomic positions were identified: the *4g* and *4j* for Ce atoms, *2a* for Ge atom, and *4g*, *4i*, *8l* and *8n* were assigned to Ga atoms. Crystallographically, it is very difficult to distinguish between the Ga and Ge atoms using X-ray data only due to the very small difference in their scattering. In this work, the differentiation between Ga and Ge was made on the basis of reasonable bond lengths and consistency with EDS elemental analysis, as was done in previous work¹⁷. Because of the smaller covalent radius of Ge compare to Ga, the shorter Ce-M distances (where M could be Ga or Ge) were assigned to Ge. In previous investigations such assignments have proven correct by neutron crystallographic studies^{18,19,20}. The resulting empirical formula Ce₃Ga₉Ge agreed well with the composition given by the EDS analysis. Further investigation of the Ga/Ge

distribution should be done with methods able to distinguish between these elements, such as neutron diffraction or anomalous X-ray scattering with the use of synchrotron radiation.

In the sub-structure, the Ce(1), Ga(1) and Ga(2) atoms form a monoatomic plane at $z = 0; 1/2$, where Ce-Ga and Ga-Ga are found at distances as close as 1.452(2) Å, and 1.629(3) Å from each other, respectively, see Figure III.A.2. Since such close proximity of the atoms does not represent a realistic picture, the occupancy parameters of the disorder atoms were freely refined. The resulting occupancies of disordered atoms varied between 0.49 and 0.51, and therefore in the final refinement cycle they were constrained to $1/2$.

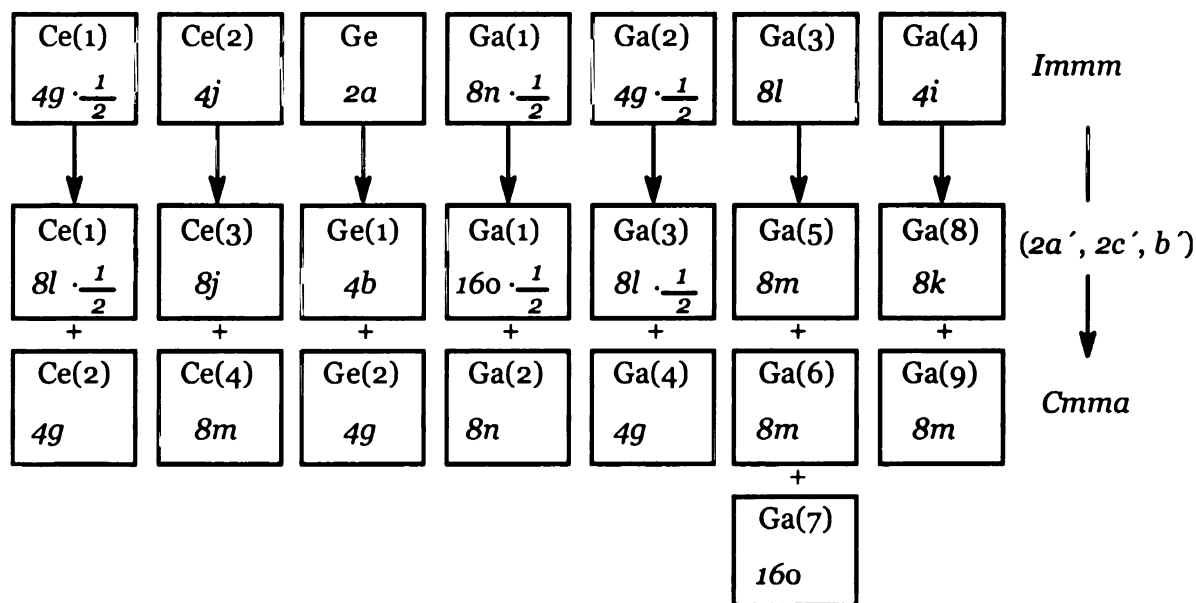
(b) Superstructure

After achieving the sub-structure solution, we returned to the originally obtained larger *C*-centered cell, so that the observed super-structure reflections, although weak, could be taken into consideration. The ambiguity of the systematic absences can be resolved by discarding the condition on either one of *hk0* or *00l* set of reflections. Since the overall number of reflections satisfying the $h, k = 2n$ condition for the *hk0* set was much larger than the $l = 2n$ in *00l* set, the latter was neglected. This yielded two possible space groups *Cm2a* and *Cmma*, of which the centro-symmetric one was found to be correct during the structure refinement.

The group-subgroup relationship between sub-structure $Immm (a' b' c')$ and super-structure $Cmma (2a', 2c' b')$ goes through two subsequent *klassengleiche* transformations to a minimal non-isomorphic subgroup of index 2: $Pmmm (a', b', c')$, and $Cmma (2a', 2c', b')$, the latter with a quadrupled cell volume.

$$Immm \quad -k2 (a', b', c') \rightarrow Pmmm \quad -k2 (2a', 2c', b') \rightarrow Cmma$$

In the super-structure, a total of 15 independent crystallographic atomic positions were refined; the correspondence of the sub-structure and superstructure atomic positions and their multiplicities combined with the occupancies (if partial) are given in the diagram below.



It is very important to note that the only difference between the super-structure with quadrupled cell and the sub-structure lies in the existence of two crystallographically distinct RE-Ga-Ge monoatomic planes. Thus, in the superstructure the planes located at $y = 0, 1/2$ are identical to the ones found in the sub-structure, *i.e.* disordered. On the contrary, the monoatomic planes at $y = \pm 1/4$ are perfectly ordered. Although the Fourier difference map shows the existence of high peak and hole (located at 0.11 Å and 1.44 Å from the Ce(2) and Ga(4) atoms, respectively), this electron density cannot be accounted for by including it during the structure refinement. Thus, this high residual density is possibly a “Fourier noise” arising from the lack of sufficiently good data supporting the superstructure. The unconstrained refinement of the occupancy parameters of all atoms yielded the values of 0.956(15) to 1.02(3) for the atomic positions of the ordered atoms, and 0.464(11), 0.487(18) and 0.506(11) for the disordered sites Ga(1), Ga(3) and Ce(1), respectively. These occupancy values were included in the final refinement. The positional parameters for both structures were standardized using the STRUCTURE TIDY²¹ software.

Details of the data collection and structure refinement for the sub- and superstructure solutions are listed in Table III.A.1. The final atomic positions, equivalent thermal displacement parameters and occupancies for the sub- and super-structure are given in Tables III.A.2a and III.A.2b, respectively. The interatomic distances up to 3.5 Å are listed in Tables III.A.3a and III.A.3b for sub- and super-cell, respectively. Selected bond angles for the substructure are given in Table III.A.4. Anisotropic displacement parameters for all atoms are presented in Table III.A.5a and III.A.5b for the sub- and super-structure, respectively.

Table III.A.1. Crystal data, (a) sub-structure and (b) superstructure refinement for Ce₃Ga₉Ge.

Identification code	(a)	(b) Ce _{2.93} Ga _{8.66} Ge _{1.02}
Formula weight	1120.43	1120.43
Temperature (K)	296(2)	296(2) K
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Immm</i>	<i>Cmma</i>
Unit cell dimensions (Å)	<i>a</i> = 4.3400(12) <i>b</i> = 10.836(3) <i>c</i> = 11.545(3)	<i>a</i> = 8.680(3) <i>b</i> = 23.090(7) <i>c</i> = 10.836(3)
Volume (Å ³)	542.9(3)	2171.8(11)
Z	2	8
d _{calc} (g/cm ³)	6.854	6.654
Absorption coefficient (mm ⁻¹)	36.866	35.788
F(000)	970	3766
Crystal size (mm ³)	0.2 × 0.06 × 0.05	0.2 × 0.06 × 0.05
θ range for data collection (°)	2.58 to 29.19 -5 ≤ <i>h</i> ≤ 5	2.58 to 29.19 -11 ≤ <i>h</i> ≤ 11
Index ranges	-14 ≤ <i>k</i> ≤ 12 -15 ≤ <i>l</i> ≤ 13	-31 ≤ <i>k</i> ≤ 26 -12 ≤ <i>l</i> ≤ 14
Reflections collected	1769	6931
Independent reflections	429 [R(int) = 0.0265]	1515 [R(int) = 0.0449]
Completeness to θ	95.8 %	94.9 %
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / parameters	429 / 33	1515 / 99
Goodness-of-fit on F ²	1.062	0.785
Final R indices [I>2σ(I)]*	R ₁ = 0.0226, wR ₂ = 0.0528	R ₁ = 0.0729, wR ₂ = 0.1569
R indices (all data)	R ₁ = 0.0247, wR ₂ = 0.0536	R ₁ = 0.1014, wR ₂ = 0.1748
Extinction coefficient	0.00095(13)	0.00098(9)
Largest diff. peak and hole (e/Å ³)	1.474 and -1.162	8.577 and -10.187

* $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table III.A.2. Atomic coordinates and equivalent isotropic displacement parameters*($\text{\AA}^2 \times 10^3$) for (a) sub-structure and (b) superstructure of $\text{Ce}_3\text{Ga}_9\text{Ge}$.

(a)

Atomic	Wyckoff					
Position	Symbol	x	y	z	U_{eq}	Occ.
Ce(1)	$4g$	0.00000	0.2860(1)	0.00000	9(1)	0.5
Ce(2)	$4j$	0.00000	0.50000	0.3101(1)	8(1)	1.0
Ge(1)	$2a$	0.00000	0.00000	0.00000	9(1)	1.0
Ga(1)	$8n$	0.3123(3)	0.2041(1)	0.00000	12(1)	0.5
Ga(2)	$4g$	0.00000	0.4200(2)	0.00000	15(1)	0.5
Ga(3)	$8l$	0.00000	0.2100(1)	0.2937(1)	11(1)	1.0
Ga(4)	$4i$	0.00000	0.00000	0.3868(1)	11(1)	1.0

Table III.A.2. (continued)

(b)

Atomic	Wykoff					
Position	Symbol	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Occ.
Ce(1)	<i>8l</i>	¼	0	0.2137(2)	16(1)	0.506(11)
Ce(2)	<i>4g</i>	0	¼	0.2858(1)	6(1)	1
Ce(3)	<i>8j</i>	¼	0.1551(1)	0	11(1)	0.960(12)
Ce(4)	<i>8m</i>	0	0.0950(1)	0.4998(1)	11(1)	0.960(12)
Ge(1)	<i>4b</i>	¼	0	½	12(1)	1.01(2)
Ge(2)	<i>4g</i>	0	¼	0.0003(2)	14(1)	1.02(3)
Ga(1)	<i>16o</i>	0.0943(4)	0.0025(1)	0.2957(3)	15(1)	0.464(11)
Ga(2)	<i>8n</i>	0.3442(2)	¼	0.2036(2)	10(1)	0.972(13)
Ga(3)	<i>8l</i>	¼	0	0.0802(5)	22(2)	0.487(18)
Ga(4)	<i>4g</i>	0	¼	0.5802(2)	14(1)	0.971(18)
Ga(5)	<i>8m</i>	0	0.1054(1)	0.2094(2)	12(1)	0.959(15)
Ga(6)	<i>8m</i>	0	0.6006(1)	0.2108(2)	12(1)	0.956(15)
Ga(7)	<i>16o</i>	0.2554(1)	0.1470(1)	0.2898(2)	13(1)	0.962(13)
Ga(8)	<i>8k</i>	¼	0.1935(1)	½	14(1)	0.976(19)
Ga(9)	<i>8m</i>	0	0.0566(1)	0.0011(1)	14(1)	0.975(18)

**U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table III.A.3. Selected bond lengths [$\text{\AA}$] for (a) sub-structure and (b) superstructure of $\text{Ce}_3\text{Ga}_9\text{Ge}$.

(a)

Bond	Distance	Mult.	Bond	Distance	Mult.
Ce(1)-Ga(2)	1.452(2)	$\times 1$	Ga(1)-Ga(1)	1.629(3)	$\times 1$
Ce(1)-Ga(1)	1.6203(14)	$\times 2$	Ga(1)-Ga(3)	2.6843(11)	$\times 2$
Ce(1)-Ge(1)	3.0991(13)	$\times 1$	Ga(1)-Ga(2)	2.704(2)	$\times 1$
Ce(1)-Ga(1)	3.1139(16)	$\times 2$	Ga(1)-Ga(1)	2.711(3)	$\times 1$
Ce(1)-Ga(2)	3.185(2)	$\times 1$	Ga(2)-Ga(2)	1.733(4)	$\times 1$
Ce(1)-Ga(3)	3.2228(8)	$\times 6$	Ga(2)-Ga(4)	2.6772(9)	$\times 4$
Ce(1)-Ga(4)	3.4342(9)	$\times 4$	Ga(2)-Ga(1)	2.704(2)	$\times 2$
Ce(2)-Ge(1)	3.0847(7)	$\times 2$	Ga(3)-Ga(4)	2.5172(10)	$\times 2$
Ce(2)-Ga(4)	3.1428(9)	$\times 2$	Ga(3)-Ga(3)	2.5446(9)	$\times 2$
Ce(2)-Ga(3)	3.1478(11)	$\times 2$	Ga(3)-Ga(1)	2.6843(11)	$\times 2$
Ce(2)-Ga(1)	3.2187(12)	$\times 4$	Ga(4)-Ga(3)	2.5172(10)	$\times 2$
Ce(2)-Ga(3)	3.3650(8)	$\times 4$	Ga(4)-Ga(4)	2.614(2)	$\times 1$
Ge(1)-Ga(1)	2.5936(14)	$\times 4$	Ga(4)-Ga(2)	2.6772(9)	$\times 4$

Table III.A.3 (continued)

(b)

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
Ce(1)-Ga(3)	1.447(6)	× 1	Ce(4)-Ga(1)	3.180(3)	× 2
Ce(1)-Ga(1)	1.619(4)	× 2	Ce(4)-Ga(1)	3.262(3)	× 2
Ce(1)-Ge(1)	3.102(3)	× 1	Ce(4)-Ga(7)	3.3396(18)	× 4
Ce(1)-Ga(1)	3.118(3)	× 2	Ge(1)-Ga(1)	2.594(3)	× 4
Ce(1)-Ga(6)	3.1792(15)	× 2	Ge(2)-Ga(2)	2.585(3)	× 2
Ce(1)-Ga(3)	3.185(5)	× 1	Ga(1)-Ga(1)	1.637(7)	× 1
Ce(1)-Ga(5)	3.2618(16)	× 2	Ga(1)-Ga(6)	2.680(3)	× 1
Ce(1)-Ga(9)	3.424(2)	× 2	Ga(1)-Ga(5)	2.683(3)	× 1
Ce(1)-Ga(9)	3.440(2)	× 2	Ga(1)-Ga(3)	2.699(6)	× 1
Ce(2)-Ge(2)	3.100(2)	× 1	Ga(1)-Ga(1)	2.705(7)	× 1
Ce(2)-Ga(2)	3.1178(19)	× 2	Ga(2)-Ga(7)	2.6688(19)	× 2
Ce(2)-Ga(4)	3.190(3)	× 1	Ga(2)-Ga(2)	2.704(3)	× 2
Ce(2)-Ga(7)	3.2510(15)	× 4	Ga(2)-Ga(4)	2.705(3)	× 1
Ce(2)-Ga(8)	3.4347(14)	× 4	Ga(3)-Ga(3)	1.738(10)	× 1
Ce(3)-Ge(2)	3.0845(10)	× 2	Ga(3)-Ga(9)	2.674(2)	× 2
Ce(3)-Ga(9)	3.143(2)	× 2	Ga(3)-Ga(9)	2.681(2)	× 2
Ce(3)-Ga(7)	3.147(2)	× 2	Ga(4)-Ga(8)	2.6770(15)	× 4
Ce(3)-Ga(2)	3.2158(16)	× 2	Ga(5)-Ga(9)	2.524(3)	× 1
Ce(3)-Ga(5)	3.3419(17)	× 2	Ga(5)-Ga(7)	2.5680(16)	× 2
Ce(3)-Ga(6)	3.3925(18)	× 2	Ga(6)-Ga(9)	2.512(3)	× 1
Ce(4)-Ge(1)	3.0847(10)	× 2	Ga(6)-Ga(7)	2.5278(16)	× 2
Ce(4)-Ga(6)	3.139(2)	× 1	Ga(7)-Ga(8)	2.518(2)	× 1
Ce(4)-Ga(8)	3.144(2)	× 2	Ga(7)-Ga(6)	2.5278(16)	× 1
Ce(4)-Ga(5)	3.156(2)	× 1	Ga(8)-Ga(8)	2.609(5)	× 1
			Ga(9)-Ga(9)	2.612(5)	× 1

Table III.A.4. Selected bond angles [°] for sub-structure of Ce₃Ga₉Ge.

Bond	Angle	Bond	Angle
Ga(2)-Ce(1)-Ga(1)	123.23(5)	Ga(3)-Ce(1)-Ga(3)	178.47(4)
Ga(1)-Ce(1)-Ga(1)	113.55(10)	Ga(2)-Ce(1)-Ga(4)	47.528(16)
Ga(2)-Ce(1)-Ge(1)	180.0	Ga(1)-Ce(1)-Ga(4)	153.97(3)
Ga(1)-Ce(1)-Ge(1)	56.77(5)	Ga(1)-Ce(1)-Ga(4)	80.88(5)
Ga(2)-Ce(1)-Ga(1)	106.57(3)	Ge(1)-Ce(1)-Ga(4)	132.472(16)
Ga(1)-Ce(1)-Ga(1)	16.66(4)	Ga(1)-Ce(1)-Ga(4)	142.96(3)
Ga(1)-Ce(1)-Ga(1)	130.21(7)	Ga(1)-Ce(1)-Ga(4)	65.60(3)
Ge(1)-Ce(1)-Ga(1)	73.43(3)	Ga(2)-Ce(1)-Ga(4)	47.528(16)
Ga(1)-Ce(1)-Ga(1)	146.87(6)	Ga(3)-Ce(1)-Ga(4)	134.25(3)
Ge(1)-Ce(1)-Ga(2)	180.0	Ga(3)-Ce(1)-Ga(4)	44.295(19)
Ga(2)-Ce(1)-Ga(3)	89.236(19)	Ga(3)-Ce(1)-Ga(4)	81.19(2)
Ga(1)-Ce(1)-Ga(3)	124.79(3)	Ga(3)-Ce(1)-Ga(4)	97.77(3)
Ge(1)-Ce(1)-Ga(3)	90.764(19)	Ge(1)-Ce(2)-Ga(4)	91.63(3)
Ga(1)-Ce(1)-Ga(3)	50.090(16)	Ga(4)-Ce(2)-Ga(4)	87.34(3)
Ga(1)-Ce(1)-Ga(3)	56.22(3)	Ge(1)-Ce(2)-Ga(3)	92.458(10)
Ga(3)-Ce(1)-Ga(3)	178.47(4)	Ga(3)-Ce(2)-Ga(3)	173.08(3)
Ga(1)-Ce(1)-Ga(3)	130.481(18)	Ge(1)-Ce(2)-Ga(1)	48.54(2)
Ga(3)-Ce(1)-Ga(3)	95.33(3)	Ga(3)-Ce(1)-Ga(3)	84.65(3)
Ge(1)-Ce(2)-Ga(1)	72.18(3)	Ga(4)-Ce(2)-Ga(3)	45.352(16)
Ga(4)-Ce(2)-Ga(1)	131.87(2)	Ga(4)-Ce(2)-Ga(3)	100.82(2)
Ga(4)-Ce(2)-Ga(1)	108.54(3)	Ga(3)-Ce(2)-Ga(3)	45.846(16)
Ga(3)-Ce(2)-Ga(1)	136.62(3)	Ga(1)-Ce(2)-Ga(3)	150.50(3)
Ga(3)-Ce(2)-Ga(1)	49.86(2)	Ga(1)-Ce(2)-Ga(3)	122.95(3)
Ga(1)-Ce(2)-Ga(1)	29.32(5)	Ga(1)-Ce(2)-Ga(3)	86.62(3)
Ga(1)-Ce(2)-Ga(1)	86.79(4)	Ga(1)-Ce(2)-Ga(3)	67.33(3)
Ga(1)-Ce(2)-Ga(1)	94.14(4)	Ge(1)-Ce(2)-Ga(3)	134.962(16)
Ge(1)-Ce(2)-Ga(3)	78.424(19)	Ga(3)-Ce(2)-Ga(3)	138.30(3)

Table III.A.4 (continued)

Bond	Angle	Bond	Angle
Ga(1)-Ge(1)-Ga(1)	180.0	Ga(4)-Ga(2)-Ga(4)	142.23(8)
Ga(1)-Ge(1)-Ga(1)	116.99(6)	Ga(4)-Ga(2)-Ga(4)	108.30(5)
Ga(1)-Ge(1)-Ga(1)	63.01(6)	Ga(2)-Ga(2)-Ga(1)	149.92(4)
Ga(1)-Ge(1)-Ga(1)	180.00(6)	Ga(4)-Ga(2)-Ga(1)	133.34(6)
Ga(1)-Ga(1)-Ge(1)	121.51(3)	Ga(4)-Ga(2)-Ga(1)	82.75(4)
Ga(1)-Ga(1)-Ga(3)	72.33(3)	Ga(1)-Ga(2)-Ga(1)	60.16(7)
Ge(1)-Ga(1)-Ga(3)	117.02(3)	Ga(4)-Ga(3)-Ga(1)	86.23(4)
Ga(3)-Ga(1)-Ga(3)	125.12(6)	Ga(3)-Ga(3)-Ga(1)	119.49(5)
Ga(1)-Ga(1)-Ga(2)	120.08(4)	Ga(3)-Ga(3)-Ga(1)	88.55(4)
Ge(1)-Ga(1)-Ga(2)	118.42(6)	Ga(1)-Ga(3)-Ga(1)	35.33(6)
Ga(3)-Ga(1)-Ga(2)	81.49(3)	Ga(3)-Ga(4)-Ga(3)	129.41(5)
Ga(1)-Ga(1)-Ga(1)	180.0	Ga(3)-Ga(4)-Ga(4)	115.29(3)
Ge(1)-Ga(1)-Ga(1)	58.50(3)	Ga(3)-Ga(4)-Ga(2)	85.18(4)
Ga(3)-Ga(1)-Ga(1)	107.67(3)	Ga(4)-Ga(4)-Ga(2)	60.78(2)
Ga(2)-Ga(1)-Ga(1)	59.92(4)	Ga(2)-Ga(4)-Ga(2)	37.77(8)
Ga(2)-Ga(2)-Ga(4)	71.11(4)	Ga(2)-Ga(4)-Ga(2)	121.57(4)

Table III.A.5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for (a) sub-structure and (b) superstructure of $\text{Ce}_3\text{Ga}_9\text{Ge}$.

(a)

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ce(1)	6(1)	10(1)	10(1)	0	0	0
Ce(2)	7(1)	9(1)	8(1)	0	0	0
Ge(1)	8(1)	9(1)	10(1)	0	0	0
Ga(1)	10(1)	12(1)	14(1)	0	0	-2(1)
Ga(2)	10(1)	11(1)	24(1)	0	0	0
Ga(3)	10(1)	10(1)	14(1)	1(1)	0	0
Ga(4)	12(1)	11(1)	9(1)	0	0	0

(b)

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Ce(1)	12(1)	18(1)	18(2)	0	0	-1(1)
Ce(2)	4(1)	7(1)	7(1)	0	0	0
Ce(3)	10(1)	12(1)	12(1)	0	0(1)	0
Ce(4)	10(1)	12(1)	12(1)	0(1)	0	0
Ge(1)	9(2)	13(2)	13(2)	0	0	0
Ge(2)	11(2)	16(2)	15(2)	0	0	0
Ga(1)	15(2)	14(2)	16(2)	1(1)	-2(1)	0(1)
Ga(2)	9(1)	13(1)	9(1)	0	2(1)	0
Ga(3)	16(3)	33(3)	16(3)	0	0	0(1)
Ga(4)	6(1)	22(2)	8(1)	0	0	0
Ga(5)	12(1)	13(1)	12(1)	-1(1)	0	0
Ga(6)	13(1)	13(1)	12(1)	-1(1)	0	0
Ga(7)	10(1)	17(1)	12(1)	-1(1)	0(1)	1(1)
Ga(8)	16(2)	12(1)	14(1)	0	-1(1)	0
Ga(9)	16(2)	12(1)	14(1)	0(1)	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Magnetic Measurements

The magnetic susceptibility measurements were performed on a MPMS SQUID magnetometer (Quantum Design, Inc.) in the temperature range 2 – 350 K with an external applied magnetic field 500 Gauss. A polycrystalline sample of $\text{Ce}_3\text{Ga}_9\text{Ge}$ and $\text{Gd}_3\text{Ga}_9\text{Ge}$ were used for the isotropic measurements. A single crystal sample of $\text{Gd}_3\text{Ga}_9\text{Ge}$ was used to investigate the magnetic anisotropy with respect to the crystallographic axes. The crystals were positioned with the [100] crystallographic direction parallel and perpendicular to the external magnetic field. The data on field-dependence of magnetization was collected for both analogs at 3 K for the fields up to ± 5 Tesla.

3. Results and Discussion

Reaction Chemistry

The new ternary polygallides $\text{RE}_3\text{Ga}_9\text{Ge}$ were isolated from the Ga-flux reactions containing RE, Cu, Ga and Ge (the ratio used was 4 : 1 : 30 : 4). From these reactions the Gd and Y analogs were initially obtained, along with binary CuGa_2 and Ge. Similarly, it was found that if the reaction involves Fe instead of Cu, the ternary polygallides are produced as a major phase, and Fe is found in the binary compound FeGa_3 . However, the $\text{RE}_3\text{Ga}_9\text{Ge}$ phase was detected only in minor quantities if the reactions involved Ni or Co. The presence of Ni and Co favors the formation of quaternary compounds such as

$\text{RE}_{0.67}\text{M}_2\text{Ga}_{5+n-x}\text{Ge}_x$ ², REMGa_3Ge ²², $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ ²², $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ ²², $\text{RE}_2\text{MGa}_9\text{Ge}_2$ ²³.

$\text{RE}_3\text{Ga}_9\text{Ge}$ phases formed at low M : RE ratios ($\leq 1 : 4$) and, of course, in the absence of the transition metal.

The large, well-formed single crystals of $\text{RE}_3\text{Ga}_9\text{Ge}$ can grow easily in liquid Ga. The crystals adopt needle or bar-like crystal morphology, see Figure III.A.1. The aggregation of needles into bundles is found in some cases, and it is more common for the Ce analog or when short synthesis times were employed. The face-indexing procedure showed that the direction of the needle growth coincides with the [100] crystallographic axis, *i.e.* the crystal growth terminates quicker in the (*bc*)-plane but continues to propagate in the direction of the shorter *a*-axis.

The $\text{RE}_3\text{Ga}_9\text{Ge}$ phases are very stable and form in a wide range of reaction conditions. For example, we have employed four different heating profiles seeking an improvement in the microscopic ordering in the crystal structures of the $\text{RE}_3\text{Ga}_9\text{Ge}$ compounds. The temperature regimes with the subsequently increasing time of the isothermal step (6, 10 and 30 days) and, oppositely, with an extremely short (5 hours) isothermal step were carried out. For all the RE elements we tried, the final product was pure $\text{RE}_3\text{Ga}_9\text{Ge}$ phase, independent of the temperature profile. An exception was seen for Ce using the short profile, where a different ternary Ce/Ga/Ge phase²⁴ formed instead. Interestingly, neither the prolonged, nor shortened temperature profiles resulted in noticeably improved microcrystalline quality of the material.

Crystal Structure

(a) Substructure Description

A projection of the $\text{RE}_3\text{Ga}_9\text{Ge}$ sub-structure onto the bc plane is presented in Figure III.A.2A. The structure is three-dimensional, however, for the sake of simplicity it is worthwhile to sub-divide it into two 2D units: a monoatomic Ce-Ga-Ge plane and a Ga-only puckered layer. These 2D motifs alternate along the c -axis building a 3D structure, and the additional Ce(2) atoms are inserted in the remaining voids. Alternatively, the structure can be viewed as constructed of two independent interpenetrating sub-lattices: an open 3D Ga-network (see Figure III.A.3) and Ce-Ga-Ge monoatomic planes. Ce(2) atoms fill in the remaining cavities.

The Ga-only puckered layer is depicted in Figure III.A.2B. In this layer, the Ga(3) and Ga(4) are arranged in the form of 8-member rings in the boat conformation. The rings are condensed into a 2D puckered layer by sharing each of the eight sides with neighboring rings. The puckered layers extend in the direction perpendicular to the c -axis, and bind to each other through Ga(4)-Ga(4) interactions, thus forming a 3D Ga-only network with large tunnels running parallel to the a -axis. This Ga-only open framework unit is shown in Figure III.A.3. The shortest Ga-Ga distance in this structure (excluding the disordered atoms) occur in the 3D Ga-only framework; overall, Ga-Ga distances span the range from 2.5172(10) Å to 2.614(2) Å. These bonding contacts, thus, reflect rather strong Ga-Ga interactions, making the 3D Ga-only sub-structural unit a rigid polyatomic network. The observed distances are close to the sum of single-bonded metallic radii for Ga²⁵ (2.50 Å) and also comparable to those found in elemental Ga²⁶ (2.484 Å - 2.788 Å).

Figure III.A.2. (A) Projection of the sub-structure (*Immm*) of $\text{Ce}_3\text{Ga}_9\text{Ge}$ onto *bc*-plane. Larger grey spheres represent Ce atoms, filled and open circles correspond to Ga and Ge atoms, respectively. The unit cell is shown in bold. For clarity, the bonds to Ce atoms are not drawn; (B) Fragment of the Ce-Ga-Ge plane viewed along the *c*-axis; (C) The Ga-only 2D puckered layer.

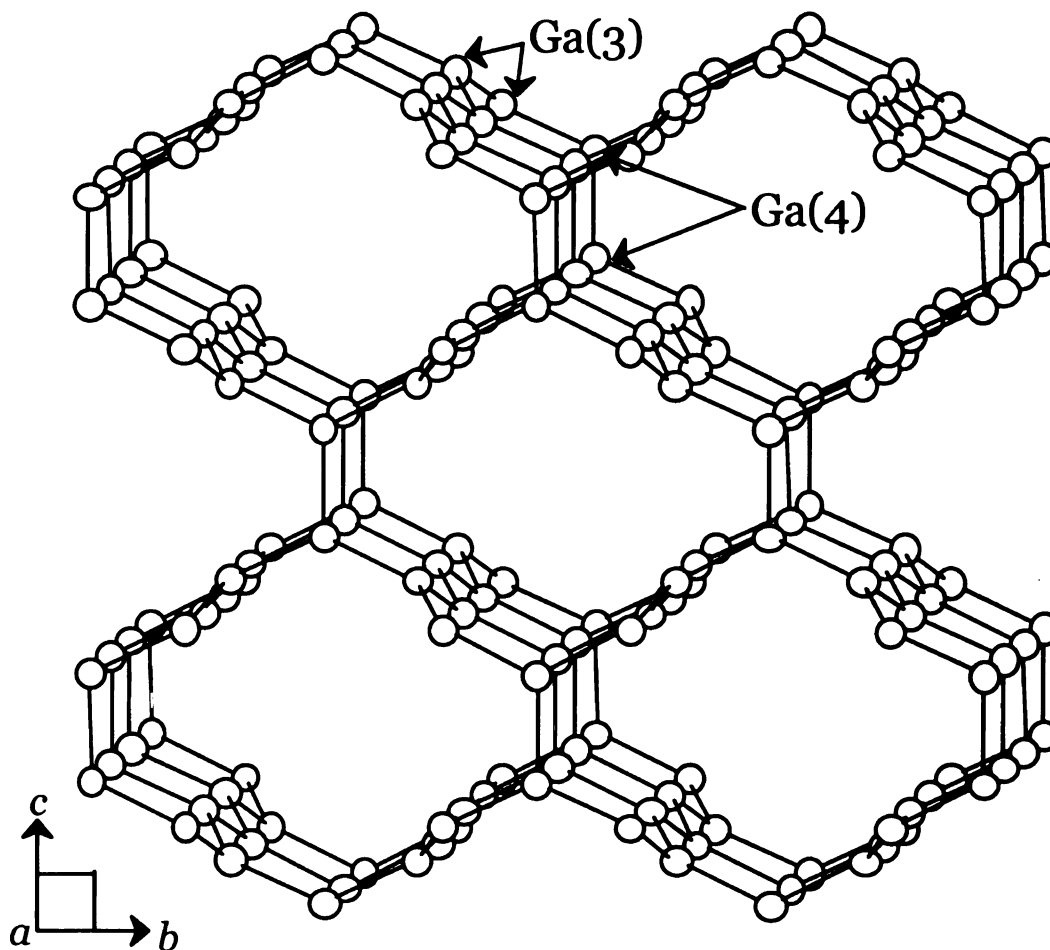


Figure III.A.3. The ordered Ga-only open 3D framework viewed along the a -axis ($Immm$). The Ga atoms are represented by open circles. The bonds between the Ga atoms are drawn up to 2.62 Å. The tunnel openings (shown by arrows) measure ~ 11 Å in width and ~ 8 Å in height.

The fragment of the Ce-Ga-Ge plane, viewed along the c -axis is shown in Figure III.A.2C. In this plane, the Ga atoms appear in a disordered arrangement forming a triangular mesh with unrealistic Ga-Ga bond distances (1.629(3) Å) between the triangles, while the Ga-Ga bonds within the triangle are regular and close to 2.71 Å. The Ce(1) atoms fill in the center of the triangles, additionally creating unreasonably short Ce-Ga bonds (1.452(2) Å and 1.6203(14) Å). A similar type of disorder between RE and Ga (or Al) was observed for RENi_3Al_9 ²⁷, $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Ge}_x$ ² ($n = 0, 1$), $\text{RE}_{1.34}\text{Pt}_4\text{Ga}_{10}$ ⁴ and $\text{RE}_4\text{Pt}_9\text{Al}_{24}$ ²⁸. As mentioned above, the occupancy parameter of each disordered atom refined to 50%, and this points to a simple ordering model. It is thus plausible to assume that the ordered arrangement is achieved when either the Ga_3 triangle is present and the Ce atom is removed from its center, or the Ce position is occupied while the Ga position comprising the triangle around it is vacant. This simple ordering scheme is shown in Figure III.A.4 (note that the cell parameters in the ordered plane have doubled along the a -axis).

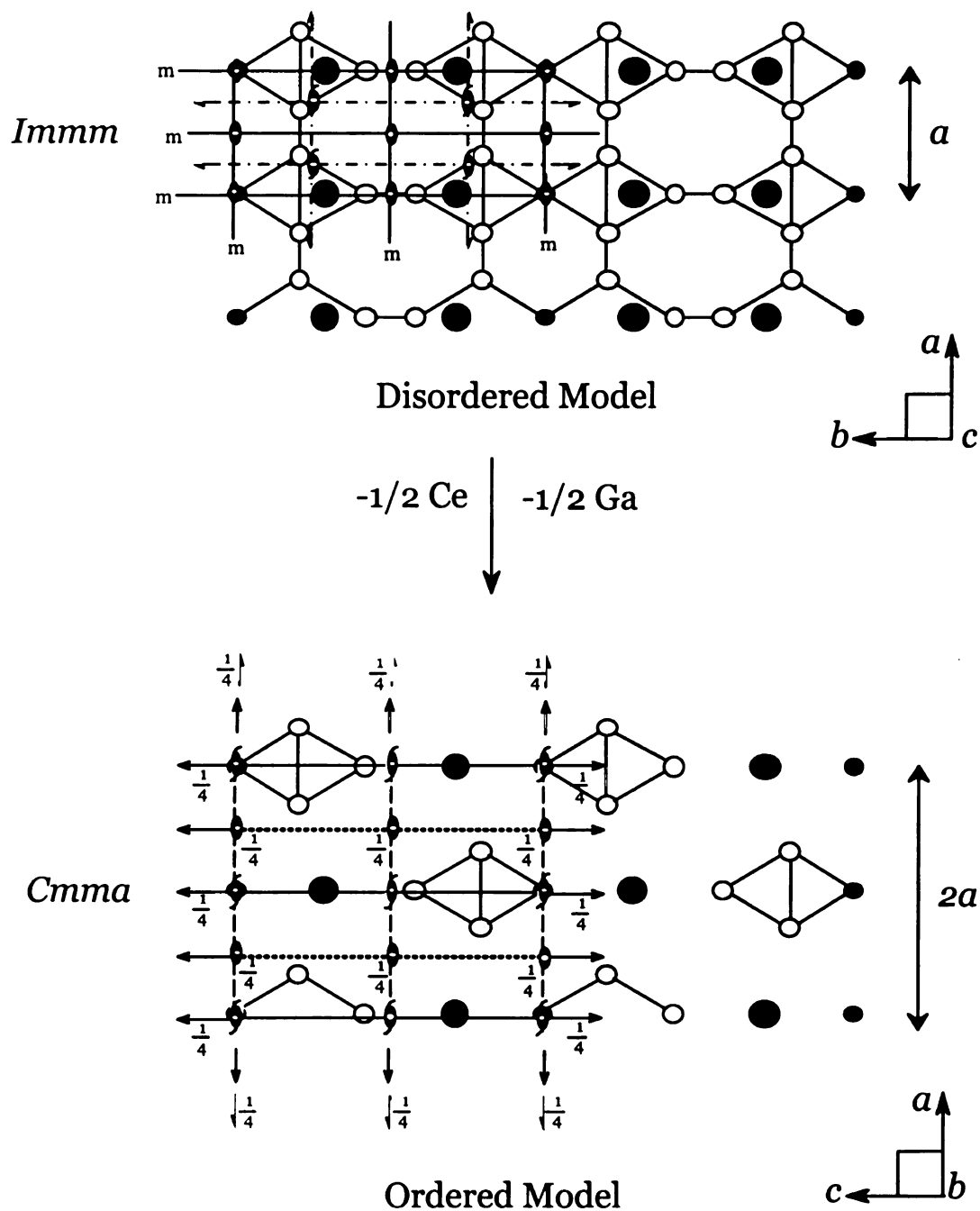


Figure III.A.4. Ordering scheme of the Ce, Ga, and Ge atoms in a selected monoatomic plane. An ordered arrangement (down) is achieved when half of Ce(1) and half of Ga(1) and Ga(2) atoms are removed from the disordered plane (up). The symmetry of the corresponding space group is superimposed onto the pattern of the plane to clarify the descent in symmetry in going from the sub-structure (*Immm*) to the superstructure (*Cmma*).

The local coordination of Ce, Ga and Ge atoms is shown in Figure III.A.5. For clarity, only the ordered atoms are depicted. The Ce(1) and Ce(2) atoms have 14 and 12 neighbors within the distance of 3.5 Å, respectively. The coordination environment of Ce(1) includes thirteen Ga atoms with Ce(1)-Ga bonds ranging between 3.1139(16) Å and 3.4342(9) Å, and one Ge atom at 3.0991(13) Å. Similarly, Ce(2) has ten Ga atoms bonded within 3.1428(9) Å to 3.3650(8) Å, plus two Ge atoms connected at 3.0847(7) Å. Considering the sum of single-bonded metallic radii²⁵ of Ce (1.818 Å for CN = 12) and Ga (1.25 Å) these interactions could be regarded weakly bonding. The Ce-Ga bond distances found in Ce₃Ga₉Ge are similar to those in CeRu₂Ga₈³ which cover the range from 3.135 Å to 3.387 Å. Note that the Ce-Ge distances are substantially shorter than the corresponding Ce-Ga bonds in accordance with the original Ga/Ge assignment. The local coordination sphere of Ge atoms within 3.0 Å is comprised of four Ga(1) atoms that are located in-plane with the Ge atom at 2.5936(14) Å. The Ga atoms within 3.0 Å adopt rather irregular coordination environments that include four to six other Ga atoms and a Ge atom, as shown in Figure III.A.5. The average distance found in Ce₃Ga₉Ge is 2.64 Å, quite shorter than the average Ga-Ga distance of 2.70 Å in metallic Ga²⁶. This further reinforces the idea of strong covalent bonding within the Ga-only 3D network.

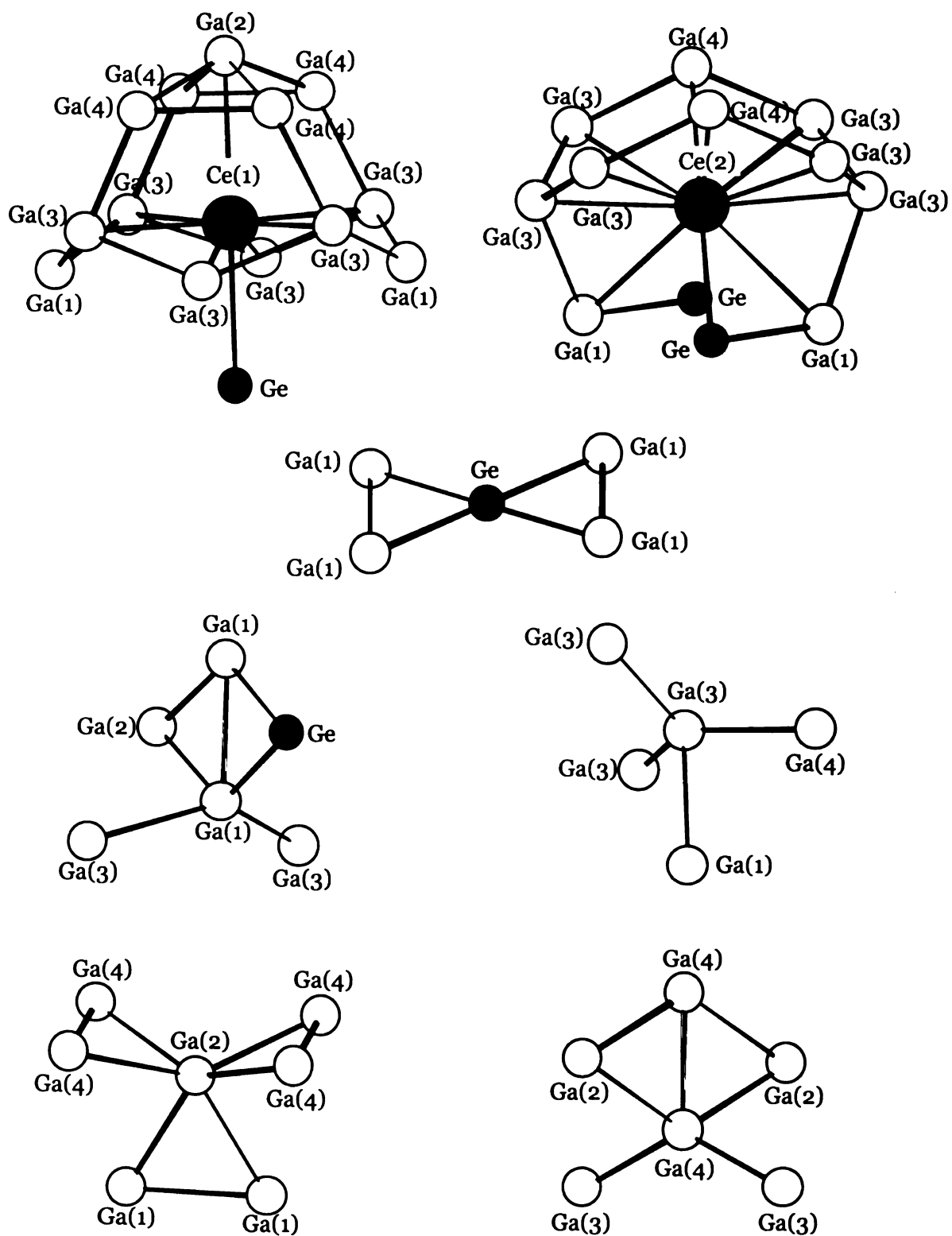


Figure III.A.5. Near-neighbor coordination environment of Ce atoms up to 3.5 Å and Ga, Ge atoms up to 3.0 Å.

(b) Superstructure Description. Substructure – Superstructure Relationship

Although the solution for the fully ordered superstructure has not been obtained due to the lack of data, the intermediate superstructure solution exhibiting partially ordered arrangement was refined. This superstructure of $\text{Ce}_3\text{Ga}_9\text{Ge}$ viewed along the a -axis is depicted in Figure III.A.6A, and it too could be thought as built of 2D units: a Ga-only puckered slab and a Ce-Ga-Ge monoatomic sheet. Again, the difference between the sub-structure and the super-structure lies in the packing and registry of the monoatomic layers along the b -axis. For example, in the superstructure the layers located at $y = 0, \frac{1}{2}$ are identical to the one found for the substructure and characterized by short distances between Ga(1), Ga(3) and Ce(1). The fragment of the disordered monoatomic layer at $y = 0, \frac{1}{2}$ viewed along the b -axis is depicted in Figure III.A.6B. In contrast, the monoatomic planes situated at $y = \pm 1/4$ contain Ce(2), Ga(2) and Ga(4) that are arranged with regular interatomic distances. For example, in the Ga(4)Ga(2)_2 triangle the Ga-Ga distance is $2.705(3) \text{ \AA}$, and the Ce(2)-Ga distance is $3.142 \text{ \AA}$ on average. This ordered type of plane is shown in Figure III.A.6C. Note that the ordered plane found in the super-structure and given in Figure III.A.6C is identical to the model shown in Figure III.A.4.

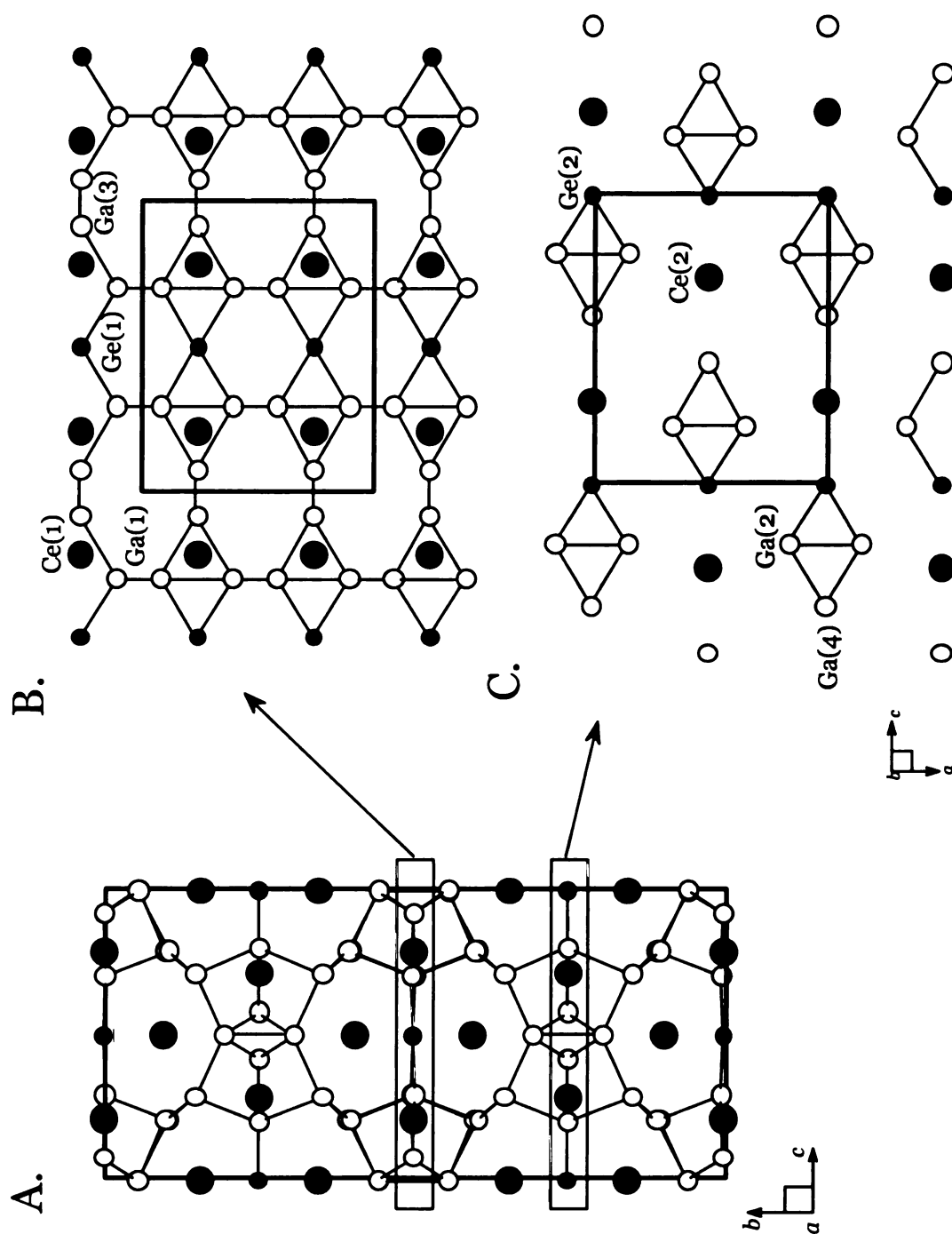


Figure III.A.6. (A) The superstructure of $\text{Ce}_3\text{Ga}_9\text{Ge}$ projected on bc -plane. The atoms are depicted in the same manner as for sub-structure. The cut-out of the (B) disordered and (C) ordered monoatomic planes viewed along the b -axis.

It is possible now to recognize the mechanism by which ordering of the Ce-Ga-Ge planes can take place by looking at the relationship between the sub- and the super-structure. It is evident from geometrical considerations that the disordered plane results from a superposition of two ordered planes shifted with respect to each other by the length of cell parameter a' . Figure III.A.7A illustrates a few unit cells of the disordered sub-structure ($Immm$, a' , b' , c') stacked along the c' -axis. If we were to glide every second unit cell along a' with respect to the one above and below, we would obtain a new structure shown in Figure III.A.7B. This super-structure is now defined by unit cell parameters that are $a = 2a'$, and $c = 2c'$. It is also clear that the lattice centering has changed from I -centered to C -centered²⁹. Most importantly, the transformation results in ordering of half of the Ce-Ga-Ge planes. However, the other half of the planes that were located inside of the sub-cell (symmetry equivalent due to I -centering) have not changed and remained disordered. In Figure III.A.7 the ordered and the disordered planes of the super-cell are represented with the letters "O" and "D", respectively. The refined super-cell ($Cmma$, $2a'$, $2b'$, c') is given for comparison in Figure III.A.7C. It is evident that the proposed model for the superstructure has a full correspondence with the one refined from the X-ray diffraction data. This is a C -centered 4-fold super-cell with alternating ordered and disordered planes of Ce-Ga-Ge.

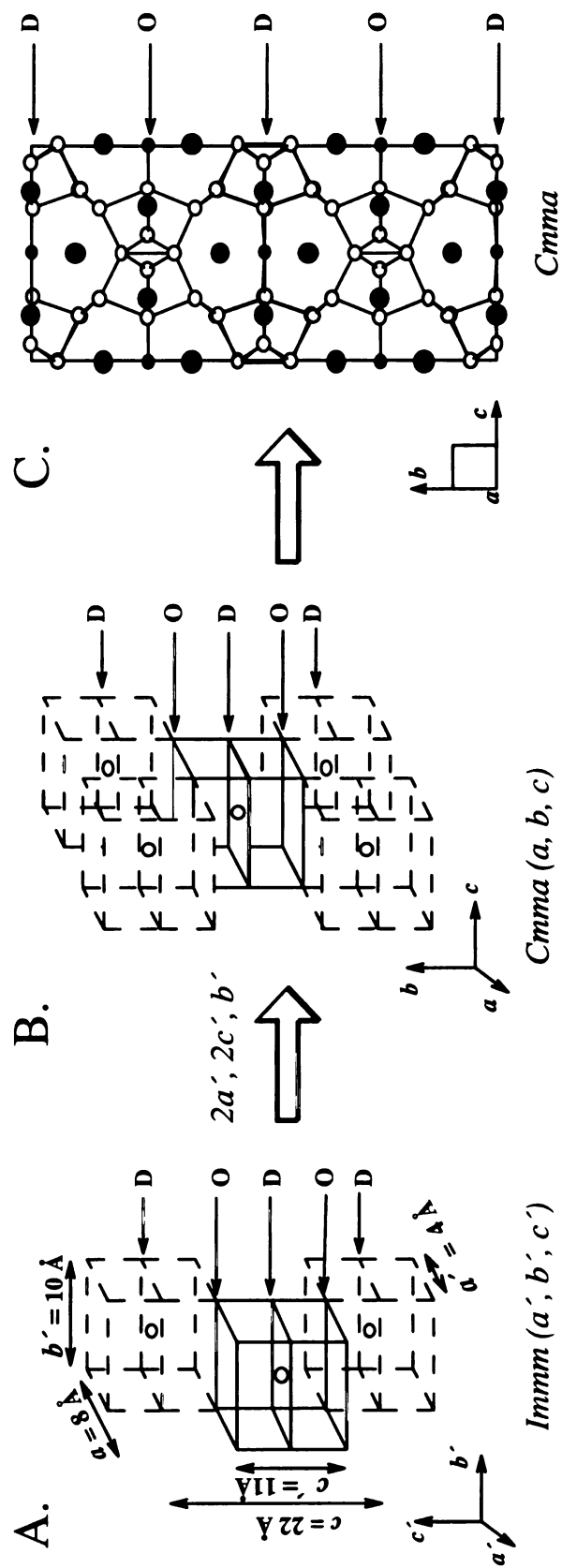


Figure III.A.7. (A - B) The transformation from the disordered sub-structure (*Immm*, a', b', c') to the partially ordered super-structure (*Cmma*, $2a', 2c', b$) via “sliding” of the sub-structure blocks by a' . (C) The refined super-structure (*Cmma*, $2a', 2c', b$) is given for comparison. The ordered and disordered monoatomic planes are marked with letters “O” and “D”, respectively.

The presented model helps us to get an insight into the process that takes place during the crystal growth. Apparently, the crystal planes containing the monoatomic layer of RE-Ga-Ge can “slide” easily with respect to the rest of the structure. In other words, the energy barrier for this transformation seems to be comparable to the thermal energy, so that the process is activated at the temperatures at which the synthesis is carried out. Employing different synthesis regimes with prolonged or shortened time we anticipated obtaining either the thermodynamic or the kinetic product that could possibly contain an ordered arrangement, where the planes are “locked” in place due to the energy stabilization of given configuration. Unfortunately, a product with fully ordered planes was not obtained from these experiments.

It is also plausible to assume that an ordered arrangement could exist at the microscopic level, however, for the crystal of given size the stacking faults of the microscopic domains would produce a statistical averaging of the X-ray data, and as a result a disordered picture. On the other hand, the completely opposite situation could hold true: in the absence of the short-range ordering of the planes, the infinitely large super-cell (up to a physical size of the crystal) would adequately describe the structure. Thus far, the data collected on a number of crystals with different rare-earth elements, crystal sizes, and different synthetic regimes did not lead to fully ordered structure solutions. Despite these indications, we searched for yet higher order superstructures looking at X-ray diffraction axial photographs. The $[hk0]$ and $[0kl]$ zone photographs are presented in Figure III.A.8A and III.A.8B, respectively. The photographs were taken on $\text{Y}_3\text{Ga}_9\text{Ge}$ with an exposure time of 1480 and 800 s for the $[hk0]$ and $[0kl]$ zones, respectively. All the diffraction spots present in the pattern are well defined, leaving no

indication for diffuse scattering. All present reflections could be indexed in the super-cell $(2a', 2c', b')$. No additional spots referring to a higher order super-cell were detected.

We emphasize that the collected intensity data that corresponds to the partially ordered super-structure was rather weak. The chance to obtain reliable X-ray data from an even higher order superstructure is thus greatly reduced. Perhaps, electron diffraction studies could provide more valuable information on the existence of the high-order super-cell due to stronger interaction of electrons with matter. The work is in progress to obtain electron diffraction patterns from the single crystal sample of $\text{RE}_3\text{Ga}_9\text{Ge}$.

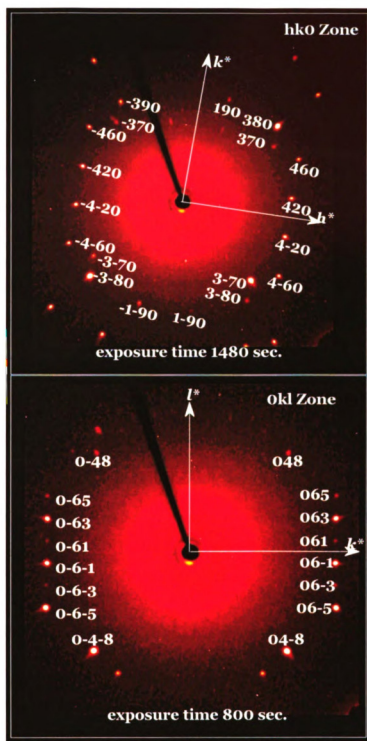


Figure III.A.8. (A) $[hk0]$ and (B) $[0kl]$ X-ray diffraction zone photographs for $\text{Y}_3\text{Ga}_5\text{Ge}$.

The Bragg spots are indexed in the $2a^*, 2c^*, b^*$ super-cell.

Magnetic Properties

(a) Gd-analog

The temperature dependence of the magnetic susceptibility and the inverse magnetic susceptibility of a single crystal sample of $\text{Gd}_3\text{Ga}_9\text{Ge}$ measured with the [100] crystallographic direction oriented parallel and perpendicular to the external field is presented in Figures III.A.9A and III.A.10A. In the high-temperature region (50 – 350 K) the molar magnetic susceptibility (χ_m) obeys the Curie-Weiss law. The extrapolation of the inverse susceptibility to zero yielded negative values of Weiss constants $\theta_{\parallel} = -48$ K and $\theta_{\perp} = -50$ K. The effective magnetic moments $\mu_{\text{eff}}^{\parallel} = 8.66$ BM and $\mu_{\text{eff}}^{\perp} = 9.0$ BM were obtained from the linear part of χ_m^{-1} vs T, and appear to be rather high compared to the free-ion values³⁰ for Gd^{3+} (7.94 BM). Relatively large values of μ_{eff} were also observed for the $\text{GdAl}_{3-x}\text{Ge}_x$ ³¹ and Gd-containing equiatomic intermetallides^{32,33}. An expanded region of χ_m at low temperatures is shown in the inset of Figure III.A.9B and III.A.10B. Below 30 K an onset of an antiferromagnetic ordering is observed. The broad maximum centered at ~ 15 K is seen in the case of $\chi_m^{\perp}$, but not in $\chi_m^{\parallel}$, which continues to rise up to the lowest measured temperature of 2 K. Additionally, a minor variation in zero-field-cooled (ZFC) – field-cooled (FC) parts of $\chi_m^{\parallel}$ was observed below 20 K indicating weak history dependence. The isotropic data of magnetic susceptibility for Gd analog is shown in Figure III.A.11, and it is consistent with the anisotropic measurements with a μ_{eff} of 8.39 BM and negative Weiss constant $\theta = -49$ K.

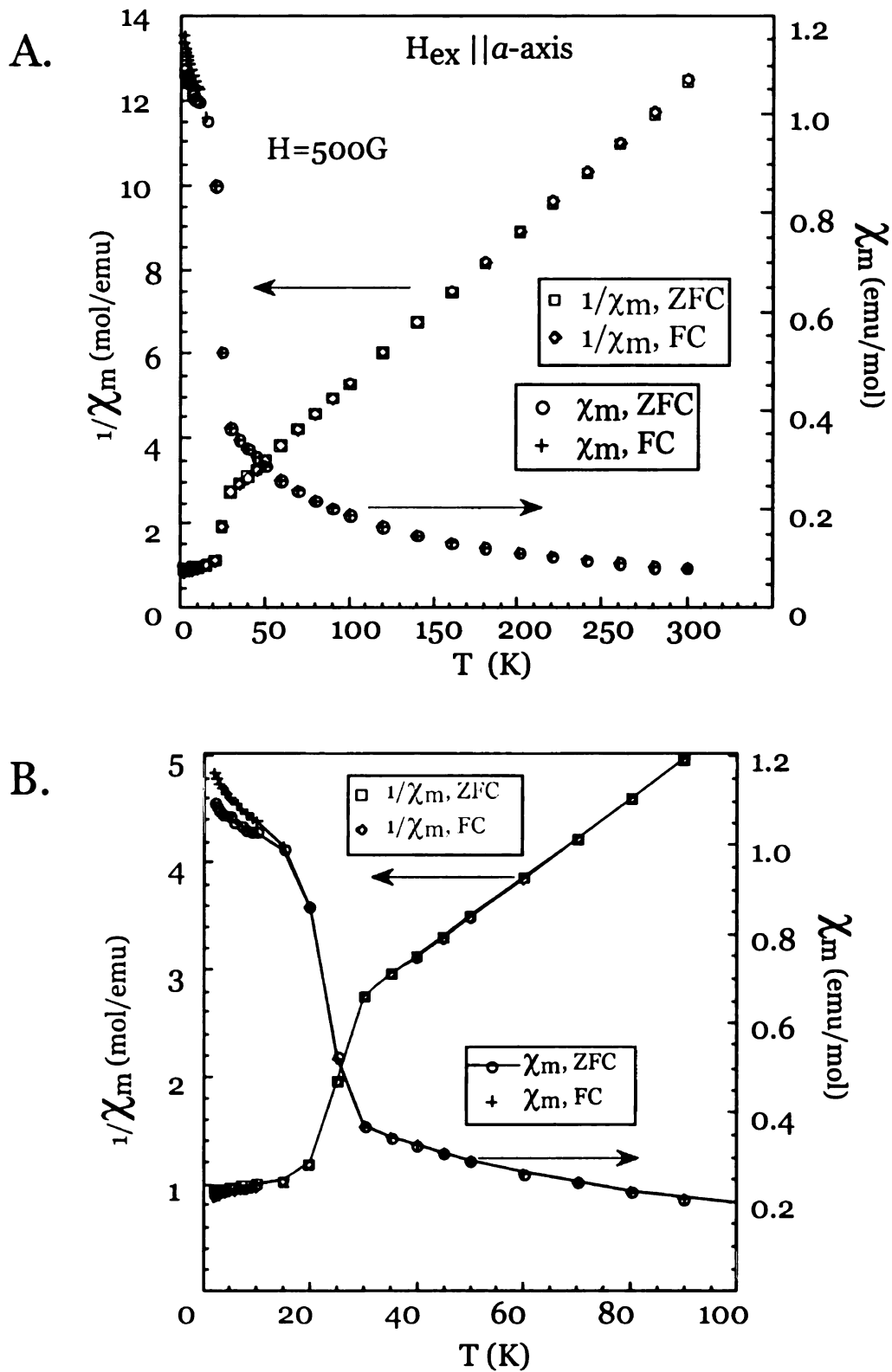


Figure III.A.9. (A) Temperature dependence of molar magnetic susceptibility and inverse susceptibility of a $\text{Gd}_3\text{Ga}_9\text{Ge}$ single crystal oriented with the $[100]$ axis parallel to the external magnetic field (H_{ex}); (B) χ_m and χ_m^{-1} in the vicinity of antiferromagnetic ordering.

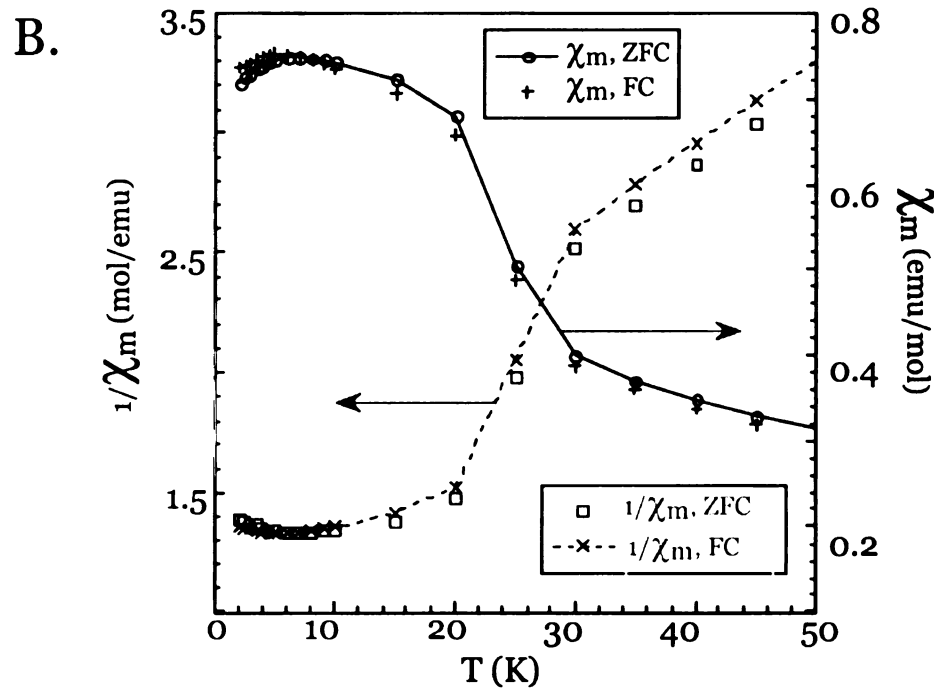
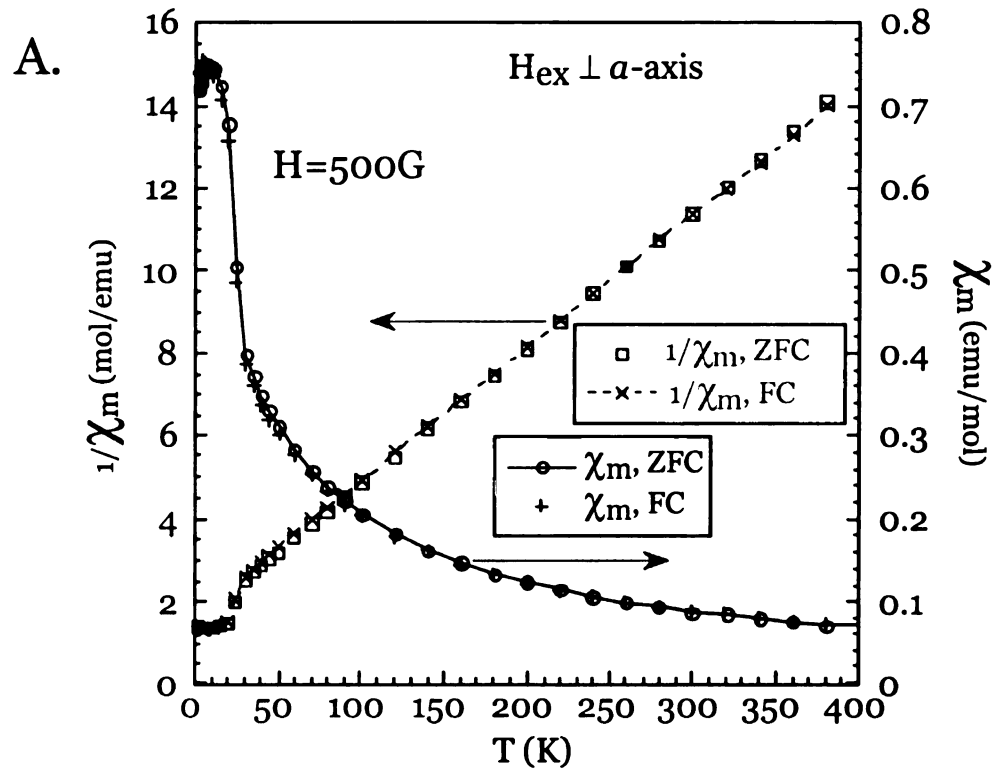


Figure III.A.10. (A) Temperature dependence of molar magnetic susceptibility and inverse susceptibility of $\text{Gd}_3\text{Ga}_9\text{Ge}$ single crystal oriented with $[100]$ axis perpendicular to the external magnetic field (H_{ex}); (B) χ_m and χ_m^{-1} in the vicinity of antiferromagnetic ordering.

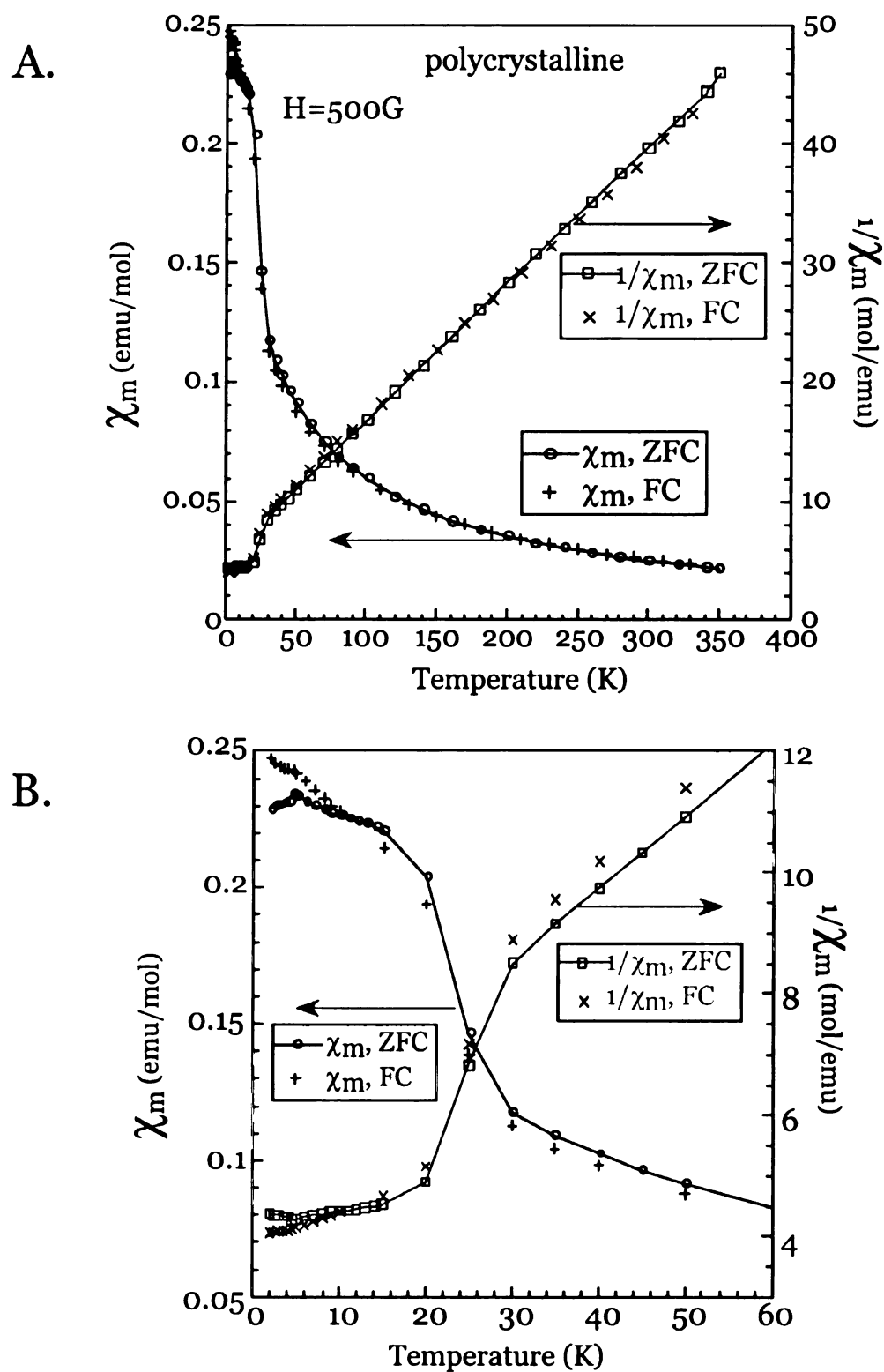
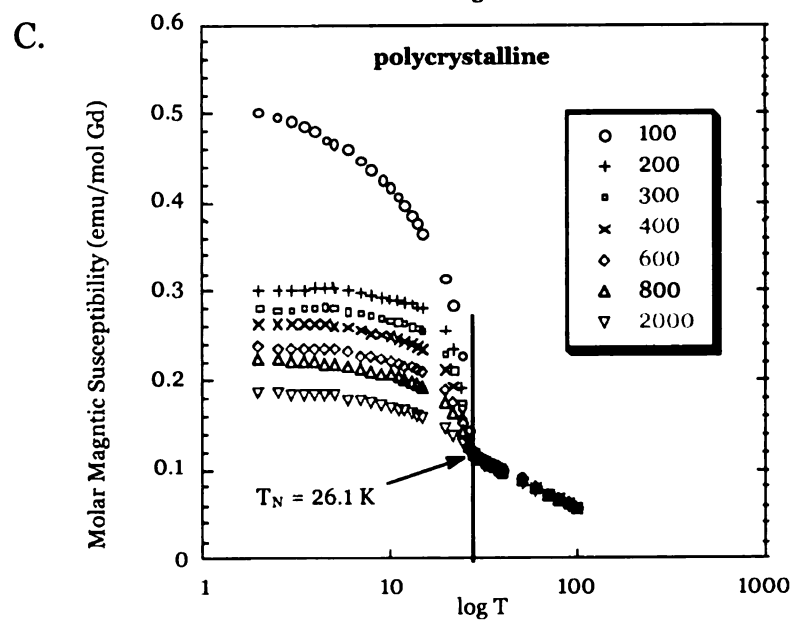
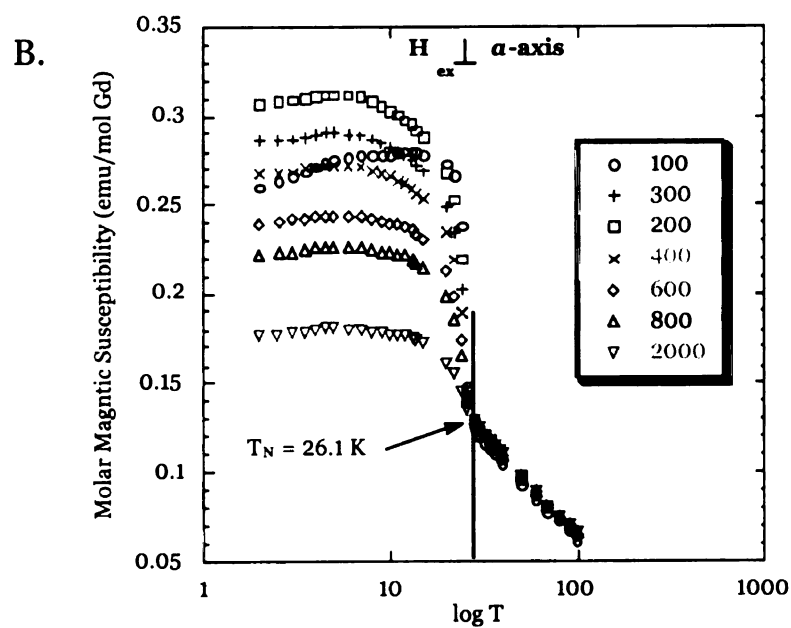
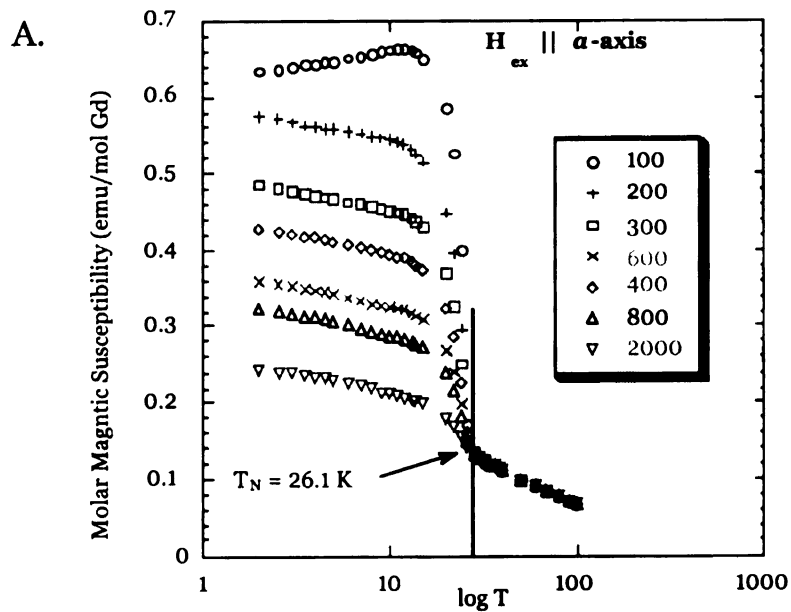


Figure III.A.11. (A) Temperature dependence of isotropic molar magnetic susceptibility and inverse susceptibility of $\text{Gd}_3\text{Ga}_9\text{Ge}$ (B) χ_m and χ_m^{-1} in the vicinity of antiferromagnetic ordering.

In order to deduce the Néel temperature (T_N) of the antiferromagnetic transition for Gd_3Ga_9Ge , a set of isofield susceptibility measurements were done. The corresponding Néel temperature determined from the $\chi_m - \log T$ plots is 26.1 K, see Figure III.A.12A-C.

The field dependence of magnetization of the single crystal and polycrystalline samples measured in the fields up to ± 5 Tesla is shown in Figure III.A.13. The saturation magnetization was fully developed neither in isotropic, nor anisotropic type of measurements. The maximal effective magnetic moment of only $\mu_{eff} \sim 4$ BM was reached in the field of 5 Tesla. Thus, the magnetic properties were found to be unaffected by the crystal orientation in both the temperature- and field-dependent susceptibility measurements. Similar results were obtained in the study of the quaternary $RE_{0.67}Ni_2Ga_{5-x}Ge_x^2$ compounds of the late RE series (Sm, Gd-Tm), where the crystal field anisotropy was not expressed for the Gd analog solely. A negligible effect of the crystal field in these cases is connected to the properties of the S-ground state of the Gd^{3+} ion. It was shown³⁴ that in the absence of an angular momentum contribution to the total angular momentum the anisotropy effects due to the crystal field vanish.

Figure III.A.12. Isofield plots of the molar magnetic susceptibility vs temperature measured (A) parallel; (B) perpendicular to the external magnetic field and (C) isotropic. The applied fields were varied from 100 to 2000 Gauss. The Néel temperature is the point at which the susceptibility measured at different fields diverges.

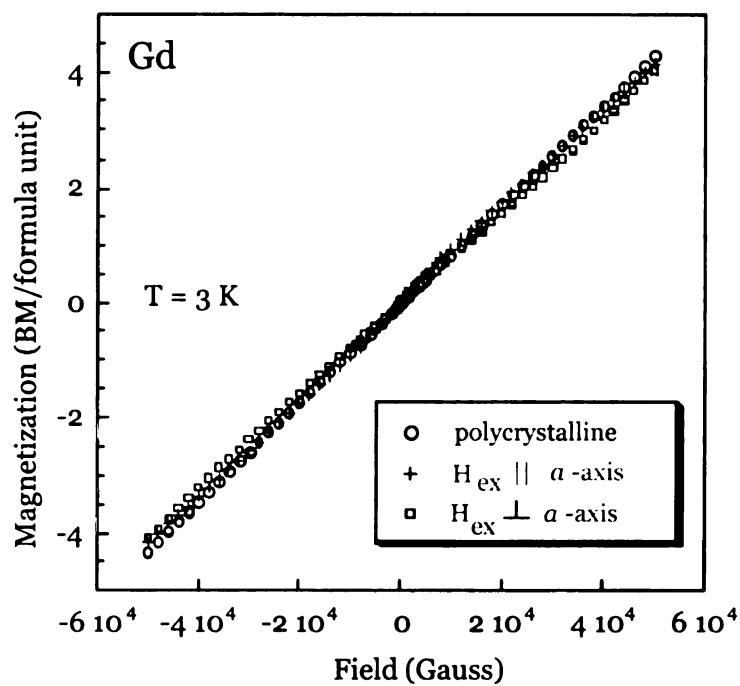


b) Ce analog

The temperature dependence of χ_m and χ_m^{-1} is given in Figure III.A.14. The effective magnetic moment of 2.53 BM per Ce atom calculated from the linear part of the χ_m^{-1} vs T plot, is in very good agreement with the free-ion value for the Ce^{3+} ion (2.54 BM). The Weiss constant has small negative value of -7.7 K, indicating possible weak antiferromagnetic ordering. In the low temperature region, see Figure III.A.14B, the ZFC-FC part of susceptibility diverges at about 6 K, however continues to rise. Thus, up to 2 K no maximum in the χ_m vs T plot was detected.

The plot of the field dependence of magnetization is given in Figure III.A.13B. For the Ce analog, saturation magnetization is reached at about 1 BM, which is rather characteristic for Ce-containing ternary intermetallics^{35,36,37} and is due to the effect of the crystal field splitting on $J = 5/2$ of the ground multiplet of the Ce^{3+} atom^{38,39}. This also is a possible cause of the slight non-linearity of the reciprocal magnetic susceptibility observed at higher temperatures.

A.



B.

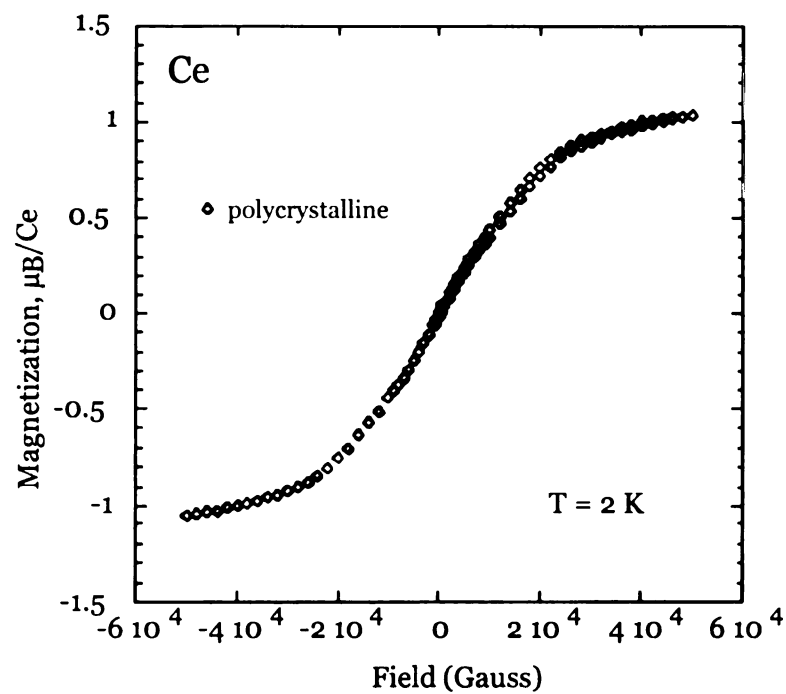


Figure III.A.13. The magnetization in fields up to ± 5 Tesla. (A) Magnetization data for a single crystal and polycrystalline samples of $\text{Gd}_3\text{Ga}_9\text{Ge}$. (B) Magnetization data for a polycrystalline sample of $\text{Ce}_3\text{Ga}_9\text{Ge}$.

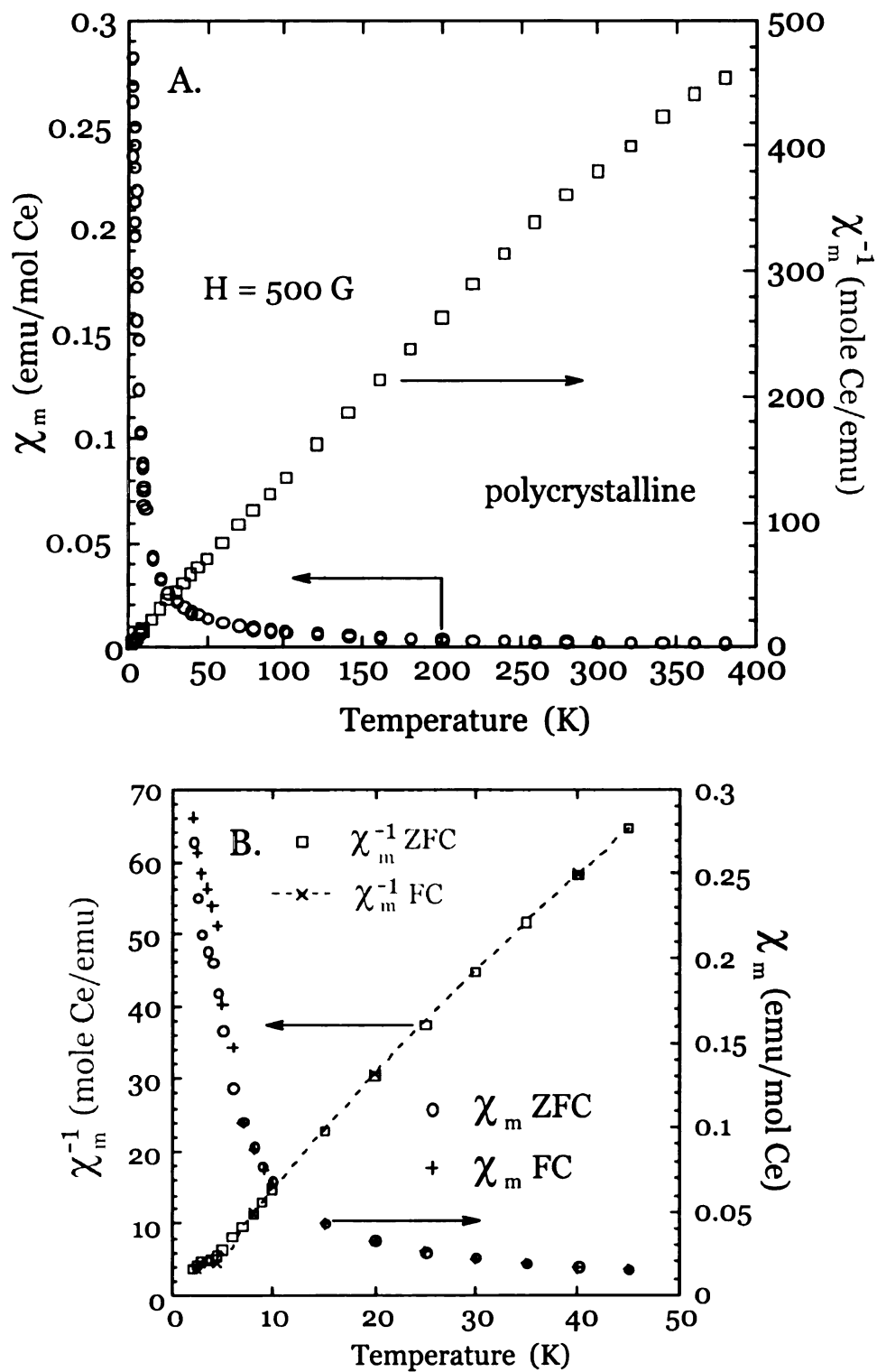


Figure III.A.14. (A) Temperature dependence of isotropic molar magnetic susceptibility and inverse susceptibility of $\text{Ce}_3\text{Ga}_9\text{Ge}$ (B) χ_m and χ_m^{-1} in the vicinity of antiferromagnetic ordering.

4. Concluding Remarks

The new ternary compounds $\text{RE}_3\text{Ga}_9\text{Ge}$ ($\text{RE} = \text{Y}, \text{Ce}, \text{Sm}, \text{Gd}$ and Yb) form from reactions in molten Ga over a broad range of synthetic conditions. The crystal structure of $\text{RE}_3\text{Ga}_9\text{Ge}$ consists of two interpenetrating sub-lattices: monoatomic RE-Ga-Ge planes and an open 3D Ga framework with large channels extending along the a -axis and filled with RE atoms. The Ga-only framework is a rigid structural unit held together via strong covalent Ga-Ga interactions with an average Ga-Ga bond distance being shorter than that in elemental Ga. Severe disorder exists between RE and Ga atoms in the monoatomic plane that is attributed to the unconstrained “sliding” of the planes during crystal growth. This “sliding” may reflect a relatively weak bonding between the two sub-lattices. On the basis of the investigation of the relationship between the sub- and the superstructure, a model for atomic ordering in the RE-Ga-Ge planes was proposed. The magnetic measurements performed on $\text{Gd}_3\text{Ga}_9\text{Ge}$ single crystals reveal no anisotropy effects associated with the crystal field, in accord with S-ground state of Gd ions.

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Chapter III

Part B

Yb₃Ga₄Ge₆ and Yb₂Ga₄Ge₆: Novel Zintl Phases Grown From Molten Ga. X-ray Structure Determination, Electronic Structure Calculations and Magnetic Properties.

1. Introduction

The Ga flux synthetic technique has proven successful not only for the synthesis of novel intermetallics, but also for the discovery of new phases of rare-earth and group 13/14 Zintl phases. We have reported a number of intermetallics grown from Ga flux including RENiSi₃¹, Sm₂NiGa₁₂², RE₄FeGa_{12-x}Ge_x³, RE_{0.67}M₂Ga_{5+n-x}Ge_x⁴ (M = Ni, Co) RE₃Ga₉Ge⁵, REMGa₃Ge and RE₃Ni₃Ga₈Ge₃^{6,7}. However, the examples of the Zintl compounds obtained from molten Ga are very scarce. The accounts on explorations in

this area come primarily from the group of G. D. Stucky. Thus, the clathrate compounds $M_8Ga_{16}Tt_{30}$ ^{8,9} (M = Ba, Sr; Tt = Si, Ge) and $Eu_4Ga_8Ge_{16}$ ¹⁰ were successfully grown from Ga solutions. The preparation of yet another two new Zintl compounds in the RE-Ga-Ge system is very inspiring.

Herein, we present Ga flux synthesis, X-ray structure determination, electronic and band structure calculations and magnetic properties of two new closely related, yet unique, Zintl compounds: $Yb_2Ga_4Ge_6$ and $Yb_3Ga_4Ge_6$.

2. Experimental

Synthesis

The $Yb_2Ga_4Ge_6$ (1) and $Yb_3Ga_4Ge_6$ (2) compounds were initially isolated from Ni-containing reactions intended for the synthesis of $Yb_{0.67}Ni_2Ga_{5+n-x}Ge_x$ ^{4,11}. For rational synthesis of $Yb_3Ga_4Ge_6$, elemental Yb, Ga and Ge of typical purity 99.9% and higher (CERAC Inc.) were combined in the molar ratios 1 : 10 : 2 (Yb 0.985 mmol, Ga 9.85 mmol; Ge 1.97 mmol) and placed in alumina crucibles. The metals were handled in a glove box under nitrogen atmosphere. The crucibles were then sealed in silica ampoules under vacuum ($\sim 1 \cdot 10^{-4}$ Torr). The reaction mixtures were heated to 1000°C in 15h, left at 1000°C for 5 hours, then cooled to 850°C and kept there for 3 days, and finally cooled to 200°C at the rate 18°/h. Most of the unused flux was then removed by span filtration at $\sim 200^\circ\text{C}$ through a specially designed silica filter with coarse frit. Further isolation was

done in a 3-5 molar solution of iodine in dimethylformamide (DMF) over 24 hours at room temperature. The product was rinsed with DMF, water, and dried with acetone and ether. From these reactions, crystals of monoclinic $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ phase were recovered at a ~100% yield. The presence of the $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ phase was detected only in the Ni-containing reactions mentioned above. The reaction conditions that lead to the enriched $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ phase have not yet been optimized. The crystals of **1** and **2** have characteristic dark grey color and metallic luster. The size of the grown crystals reaches a few millimeters in one dimension. An image of typical crystals of $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ and $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ grown under the above conditions taken on a scanning electron microscope (SEM) is shown in Figure III.B.1.A and III.B.1.B, respectively.

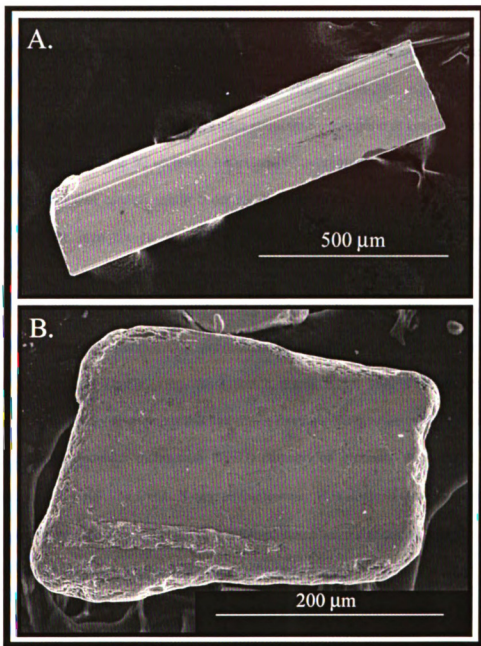


Figure III.B.1. SEM photograph of typical Ga flux grown (A) $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ and (B) $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ crystals.

Elemental Analysis and X-Ray Powder Diffraction

The elemental composition was studied by Energy Dispersive Spectroscopy (EDS) semi-quantitative analysis on the SEM JEOL JSM-35C equipped with the NORAN Inc. EDS detector. The routine data acquisition was done at acceleration voltage 20 kV and collection time 30 seconds. An extensive averaging of the results obtained on different crystals was carried out in order to attain accurate values of the atomic ratios. Additionally, the analysis on the freshly exposed cross-section of the crystals was performed in order to eliminate possible contamination with the surface-adhered impurities. The EDS results obtained from the surface and cross-section areas were then compared. The average composition (normalized to the amount of Yb) was determined to be $\text{Yb}_2\text{Ga}_{4.3}\text{Ge}_{5.1}$ and $\text{Yb}_3\text{Ga}_{4.2}\text{Ge}_{4.7}$ for **1** and **2**, respectively. This is in agreement with the single crystal X-ray refinement that led to the formula $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ and $\text{Yb}_3\text{Ga}_4\text{Ge}_6$.

The X-ray powder diffraction (XRD) patterns of products were taken at room temperature on a CPS 120 INEL X-ray diffractometer (Cu $K\alpha$ radiation) equipped with position-sensitive detector. Experimental XRD patterns were compared to that calculated from single crystal data using the CERIUS² software package¹².

Single Crystal X-Ray Diffraction

The intensity data was collected on single crystals of $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (**1**) and $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (**2**) at room temperature with a Siemens Platform SMART¹³ CCD X-ray diffractometer. For **1**, a crystal of suitable size $0.12 \times 0.10 \times 0.08 \text{ mm}^3$ was cut off from a

larger crystal and mounted on glass fiber. A needle-like single crystal with the dimensions $0.06 \times 0.08 \times 0.30 \text{ mm}^3$ was selected for data collection of **2**. For each compound, a full sphere of reciprocal data (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$) was acquired up to 60° in 2θ . The individual frames were measured using the ω -steps of 0.30° and an exposure time 20 s and 25 s per frame for **1** and **2**, respectively. The data acquisition and cell reduction was done with SMART¹³, and data reduction was performed with the SAINTPLUS¹⁴ software package. The face-indexing routine was applied for analytical absorption corrections. An empirical correction for absorption based on symmetry equivalent reflections was applied with the SADABS¹⁵ program. The structure solution and refinement were done by direct methods with the SHELXTL¹⁶ software package. All atomic positions were refined anisotropically. The setting of the cell was standardized with the STRUCTURE TIDY program¹⁷.

Structure Refinement of 1

The first unit cell reduction in SMART¹³ initially gave a *C*-centered monoclinic lattice with parameters $a = 23.257(4) \text{ \AA}$, $b = 4.1699(7) \text{ \AA}$, $c = 10.744(1) \text{ \AA}$ and β angle very close to 90° ($\beta = 90.07(1)^\circ$). However, the subsequent cell determinations using a larger number of frames (total of 1000 frames) yielded orthorhombic *C*-centered lattice with cell parameters $a = 4.1732(6) \text{ \AA}$, $b = 23.276(3) \text{ \AA}$, $c = 10.738(2) \text{ \AA}$. Following space group determination in SAINTPLUS¹⁴, based on the systematic absences statistics, led to four possible space groups *Cmc2*₁ (#36), *Cmcm* (#63) and *Ama2* (#40). The mean $|E^2 - 1|$

value of 0.666 pointed to a possibility of a non-centrosymmetric space group*. The combined figure of merit (CFOM) also favored the choice of non-centrosymmetric space groups *Cmc2₁* and *Ama2*; of those *Cmc2₁* had lowest CFOM value (1.82 %). Thus, the non-centrosymmetric *Cmc2₁* space group was chosen for the structure solution and was found to be correct during the structure refinement. However, the attempt to solve the structure in the centrosymmetric *Cmcm* space group was also made. As a result, an extremely poor convergence (~ 50 %) of the calculated versus observed structure was found. Thus, the correctness of the structure solution in *Cmc2₁* was reconfirmed.

The information relevant to the data collection and structure refinement of **1** is given in the Table III.B.1. The final atomic positions and the equivalent thermal displacement parameters are listed in Table III.B.2. The selected interatomic distances (up to 3.5 Å) and bond angles are presented in Table III.B.3 and III.B.4, respectively. The anisotropic displacement parameters for all atoms are given in Table III.B.5.

Structure Refinement of 2

The initial cell of **2** suggested by the program was a monoclinic *C*-centered cell with the volume 8-fold larger than the one of true structure (cell parameters $a = 47.948(6)$ Å, $b = 8.4025(9)$ Å, $c = 21.892(4)$ Å; $\beta = 91.41(1)^\circ$). The cell enlargement was most likely caused by the $\lambda/2$ radiation problem. Further cell reductions yielded a correct cell with parameters $a = 23.941(6)$ Å, $b = 4.1928(11)$ Å, $c = 10.918(3)$ Å, $\beta = 91.426(4)^\circ$

* The estimated $|E^2-1|$ values for non-centrosymmetric space group is 0.736 and for the centrosymmetric one 0.968.

which was then used for data integration and structure solution. The monoclinic space group $C2/m$ was chosen and was found to be correct during the structure refinement. The final convergence factor $R_1 = 4.26\%$ was obtained upon correcting for secondary extinction and refining all atoms anisotropically. However, further reduction of the R -values to 4.11% was possible by introducing the twinning law matrix (001, 0-10, 100) that accounted for the 2-fold rotational twin about the b -axis. This particular type of twinning is likely to occur in the monoclinic systems with β angle close to 90° .

Details of the data collection and structure refinement of **2** is given in the Table III.B.6. The final atomic positions and the equivalent thermal displacement parameters are listed in Table III.B.7. The selected interatomic distances (up to $3.5 \text{ \AA}$) and bond angles are presented in Table III.B.8 and III.B.9, respectively. The anisotropic displacement parameters for all atoms are given on Table III.B.10.

The Ga/Ge Assignment in 1 and 2

Because of very similar X-ray scattering lengths of Ga and Ge atoms, the assignment of their positions in the structure is very difficult. In our previous studies, we have been using the connectivity data coupled with thorough elemental analysis in assigning Ga/Ge and Al/Si from X-ray data. In a number of instances, such approach had been proven correct by additional neutron* crystallographic studies^{18,19,6}. Although the

* The neutron scattering lengths of Ga and Ge atoms differ $\sim 10\%$, compared to that of X-ray (3%).

neutron diffraction studies are currently in progress for the compound **2**, we decided to investigate the Ga/Ge distribution of Ga/Ge with the information at hand.

First of all, careful elemental analysis performed on the crystalline samples of **1** and **2** indicated a slightly higher content of Ge compare to Ga. This makes the composition “Yb₂Ga₄Ge₆” and “Yb₃Ga₄Ge₆” more favorable as opposed to “Yb₂Ga₅Ge₅” and “Yb₃Ga₅Ge₅” and even more favorable than, for example, “Yb₂Ga₆Ge₄” and “Yb₃Ga₆Ge₄”. Secondly, using the fact that the covalent radius of Ge is slightly smaller than that of Ga, in the original X-ray structure solution the shorter Yb-M distances were assigned to Yb-Ge, while the longer to Yb-Ga. This narrowed down the number of possible structures to 2 – 3. Using the assignments made above, two models for each compound were generated, where (a) the shortest homoatomic distances were ascribed to Ge-Ge and the longer to Ga-Ga; (b) the distribution of Ga and Ge throughout the structure was even. For compound **1**, the structural refinement immediately yielded a better convergence factor (2.29% vs 2.33%) for the combination (b). For **2**, the convergence factor remained invariant for both (a) and (b) assignments. The configurations (a) and (b) for the structures of **1** and **2** were further tested using electronic band structure calculations. For **1**, the configuration (b) showed to be more stable in energy than (a) by a substantial amount of 3 eV per formula unit*. This result was consistent with the X-ray refinement data pointing to the validity of the of the Ga/Ge assignment using the configuration (b). This particular assignment is used in this work to report the structure of **1**.

* The formula unit in this case is (2 × Yb₂Ga₄Ge₆).

In the case of **2**, theoretical structure calculations showed that configuration (b) is more stable by 0.04 eV than (a), in accord with the results obtained for **1**. However, by choosing configuration (b) for **2**, one of the bonds which is more typical for Yb-Ge bonding (3.0072(17) Å) had to be assigned as Yb-Ga. For this reason, further tests using modified configuration (b) were carried out. In the next run of electronic structure calculations, the Ga atom at 3.0072(17) Å from Yb was exchanged for a Ge atom, to conform to the original assignment requiring shorter Yb-Ge connectivities. However, in order to keep the number of electrons constant, one of the Ge sites had to be exchanged with Ga. For this reason, the Ge atom at the trigonal planar site was substituted for Ga, as the corresponding Yb distances allowed. Interestingly, the obtained structure was the least stable in energy, lying higher by ~ 1 eV per formula unit*. Thus, the original configuration (b) was chosen in case of **2** as well, and it is reported below.

For both structures **1** and **2**, the determined Ga/Ge distribution was later found to be in accordance with the magnetic measurements and the Zintl concept of bonding, further validating the atomic assignment.

* The formula unit in this case is $(2 \times \text{Yb}_3\text{Ga}_4\text{Ge}_6)$.

Table III.B.1. Crystal data and structure refinement for Yb₂Ga₄Ge₆ (1).

Empirical formula	Yb ₂ Ga ₄ Ge ₆
Formula weight	1060.50
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Cmc</i> 2 ₁ (#36)
Unit cell dimensions (Å)	<i>a</i> = 4.1698(7) <i>b</i> = 23.254(4) <i>c</i> = 10.7299(18)
Volume (Å ³)	1040.4(3)
Z	4
Density (calculated) (g/cm ³)	6.770
Absorption coefficient (mm ⁻¹)	44.936
F(000)	1824
Crystal size (mm ³)	0.12 × 0.1 × 0.08
θ range for data collection (°)	2.58 to 29.16
Index ranges	-5 ≤ <i>h</i> ≤ 5, -31 ≤ <i>k</i> ≤ 30, -14 ≤ <i>l</i> ≤ 14
Reflections collected	5431
Independent reflections	1479 [<i>R</i> _{int} = 0.0395]
Completeness to θ = 29.16°	96.8 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1479 / 1 / 74
Goodness-of-fit on <i>F</i> ²	1.109
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] *	<i>R</i> ₁ = 0.0229, <i>wR</i> ₂ = 0.0589
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0234, <i>wR</i> ₂ = 0.0591
Absolute structure parameter	-0.03(3)
Extinction coefficient	0.00047(5)
Largest diff. peak and hole (e/Å ³)	1.452 and -1.315

* $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table III.B.2. Atomic coordinates and equivalent isotropic displacement parameters*
($\text{\AA}^2 \times 10^3$) for $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (1).

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Yb(1)	<i>4a</i>	0	0.0187(1)	0.1308(1)	14(1)
Yb(2)	<i>4a</i>	0	0.3006(1)	0.3130(1)	14(1)
Ge(1)	<i>4a</i>	0	0.1411(1)	0.0213(1)	13(1)
Ge(2)	<i>4a</i>	0	0.4285(1)	0.2255(1)	11(1)
Ge(3)	<i>4a</i>	0	0.0709(1)	0.4079(1)	12(1)
Ge(4)	<i>4a</i>	0	0.2226(1)	0.6074(1)	12(1)
Ge(5)	<i>4a</i>	0	0.4124(1)	0.4626(1)	12(1)
Ge(6)	<i>4a</i>	0	0.7049(1)	0.2878(1)	12(1)
Ga(1)	<i>4a</i>	0	0.2501(1)	-0.0002(2)	11(1)
Ga(2)	<i>4a</i>	0	0.1497(1)	0.2540(1)	11(1)
Ga(3)	<i>4a</i>	0	0.5143(1)	0.3790(1)	14(1)
Ga(4)	<i>4a</i>	0	0.1144(1)	0.6287(1)	13(1)

*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table III.B.3. Selected bond lengths [$\text{\AA}$] for $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (1).

Bond	Distance	Mult.	Bond	Distance	Mult.
Yb(1)-Ge(1)	3.0774(14)	$\times 1$			
Yb(1)-Ga(4)	3.0957(15)	$\times 1$	Ge(1)-Ga(2)	2.5050(18)	$\times 1$
Yb(1)-Ge(2)	3.1273(11)	$\times 2$	Ge(1)-Ge(5)	2.5081(11)	$\times 2$
Yb(1)-Ge(3)	3.1726(15)	$\times 1$	Ge(1)-Ga(1)	2.547(2)	$\times 1$
Yb(1)-Ge(5)	3.1884(11)	$\times 2$	Ge(2)-Ga(4)	2.5340(12)	$\times 2$
Yb(1)-Ge(3)	3.2106(15)	$\times 1$	Ge(2)-Ge(5)	2.5713(19)	$\times 1$
Yb(1)-Ga(2)	3.3202(15)	$\times 1$	Ge(2)-Ga(3)	2.5863(19)	$\times 1$
Yb(1)-Ga(3)	3.3836(13)	$\times 2$	Ge(3)-Ga(2)	2.4666(18)	$\times 1$
Yb(1)-Ga(3)	3.4982(13)	$\times 2$	Ge(3)-Ga(3)	2.4849(10)	$\times 2$
Yb(2)-Ge(5)	3.0567(14)	$\times 1$	Ge(3)-Ga(4)	2.577(2)	$\times 1$
Yb(2)-Ge(6)	3.0616(10)	$\times 2$	Ge(4)-Ga(1)	2.4658(12)	$\times 2$
Yb(2)-Ge(4)	3.0833(11)	$\times 2$	Ge(4)-Ga(4)	2.5271(19)	$\times 1$
Yb(2)-Ge(2)	3.1200(15)	$\times 1$	Ge(4)-Ge(6)	2.5672(19)	$\times 1$
Yb(2)-Ga(1)	3.1231(13)	$\times 2$	Ge(5)-Ga(3)	2.5326(19)	$\times 1$
Yb(2)-Ge(1)	3.3445(11)	$\times 2$	Ge(6)-Ga(2)	2.4745(10)	$\times 2$
Yb(2)-Ga(4)	3.4882(13)	$\times 2$	Ge(6)-Ga(1)	2.505(2)	$\times 1$

Table III.B.4. Selected bond angles [°] for Yb₂Ga₄Ge₆ (1).

Bond	Angle	Bond	Angle
Ge(1)-Yb(1)-Ga(4)	157.14(4)	Ge(3)-Yb(1)-Ga(3)	44.18(2)
Ge(1)-Yb(1)-Ge(2)	138.076(18)	Ga(2)-Yb(1)-Ga(3)	73.42(3)
Ga(4)-Yb(1)-Ge(2)	48.05(2)	Ge(1)-Yb(1)-Ga(3)	109.19(3)
Ge(2)-Yb(1)-Ge(2)	83.62(4)	Ge(2)-Yb(1)-Ga(3)	46.60(3)
Ge(1)-Yb(1)-Ge(3)	108.62(4)	Ga(3)-Yb(1)-Ga(3)	76.08(4)
Ga(4)-Yb(1)-Ge(3)	48.53(4)	Ge(1)-Yb(1)-Ga(3)	84.72(3)
Ge(2)-Yb(1)-Ge(3)	78.72(3)	Ga(4)-Yb(1)-Ga(3)	76.99(3)
Ge(1)-Yb(1)-Ge(5)	47.15(2)	Ge(2)-Yb(1)-Ga(3)	72.93(3)
Ga(4)-Yb(1)-Ge(5)	119.86(3)	Ge(2)-Yb(1)-Ga(3)	120.07(3)
Ge(2)-Yb(1)-Ge(5)	94.86(3)	Ge(3)-Yb(1)-Ga(3)	43.40(2)
Ge(2)-Yb(1)-Ge(5)	163.06(4)	Ge(5)-Yb(1)-Ga(3)	44.21(3)
Ge(3)-Yb(1)-Ge(5)	84.43(3)	Ge(5)-Yb(1)-Ga(3)	93.59(3)
Ge(5)-Yb(1)-Ge(5)	81.67(3)	Ge(3)-Yb(1)-Ga(3)	142.948(17)
Ge(1)-Yb(1)-Ge(3)	90.25(4)	Ga(2)-Yb(1)-Ga(3)	120.59(3)
Ga(4)-Yb(1)-Ge(3)	112.61(4)	Ga(3)-Yb(1)-Ga(3)	165.564(16)
Ge(2)-Yb(1)-Ge(3)	87.28(3)	Ga(3)-Yb(1)-Ga(3)	103.530(14)
Ge(3)-Yb(1)-Ge(3)	161.13(3)	Ge(5)-Yb(2)-Ge(6)	131.69(2)
Ge(5)-Yb(1)-Ge(3)	109.54(3)	Ge(6)-Yb(2)-Ge(6)	85.84(4)
Ge(1)-Yb(1)-Ga(2)	45.91(3)	Ge(5)-Yb(2)-Ge(4)	121.64(3)
Ga(4)-Yb(1)-Ga(2)	156.95(4)	Ge(6)-Yb(2)-Ge(4)	49.39(3)
Ge(2)-Yb(1)-Ga(2)	119.07(3)	Ge(6)-Yb(2)-Ge(4)	105.66(3)
Ge(3)-Yb(1)-Ga(2)	154.53(4)	Ge(5)-Yb(2)-Ge(4)	121.64(3)
Ge(5)-Yb(1)-Ga(2)	76.40(3)	Ge(6)-Yb(2)-Ge(4)	105.66(3)
Ge(3)-Yb(1)-Ga(2)	44.34(3)	Ge(4)-Yb(2)-Ge(4)	85.09(4)
Ge(1)-Yb(1)-Ga(3)	109.19(3)	Ge(5)-Yb(2)-Ge(2)	49.19(4)
Ga(4)-Yb(1)-Ga(3)	88.57(3)	Ge(6)-Yb(2)-Ge(2)	131.80(2)
Ge(2)-Yb(1)-Ga(3)	97.73(3)	Ge(4)-Yb(2)-Ge(2)	87.22(3)
Ge(2)-Yb(1)-Ga(3)	46.60(3)	Ge(6)-Yb(2)-Ga(1)	103.71(4)
Ge(3)-Yb(1)-Ga(3)	124.98(3)	Ge(6)-Yb(2)-Ga(1)	47.77(4)
Ge(5)-Yb(1)-Ga(3)	149.74(4)	Ge(4)-Yb(2)-Ga(1)	147.64(4)
Ge(5)-Yb(1)-Ga(3)	93.32(3)	Ge(4)-Yb(2)-Ga(1)	86.67(3)

Table III.B.4. (continued)

Bond	Angle	Bond	Angle
Ge(2)-Yb(2)-Ga(1)	123.58(3)	Ge(5)-Ge(2)-Ga(3)	58.82(5)
Ga(1)-Yb(2)-Ga(1)	83.76(4)	Ga(4)-Ge(2)-Ga(4)	110.73(7)
Ge(5)-Yb(2)-Ge(1)	45.86(2)	Ga(2)-Ge(3)-Ga(3)	108.07(5)
Ge(6)-Yb(2)-Ge(1)	141.15(4)	Ga(3)-Ge(3)-Ga(3)	114.07(7)
Ge(6)-Yb(2)-Ge(1)	85.97(3)	Ga(2)-Ge(3)-Ga(4)	108.89(6)
Ge(4)-Yb(2)-Ge(1)	166.12(4)	Ga(3)-Ge(3)-Ga(4)	108.82(5)
Ge(4)-Yb(2)-Ge(1)	97.34(3)	Ga(1)-Ge(4)-Ga(1)	115.45(8)
Ge(2)-Yb(2)-Ge(1)	79.28(3)	Ga(1)-Ge(4)-Ga(4)	107.37(5)
Ga(1)-Yb(2)-Ge(1)	46.22(4)	Ga(1)-Ge(4)-Ge(6)	100.60(5)
Ga(1)-Yb(2)-Ge(1)	98.07(4)	Ga(4)-Ge(4)-Ge(6)	125.86(7)
Ge(5)-Yb(2)-Ge(1)	45.86(2)	Ge(1)-Ge(5)-Ge(1)	112.46(7)
Ge(1)-Yb(2)-Ge(1)	77.13(3)	Ge(1)-Ge(5)-Ga(3)	123.55(4)
Ge(5)-Yb(2)-Ga(4)	79.35(3)	Ge(1)-Ge(5)-Ge(2)	108.70(4)
Ge(6)-Yb(2)-Ga(4)	140.26(4)	Ga(3)-Ge(5)-Ge(2)	60.89(5)
Ge(6)-Yb(2)-Ga(4)	87.41(3)	Ga(2)-Ge(6)-Ga(2)	114.82(7)
Ge(4)-Yb(2)-Ga(4)	95.60(3)	Ga(2)-Ge(6)-Ga(1)	110.46(5)
Ge(4)-Yb(2)-Ga(4)	44.71(3)	Ga(2)-Ge(6)-Ge(4)	103.31(5)
Ge(2)-Yb(2)-Ga(4)	44.67(2)	Ga(1)-Ge(6)-Ge(4)	114.23(6)
Ga(1)-Yb(2)-Ga(4)	100.30(3)	Ge(4)-Ga(1)-Ge(4)	115.45(8)
Ga(1)-Yb(2)-Ga(4)	167.63(4)	Ge(4)-Ga(1)-Ge(6)	108.52(5)
Ge(1)-Yb(2)-Ga(4)	77.06(3)	Ge(4)-Ga(1)-Ge(1)	102.34(5)
Ge(1)-Yb(2)-Ga(4)	121.42(4)	Ge(6)-Ga(1)-Ge(1)	119.90(7)
Ge(5)-Yb(2)-Ga(4)	79.35(3)	Ge(3)-Ga(2)-Ge(6)	106.70(5)
Ge(6)-Yb(2)-Ga(4)	87.41(3)	Ge(3)-Ga(2)-Ge(1)	127.40(7)
Ga(4)-Yb(2)-Ga(4)	73.41(3)	Ge(6)-Ga(2)-Ge(1)	100.81(5)
Ga(2)-Ge(1)-Ge(5)	106.87(5)	Ge(3)-Ga(3)-Ge(5)	116.81(5)
Ge(5)-Ge(1)-Ge(5)	112.46(7)	Ge(3)-Ga(3)-Ge(2)	119.20(4)
Ga(2)-Ge(1)-Ga(1)	90.59(6)	Ge(5)-Ga(3)-Ge(2)	60.30(5)
Ge(5)-Ge(1)-Ga(1)	118.11(4)	Ge(4)-Ga(4)-Ge(2)	115.43(4)
Ga(4)-Ge(2)-Ga(4)	110.73(7)	Ge(2)-Ga(4)-Ge(2)	110.73(7)
Ga(4)-Ge(2)-Ga(3)	124.38(4)	Ge(4)-Ga(4)-Ge(3)	107.91(7)

Table III.B.5. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (1).

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Yb(1)	13(1)	11(1)	17(1)	1(1)	0	0
Yb(2)	11(1)	13(1)	17(1)	-2(1)	0	0
Ge(1)	11(1)	11(1)	16(1)	0(1)	0	0
Ge(2)	9(1)	12(1)	13(1)	-1(1)	0	0
Ge(3)	11(1)	11(1)	13(1)	0(1)	0	0
Ge(4)	9(1)	12(1)	14(1)	0(1)	0	0
Ge(5)	11(1)	11(1)	15(1)	0(1)	0	0
Ge(6)	11(1)	13(1)	14(1)	-1(1)	0	0
Ga(1)	8(1)	13(1)	12(1)	0(1)	0	0
Ga(2)	11(1)	9(1)	13(1)	1(1)	0	0
Ga(3)	11(1)	11(1)	20(1)	0(1)	0	0
Ga(4)	12(1)	10(1)	18(1)	0(1)	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Table III.B.6. Crystal data and structure refinement for Yb₃Ga₄Ge₆ (2).

Empirical formula	Yb ₃ Ga ₄ Ge ₆
Formula weight	1233.54
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	<i>C2/m</i> (#12)
Unit cell dimensions (Å)	<i>a</i> = 23.941(6) <i>b</i> = 4.1928(11) β = 91.426(4)° <i>c</i> = 10.918(3)
Volume (Å ³)	1095.6(5)
Z	4
Density (calculated) (g/cm ³)	7.478
Absorption coefficient (mm ⁻¹)	51.107
F(000)	2104
Crystal size (mm ³)	0.06 × 0.08 × 0.30
θ range for data collection (°)	1.70 to 28.37
Index ranges	-27 ≤ <i>h</i> ≤ 30, -5 ≤ <i>k</i> ≤ 5, -13 ≤ <i>l</i> ≤ 13
Reflections collected	4673
Independent reflections	1412 [<i>R</i> _{int} = 0.0447]
Completeness to θ = 29.16°	90.5 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	1412 / 0 / 81
Goodness-of-fit on <i>F</i> ²	1.095
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] *	<i>R</i> ₁ = 0.0411, <i>wR</i> ₂ = 0.1114
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0425, <i>wR</i> ₂ = 0.1129
Extinction coefficient	0.00065(8)
Largest diff. peak and hole (e/Å ³)	3.118 and -2.778

* $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table III.B.7. Atomic coordinates and equivalent isotropic displacement parameters*
($\text{\AA}^2 \times 10^3$) for $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (2).

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)
Yb(1)	4 <i>c</i>	0.1759(1)	0	0.5475(1)	13(1)
Yb(2)	4 <i>c</i>	0.4764(1)	0	0.1682(1)	10(1)
Yb(3)	4 <i>c</i>	0.6447(1)	0	0.1063(1)	10(1)
Ge(1)	4 <i>c</i>	0.0225(1)	0	0.6040(2)	12(1)
Ge(2)	4 <i>c</i>	0.2254(1)	0	0.0262(1)	10(1)
Ge(3)	4 <i>c</i>	0.2917(1)	0	0.6416(1)	9(1)
Ge(4)	4 <i>c</i>	0.3478(1)	0	0.2359(1)	9(1)
Ge(5)	4 <i>c</i>	0.6040(1)	0	0.3662(1)	12(1)
Ge(6)	4 <i>c</i>	0.0515(1)	0	0.0340(1)	11(1)
Ga(1)	4 <i>c</i>	0.4210(1)	0	0.4124(1)	8(1)
Ga(2)	4 <i>c</i>	0.2408(1)	0	0.2572(2)	11(1)
Ga(3)	4 <i>c</i>	0.0652(1)	0	0.2674(2)	10(1)
Ga(4)	4 <i>c</i>	0.8644(1)	0	0.1146(1)	10(1)

*U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table III.B.8. Selected bond distances [$\text{\AA}$] for $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (2).

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
Yb(1)-Ge(3)	2.9321(17)	$\times 1$	Yb(3)-Ga(3)	3.3579(14)	$\times 2$
Yb(1)-Ge(3)	3.0563(13)	$\times 2$	Yb(3)-Ge(2)	3.4618(18)	$\times 1$
Yb(1)-Ga(1)	3.1654(13)	$\times 2$	Yb(3)-Ga(2)	3.4949(15)	$\times 1$
Yb(1)-Ge(4)	3.2213(13)	$\times 2$	Ge(1)-Ge(1)	2.490(3)	$\times 1$
Yb(1)-Ge(5)	3.3323(14)	$\times 2$	Ge(1)-Ga(1)	2.5036(13)	$\times 2$
Yb(1)-Ga(2)	3.564(2)	$\times 1$	Ge(1)-Ga(3)	2.555(2)	$\times 1$
Yb(1)-Ga(2)	3.5650(15)	$\times 2$	Ge(2)-Ge(2)	2.4775(16)	$\times 2$
Yb(2)-Ga(1)	3.0072(17)	$\times 1$	Ge(2)-Ga(2)	2.540(2)	$\times 1$
Yb(2)-Ge(6)	3.1046(13)	$\times 2$	Ge(2)-Ga(4)	2.611(2)	$\times 1$
Yb(2)-Ge(6)	3.1479(13)	$\times 2$	Ge(3)-Ge(5)	2.501(2)	$\times 1$
Yb(2)-Ga(3)	3.1587(14)	$\times 2$	Ge(3)-Ga(2)	2.5020(13)	$\times 2$
Yb(2)-Ge(4)	3.1838(18)	$\times 1$	Ge(4)-Ga(4)	2.5165(13)	$\times 2$
Yb(2)-Ge(1)	3.2521(15)	$\times 2$	Ge(4)-Ga(1)	2.573(2)	$\times 1$
Yb(2)-Ga(4)	3.4427(15)	$\times 2$	Ge(4)-Ga(2)	2.579(2)	$\times 1$
Yb(3)-Ge(2)	2.9970(12)	$\times 2$	Ge(5)-Ga(1)	2.504(2)	$\times 1$
Yb(3)-Ge(5)	3.0232(18)	$\times 1$	Ge(5)-Ga(3)	2.5241(13)	$\times 2$
Yb(3)-Ge(3)	3.1125(17)	$\times 1$	Ge(6)-Ge(6)	2.558(3)	$\times 1$
Yb(3)-Ge(6)	3.1475(13)	$\times 2$	Ge(6)-Ga(3)	2.562(2)	$\times 1$
Yb(3)-Ga(4)	3.1985(14)	$\times 2$	Ge(6)-Ga(4)	2.617(2)	$\times 1$

Table III.B.9. Selected bond angles [°] for Yb₃Ga₄Ge₆ (2).

Bond	Angle	Bond	Angle
Ge(3)-Yb(1)-Ge(3)	89.03(4)	Ga(2)-Yb(1)-Ga(2)	106.38(4)
Ge(3)-Yb(1)-Ge(3)	86.62(5)	Ge(3)-Yb(1)-Ga(2)	43.97(3)
Ge(3)-Yb(1)-Ga(1)	129.88(3)	Ga(2)-Yb(1)-Ga(2)	72.04(4)
Ge(3)-Yb(1)-Ga(1)	80.71(4)	Ga(1)-Yb(2)-Ge(6)	122.59(4)
Ge(3)-Yb(1)-Ga(1)	138.34(5)	Ge(6)-Yb(2)-Ge(6)	84.95(4)
Ga(1)-Yb(1)-Ga(1)	82.95(4)	Ga(1)-Yb(2)-Ge(6)	133.04(3)
Ge(3)-Yb(1)-Ge(4)	85.69(4)	Ge(6)-Yb(2)-Ge(6)	103.53(3)
Ge(3)-Yb(1)-Ge(4)	174.12(4)	Ge(6)-Yb(2)-Ge(6)	48.29(5)
Ge(3)-Yb(1)-Ge(4)	95.85(3)	Ge(6)-Yb(2)-Ge(6)	83.51(4)
Ga(1)-Yb(1)-Ge(4)	100.74(4)	Ga(1)-Yb(2)-Ga(3)	90.23(4)
Ga(1)-Yb(1)-Ge(4)	47.50(4)	Ge(6)-Yb(2)-Ga(3)	145.39(5)
Ge(4)-Yb(1)-Ge(4)	81.20(4)	Ge(6)-Yb(2)-Ga(3)	85.80(4)
Ge(3)-Yb(1)-Ge(5)	132.69(3)	Ge(6)-Yb(2)-Ga(3)	47.93(4)
Ge(3)-Yb(1)-Ge(5)	45.85(4)	Ge(6)-Yb(2)-Ga(3)	102.35(4)
Ge(3)-Yb(1)-Ge(5)	99.58(4)	Ga(1)-Yb(2)-Ga(3)	90.23(4)
Ga(1)-Yb(1)-Ge(5)	45.24(4)	Ga(3)-Yb(2)-Ga(3)	83.17(5)
Ga(1)-Yb(1)-Ge(5)	97.42(4)	Ga(1)-Yb(2)-Ge(4)	49.00(4)
Ge(4)-Yb(1)-Ge(5)	138.38(4)	Ge(6)-Yb(2)-Ge(4)	88.45(4)
Ge(4)-Yb(1)-Ge(5)	85.91(4)	Ge(6)-Yb(2)-Ge(4)	132.46(3)
Ge(5)-Yb(1)-Ge(5)	77.97(4)	Ga(3)-Yb(2)-Ge(4)	124.55(4)
Ge(3)-Yb(1)-Ga(2)	83.26(4)	Ga(1)-Yb(2)-Ge(1)	46.95(3)
Ge(3)-Yb(1)-Ga(2)	43.58(2)	Ge(6)-Yb(2)-Ge(1)	167.53(5)
Ga(1)-Yb(1)-Ga(2)	117.39(3)	Ge(6)-Yb(2)-Ge(1)	96.07(3)
Ge(4)-Yb(1)-Ga(2)	137.86(2)	Ge(6)-Yb(2)-Ge(1)	86.15(4)
Ge(5)-Yb(1)-Ga(2)	72.66(4)	Ge(6)-Yb(2)-Ge(1)	142.32(4)
Ge(3)-Yb(1)-Ga(2)	43.97(3)	Ga(3)-Yb(2)-Ge(1)	99.97(4)
Ge(3)-Yb(1)-Ga(2)	131.27(4)	Ge(4)-Yb(2)-Ge(1)	79.17(4)
Ge(3)-Yb(1)-Ga(2)	81.54(4)	Ge(1)-Yb(2)-Ge(1)	80.28(5)
Ga(1)-Yb(1)-Ga(2)	135.07(4)	Ga(1)-Yb(2)-Ga(4)	78.00(4)

Table III.B.9. (continued)

Bond	Angle	Bond	Angle
Ga(1)-Yb(1)-Ga(2)	85.93(4)	Ge(2)-Yb(3)-Ga(4)	49.72(4)
Ge(4)-Yb(1)-Ga(2)	92.85(4)	Ge(5)-Yb(3)-Ga(4)	133.66(3)
Ge(4)-Yb(1)-Ga(2)	44.31(4)	Ga(4)-Yb(3)-Ga(3)	140.86(4)
Ge(5)-Yb(1)-Ga(2)	176.59(3)	Ge(6)-Yb(3)-Ga(3)	46.24(4)
Ge(5)-Yb(1)-Ga(2)	104.97(3)	Ga(3)-Yb(3)-Ga(3)	77.27(4)
Ge(6)-Yb(2)-Ga(4)	141.09(4)	Ge(2)-Yb(3)-Ge(2)	44.39(2)
Ge(6)-Yb(2)-Ga(4)	88.11(4)	Ge(5)-Yb(3)-Ge(2)	134.89(4)
Ga(3)-Yb(2)-Ga(4)	167.83(5)	Ge(3)-Yb(3)-Ge(2)	86.80(4)
Ga(3)-Yb(2)-Ga(4)	99.74(3)	Ge(6)-Yb(3)-Ge(2)	122.25(4)
Ge(4)-Yb(2)-Ga(4)	44.42(3)	Ga(4)-Yb(3)-Ge(2)	74.32(4)
Ge(1)-Yb(2)-Ga(4)	120.94(4)	Ga(3)-Yb(3)-Ge(2)	138.19(2)
Ge(1)-Yb(2)-Ga(4)	74.27(4)	Ge(2)-Yb(3)-Ga(2)	45.27(4)
Ga(1)-Yb(2)-Ga(4)	78.00(4)	Ge(2)-Yb(3)-Ga(2)	97.78(4)
Ge(6)-Yb(2)-Ga(4)	46.77(4)	Ge(5)-Yb(3)-Ga(2)	77.35(4)
Ge(6)-Yb(2)-Ga(4)	141.09(4)	Ge(3)-Yb(3)-Ga(2)	44.03(3)
Ga(3)-Yb(2)-Ga(4)	99.74(3)	Ge(6)-Yb(3)-Ga(2)	166.39(4)
Ga(4)-Yb(2)-Ga(4)	75.03(4)	Ge(6)-Yb(3)-Ga(2)	99.95(3)
Ge(6)-Yb(2)-Ga(4)	46.77(4)	Ga(4)-Yb(3)-Ga(2)	141.26(4)
Ge(6)-Yb(2)-Ga(4)	97.90(4)	Ga(4)-Yb(3)-Ga(2)	89.64(3)
Ge(2)-Yb(3)-Ge(2)	88.77(5)	Ga(3)-Yb(3)-Ga(2)	120.16(4)
Ge(2)-Yb(3)-Ge(5)	119.95(3)	Ga(3)-Yb(3)-Ga(2)	75.72(4)
Ge(2)-Yb(3)-Ge(3)	87.30(4)	Ge(2)-Yb(3)-Ga(2)	67.00(4)
Ge(5)-Yb(3)-Ge(3)	48.09(4)	Ge(3)-Yb(3)-Ga(4)	133.56(3)
Ge(2)-Yb(3)-Ge(6)	148.32(4)	Ge(6)-Yb(3)-Ga(4)	48.70(4)
Ge(2)-Yb(3)-Ge(6)	85.36(4)	Ge(6)-Yb(3)-Ga(4)	102.31(4)
Ge(5)-Yb(3)-Ge(6)	89.58(4)	Ga(4)-Yb(3)-Ga(4)	81.91(4)
Ge(3)-Yb(3)-Ge(6)	123.38(3)	Ge(2)-Yb(3)-Ga(3)	165.38(4)
Ge(6)-Yb(3)-Ge(6)	83.53(4)	Ge(2)-Yb(3)-Ga(3)	95.41(3)
Ge(2)-Yb(3)-Ga(4)	105.69(4)	Ge(5)-Yb(3)-Ga(3)	46.23(3)

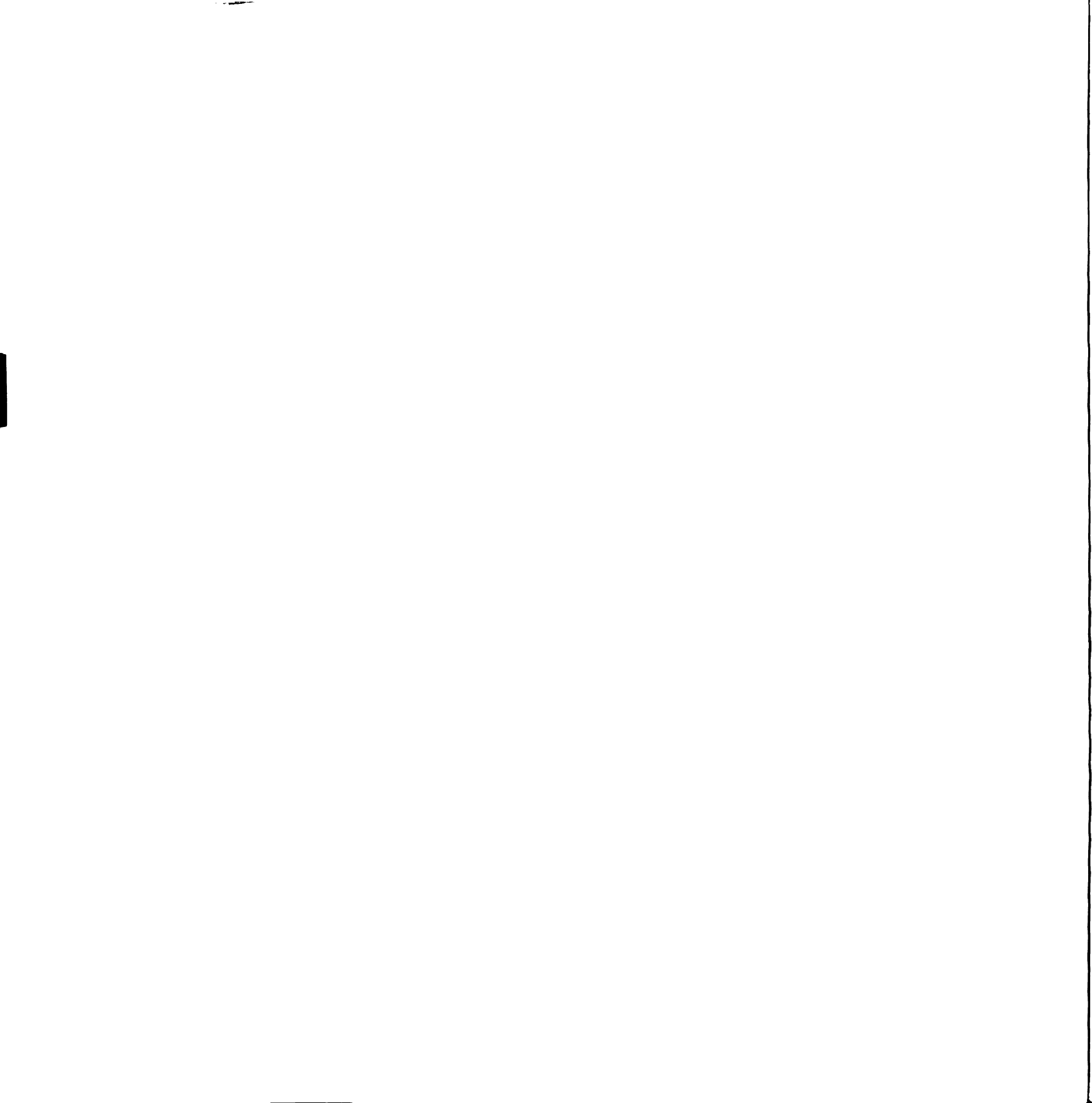


Table III.B.9. (continued)

Bond	Angle	Bond	Angle
Ge(3)-Yb(3)-Ga(3)	78.93(4)	Ga(3)-Ge(5)-Ga(3)	112.31(8)
Ge(6)-Yb(3)-Ga(3)	46.24(4)	Ge(6)-Ge(6)-Ga(3)	112.78(9)
Ge(6)-Yb(3)-Ga(3)	98.05(4)	Ge(6)-Ge(6)-Ga(4)	124.88(10)
Ga(4)-Yb(3)-Ga(3)	87.54(4)	Ga(3)-Ge(6)-Ga(4)	122.34(8)
Ge(1)-Ge(1)-Ga(1)	99.02(7)	Ge(1)-Ga(1)-Ge(1)	113.72(8)
Ga(1)-Ge(1)-Ga(1)	113.72(8)	Ge(1)-Ga(1)-Ge(5)	102.23(6)
Ge(1)-Ge(1)-Ga(3)	99.09(10)	Ge(1)-Ga(1)-Ge(4)	107.78(6)
Ga(1)-Ge(1)-Ga(3)	119.49(5)	Ge(5)-Ga(1)-Ge(4)	123.24(8)
Ge(2)-Ge(2)-Ge(2)	115.59(12)	Ge(3)-Ga(2)-Ge(3)	113.84(8)
Ge(2)-Ge(2)-Ga(2)	99.86(8)	Ge(3)-Ga(2)-Ge(2)	113.55(5)
Ge(2)-Ge(2)-Ga(4)	104.66(7)	Ge(3)-Ga(2)-Ge(4)	111.09(5)
Ga(2)-Ge(2)-Ga(4)	132.92(8)	Ge(2)-Ga(2)-Ge(4)	91.71(7)
Ge(5)-Ge(3)-Ga(2)	109.66(5)	Ge(5)-Ga(3)-Ge(1)	93.66(6)
Ga(2)-Ge(3)-Ga(2)	113.84(8)	Ge(5)-Ga(3)-Ge(6)	117.51(5)
Ga(4)-Ge(4)-Ga(4)	112.83(8)	Ge(5)-Ga(3)-Ge(5)	112.30(8)
Ga(4)-Ge(4)-Ga(1)	106.32(6)	Ge(1)-Ga(3)-Ge(6)	117.37(8)
Ga(4)-Ge(4)-Ga(2)	102.56(6)	Ge(4)-Ga(4)-Ge(4)	112.83(8)
Ga(1)-Ge(4)-Ga(2)	126.32(8)	Ge(4)-Ga(4)-Ge(2)	99.87(6)
Ge(3)-Ge(5)-Ga(1)	107.22(7)	Ge(4)-Ga(4)-Ge(6)	117.38(5)
Ga(1)-Ge(5)-Ga(3)	108.55(6)	Ge(2)-Ga(4)-Ge(6)	105.69(7)
Ge(3)-Ge(5)-Ga(3)	110.02(6)		

Table III.B.10. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (2).

Atomic Position	U11	U22	U33	U23	U13	U12
Yb(1)	11(1)	14(1)	16(1)	0	4(1)	0
Yb(2)	11(1)	11(1)	8(1)	0	5(1)	0
Yb(3)	9(1)	12(1)	10(1)	0	4(1)	0
Ge(1)	10(1)	12(1)	13(1)	0	4(1)	0
Ge(2)	7(1)	11(1)	12(1)	0	5(1)	0
Ge(3)	7(1)	11(1)	10(1)	0	5(1)	0
Ge(4)	7(1)	11(1)	9(1)	0	5(1)	0
Ge(5)	11(1)	14(1)	10(1)	0	4(1)	0
Ge(6)	7(1)	19(1)	8(1)	0	3(1)	0
Ga(1)	5(1)	11(1)	7(1)	0	5(1)	0
Ga(2)	11(1)	12(1)	11(1)	0	4(1)	0
Ga(3)	9(1)	10(1)	10(1)	0	5(1)	0
Ga(4)	11(1)	11(1)	9(1)	0	4(1)	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Physical Properties

A conventional four-probe method and a slow AC technique were used for electrical conductivity and thermopower measurements²⁰ conducted in the temperature range of 4–300 K.

The magnetic susceptibility measurements were performed on a MPMS SQUID magnetometer (Quantum Design, Inc.) in the temperature range 2 - 400 K with an external applied magnetic field 10000 Gauss. Single crystal and polycrystalline samples of $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ were used for the magnetic measurements. The magnetization data were corrected for sample holder contribution.

Electronic Properties and Band Structure Calculations

The band structure calculations were performed on the compounds $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (1) and $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (2) and hypothetical compounds “ $\text{Sr}_2\text{Ga}_4\text{Ge}_6$ ” and “ $\text{Sr}_3\text{Ga}_4\text{Ge}_6$ ” obtained via substitution of the Yb sites with Sr. The latter was essential for the calculations where the presence of highly localized close-lying to Fermi level *4f*-states of Yb were undesirable. Electronic structure calculations were performed using the self-consistent full-potential linearized augmented plane wave method (FPLAPW)²¹ within density functional theory (DFT)²² using the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof²³ for the exchange and correlation potential. The values of the atomic radii were taken to be: 2.3 a.u. for Ga and Ge atoms, and 2.5 a.u. for Yb and Sr atoms where a.u. is the atomic unit (0.529 Å). Convergence of the self-consistent iterations was performed for 25 k points inside the reduced Brillouin zone to within 0.0001 Ry with a cutoff of -6.0 Ry between the valence and the core states. Scalar relativistic corrections were included and spin-orbit interaction was incorporated using a second variational procedure²⁴. The calculations were performed using WIEN97 program²⁵.

3. Results and Discussions

Reaction Chemistry

The compounds $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (**1**) and $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (**2**) were first obtained from the Yb/Ni/Ga/Ge reactions conducted in liquid Ga. From these reactions, the $\text{Yb}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ ($x \sim 0.67$) hexagonal phase was isolated in a high yield, whereas compounds **1** and **2** were present in only minor quantities. Nevertheless, the formation of **1** and **2** at the reaction stoichiometries far from their ideal compositions evidences the high stability of their crystal lattices. Consequently, when the reaction was conducted in the absence of Ni and with the appropriate Yb : Ge ratio, the pure phase of **2** results. However, the formation of **1** in pure or enriched form has not been observed yet. To investigate the range of the stability of **1**, the experiments using various RE : Ge ratios (note that Ga is always taken in excess, as a flux) were carried out. These reactions did not lead to **1**. Instead, for up to Yb : Ge ratios of 1 : 1, the phase **2** results. When the RE : Ge reaches 1 : 1, $\text{Yb}_3\text{Ga}_9\text{Ge}^5$ is produced in pure form*. The experiments conducted at different reaction times and heating/cooling regimes have also resulted in **2**. These results may indicate that phase **2** is far more thermodynamically stable than **1**, so that even if **1** forms initially, it is eventually converted to **2**. For these reasons, experiments conducted at much lower temperatures (possibly $\approx 700^\circ\text{C}$) could be suggested; those are currently in progress. Additionally, there is a chance that Ni in some way catalyzes the reaction that

* The reaction product could also contain unreacted Ge.

favors **1**, since the phases **1** and **2** were obtained in equal amounts from the Ni-containing reaction.

Crystal Structure of 1

The structure of $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (**1**) is presented in Figure III.B.2. The Yb atoms are shown in larger grey spheres, the Ga and Ge atoms are depicted as open and filled circles, respectively. In Figure III.B.2, the polar, non-centrosymmetric $[\text{Ga}_4\text{Ge}_6]^{4-}$ network is outlined, while the Yb atoms are shown as inserted in the channels of this network, but not bonded to it. The channels in $[\text{Ga}_4\text{Ge}_6]^{4-}$ have various shapes and sizes. The smaller three-, five- and six-membered channels are vacant, whereas bigger seven- and nine-membered channels are occupied with Yb(2) and Yb(1), respectively.

The 3D four-coordinate $[\text{Ga}_4\text{Ge}_6]$ framework easily conforms to the requirements of the Zintl concept. Following the octet rule, the framework is electron deficient, as each Ga atom has four neighbors, but only three electrons (see below for Ga and Ge coordination environments). The extra one electron per Ga atom (a total of four per formula unit) is donated to the network by the electropositive Yb atoms. The Yb atoms are thus expected to be in a 2+ oxidation state. The theoretical electronic structure calculations strongly support the Yb^{2+} electron configuration in **1** (see below). The charge balanced formula of **1** consequently appears as $\text{Yb}_2^{4+}[\text{Ga}_4\text{Ge}_6]^{4-}$.

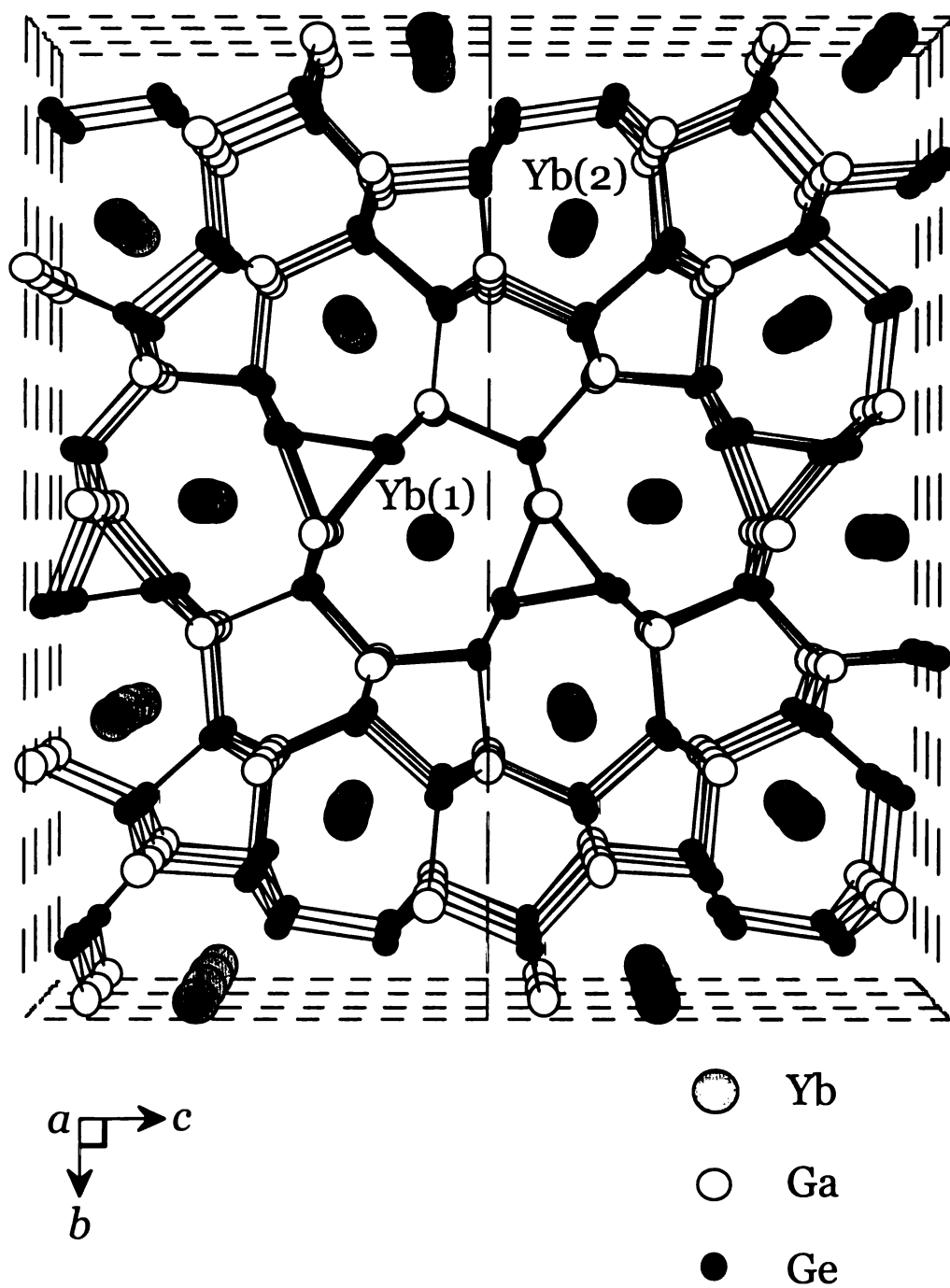


Figure III.B.2. The non-centrosymmetric structure of $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (1) viewed down the a -axis. Two Yb sites are labeled. The dashed lines indicate the unit cell (two unit cells are shown).

The local coordination polyhedra of Ge, Ga and Yb atoms are shown in Figure III.B.3.A – C, respectively. As follows from Figure III.B.3, all of Ga and Ge atoms are four-coordinate, with the geometries of their coordination environments being close to tetrahedral. For example, all Ge atoms occupy centers of distorted tetrahedra, see Figure III.B.3.A. For some of the Ge atoms, the angles only slightly diverge from the ideal tetrahedral, as it is for the Ge(3) and Ge(6) atoms (the angles vary within the range $108.07(5)^\circ$ - $114.07(7)^\circ$ for Ge(3), and within $103.31(5)^\circ$ - $114.82(7)^\circ$ for Ge(6)). Other Ge-centered tetrahedra are moderately distorted, like the ones with Ge(1) and Ge(4) in the centers. Here, the tetrahedral angles fall in the range $90.59(6)^\circ$ - $118.11(4)^\circ$ for Ge(1) and $100.60(5)^\circ$ - $125.86(7)^\circ$ for Ge(4). The remaining two Ge atoms have grossly distorted environment that include angle variations from $58.82(5)^\circ$ - $124.38(4)^\circ$ for Ge(2) and $60.89(6)^\circ$ - $123.55(4)^\circ$ for Ge(5). The average Ge-Ge distance is 2.54 Å; in view of the sum of covalent radii²⁶ for Ge (2.44 Å) it could be considered as bonding. It also close to the Ge-Ge distances found in elemental Ge²⁷ (2.45 Å).

The atoms of Ga contain only Ge in their immediate coordination spheres, see Figure III.B.3.B. The Ga(1), Ga(2) and Ga(4) tetrahedra are only slightly distorted. The corresponding Ge-Ga-Ge angles vary from $102.34(5)^\circ$ to $119.90(7)^\circ$ for Ga(1); from $100.81(5)^\circ$ to $127.40(7)^\circ$ for Ga(2) and from $102.85(5)^\circ$ to $115.43(4)^\circ$ for Ga(4). However, the tetrahedron formed around Ga(3) is greatly compressed, as one of the angles became as small as $60.30(5)^\circ$.

A.

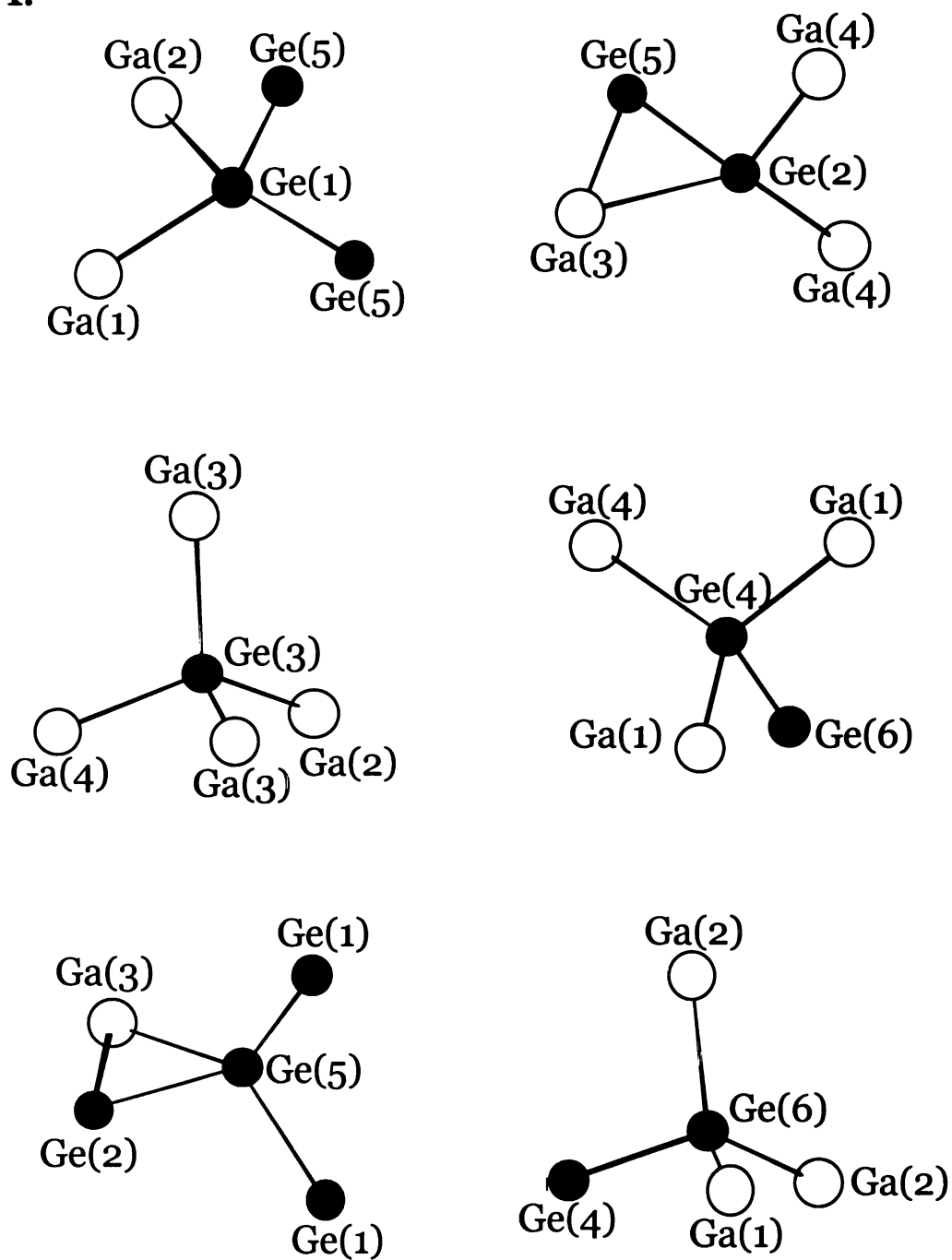


Figure III.B.3. (A) The local coordination environments of Ge atoms (Ge(1) – Ge(6)) in the structure of **1** within the sphere of radius 3.0 Å.

B.

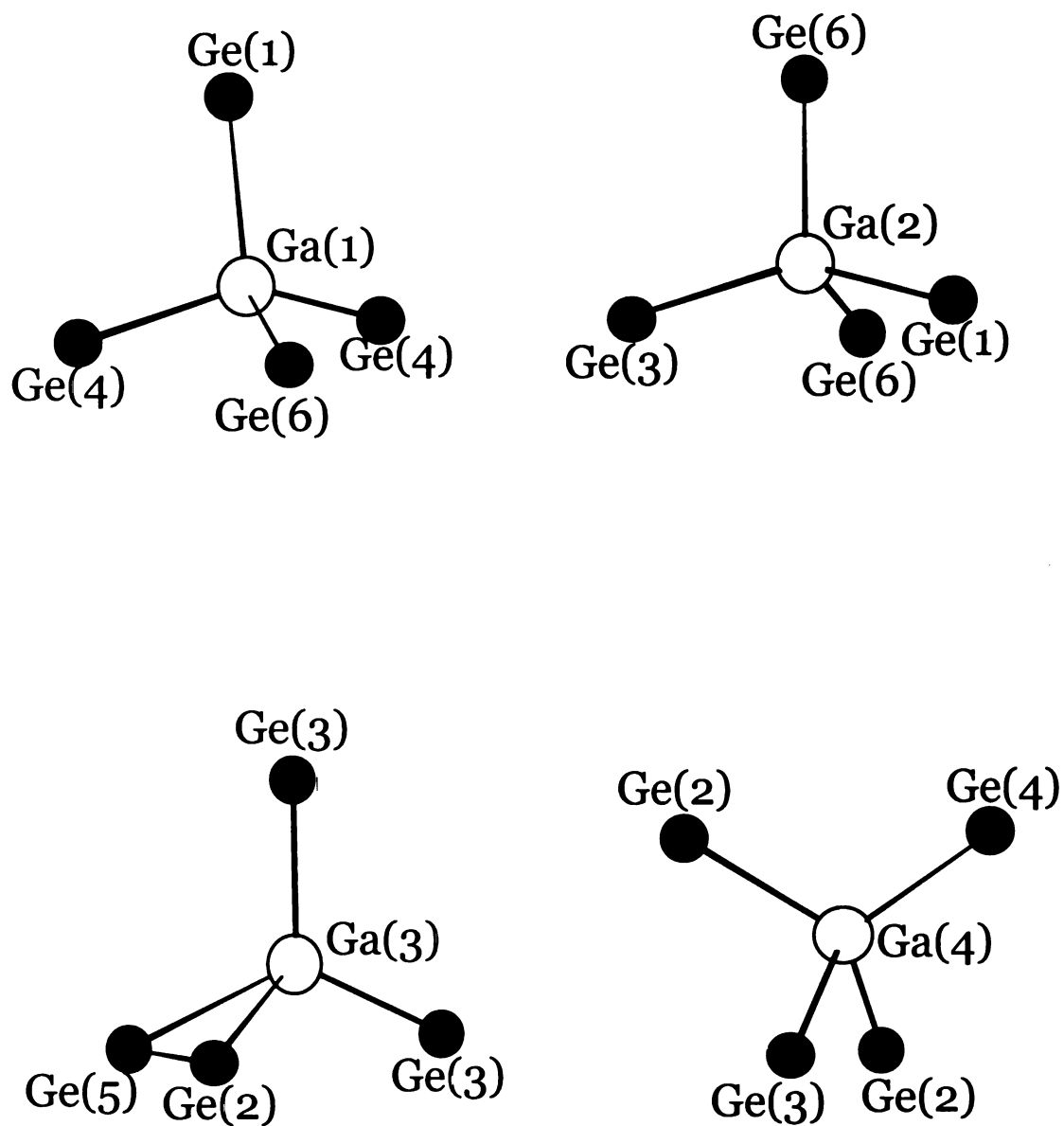


Figure III.B.3. (B) The local coordination environments of Ga atoms (Ga(1) – Ga(4)) in the structure of **1** within the sphere of radius 3.0 Å.

The average Ga-Ge distance found in **1** is quite short, about 2.51 Å. Compared to the sum of single bonded metallic radii for Ga²⁶ and covalent radii for Ge²⁷ (2.47 Å), the Ga-Ge interactions are certainly strongly bonding. Thus, from the connectivity data we could conclude that the rigidity of the [Ga₄Ge₆] network is primarily held by the strong Ga-Ga interactions, although corresponding Ge-Ge interactions are also quite strong.

The nearest neighbor coordination environments of Yb atoms are shown in Figure III.B.3.C. The Yb(1) atom is located in the center of a cage consisting of thirteen Ga and Ge atoms. The Yb(2) has twelve Ga and Ge neighbors in its immediate coordination sphere of a 3.5 Å radius. In the projection along the *a*-axis, the Yb(1) and Yb(2) appear as residing in respectively 9- and 7-membered channels of the Ga-Ge framework. Interestingly, the connectivity between the Yb atoms and the framework is also strongly bonding. Thus, the Yb-Ga bond distances vary from 3.0957(15) Å to 3.4882(13) Å, and Yb-Ge distances range from 3.0567(14) Å to 3.3445(11) Å. The average Yb-Ge and Yb-Ga connectivities in **1** are 3.15 Å and 3.34 Å, respectively. Note that the Yb-Ge distances are shorter than the corresponding Yb-Ga, in accordance with the original Ga/Ge assignment. Allowing for the sum of single-bonded metallic radii (coordination number 12 for Yb(II) is considered) for Yb and Ge (3.15 Å) and Yb and Ga (3.18 Å), these interactions are strongly bonding with a considerable covalent contribution to the bonding character.

Interestingly, in the related clathrate compound such as Eu₈Ga₁₆Ge₃₀, the Eu atoms were found in much larger cages with corresponding Eu-Ga or Eu-Ge contacts ranging between 3.37 Å and 3.58 Å. The Eu atoms were also found to be “rattling” in the cages, which was reflected in the enlarged thermal displacement parameters of Eu atoms

and reduced thermal conductivity of this material. However, in case of **1**, no “rattling” or any abnormality in the thermal ellipsoids was observed, see Table III.B.1 and III.B.5. Thus in **1**, the Yb atoms could not be regarded as being merely “guests” in a host $[\text{Ga}_4\text{Ge}_6]$ framework, but evidently participate in the covalent bonding with the network. Apparently this interaction further stabilizes the structure of **1**.

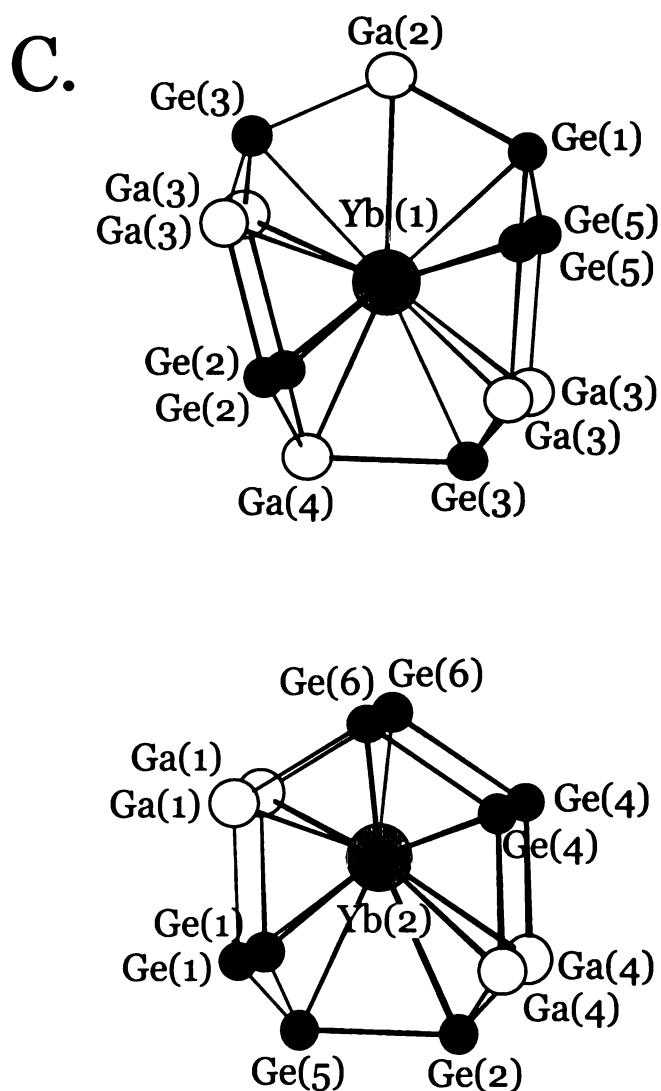


Figure III.B.3. (C) The local coordination environments of Yb atoms (Yb(1) and Yb(2)) within the sphere of radius 3.5 Å.

Crystal Structure of 2

The structure of $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (**2**) is presented in Figure III.B.4. For consistency, the Yb, Ga and Ge atoms are depicted in the same way as for **1**. As it is in case of **1**, a three-dimensional (3D) $[\text{Ga}_4\text{Ge}_6]$ framework could be marked out in the structure of **2** as well. The difference between the Ga-Ge framework in **1** and **2** is the number of electrons, i.e. $[\text{Ga}_4\text{Ge}_6]^{4+}$ versus $[\text{Ga}_4\text{Ge}_6]^{6-}$. The tunnels formed by the framework in **2** are quite different from those found in **1**. Thus, the only unfilled tunnels are five-membered. The remaining channels are larger and occupied with Yb atoms. A pair of Yb(1) atoms (Yb(1)-Yb(1) distance is 4.271 Å) reside inside of a large ten-membered tunnel. Additionally, there are two types of seven-membered channels; each of them is centered with Yb(2) or Yb(3) atoms.

In contrast to **1**, the $[\text{Ga}_4\text{Ge}_6]$ 3D net in **2** consists of both four- and three-coordinated Ga and Ge atoms. This can be understood by the additional two electrons added which reduce the certain atoms from four- to three-coordinate. The bonding in **2** could still be explained within the Zintl concept. First, the direct indications of Yb being in the 2+ oxidation state are found in magnetic data (see below). The position of the Yb peaks (below the Fermi level) in the calculated density of states of Yb atoms in **2** also points to the Yb 2+ state as opposed to Yb 3+ (discussed below). Thus, the possibility of finding Yb in the 3+ state in **2** is absolutely ruled out. The assignment of the charge distribution on the remaining ten Ga and Ge atoms was done using the octet rule as follows. All of the Ga atoms were found at the four-coordinate sites, and therefore the 1- charge was assigned to each of them in order to complete the octet.

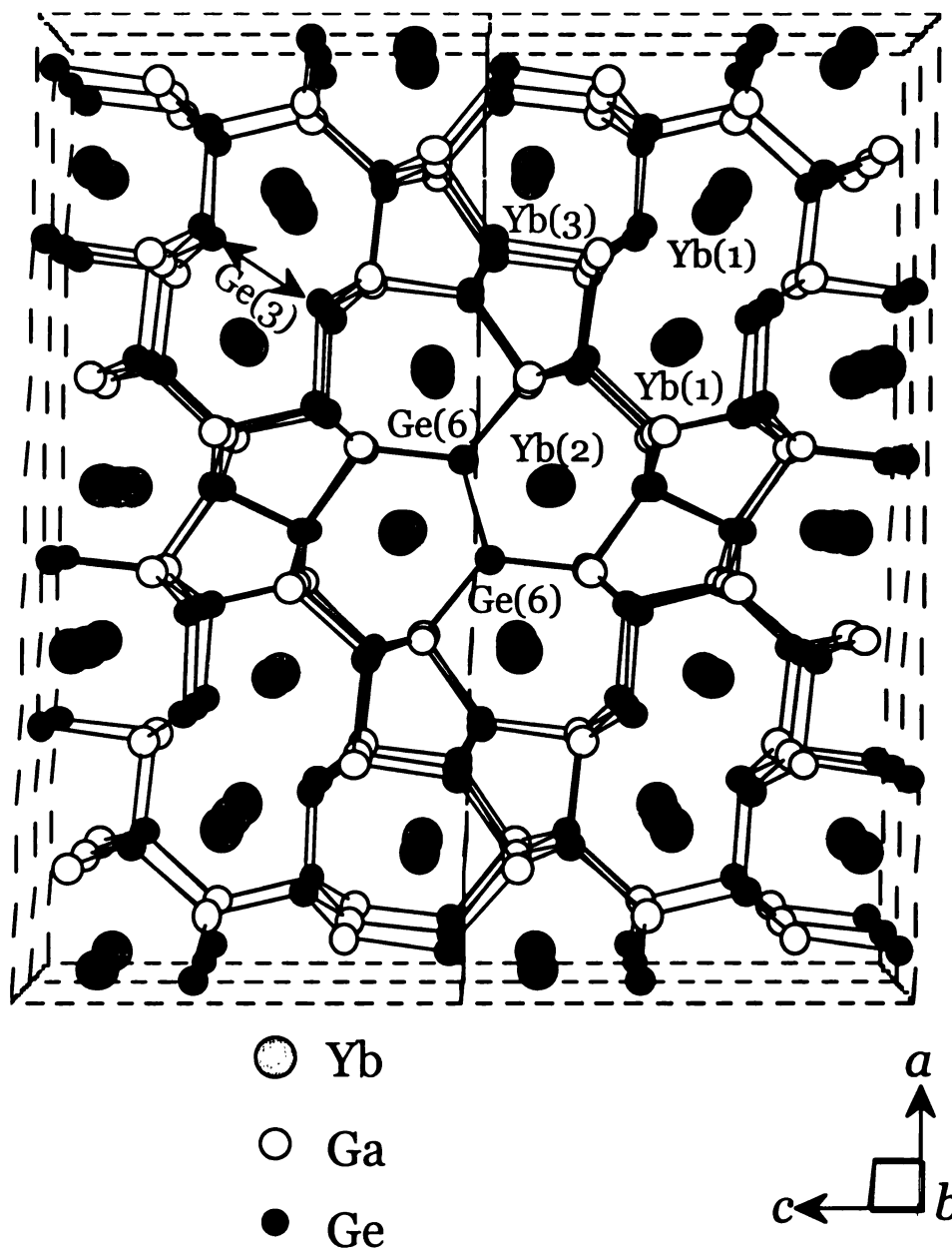


Figure III.B.4. The structure of $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (2) projected onto ac -plane. Three crystallographically different Yb sites are marked. Three-coordinated Ge atoms (Ge(3) and Ge(6)) are also labeled. The unit cell is shown in dashed lines.

Next, to four Ge atoms in the tetrahedral environments a zero charge was assigned, and to the remaining two Ge atoms with three-coordinated (trigonal planar and pyramidal) environments, a charge of 1- was ascribed. Thus, the resulting charge-balanced formula is $\text{Yb}_3^{6+}[\text{Ga}_4^{4-}\text{Ge}_4^0\text{Ge}_2^{2-}]$. The doubtful sites containing three-coordinated atoms were especially carefully tested: first, using bonding considerations and then, by the way of minimization of the energy of the system using electronic band structure calculations, as described in the “Experimental Section”. The location of the Ga^{2-} versus Ge^{1-} on the three-coordinated site is also less likely from the chemical stand point.

The local coordination environments of Ga, Ge and Yb atoms are shown in Figures III.B.5 A – D. The local environment of all Ga atoms within 3.0 Å is tetrahedral, see Figure III.B.5.A. The departure from the ideal tetrahedral angles is not substantial, as could be seen from the ranges of corresponding tetrahedral angles: 102.23(6)° - 123.24(8)° for Ga(1); 91.71(7)° - 113.84(8)° for Ga(2); 93.66(6)° - 117.51(5)° for Ga(3); and 99.87(6)° - 117.38(5)° for Ga(4). The Ga-Ge bond contacts range from 2.501(2) Å to 2.617(2) Å with the average Ga-Ge bond distance of 2.54 Å, comparable to that observed in **1** (2.51 Å). The average Ge-Ge bond distances are even stronger than that found in **1** (2.54 Å) with the average bonding contact of 2.50 Å. Thus the $[\text{Ga}_4\text{Ge}_6]$ framework in **2** is an extremely rigid unit, held together by strong Ga-Ge and Ge-Ge interactions.

A.

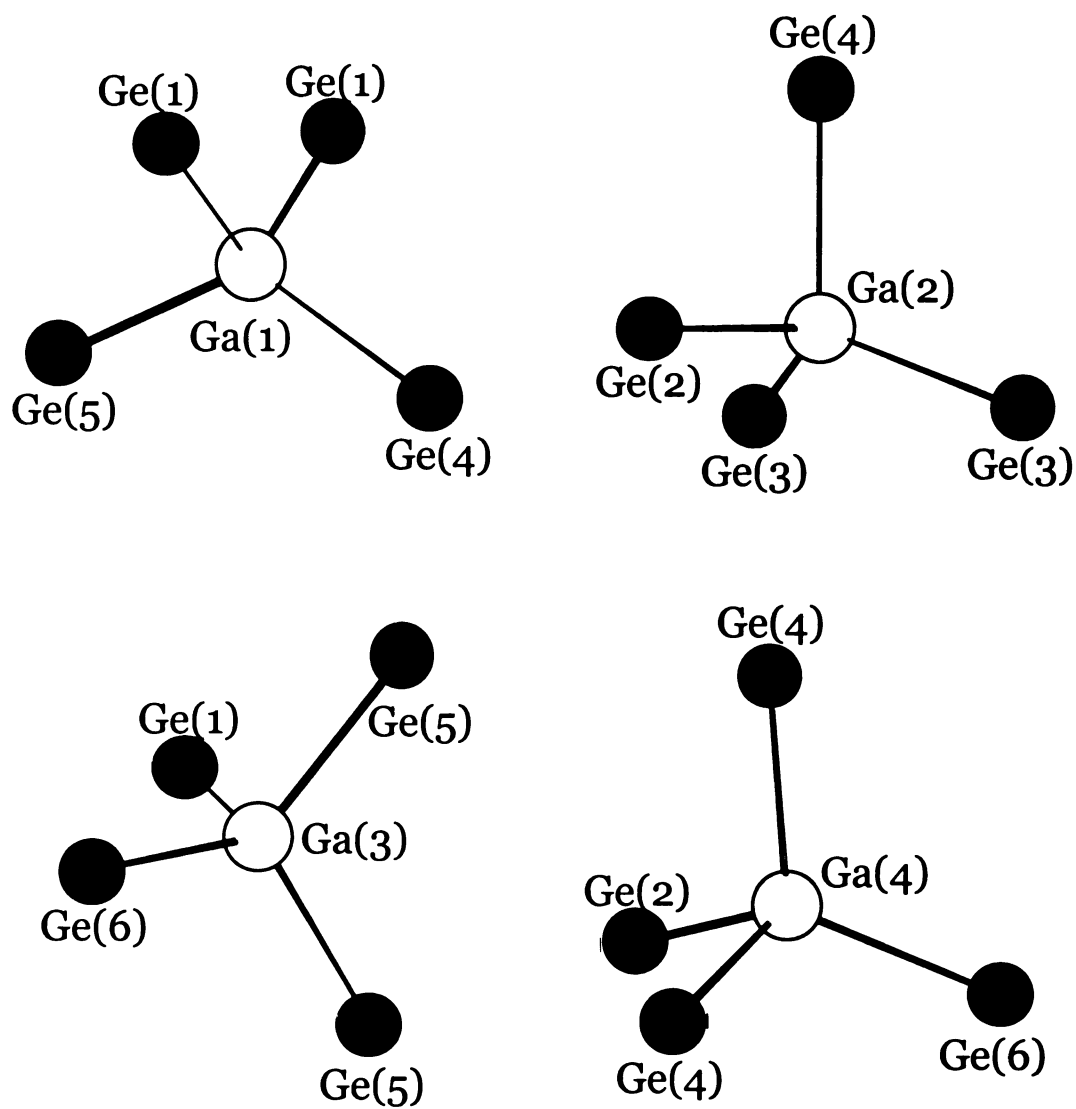


Figure III.B.5. (A) The local coordination environments of Ga atoms (Ga(1) – Ga(4)) in the structure of **2** within the sphere of radius 3.0 Å.

The Ge coordination environments that contain only the Ga and Ge neighbors (Yb atoms were excluded for clarity) are shown in Figure III.B.5.B. Here, the Ge(1), Ge(2), Ge(4) and Ge(5) atoms are four-coordinate, whereas Ge(3) and Ge(6) are three-coordinate. Within the four-coordinate environment of Ge atoms, the angles are close to the ideal tetrahedral. For example, those fall in the range of $99.02(7)^\circ$ - $119.49(5)^\circ$ for the Ge(1); $99.86(8)^\circ$ - $132.92(8)^\circ$ for Ge(2); $102.56(6)^\circ$ - $126.32(8)^\circ$ for Ge(4) and $107.22(7)^\circ$ - $112.31(8)^\circ$ for Ge(5). The Ge(3) atom is in the apex position of distorted trigonal pyramid with the base of two Ga(2) atoms and one Ge(5) atom. The corresponding Ge(5)-Ge(3)-Ga(2) and Ga(2)-Ge(3)-Ga(2) angles are $109.66(5)^\circ$ and $113.84(8)^\circ$, respectively. The Ge(6) atom is in the trigonal planar environment of Ga(3), Ga(4) and Ge(6). The angles only slightly vary from true trigonal and correspond to $112.31(8)^\circ$, $112.78(9)^\circ$ and $124.88(10)^\circ$. The plane of a Ge(6)-centered triangle is perpendicular to the *b*-axis.

However, the near-neighbor environment of some Ge atoms is incomplete unless the Yb atoms are included. A few examples of such Ge environments containing close-lying Yb atoms (spheres of radii 3.0 Å to 3.15 Å are considered) are presented in Figure III.B.5.C. It should be noted that the three-coordinate Ge atoms have in general more Ge-Yb contacts than the other Ge atoms (up to six, as it is for Ge(6)). Interestingly, some of the Yb-Ge bonding contacts are as short as 2.9321(17) Å, as it is the case for Yb(1)-Ge(3). The average Yb-Ge bond length in **2** is 3.15 Å (identical to that found in **1**), thus suggesting that the bonding interactions between Yb and Ge are very strong. The corresponding Yb-Ge contacts in **2** are 3.33 Å on average, which is again bonding and very close to that found in **1** (3.34 Å).

B.

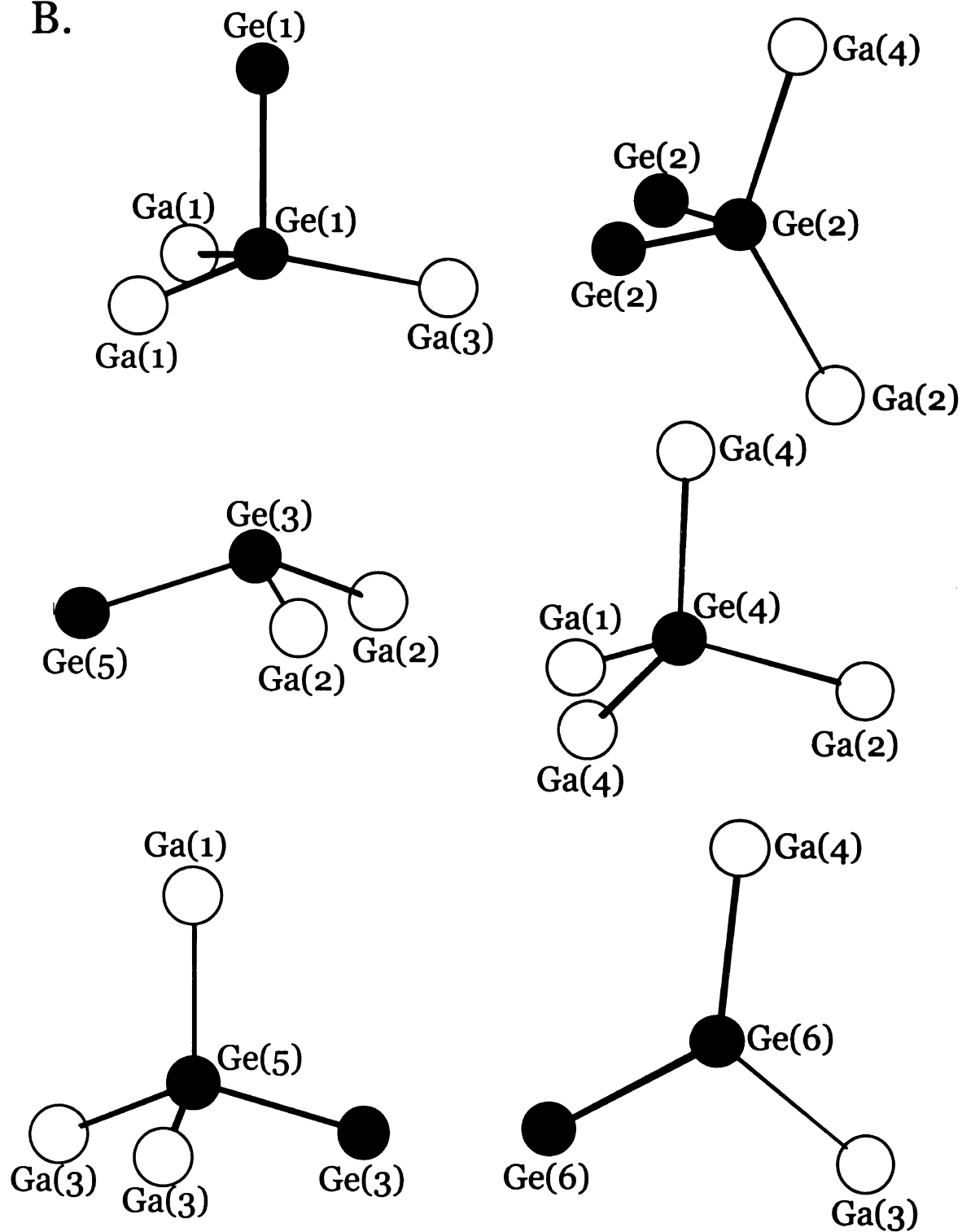


Figure III.B.5. (B) The local coordination environments of Ge atoms (Ge(1) – Ge(6)) in the structure of **2** within the sphere of radius 3.0 Å. Only Ga and Ge neighbors are shown.

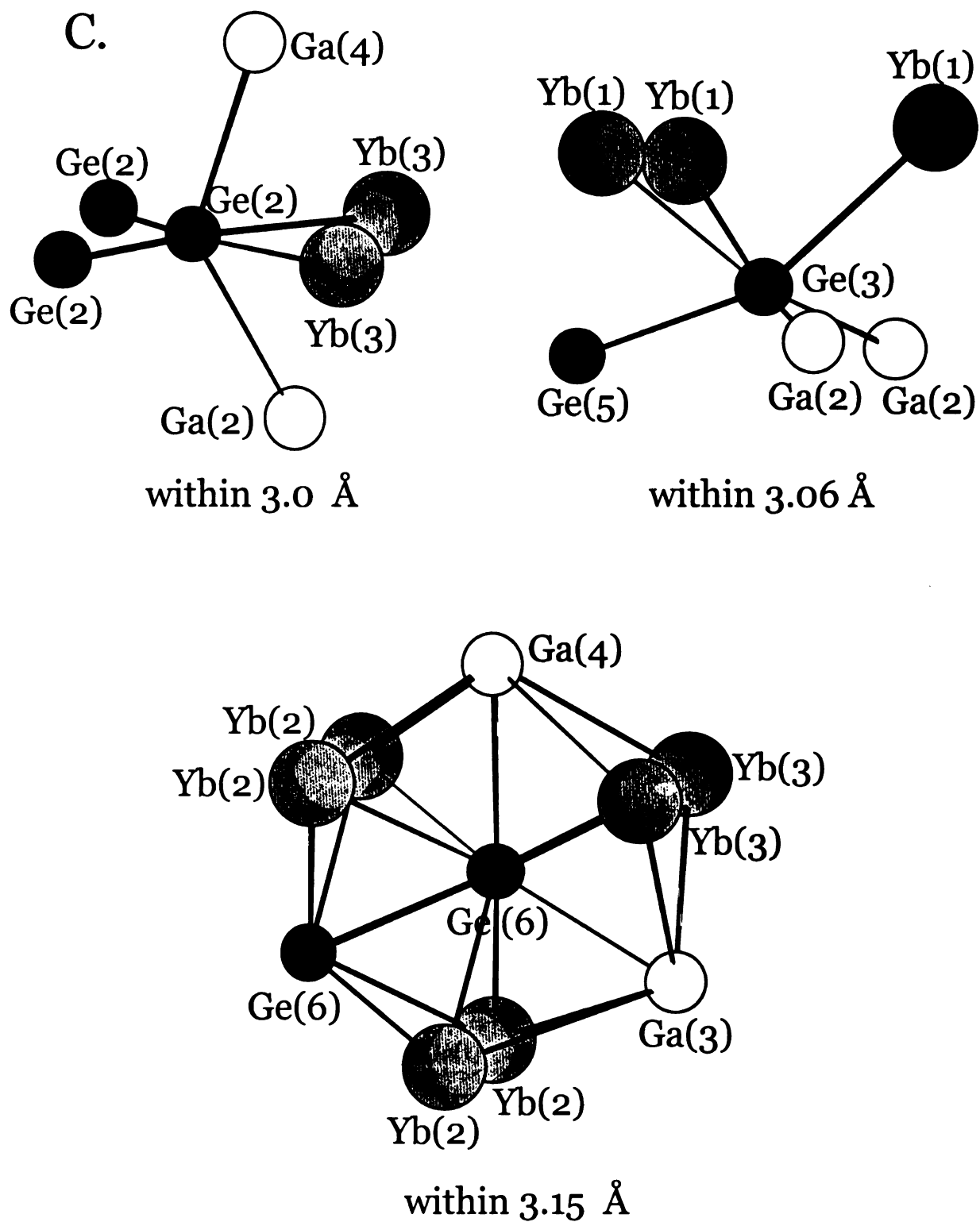


Figure III.B.5. (C) The local coordination environments of Ge atoms in **2** within the sphere of radius 3.0 Å– 3.15 Å with all neighboring atoms shown.

The immediate coordination spheres of Yb atoms within the radius of 3.6 Å are depicted in Figure III.B.5.D. The Yb(1) and Yb(2) atoms have twelve Ga and Ge neighbors, while Yb(3) has thirteen. Both the Yb(2) and Yb(3) coordination shells are closed, as it is also the case for Yb atoms in **1**. However, because the Yb(1) atoms have a “double occupancy” cage, the Yb(1) shell is open. In the opening between the Ga(2) and Ge(3) atoms an Yb(1)-Yb(1) interaction is directed (Yb(1) is self-bonded at 4.27 Å).

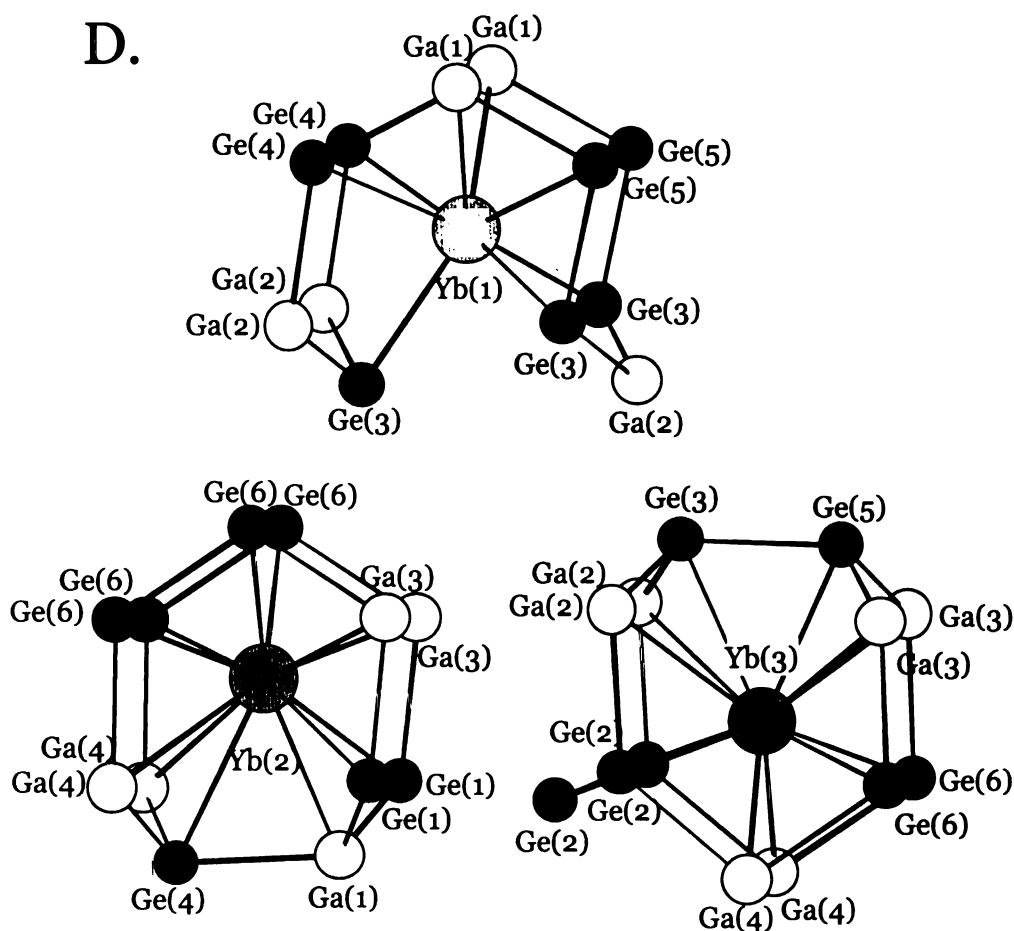


Figure III.B.5. (D) The local coordination environments of Yb atoms (Yb(1) – Yb(3)) in the structure of **2** within the sphere of radius 3.5 Å.

To obtain further insight into the bonding and transport properties of $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (**1**) and $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (**2**), band structure calculations were carried out. The total density of states (DOS) for the compounds **1** and **2** are shown in Figures III.B.6.A and III.B.9.A, respectively. The DOS calculation predicts both compounds **1** and **2** to be poor metals, with a low DOS at the Fermi energy (E_F). However, the determination of the precise DOS at the E_F was obstructed due to the presence of close-lying to E_F Yb $4f$ -levels. The supplementary calculations performed on the hypothetical Sr compounds “ $\text{Sr}_2\text{Ga}_4\text{Ge}_6$ ” and $\text{Sr}_3\text{Ga}_4\text{Ge}_6$ (which do not have f -electrons) show that these compounds are semimetals with a very low DOS at E_F of ~ 1 eV per formula unit.

The partial DOS analysis for **1** and **2** reveals that the largest contribution to the total DOS ranging from -2 eV to ~ 0 eV comes from the Yb f -levels, as could be seen in Figures III.B.6.B and III.B.9.B, respectively. The observed two narrow peaks is a result of splitting of Yb states due to spin-orbit interaction. The location of Yb peaks close, yet below the E_F suggests that Yb f -states are fully occupied, thus pointing to the f^{14} electron configuration corresponding to Yb^{2+} . For the compound **2**, the results of magnetic measurements show diamagnetic temperature independent behavior consistent with the completely filled f^{14} shell. Although for **1** similar magnetic measurements were not performed, the position of the Yb peaks in the DOS plots of **1** is identical to that in **2**, this signifying that the Yb atoms in **1** are in $2+$ state as well.

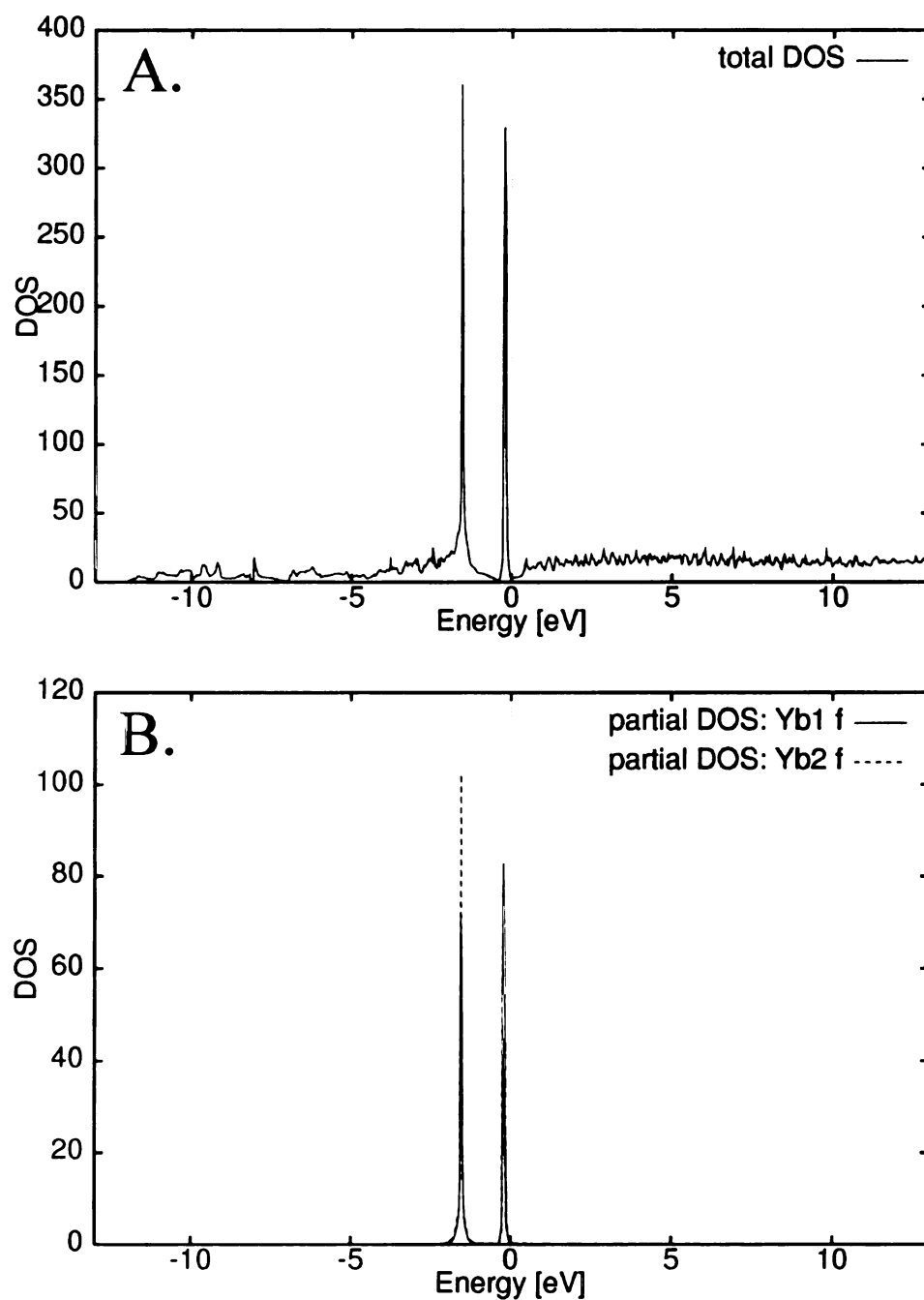


Figure III.B.6. (A) A total density of states (DOS) plot (states/eV· $\text{Yb}_4\text{Ga}_8\text{Ge}_{12}$) for $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ (1). The Fermi level (E_F) is drawn as a dotted line. (B) Yb(1) and Yb(2) f -states contribution to DOS.

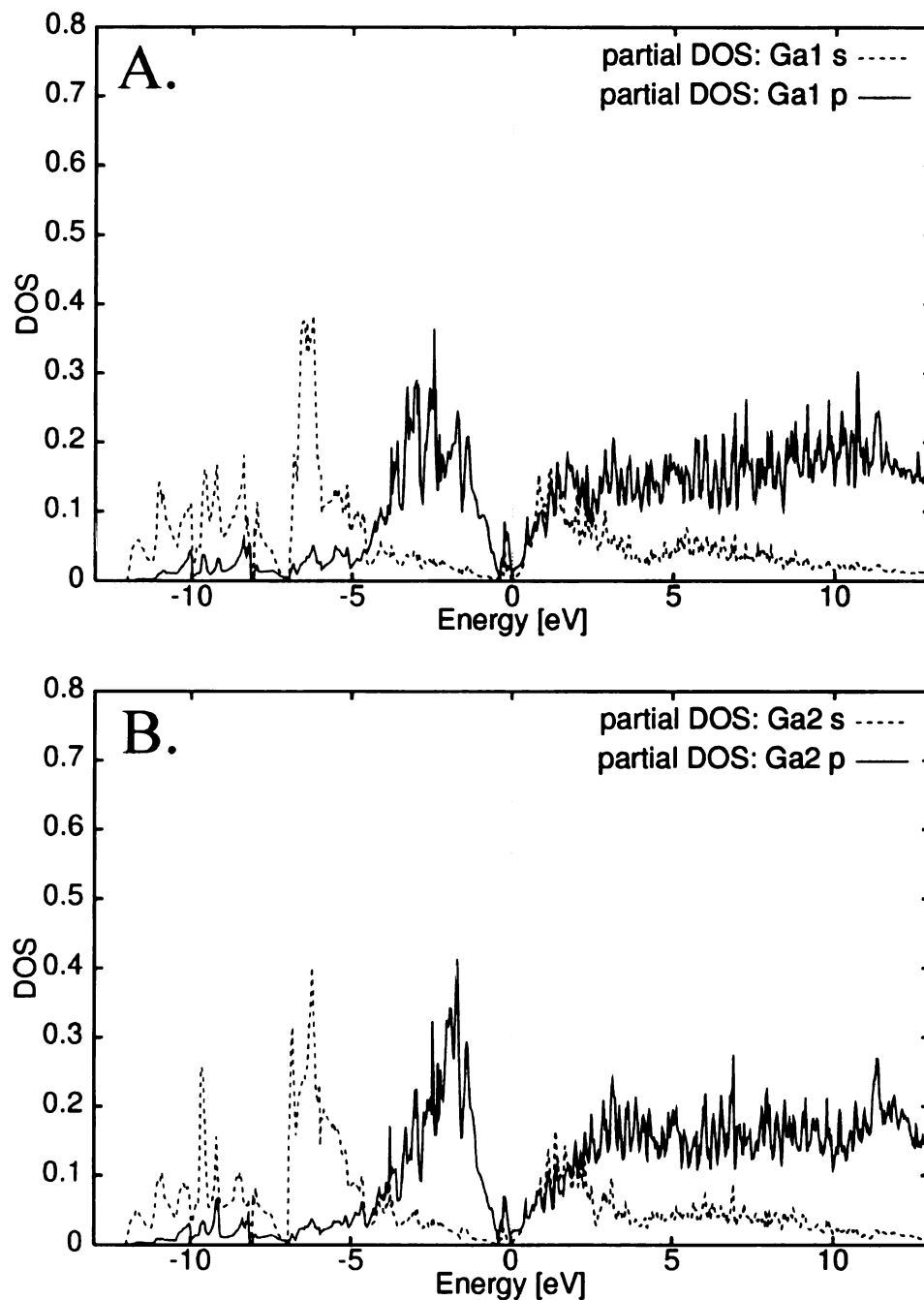


Figure III.B.7. The partial density of states (DOS) plot for 1. (A) Contribution from Ga(1) *s*-states (dashed line) and *p*-states (solid line) to the DOS. (B) Contribution from Ga(2) *s*-states (dashed line) and *p*-states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

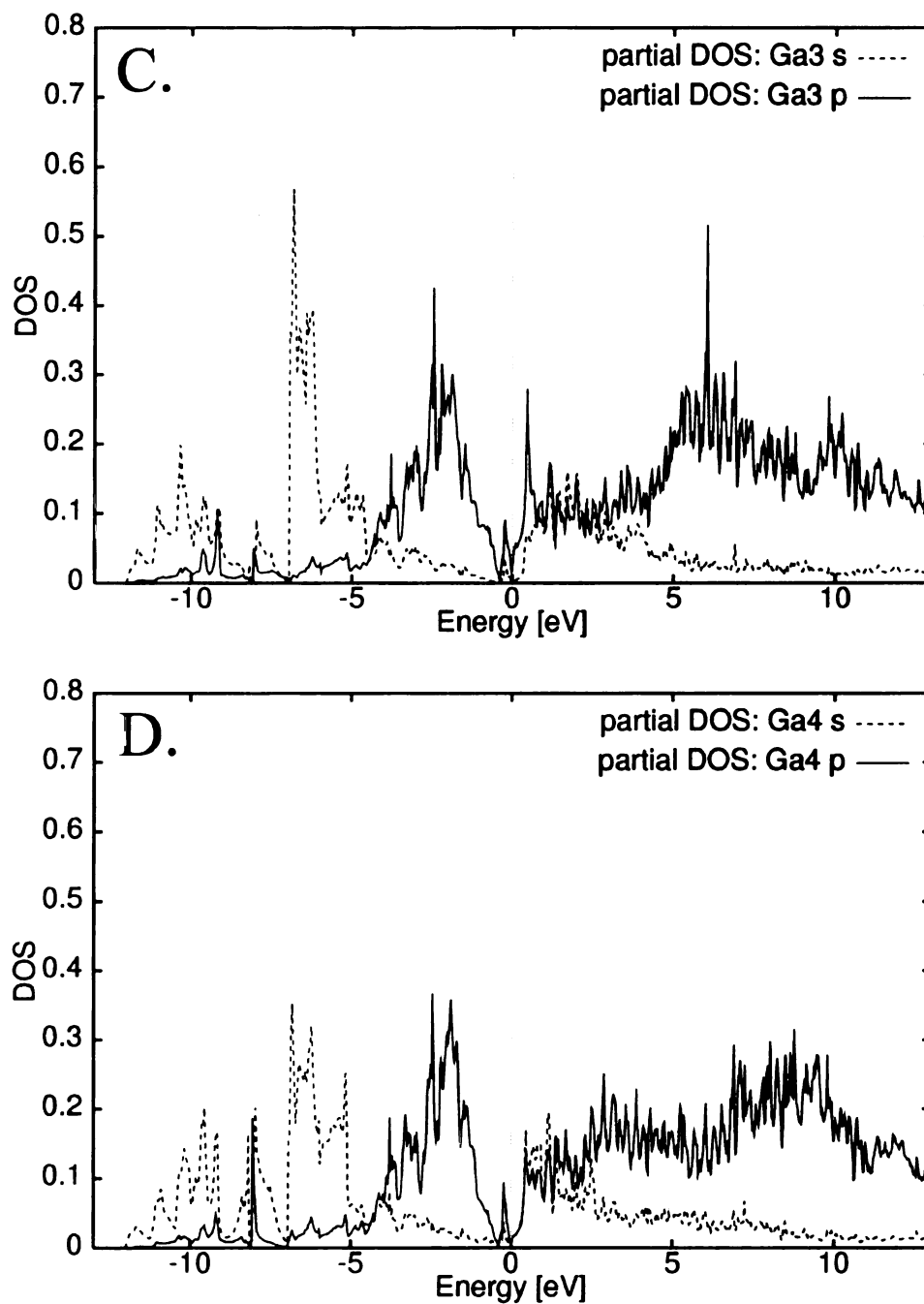


Figure III.B.7. The partial density of states (DOS) plot for 1. (C) Contribution from Ga(3) s -states (dashed line) and p -states (solid line) to the DOS. (D) Contribution from Ga(4) s -states (dashed line) and p -states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

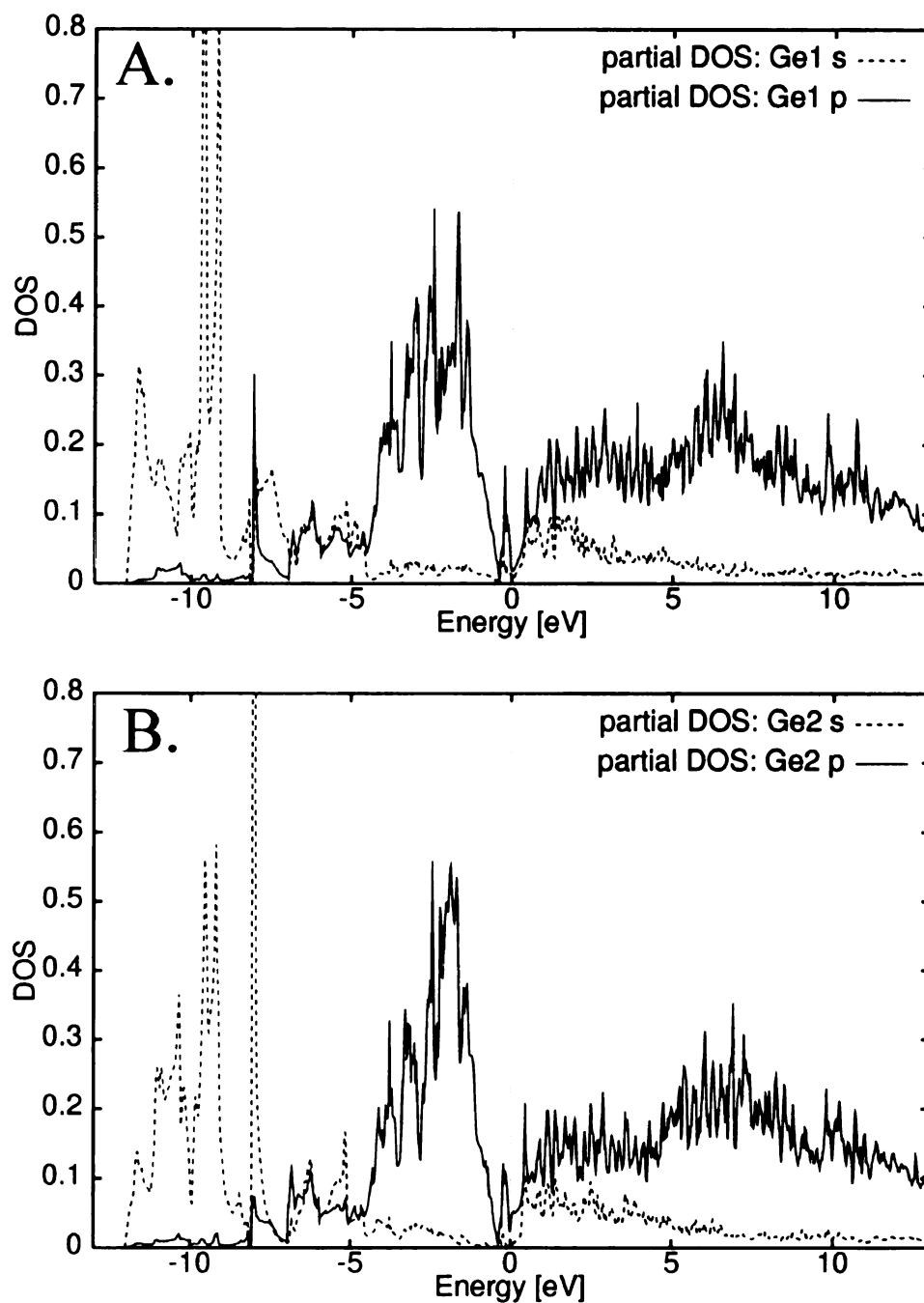


Figure III.B.8. The partial density of states (DOS) plot for 1. (A) Contribution from Ge(1) *s*-states (dashed line) and *p*-states (solid line) to the DOS. (B) Contribution from Ge(2) *s*-states (dashed line) and *p*-states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

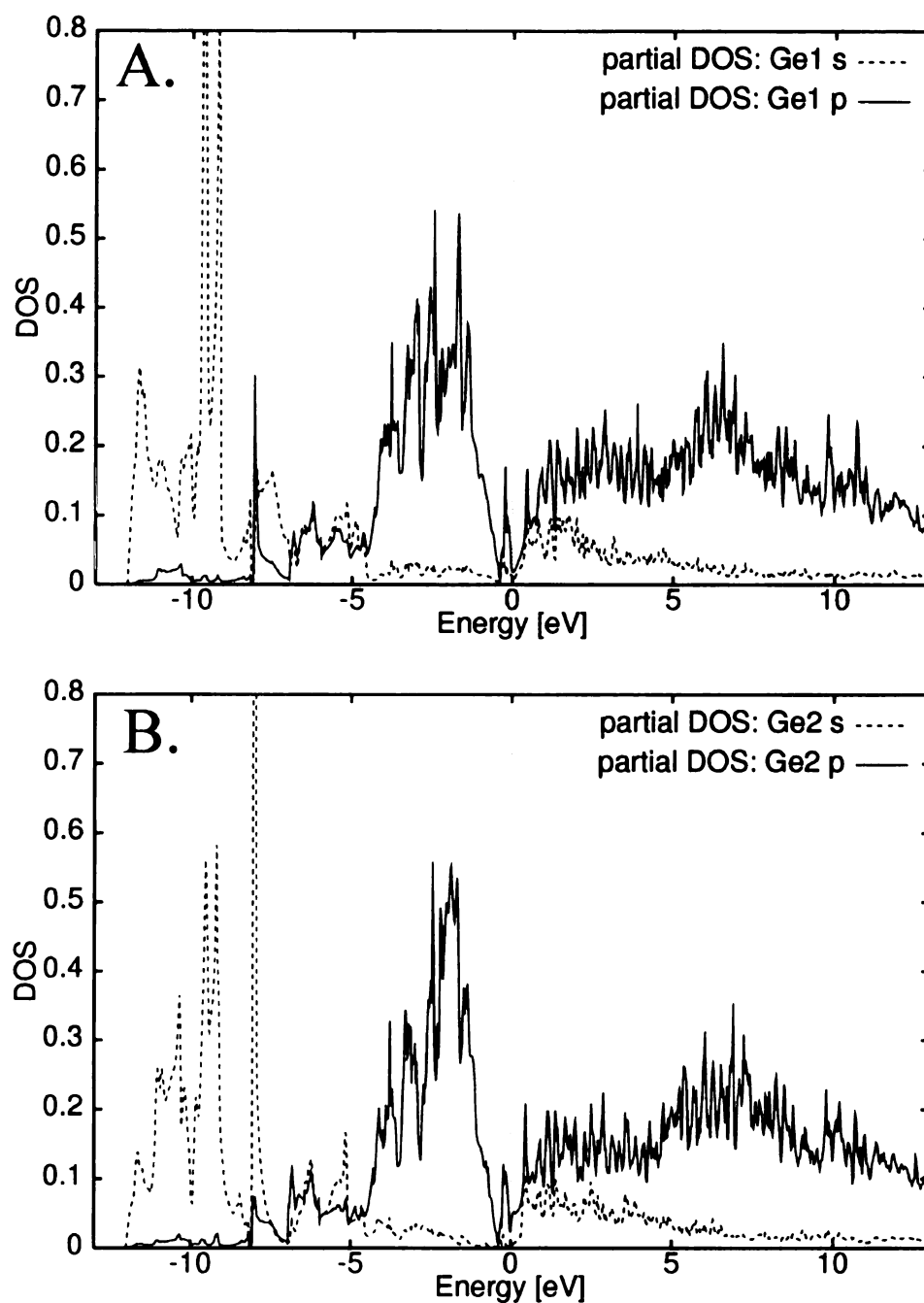


Figure III.B.8. The partial density of states (DOS) plot for 1. (A) Contribution from Ge(1) *s*-states (dashed line) and *p*-states (solid line) to the DOS. (B) Contribution from Ge(2) *s*-states (dashed line) and *p*-states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

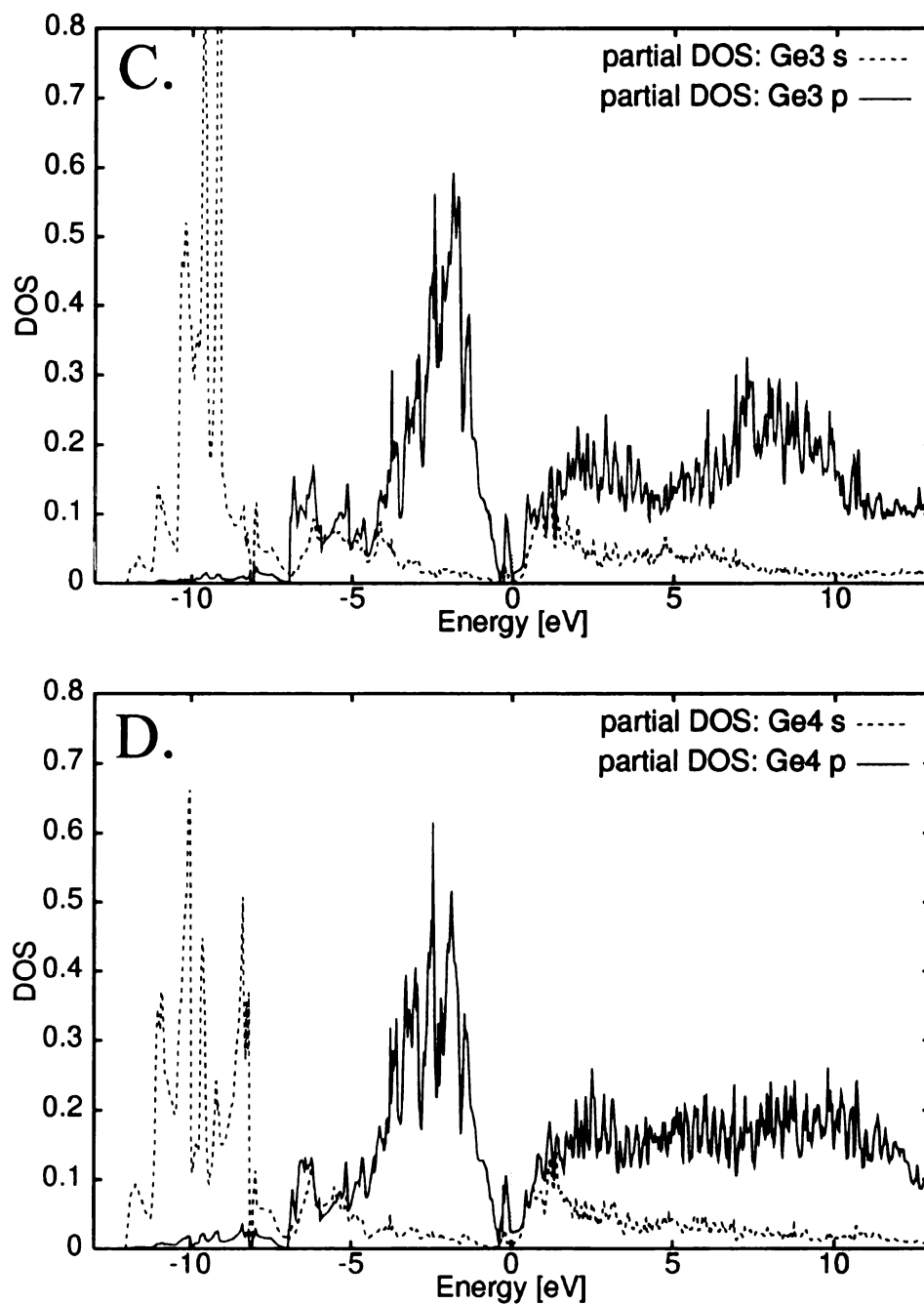


Figure III.B.8. The partial density of states (DOS) plot for 1. (C) Contribution from Ge(3) *s*-states (dashed line) and *p*-states (solid line) to the DOS. (D) Contribution from Ge(4) *s*-states (dashed line) and *p*-states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

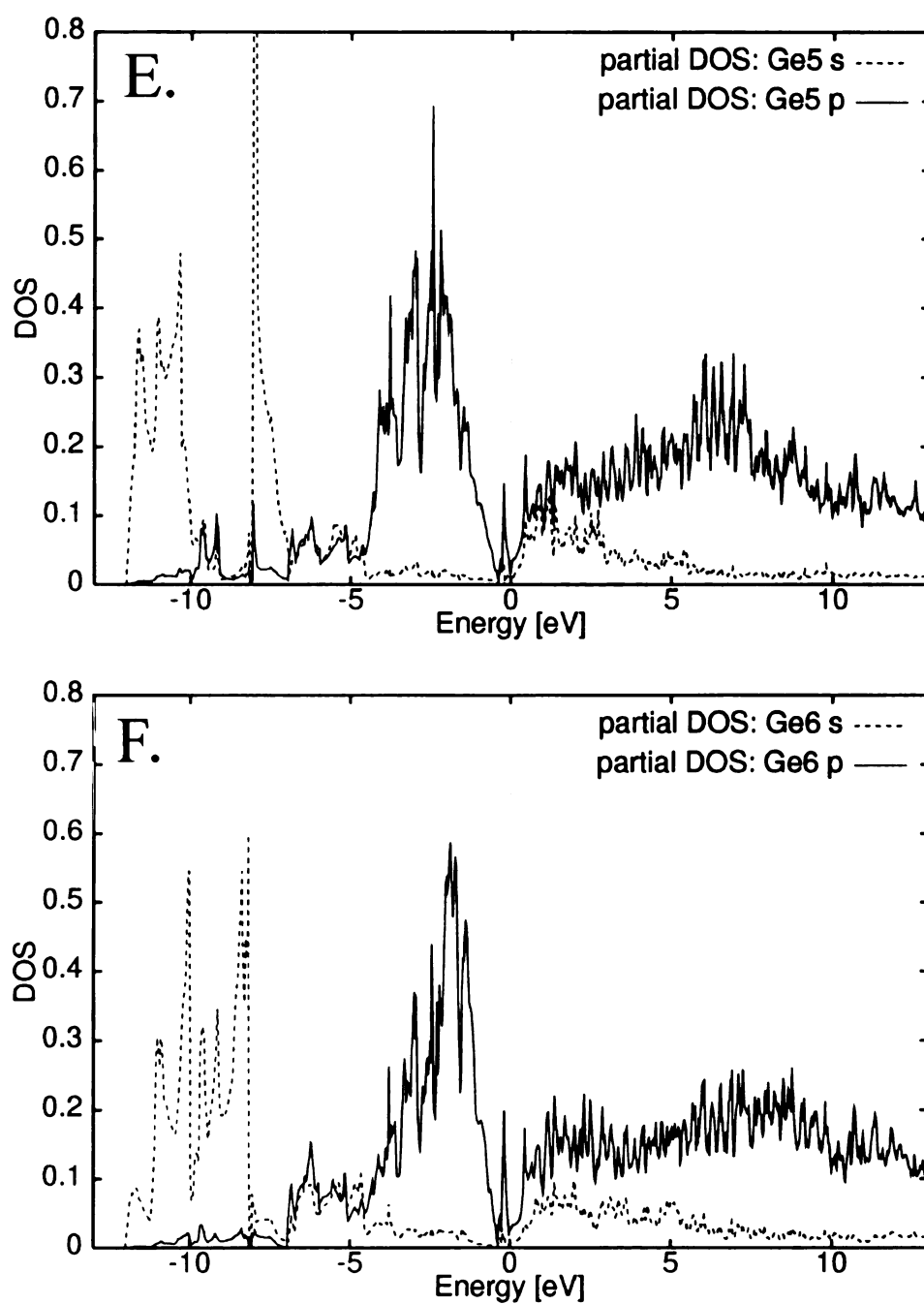


Figure III.B.8. The partial density of states (DOS) plot for 1. (E) Contribution from Ge(5) *s*-states (dashed line) and *p*-states (solid line) to the DOS. (F) Contribution from Ge(6) *s*-states (dashed line) and *p*-states (solid line) to the DOS. The Fermi energy is shown with a dotted line.



If we suppose the f^{d3} electron configuration corresponding to Yb^{3+} , the Yb f -levels would lie above E_F , suggestive of unfilled f -states, which is in disagreement with the results of theoretical structure calculations. Additionally, unpaired electrons on the unfilled f^{d3} shell would result in temperature-dependent paramagnetic behavior, which again contradicts experimentally observed diamagnetism.

The partial DOS of Ga atoms in **1** and **2** are presented in Figures III.B.7.A – D and III.B.10 A – D, respectively. The Ga s -levels in **1** and **2** range from -12 eV and -5 eV, whereas the Ga p -levels from -5 eV to 10 eV. Similarly, the position of the Ge s -levels in **1** and **2** mainly falls in the interval between -12 eV and -5 eV and for the Ge p -levels between -5 eV and 10 eV, see Figures III.B.8 A – D and III.B.11 A – F, respectively. As can be seen from the partial DOS, the Ga p - and Ge p - states between -5 eV and 10 eV are highly hybridized, suggesting a strong covalent interaction within $[\text{Ga}_4\text{Ge}_6]$ framework. The manifestation of the strong covalent interaction within the $[\text{Ga}_4\text{Ge}_6]$ framework has already been seen in the short Ga-Ge and Ge-Ge bonding interactions, as discussed above. Additionally, the Yb s - and Yb f -states also hybridize with the Ga p - and Ge p -states, indicating that the Yb atoms acts not only as electron donors (Yb^{2+}) to the $[\text{Ga}_4\text{Ge}_6]$ framework, but also participate in the covalent bonding with it. The observed weak hybridization of Yb and Ga/Ge states further reinforces the idea of covalent bonding between the Yb atoms and the $[\text{Ga}_4\text{Ge}_6]$ framework found from the connectivity data regarded in the previous section.

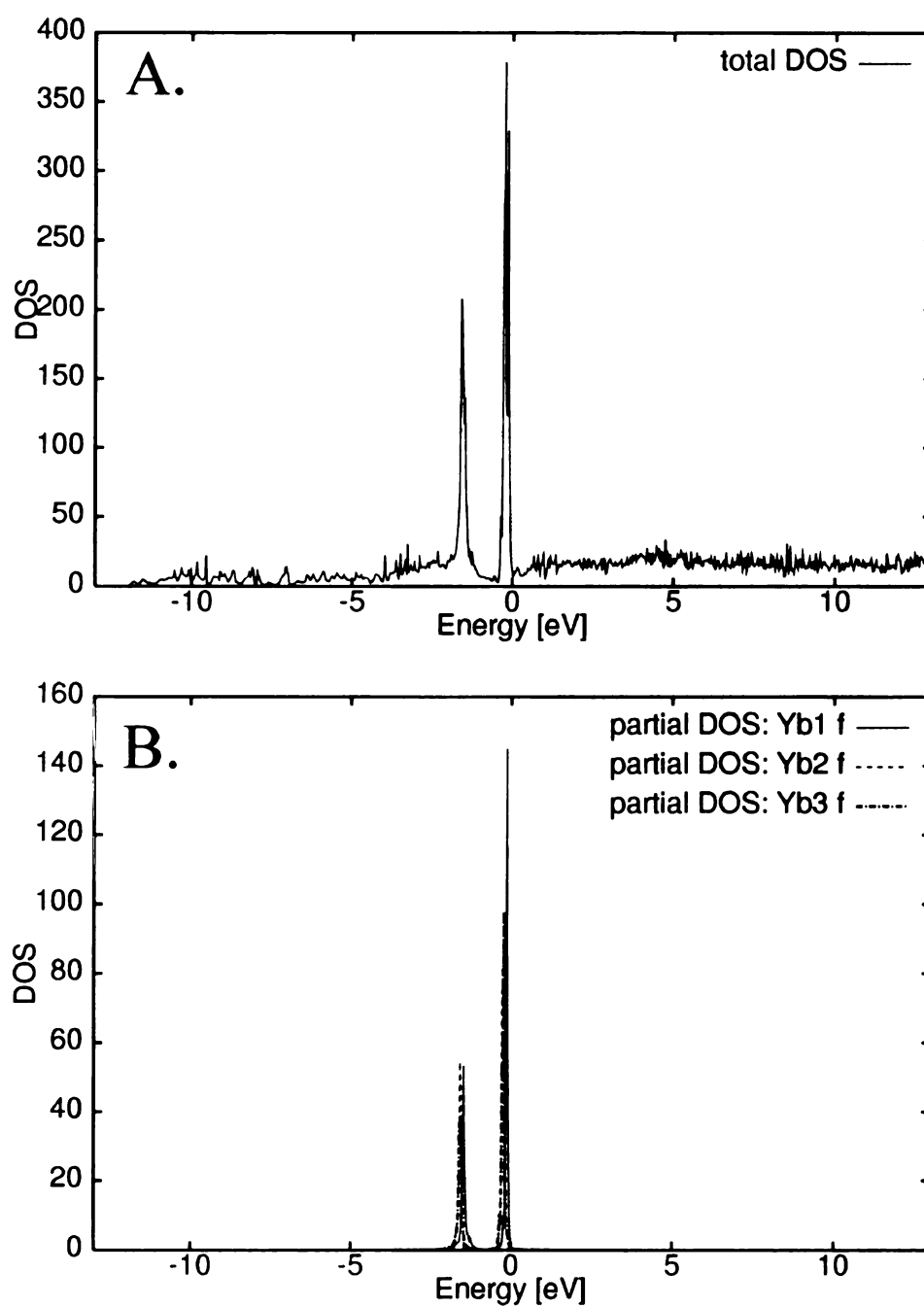


Figure III.B.9. (A) A total density of states (DOS) plot (states/eV· $\text{Yb}_6\text{Ga}_8\text{Ge}_{12}$) for $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (2). The Fermi level (E_F) is drawn as a dotted line. (B) Yb(1), Yb(2) and Yb(3) *f*-states contribution to DOS.

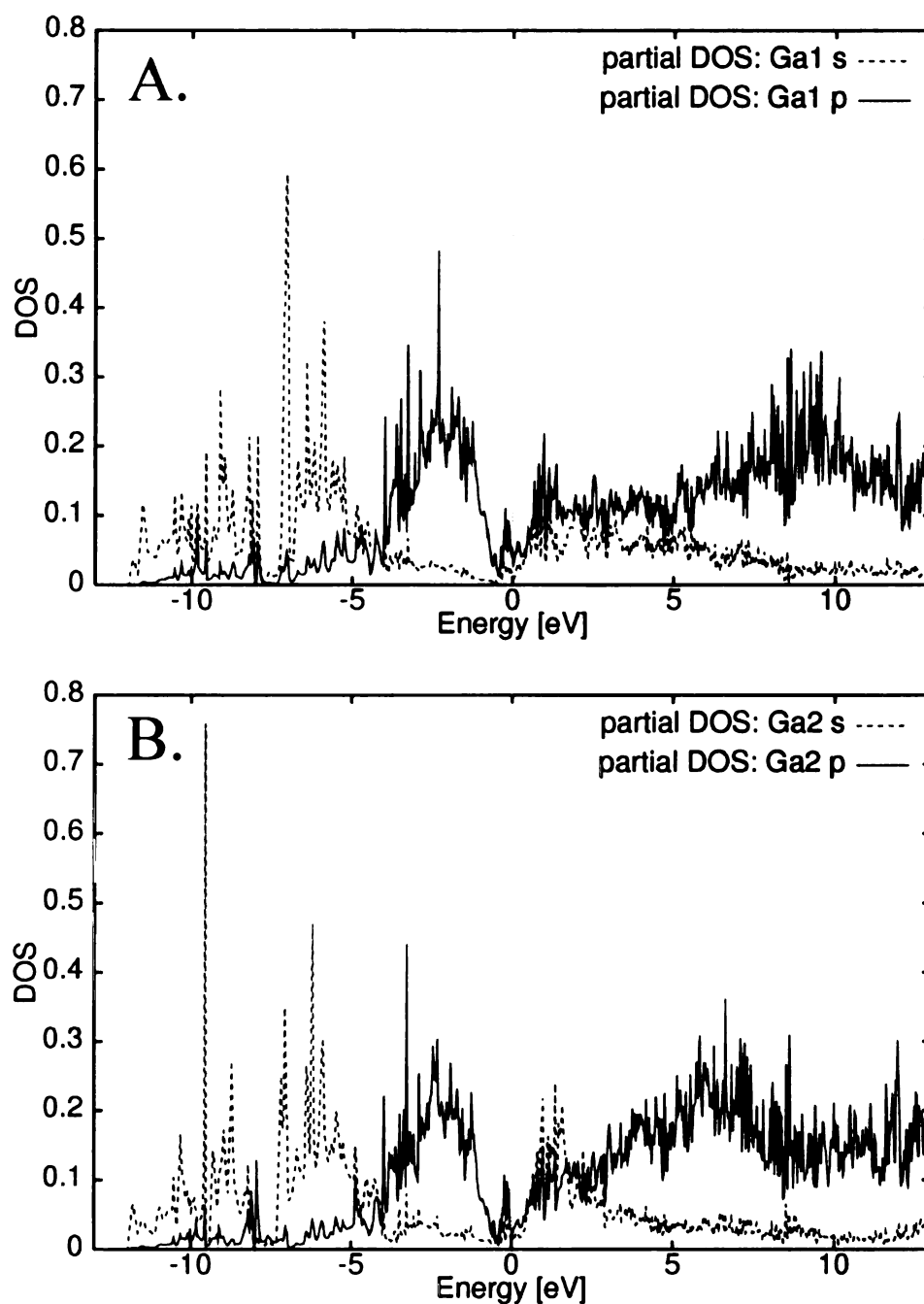


Figure III.B.10. The partial density of states (DOS) plot for 2. (A) Contribution from Ga(1) *s*-states (dashed line) and *p*-states (solid line) to the DOS. (B) Contribution from Ga(2) *s*-states (dashed line) and *p*-states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

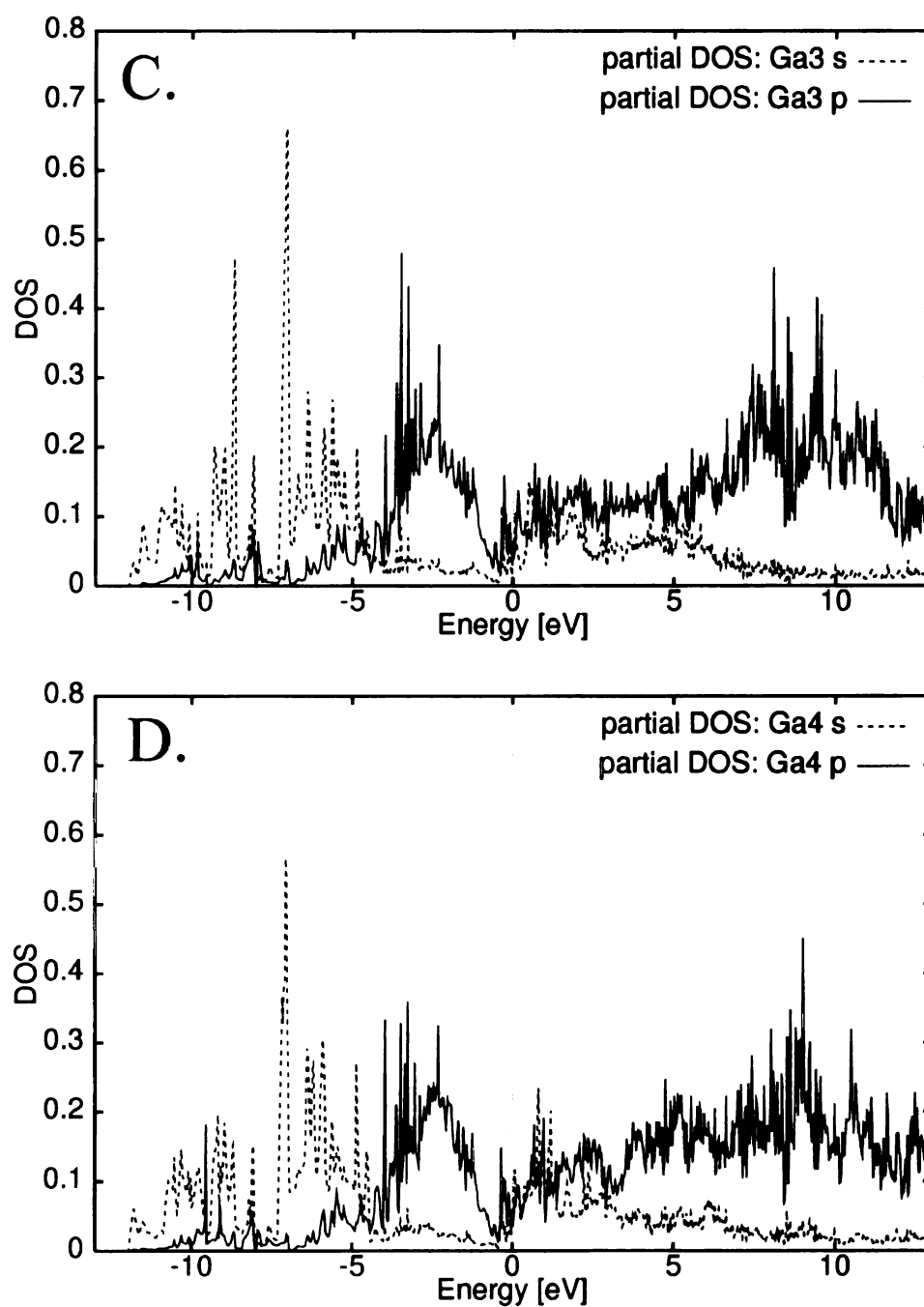


Figure III.B.10. The partial density of states (DOS) plot for 2. (C) Contribution from Ga(3) s -states (dashed line) and p -states (solid line) to the DOS. (D) Contribution from Ga(4) s -states (dashed line) and p -states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

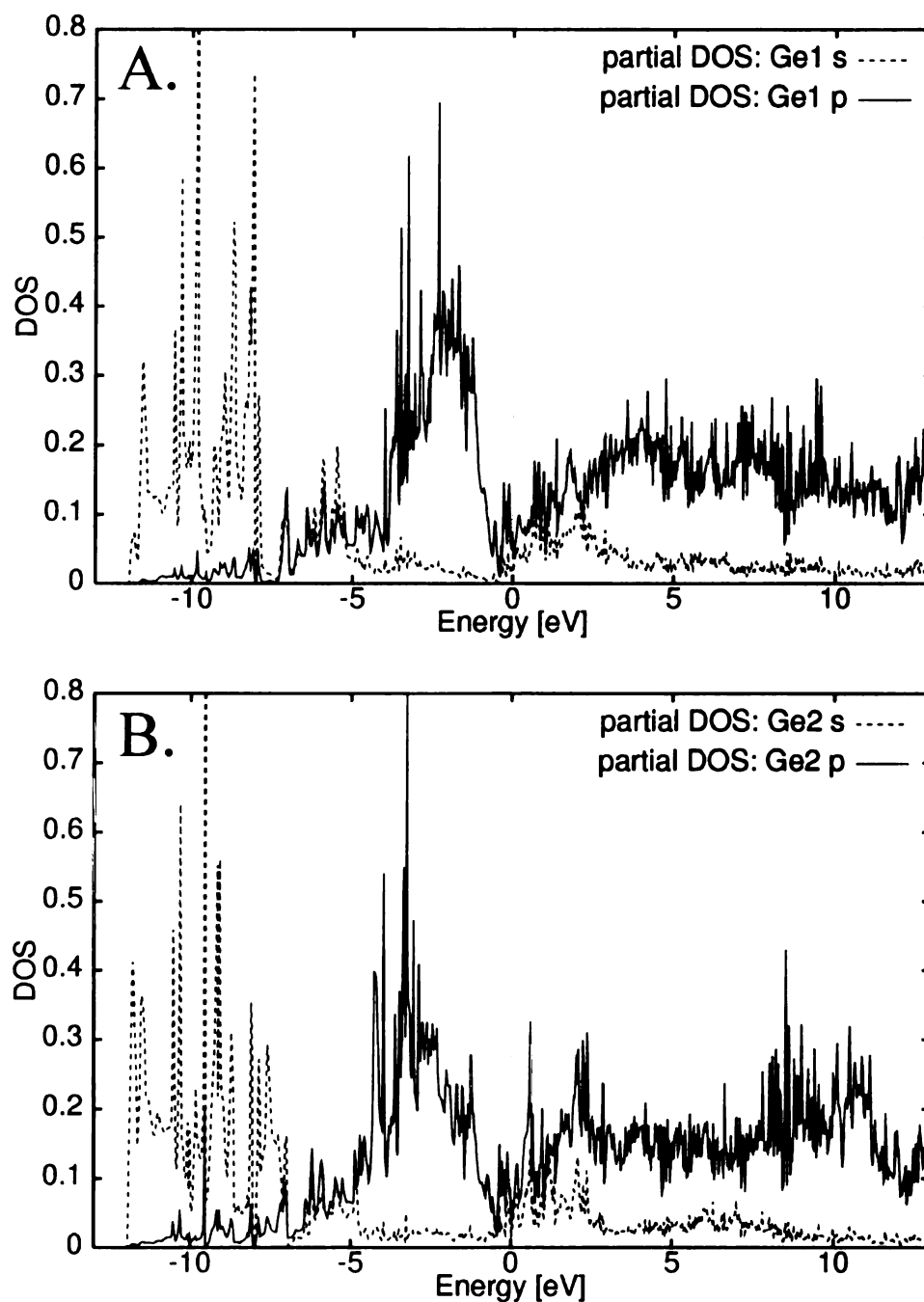


Figure III.B.11. The partial density of states (DOS) plot for 2. (A) Contribution from Ge(1) s -states (dashed line) and p -states (solid line) to the DOS. (B) Contribution from Ge(2) s -states (dashed line) and p -states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

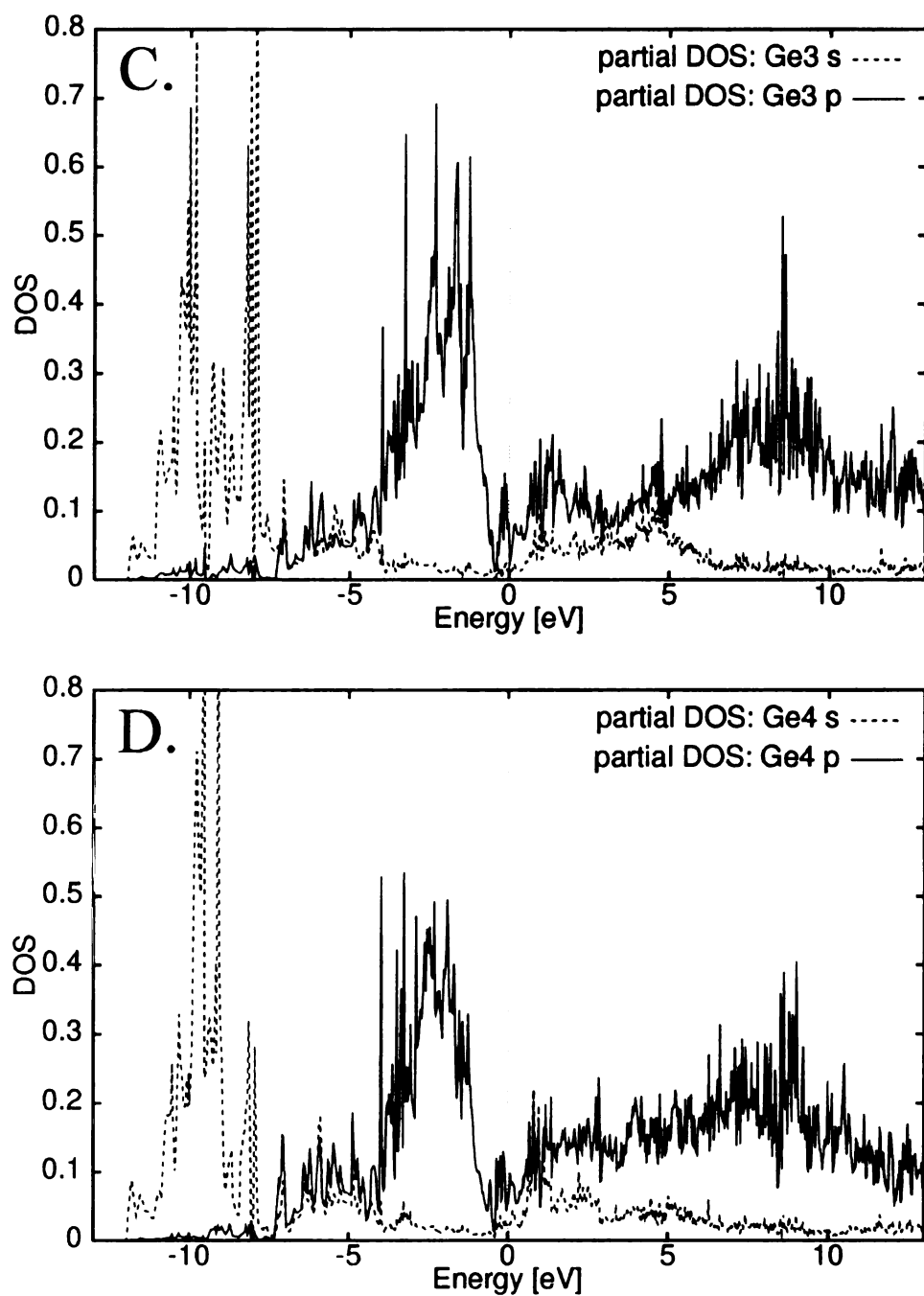


Figure III.B.11. The partial density of states (DOS) plot for 2. (C) Contribution from Ge(3) *s*-states (dashed line) and *p*-states (solid line) to the DOS. (D) Contribution from Ge(4) *s*-states (dashed line) and *p*-states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

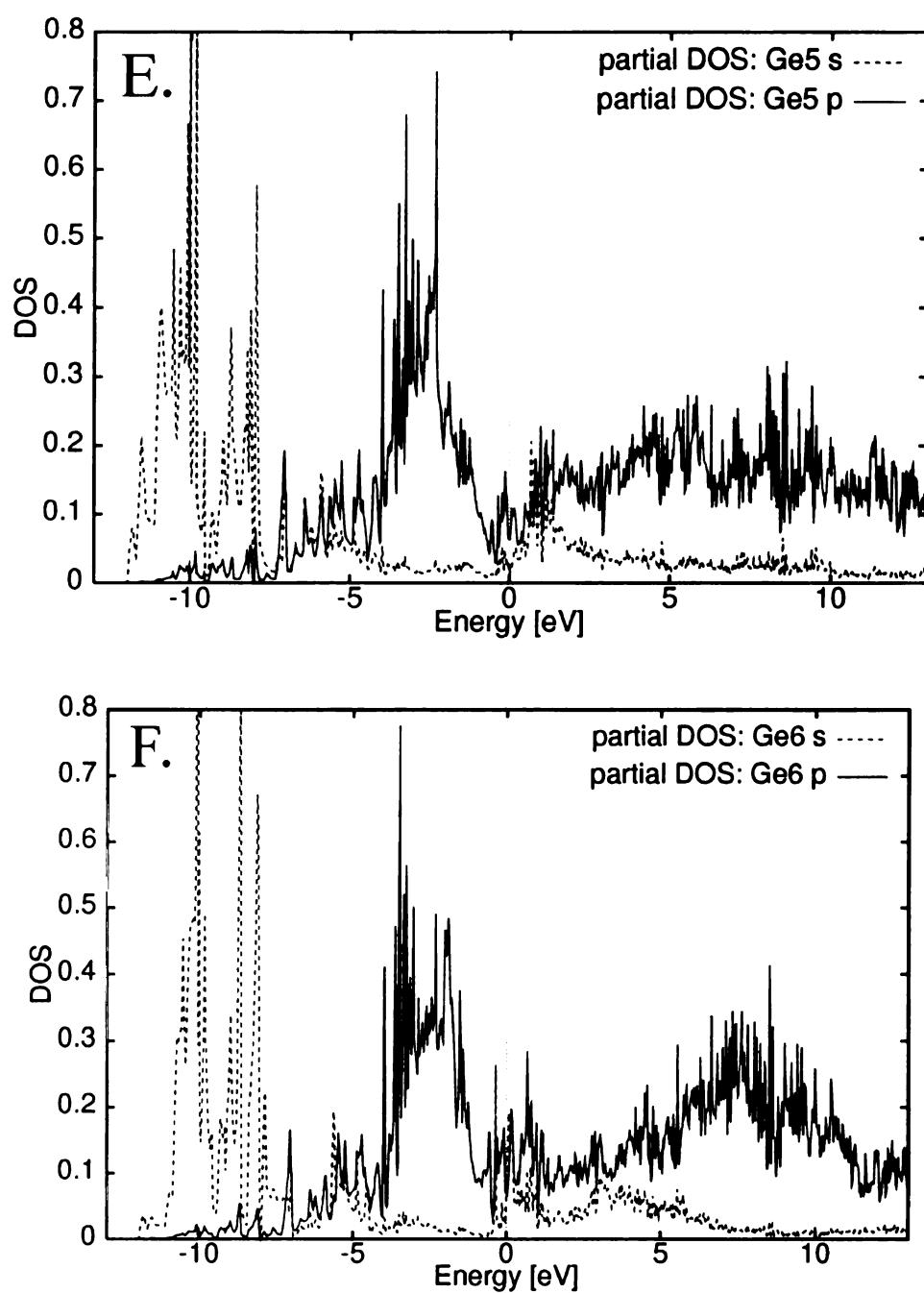


Figure III.B.11. The partial density of states (DOS) plot for 2. (E) Contribution from Ge(5) s -states (dashed line) and p -states (solid line) to the DOS. (F) Contribution from Ge(6) s -states (dashed line) and p -states (solid line) to the DOS. The Fermi energy is shown with a dotted line.

Considering these discoveries, the metallic property of **1** and **2**, as opposed to a semiconducting behavior characteristic for classic Zintl phases, could be accounted for. As has been noted by a number of researchers, the predicted semiconducting behavior has been seen in a relatively few “closed shell” Zintl compounds²⁸. The question on whether this phenomenon is caused by adventitious doping effects, or incomplete charge transfer from the guest species to the host framework still remains¹⁰. In the case of **1** and **2**, a combined approach of X-ray structural data and theoretical electronic calculations seem to suggest poor metallic behavior, although the possibility of overdoping can not be ruled out given the electrical conductivity data to be presented in the section below. In particular, it is worthwhile noticing that the incomplete charge transfer is supported by both connectivity considerations (single crystal X-ray data) and theoretical calculations.

Magnetic Properties

The plot of the molar susceptibility (χ_m) of crystalline sample of $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (**2**) as a function of temperature is presented in Figure III.B.12. The susceptibility of **2** has a very low negative value of $-0.56 \cdot 10^{-3}$ emu/mol Yb and is nearly independent of temperature which is characteristic for diamagnetism. The small upturn of χ_m at low temperatures is most likely due to the presence of impurities. The temperature-independent behavior of χ_m evidences the non-magnetic state of Yb ions (Yb^{2+}) with completely filled f^{14} configuration. Moreover, from the negative sign of χ_m it follows that the contribution to the magnetic susceptibility from the core diamagnetism of constituting atoms surpasses the paramagnetic contribution caused by presence of conduction

electrons (Pauli paramagnetism). Interestingly, in our previous studies of intermetallic compounds with non-magnetic RE, we find that the systems which exhibit metallic conductivity²⁹ typically behave as Pauli paramagnetics. The examples of the latter include $\text{Y}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ ($+0.13 \cdot 10^{-3}$ emu/mol Y), $\text{Y}_{0.67}\text{Co}_2\text{Ga}_{6-x}\text{Ge}_x$ ($+0.11 \cdot 10^{-3}$ emu/mol Y), $\text{La}_{5-x}\text{Ni}_{12}\text{Sn}_{24}$ ($+2.83 \cdot 10^{-3}$ emu/mol La) and YCoGa_3Ge ($+0.6 \cdot 10^{-3}$ emu/mol Y).

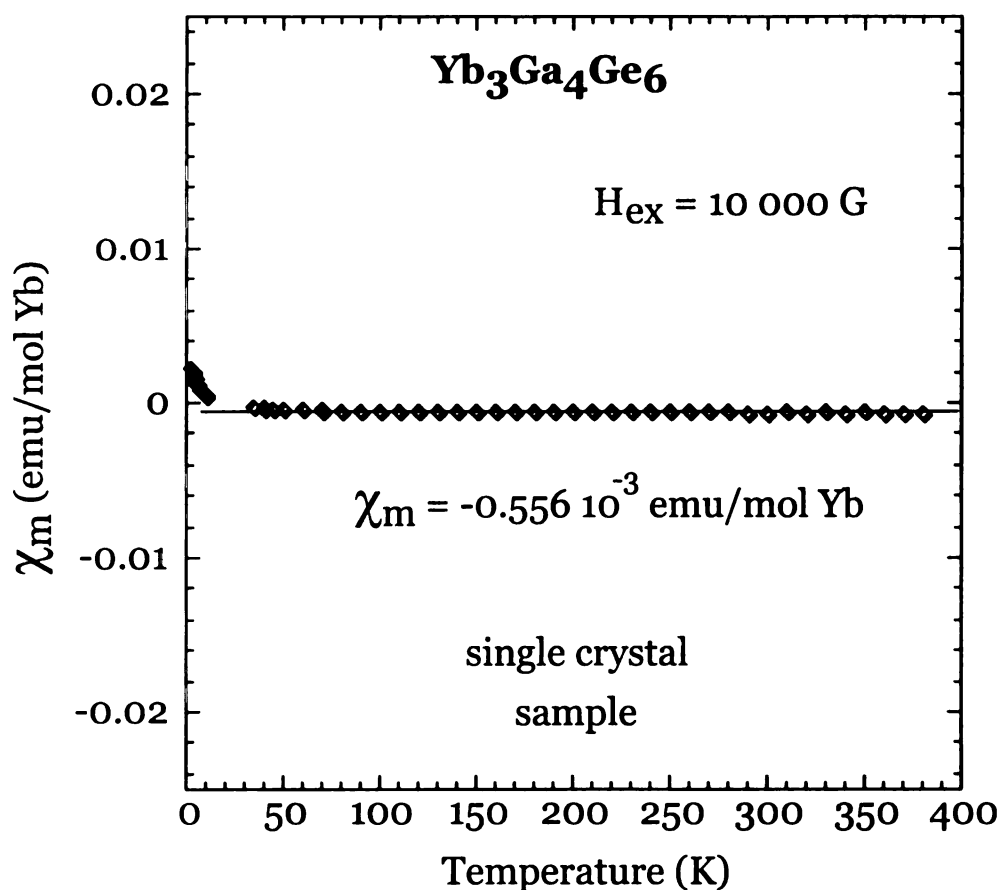


Figure III.B.12. Temperature dependence of the magnetic susceptibility of crystalline sample of $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (2) calculated per mole of Yb. The measurements were done with 10000 Gauss of applied magnetic field.

Transport Properties

Electrical conductivity and thermopower measurements were performed on single crystal samples of $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ (**2**). Figure III.B.13.A depicts conductivity measured as a function of temperature in the region 70 – 350 K. The conductivity decreases linearly with temperature, indicating metallic behavior. The room temperature conductivity is $\sim 10^4$ S/cm, typical of metals. The temperature dependence of the thermoelectric power measured between 80 and 300 K is shown in Figure III.B.13.B. The thermopower has small positive values (~ 10 $\mu\text{V/K}$), signifying that charge carriers are holes. The calculated power factor, see Figure III.B.13.C is quite low, reaching values of ~ 1 $\mu\text{W/K}^2\cdot\text{cm}$ at room temperature.

The occurrence of metallic behavior for compounds **1** and **2** lies in the position of the Yb *f*-levels. As evident from the spaghetti plots for **1** and **2**, see Figures III.B.14 A and C, respectively, the Yb *f*-bands are very flat and pinned to the E_F . Although there is no direct crossover between the conduction and valence bands, the E_F slightly cuts through the part of the *f*-levels. However, when integrated, the resulting number of electrons contributing to the conduction is substantial, owing to the flatness of the *f*-bands. This is not the case for the hypothetical Sr analog (see Figure III.B.14 B and D), where, in the absence of *f*-levels, the bands are sharp, and even though the bands cross the E_F , the concentration of conduction electrons is small, typical to semimetals.

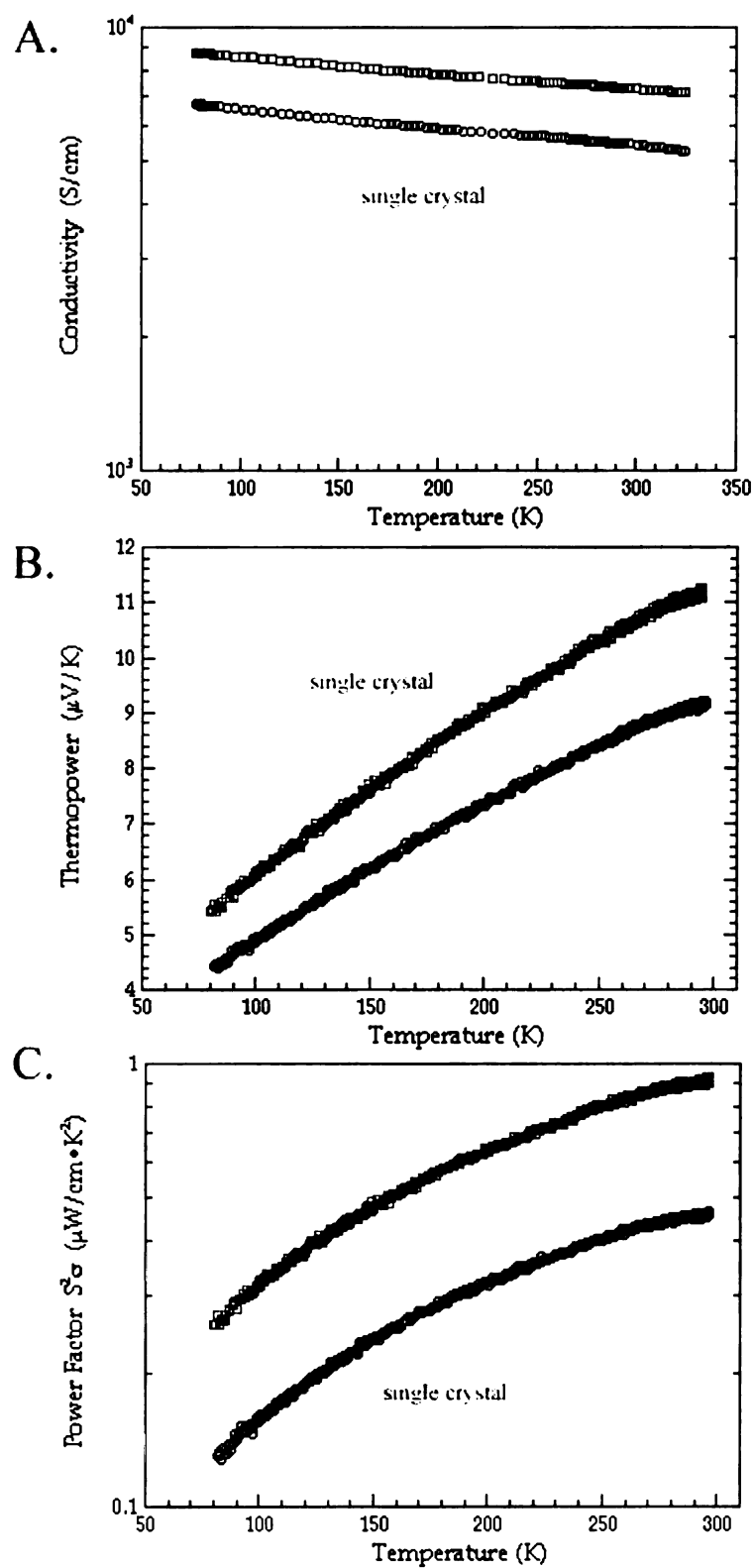


Figure III.B.13. Transport properties of the $\text{Yb}_3\text{Ga}_4\text{Ge}_6$. Temperature dependence of (A) electrical conductivity; (B) thermopower and (C) power factor.

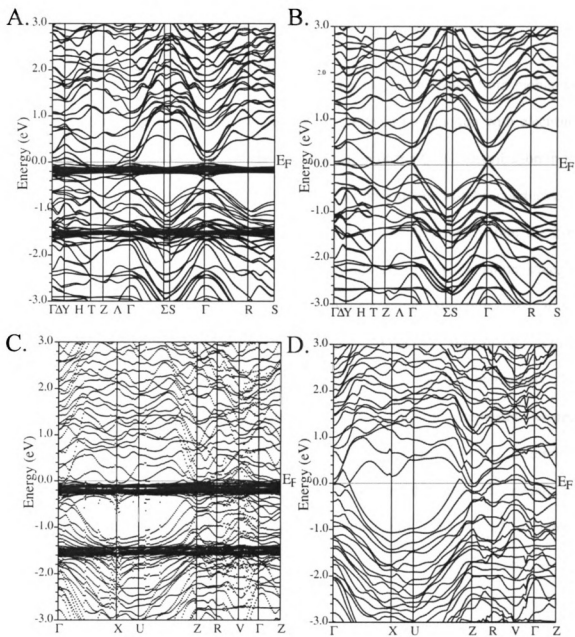
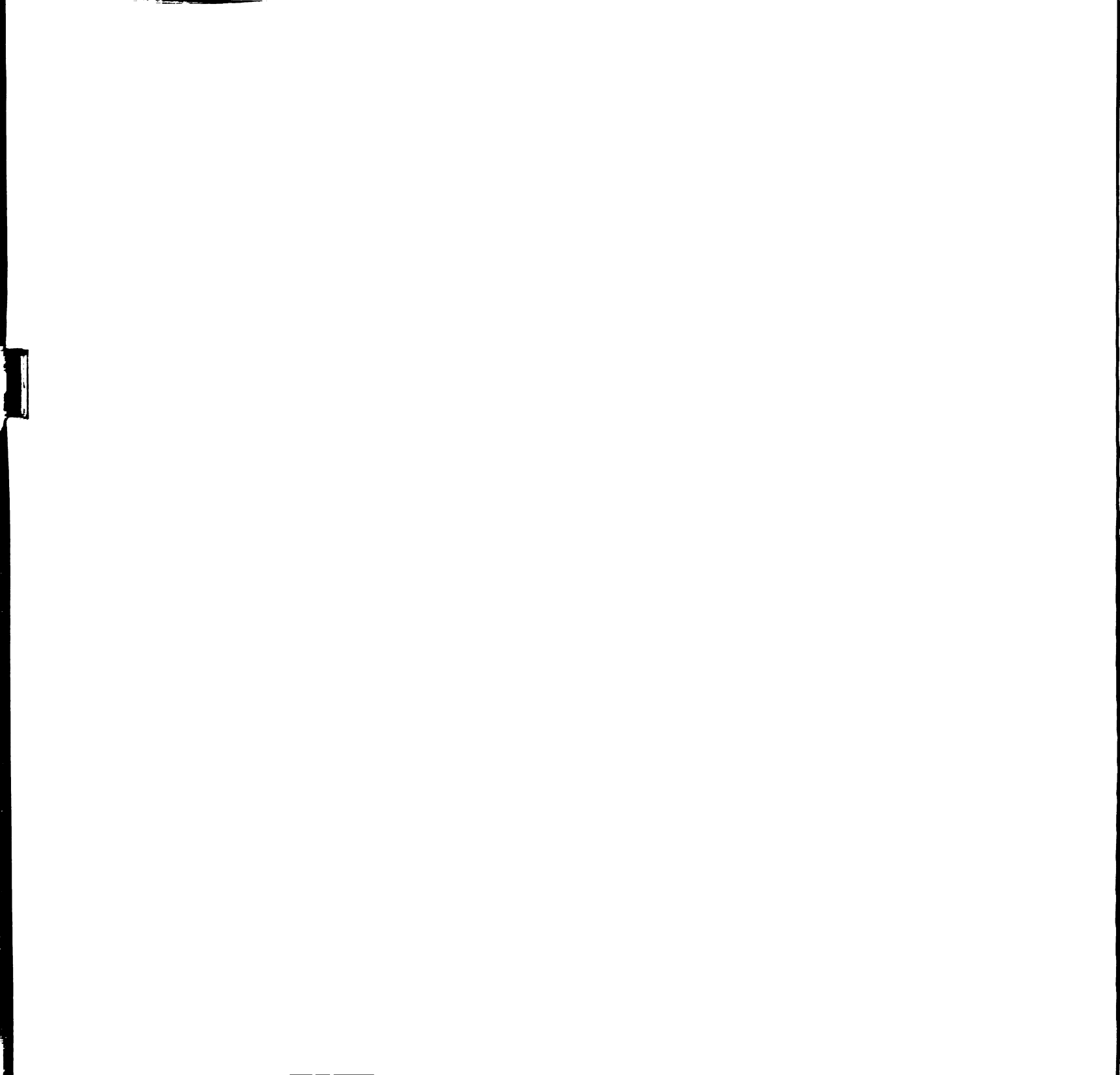


Figure III.B.14. Calculated band structure for (A) $\text{Yb}_2\text{Ga}_4\text{Ge}_6$; (B) hypothetical $\text{Sr}_2\text{Ga}_4\text{Ge}_6$; (C) $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ and (D) hypothetical $\text{Sr}_3\text{Ga}_4\text{Ge}_6$. The Fermi level (E_F) is shown with solid grey line.

4. Concluding Remarks

The novel compounds $\text{Yb}_2\text{Ga}_4\text{Ge}_6$ and $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ were grown from molten Ga solutions at 850°C . X-ray crystal structure investigation in conjunction with electronic structure calculations allowed preliminary determination of the Ga/Ge distribution in the structure of these two compounds. Neutron diffraction studies will be conducted in future. The structure and bonding of these compounds was described within the Zintl bonding concept. The Yb atoms in both compounds are in $2+$ oxidation state, as evidenced by both magnetic measurements and electronic structure calculations. Electropositive Yb atoms are hosted by the polyanionic $[\text{Ga}_4\text{Ge}_6]^{n-}$ framework – a three dimensional rigid unit held together by strong Ga-Ge and Ge-Ge interactions. The theoretical calculations predict these materials to possess metallic properties, whereas hypothetical Sr analogs are expected to be semimetals. Experimentally determined transport properties of $\text{Yb}_3\text{Ga}_4\text{Ge}_6$ show metallic p-type conductivity. The metallic as opposed to the semiconducting behavior of these compounds is a result of incomplete charge transfer from the guest Yb atoms to the host $[\text{Ga}_4\text{Ge}_6]$ network, which is also apparent from the strong covalent Yb-Ge connectivities and possible doping effects. Magnetic susceptibility measurements performed for $\text{Yb}_3\text{Ga}_4\text{Ge}_6$, indicated temperature-independent diamagnetism, in accord with fully filled f^{14} shell of Yb^{2+} ions.



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Chapter IV

Isolation of the New Cubic Phases $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ (RE = Sm, Tb; $x = 2.5$) from Molten Gallium. Single Crystal Neutron Diffraction Study of the Ga/Ge distribution.

1. Introduction

Crystal growth employing molten metals¹, and molten salts² has been known for a long time, however their use in deliberate solid state synthesis has attracted increasing attention in recent years^{3, 4, 5}. Because of the huge potential for new materials discovery in the realm of intermetallics, the molten metal flux technique is proving to be an outstanding tool for exploration^{6, 7-10}. The advantages of this method lie in the enhanced diffusion of the elements facilitated by the solvent and the lower reaction temperatures that can be tolerated. The latter allows better kinetic control that gives more flexibility to

adopt novel compositions and atomic arrangements in the structure. Recently, we suggested the use of liquid Al for the synthesis of new Si and Ge containing materials and have reported on the $\text{Ho}_2\text{Al}_3\text{Si}_2$ ⁸, $\text{Sm}_2\text{Ni}(\text{Si}_{1-x}\text{Ni}_x)\text{Al}_4\text{Si}_6$ ⁹, $\text{RENiAl}_4\text{Ge}_2$ ¹⁰ (RE = Sm, Tb, Y), $\text{RE}_4\text{Fe}_{2+x}\text{Al}_{7-x}\text{Si}_8$ ¹¹ (RE = Ce, Pr, Nd, Sm), and $\text{RE}_8\text{Ru}_{12}\text{Al}_{49}\text{Si}_9(\text{Al}_x\text{Si}_{12-x})$ ¹² (RE = Pr, Sm). The success of molten Al to uncover new materials stimulated us to explore the related Ga system. The known binary and ternary compounds of Ga are numerous¹³, however, there is still a paucity of data on quaternary intermetallic phases such as silicides and germanides. Using liquid Ga we have already discovered ternary rare-earth nickel silicides $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ¹⁴, RENiSi_3 ¹⁵, germanide Tb_4FeGe_8 ¹⁶, as well as ternary gallides $\text{Yb}_3\text{Ga}_5\text{Ge}_5$, $\text{Yb}_2\text{Ga}_5\text{Ge}_5$ ¹⁷, and polygallides $\text{Sm}_2\text{NiGa}_{12}$ ¹⁸ and $\text{RE}_3\text{Ga}_9\text{Ge}$ ¹⁹. Our continued investigations with Ga targeting quaternary silicides and germanides focused further on the systems RE/M/Ga/Ge encompassing different transition metals M = Fe, Co, Ni, Cu.

In this Chapter, we report results regarding the Fe system and describe the synthesis, crystal structure, transport and magnetic properties of the cubic phases $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ (RE = Sm, Tb) obtained from the reactions in molten Ga and $\text{Y}_4\text{FeGa}_{12-x}\text{Ge}_x$ found in the direct combination reactions.

2. Experimental Section

Synthesis

(a) Flux Synthesis

Rare-earth, Fe and Ge were combined with a large excess of Ga under a nitrogen atmosphere. Alumina crucibles containing the reaction mixtures: Sm (Tb) (3.6 mmol), Fe (0.9 mmol), Ge (2.7 mmol), Ga (27 mmol) were placed into silica tubes and sealed under high vacuum $<1 \cdot 10^{-4}$ Torr. The heating profile included slow heating (60°/hour) up to 1000°C, a short isothermal step at 1000°C to allow proper homogenization, cooling (75°/hour) to 850°C and a long isothermal step of 72 hours at 850°C. The system was then allowed to cool slowly (15°/hour) to ~200 - 250°C, and the tubes were taken out for hot-filtration to remove liquid Ga. The filtration was done using specially designed silica filters with coarse frit by centrifuging at high speed > 3000 rpm for approximately 30 seconds. After filtration the residual Ga flux was removed with ~3 M solution of I_2 in dimethylformamide (DMF) overnight. The resultant crystalline product was subsequently washed in DMF, hot water, and dried by washing with acetone and ether. The product was $RE_4FeGa_{12-x}Ge_x$ as a major phase (about 75%), and $FeGa_3$ and Ge as minor phases. For RE = Sm, the formation of the ternary phase Sm_3Ga_9Ge was also observed.

(b) Direct Combination Synthesis

The Y analog of $RE_4FeGa_{12-x}Ge_x$ was obtained from the direct combination reactions intended for synthesis of $YFe_{4+x}Ga_{8-x}$ and $YFe_6Ga_4Ge_2$ compounds, derivatives

of the ThMn_{12} structure type. In these reactions, the elements: Y, Fe, Ga and Ge were combined in the proportions Y : Fe : Ga : Ge as 5 : 2 : 8 : 8 and loaded into alumina crucibles under inert atmosphere. The temperature variation scheme included slow heating ($60^\circ/\text{hour}$) up to 1000°C , a short isothermal step at 1000°C to allow proper homogenization, cooling ($75^\circ/\text{hour}$) to 850°C and a long isothermal step of 72 hours at 850°C . The system was then allowed to cool slowly ($22^\circ/\text{hour}$) to 50°C . Upon completion of the reactions, the product was treated shortly with I_2/DMF solution to remove possibly unreacted Ga, Y and Fe, sonicated in water and, finally, dried with few aliquots of acetone and ether.

Scanning Electron Microscopy and Elemental Analysis

The micrographs of the samples were taken with a scanning electron microscope (SEM) JEOL JSM-35C. A semi-quantitative elemental analysis by Energy Dispersive Spectroscopy (EDS) was done on the SEM equipped with NORAN Inc. EDS detector. The analysis was conducted at an accelerating voltage 20 kV and collection time 30 seconds. Data were taken from several samples, and the results were averaged. The EDS analysis shows that the elemental composition of the samples under investigation (normalized per amount of Fe) corresponds to the formula $\text{RE}_3\text{FeGa}_8\text{Ge}_3$. The composition was consistent for both Sm and Tb analogs, despite the complication caused by partial overlap of energies of Fe $\text{K}\alpha$ -line (6.403 keV) and Tb $\text{L}\alpha$ -lines (6.272 keV) in the X-ray fluorescence spectra. Composition of the Y analog corresponded to the formula $\text{Y}_{5.1}\text{FeGa}_{10}\text{Ge}_{2.6}$ if normalized per content of Fe.

Single Crystal X-ray Crystallography

Single crystal X-ray diffraction data was collected at room temperature on a Siemens Platform SMART CCD diffractometer. The samples of size $0.06 \times 0.06 \times 0.04$ mm³ for RE = Sm, $0.1 \times 0.16 \times 0.02$ mm³ for RE = Tb and $0.1 \times 0.08 \times 0.04$ mm³ for RE = Y were cut from larger crystals and mounted on glass fibers. A hemisphere of data (Mo K α radiation, $\lambda = 0.71073$ Å) was acquired, using an exposure time 60 seconds per frame for Sm, and 30 seconds per frame for Y and Tb analogs. The data collection and acquisition was done with the SMART²⁰ software package and the SAINTPLUS²¹ program was used for data reduction. An empirical correction for absorption based on symmetry equivalent reflections was applied using SADABS²². Systematic absences led to the following possible space groups: $I23$, $I2_13$, $Im\bar{3}$, $I432$, $\bar{I}3m$, $Im\bar{3}m$. The highest symmetry space group $Im\bar{3}m$ was chosen. The structures were solved with direct methods and refined using the full-matrix least-squares technique with the SHELXTL²³ software package. All atoms were refined anisotropically. The positional parameters were standardized using STRUCTURE TIDY program²⁴.

Details of the data collection and structure refinement are listed in Table IV.1. The final atomic positions, the equivalent thermal displacement parameters, and occupancies are given in Table IV.2. The interatomic distances up to 3.5 Å and selected bond angles are listed in Tables 3 and 4, respectively. The anisotropic displacement parameters are given in Table IV.5.

In the structure a total of four atomic sites RE ($8c, 1/4\ 1/4\ 1/4$), Fe ($2a, 0\ 0\ 0$), Ga ($12d, 1/4\ 0\ 1/2$) and Ge ($12e, x\ 0\ 0$) one for each element were identified. For the Sm and Y analogs a mixed occupancy of Fe with Ge was observed on the $12e$ crystallographic site. It is not possible however to distinguish between Ga and Ge atoms relying on X-ray diffraction data only. The R-values and the values of the resulting thermal displacement parameters were entirely satisfactory for the assignment of Ga atoms to $12d$ and Ge to $12e$ positions. However, the resulting formula $\text{RE}_4\text{FeGa}_6\text{Ge}_6$ is in disagreement with the composition given by EDS " $\text{RE}_4\text{FeGa}_8\text{Ge}_3$ ". Thus, the uncertainty about the Ga/Ge distribution motivated us to undertake a single crystal neutron diffraction crystallographic analysis. In contrast to the small difference in X-ray scattering lengths ($\sim 3\%$) between Ga and Ge atoms, the neutron scattering lengths for Ga and Ge atoms differ significantly ($\sim 10\%$). Thus neutron diffraction provides a better means for distinguishing these two elements in a crystalline sample.

Table IV.1. Crystal data and structure refinement for RE₄Fe_{1+y}Ga₆Ge_{6-y} (RE = Sm, Tb).

	(a) RE = Sm	(b) RE = Tb
Empirical formula	Sm ₄ Fe _{1+y} Ga ₆ Ge _{6-y}	Tb ₄ FeGa ₆ Ge ₆
y	0.98(1)	–
Formula weight	1493.98	1545.39
Temperature (K)	298(2)	298(2) K
Wavelength (Å)	0.71073	0.71073 Å
Crystal system	Cubic	Cubic
Space group	$Im\bar{3}m$	$Im\bar{3}m$
Unit cell dimensions (Å)	$a = 8.657(4)$	$a = 8.5620(9)$
Volume	648.7(6)	627.66(11) Å ³
Z	2	2
Density (calculated) (g/cm ³)	7.648	8.177
Absorption coefficient (mm ⁻¹)	43.496	50.017
F(000)	1292	1328
Crystal size (mm ³)	0.06 × 0.06 × 0.04	0.02 × 0.10 × 0.16
θ range for data collection	3.33 to 27.91°	3.37 to 28.72°
Index ranges	$-11 \leq h \leq 9$ $-11 \leq k \leq 11$ $-11 \leq l \leq 9$	$-11 \leq h \leq 11$ $-11 \leq k \leq 10$ $-10 \leq l \leq 6$
Reflections collected	1907	2000
Independent reflections	99 [$R_{\text{int}} = 0.0439$]	104 [$R_{\text{int}} = 0.0645$]
Completeness to θ	99.0 %	98.1 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	99 / 1 / 12	104 / 0 / 12
Goodness-of-fit on F^2	1.251	1.481
Final R indices [$I > 2\sigma(I)$] [*]	$R_1 = 0.0147$, $wR_2 = 0.0413$	$R_1 = 0.0229$, $wR_2 = 0.0712$
R indices (all data)	$R_1 = 0.0161$, $wR_2 = 0.0417$	$R_1 = 0.0234$, $wR_2 = 0.0713$
Extinction coefficient	0.00141(12)	0.0024(3)
Largest difference peak and hole (e·Å ⁻³)	0.669 and -0.852	0.914 and -1.686

^{*} $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table IV.1. (c) Crystal data and structure refinement for $\text{Y}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$.

	(c) RE = Y
Empirical formula	$\text{Y}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$
y	1.7(4)
Formula weight	1239.04
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Cubic
Space group	$\bar{Im}3m$
Unit cell dimensions (Å)	$a = 8.5683(12)$
Volume	629.05(15)
Z	2
Density (calculated) (g/cm^3)	6.542
Absorption coefficient (mm^{-1})	43.946
F(000)	1101
Crystal size (mm^3)	$0.1 \times 0.08 \times 0.04$
θ range for data collection	3.36 to 28.22°
Index ranges	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-11 \leq l \leq 5$
Reflections collected	1927
Independent reflections	99 [$R_{\text{int}} = 0.0342$]
Completeness to θ	99.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	99 / 1 / 12
Goodness-of-fit on F^2	1.436
Final R indices [$I > 2\sigma(I)$] [*]	$R_1 = 0.0251$, $wR_2 = 0.0788$
R indices (all data)	$R_1 = 0.0261$, $wR_2 = 0.0791$
Extinction coefficient	0.0027(4)
Largest difference peak and hole ($\text{e} \cdot \text{\AA}^{-3}$)	0.874 and -0.958

^{*} $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table IV.2. Atomic coordinates, equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and occupancies for (a) $\text{Sm}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$, (b) $\text{Tb}_4\text{FeGa}_6\text{Ge}_6$ and (c) $\text{Y}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$.

(a)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*	Occupancy
Sm	<i>8c</i>	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	9(1)	1.0
Fe	<i>2a</i>	0	0	0	10(1)	1.0
Ga	<i>12d</i>	$\frac{1}{4}$	0	$\frac{1}{2}$	10(1)	1.0
M	<i>12e</i>	0.2879(2)	0	0	9(1)	0.83(4) Ge + 0.16(5) Fe

*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

(b)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*	Occupancy
Tb	<i>8c</i>	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	8(1)	1.0
Fe	<i>2a</i>	0	0	0	10(1)	1.0
Ga	<i>12d</i>	$\frac{1}{4}$	0	$\frac{1}{2}$	9(1)	1.0
Ge	<i>12e</i>	0.2869(3)	0	0	10(1)	1.0

*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table IV.2 (continued)

(c)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)	Occupancy
Y	<i>8c</i>	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	9(1)	1.0
Fe	<i>2a</i>	0	0	0	13(2)	1.0
Ga	<i>12d</i>	$\frac{1}{4}$	0	$\frac{1}{2}$	12(1)	1.0
M	<i>12e</i>	0.2864(3)	0	0	10(1)	0.72(7) Ge + 0.28(7) (Fe)

*U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table IV.3. Selected bond lengths [$\text{\AA}$] for (a) $\text{Sm}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$, (b) $\text{Tb}_4\text{FeGa}_6\text{Ge}_6$ and (c) $\text{Y}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$.

(a)

Bond	Distance	Multiplicity
Sm-Ga	3.0606(15)	$\times 6$
Sm-Ge	3.0781(15)	$\times 6$
Fe-Ge	2.492(2)	$\times 6$
M-Ga	2.8381(17)	$\times 4$

(b)

Bond	Distance	Multiplicity
Tb-Ga	3.0271(3)	$\times 6$
Tb-Ge	3.0436(4)	$\times 6$
Fe-Ge	2.457(3)	$\times 6$
Ge-Ga	2.8125(17)	$\times 4$

(c)

Bond	Distance	Multiplicity
Y-Ga	3.0294(4)	$\times 6$
Y-M	3.0454(5)	$\times 6$
Fe-M	2.454(3)	$\times 6$
M-Ga	2.8172(17)	$\times 4$

Table IV.4. Selected bond angles [°] for (a) $\text{Sm}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$, (b) $\text{Tb}_4\text{FeGa}_6\text{Ge}_6$ and (c) $\text{Y}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$.

(a)

Bond	Angle	Bond	Angle
Ga-Sm-Ga	60.0	M-Fe-M	90.0
Ga-Sm-Ga	120.0	M-Fe-M	180.0
Ga-Sm-Ga	180.0	M-Ga-M	125.55(3)
Ga-Sm-M	55.07(2)	M-Ga-M	0.0
Ga-Sm-M	124.93(2)	M-Ga-M	0.00(5)
Ga-Sm-M	90.0	M-Ga-M	80.62(5)
M-Sm-M	69.85(5)	Fe-M-Ga	130.31(2)
M-Sm-M	110.15(5)	Ga-M-Ga	65.26(3)
M-Sm-M	180.0	Ga-M-Ga	99.38(5)

(b)

Bond	Angle	Ga-Tb-Ge	90.0
Ga-Tb-Ga	60.0	Ge-Tb-Ge	180.00(10)
Ga-Tb-Ga	120.0	Ge-Fe-Ge	90.0
Ga-Tb-Ga	180.0	Ge-Fe-Ge	180.0
Ga-Tb-Ge	55.20(4)	Fe-Ge-Ga	130.44(4)
Ga-Tb-Ge	124.80(4)	Ga-Ge-Ga	65.12(4)
Ge-Tb-Ge	110.40(8)	Ga-Ge-Ga	99.12(8)
Ge-Tb-Ge	69.60(8)	Ge-Ga-Ge	125.40(5)
Ge-Tb-Ge	180.0	Ge-Ga-Ge	80.88(8)

Table IV.4 (continued)

(c)

Bond	Angle	M-Y-M	69.48(7)
Fe-M-Ga	130.51(4)	M-Y-M	180.00(9)
Ga-M-Ga	65.05(4)	M-Y-M	110.52(7)
Ga-M-Ga	98.99(8)	M-Y-M	180.0
Ga-Y-Ga	60.0	M-Fe-M	90.0
Ga-Y-Ga	120.0	M-Fe-M	180.0
Ga-Y-Ga	180.0	M-Ga(1)- M	125.32(5)
Ga-Y-M	55.26(4)	M -Ga(1)- M	0.00(8)
Ga-Y-M	124.74(4)	M-Ga(1)- M	81.01(8)
Ga-Y-M	90.0	M-Ga(1)- M	0.0

Table IV.5. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for (a) $\text{Sm}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$,
(b) $\text{Tb}_4\text{FeGa}_6\text{Ge}_6$ and (c) $\text{Y}_4\text{Fe}_{1+y}\text{Ga}_6\text{Ge}_{6-y}$.

(a)

Atomic Position	U11	U22	U33	U23	U13	U12
Sm	9(1)	9(1)	9(1)	2(1)	2(1)	2(1)
Fe	10(1)	10(1)	10(1)	0	0	0
Ga	14(1)	8(1)	8(1)	0	0	0
Ge	8(1)	10(1)	10(1)	0	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

(b)

Atomic Position	U11	U22	U33	U23	U13	U12
Tb	8(1)	8(1)	8(1)	2(1)	2(1)	2(1)
Fe	10(1)	10(1)	10(1)	0	0	0
Ge	9(1)	11(1)	11(1)	0	0	0
Ga	12(1)	7(1)	7(1)	0	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Table IV.5 (continued)

(c)

Atomic	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Position						
Y	9(1)	9(1)	9(1)	2(1)	2(1)	2(1)
Fe	13(2)	13(2)	13(2)	0	0	0
Ga	16(1)	10(1)	10(1)	0	0	0
M	10(1)	11(1)	11(1)	0	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Single Crystal Neutron Crystallography

Neutron diffraction data were collected from a single crystal of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ weighing 30.1 mg ($2.3 \times 2.3 \times 1.8 \text{ mm}^3$) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory on the single-crystal diffractometer (SCD). A detailed description of the SCD instrument and data collection and analysis procedures has been published.^{25,26} An auto-indexing algorithm²⁷ was used to obtain an initial orientation matrix from the peaks in one histogram. For intensity data collection, a total of 18 histograms were measured - each for a different crystal setting. Bragg peaks were integrated in three dimensions about their predicted locations and were corrected for the incident neutron spectrum, detector efficiency and dead-time loss. Lorenz and absorption corrections were also applied. The GSAS software package²⁸ was used for structural analysis. The initial coordinates were based on the single crystal X-ray diffraction.

The refinement based on the original assignment of Ga at *12d* and Ge at *12e* positions yielded $R(F)/R_w(F) = 0.068/0.083$, and slightly enlarged thermal displacement parameter for Ge. After introducing a mixed occupancy model between Ga/Ge in both *12d* and *12e* sites (with occupancy refinement), the resulting R-values dropped and the temperature factor of the *12e* site improved. Occupancies of the Ga and Ge atoms at sites were found to be 0.89(4) for Ga(1) and 0.11(4) for Ge(1) at *12d*, and 0.70(4) for Ga(2) and 0.30(4) for Ge(2) at *12e*. All atoms were refined with anisotropic atomic displacement parameters and the final refinement converged to $R(F) = 0.062$ and $R_w(F) = 0.073$. The resulting formula $\text{Tb}_4\text{FeGa}_{9.54}\text{Ge}_{2.46}$ is in fair agreement with EDS elemental

analysis. A summary of parameters related to the neutron diffraction analysis is presented in Table IV.6. Atomic coordinates and site occupancies are listed in Table IV.7.

Table IV.6. Crystal data and structural refinement parameters for $\text{Tb}_4\text{FeGa}_{9.54}\text{Ge}_{2.46}$ obtained from neutron diffraction.

Formula	$\text{Tb}_4\text{FeGa}_{9.5(3)}\text{Ge}_{2.5(3)}$
Formula Weight	1535.325
Temperature, K	298(2)
Crystal system	<i>Cubic</i>
Space group	$Im\bar{3}m$
a , Å	8.6054(6)
V , Å ³	637.25(8)
Z	2
d_{calc} , g cm ⁻³	8.002
Size, mm ³	$2.3 \times 2.3 \times 1.8$
Radiation	Neutrons
Data collection technique	Time-of-flight Laue
$\mu(\lambda)$, cm ⁻¹	$0.393 + 0.2223\lambda$
Reflections collected ($I > 3\sigma(I)$)	1454
Parameters refined	34
Refinement method	Full-matrix least-squares on F
R indices $R_w(F)$ ^a $R(F)$, ^b	0.073, 0.062
Goodness-of-fit	1.49

$$^a R_w(F) = \left\{ \sum [w(F_o - F_c)^2] / \sum [w(F_o)^2] \right\}^{1/2} \quad ^b R(F) = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$$

Table IV.7. Fractional atomic coordinates for Tb₄FeGa_{9.5(3)}Ge_{2.5(3)} obtained from neutron diffraction.

Atomic Position	Site Symmetry	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	U (eq)
Fe(1)	<i>2a</i>	0	0	0	1.0	0.0101
Tb(1)	<i>8c</i>	¼	¼	¼	1.0	0.0085
M(1)	<i>12d</i>	¼	0	½	0.89(4) Ga + 0.11(4) Ge	0.0091
M(2)	<i>12e</i>	0.28378	0	0	0.70(4) Ga + 0.30(4) Ge	0.0101

Magnetic Properties and Mössbauer Spectroscopy

The magnetization of a 33.0 mg single crystal sample of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ was measured in the temperature range 2–300 K with an applied external field of 500 G using a Quantum Design MPMS SQUID magnetometer. The field dependence of the magnetic susceptibility was examined up to fields of ± 1 Tesla at 2 K. Raw susceptibility data were corrected for the sample holder contribution.

The Mössbauer spectra were taken on polycrystalline sample of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ with a constant acceleration spectrometer, equipped with a ^{57}Co source in Rh matrix. The spectrometer was calibrated with metallic iron and the isomer shift values are reported relative to $\alpha\text{-Fe}$. A closed-loop refrigerator system was used for the low temperature measurements. An Oxford Instrument Variox 316 cryostat was used for measurements at liquid helium temperature.

Transport Measurements

The Seebeck coefficient of single crystal sample of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ was measured between 50 and 400 K by using a SB-100 Seebeck Effect Measurement System MMR Technologies. The samples were glued to the stage with CW220MPT Conductive Pen silver paste.

3. Results and Discussion

General Chemistry

The compounds $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ were discovered from reactions in liquid Ga involving RE, M and Ge, where RE is Y, Ce, Sm, Gd, Tb; and M is Fe, Co, Ni, Cu. These systems were investigated at various metal ratios and different heating regimes. A heating regime with a shorter isothermal step was shown to favor the formation of cubic phases $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$. For example, when a six day isothermal step was used in the system Tb/Fe/Ga/Ge, the products were Tb_4FeGe_8 ¹⁶ and $\text{Tb}_2\text{Ga}_2\text{Ge}_5$ ²⁹, along with the cubic phase as a minor product. The shorter isothermal step of three days at 850°C, on the other hand, produced the cubic phase in high yield. For RE = Sm, the situation was similar, as the six day isothermal heating gave rise to $\text{Sm}_3\text{Ga}_9\text{Ge}$ as the major component, and the cubic phase, FeGa_3 and Ge as minor components. Reducing the time by half brought about an increase in the yield of the cubic phase. From this we conclude that the cubic phases are essentially a kinetic product of the reaction.

It is interesting that we did not observe isostructural phases as M was changed from Co to Ni, or to Cu. Instead, a variety of other quaternary compounds $\text{RE}_{0.67}\text{M}_2\text{Ga}_{5+n-x}\text{Ge}_x$ ^{30,31}, REMGa_3Ge ³², $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ ³², $\text{RE}_2\text{MGa}_9\text{Ge}_2$ ²⁹ and $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ ³² were detected. In addition, the type of RE appears to be important in phase formation. Thus, in the system RE/Fe/Ga/Ge, when RE was Y, Ce and Gd, the ternary $\text{RE}_3\text{Ga}_9\text{Ge}$ ¹⁹ phases were predominantly found. Remarkably, the Y analog $\text{Y}_4\text{FeGa}_{12-x}\text{Ge}_x$ does exist, however, it was obtained from a direct combination reaction. It is unclear at this point

whether the analogs of $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$, with RE other than Y, Sm and Tb, are unstable, or if the window of proper experimental synthetic conditions for these is rather narrow and was not accessed in this study.

Unlike conventional solid state techniques used for the synthesis of isostructural to $\text{U}_4\text{Re}_7\text{Si}_6$ -type compounds (see below), the molten metal method enables faster diffusion of the elements in the reaction mixture and promotes crystal growth. Thus, large single crystals of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$, measuring up to 2 mm each side, could be grown from molten Ga, see Figure IV.1. The incorporation of Ga in these phases shows that in this case the solvent is reactive. This is in contrast to the Sm/Ni/Ga/Si system in which the Ga-free $\text{Sm}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ¹⁴ and SmNiSi_3 ¹⁵ phases could be obtained.



Figure IV.1. SEM image of a typical Ga-grown $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ crystal. The roughening of the surface is caused by an etching process during isolation.

Crystal Structure

The $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ compounds crystallize in the $\text{U}_4\text{Re}_7\text{Si}_6$ ³³ structure type. This is a rather stable structural arrangement as a large number of isotypic ternary phases with Sc³⁴, lanthanides^{35,36}, actinides³⁷, as well as group IVA metals³⁸ are known. The $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ compounds seem to be the first quaternary analogs of the $\text{U}_4\text{Re}_7\text{Si}_6$ structure type. The general formula for these compounds could be written as $\text{A}_4\text{M}(\text{M}'_6\text{T}_6)$, where A = Sc, Ln, Ac, Zr, Hf, M = transition metal, M' = transition metal or Ga, and Tt = tetrelide or Ga. The examples of those are: $\text{Sc}_4\text{M}_7\text{Ge}_6$ ³⁴, $\text{RE}_4\text{M}_7\text{Ge}_6$ ³⁵ (M = Ru, Os, Rh, Ir), $\text{U}_4\text{Tc}_7\text{T}_6$ (Tt = Si, Ge), $\text{Np}_4\text{Ru}_7\text{Ge}_6$ ³⁷, $\text{U}_4\text{Re}_7\text{Si}_6$, $\text{M}_4\text{Co}_7\text{Ge}_6$ ³⁸ (M = Zr, Hf), and even $\text{RE}_4\text{MGe}_{12}$ ³⁶ (RE = Ho, Tm; M = Ni, Pd).

The position of the transition metal in the structure of these compounds is rather interesting: it could occupy only one crystallographic position with the lowest multiplicity ($2a, 0, 0, 0$) as it is for $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ and $\text{RE}_4\text{MGe}_{12}$, or two positions ($2a, 0, 0, 0$ and $12d, \frac{1}{4}, 0, \frac{1}{2}$), as it is in all other cases reported earlier. There seems to be a tendency that if the compound does not contain a group III element (*e.g.* Ga), the two sites are occupied with transition metal. However, in the presence of Ga, the transition metal adopts only the lowest multiplicity site, while the higher multiplicity site becomes preferably stabilized with Ga. In effect, as we can see in the example of $\text{Tm}_4\text{NiGa}_{12}$, Ga could occupy both the transition metal and a tetrelide position.

The structure of $\text{Sm}_4\text{FeGa}_{12-x}\text{Ge}_x$ viewed along the $[001]$ direction is depicted in Figure IV.2. The striped grey spheres represent Sm atoms, small filled circles are Fe atoms, and the mixed occupied positions $\text{M}(1) = \text{Ga}(1)/\text{Ge}(1)$ and $\text{M}(2) = \text{Ga}(2)/\text{Ge}(2)$ are drawn in open and shaded circles, respectively.

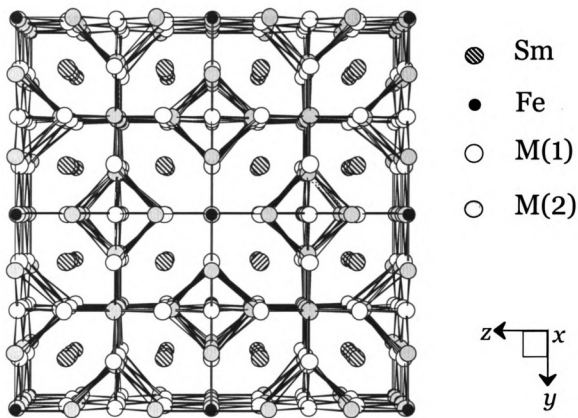


Figure IV.2. Structure of the $\text{Sm}_4\text{FeGa}_{12-x}\text{Ge}_x$ viewed along the $[100]$ direction.

This structure, as shown, is rather complicated, however, it becomes clearer when described in polyhedral representation. The two types of polyhedra found in this structure are shown in Figure IV.3a. The first, is a highly distorted tetrahedron of $M(1)M(2)_4$, with $M(1)$ atom in the center and $M(2)$ atoms in its corners. The distortion occurs in a way that two out of six edges are short (3.667 Å) and four are long (5.046 Å). The second polyhedron consists of the Fe atoms octahedrally coordinated within 2.495(2) Å to six $M(2)$ atoms. In this structure, the tetrahedra share their edges, forming a three-dimensional $[Ga_{12-x}Ge_x]$ substructure, see Figure IV.3b. The $FeM(2)_6$ octahedra occupy every corner and the center of the cubic unit cell, sharing their corners with the $[Ga_{12-x}Ge_x]$ framework, as shown in Figure IV.3c, and giving rise to a $Fe[Ge_{12-x}Ge_x]$ substructural unit. The octahedra are not connected with each other, and the closest distance between two apical $M(2)$ atoms is about 3.66 Å. The Sm atoms are situated in the pockets formed by the $Fe[Ge_{12-x}Ge_x]$ substructure, at the positions 8c ($\frac{1}{4} \frac{1}{4} \frac{1}{4}$), see Figure IV.3d.

(a)

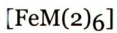
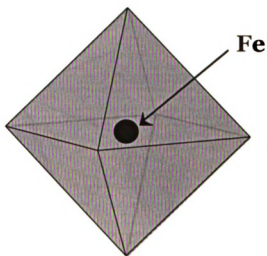
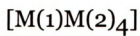
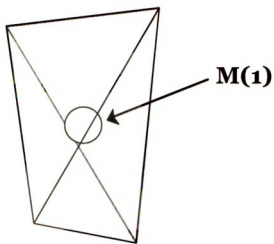


Figure IV.3a. An isolated $[M(1)M(2)_4]$ tetrahedron with M(1) atom in the center and four M(2) atoms in its corners (up). The octahedral unit $[FeM(2)_6]$ is built on the central Fe atom and six M(2) atoms in its corners (down).

(b)

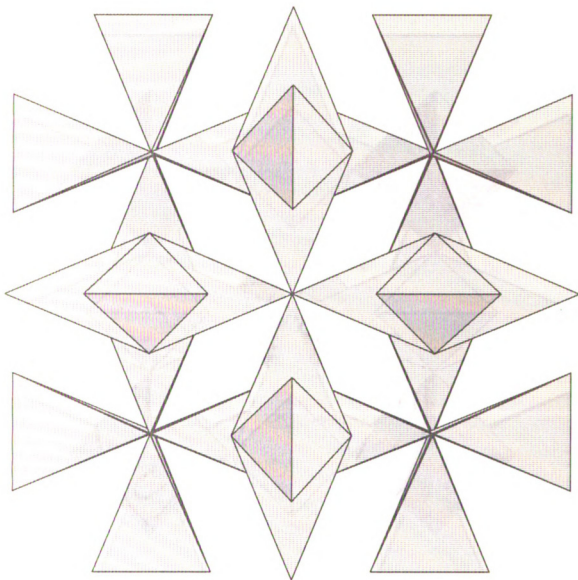


Figure IV.3b. The $[\text{Ga}_{12-x}\text{Ge}_x]$ three-dimensional framework built on $[\text{M}(1)\text{M}(2)_4]$ tetrahedra. The tetrahedra share all four of their edges with each other.

(c)

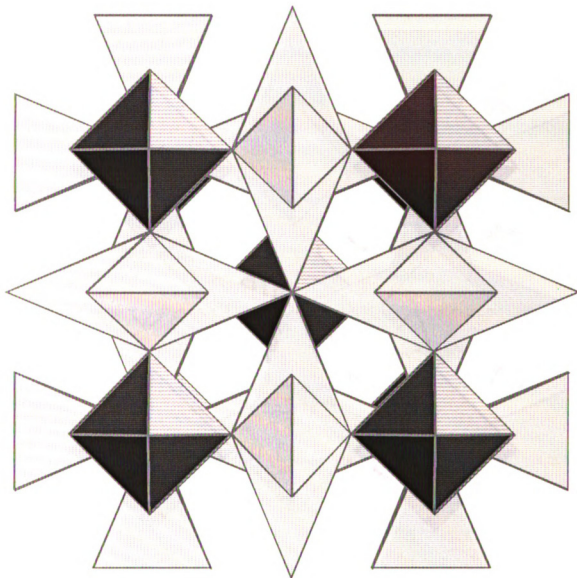


Figure IV.3c. Polyhedral representation of $\text{Fe}[\text{Ga}_{12-x}\text{Ge}_x]$ substructure. $[\text{FeM}(2)_6]$ octahedral share corners with $[\text{Ga}_{12-x}\text{Ge}_x]$ framework, but not connected to each other.

(d)

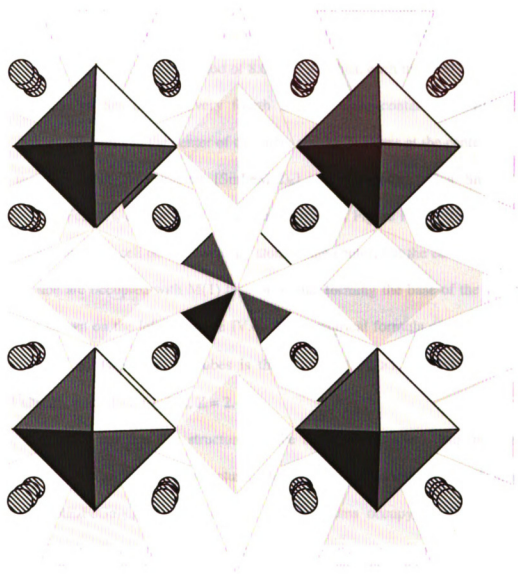
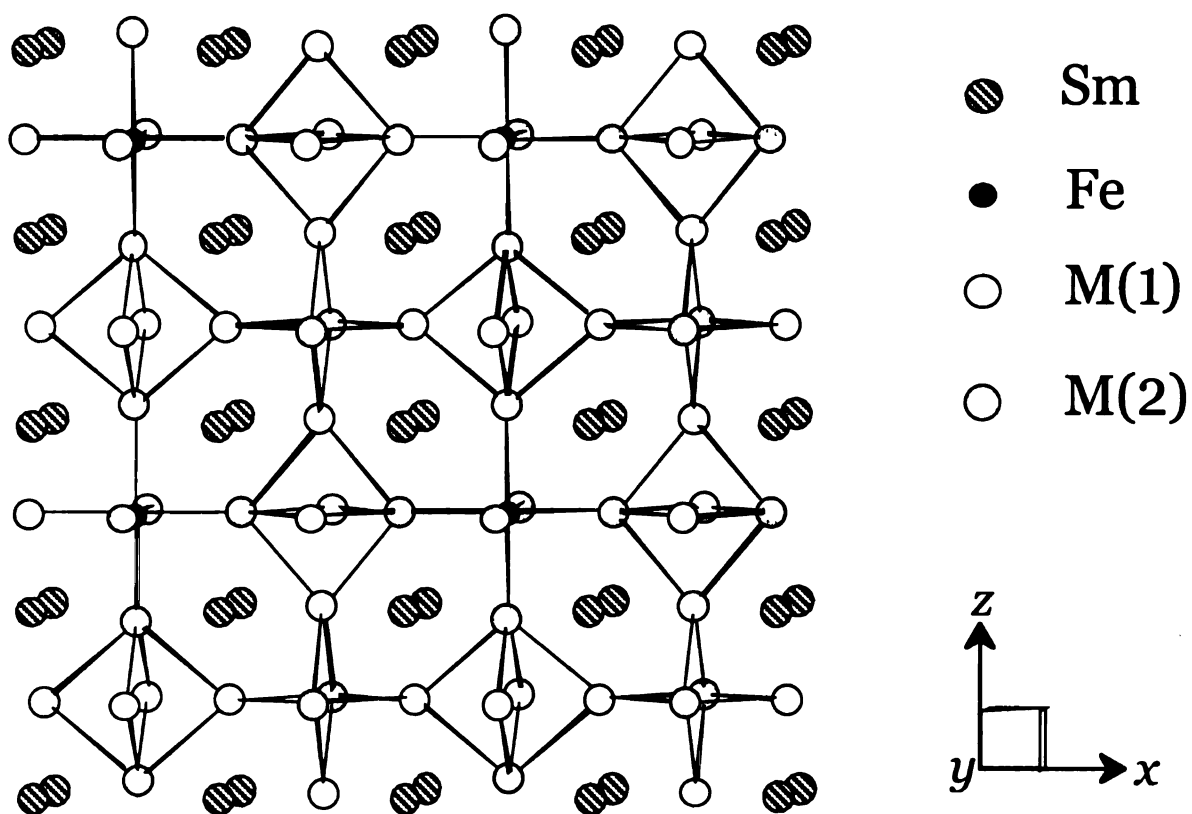


Figure IV.3d. The $\text{Sm}_4\text{FeGa}_{12-x}\text{Ge}_x$ structure as a whole in polyhedral representation. The Sm atoms occupy three-dimensional voids formed by the $\text{Fe}[\text{Ga}_{12-x}\text{Ge}_x]$ network.

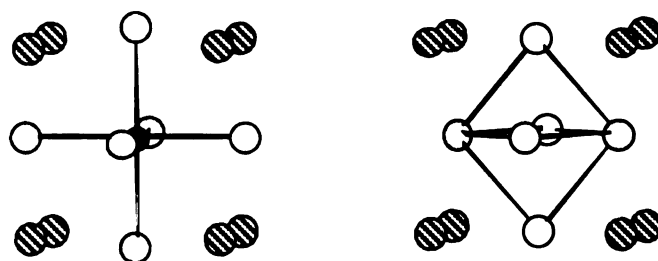
Another way to view this structure is to sub-divide it into two slabs, one of which is shown on Figure IV.4a. The superposition of this slab on an identical one, but shifted by the centering operation to $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ will produce the whole structure. As seen from Figure IV.4a, the Sm atoms form an ideal cubic framework, in which the Sm-Sm distance is 4.328 Å, exactly half the unit cell period of 8.657(4) Å. Thus, each unit cell consists of eight cubes made of Sm atoms. Every fourth of such cube contains the FeM(2)₆ octahedra, having Fe atoms in the center of the cube, and M(2) atoms at the center of the faces of the Sm cube. An isolated [SmFeM(2)₆] unit consisting of a Sm cube encapsulating the FeM(2)₆ octahedra is shown on the right of Figure IV.4b. Three out of four Sm cubes of the unit cell do not have any atom in the center, but the centers of four faces of the cube are occupied with M(1) type of atoms, forming the base of the square bipyramid, as shown on the left of Figure IV.4b. The empirical formula of the unit cell content comprised by two types of cubes is then $[\text{SmFeM}(2)_6] \times 1 + [\text{SmM}(1)_2] \times 3 = \text{Sm}_4\text{FeM}(1)_6\text{M}(2)_6 = \text{Sm}_4\text{FeGa}_{12-x}\text{Ge}_x$, $Z = 2$.

We also point out that this structure can be thought as stuffed (and therefore distorted) form the AuCu₃ [Au₄Cu₁₂] structure, where the Au atoms occupy the RE atom position in the RE₄FeGa_{12-x}Ge_x structure, and the Cu atoms occupy the Ga and Ge positions. The Fe atom can be thought of as an interstitial, sitting in only a fraction of the octahedral pockets.

(a)



(b)



[SmFeM(2)₆]

[SmM(1)₂]

Figure IV.4. (a) The $\text{Sm}_4\text{FeGa}_{12-x}\text{Ge}_x$ structure in ball-and-stick representation; (b)

Isolated $[\text{SmFeM}(2)_6]$ and $[\text{SmM}(1)_2]$ structural units.

The local coordination of the Sm (within 3.5 Å), the Fe and the disordered Ga/Ga atoms M(1) and M(2) (within 3.0 Å) are shown in Figure IV.5. The Sm atom has 12 neighbors in its immediate coordination sphere. These include six M(1) atoms within 3.0606(15) Å in the form of a flat hexagon (with the Sm is the center), and six additional M(2) atoms with three located below and three above the hexagon in a trigonal antiprismatic geometry (the Sm-M(2) distance is 3.0784(15) Å). The Fe atoms are in a perfect octahedral environment of six M(2) atoms at 2.492(2) Å. The next nearest to M(2) atoms are the Sm atoms located at 3.75 Å. The M(1) atom is in the distorted tetrahedral environment of M(2) atoms. The M(2) atoms are bonded to four M(1) atoms in the form of a square pyramid, defined by a base of four M(1) atoms and an apex of a Fe atom. For a list of selected bond distances see Table IV.3.

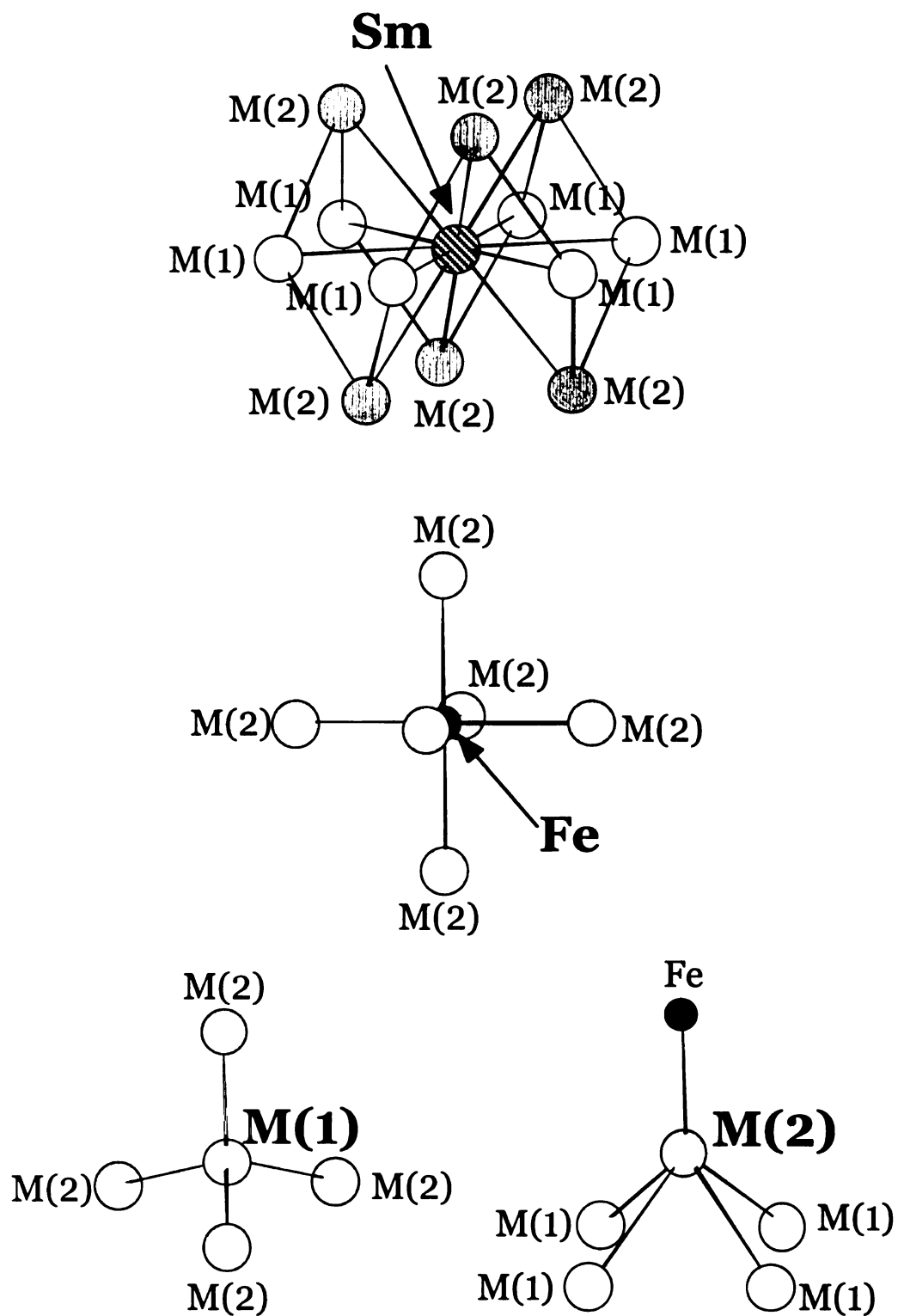


Figure IV.5. Local coordination environment of Sm, Fe, and M(1) = Ga(1)/Ge(1) and M(2) = Ga(2)/Ge(2) atoms.

Seebeck coefficient measurements done on single crystals of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ show extremely low values of thermopower which is a characteristic of metallic conductors. The thermopower is on the order of $\pm 2 \mu\text{V/K}$ and stays low in the entire temperature range of 50 – 400 K.

The magnetic properties of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ were studied, and a plot of the temperature dependent magnetic susceptibility and the inverse magnetic susceptibility, calculated per mole of Tb, is shown in Figure IV.6.

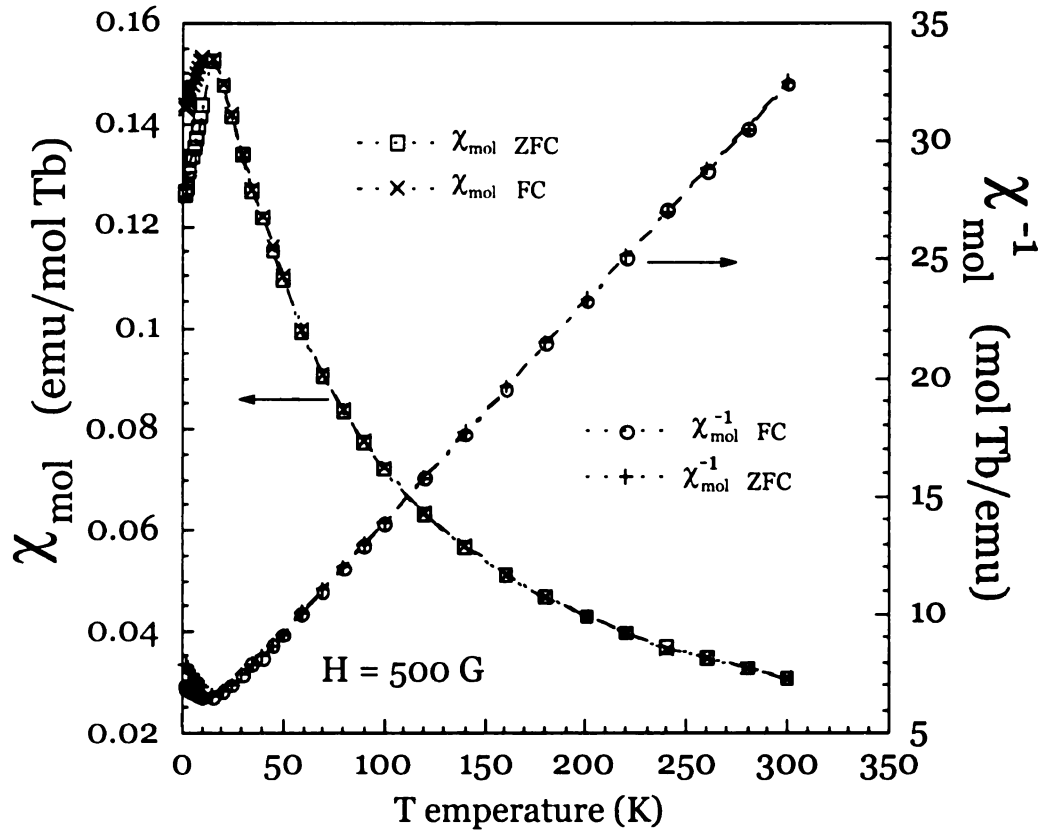


Figure IV.6. Temperature dependence of the molar magnetic susceptibility and the inverse molar magnetic susceptibility of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$.

At low temperatures, a maximum in the magnetic susceptibility, $T_{\max}$, is observed at 12 K, indicative of anti-ferromagnetic ordering. As the temperature drops below the $T_{\max}$ of 12 K, the difference in the zero-field cooled (ZFC) and field cooled (FC) parts of susceptibility becomes substantial, see Figure IV.7. The Néel temperature $T_N = 13.0$ K was obtained from a set of the isofield $\chi_{\text{mol}} - T$ measurements, as a point where the susceptibility measured in different fields diverge, see Figure IV.8.

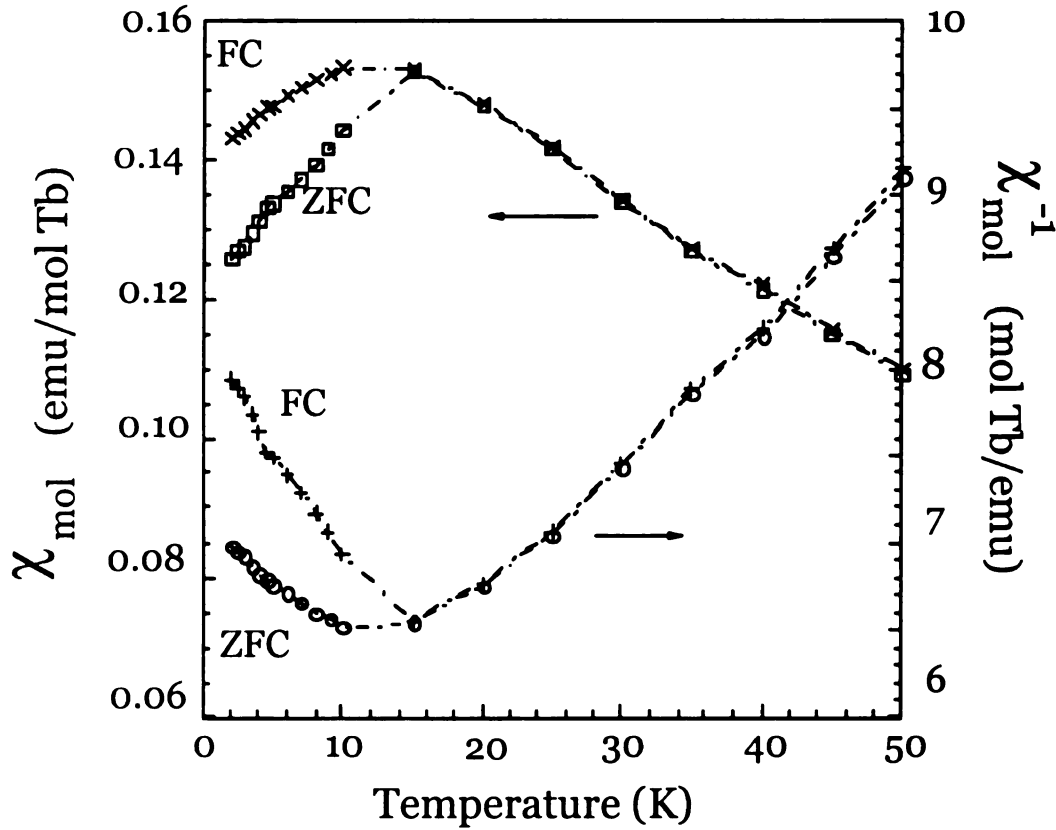


Figure IV.7. Temperature dependence of molar magnetic susceptibility and the inverse molar magnetic susceptibility of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ in the vicinity of the temperature of the maximal magnetic susceptibility.

Above T_N the magnetic susceptibility follows Curie-Weiss behavior, as given in the linear $(\chi_{\text{mol}})^{-1}$ vs T plot, with a Weiss constant of -48 K. The effective magnetic moment μ_{eff} , calculated from the slope of the line and normalized per one Tb atom gave a value of 9.25 BM. This is in a fairly good agreement with the one calculated using the Van Vleck equation³⁹ for a free Tb^{3+} atom, $\mu_{\text{eff}} = 9.72$ BM, showing that the RE atoms in the structure are in a +3 state, whereas the Fe atoms do not contribute to the magnetic susceptibility.

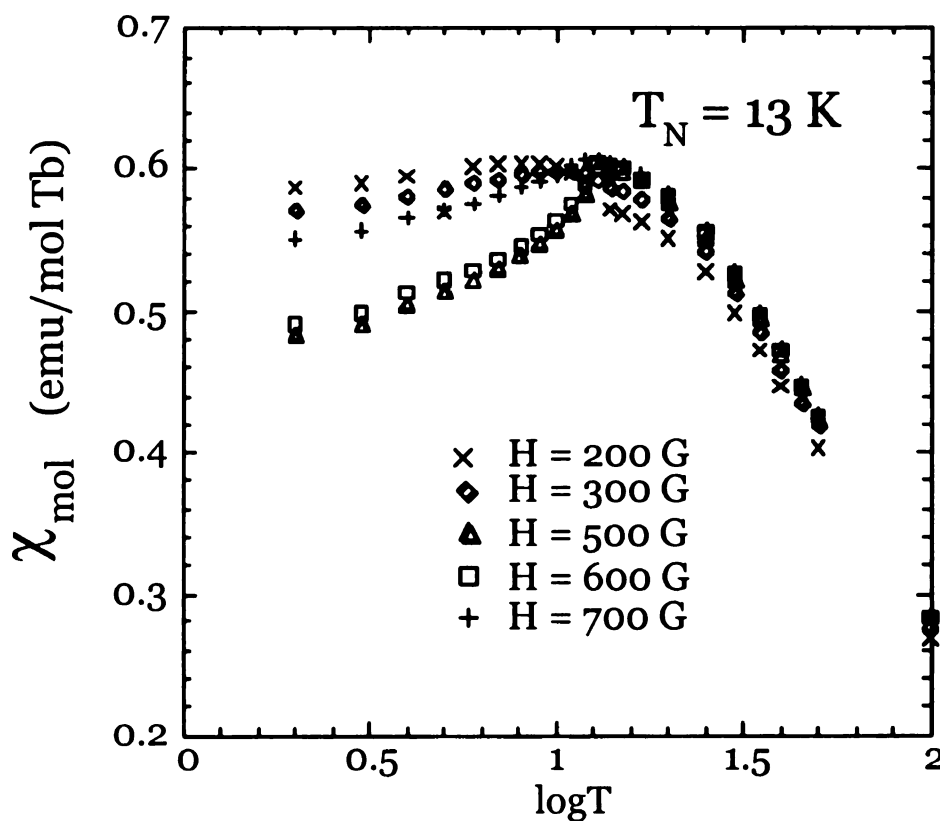


Figure IV.8. Isofield temperature dependence of the magnetic susceptibility of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$. The strength of the applied magnetic field was varied from 200 to 700 Gauss.

The field dependence of the magnetic moment measured at 2 K did not exhibit any hysteresis and stays linear up to the fields of ± 1 Tesla, see Figure IV.9. The full saturation moment of an ion is given by the formula $\mu_{\text{sat}} = g_J J$, where g_J is a Landé factor and J is a total angular momentum of the ion, and equals 9 BM for Tb^{3+} . Clearly, no saturation is observed in the fields of 1 Tesla, as only 3% of full saturation value is developed. Analogous situation was observed for other Tb-containing intermetallics such as Tb_2FeGe_8 ¹⁶, $\text{Tb}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ¹⁴ and $\text{TbAl}_{3-x}\text{Ge}_x$ ⁴⁰ and TbNiGa_3Ge ³⁰.

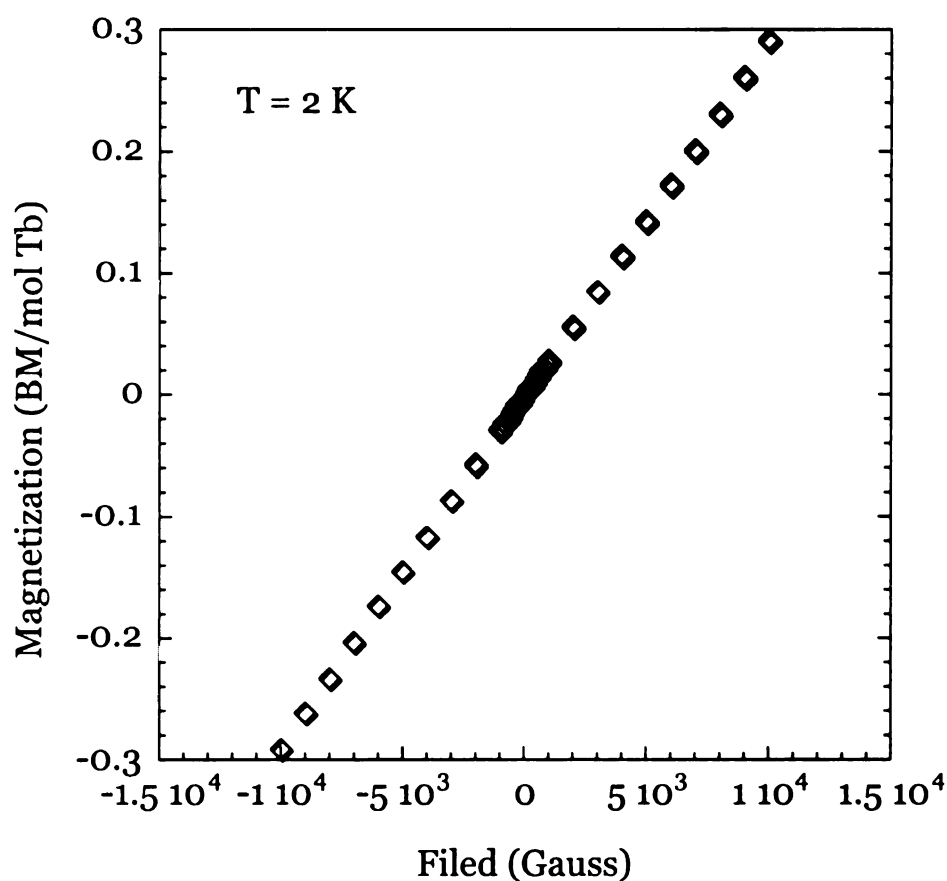


Figure IV.9. Magnetization as a function of field calculated in Bohr magnetons per mole of Tb. The strength of the external magnetic field varied in a ± 10000 Gauss range.

The non-magnetic state of Fe atoms was also confirmed with ^{57}Fe Mössbauer spectroscopy taken at 4.2 K and 18 K. The 18 K spectrum fitted in Lorentzian form is shown in Figure IV.10. Two components we identified with hyperfine parameters: isomer shift, $\hat{c}$ (0.56 mm/s, 0.41 mm/s), quadrupole splitting, ΔE_q (0.17 mm/s, 0.26 mm/s) and relative areas (85%, 15%). The larger-area sub-component with the lower value of quadrupole splitting reflects the fact that Fe is in a perfect octahedral environment of Ga atoms. Because the coordination sphere of Fe atoms also contains some Ge atoms partially occupying the Ga position, the symmetry of this particular local Fe sites is slightly lowered. The disorder between Ga and Ge may be responsible for the appearance of the minor sub-component with a higher value of ΔE_q . No indication is observed in the spectra taken at 18 K and 4.2 K for magnetic splitting due to the ordering of magnetic moments centered on Fe atoms. Similar non-magnetic character of the Fe atoms was observed in the intermetallic compounds Tb_4FeGe_8 ¹⁶ and $\text{RE}_4\text{Fe}_{2+x}\text{Al}_{7-x}\text{Si}_8$ ¹¹.

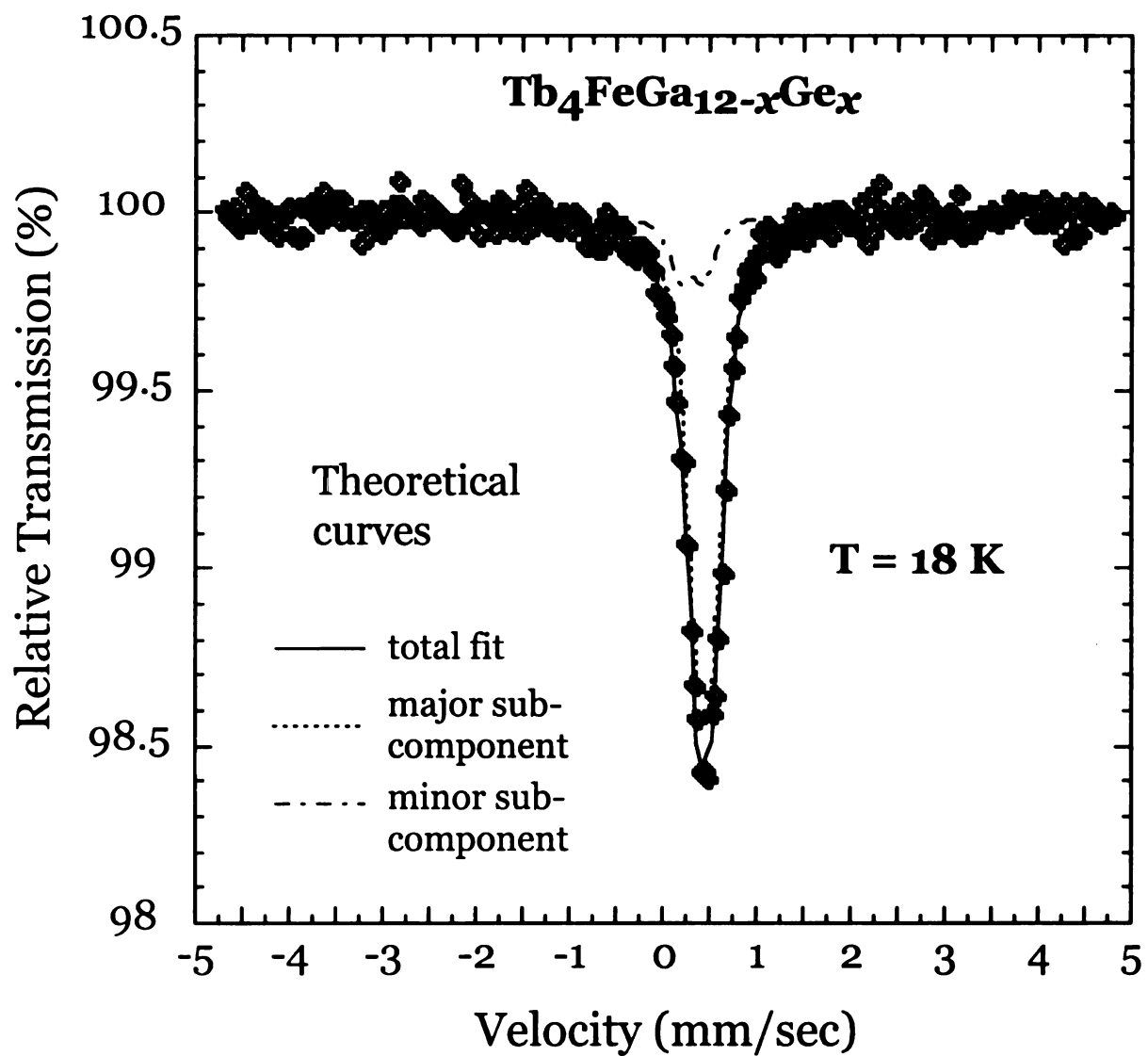


Figure IV.10. ^{57}Fe Mössbauer spectrum of $\text{Tb}_4\text{FeGa}_{12-x}\text{Ge}_x$ at 18 K. The solid line is the least-square fit of the experimental data.

4. Concluding Remarks

Exploratory synthesis in the system RE/M/Ga/Ge (RE = Y, Ce, Sm, Gd, Tb; M = Fe, Co, Ni, Cu) with the liquid Ga as a solvent gave rise to new compounds of the general formula $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ (RE = Sm, Tb). The formation of isostructural phases was not observed for M = Co, Ni, or Cu suggesting that Fe is critical to the stabilization of these cubic phases. The $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ are the first quaternary analogs of the cubic $\text{U}_4\text{Re}_7\text{Si}_6$ structure type and contain a three-dimensional $[\text{Ga}_{12-x}\text{Ge}_x]$ framework, which accommodates Fe in octahedral pockets and RE atoms in the remaining 3D voids. The rare-earth atoms are in a +3 formal oxidation state whereas the Fe atoms are in non-magnetic state. Antiferromagnetic ordering of spins localized on Tb atoms occurs at the Néel temperature of 13 K.

5. References

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EXPLORATORY SYNTHESIS IN THE QUATERNARY SYSTEM INCLUDING
RARE-EARTH, TRANSITION METAL, GALLIUM AND A TETRELIDE USING
LIQUID GALLIUM AS A SOLVENT.

VOLUME II

By

Marina A. Zhuravleva

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

2002

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Chapter V

New quaternary phases $\text{RE}_{0.67}\text{M}_2\text{Ga}_{5+n-x}\text{Tt}_x$ of homologous series $n = 0, 1$ (Tt = Ge or Si; M = Ni, Co; RE = Y, Sm, Gd, Tb, Dy, Ho, Er, Tm and Yb) Synthesized in Liquid Ga. X-Ray, Neutron and Electron Structure Determination and Magnetic Properties.

1. Introduction

We have recently demonstrated in the example of the RE–Ni–Ga–Si system that a molten Ga flux could efficiently serve as a non-reactive solvent to produce ternary rare-earth nickel silicides such as $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ¹ and RENiSi_3 ². In these reactions, the ratio of RE : Ni in the initial composition was typically greater than unity. When we employed liquid Ga flux to perform similar reaction chemistry in the same system but with RE : Ni < 1, we noticed that it was more feasible to incorporate Ga in the final products.

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However, when compared to the related systems with Al (such as RE–Ni–Al–Si), we find that the effectiveness of integration of Al in the reaction product to give rise to quaternary metal aluminides silicides is far greater than that of Ga. The examples of Al-containing phases include $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Si}_{1-x})\text{Al}_4\text{Si}_6$ ³ obtained from Al flux at $\text{Sm} : \text{Ni} > 1$ and $\text{RE}_{1-x}\text{Ni}_2\text{Al}_{5-y}\text{Si}_y$ ⁴, $\text{RE}_{2-x}\text{Ni}_2\text{Al}_4\text{Si}_2(\text{Al}_{1-y}\text{Si}_y)(\text{Al}_{1-z}\text{Si}_z)_2$ ⁴ found at $\text{RE} : \text{Ni} \leq 1$. Since Ga and Al are isoelectronic and have similar sizes, it is hard to explain the above bifurcation in their chemistry, especially when the solubility of Si in Al is similar to that in Ga⁵. For this reason, we decided to study the Ga systems in more detail, and also to compare and contrast the chemistry of Ge analogs vis-à-vis Si. Remarkably, we find that the RE–M–Ga–Ge systems (M = Ni, Co) promptly proceed to give quaternary compounds regardless of the RE : M ratio (again, the RE–Ni–Ga–Si system produced quaternaries only when RE : Ni < 1). Among the RE–M–Ga–Ge systems with different transition metals M, the one with M = Ni was studied in more detail in order to contrast it to the corresponding RE–Ni–Ga–Si. The related system with M = Co is also of interest, however, fewer investigations with it have been performed. Nevertheless, we find similar tendencies to Ni with several isostructural analogs.

Here we report the results of exploratory investigations in the system RE/M/Ga/Tt at RE : M < 1. The synthesis, structure and physical properties of two new types of quaternary compounds of homologous series $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Tt}_x$ (n = 0; 1): $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Si}_x$ (RE = Y, Sm, Gd and Tb); $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (RE = Y, Sm, Gd, Tb, Ho, Er and Tm); $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Si}_x$ (RE = Y, Sm and Gd); $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ (RE = Y, Sm, Gd, Dy and Yb); and $\text{RE}_{0.67}\text{Co}_2\text{Ga}_{6-x}\text{Ge}_x$ (RE = Y and Gd) are presented.

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2. Experimental Section

Synthesis

The reactions between the rare-earth element, nickel and a tetrelide (Tt = Si, Ge), taken in the ratio RE : Ni : Ga : Tt as 1 : 2 : 30 : 2, were performed in liquid Ga as a reactive solvent at 850°C. Elemental rare-earth (Y, Sm, Dy, Gd, Tb, Ho, Er, Tm and Yb), typically of purity 99.9% (CERAC Inc.), nickel powder 99.99% (Aldrich Inc.), Ge powder (99.999%, CERAC Inc.), Si powder (99.999%, CERAC Inc.), and Ga (3 mm shots 99.999%, CERAC Inc.) were taken in the amounts: RE 1.2 mmol, Ni 2.4 mmol, Ga 36 mmol, Ge(Si) 2.4 mmol, and loaded into alumina crucibles under inert (N₂) atmosphere. The crucibles were then placed into fused silica tubes, sealed under the vacuum ($\sim 1 \cdot 10^{-4}$ Torr) and subjected to the following treatment: heated to 1000° at the rate 60°/h, kept at 1000°C for 5h to allow proper homogenization, then cooled down to 850°C in 2h and kept isothermally at 850°C for 3 days and, finally, slowly cooled down to 250°C at the rate 18°/h. The excess of Ga was next filtered through a specially designed quartz filter with coarse frit by centrifuging at 250°C (30 seconds at 3000 rpm). The residual Ga was then removed using ~5 M solution of iodine in dimethylformamide (DMF) over 12 hours at room temperature. Resulting crystalline product was subsequently washed in water, DMF and dried with acetone and ether. A typical product of the reaction batch is shown in Figure V.1 (the Y/Ni/Ga/Ge system is depicted). The crystalline material is very homogeneous and mostly consists of large, rod-like crystals of quaternary phase(s) $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Tt}_x$ ($n = 0; 1$).

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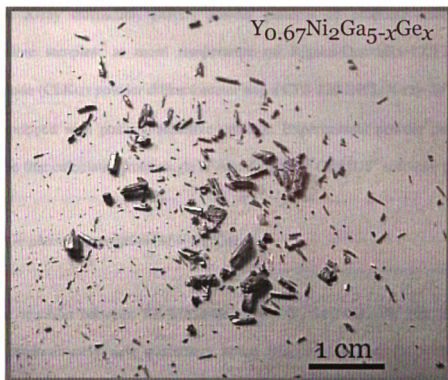


Figure V.1. A typical product of the RE-M-Ga-Ge reaction (RE : M <1) conducted in liquid Ga at 850°C; RE = Y, Sm, Gd, Tb, Ho, Er and Tm.

Elemental Analysis and X-ray Powder Diffraction

The chemical composition of the products was determined by Energy Dispersive Spectroscopy (EDS) performed on scanning electron microscope (SEM) JEOL JSM-35C equipped with Noran Inc. EDS detector. The routine analysis was conducted at accelerating voltage 20 kV and collection time 30 seconds. Several samples from each batch were analyzed, and the results averaged.

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The X-ray diffraction (XRD) powder patterns of products were taken on polycrystalline samples* at room temperature on Rigaku-Denki/Rw400F2 (rotaflex) rotating-anode (CuK α) powder diffractometer and a CPS 120 INEL X-ray diffractometer (CuK α) equipped with position-sensitive detector. Experimental powder patterns were compared to that calculated from single crystal data using CERIUS² software package⁶.

RE/M/Ga/Ge phase composition (M = Ni, Co)

The reaction between RE/Ni/Ga/Ge (RE = Y, Sm, Gd, Tb, Ho, Er and Tm) produced predominately new quaternary phase RE_{0.67}Ni₂Ga_{5-x}Ge_x (**1**) with elemental composition “RE_{0.67}Ni₂Ga_{3.5}Ge_{0.8}”, as determined by EDS. On average, more than 90% of the Bragg peaks of XRD pattern were attributed to **1**, and less than 10% were due to recrystallized but unreacted Ge. A typical powder XRD pattern of the reaction product (Sm/Ni/Ga/Ge system was used) is shown in Figure V.2.

Another more Ga-rich phase RE_{0.67}M₂Ga_{6-x}Ge_x (**2**) was found in the systems Gd/Ni/Ga/Ge, Gd/Co/Ga/Ge, Y/Ni/Ga/Ge, Y/Co/Ga/Ge, Dy/Ni/Ga/Ge and Yb/Ni/Ga/Ge, although high yield (> 90%) was observed only for the three latter cases. The average EDS composition of Ni-containing analogs of **2** is “RE_{0.5}Ni_{2.4}Ga_{5.5}Ge_{0.6}”. Slightly lowered RE amount and increased Ni amount are caused by partial overlap of the Ni K α (7.477 keV) and Yb L α (7.414 keV) lines in the X-ray fluorescence spectra. The average elemental composition of Co analogs of **2** is given by the formula “RE_{0.7}Co₂Ga_{4.2}Ge_{1.5}”. For some unknown reason the Co-analogs show as much as doubled amount of Ge per

* Crystals were hand-ground with mortar and pestle to obtain powdered material.

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formula compared to the Ni-analogs. However, the overall composition is still in fair agreement with the single crystal X-ray and neutron data.

For some RE analogs of **1** and **2** the formation of an additional binary Ni-Ga side product was detected with EDS analysis. This side phase⁷ forms a film on the surface of the crystals of quaternary phases. The presence of the Ni-Ga binary phases was not detected with powder diffraction due to the minor quantities or lack of crystallinity. To reduce the formation of undesirable Ni-Ga side-phase, as it certainly will interfere with the results of magnetic measurements, we used higher than stoichiometric amounts of Ge in order to shift the reaction equilibrium toward the formation of quaternary phases.

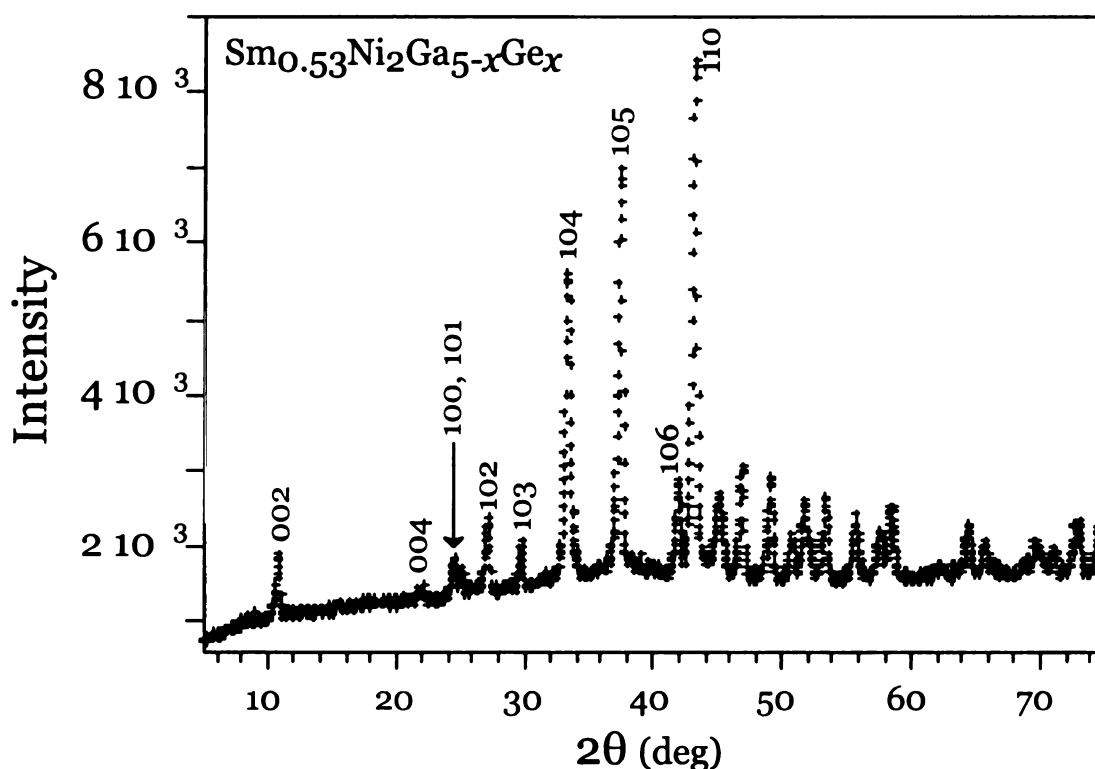


Figure V.2. X-ray powder pattern of a typical product of RE-Ni-Ga-Ge reaction (RE : M < 1); (RE = Y, Sm, Gd, Tb, Ho, Er and Tm).

RE/Ni/Ga/Si phase composition

The products of the reaction conducted under similar conditions in the RE/Ni/Ga/Si system are very different from RE/Ni/Ga/Ge system. The XRD patterns show a multi-phase composition which varies from rare-earth to rare-earth and includes phases **1** and **2**, the ternary phases RENiSi_3 ², $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ¹, and NiGaSi ⁸, the binary Ni_3Ga_2 ⁹, and Si. The yield of the quaternary phases was studied as a function of the duration of isothermal step, cooling rate, and the flux amount. The maximal yield of 50/50% for the quaternary phases **1** and **2** was observed for Sm/Ni/Ga/Si under the synthesis conditions indicated in the experimental section.

Single Crystal X-ray Diffraction

Single crystals of the four isotopic compounds of **1** (RE = Y, Sm, Ho with Tt = Ge, and RE = Tb with Tt = Si) and three analogs of **2** (RE = Dy, Gd with Tt = Ge and RE = Sm with Tt = Si) were mounted on glass fibers. The crystallographic data corresponding to a hemi- or full sphere of reciprocal space were collected on a Siemens Platform SMART CCD diffractometer using crystal monochromator and Mo K α ($\lambda = 0.71073 \text{ \AA}$) radiation. The SMART¹⁰ software was used for data acquisition and cell reduction, and the integration was done with SAINT¹¹ software package. The face-indexing routine was used for analytical absorption corrections. The empirical absorption corrections were subsequently applied with SADABS¹² crystallographic program. The structure solution and refinement were done by direct methods with the SHELXTL¹³

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X-ray Refinement of 1

The $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Tt}_x$ (**1**) crystallizes in a primitive cell in high-symmetry hexagonal space group $P6_3/mmc$. The structure type of **1** is related to that of $\text{RE}_2\text{Pt}_4\text{Ga}_{8+y}$ ¹⁵, incidentally also grown from Ga flux, although the latter has been refined in a different space group $P\bar{3}1c$. There are a total of five atomic sites in the structure. The two $4f$ ($1/3$ $2/3$ z) positions were unambiguously assigned to Ni and Ga, and the $2c$ ($1/3$ $2/3$ $1/4$) site to a RE atom. The $6h$ (x $2x$ $1/4$) M(1) site can be refined either as Ga or Ge. Likewise, the $4e$ (0 0 z) position could be occupied either with Ga, or have mixed occupancy M(2) with Ga and a tetrelide (Tt). The interchange of Ga and Tt on the $6h$ M(1) position, or introduction the $4e$ M(2) disordered position instead of full occupancy with Ga, brought about only subtle changes in the R-values. However, the best convergence factor was obtained when M(1) is occupied with Ga and M(2) has a mixed-occupancy with Ga and Tt (65 to 88% of Ga and 35 to 12% of Tt respectively, depending on the type of RE metal).

Another type of disorder was observed between the RE and M(1)-type atoms. The symmetry equivalents of the RE atoms at $2c$ ($1/3$ $2/3$ $1/4$) and the M(1) at $6h$ (x $2x$ $1/4$) form a monoatomic plane at $z = \pm 1/4$ with a triangular mesh pattern. This disorder will be discussed later in detail. The disorder occurs in a way that every RE atom has three neighboring M(1)₃ triangles at a very close distance of ~ 1.4 Å, while the M(1) atoms

within the triangles are located at $\sim 1.6 \text{ \AA}$ to each other. Furthermore, the occupancies of the RE and M(1) atoms were lower than the full amount allowed by that specific crystallographic position. For example, the occupancy of 33% was obtained for the M(1) site, while the RE site is 67% occupied for RE = Tb, Ho, and only 53% and 59% occupied for RE = Sm and Y, respectively. More careful examination of the disorder in the RE-M(1) plane will be discussed in the section devoted to the crystal structure of 1. Details of the data collection and structure refinement of all four analogs are listed in the Table V.1 and Table V.2. The atomic coordinates, occupancies and isotropic displacement parameters for $\text{Ho}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ and $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Si}_x$ (as the representatives of Ge and Si families, respectively) are given in Tables V.3a and V.3b. The interatomic distances up to $3.5 \text{ \AA}$ are presented in the Tables V.4a and V.4b for the $\text{Ho}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ and $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Si}_x$ analogs, respectively. Selected bond angles are listed in Tables V.5a and V.5b, and anisotropic displacement parameters are contained in the Tables V.6a and V.6b.

Table V.1. Crystal X-ray data and structure refinement details for **1**: $\text{Y}_{0.59}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ and $\text{Sm}_{0.53}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$.

Empirical formula	$\text{Y}_{0.59}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1)	$\text{Sm}_{0.53}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1)
Parameter x	0.60	0.44
Formula weight	520.20	546.97
Temperature	293(2) K	293(2) K
Wavelength (Å)	0.71073	0.71073
Space group	$P6_3/mmc$	$P6_3/mmc$
Lattice Constants (Å)	$a = 4.1344(11)$ $c = 15.887(6)$	$a = 4.1748(7)$ $c = 16.007(4)$
Volume (Å ³)	235.18(12)	241.61(8)
Z	2	2
Calculated density (g/cm ³)	7.346	7.518
Absorption coefficient (mm ⁻¹)	43.409	41.484
F(000)	469	489
Crystal size, (mm ³)	0.12 x 0.06 x 0.02	0.14 x 0.08 x 0.04
θ range (°)	2.56 to 23.14.	5.09 to 23.20
Limiting indices	$-4 \leq h \leq 4$ $-4 \leq k \leq 4$ $-17 \leq l \leq 17$	$-4 \leq h \leq 4$ $-4 \leq k \leq 4$ $-17 \leq l \leq 17$
Reflections collected	1263	1379
Unique reflections	89 [$R_{\text{int}} = 0.0678$]	91 [$R_{\text{int}} = 0.0535$]
Completeness to θ	100.0 %	98.9%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Variables	19	19
Goodness-of-fit on F^2	1.133	1.164
Final R indices [$I > 2\sigma(I)$] [*]	$R_1=0.0314$, $wR_2=0.0739$	$R_1=0.0311$, $wR_2=0.0721$
R indices (all data)	$R_1=0.0314$, $wR_2=0.0739$	$R_1=0.0320$, $wR_2=0.0724$
Extinction coefficient	0.100(11)	0.014(2)
Highest residual peak (e/Å ³)	2.035 and -1.008	3.028 and -1.282

^{*} $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table V.2. Crystal X-ray data and structure refinement details for **1**: Ho_{0.67}Ni₂Ga_{5-x}Ge_x and Tb_{0.67}Ni₂Ga_{5-x}Si_x.

Empirical formula	Ho _{0.67} Ni ₂ Ga _{5-x} Ge _x (1)	Tb _{0.67} Ni ₂ Ga _{5-x} Si _x (1)
Parameter <i>x</i>	0.60	0.24
Formula weight	577.42	561.71
Temperature	293(2) K	293(2) K
Wavelength (Å)	0.71073	0.71073
Space group	<i>P6₃/mmc</i>	<i>P6₃/mmc</i>
Lattice Constants (Å)	<i>a</i> = 4.1491(4) <i>c</i> = 15.877(2)	<i>a</i> = 4.1415(11) <i>c</i> = 15.843(6)
Volume (Å ³)	236.71(5)	235.33(12)
Z	2	2
Calculated density (g/cm ³)	8.101	7.927
Absorption coefficient (mm ⁻¹)	46.957	44.364
F(000)	512	500
Crystal size (mm ³)	0.1 x 0.08 x 0.06	0.10 x 0.10x 0.04
θ range (°)	6.87 to 32.55	2.57 to 27.09
Limiting indices	-4 ≤ <i>h</i> ≤ 6 -6 ≤ <i>k</i> ≤ 3 -22 ≤ <i>l</i> ≤ 23	-3 ≤ <i>h</i> ≤ 5 -5 ≤ <i>k</i> ≤ 5 -19 ≤ <i>l</i> ≤ 18
Reflections collected	1641	1184
Unique reflections	199 [R _{int} = 0.0524]	129 [R _{int} = 0.0321]
Completeness to θ	95.7 %	97.7%
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Variables	19	19
Goodness-of-fit on F ²	1.317	1.374
Final R indices [I>2σ(I)] [*]	R ₁ =0.0332, wR ₂ =0.0846	R ₁ =0.0292, wR ₂ =0.0838
R indices (all data)	R ₁ =0.0338, wR ₂ =0.0849	R ₁ =0.0324, wR ₂ =0.0849
Extinction coefficient	0.057(6)	0.0096(18)
Highest residual peak (e/Å ³)	3.780 and -2.774	1.053 and -1.307

^{*} $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table V.3. Atomic coordinates, equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and the occupancies for (a) $\text{Ho}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ and (b) $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Si}_x$.

(a)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*	Occupancy
Ho	2 <i>c</i>	1/3	2/3	1/4	7(1)	0.67
M(1)	6 <i>h</i>	0.5393(4)	0.0786(8)	1/4	10(1)	0.33
M(2)	4 <i>e</i>	0	0	0.1342(1)	9(1)	0.65(15) Ga 0.35(15) Ge
Ga	4 <i>f</i>	1/3	2/3	0.0459(1)	7(1)	1.0
Ni	4 <i>f</i>	1/3	2/3	0.6091(1)	7(1)	1.0

*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

(b)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)	Occupancy
Tb	2 <i>c</i>	1/3	2/3	1/4	6(1)	0.67
M(1)	6 <i>h</i>	0.5408(10)	0.0820(20)	1/4	21(2)	0.33 (Ga)
M(2)	4 <i>e</i>	0	0	0.1333(2)	9(1)	0.88(2) Ga 0.12(3) Si
Ga	4 <i>f</i>	1/3	2/3	0.0461(2)	6(1)	1.0
Ni	4 <i>f</i>	1/3	2/3	0.6098(2)	7(1)	1.0

*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table V.4. Selected bond lengths [Å] for 1: (a) Ho_{0.67}Ni₂Ga_{5-x}Ge_x and (b) Tb_{0.67}Ni₂Ga_{5-x}Si_x.

(a)

Bond	Distance	Mult.	Bond	Distance	Mult.
Ho-M(1)	1.480(3)	× 3	M(1)-M(2)	2.7859(9)	× 4
Ho-M(1)	2.961(2)	× 6	M(2)-Ni	2.4286(4)	× 3
Ho-M(2)	3.0193(8)	× 6	M(2)-Ga	2.7763(9)	× 3
M(1)-M(1)	1.585(5)	× 2	Ga-Ga	2.8033(13)	× 3
M(1)-M(1)	2.564(5)	× 2	Ni-Ga	2.460(2)	× 1
M(1)-Ni	2.4174(17)	× 2	Ni-Ga	2.5973(7)	× 3

(b)

Bond	Distance	Mult.	Bond	Distance	Mult.
Tb-M(1)	1.488(7)	× 3	M(2)-M(1)	2.791(2)	× 4
Tb-M(1)	2.948(5)	× 6	M(2)-Ni	2.4198(9)	× 3
Tb-M(2)	3.0224(17)	× 6	M(2)-Ga	2.7612(19)	× 3
M(1)-M(1)	1.564(13)	× 2	Ga-Ga	2.803(3)	× 3
M(1)-M(1)	2.577(13)	× 2	Ni-Ga	2.471(4)	× 1
M(1)-Ni	2.397(4)	× 2	Ni-Ga	2.5953(15)	× 3

Table V.5. Selected bond angles [°] for **1**: (a) $\text{Ho}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ and (b) $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Si}_x$.

(a)

Bond	Angle	Bond	Angle	Bond	Angle
M(1)-Ho-M(1)	120.0	Ni-M(1)-M(2)	55.10(2)	Ni-Ga-M(2)	53.611(16)
M(1)-Ho-M(1)	120.001(1)	Ni-M(1)-M(2)	130.46(4)	Ni-Ga-M(2)	126.90(6)
M(1)-Ho-M(1)	15.53(4)	M(1)-M(1)-M(2)	62.60(5)	Ni-Ga-M(2)	53.611(16)
M(1)-Ho-M(1)	135.53(4)	M(1)-M(1)-M(2)	106.53(5)	M(2)-Ga-M(2)	96.70(4)
M(1)-Ho-M(1)	104.47(4)	M(2)-M(1)-M(2)	96.26(4)	Ni-Ga-Ga	58.71(4)
M(1)-Ho-M(1)	88.95(8)	Ni-M(2)-Ni	117.35(2)	Ni-Ga-Ga	54.03(4)
M(1)-Ho-M(1)	151.05(8)	Ni-M(2)-Ga	59.42(2)	Ni-Ga-Ga	126.499(12)
M(1)-Ho-M(1)	31.05(8)	Ni-M(2)-Ga	140.17(7)	M(2)-Ga-Ga	83.91(2)
M(1)-Ho-M(2)	142.51(2)	Ga-M(2)-Ga	96.70(4)	M(2)-Ga-Ga	179.07(7)
M(1)-Ho-M(2)	66.629(7)	Ni-M(2)-M(1)	102.04(6)	Ga-Ga-Ga	95.47(6)
M(1)-Ho-M(2)	139.86(2)	Ni-M(2)-M(1)	54.72(5)	M(1)-Ni-M(1)	38.28(11)
M(1)-Ho-M(2)	78.56(3)	Ni-M(2)-M(1)	134.00(6)	M(1)-Ni-M(2)	70.18(5)
M(1)-Ho-M(2)	55.52(3)	Ga-M(2)-M(1)	159.01(6)	M(1)-Ni-M(2)	102.78(8)
M(1)-M(1)-M(1)	60.0	Ga-M(2)-M(1)	79.67(3)	M(2)-Ni-M(2)	117.35(2)
M(1)-M(1)-Ni	70.86(5)	M(1)-M(2)-M(1)	54.79(11)	M(1)-Ni-Ga	157.75(6)
Ni-M(1)-Ni	135.50(13)	M(1)-M(2)-M(1)	33.06(11)	M(2)-Ni-Ga	99.47(4)
M(1)-M(1)-M(1)	120.0	M(1)-M(2)-M(1)	81.21(3)	M(1)-Ni-Ga	122.16(4)
M(1)-M(1)-M(1)	179.997(4)	M(1)-M(2)-M(1)	96.26(4)	M(1)-Ni-Ga	90.49(7)
Ni-M(1)-M(1)	109.14(5)	Ni-Ga-Ni	112.74(4)	M(2)-Ni-Ga	66.967(18)
M(1)-M(1)-M(2)	73.47(5)	Ni-Ga-Ni	106.02(4)	Ga-Ni-Ga	67.26(4)
M(1)-M(1)-M(2)	117.40(5)	Ni-Ga-M(2)	120.36(3)	Ga-Ni-Ga	106.02(4)

Table V.5. (continued)

(b)

Bond	Angle	Bond	Angle	Bond	Angle
M(1)-Tb-M(1)	120.001(2)	M(1)-M(1)-M(2)	117.50(14)	Ni-Ga-Ni	112.88(7)
M(1)-Tb-M(1)	119.999(1)	Ni-M(1)-M(2)	54.97(4)	Ni-Ga-Ni	105.86(8)
M(1)-Tb-M(1)	104.62(10)	Ni-M(1)-M(2)	130.77(10)	Ni-Ga-M(2)	120.01(7)
M(1)-Tb-M(1)	15.38(10)	M(1)-M(1)-M(2)	62.51(14)	Ni-Ga-M(2)	127.11(12)
M(1)-Tb-M(1)	135.38(10)	M(1)-M(1)-M(2)	106.27(14)	Ni-Ga-M(2)	53.60(3)
M(1)-Tb-M(1)	89.2(2)	M(2)-M(1)-M(2)	95.78(9)	M(2)-Ga-M(2)	97.17(9)
M(1)-Tb-M(1)	30.8(2)	Ni-M(2)-Ni	117.68(4)	Ni-Ga-Ga	58.55(8)
M(1)-Tb-M(1)	150.8(2)	Ni-M(2)-Ga	59.69(4)	Ni-Ga-Ga	54.33(7)
M(1)-Tb-M(2)	142.29(4)	Ni-M(2)-Ga	141.15(13)	Ni-Ga-Ga	126.57(2)
M(1)-Tb-M(2)	66.701(14)	Ga-M(2)-Ga	97.17(9)	M(2)-Ga-Ga	178.56(13)
M(1)-Tb-M(2)	139.71(5)	Ni-M(2)-M(1)	101.85(16)	M(2)-Ga-Ga	83.77(4)
M(1)-Tb-M(2)	78.48(8)	Ni-M(2)-M(1)	54.21(10)	Ga-Ga-Ga	95.26(11)
M(1)-Tb-M(2)	55.73(7)	Ni-M(2)-M(1)	133.22(14)	M(1)-Ni-M(1)	38.1(3)
M(1)-M(1)-M(1)	60.000(1)	Ga-M(2)-M(1)	158.90(15)	M(1)-Ni-M(2)	103.3(2)
M(1)-M(1)-Ni	70.96(14)	Ga-M(2)-M(1)	103.91(14)	M(1)-Ni-M(2)	70.82(10)
Ni-M(1)-Ni	135.7(3)	Ga-M(2)-M(1)	79.64(8)	M(1)-Ni-Ga	157.87(17)
M(1)-M(1)-M(1)	120.004(1)	M(1)-M(2)-M(1)	80.91(7)	M(1)-Ni-Ga	90.75(17)
M(1)-M(1)-M(1)	179.995(1)	M(1)-M(2)-M(1)	32.5(3)	M(1)-Ni-Ga	122.25(9)
Ni-M(1)-M(1)	109.04(14)	Ni-M(2)-M(1)	133.22(14)	M(2)-Ni-Ga	165.96(14)
M(1)-M(1)-M(1)	120.0	M(1)-M(2)-M(1)	55.0(3)	M(2)-Ni-Ga	66.71(4)
M(1)-M(1)-M(2)	73.73(14)	M(1)-M(2)-M(1)	80.91(7)	Ga-Ni-Ga	67.12(7)

Table V.6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1: (a) $\text{Ho}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ and (b) $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Si}_x$.

(a)

Atomic Position	U11	U22	U33	U23	U13	U12
Ho	8(1)	8(1)	6(1)	0	0	4(1)
M(1)	14(1)	13(1)	4(1)	0	0	6(1)
M(2)	8(1)	8(1)	10(1)	0	0	4(1)
Ga	9(1)	9(1)	5(1)	0	0	4(1)
Ni	7(1)	7(1)	6(1)	0	0	4(1)

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U11 + \dots + 2hka^*b^*U12]$.

(b)

Atomic Position	U11	U22	U33	U23	U13	U12
Tb	6(1)	6(1)	6(1)	0	0	3(1)
M(1)	21(2)	24(4)	17(3)	0	0	12(2)
M(2)	8(1)	8(1)	10(2)	0	0	4(1)
Ga	6(1)	6(1)	6(1)	0	0	3(1)
Ni	7(1)	7(1)	7(1)	0	0	4(1)

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U11 + \dots + 2hka^*b^*U12]$.

Because of the disorder in the structure and the very similar X-ray scattering power of Ga and Ge, the location of Ge atoms in the unit cell based solely on X-ray data was difficult. We employed careful semi-quantitative elemental EDS analysis with extensive averaging over several crystals to obtain accurate composition for **1**. The analytical results showed that the average composition of **1** is “RE_{0.67}Ni₂Ga_{3.5}Tt_{0.8}”. If we suppose that the M(1) site belongs to a Ge atom and M(2) to a Ga atom, the empirical formula would be RE_{0.67}Ni₂Ga₄Tt, which is close to the EDS experimental values. On the contrary, if M(1) = Ga, and M(2) is mixed-occupied with Ga and Tt (65% and 35%), the formula becomes RE_{0.67}Ni₂Ga_{4.3}Tt_{0.7}, which is again comparable to the composition given by EDS. Thus, an independent method capable of distinguishing between Ga and Ge such as neutron scattering had to be employed.

X-ray Refinement of 2

The second compound RE_{0.67}Ni₂Ga_{6-x}Tt_x was refined in a structure that can be viewed as a sub-cell of the ErNi₃Al₉²⁴ structure type with a volume nine times smaller (cell parameters $a'/\sqrt{3}$, $c'/3$). The reason for choosing a sub-cell for structure description is disorder, similar to that observed between RE atoms and M(1) atoms in **1**.

The sub-cell structure solution of **2** was done in the hexagonal space group $P\bar{6}m2$ for the Gd_{0.67}Ni₂Ga_{6-x}Ge_x, Yb_{0.67}Ni₂Ga_{6-x}Ge_x and Sm_{0.67}Ni₂Ga_{6-x}Si_x analogs. A total of six atomic sites were identified, three of which $2i$ ($2/3$ $1/3$ z), $2g$ (0 0 z), and $1d$ ($1/2$ $2/3$ $1/2$) were ascribed to Ga; the other two $2h$ ($1/3$ $2/3$ z) and $1a$ (0 0 0) were assigned to Ni and RE, respectively. The remaining position $3j$ (x $-x$ 0) could be occupied with Ga or Ge, however, in contrast to **1** $3j$ is the only site where Ge can be located without a sensible

increase in R-values. The structure of **2** has a disorder between RE atoms and M(1)-type atoms identical to that observed in **1**, namely a triangular mesh in the RE–M(1) plane. As it is for **1**, the distances between M(1)–M(1) and RE–M(1) are too short to allow full occupancy in these sites, and therefore the occupancy parameters of these disordered atoms were freely refined. As a result, a decrease from full occupancy of the RE and M(1) positions to 67% and 33% respectively was observed. If the M(1) site was indeed occupied with Ge, the formula of **2** would be $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_5\text{Ge}$, which is close to the one obtained from elemental analysis “ $\text{RE}_{0.6}\text{Ni}_{2.3}\text{Ga}_{5.1}\text{Ge}_{0.6}$ ”. Yet, X-ray diffraction does not provide information to discern between Ga and Ge at M(1).

It is interesting that the Dy analog of **2** $\text{Dy}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ shows a higher-order sub-structure with the cell volume $2/3$ of that of a “super-cell” of ErNi_3Al_9 (parameters a' , $2/3c$) or six times larger than that of other analogs of **2**. Although the in-plane disorder between RE and M(1) is still observed, the extent of it is much less. Further details on the structural peculiarities of the sub-cells and a super-cell, as well as their relationship will be discussed later in the section devoted to the superstructure of **2**. The information relevant to the details of the data collection and structure refinement for all three analogs are given in Tables V.7 and V.8. The atomic coordinates, occupancies and isotropic displacement parameters for two analogs (representatives of Ge and Si families) $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ and $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Si}_x$ are given in Tables V.9a and V.9b, respectively. The bond distances up to 3.5 Å for the latter two analogs are presented in Tables V.10a and V.10b; and selected bond angles are listed in Tables V.11a and V.11b, respectively. The list of anisotropic thermal displacement parameters could be found in Tables V.12a and V.12b.

Table V.7. Crystal data and structure refinement details for **2**: Sm_{0.67}Ni₂Ga_{6-x}Si_x and Gd_{0.67}Ni₂Ga_{6-x}Ge_x.

Empirical formula	Sm _{0.67} Ni ₂ Ga _{6-x} Si _x (2)	Gd _{0.58} Ni ₂ Ga _{6-x} Ge _x (2)
Parameter <i>x</i>	0.06	0.67
Formula weight	633.98	546.97
Temperature	298(2) K	298(2) K
Wavelength (Å)	0.71073	0.71073
Space group	$P\bar{6}m2$	$P\bar{6}m2$
Lattice Constants (Å)	$a = 4.1976(8)$ $c = 9.159(3)$	$a = 4.1856(10)$ $c = 9.167(3)$
Volume (Å ³)	139.76(5)	139.08(7)
Z	1	1
Calculated density (g/cm ³)	7.533	7.677
Absorption coefficient (mm ⁻¹)	41.508	43.272
F(000)	283	286
Crystal size (mm ³)	0.1 × 0.06 × 0.01	0.14 × 0.1 × 0.06
θ range (°)	4.45 to 30.35	4.45 to 30.72
Limiting indices	$-5 \leq h \leq 5$ $-5 \leq k \leq 5$ $-12 \leq l \leq 12$	$-5 \leq h \leq 6$ $-5 \leq k \leq 5$ $-12 \leq l \leq 12$
Reflections collected	1618 [<i>R</i> _{int} = 0.0604]	1631 [<i>R</i> _{int} = 0.0574]
Unique reflections	204	207
Completeness to θ	97.6 %	97.6%
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Variables/Restraints	22	21
Goodness-of-fit on <i>F</i> ²	1.100	1.095
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] [*]	<i>R</i> ₁ = 0.0233, <i>wR</i> ₂ = 0.0497	<i>R</i> ₁ = 0.0268, <i>wR</i> ₂ = 0.0647
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0234, <i>wR</i> ₂ = 0.0497	<i>R</i> ₁ = 0.0274, <i>wR</i> ₂ = 0.0649
Absolute structure parameter	0.0(2)	0.0(6)
Extinction coefficient	0.036(3)	0.034(5)
Highest residual peak (e/Å ³)	1.248 and -0.802	3.738 and -2.005

^{*} $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table V.8. Crystal data and superstructure refinement details for **2**: Dy_{0.67}Ni₂Ga_{6-x}Ge.

Empirical formula	Dy _{0.62} Ni ₂ Ga _{5.25} Ge (2)
Formula weight	656.52
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Space group	$P\bar{3}1c$
Lattice Constants (Å)	$a = 7.2536(8)$ $c = 18.308(3)$
Volume (Å ³)	834.23(19)
Z	6
Calculated density (g/cm ³)	7.841
Absorption coefficient (mm ⁻¹)	44.986
F(000)	1749
Crystal size (mm ³)	0.08 × 0.08 × 0.08
θ range (°)	6.45 to 32.51
Limiting indices	$-10 \leq h \leq 10$ $-10 \leq k \leq 9$ $-17 \leq l \leq 27$
Reflections collected	5914
Unique reflections	1530
R _{int}	0.0775
Completeness to θ	96.2 %
Refinement method	Full-matrix least-squares on F ²
Variables/Restraints	93/1
Goodness-of-fit on F ²	0.840
Final R indices [I>2σ(I)] [*]	R ₁ = 0.0487, wR ₂ = 0.1327
R indices (all data)	R ₁ = 0.0716, wR ₂ = 0.1389
Absolute structure parameter	0.0(2)
Extinction coefficient	0.00040(10)
Highest residual peak (e/Å ³)	3.218 and -3.770

^{*} $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table V.9. Atomic coordinates and equivalent isotropic displacement parameters($\text{\AA}^2 \times 10^3$), and the occupancies for **2**: (a) $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ and (b) $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Si}_x$.

(a)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*	Occupancy
Gd(1)	<i>1a</i>	0	0	0	9(1)	0.580(6)
Ni(1)	<i>2h</i>	1/3	2/3	0.2455(2)	10(1)	1.0
M(1)	<i>3j</i>	0.2012(7)	-0.2012(7)	0	22(1)	0.33 Ga
M(2)	<i>2i</i>	2/3	1/3	0.2003(2)	14(1)	1.0 Ge
Ga(3)	<i>2g</i>	0	0	0.3490(2)	12(1)	1.0
Ga(4)	<i>1d</i>	1/3	2/3	1/2	15(1)	1.0

*U_(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

(b)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*	Occupancy
Sm	<i>1a</i>	0	0	0	6(1)	0.67
Ni	<i>2h</i>	1/3	2/3	0.2456(2)	8(1)	1.0
M(1)	<i>3j</i>	0.2074(5)	-0.2074(5)	0	12(1)	0.33 Ga
M(2)	<i>2i</i>	2/3	1/3	0.2025(2)	9(1)	0.972(4) Ga 0.03(2) Si
Ga(3)	<i>2g</i>	0	0	0.3491(2)	9(1)	1.0
Ga(4)	<i>1d</i>	1/3	2/3	1/2	11(1)	1.0

*U_(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table V.10. Selected bond lengths [Å] for **2**: (a) $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ and (b) $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Si}_x$.

(a)

Bond	Distance	Mult.	Bond	Distance	Mult.
Gd-M(1)	1.458(5)	× 3			
Gd-M(1)	3.012(4)	× 6	M(1)-M(1)	1.660(9)	× 2
Gd-M(2)	3.0351(14)	× 6	M(1)-M(1)	2.526(9)	× 2
Ni-Ga(4)	2.3326(18)	× 1	M(1)-M(2)	2.7954(15)	× 4
Ni-M(1)	2.446(3)	× 2	M(2)-Ga(3)	2.7742(13)	× 3
Ni-M(2)	2.4519(7)	× 3	Ga(3)-Ga(3)	2.769(3)	× 1
Ni-Ga(3)	2.5958(10)	× 3	Ga(3)-Ga(4)	2.7851(10)	× 3

(b)

Bond	Distance	Mult.	Bond	Distance	Mult.
Sm-M(1)	1.508(4)	× 3	M(2)-Ga(3)	2.7706(11)	× 3
Sm-M(1)	2.989(3)	× 6	M(2)-M(1)	2.8165(13)	× 4
Sm-M(2)	3.0518(12)	× 6	Ga(3)-Ga(3)	2.764(3)	× 1
Ni-Ga(4)	2.3296(17)	× 1	Ga(3)-Ga(4)	2.7898(9)	× 3
Ni-M(1)	2.429(2)	× 2	M(1)-M(1)	1.586(7)	× 2
Ni-M(2)	2.4555(6)	× 3	M(1)-M(1)	2.611(7)	× 2
Ni-Ga(3)	2.6021(8)	× 3			

Table V.11. Selected bond angles [°] for **2**: (a) $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ and (b) $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Si}_x$.

(a)

Bond	Angle	Bond	Angle
M(1)-Gd-M(1)	120.0	Ni-M(2)-Ni	117.20(3)
M(1)-Gd-M(1)	104.01(7)	Ni-M(2)-Ga(3)	59.18(2)
M(1)-Gd-M(1)	15.99(7)	Ni-M(2)-Ga(3)	140.85(9)
M(1)-Gd-M(1)	31.98(13)	Ni-M(2)-M(1)	134.91(10)
M(1)-Gd-M(1)	135.99(7)	Ni-M(2)-M(1)	55.11(7)
M(1)-Gd-M(1)	88.02(13)	Ni-M(2)-M(1)	101.49(11)
M(1)-Gd-M(1)	120.000(1)	Ga(3)-M(2)-M(1)	104.16(10)
M(1)-Gd-M(1)	151.98(13)	Ga(3)-M(2)-M(1)	78.28(6)
M(1)-Gd-M(2)	66.541(11)	Ga(3)-M(2)-M(1)	157.87(10)
M(1)-Gd-M(2)	142.77(3)	M(1)-M(2)-M(1)	53.72(19)
M(1)-Gd-M(2)	55.06(5)	M(1)-M(2)-M(1)	34.54(19)
M(1)-Gd-M(2)	78.89(5)	M(1)-M(2)-M(1)	81.53(5)
M(1)-Gd-M(2)	139.94(4)	M(1)-M(2)-M(1)	96.95(7)
M(2)-Gd-M(2)	87.19(5)	Ni-Ga(3)-Ga(3)	111.42(4)
M(2)-Gd-M(2)	133.08(2)	Ni-Ga(3)-M(2)	129.16(8)
M(2)-Gd-M(2)	74.46(7)	Ni-Ga(3)-M(2)	54.210(19)
Ga(4)-Ni-M(1)	156.94(11)	Ga(3)-Ga(3)-M(2)	119.42(4)
M(1)-Ni-M(1)	39.66(18)	M(2)-Ga(3)-M(2)	97.94(6)
Ga(4)-Ni-M(2)	99.74(6)	Ni-Ga(3)-Ga(4)	51.23(4)
M(1)-Ni-M(2)	69.60(6)	Ni-Ga(3)-Ga(4)	125.833(16)
M(1)-Ni-M(2)	103.32(13)	Ga(3)-Ga(3)-Ga(4)	60.19(3)
Ga(4)-Ni-Ga(3)	68.58(4)	M(2)-Ga(3)-Ga(4)	179.60(6)
M(1)-Ni-Ga(3)	121.22(6)	M(2)-Ga(3)-Ga(4)	82.31(3)
M(1)-Ni-Ga(3)	88.36(11)	Ni-Ga(4)-Ni	180.0
M(2)-Ni-Ga(3)	66.61(2)	Ga(3)-Ga(4)-Ga(3)	128.578(17)
M(2)-Ni-Ga(3)	168.32(9)	Ga(3)-Ga(4)-Ga(3)	97.43(4)
Ga(3)-Ni-Ga(3)	107.46(5)	Ga(3)-Ga(4)-Ga(3)	59.62(6)

Table V.11 (continued)

(b)

Bond	Angle	Bond	Angle
M(1)-Sm-M(1)	120.0	Ni-M(2)-M(1)	133.72(8)
M(1)-Sm-M(1)	104.61(5)	Ni-M(2)-M(1)	54.35(5)
M(1)-Sm-M(1)	15.39(5)	Ni-M(2)-M(1)	102.10(8)
M(1)-Sm-M(1)	135.39(5)	Ga(3)-M(2)-M(1)	103.14(8)
M(1)-Sm-M(1)	89.22(10)	Ga(3)-M(2)-M(1)	78.50(5)
M(1)-Sm-M(1)	30.78(10)	Ga(3)-M(2)-M(1)	158.37(8)
M(1)-Sm-M(1)	120.000(1)	M(1)-M(2)-M(1)	32.72(15)
M(1)-Sm-M(1)	150.78(10)	M(1)-M(2)-M(1)	55.23(15)
M(1)-Sm-M(2)	66.605(9)	M(1)-M(2)-M(1)	81.34(5)
M(1)-Sm-M(2)	142.57(3)	M(1)-M(2)-M(1)	96.35(6)
M(1)-Sm-M(2)	55.57(4)	Ni-Ga(3)-Ni	107.52(4)
M(1)-Sm-M(2)	78.45(4)	Ni-Ga(3)-Ga(3)	111.35(4)
M(1)-Sm-M(2)	139.96(3)	Ni-Ga(3)-M(2)	54.280(17)
Ga(4)-Ni-M(1)	157.85(9)	Ni-Ga(3)-M(2)	129.66(7)
M(1)-Ni-M(1)	38.12(15)	Ga(3)-Ga(3)-M(2)	118.99(4)
Ga(4)-Ni-M(2)	99.26(5)	M(2)-Ga(3)-M(2)	98.49(5)
M(1)-Ni-M(2)	70.42(5)	Ni-Ga(3)-Ga(4)	51.05(3)
M(1)-Ni-M(2)	102.89(10)	Ni-Ga(3)-Ga(4)	125.797(14)
M(2)-Ni-M(2)	117.46(3)	Ga(3)-Ga(3)-Ga(4)	60.31(3)
Ga(4)-Ni-Ga(3)	68.64(4)	M(2)-Ga(3)-Ga(4)	81.96(2)
M(1)-Ni-Ga(3)	120.85(5)	M(2)-Ga(3)-Ga(4)	179.29(6)
M(1)-Ni-Ga(3)	89.20(9)	Ga(3)-Ga(3)-Ga(4)	60.31(3)
M(2)-Ni-Ga(3)	66.36(2)	Ni-Ga(4)-Ni	180.0
M(2)-Ni-Ga(3)	167.91(7)	Ni-Ga(4)-Ga(3)6	119.69(3)
Ga(3)-Ni-Ga(3)	107.52(4)	Ga(3)-Ga(4)-Ga(3)	59.39(5)
Ni-M(2)-Ga(3)	59.36(2)	Ga(3)-Ga(4)-Ga(3)	128.513(16)
Ni-M(2)-Ga(3)	141.75(8)	Ga(3)-Ga(4)-Ga(3)	97.58(4)

Table V.12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**: (a) $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ and (b) $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Si}_x$.

(a)

	U11	U22	U33	U23	U13	U12
Gd	8(1)	8(1)	12(1)	0	0	4(1)
Ni	8(1)	8(1)	15(1)	0	0	4(1)
M(1)	23(1)	23(1)	15(2)	0	0	9(2)
M(2)	10(1)	10(1)	20(1)	0	0	5(1)
Ga(3)	10(1)	10(1)	15(1)	0	0	5(1)
Ga(4)	15(1)	15(1)	14(1)	0	0	8(1)

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U11 + \dots + 2hka^*b^*U12]$.

(b)

Atomic Position	U11	U22	U33	U23	U13	U12
Sm	6(1)	6(1)	6(1)	0	0	3(1)
Ni	8(1)	8(1)	7(1)	0	0	4(1)
M(1)	12(1)	12(1)	11(2)	0	0	5(1)
M(2)	9(1)	9(1)	11(1)	0	0	4(1)
Ga(3)	9(1)	9(1)	8(1)	0	0	5(1)
Ga(4)	15(1)	15(1)	4(1)	0	0	7(1)

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U11 + \dots + 2hka^*b^*U12]$.

Single Crystal Neutron Diffraction

In order to determine with certainty the nature of the M(1) triangles and to locate the tetrelide atoms in the structure, neutron diffraction experiments on single crystal samples of **1** and **2** were performed. In contrast to the small difference in X-ray scattering lengths ($\sim 3\%$) between Ga and Ge atoms, the neutron scattering lengths for Ga and Ge atoms differ more significantly ($\sim 10\%$). Thus neutron diffraction provides a better means for distinguishing these two elements in a crystalline sample.

Diffraction data were collected from single crystals of **1** ($\text{Y}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$) and **2** ($\text{Y}_{0.67}\text{Co}_2\text{Ga}_{6-x}\text{Ge}_x$) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory on the single-crystal diffractometer (SCD). A detailed description of the SCD instrument, data collection and analysis procedures has been published elsewhere.^{16, 17} A total of 13 and 18 histograms for compounds **1** and **2**, respectively were measured at χ and ϕ values suitable to cover a unique octant of reciprocal space. An auto-indexing algorithm¹⁸ was used to obtain an initial orientation matrix from the peaks in one histogram. Data were indexed using individual orientation matrices for each histogram to allow for any misalignment of the sample. Bragg peaks were integrated in three dimensions about their predicted locations and were corrected for the incident neutron spectrum and detector efficiency. The intensities were corrected for absorption using a local program ANVRED assuming a crystal of spherical shape. The GSAS software package¹⁹ was used for structural analysis. The refinement was based on F_o using reflections with $|F_o| > 3\sigma(F_o)$. For structure solution, the space group and initial coordinates obtained from the single crystal X-ray analysis were used.

Neutron Refinement of 1

For compound **1**, two solutions, one based on Y/Ga disorder ($M(1) = \text{Ga}$) and the other one based on Y/Ge disorder ($M(1) = \text{Ge}$), were tested with the use of neutron data. The occupancies were refined to 0.680(6) for Y and 0.320(6) for Ga if Y/Ga model was considered. If Ge instead of Ga atoms were placed in the $M(1)$ $6h$ position, these parameters refined to 0.708(6) for Y and 0.292(6) for Ge, and a higher residual R -value was obtained. The result is consistent with Ga atom occupying the $M(1)$ $6h$ position. The refinement also indicates that $M(2)$ $4e$ position in **1** contains both Ga and Ge atoms, and their occupancies were refined to 0.69(8) and 0.31(8), respectively. The model, where $M(1) = \text{Ga}(1)$, and $M(2) = \text{Ga}(2) + \text{Ge}(2)$ was included in the final structural refinement. In the final refinement cycle the occupancies were additionally fixed to 2/3 for Y at $2c$ and Ga(2) at $4e$ and to 1/3 for Ga(1) at $6h$ and Ge(2) at $4e$, respectively (see Table V.14). According to this solution, the unit cell composition of **1** is then represented as $\text{Y}_{0.67}\text{Ni}_2\text{Ga}_{4.33}\text{Ge}_{0.67}$ ($Z = 2$). The obtained formula is in good agreement with the composition given by the EDS elemental analysis. A summary of parameters related to the neutron diffraction analysis of **1** is given in Table V.13. Atomic coordinates and occupancies are listed in Table V.14; selected interatomic distances are contained in Table V.15.

Table V.13. Neutron crystal data and structural refinement parameters for **1**.

Formula	$\text{Y}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$
x	0.67
Formula weight (g mol^{-1})	527.19
Temperature (K)	295
Crystal system	Hexagonal
Space group	$P6_3/mmc$
a ($\text{\AA}$)	4.179(1)
c ($\text{\AA}$)	15.993(5)
V ($\text{\AA}^3$)	241.9(1)
Z	2
d_{calc} (g cm^{-3})	7.24
Radiation	Neutrons
Data collection technique	Time-of-flight Laue
$\mu(\lambda)$ (cm^{-1})	$0.640 + 0.107 \lambda$
No. of refl. ($I > 3\sigma(I)$)	459
No. of parameters refined	29
Refinement method	Full-matrix least-squares on F
R indices $R_w(F)$ ^a $R(F)$, ^b	0.059, 0.055

$$^a R_w(F) = \left\{ \sum [w(F_o - F_c)^2] / \sum [w(F_o)^2] \right\}^{1/2} \quad ^b R(F) = \sum |F_o| - |F_c| / \sum |F_o|$$

Table V.14. Fractional coordinates and site occupancy of **1**.

Position	Wyckoff	x	y	z	Occupancy
Symbol					
Y	<i>2c</i>	1/3	2/3	1/4	0.67
Ga(1)	<i>6h</i>	0.5408(6)	0.0817(12)	1/4	0.33
M(2)	<i>4e</i>	0	0	0.13351(9)	0.67 Ga(2)
	<i>4e</i>	0	0	0.13350(9)	0.33 Ge(2)
Ga(3)	<i>4f</i>	1/3	2/3	0.04590(9)	1.0
Ni	<i>4f</i>	1/3	2/3	0.60897(7)	1.0

Table V.15. Selected interatomic distances (Å) for **1**.

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
Y-Ga(1)	1.502(4)	× 3	Ga(1)-M(2)	2.815(1)	× 4
Y-Ga(1)	2.975(3)	× 6	Ni-Ga(3)	2.477(2)	× 1
Y-M(2)	3.049(1)	× 6	Ni-Ga(3)	2.6151(9)	× 3
Y-Ga(3)	3.264(2)	× 2	Ni-M(2)	2.4445(7)	× 3
Ga(1)-Ga(1)	1.578(8)	× 2	Ga(3)-M(2)	2.790(1)	× 3
Ga(1)-Ga(1)	2.601(8)	× 2	Ga(3)-Ga(3)	2.824(2)	× 3
Ga(1)-Ni	2.433(2)	× 2			

Neutron Refinement of 2

Because of the close structural relationship of **1** and **2**, we expected to see a similar type of disordered arrangement between Ga and Ge atoms in compound **2** as well. Indeed, the neutron structural refinement for **2** with the best convergence factor corresponds to the model where the M(1) site is occupied with Ga atoms (Ga(1), multiplicity site $3j$). The Ga(1) atoms are disordered in the same layer with Y atoms with occupancies of $1/3$ and 0.60 , respectively. Like the telluride atoms in **1**, the Ge atoms do not possess any particular crystallographic position in the structure, but they are disordered with Ga atoms on the same site of multiplicity $2i$. The mixed occupancy $2i$ site consists of $2/3$ of Ga(1) and $1/3$ of Ge(1). The neutron diffraction analysis gave a formula of $\text{Y}_{0.6}\text{Co}_2\text{Ga}_{5.33}\text{Ge}_{0.67}$ for **2** which is in fair agreement with the EDS elemental analysis data. The details of neutron diffraction analysis for **2** are presented in Table V.16. The atomic coordinates and occupancies are given in Table V.17. Selected bond distances are listed in the Table V.18.

Table V.16. Crystal data and structural refinement parameters for **2** from neutron diffraction.

Formula	$\text{Y}_{0.60}\text{Co}_2\text{Ga}_{5.33}\text{Ge}_{0.67}$
Formula weight	389.859
Temperature (K)	298(2)
Crystal system	Hexagonal
Space group	$P\bar{6}m2$
a (Å)	4.1822(6)
c (Å)	9.240(2)
V (Å ³)	139.96(4)
Z	1
d_{calc} , g cm ⁻³	6.998
Radiation	Neutrons
Data collection technique	Time-of-flight Laue
$\mu(\lambda)$, cm ⁻¹	$0.413 + 0.362\lambda$
Reflections ($I > 3\sigma(I)$)	806
Parameters refined	39
Refinement method	Full-matrix least-squares on F
R indices $R_w(F)$ ^a $R(F)$, ^b	0.063, 0.048
goodness-of-fit	1.52

$$^a R_w(F) = \left\{ \frac{\sum [w(F_o - F_c)^2]}{\sum [w(F_o)^2]} \right\}^{1/2} \quad ^b R(F) = \sum |F_o| - |F_c| / \sum |F_o|$$

Table V.17. Atomic coordinates, isotropic thermal displacement parameters and site occupancies for **2**.

Name	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	U (eq)
Y	<i>1a</i>	0	0	0	0.597(7)	0.0077
Co	<i>2h</i>	1/3	2/3	0.2440(3)	1.0	0.0105
Ga(1)	<i>3j</i>	0.2081(3)	-0.2081(3)	0	0.327(5)	0.0103
M(2)	<i>2i</i>	2/3	1/3	0.2018(1)	0.67(5) Ga(2)	0.0104
	<i>2i</i>	2/3	1/3	0.2018(1)	0.33(5) Ge(2)	0.0104
Ga(3)	<i>2g</i>	0	0	0.3495(1)	1.0	0.0104
Ga(4)	<i>1d</i>	1/3	2/3	1/2	1.0	0.0116

Table V.18. Selected interatomic distances (Å) for **2**.

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
Y-Ga(3)	3.230(1)	× 2	Ga(3)-Ga(3)	2.781(2)	× 1
Y-M(2)	3.0509(8)	× 6	Ga(3)-Ga(4)	2.7864(6)	× 3
Y-Ga(1)	2.974(2)	× 6	Co-Ga(3)	2.604(1)	× 3
Y-Ga(1)	1.508(2)	× 3	Co-Ga(4)	2.366(3)	× 1
M(2)-Ga(1)	2.8179(8)	× 4	Co-M(2)	2.4458(5)	× 3
M(2)-Ga(3)	2.7735(7)	× 3	Co-Ga(1)	2.430(3)	× 2

Transmission Electron Microscopy and Electron Diffraction

The transmission electron microscopy (TEM) studies were performed on a TEM microscope JEOL 100CX. The electron beam was generated from the CeB₆ filament at accelerating voltage 120 kV. Both the imaging mode and the selected area electron diffraction (SAED) were used. The samples were stable under the impact of electron beam. *Sample preparation:* large, rod-like single crystals of **1** and “fat” rod-like single crystals of **2** were selected. The crystals were cut with a wire saw in a way that either *ab*-plane (with hexagonal cross-section) or the direction perpendicular to it was exposed. The samples were next hand-polished using sand paper with subsequently increasing grit (600 – 1500) to approximately 200 – 300 μm in thickness. If necessary, the core drill was then used to cut out circular shape specimen suitable to use in the TEM holder, usually 3 mm in diameter. As-prepared samples were electrochemically thinned using Tenupole-3 twin jet polishing unit equipped with an infrared detector. The electropolishing experiment was conducted at the temperature range from -15°C to -35°C with applied potential 15V using four-component acidic electrolyte²⁰. The size of the resultant hole is larger than typical, ~ 180 μm in diameter, see Figure V.3, with the estimated area lucent to the electron beam of over 1000 μm^2 .

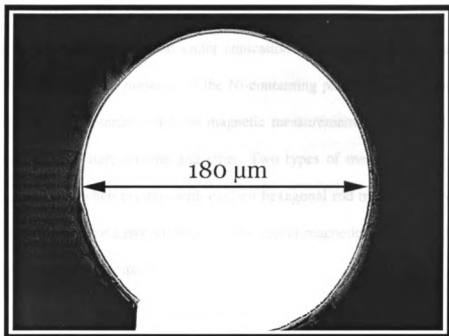


Figure V.3. The low magnification TEM image of the $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5.3}\text{Ge}_x$ electropolished sample. The thin, electron lucent area could be seen around the hole.

Physical Properties

A conventional four-probe method and a slow AC technique were used for electrical conductivity and thermopower measurements²¹ conducted in the temperature range of 4–300 K.

The magnetic susceptibility was measured on single crystal and polycrystalline samples as a function of temperature in the range 2 – 400 K in an applied external magnetic field of 500 Gauss with MPMS Quantum Design Inc. SQUID magnetometer. The field dependence of the magnetic susceptibility was determined at $T = 2$ K in the

fields up to ± 5 T. *Sample preparation:* for the magnetic measurements the crystals were selected manually, treated under sonication with *aqua regia*, for about 30 seconds to eliminate possible presence of the Ni-containing phases from the surface of the crystals, which could interfere with the magnetic measurements. The crystals were subsequently washed in water, acetone and ether. Two types of measurements were performed: (a) anisotropic, when crystals with explicit hexagonal rod morphology were placed with the *c*-axis parallel or perpendicular to the external magnetic field; (b) isotropic, using ground polycrystalline samples.

3. Results and Discussion

Reaction Chemistry

The reactions between rare earth, Ni, and a tetrelide in liquid Ga yielded large, well-formed crystals of the new quaternary phases $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Tt}_x$ (Tt = Si, Ge) (**1**). These crystals have an unusual tapered rod or arrow head morphology with hexagonal cross-section, see Figure V.4. A homologous quaternary compound, $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Tt}_x$ (**2**), with a related structure was first found as a side-phase in the system Sm/Ni/Ga/Si. The $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Tt}_x$ phases are very stable and readily form as nearly pure products according to EDS and powder XRD. Originally, the formation of **1** was detected in the Sm/Ni/Al/Si system by its unusual morphology⁴. The isostructural compounds with Y, Sm and the heavy rare-earth metals with the exception of Dy, Yb and Lu with Si and Ge were obtained. For these analogs, the volume of the unit cell plotted against the atomic

number is shown in Figure V.5. The observed linear decrease of the cell volume with increasing atomic number is consistent with the lanthanide contraction.

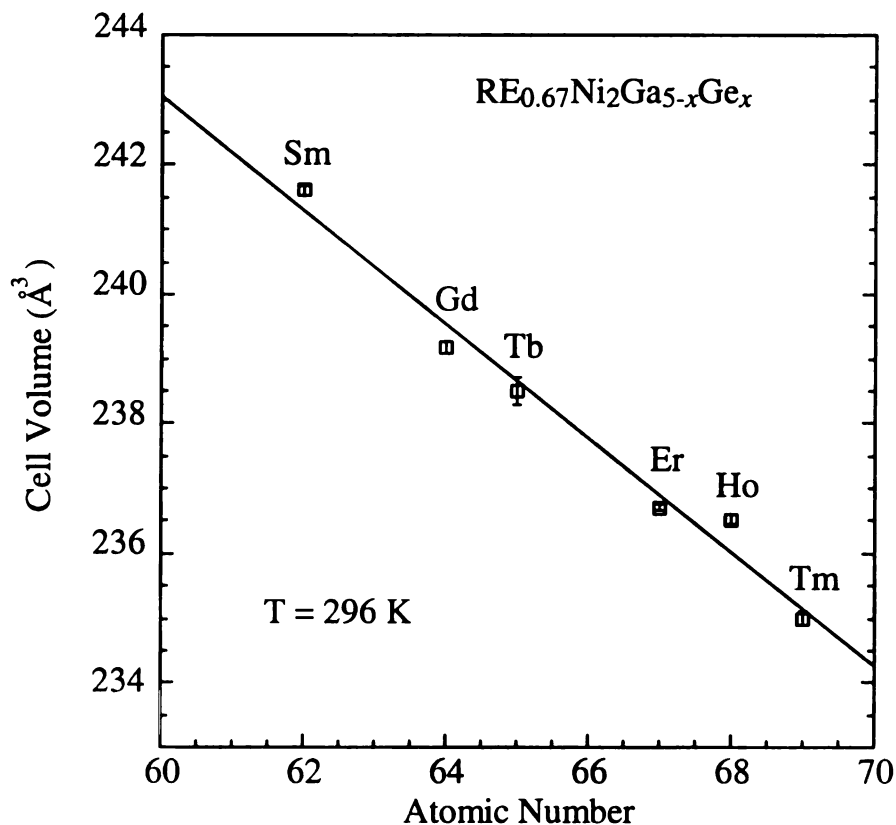


Figure V.4. The cell volume of the $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ compounds obtained at room temperature with single crystal X-ray diffraction data versus the atomic number of the corresponding RE.

The representatives of the $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Tt}_x$ and $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Tt}_x$ phases are chemically stable even in the aggressive environments. Only slow decomposition was observed in highly basic (5 M solution of NaOH) or acidic/oxidative environments as *aqua regia*.

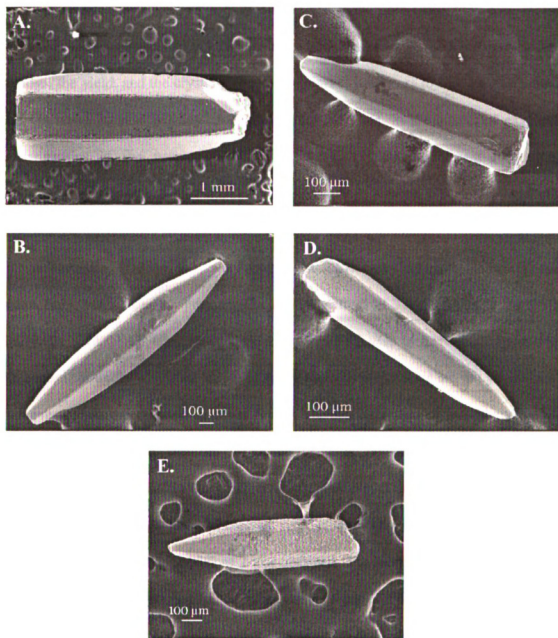


Figure V.5. SEM micrographs of crystals of $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1): (A), (B) $\text{Tm}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$; (C), (D) $\text{Er}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$; (E) $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$.

It was found that Ge analogs of **1** form and grow more easily than corresponding Si analogs. For example, the ‘window’ of synthesis conditions is much broader for the Ge analogs, the yield, and the crystal size are also higher. It appears to be a general tendency that Ga has a greater “affinity” for Ge than for Si. Thus, in the course of exploratory investigations in the system RE/Ni/Ga/Tt, we observed predominant formation of quaternary phases $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$, $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ ²² when Tt = Ge, and phase separation onto ternaries RENiSi_3 , NiGaSi , $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$, and binary Ni_3Ga_2 ⁸ if Tt = Si.

The $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Tt}_x$ phase coexists in some cases with the $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Tt}_x$ phase, but often as a minor product. The representatives of **2** were found in the systems Sm/Ni/Ga/Si, Y/Ni/Ga/Ge, Gd/Co/Ga/Ge, and Gd/Ni/Ga/Ge in trace amounts, although the conditions under which the single phase of these analogs forms are not yet optimized. However, when the reaction involves Dy or Yb, the formation of the otherwise stable phase **1** is suppressed and the formation of **2** is favored. Thus, in the systems Dy/Ni/Ga/Ge and Yb/Ni/Ga/Ge a nearly single phase of **2** was obtained under similar conditions to those that yield phases of type **1**. Similarly in the reaction containing Y/Co/Ga/Ge, a yield of over 95% of **2** was obtained. The morphology of the crystals of **2** varies from chunks with hexagonal faces, as it is for Sm/Ni/Ga/Si, Y/Ni/Ga/Ge, and Gd/Ni/Ga/Ge, to “fat” tapered rods, as it is in the case of Dy/Ni/Ga/Ge and Y/Co/Ga/Ge, see Figure V.6. In case of Yb/Ni/Ga/Ge, the crystals grow mostly as agglomerates with no explicit hexagonal faceting.

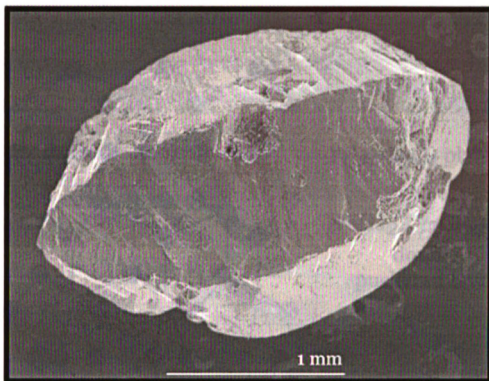


Figure V.6. SEM micrograph of a crystal of $\text{Y}_{0.67}\text{Co}_2\text{Ga}_{6-x}\text{Ge}_x$ (**2**).

Crystal Structure

Crystal Structure of 1

A drawing of **1** $\text{Y}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ ($x = 0.67$) is shown in Figure V.7. The larger gray spheres represent Y atoms, the open circles and the solid circles correspond to Ni and Ga atoms respectively. The Ga(2)/Ge(2) mixed-occupied M(2) position is shown as spheres with checker pattern. The structure of **1** can be viewed as constructed of two types of layers, namely a $[\text{NiGa}_{2-x/2}\text{Ge}_{x/2}]_2$ bi-layer and a disordered $\text{Y}_{0.67}\text{Ga}(1)$ monoatomic plane.

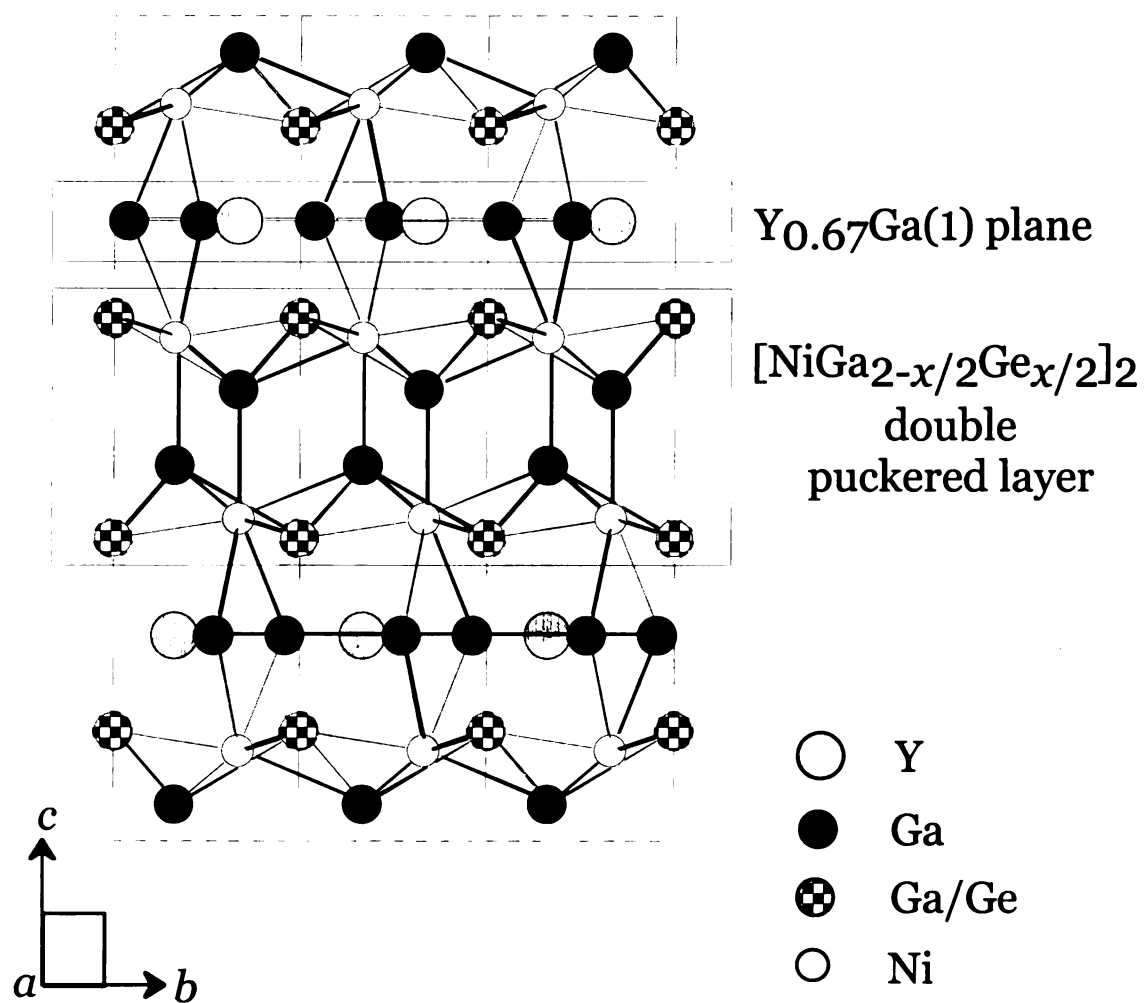
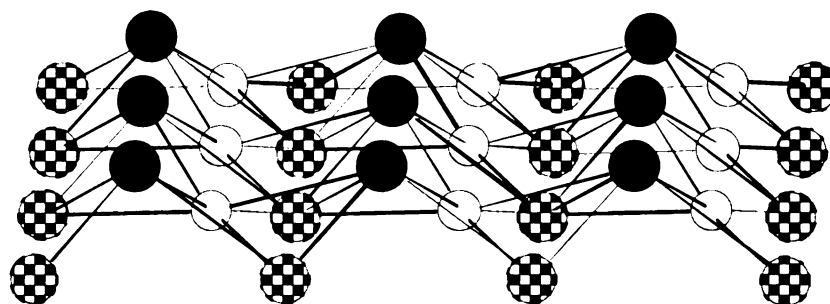


Figure V.7. Structure of Y_{0.67}Ni₂Ga_{5-x}Ge_x (1) viewed along the *a*-axis. The dashed lines represent the unit cell.

The $[\text{NiGa}_{2-x/2}\text{Ge}_{x/2}]$ layer consists of arsenic-type layer of M(2) and Ga(3) atoms “stuffed” with Ni atoms,^{1,24} see Figure V.8. The Ni-M(2) and Ni-Ga(3) bond distances within the layer are 2.4445(7) Å and 2.6151(9) Å respectively, the M(2)–Ga(3) are connected at 2.790(1) Å. In this structure, the two single $[\text{NiGa}_{2-x/2}\text{Ge}_{x/2}]$ layers are joined together via Ni–Ga(3) interactions at 2.477(2) Å to form a bi-layer.



$[\text{NiGa}_{2-x/2}\text{Ge}_{x/2}]$ single puckered layer

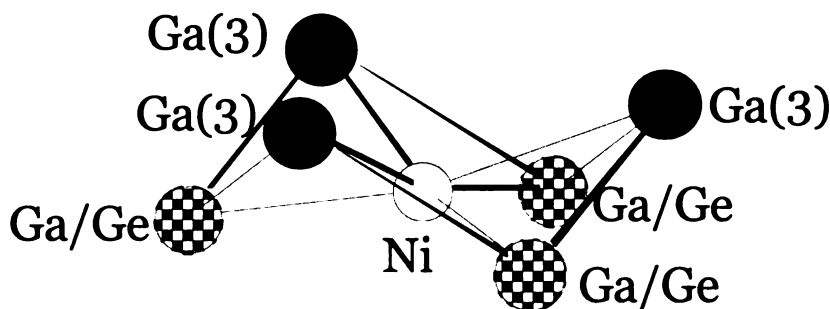


Figure V.8. A single $[\text{NiGa}_{2-x/2}\text{Ge}_{x/2}]$ puckered layer. An As-type infinite sheet of Ga/Ge atoms is stuffed with Ni atoms. A single $\text{Ga}_{6-x}\text{Ge}_x$ hexagon in chair conformation with Ni atom in the center is shown below.

Another structural fragment is the disordered $Y_{0.67}Ga$ plane shown in Figure V.9. The ordered type model is shown on the right for reference. In the disordered $Y_{0.67}Ga$ plane unreasonably short distances are produced between the Ga(1) and Y atoms: Ga(1)–Ga(1) ~ 1.6 Å, and Y–Ga(1) ~ 1.5 Å owing to the symmetry equivalent positions of Y atoms at $2c$ ($1/3$ $2/3$ $1/4$) and Ga(1) atoms at $6h$ (x $2x$ $1/4$). Since such disorder does not represent the realistic picture of the atomic arrangement, partial occupancies of $2/3$ and $1/3$ were found for Y and Ga(1) sites respectively. The $[NiGa_{2-x/2}Ge_{x/2}]_2$ slabs then alternate with the $Y_{0.67}Ga$ planes as shown in Figure V.7.

The local coordination environment of Y, Ni, Ga(3) and M(2) = Ga/Ge types of atoms are shown in Figure V.10 (the disordered M(1) atoms were excluded). The Y atoms are in the center of a bi-capped trigonal prism, formed by six M(2) atoms and two Ga(3) atoms bonded at 3.049(1) Å and 3.264(2) Å respectively. The Ni atoms are linked to the 6-membered ring consisting of M(2) and Ga(3) atoms in a chair conformation. The bond distances from the central Ni atom to M(2) and Ga(3) are 2.4445(7) Å and 2.6151(9) Å respectively. The Ni atom has an additional Ni–Ga(3) bond out of the $[NiGa_{2-x/2}Ge_{x/2}]$ puckered layer (Ni–Ga(3) = 2.477(2) Å), which connects two $[NiGa_{2-x/2}Ge_{x/2}]$ slabs into a double-layer. The M(2) atoms are bonded to a $Ni_3Ga(3)_3$ six-member rings, with M(2)–Ga(3) distance of 2.790(1) Å. The Ga(3) site is found in a cage of 10 atoms and is connected to a $Ni_3M(2)_3$ six-member ring, and also capped with $NiGa(3)_3$ “umbrella”, see Figure V.5. The Ga(3)–Ga(3) bond distance is 2.824(2) Å.

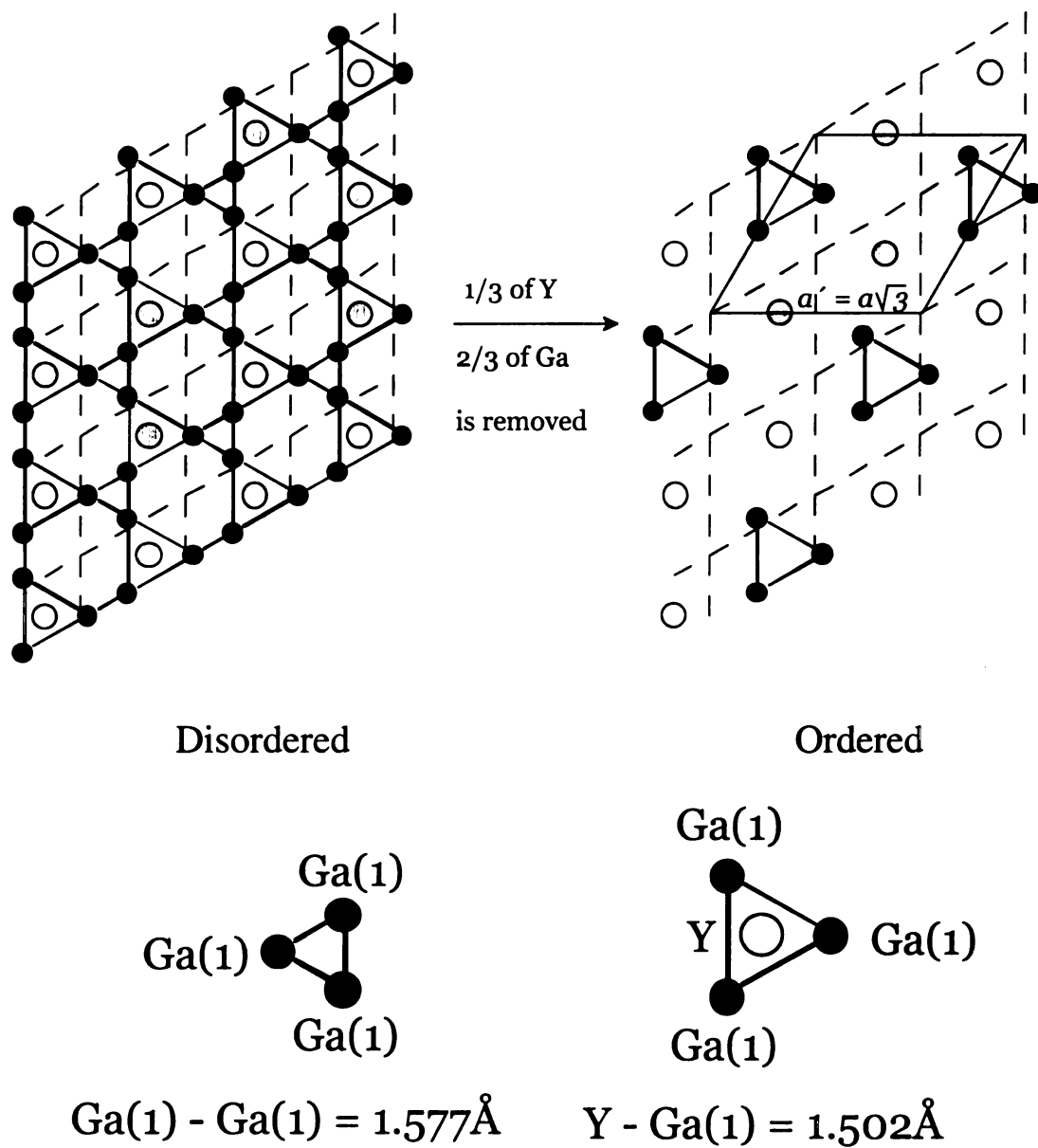


Figure V.9. The Y-Ga plane in **1** viewed along *c*-axis (left). An ordered model of the $\text{Y}_{0.67}\text{Ga}$ plane is given for comparison (right). The disordered Ga(1)_3 triangle and Y-centered Ga(1)_3 triangle, shown below, create unreasonably short interatomic distances.

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Figure

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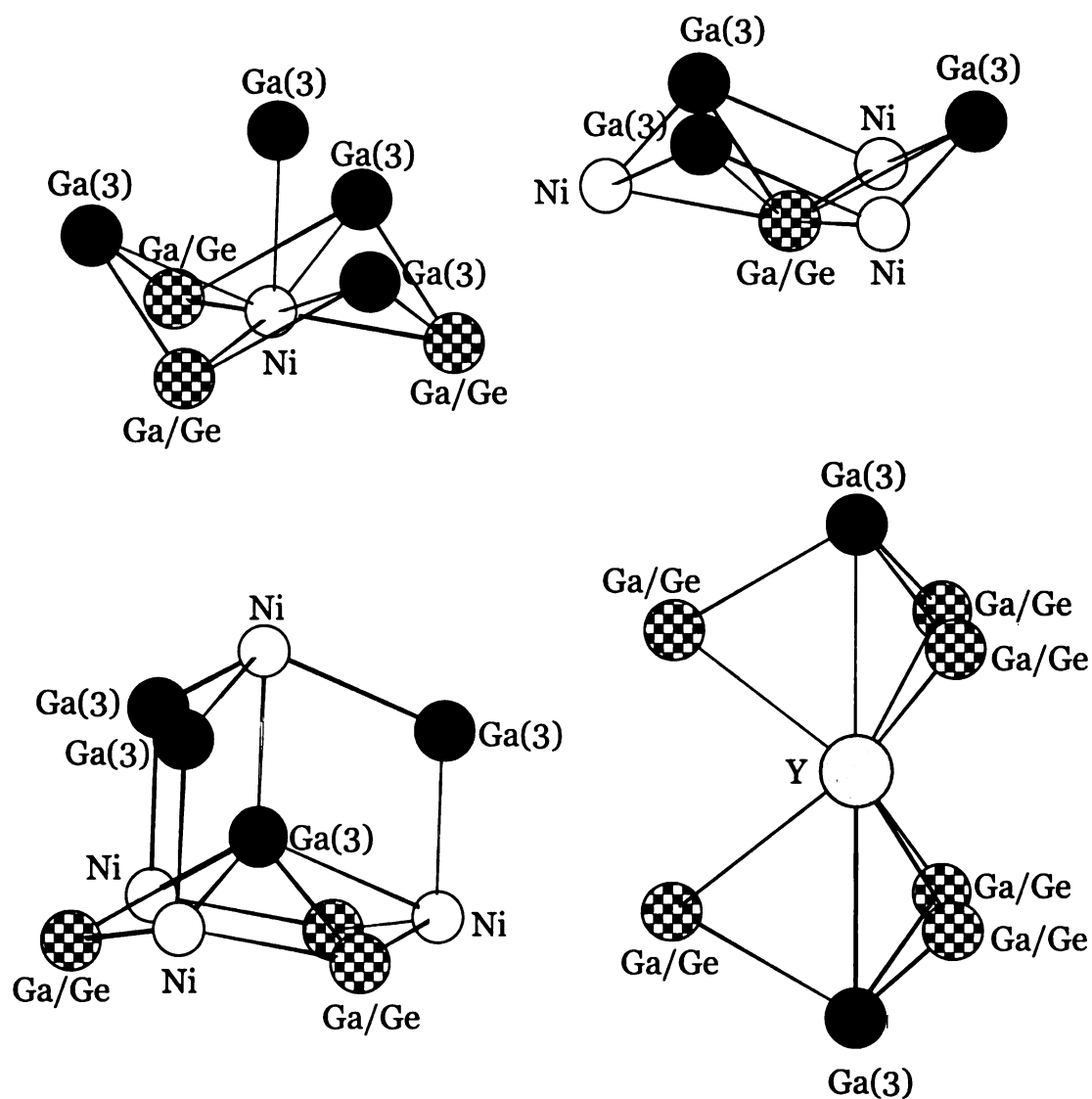


Figure V.10. Local coordination of Y (within 3.5 Å), Ni, Ga and Ga/Ge atoms (within 3.0 Å) in the structure of $\text{Y}_{0.67}\text{Ni}_2\text{Ga}_{5.5}\text{Ge}_{0.5}$ (1). The disordered Ga(1) atoms are omitted for clarity.

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Crystal Structure of **2**

The structure of **2** is even more complicated than that of **1** in terms of the disorder taking place in the $\text{RE}_{0.67}\text{Ga}$ plane. Two crystal structures differing in the degree of order in this plane were found in the analogs of **2**. For instance, in the case of $\text{RE} = \text{Y}, \text{Sm}$ and Gd a satisfactory solution in the $P\bar{6}m2$ hexagonal space group was found. The structure of the Co analog $\text{Y}_{0.67}\text{Co}_2\text{Ga}_{6-x}\text{Ge}_x$ of **2** was studied and refined by neutron diffraction, and is depicted in Figure V.11; the atoms of Y, Co, Ga and $\text{M}(2) = \text{Ga/Ge}$ are drawn analogous to those in **1**. Similar to **1**, the crystal structure of **2** can be represented as a stacking of alternating $\text{Ga}[\text{CoGa}_{2-x/2}\text{Ge}_{x/2}]_2$ thick slabs and $\text{Y}_{0.67}\text{Ga}$ planes along the long (*c*) axis, see Figure V.11. The thick slab consisting of Co, Ga and Ge atoms is reminiscent of the $[\text{NiGa}_{2-x/2}\text{Ge}_{x/2}]_2$ double puckered layer in **1**.

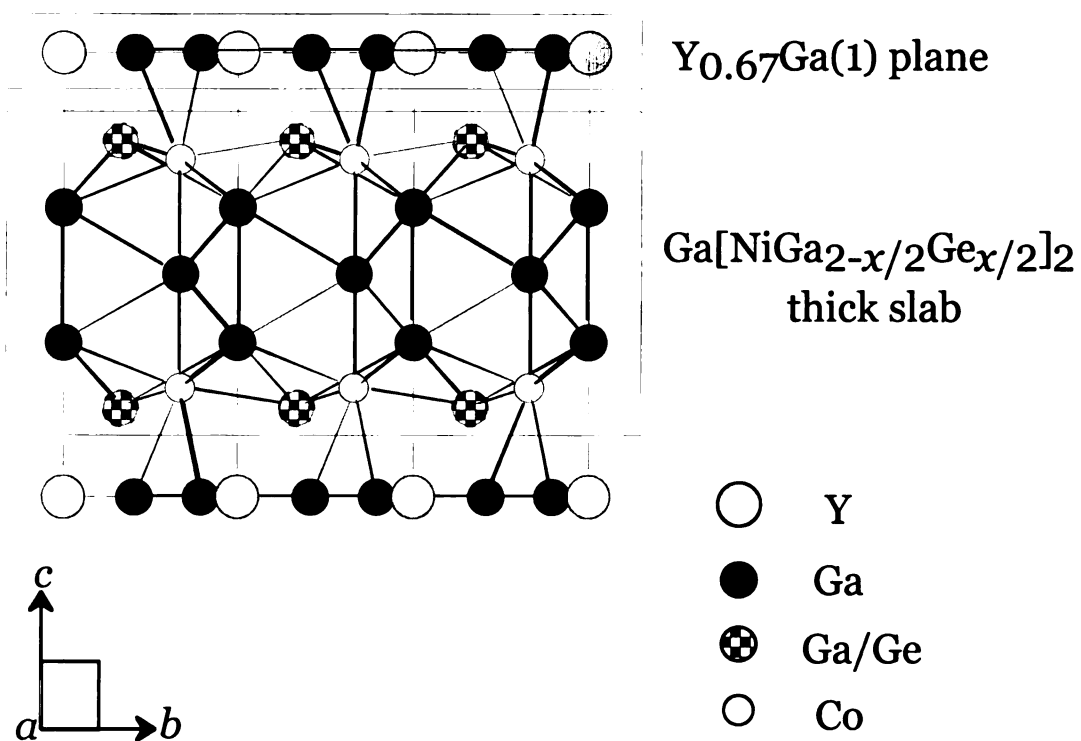


Figure V.11. Structure of Y_{0.67}Co₂Ga_{6-x}Ge_x (2) viewed along a -axis. The unit cells are shown in dashed lines.

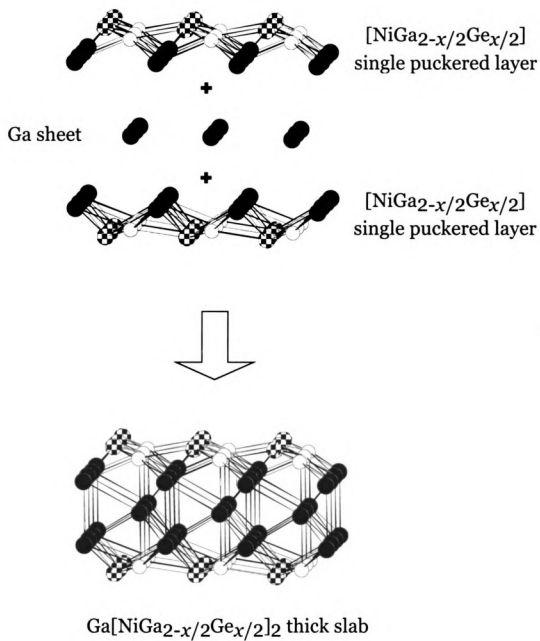


Figure V.12. The $[\text{NiGa}_{5-x}\text{Ge}_x]$ thick slab as a combination of Ga sheet sandwiched between two single $[\text{NiGa}_{2-x/2}\text{Ge}_{x/2}]$ puckered layers.

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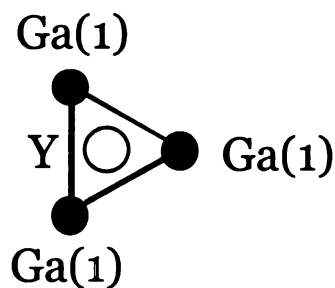
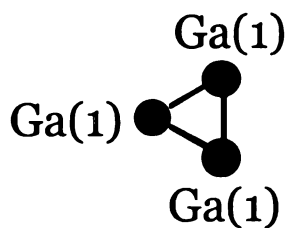
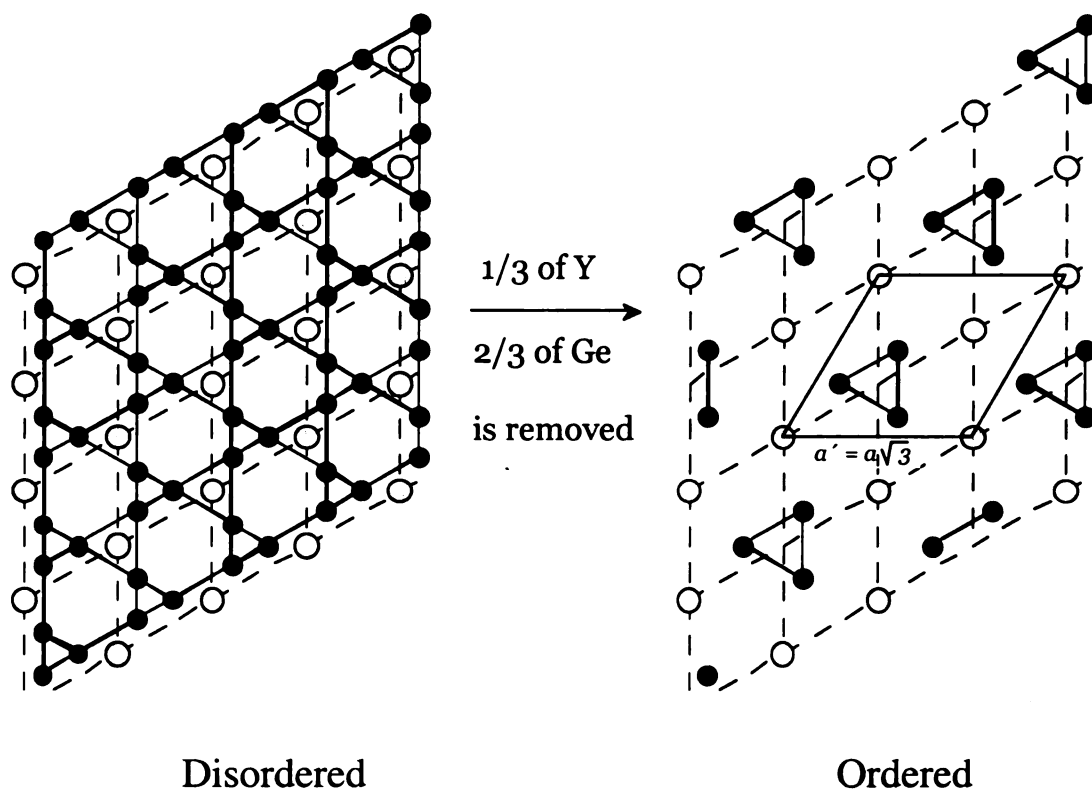
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The difference lies in the thickness of the layer and the way the single puckered layers are oriented against each other. As shown in Figure V.12, the $\text{Ga}[\text{CoGa}_{2-x/2}\text{Ge}_{x/2}]_2$ thick slab is constructed of two single puckered layers, identical to those of **1**, but this time an additional Ga sheet is sandwiched between them. The two puckered layers in **2** are related to each other by mirror symmetry (mirror plane contains the extra Ga sheet), and connected via Ga atoms ($\text{Ga}(3)\text{--Ga}(3) = 2.781(2) \text{ \AA}$) and through Co atoms bonded to Ga(4) atoms of Ga sheet ($\text{Co--Ga}(4) = 2.366(3) \text{ \AA}$). In **1**, the puckered layers in addition to the mirror symmetry are rotated 60° with respect to each other.

The $\text{Y}_{0.67}\text{Ga}$ planes in the structure of **2** are identical to those found in **1**, see Figure V.13. A similar type of disorder between Y and Ga(1) atoms is observed with short Ga-Ga ($1.57 \text{ \AA}$) and Y-Ga ($1.51 \text{ \AA}$) distances. As it was discussed above, the ordered arrangement (with the super-cell parameter $a' = a\sqrt{3}$) of Y and Ga atoms in the plane can be achieved if 1/3 of Y atoms and 2/3 of Ga atoms were removed. This ordered type of plane is given on the right of Figure V.13.

enter



$$\text{Ga(1)} - \text{Ga(1)} = 1.57(3) \text{ \AA} \quad \text{Y} - \text{Ga(1)} = 1.508(2) \text{ \AA}$$

Figure V.13. The Y-Ga plane in **2** viewed along *c*-axis (left). An ordered model of $\text{Y}_{0.67}\text{Ga}$ plane given for comparison (right). The disordered Ga(1)_3 triangle and Y-centered Ga(1)_3 triangle, shown below, create unreasonably short interatomic distances.

The local coordination environments of Y, Co, Ga, and M(2) atoms are depicted in Figure V.14. The disordered M(1) atoms are omitted for clarity. The Y atoms are in the center of the trigonal prism formed by six M(2) atoms (Y–M(2) bond distance is 3.0509(8) Å) and two Co atoms (Y–Co = 3.230(1) Å). The Co atoms are seven-coordinate, and bonded to three Ga(3) and three M(2) atoms of the puckered layer, and to one Ga(4) atom at 2.366(3) Å of Ga sheet. The atoms on the mixed-occupancy M(2) site, being part of the puckered layer, are connected to three Co and three Ga(3) atoms at a distance of 2.4458(5) Å and 2.7735(7) Å, respectively. The Ga(3) atoms are ten-coordinate, self-bonded at 2.781(2) Å and also connected to three Ga(4) atoms of the Ga-sheet at 2.7864(6) Å to link two puckered layers. The Ga(3) coordination environment includes another six atoms: three Co at 2.604(1) Å and three M(2) atoms. The bi-capped trigonal prism of two Co and six Ga(3) atoms comprises the coordination polyhedron of Ga(4).

Figur

$Y_{t,5}$ -C

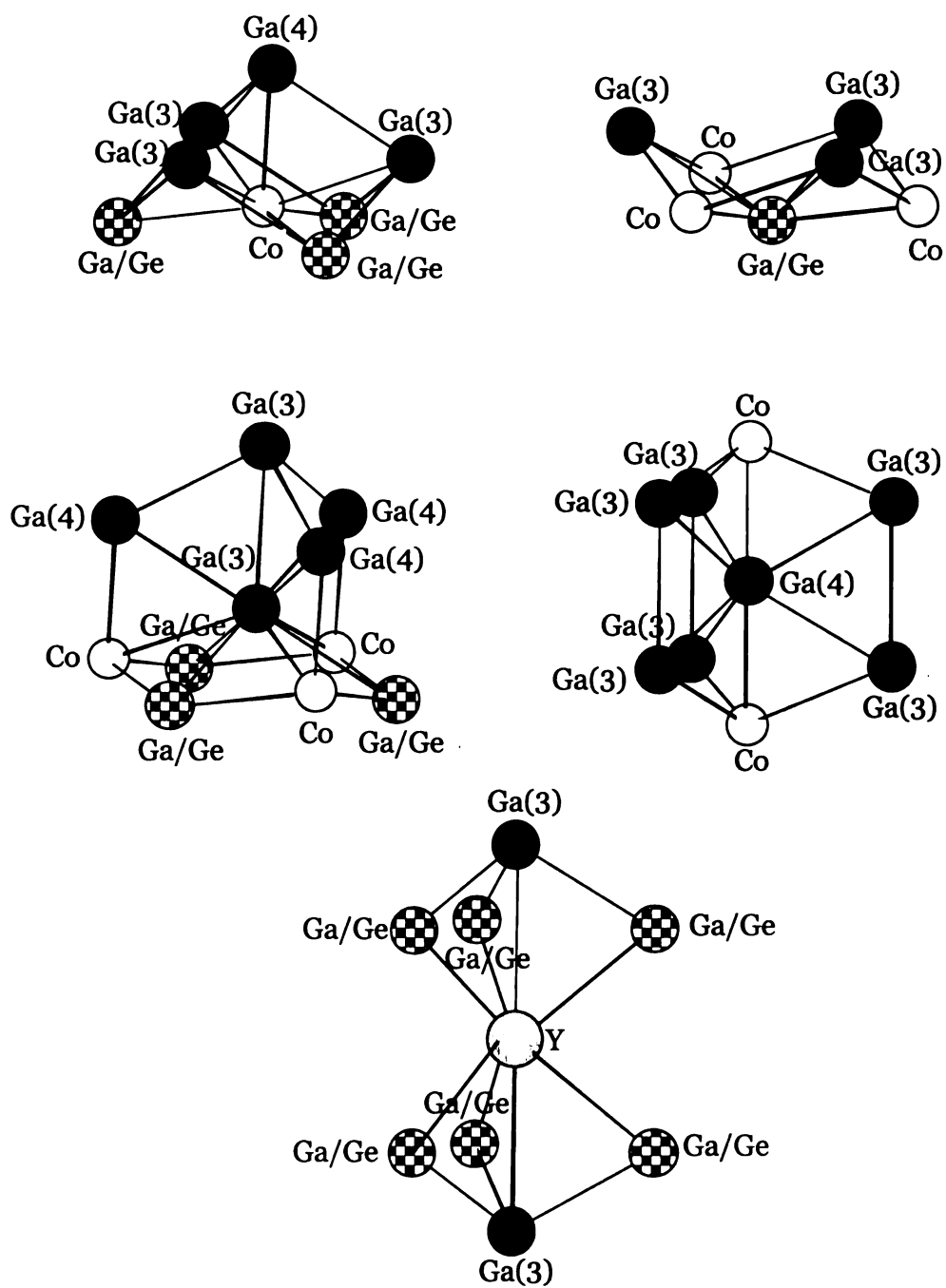


Figure V.14. Local coordination of Y, Co, Ga and Ga/Ge atoms in the structure of

$Y_{0.67}Co_2Ga_{6-x}Ge_x$ (2); the disorder Ga(1) atoms are omitted for clarity.

Superstructure of 1

The disorder observed in the analogs of **1** and **2** is not the only one of its kind. Similar disorder between RE and Al atoms in the RE-Al plane was observed in the RE₂._xPt₄Ga_{8+y}¹⁵, RENi₃Al₉²⁴ and RE₄Pt₉Al₂₄²⁵ family of compounds. As found by Gladyshevskii *et al.*²⁴, the Y and Dy analogs of RENi₃Al₉ exhibit partially disordered arrangements of RE and Al atoms in a triangular mesh. In this case, the apparent distance between RE and Al in the Al₃ triangle was reported to be ~1.5 Å. Interestingly, the Er and Gd analogs show an ordered arrangement with regular interatomic distances. Following the description given by Gladyshevskii, it is easy to model an ordered atomic arrangement from the disordered YGa(1)₃ plane by removing 1/3 of Y atoms and 2/3 of Ga(1) atoms: $Y \times 2/3 + Ga(1)_3 \times 1/3 = Y_{0.67}Ga(1)$, see Figure V.3c. Thus, if every third Y atom is removed, and the three Ga atoms that surround the remaining Y atom are also removed, as shown on the right of Figure V.3c, one obtains a perfectly ordered structure with reasonable Ga(1)–Ga(1) bond distances of about 2.5 Å. This larger unit cell is now characterized by a lattice parameter $a' = a\sqrt{3}$, where a is the parameter of the original sub-cell. The partial occupancies of 2/3 and 1/3 found for the Y and Ga(1) atoms respectively in **1** point to the validity of the given model. This exact type of arrangement, with $a\sqrt{3}$ super-cell, was observed in the ordered GdNi₃Al₉, ErNi₃Al₉ and in SmNi₃Ga₉²⁶. A similar ordered arrangement was reported by Thiede²⁵ *et al.* for Er₄Pt₉Al₂₄ described in a triclinic (space group $P\bar{1}$) super-cell.

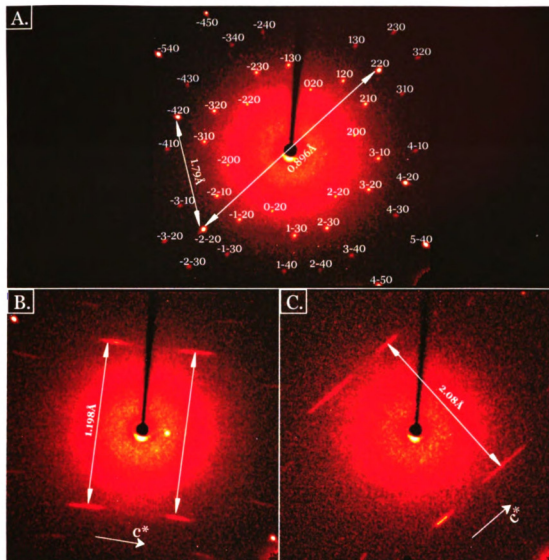


Figure V.15. Zone photographs of $\text{Ho}_{0.67}\text{Ni}_2\text{Ga}_{5.4}\text{Ge}_8$. (A) $hk0$ zone; (B) $h0l$ zone; (C) okl zone. Exposure time 360 seconds.

Despite these indications, numerous cell refinements using the collected X-ray data, performed on a number of analogs of **1**, failed to prove the existence of a proper $a\sqrt{3} \times a\sqrt{3} \times 3c$ superstructure. However, long exposure zone photographs ($hk0$, $0kl$, $h0l$) recorded on various crystals shed considerable light on the nature of the disorder and the presence of the $a\sqrt{3} \times a\sqrt{3}$ super-structure and provided useful information in understanding the mechanism of the crystal structure formation of this phase. Two features of the zone photographs are of extreme importance. First, in the $hk0$ zone photograph the reflection spots do indeed correspond to a $a\sqrt{3} \times a\sqrt{3}$ super-cell of 7.1864(7) Å, see Figure V.15A. This diffraction pattern shows that the true cell (in the ab plane) is three times larger than the original one, and hence, the arrangement of RE and Ga atoms in the plane may in fact be ordered. Second, the $h0l$ and $0kl$ zone photographs, shown in Figures 15B and 15C, reveal diffuse scattering and streaking along the l -direction instead of regularly spaced discrete Bragg reflection spots.

Similarly, the $[120]$ zone selected area electron diffraction pattern taken on $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ analog of **1** and depicted in Figure V.16A exhibits diffuse scattering along the c^* -axis. The streaking occurs between the hkl lines of reflections related to the subcell. The subcell reflections appear as well-defined Bragg spots, with the extinction conditions ($hhil$; $l = 2n$) consistent with the $P6_3/mmc$ space group. The major streaks occur at the distance of a $1/3$ between the subcell reflection spots. Because the $[120]$ zone is a view along the diagonal of the reciprocal subcell, the supercell modulation thus scales as $1/3 \cdot a^*\sqrt{3}$ with respect to the reciprocal subcell parameter a^* . In real space it would translate to $a\sqrt{3}$, where a is a unit cell parameter corresponding to the subcell. This exact modulation is seen also in the X-ray zone photographs, as the $hk0$ zone for example

features the $a\sqrt{3} \times a\sqrt{3}$ supercell. The electron diffraction data is therefore in agreement with the results obtained from the X-ray diffraction. The corresponding thin area of the $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ single crystal is featureless, see Figure V.16B, and does not display any irregularities.

The observed streaks along the c^* -axis of the reciprocal unit cell are indicative of irregular non-periodic stacking of $\text{RE}_{0.67}\text{Ga}$ planes along the c -axis. In other words, the c -axis of the unit cell can be viewed as infinitely large, so that the zero-dimension reflection spots are replaced with grossly elongated diffuse lines. Therefore, we conclude that the disorder seen from diffraction experiments originates in the extensive and random stacking faults of *ordered* $\text{RE}_{0.67}\text{Ga}$ planes (with $a\sqrt{3} \times a\sqrt{3}$ super-cell) along the direction of the c -axis²⁴. Alternatively we can state that the $\text{RE}_{0.67}\text{Ga}$ planes appear to be sliding easily along the ab -plane creating stacking disorder along the c -axis. The statistical averaging of the randomly stacked planes results in a smaller unit cell (the one shown in Tables V.1 and V.2) and the observed disordered averaged picture. Thus the description of the $\text{YGa}(1)_3$ plane emerging from the refinement seems to be the result of a “folding over” or “projection” of the real structure onto a smaller unit cell.

In order to test other possibilities of preparing ordered variants of **1**, a prolonged annealing experiment was performed using ready-made crystals of $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ and $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Si}_x$. By employing extended heating times and moderate temperatures, we sought an improvement in the microscopic ordering in the crystal structures of **1** by allowing the system to arrive at its most energetically stable configuration, which, by chance could be the one that contains the ordered arrangements of RE-Ga planes. In this experiment, crystals of **1** were mixed with Al_2O_3 powder to prevent glass attack, sealed in

the quartz tube under vacuum and subjected to annealing at 750°C of one month duration. As a result, no crystals of **1** were available for further structure determination. Instead, a complete decomposition into elemental Ge (it formed spheres) or Si, Ni₃Ga₂ binary phase and pure Sm were observed upon the completion of annealing. Thus, the structures of **1** (both Ge and Si families) were not stable under the above mentioned conditions and decomposed over such a long period of time. It appears that the temperature of annealing (750 °C) is too high and causes the decay of quaternary compounds. As an alternative experiment with milder conditions (lower temperatures and shorter annealing time) may be suggested.

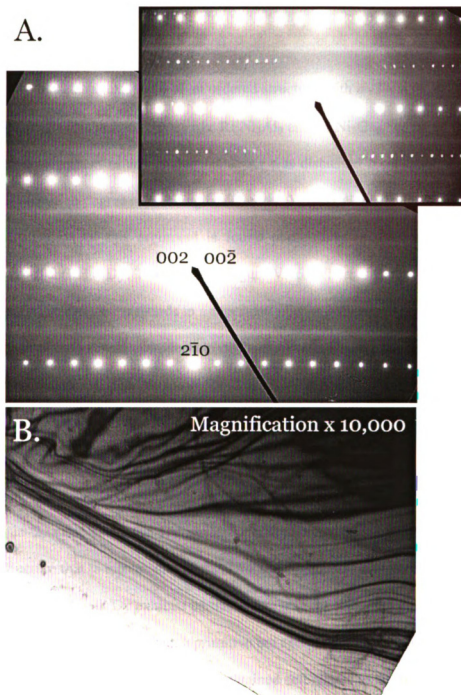


Figure V.16. (A) [120] zone selected area electron diffraction pattern of $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_5$. xGe_x single crystal. Individual Bragg spots are indexed in the subcell. (B) The TEM image of the corresponding thin area of the crystal.

Superstructure of 2

Even though the existence of an ordered structure with $a\sqrt{3} \times a\sqrt{3} \times 3c$ super-cell was found for isotopic ternary phases like RENi_3Al_9 and RENi_3Ga_9 , we could not observe an ordered arrangement in any analogs of **2**. As was discussed for **1**, such disorder can derive from the high degree of stacking faults of the $\text{Y}_{0.67}\text{Ga}$ planes in the direction of the c -axis. Justification of this argument is found particularly in the $hk0$ and $0kl$ zone photographs of **2** ($\text{RE} = \text{Dy}$, $\text{Tt} = \text{Ge}$), see Figure V.16. Whereas the indexing of the $hk0$ zone reflections clearly corresponds to a super-cell of $a' = a\sqrt{3}$, see Figure V.17A, the $0kl$ and $h0l$ zone photos reveal considerable diffuse scattering along the reciprocal c^* -axis (Figure V.17B and C). The situation for **2** is thus identical to that found in **1**, and therefore the disorder observed in these two homologous compounds is of the same origin.

Although a single crystal sample exhibiting an ordered super-structure could not be found in **2**, samples of the Dy analog appeared to be more ordered, showing an average structure that is intermediate between the sub-structure and super-structure. That is, the structure of **2** with Dy exhibits partial ordering in the $\text{RE}_{0.67}\text{Ga}$ plane. For instance, the $\text{Dy}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ crystallizes in a primitive hexagonal cell with parameters $a'' = a\sqrt{3} = 7.2536(8) \text{ \AA}$, $c'' = 2c = 18.308(3) \text{ \AA}$. The obtained cell relates to the sub-cell parameters (a, c) as $a\sqrt{3} \times a\sqrt{3} \times 2c$ and to the super-cell (a', c') as $a' \times a' \times 2/3c'$. The fully ordered super-structure unit cell, as it is for example for ErNi_3Al_9 , is $a' = 7.2716(5) \text{ \AA}$, $c' = 27.346(3) \text{ \AA}$.

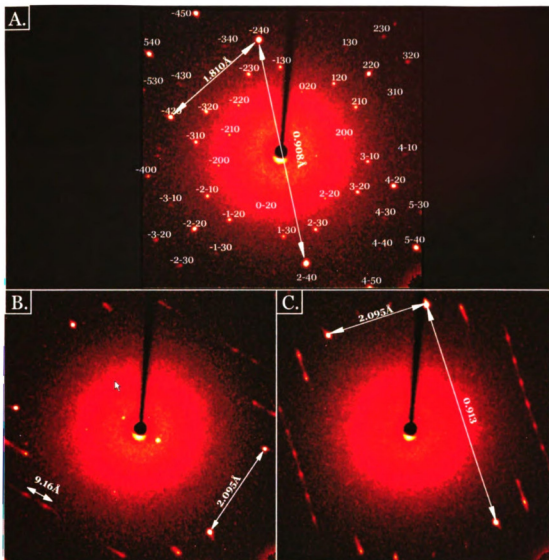


Figure V.17. Zone photographs of $\text{Dy}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$. (A) hko zone; indexing of the individual Bragg spots is given; (B) $h0l$ zone; (C) okl zone. Exposure time 360 seconds.

Because the volume of the unit cell of the Dy analogue of **2** is greater than that of the disordered substructure but, at the same time, less than that of the fully ordered superstructure, it could be regarded as an intermediate between the latter two. If measured in the volumes of the subcell, V , the volume of the intermediate supercell is $6V$, whereas the fully ordered superstructure has volume $9V$. The crystallographic result of this is a partial order in the RE–Ga(1) planes. The drawing of the RE–Ga plane of the Dy analog of **2** is depicted on Figure V.18 (center), and the RE–Ga planes of sub-structure and a super-structure are given for comparison to the left and to the right respectively. It is obvious from Figure V.18 that the central fragment depicting the Dy–Ga plane can be obtained from the disordered plane shown in the left-hand side by removing the Ga atoms from around half the Dy atoms. Those Dy atoms (Dy(1) in super-cell notation) are therefore ordered (do not have any atoms at short distances). The remaining half of Dy atoms (Dy(2)), is still disordered, i.e. three Z(2) atoms are bonded to every Dy(2) atom at very close distance defining a triangle. Likewise, Ga(1) atoms have Z(1) atoms in the center of the triangle which create short distances. If both Z(1) and Z(2) disordered atoms are removed, the ordered arrangement appearing on the right of Figure V.18 is obtained.

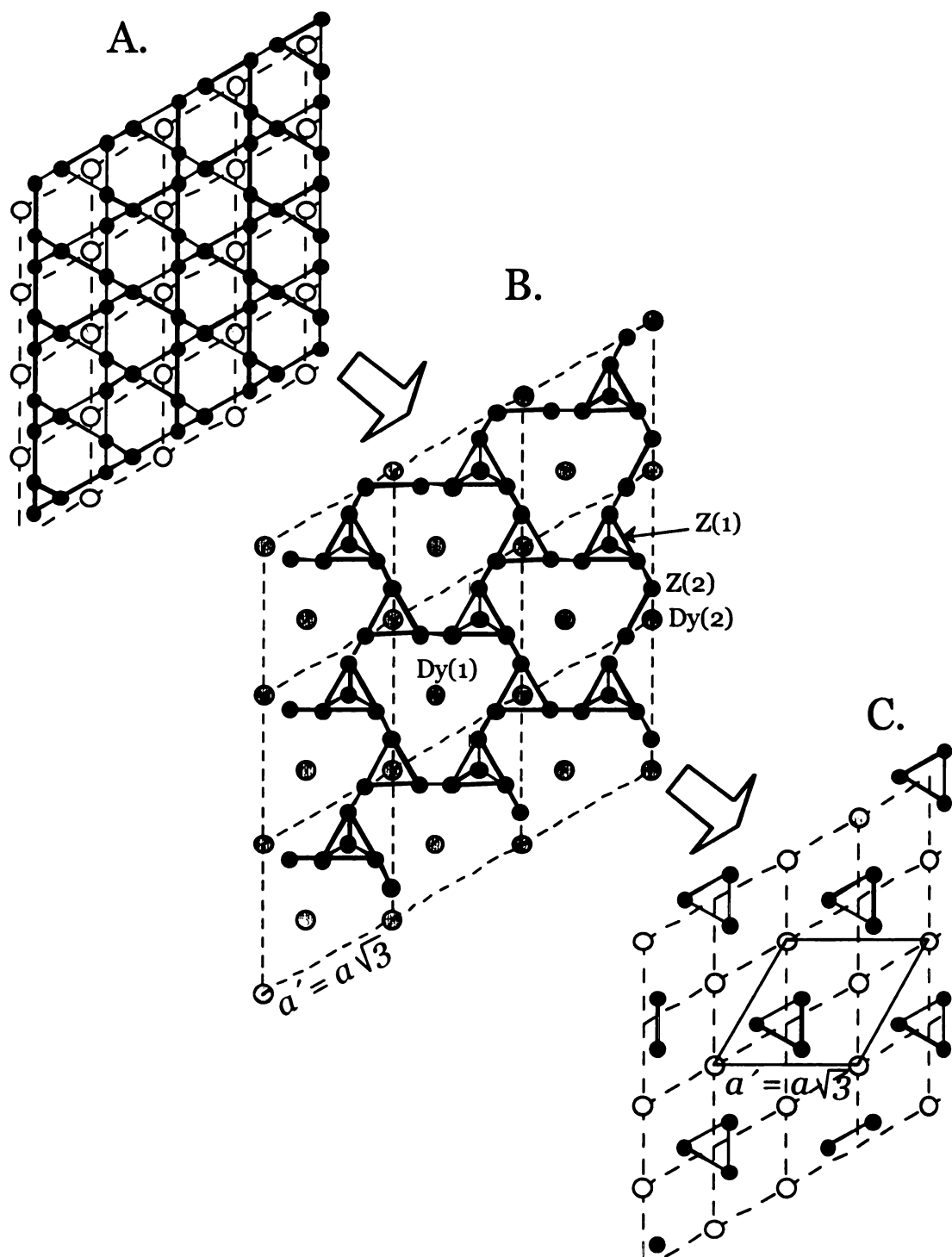


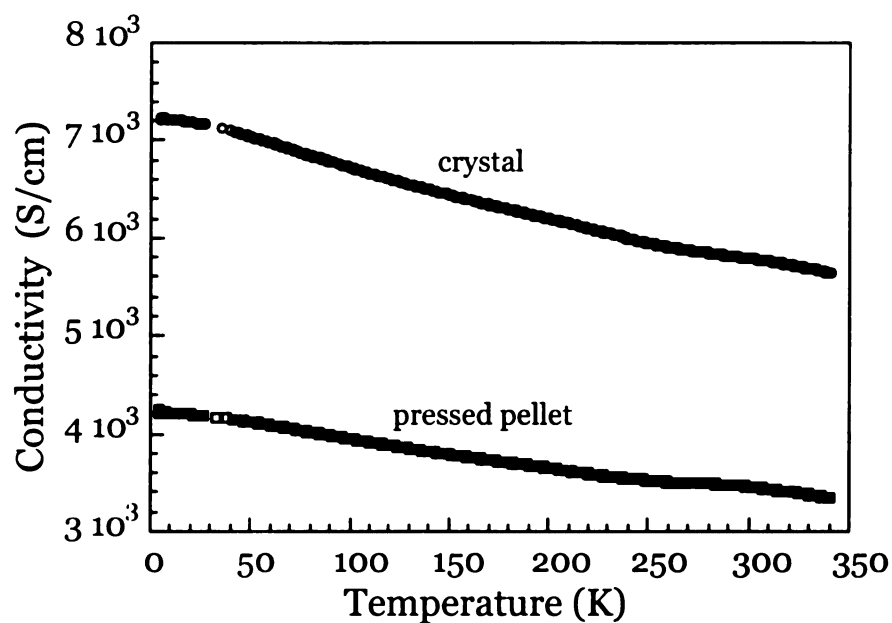
Figure V.18. The Dy-Ga plane with partial disorder found in $\text{Dy}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ (center); the RE-Ga(1) with complete disorder as found in $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (left), and ordered RE-Al plane observed in ErNi_3Al_9 structure type (right) are given for comparison.

Physical Properties

Transport Properties

Electrical conductivity and thermopower measurements were performed on single crystal and polycrystalline samples (pressed into pellets) of $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$. Figure V.19A depicts conductivity measured as a function of temperature in the region 2 – 350 K. The conductivity decreases linearly with temperature indicating metallic behavior. The room temperature conductivity is also consistent with metallic conductivity and is ~6000 S/cm for a single crystal sample, and ~3500 S/cm for a pressed pellet. Similar values (~10000 S/cm) were obtained for the related $\text{Sm}_2\text{NiGa}_{12}$ ²⁷ polygallide. The temperature dependence of the thermoelectric power measured between 20 and 300 K is shown in Figure V.19B. The values of the thermopower are very low in the whole temperature range, $\pm 0.5 \mu\text{V/K}$. Thus, a negative slope of the temperature dependence of the electrical conductivity coupled with the very low values of the thermoelectric power point to high metallic character of these compounds.

A.



B.

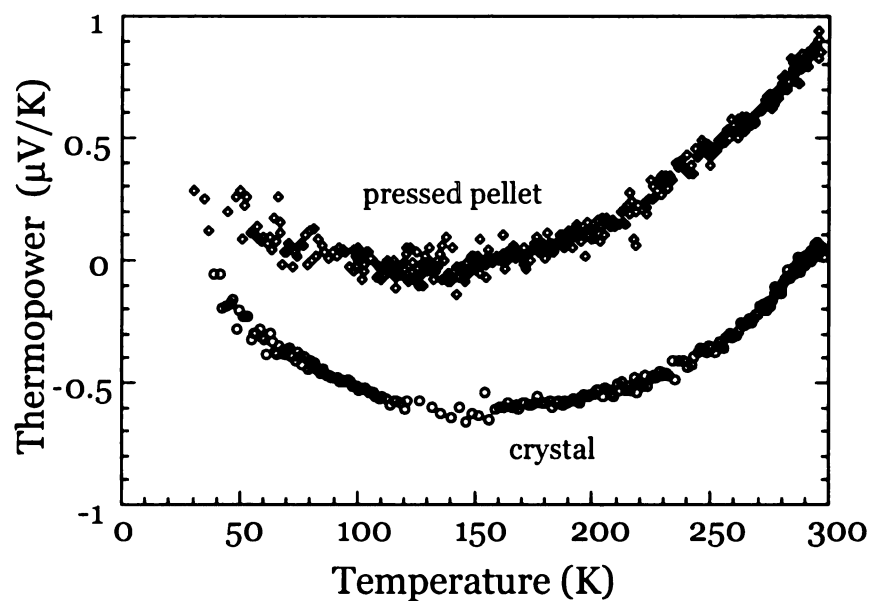


Figure V.19. (A) Electrical conductivity and (B) thermopower measurements as a function of temperature for $\text{Sm}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$.

Temperature Dependence of Susceptibility

Because of the explicit rod-like morphology and the large crystal size of **1** and **2** compounds we were able to study the magnetic response to an applied external magnetic field as a function of temperature in single crystal samples. Measurements on polycrystalline samples were also performed. Six analogs of **1** (RE = Y, Gd, Tb, Ho, Er, Tm) and two analogs of **2** (RE = Dy, and RE = Y, M = Co) with Ge were used for the measurements. The results are summarized in the Table V.19, and Figures V.20 and V.21.

The temperature dependence of the molar magnetic susceptibility χ_m (calculated per mole of RE) is shown in Figure V.20. At low temperatures (3–4 K), see inset, a well-pronounced χ_m maximum occurs for RE = Gd, Tb, Er. In the case of Dy two maxima at temperatures about 10 K and 3.5 K were observed. The RE = Ho and Tm, however, show no $T_{\max}$ which presumably lies at temperatures below 2 K, and outside of our experimental limits. Below the $T_{\max}$, some analogs such as Tb display irreversibility in the field-cooled (FC) and zero-field-cooled (ZFC) susceptibility. The ZFC part of χ_m is decreasing rapidly as the temperature drops below the $T_{\max}$, while the FC part of χ_m continues to rise even below $T_{\max}$. The maxima on the χ_m -T plots indicate possible anti-ferromagnetic ordering taking place at the temperature below $T_{\max}$.

The anisotropic measurements (with $H_{ex} \parallel c\text{-axis}$ or $H_{ex} \perp c\text{-axis}$) show that except for Gd, which magnetic response was invariant to the crystal orientation relative to the direction of H_{ex} , all other heavy RE analogues showed very different magnetic response at various crystal orientations. Hence, it could be seen from Figure V.20A that for Gd isotype of **1** the same scale was used for isotropic (χ_m^{iso}) and both of anisotropic χ_m ($\chi_m^{\parallel c}$ and $\chi_m^{\perp c}$). This is not the case for Tb, Dy, Ho, Er, Tm analogues, in which the values for $\chi_m^{\parallel c}$ could vary from $\chi_m^{\perp c}$ by up to the order of magnitude. For instance, $\chi_m^{\perp c}$ in Tb and Ho analogues, see Figure V.20B and 20D, is substantially greater than $\chi_m^{\parallel c}$, while for Er and Tm the situation is opposite, and $\chi_m^{\parallel c}$ is larger than the corresponding $\chi_m^{\perp c}$, see Figure V.20E and 20F. Thus, the interaction between the moments in Tb, Dy, Ho, Er, Tm analogues of **1** and **2** depends on the crystal orientation relative to the direction of H_{ex} . The observed phenomenon is a demonstration of the crystal field effect that results in anisotropy of the magnetic response. A closer look at the magnetic anisotropy caused by crystal field in analogues of **1** and **2** will be given soon after the field dependence of magnetization is considered.

Figure V.20.

(A) Temperature dependence of the molar magnetic susceptibility χ_m for single crystal and polycrystalline samples of $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1); the low temperature region is expanded in the inset at the upper right corner. The linear part of the inverse molar magnetic susceptibility χ_m^{-1} is shown below;

(B) Temperature dependence of the molar magnetic susceptibility χ_m for single crystal and polycrystalline samples of $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1); the low temperature region is expanded in the inset at the upper right corner. The linear part of the inverse molar magnetic susceptibility χ_m^{-1} is shown below.;

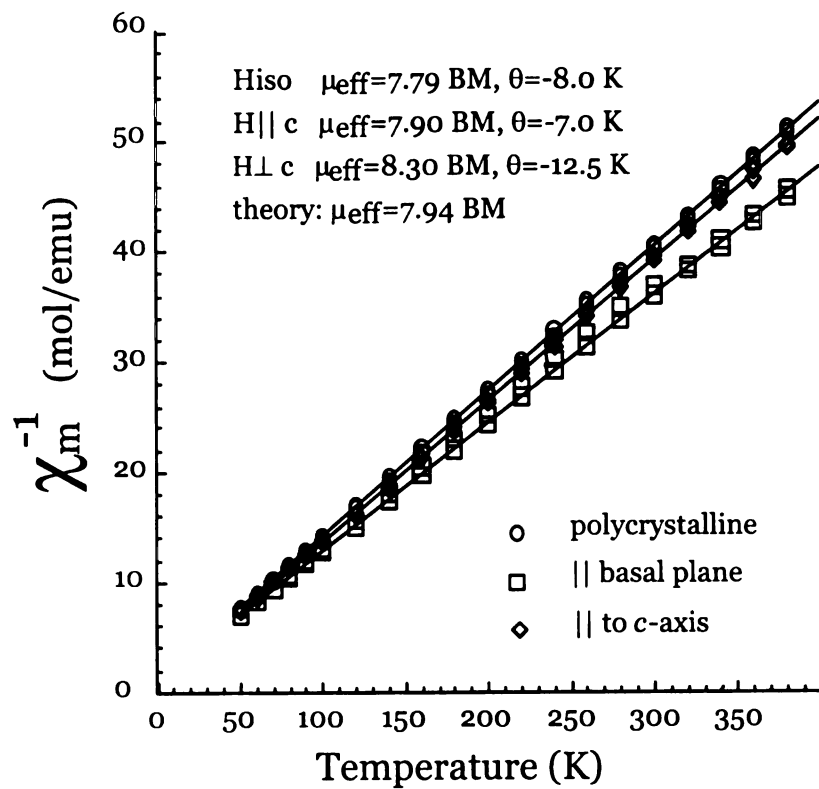
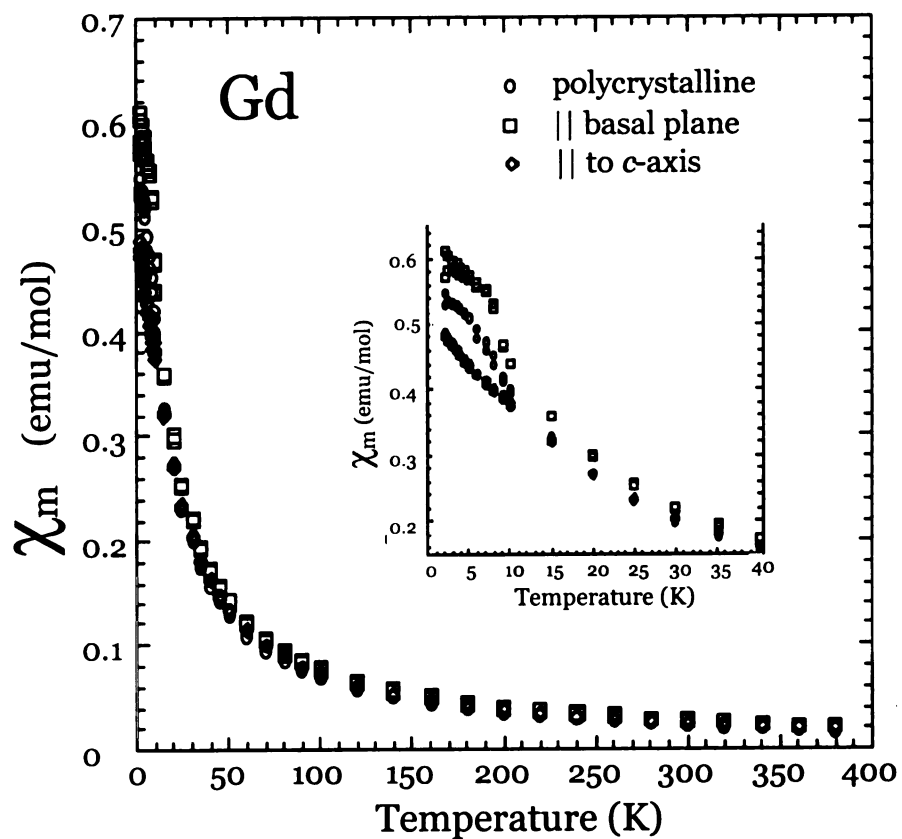
(C) Temperature dependence of the molar magnetic susceptibility χ_m for single crystal and polycrystalline samples of $\text{Dy}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ (2); the low temperature region is expanded in the inset at the upper right corner. The linear part of the inverse molar magnetic susceptibility χ_m^{-1} is shown below;

(D) Temperature dependence of the molar magnetic susceptibility χ_m for single crystal and polycrystalline samples of $\text{Er}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1); the low temperature region is expanded in the inset at the upper right corner. The linear part of the inverse molar magnetic susceptibility χ_m^{-1} is shown below;

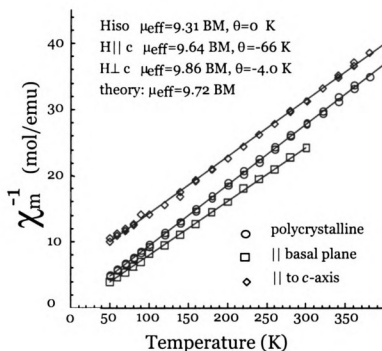
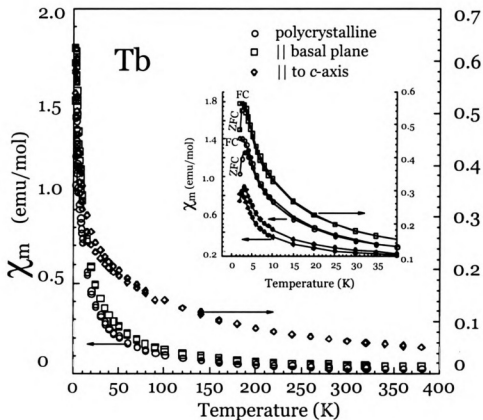
(E) Temperature dependence of the molar magnetic susceptibility χ_m for single crystal and polycrystalline samples of $\text{Ho}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1); the low temperature region is expanded in the inset at the upper right corner. The linear part of the inverse molar magnetic susceptibility χ_m^{-1} is shown below;

(F) Temperature dependence of the molar magnetic susceptibility χ_m for single crystal and polycrystalline samples of $\text{Tm}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1); the low temperature region is expanded in the inset at the upper right corner. The linear part of the inverse molar magnetic susceptibility χ_m^{-1} is shown below.

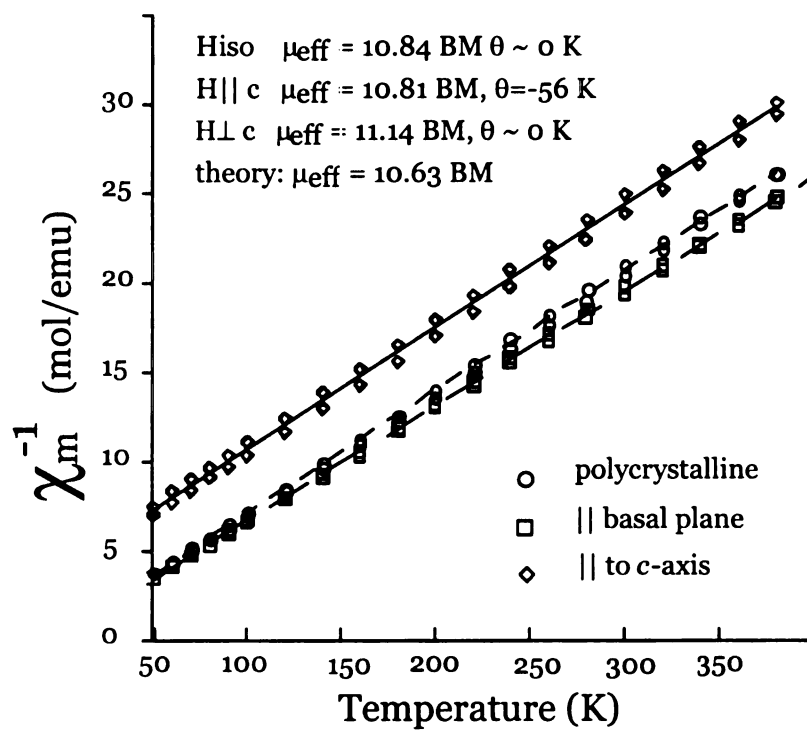
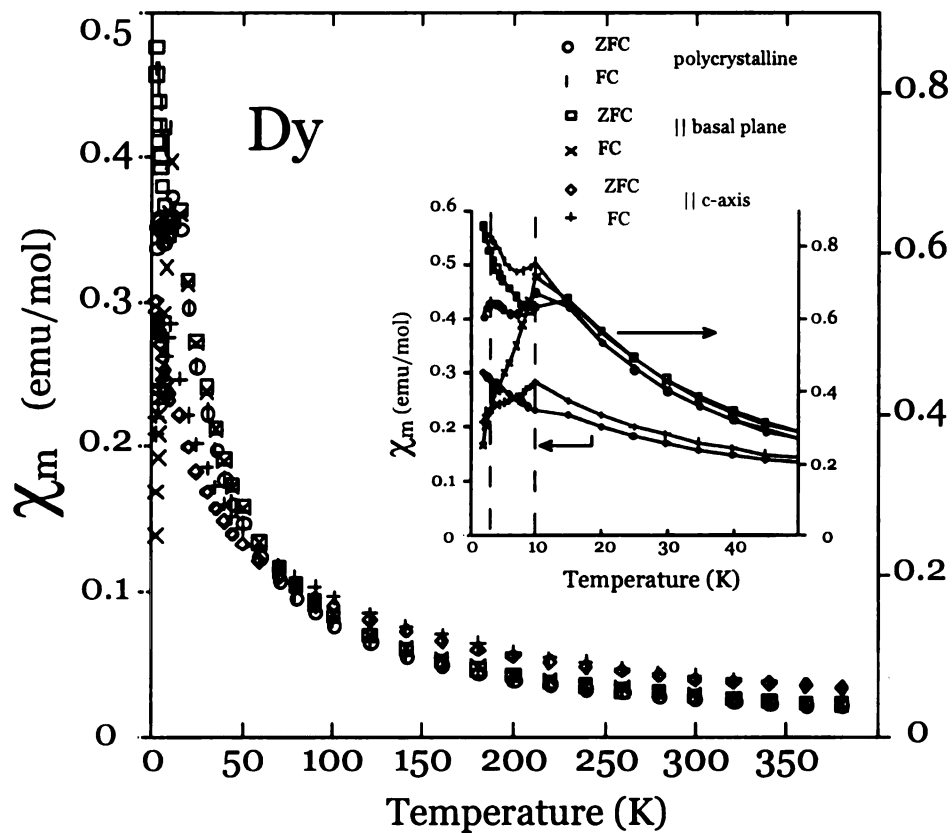
A.



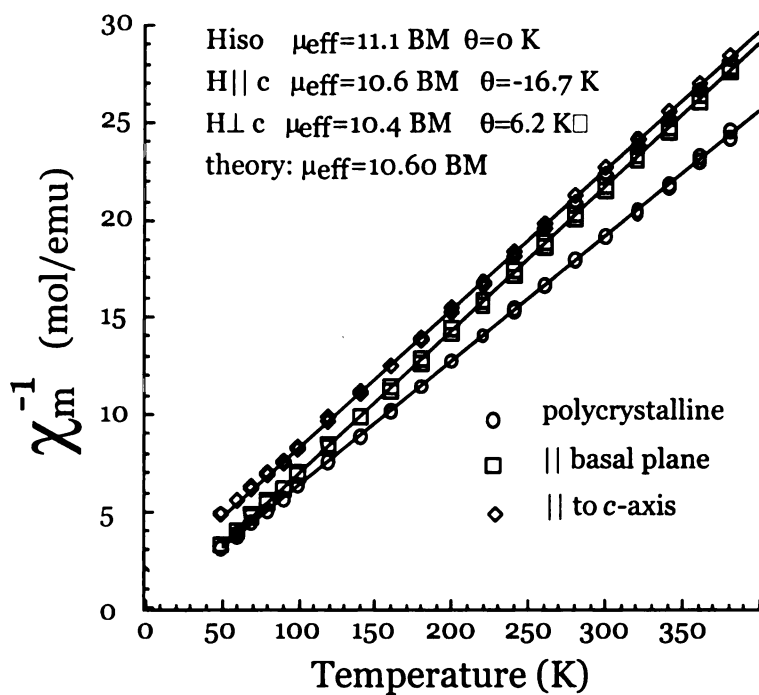
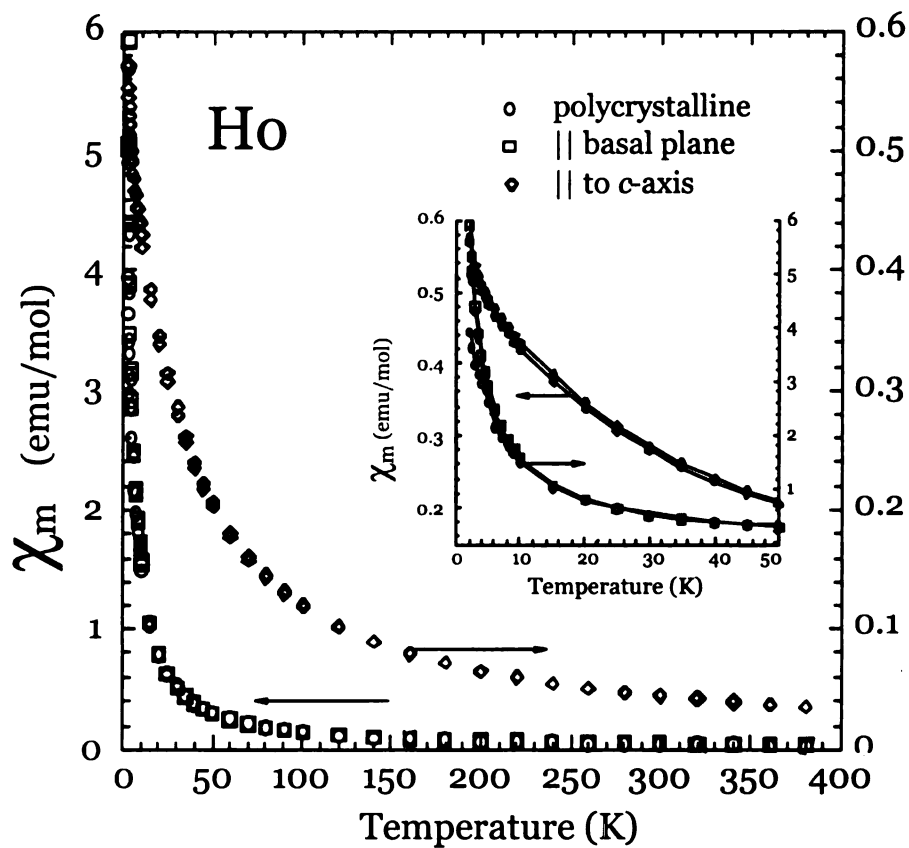
B.



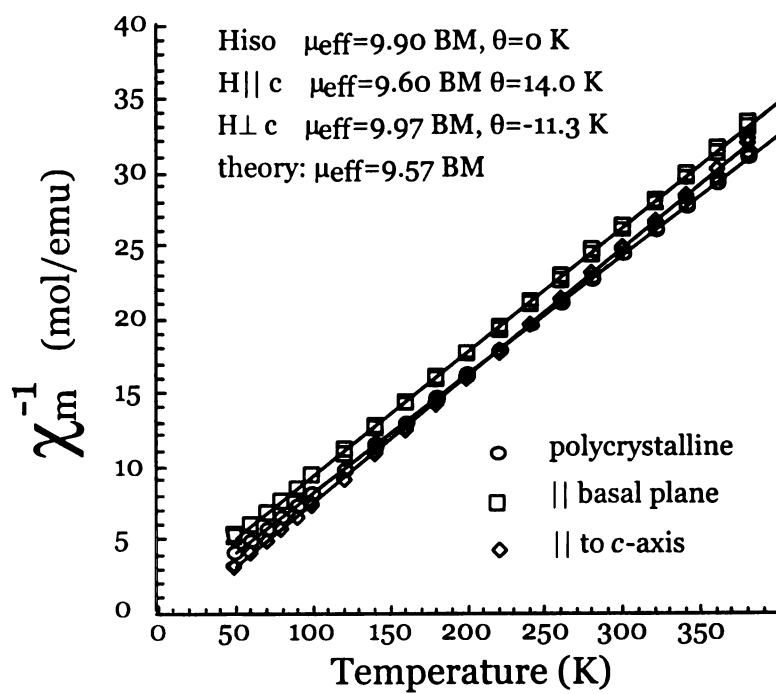
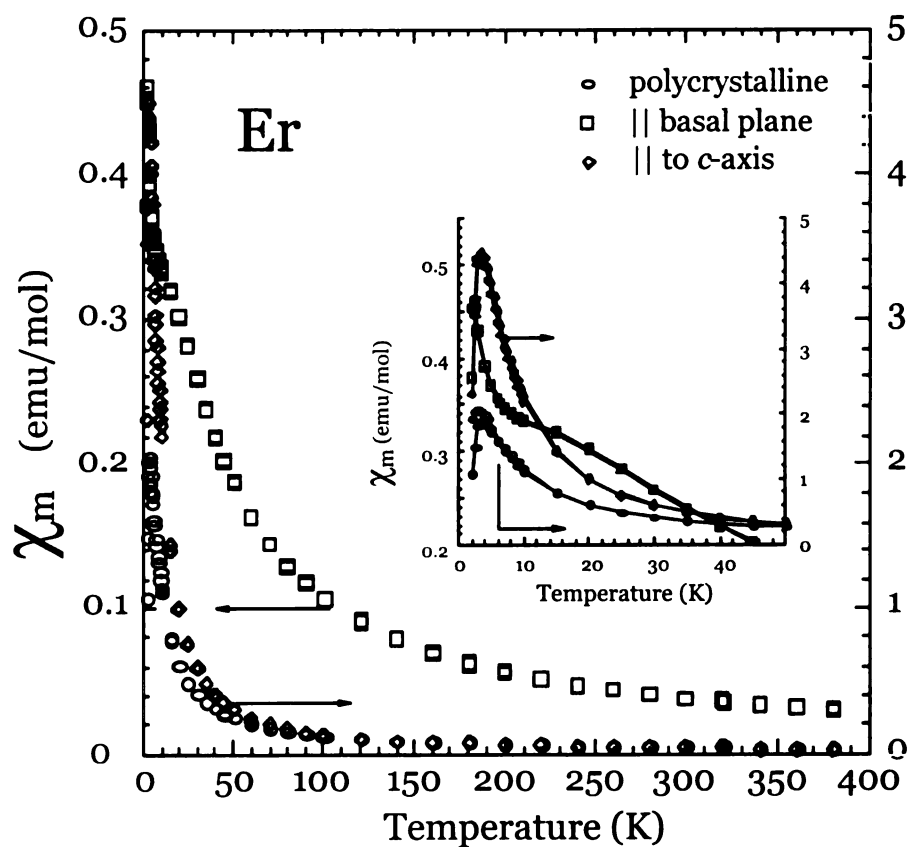
C.



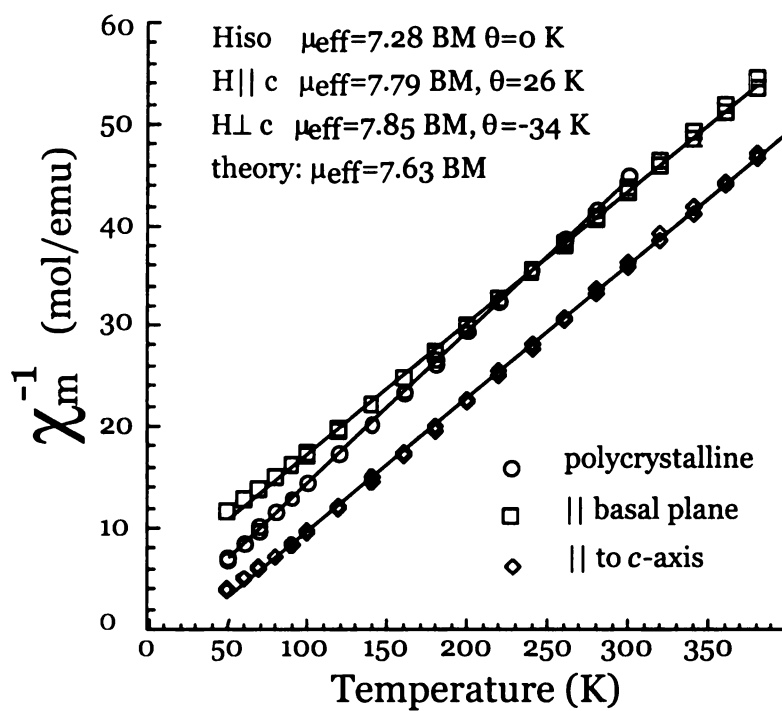
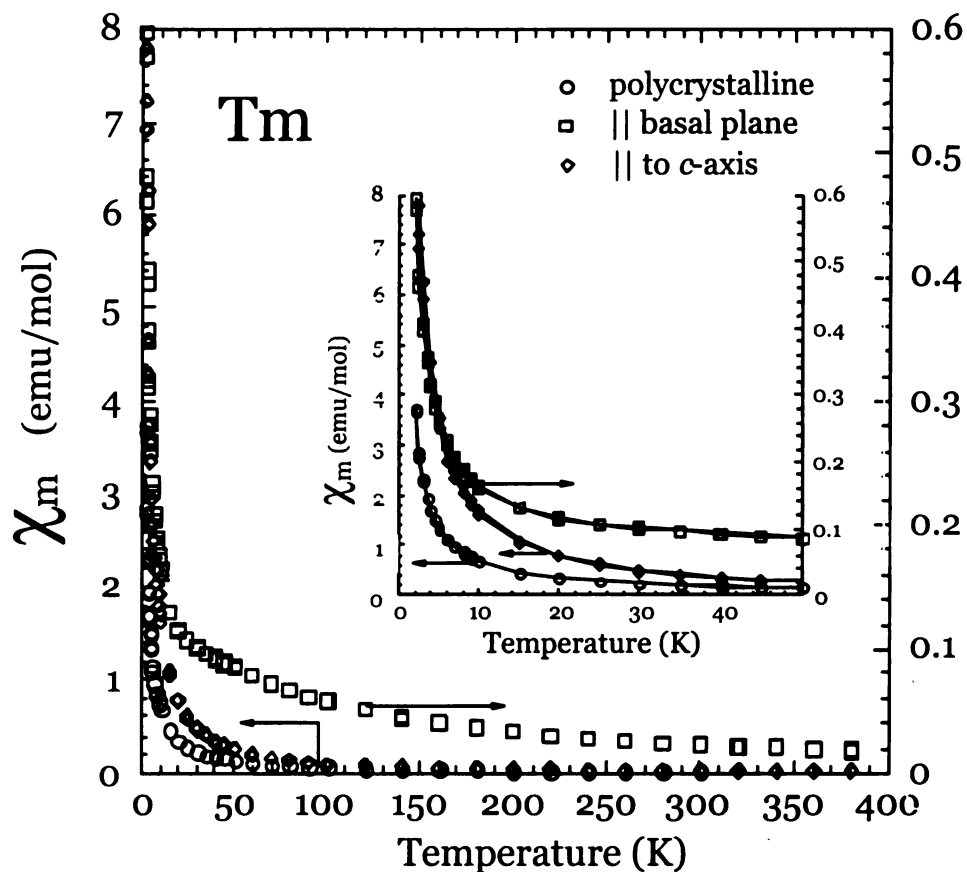
D.



E.



F.



At higher temperatures, the thermal energy becomes sufficient to disrupt the alignment of the magnetic moments, and the system falls into a paramagnetic state. The Curie law is obeyed in the isotropically averaged polycrystalline magnetic susceptibility χ_m^{iso} , while anisotropic $\chi_m^{\parallel c}$ and $\chi_m^{\perp c}$ exhibit Curie-Weiss behavior with the Weiss constant Θ ranging from -66 K to $+26$ K. The characteristic plots of the χ_m^{-1} versus T are shown in Figure V.20 (below). The effective magnetic moments (μ_{eff}) for different rare-earth analogs calculated from the linear part of the χ_m^{-1} versus T were found to be very close to the values expected for the free RE^{3+} ions²⁸. Thus the contribution to the magnetic susceptibility of these systems is due solely to the rare-earth atoms which are in +3 oxidation state, whereas the Ni atoms are in a non-magnetic state. Additionally, the temperature dependence of magnetization of **1** of the non-magnetic Y analog was measured to probe the magnetic state of Ni atoms. The results are consistent with non-magnetic behavior of Ni and show very small room temperature magnetization of about $8.77 \cdot 10^{-5} \text{ emu} \cdot \text{mol}^{-1}$ with very weak temperature variation $d\chi_m/dT$ of $-7.0 \cdot 10^{-7} \text{ emu} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. A similar diamagnetic behavior was observed for Y analog of **2** with Co ($\chi_m^{\text{RT}} = 7.50 \cdot 10^{-5} \text{ emu} \cdot \text{mol}^{-1}$; $d\chi_m/dT = -8.6 \cdot 10^{-7} \text{ emu} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), which supports the general idea that in these types of RE/M/Tt/Al(Ga) compounds the transition metals are in non-magnetic states. The values of μ_{eff} , $\Theta_{\parallel c}$, and $\Theta_{\perp c}$ for the isotropic and anisotropic measurements, as well as the average value of μ_{eff} are given in the Table V.19.

Figure V.21.

(A) Anisotropic and isotropic field dependence magnetization curves (μ_{BM} /per Gd ion) of $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1) measured at $T = 2$ K;

(B) Anisotropic and isotropic field dependence magnetization curves (μ_{BM} /per Tb ion) of $\text{Tb}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1) measured at $T = 2$ K;

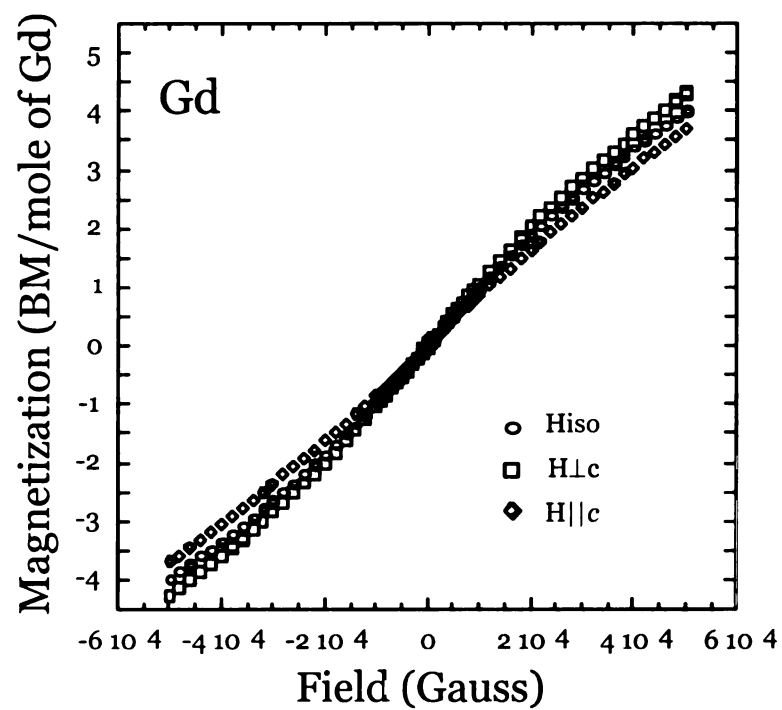
(C) Anisotropic and isotropic field dependence magnetization curves (μ_{BM} /per Dy ion) of $\text{Dy}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (2) measured at $T = 2$ K;

(D) Anisotropic and isotropic field dependence magnetization curves (μ_{BM} /per Er ion) of $\text{Er}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1) measured at $T = 2$ K;

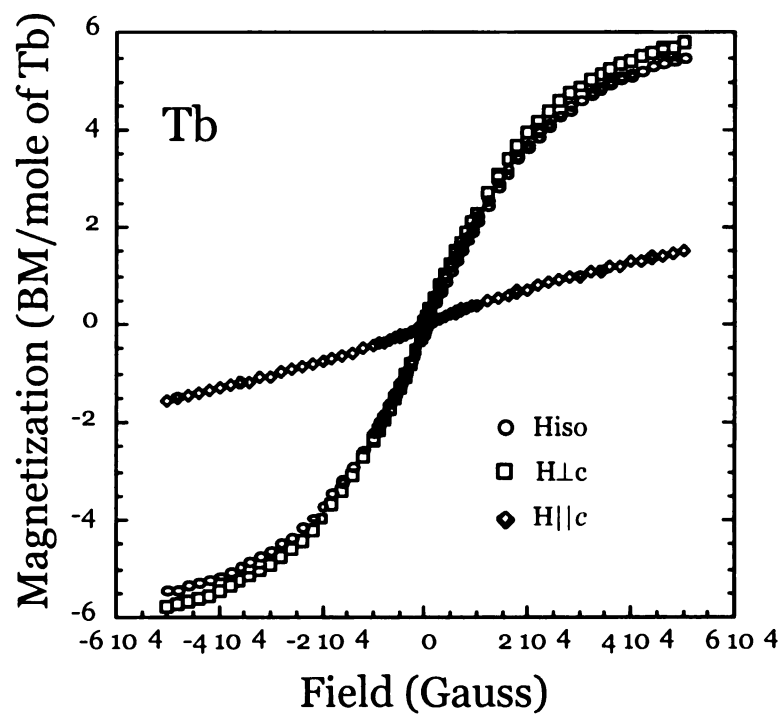
(E) Anisotropic and isotropic field dependence magnetization curves (μ_{BM} /per Ho ion) of $\text{Ho}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1) measured at $T = 2$ K;

(F) Anisotropic and isotropic field dependence magnetization curves (μ_{BM} /per Tm ion) of $\text{Tm}_{0.67}\text{Ni}_2\text{Ga}_{5-x}\text{Ge}_x$ (1) measured at $T = 2$ K.

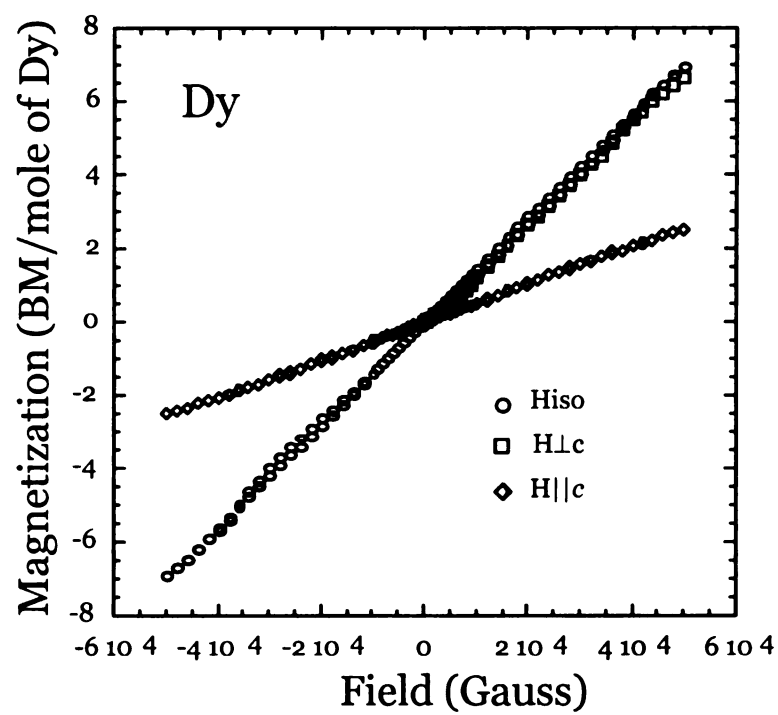
A.



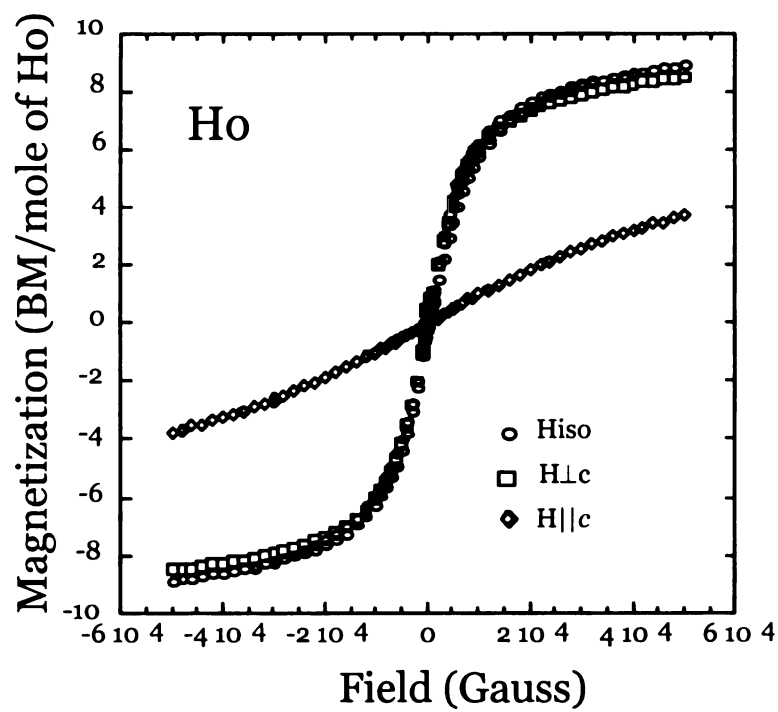
B.



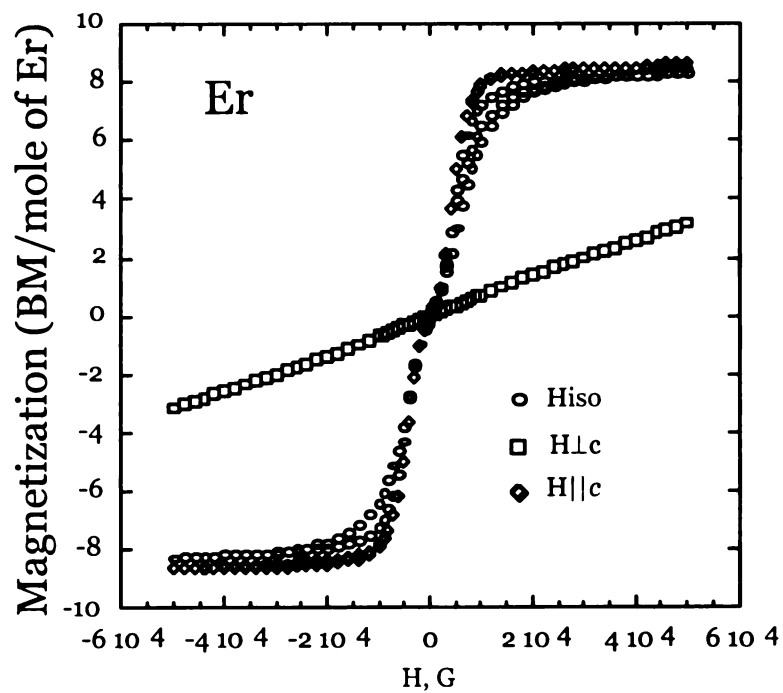
C.



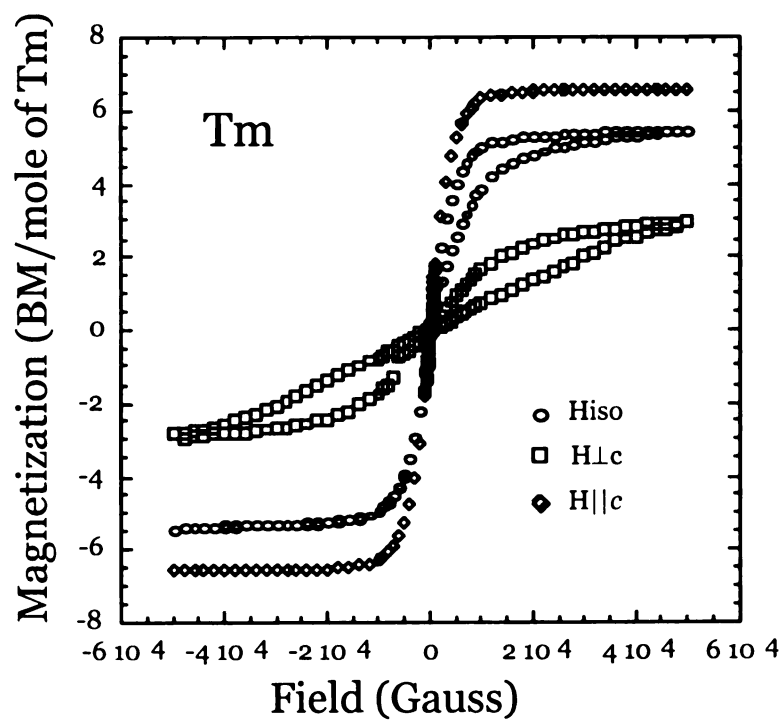
D.



E.



F.



Field Dependence of Magnetization

The field dependence magnetization curves of **1** (RE = Gd, Tb, Ho, Er and Tm) and **2** (RE = Dy) are shown in Figure V.21. The Gd analog of **1** has the only rare earth ion in this series which does not have a contribution from the orbital momentum to the total momentum. Magnetization curves do not exhibit anisotropy effects up to the fields of 5 T. The magnetization at 5 T reaches only 70% of its saturation value. In the case of Tb and Ho analogs of **1**, substantial basal plane anisotropy is observed (basal plane, or *ab*-plane lies perpendicular to the *c*-axis). Although at the fields $H \perp c$ of 5 T only the onset of the saturation is observed, the direction perpendicular to the *c*-axis is the magnetically easy axis, and the magnetic moments are constrained to the basal plane. In the case of $H \parallel c$, $\mu_{\text{eff}}^{\text{Hys}}$ yields $\sim 1.5 \mu_{\text{BM}}$ and $\sim 4 \mu_{\text{BM}}$ for Tb and Ho respectively, which is about 15% and 40 % of the saturation value. A similar situation is observed for the Dy analog of **2**. A magnetic moment of $\sim 7 \mu_{\text{BM}}$ (70 % of saturation value) is developed at 5 T when the applied magnetic field is directed parallel to the basal plane, and only $\sim 2.5 \mu_{\text{BM}}$ if it is oriented parallel to *c*-axis.

Unlike the Tb and Ho analogs, the basal plane of Er and Tm is magnetically hard, *i.e.* the easy axis does not lie in the basal plane. A moment of only $\sim 3 \mu_{\text{BM}}$ is developed in basal plane in a 5 T field. However, an application of an external field of only 1 T along the *c*-axis yields a full saturation moment of $\sim 9 \mu_{\text{BM}}$ for the case of Er, and $\sim 7 \mu_{\text{BM}}$ for the case of Tm. Thus, in these two cases the [001] direction defines the magnetically easy axis.

Magnetic Anisotropy

The large magnetic anisotropy found in the analogs of **1** and **2** parallels the behavior observed in the heavy rare-earth metals²⁹ themselves. The latter has been attributed to the interaction of Coulomb crystal field and non-spherical *4f* charge cloud distribution based on the single-ion approximation. The effect of the crystal field is small compare to the exchange and is manifested as an anisotropy, *i.e.* a tendency to align the charge clouds (and magnetic moments together with it) along the crystal axis. In a phenomenological form the effect of the crystal field of hexagonal symmetry can be expressed as the potential:^{30,31}

$$V = A_2^0 \alpha \langle r^2 \rangle Y_2^0(\mathbf{J}) + A_4^0 \beta \langle r^4 \rangle Y_4^0(\mathbf{J}) + A_6^0 \gamma \langle r^6 \rangle Y_6^0(\mathbf{J}) + A_6^6 \gamma \langle r^6 \rangle Y_6^6(\mathbf{J})$$

The numerical constants^{32,33} α , β , γ (Stevens' constants), the averages over the *4f* wave functions $\langle r^l \rangle$, and operator equivalents of spherical harmonics $Y_l^m(\mathbf{J})$ are the properties of free ion, while the electric field components A_l^m are properties of the crystal lattice. The magnetic anisotropy energy in terms of the anisotropy coefficients K_l^m and spherical harmonics $Y_l^m(\theta, \varphi)$ can be written as

$$E_K = K_2 Y_2^0(\theta, \varphi) + K_4 Y_4^0(\theta, \varphi) + K_6 Y_6^0(\theta, \varphi) + K_6^6 Y_6^6(\theta, \varphi),$$

where θ and φ are the angles between the direction of the magnetic moment and *c*- and *a*-axis respectively. The K_l (*i.e.* K_2 , K_4 , K_6) uniaxial anisotropy is dominant in the pure

heavy RE metals, and among these the two-fold anisotropy constant K_2 has the largest contribution to the anisotropy energy. Moreover, the magnitudes of K_2 scale approximately with the corresponding Stevens' constant α , while A_2^0 and $\langle r^2 \rangle$ show only small variation in the heavy RE series^{30,34}. The sign of α determines for the most part the direction of the anisotropy: $\alpha < 0$ for Tb, Dy and Ho, and the magnetically easy axis lies in basal plane; $\alpha > 0$ for Er, and Tm, and the direction of the magnetically easy axis coincides with the c -axis of the hexagonal cell. In the case of Gd, which has an S ground state, $\alpha = 0$, and as a consequence the single-ion contribution to the anisotropy vanishes, giving a nearly isotropic magnetization for Gd.

Because qualitatively similar results were obtained for the quaternary phases as for the pure RE metals^{29,30}, we became interested in the magnitude of the magnetic anisotropy energy in these compounds, particularly in K_2^0 . Although the crystal structures of **1** and **2** are far more complicated than the close packed structures of elemental RE, the local coordination of the RE atoms is somewhat similar in both structures. Yet, even with the knowledge of the symmetry and the local environment of RE atoms in **1** and **2**, it is hard to apply a point charge model approximation in order to calculate the crystal field potential.³⁵ However, the anisotropy constant K_2^{para} can be obtained experimentally from the Weiss constant anisotropy $\Delta\Theta = \Theta_{\parallel} - \Theta_{\perp}$ according to the equation³⁰:

$$k\Delta\Theta = 3[4J(J+1) - 3] K_2^{\text{para}} / 10J(2J-1)$$

where J is the total angular momentum and k is a Boltzman constant. The values of K_2^{para} for the heavy RE analogs of **1** and **2** are listed in Table V.11; the theoretical values of K_2^0

calculated for heavy RE metals are given for comparison. The agreement between K_2^{para} and K_2^0 is as surprising as it is striking, considering the large differences in the crystal structures between the quaternary phases described here and those of RE elements. It is plausible to consider that perhaps the strength of the interaction of the crystal field with the local magnetic moments is dictated primarily by the properties of the free rare-earth ion (α , $\langle r^f \rangle$, $Y,^m(J)$), and only secondarily by the properties of the crystal field.

4. Conclusion

The exploratory reaction chemistry in the quaternary system RE/Ni/Ga/Tt, where RE = Y, Sm, Dy, Gd, Tb, Ho, Er, Tm and Yb with Tt = Si or Ge, and RE/Co/Ga/Ge with RE = Y and Gd using liquid Ga led to two types of new intermetallic phases of the formula $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Tt}_x$, $n = 0, 1$. The crystal structures of these compounds were solved with single crystal X-ray diffraction and the distribution of Ga and Ge in these structures was studied with single crystal neutron diffraction. Neutron refinement revealed the location of Ge in a mixed occupancy site consisting of 67% of Ga and 33% of Ge. The structures of these phases are related and can be represented as a consequent stacking of the $\text{RE}_{0.67}\text{Ga}$ planes and $\text{Ga}_n[\text{Ni}_2\text{Ga}_{4-x}\text{Tt}_x]$ thick slabs along the c -axis. A common feature is shared by the phases, namely the disorder of the $\text{RE}_{0.67}\text{Ga}$ layer, where the atoms of RE and Ga form a triangular mesh with unreasonably close distances. The observed disorder is an average picture that emerges from the random and continuous stacking faults of ordered $\text{RE}_{0.67}\text{Ga}$ planes with a super-cell of $a\sqrt{3} \times a\sqrt{3}$. The stacking irregularities do not allow an ordered structure to develop along the c -axis. On the basis

of diffraction properties of these crystals an ordered arrangement of these planes was proposed.

Electrical conductivity and thermopower measurements show the metallic behavior of these compounds. The effective magnetic moments on the RE atoms obtained from the Curie temperature dependence are in the good agreement with the values of μ_{eff} calculated for free RE^{3+} atoms. A strong anisotropy with respect to crystallographic axis was detected for these compounds. The field dependence measurements point out that the direction of magnetically easy axis coincides with the *c*-axis for RE = Er and Tm, and lies in the basal plane in case of Tb, Dy and Ho. The single-ion two-fold anisotropy constants K_2^{para} were calculated from the Weiss constant anisotropy are in good agreement with the theoretical ones calculated for the pure RE metals.

Table V.19. Summary of magnetic results for RE_{0.67}Ni₂Ga_{5+6-x}Ge_x.

	Gd _{0.67} Ni ₂ Ga _{5-x} Ge _x			Tb _{0.67} Ni ₂ Ga _{5-x} Ge _x			Dy _{0.67} Ni ₂ Ga _{6-x} Ge _x			Ho _{0.67} Ni ₂ Ga _{5-x} Ge _x			Er _{0.67} Ni ₂ Ga _{5-x} Ge _x			Tm _{0.67} Ni ₂ Ga _{5-x} Ge _x		
	H ¹⁰⁰	H c	H⊥c	H ¹⁰⁰	H c	H⊥c	H ¹⁰⁰	H c	H⊥c	H ¹⁰⁰	H c	H⊥c	H ¹⁰⁰	H c	H⊥c	H ¹⁰⁰	H c	H⊥c
T _{max} (K) ⁽¹⁾	~3	-	~3	-	~3	~3	-	-	-	~3	-	-	-	~4	~3	~4	-	-
Θ (K) ⁽²⁾	-8	-7	+12	0	-66	-11	0	-56	0	0	-17	+6	0	+14	-11	0	+26	-34
Θ - Θ _⊥ (K) ⁽³⁾	-			-55			-56			-23			+25			+60		
K ₂ ^{para} (<10 ¹⁵ erg/ion) ⁽⁴⁾	-			9.93			10.73			4.47			-4.20			-11.04		
K ₂ ⁰ (<10 ¹⁵ erg/ion) ⁽⁵⁾	-			9.77			10.63			4.25			-4.79			-10.24		
μ _{eff} ^{CW(6)}	7.79	7.90	8.30	9.31	9.64	9.86	10.8	10.8	11.1	11.1	10.6	10.4	9.9	9.60	9.97	7.28	7.79	7.85
μ _{eff} ^{ave(7)}	8.00			9.60			10.93			10.7			9.82			7.64		
μ _{eff} ^{calc(8)}	7.94			9.72			10.63			10.6			9.57			7.63		
μ _{eff} ^{lys(9)}	~4	~4	~5	~6	~1.5	~6	~7	~2.5	~7	~6	~4	~9	~9	~9	~3	~8	~7	~3
Easy axis ⁽¹⁰⁾	Isotropic			In BASAL plane			In BASAL plane			In BASAL plane			to c-axis			to c-axis		

1. The temperature of the maximal magnetic susceptibility;
2. Paramagnetic Curie temperature (Weiss constant);
3. The difference between the paramagnetic Curie temperatures for spin directions parallel and perpendicular to *c*-axis;
4. Effective 0 K two-fold anisotropy constant calculated from the paramagnetic Curie temperature anisotropy;
5. Theoretical values of the single-ion two-fold anisotropy constant at 0 K;
6. The effective magnetic moment μ_{eff} (in Bohr Magnetons) calculated from the linear part of the reciprocal magnetic susceptibility vs temperature;
7. Averaged value of the isotropic and anisotropic values of μ_{eff} ;
8. μ_{eff} (in Bohr Magnetons) calculated based on Van Vleck equation for free RE³⁺ ion;
9. The maximal effective magnetic moment μ_{eff} (in Bohr Magnetons) obtained from the field dependence curves;
10. The direction of the magnetically easy axis with respect to the crystallographic axis obtained from the onset of the M(H) saturation magnetization

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⁷ This Ni-Ga side phase is ferromagnetic above the room temperature with a quite strong coercive force.

⁸ NiGa_{1+x}Si_{1-x} ($x \sim 0.13$) single crystal X-ray data: $F\bar{4}3m$, $a = 5.4728(13) \text{ \AA}$, $R_1/wR_2 = 0.0501/0.120$ for $I > 2\sigma(I)$, residual peak/hole +4.448 and -1.957. Ga is at $4a$ (0 0 0), Ni is at $4c$ ($\frac{1}{4} \frac{1}{4} \frac{1}{4}$) and Si/Ga is at $4d$ ($\frac{3}{4} \frac{3}{4} \frac{3}{4}$).

⁹ Ni₃Ga₂ single crystal X-ray data: $P\bar{3}m1$, $a = 4.006(2) \text{ \AA}$, $c = 4.874(2) \text{ \AA}$, $R_1/wR_2 = 0.0487/0.0491$ for $I > 2\sigma(I)$, residual peak/hole +1.746/-2.853. Two Ni positions at $1b$ and $2d$ and single Ga site at $2d$ were refined.

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Chapter VI

New Quaternary Phases REMGa_3Ge , $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ and $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ ($\text{M}=\text{Ni}$ and Co ; $\text{RE}=\text{Rare-Earth}$) Synthesized in Liquid Ga. X-Ray, Electron and Neutron Structure Determination and Magnetism.

1. Introduction

In the previous chapter we examined the chemistry in the quaternary RE/M/Ga/Tt system ($\text{Tt} = \text{Si}$ or Ge ; $\text{M} = \text{Ni}$, Co) under Ga flux conditions. From these studies, we have reported the hexagonal compounds $\text{RE}_{0.67}\text{M}_2\text{Ga}_{5-x}\text{Tt}_x$, and $\text{RE}_{0.67}\text{M}_2\text{Ga}_{6-x}\text{Tt}_x$ ¹ ($\text{M} = \text{Ni}$, Co ; $\text{Tt} = \text{Si}$ or Ge) that are very stable and readily form at the ratio $\text{RE} : \text{M} < 1$ within a rather broad range of synthetic conditions. In our earlier investigations we have also discovered a non-reactive behavior of Ga flux, when the $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ² compounds were

isolated at RE : Ni < 1. Continuing systematic investigations in this area, we decided to further explore the reactivity and phase formation in the RE/M/Ga/Ge system, but this time using RE : M $\geq$ 1. We were encouraged by the application of the molten aluminum to perform similar reaction chemistry in the related RE/M/Al/Ti system which led to the discovery of a number of new multinary phases including $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Si}_{1-x})\text{Al}_4\text{Si}_6$ ³, $\text{RENiAl}_4\text{Ge}_2$ ⁴, $\text{Tb}_2\text{NiAl}_4\text{Ge}_2$ and $\text{Ce}_2\text{NiAl}_{6-x}\text{Ge}_{4-y}$ ⁵.

Interestingly, we find that in case of RE : M $\geq$ 1 the reaction product depends on RE and is also sensitive to the reaction conditions. Specifically, we find that the hexagonal phases do not form, instead, we obtain the tetragonal REMGa_3Ge , $\text{RE}_2\text{MGa}_9\text{Ge}_2$ ⁶, $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$, and the orthorhombic $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ phases. The results are reminiscent of those obtained in the corresponding RE/Ni/Al/Si and RE/Ni/Ga/Si systems, in which the tetragonal compounds $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Si}_{1-x})\text{Al}_4\text{Si}_6$ ³, and $\text{RE}_2\text{NiGa}_{12-x}\text{Si}_x$ ⁷ were produced at Sm : Ni > 1. Here we report the synthesis, crystal structure and magnetic properties of two new families of quaternary intermetallic compounds REMGa_3Ge (RE = Y, Sm, Tb, Gd, Er, Tm; M = Ni, Co) and $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ (RE = Sm, Gd) grown from Ga flux at RE : M = 1.

2. Experimental Section

Synthesis

The reactions between the rare-earth element, transition metal (Ni or Co) and a Ge were performed in liquid Ga. Elemental rare-earth (Y, Sm, Gd, Tb, Er, Tm) typically of purity 99.9% and higher (CERAC Inc.), nickel (cobalt) powder 99.99% (Aldrich Inc.), Ge powder (99.999%, CERAC Inc.), and Ga (3 mm shots 99.999%, CERAC Inc.) were taken in the amounts: RE 0.75 mmol, Ni 0.75 mmol, Ga 11.2 mmol, Ge 0.75 mmol and loaded into alumina crucibles under inert (N_2) atmosphere. The crucibles were placed into fused silica tubes and evacuated ($\sim 1 \cdot 10^{-4}$ Torr). The following heat treatment was used for synthesis of $REMGa_3Ge$ (1) and $RE_3Ni_3Ga_8Ge_3$ (2): the temperature was raised up to 1000°C at the rate 60°/hour and kept at 1000°C for 5h to achieve proper melt, then cooled down to 850°C in 2h and kept isothermally at 850°C for 36 hours and, finally, slowly cooled down to 250°C at the rate 33°/h. To prepare $RE_4Ni_3Ga_7Ge_3$ (3) phase in high yield, substantially longer reaction and cooling times are required. The reaction mixtures were slowly heated (60°/hour) up to 1000°C, shortly (5 hours) held at 1000°C, then cooled (75°/hour) to 850°C and held there isothermally for 6 days and lastly cooled at 8°/hour to $\sim 250^\circ\text{C}$.

Upon the completion of the reactions, the majority of the unused flux was next removed by centrifuging liquid Ga through a coarse frit at $\sim 250^\circ\text{C}$. The reaction products were further isolated from the remaining Ga by soaking in a ~ 5 M solution of iodine in dimethylformamide (DMF) over 12h at room temperature. This step serves to

dissolve the residual Ga by converting it to GaI_3 . The resulting crystalline product was subsequently rinsed with DMF and dried with acetone and ether. The phases **1**, **2** and **3** were recovered in high yields (80 – 95%) from the reactions in molten Ga. The isolated crystals possessed a typical plate-like morphology, often with a phyllo-morphous character. Images of characteristic crystals of **1** and **2** are shown in the SEM micrographs in Figure VI.1.A and VI.1.B.

Elemental Analysis and X-ray Powder Diffraction

The chemical composition of the products was determined by Energy Dispersive Spectroscopy (EDS) performed on scanning electron microscope (SEM) JEOL JSM-35C equipped with NORAN Inc. EDS detector. The analysis was conducted at accelerating voltage 20 kV and collection time 30 s. After averaging the results of the elemental analysis over several crystals of each analog, the composition of compounds **1**, **2** and **3** was determined to be “ $\text{RE}_{1.1}\text{MGa}_3\text{Ge}_{1.1}$ ”, “ $\text{RE}_3\text{Ni}_{2.3}\text{Ga}_8\text{Ge}_{2.5}$ ” and “ $\text{RE}_{3.3}\text{M}_{2.8}\text{Ga}_{5.9}\text{Ge}_4$ ”, respectively. The formulae obtained from the elemental analysis agreed well with that refined from the single crystal data.

The X-ray diffraction (XRD) powder patterns of products were taken at room temperature on Rigaku-Denki/Rw400F2 (rotaflex) rotating-anode ($\text{CuK}\alpha$) powder diffractometer and a CPS 120 INEL X-ray diffractometer ($\text{CuK}\alpha$) equipped with position-sensitive detector. Experimental powder patterns were compared to that calculated from single crystal data using CERIUSt² software package⁸.

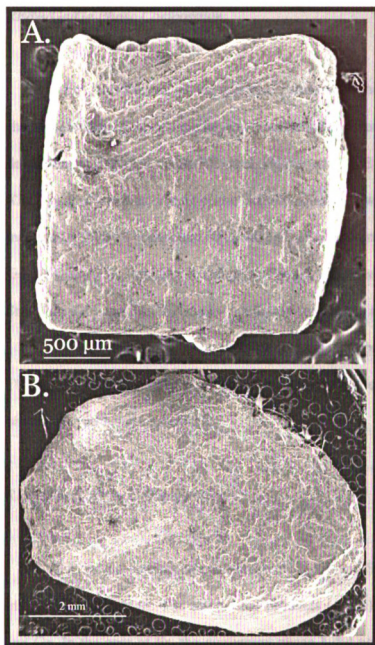


Figure VI.1. The SEM photographs of crystals of (A) GdCoGa_3Ge (1), (B) $\text{Sm}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ (2) grown from liquid Ga at 850°C.

RE/Ni/Ga/Ge Phase Composition

The examination of the powder patterns of the reaction products obtained at shorter reaction times immediately revealed the differences in the reaction products depending on the type of the RE used. Hence, when RE = Y, Tb, Er or Tm, the peaks in XRD pattern showed single-phase RENiGa_3Ge (**1**), while for RE = Gd the patterns indicated ~ 80% of compound $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ (**2**) with impurities that included hexagonal $\text{Gd}_{0.67}\text{Ni}_2\text{Ga}_{6-x}\text{Ge}_x$ ¹ and Ge. In the case of Sm, up to three quaternary phases SmNiGa_3Ge , $\text{Sm}_2\text{NiGa}_8\text{Ge}_3$ and $\text{Sm}_3\text{Ni}_3\text{Ga}_9\text{Ge}_2$ could be found in the reaction product.

At extended times of the reaction (6 days), the product of the reaction with RE = Tb and Y yielded nearly pure phase of $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (**3**), whereas at shorter times phases of type **1** were produced.

RE/Co/Ga/Ge Phase Composition:

For the Co-containing reactions with Y, Gd and Sm the yield of quaternary phases of type **1** is very high. The minor side products (~ 5%) for these reactions were CoGa_3 and Ge. In the case of Er, the quaternary phase **1** did not form; instead a single phase of ErCoGa_5 (HoCoGa_5 structure type⁹) was produced.

Single Crystal X-Ray Diffraction

Intensity data was collected on single crystals of **1** (YNiGa₃Ge) and **2** (Gd₃Ni₃Ga₈Ge₃) at room temperature and on crystal of **3** (RE₄Ni₃Ga₆Ge₄) at low temperature (173(2) K) with a Siemens Platform SMART¹⁰ CCD X-ray diffractometer. The crystals of suitable size $0.08 \times 0.12 \times 0.01 \text{ mm}^3$, $0.07 \times 0.06 \times 0.02 \text{ mm}^3$ and $0.08 \times 0.06 \times 0.12$ were cut out of a larger crystal and mounted on glass fiber. A data collection (Mo K α radiation, $\lambda = 0.71073 \text{ \AA}$) was acquired up to 66.5° in 2θ , covering either a full sphere or a hemisphere of reciprocal space. The individual frames were measured using the ω -steps of 0.30° and exposure time up to 120s per frame.

The data reduction was performed with the SAINTPLUS¹¹ software package. A face-indexing procedure was used for analytical absorption corrections. An additional correction for absorption based on symmetry equivalent reflections was consequently applied with SADABS¹² program. The structure solution and refinement were done by direct methods with SHELXTL¹³ software package. All atomic positions were refined anisotropically. The setting of the cell was standardized with STRUCTURE TIDY program¹⁴.

X-ray Structure Refinement of 1.

The YNiGa₃Ge (1) crystallizes in the tetragonal space group *I4/mmm*. The asymmetric unit of YNiGa₃Ge contains a total of seven atomic positions. The Y atoms reside at *4e* position, the Ga atoms occupy *8g* and *4d* sites, and Ni atoms are found at *2a* and *4e* sites. The Ge was refined as a split position with 50% occupancy on each of the Ge(1) and Ge(2) sites. The refinement of Ge in a single *4e* site resulted in the enlarged atomic displacement parameter (U_{eq} up to $\sim 100 \text{ \AA}^2 \times 10^{-3}$) and increased R-values (17% and higher). The partial occupancy of 50% was also refined for the Ni at *4e*, as a result of the close interatomic distances to one of the split positions of Ge. The information relevant to the data collection and structure refinement is given in Table VI.1. The final atomic positions, the equivalent thermal displacement parameters, and occupancies are listed in Table VI.2. Selected interatomic distances (up to 3.5 Å) and bond angles are presented in Tables VI.3 and VI.4, respectively. The anisotropic displacement parameters for all atoms are given in Table VI.5.

Table VI.1. X-ray single crystal data and structure refinement for YNiGa₃Ge (1)

Empirical formula	YNiGa ₃ Ge
Formula weight	429.37
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	<i>I4/mmm</i>
Unit cell dimensions (Å)	<i>a</i> = 4.1748(10) <i>c</i> = 23.710(8)
Volume (Å ³)	413.24(19)
Z	4
Density (calculated) (g/cm ³)	6.901
Absorption coefficient (mm ⁻¹)	44.575
F(000)	768
Crystal size (mm ³)	0.08 × 0.12 × 0.01
θ range for data collection	1.72 to 28.33°.
Index ranges	-5 ≤ <i>h</i> ≤ 5; -5 ≤ <i>k</i> ≤ 5; -30 ≤ <i>l</i> ≤ 30
Reflections collected	1944
Independent reflections	194 [R(int) = 0.0569]
Completeness to θ = 33.27°	97.5 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	194 / 22
Goodness-of-fit on F ²	1.087
Final R indices [I>2σ (I)]*	R ₁ = 0.0298, wR ₂ = 0.0787
R indices (all data)	R ₁ = 0.0333, wR ₂ = 0.0797
Extinction coefficient	0.0009(4)
Largest diff. peak and hole (e/Å ³)	0.987 and -1.460

* $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table VI.2. Atomic coordinates, equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and occupancies for YNiGa₃Ge (1).

Atom	Wykoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*	Occ.
Y	<i>4e</i>	0	0	0.1496(1)	8(1)	1.0
Ga(1)	<i>8g</i>	0	½	0.0551(1)	14(1)	1.0
Ga(2)	<i>4d</i>	0	½	¼	31(1)	1.0
Ni(1)	<i>2a</i>	0	0	0	9(1)	1.0
Ni(2)	<i>4e</i>	0	0	0.2831(2)	19(1)	0.5
Ge(1)	<i>4e</i>	0	0	0.3523(2)	13(1)	0.5
Ge(2)	<i>4e</i>	0	0	0.3794(2)	13(1)	0.5

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table VI.3. Selected bond lengths [$\text{\AA}$] for YNiGa_3Ge (1).

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
Y-Ge(1)	2.9524(7)	$\times 4$	Ga(2)-Ni(2)	2.2298(15)	$\times 4$
Y-Ge(2)	3.0316(13)	$\times 4$	Ga(2)-Ga(2)	2.9520(7)	$\times 4$
Y-Ga(1)	3.0622(14)	$\times 4$	Ge(1)-Ge(2)	0.645(4)	$\times 1$
Y-Ga(2)	3.1652(12)	$\times 4$	Ge(1)-Ni(2)	1.640(6)	$\times 1$
Y-Ni(2)	3.355(2)	$\times 4$	Ge(2)-Ga(1)	2.600(3)	$\times 4$
Y-Ge(2)	3.0316(13)	$\times 4$	Ga(1)-Ni(1)	2.4631(8)	$\times 2$
Ni(1)-Ga(1)	2.4632(8)	$\times 8$	Ga(1)-Ge(2)	2.600(3)	$\times 2$
Ni(2)-Ga(2)	2.2298(15)	$\times 3$	Ga(1)-Ga(1)	2.615(3)	$\times 1$
Ni(2)-Ge(2)	2.285(6)	$\times 1$	Ga(1)-Ga(1)	2.9520(7)	$\times 4$

Table VI.4. Selected bond angles [°] for YNiGa₃Ge (1).

Bond	Angle	Bond	Angle
Ge(1)-Y-Ge(1)	178.25(19)	Ni(1)-Ga(1)-Ga(1)	57.94(3)
Ge(1)-Y-Ge(1)	89.987(3)	Ge(2)-Ga(1)-Ga(1)	126.61(9)
Ge(1)-Y-Ge(2)	165.97(18)	Ni(1)-Ga(1)-Ga(1)	53.185(13)
Ge(1)-Y-Ge(2)	12.28(7)	Ni(1)-Ga(1)-Ga(1)	126.816(13)
Ge(1)-Y-Ge(2)	89.80(2)	Ge(2)-Ga(1)-Ga(1)	124.58(4)
Ge(2)-Y-Ge(2)	153.69(19)	Ge(2)-Ga(1)-Ga(1)	55.41(4)
Ge(2)-Y-Ge(2)	87.03(4)	Ga(1)-Ga(1)-Ga(1)	90.0
Ge(1)-Y-Ga(1)	118.08(9)	Ni(1)-Ga(1)-Ga(1)	53.185(13)
Ge(1)-Y-Ga(1)	60.45(8)	Ge(2)-Ga(1)-Ga(1)	55.41(4)
Ge(2)-Y-Ga(1)	50.52(7)	Ga(1)-Ga(1)-Ga(1)	180.0
Ge(2)-Y-Ga(1)	107.63(9)	Ge(2)-Ge(1)-Ni(2)	180.000(1)
Ga(1)-Y-Ga(1)	57.63(3)	Ge(1)-Ni(2)-Ga(2)	110.59(10)
Ga(1)-Y-Ga(1)	85.95(5)	Ga(2)-Ni(2)-Ga(2)	82.90(7)
Ge(2)-Y-Ga(1)	107.63(9)	Ga(2)-Ni(2)-Ga(2)	138.8(2)
Ni(2)-Ga(2)-Ni(2)	97.10(7)	Ge(1)-Ni(2)-Ge(2)	0.0
Ni(2)-Ga(2)-Ni(2)	138.8(2)	Ga(1)-Ni(1)-Ga(1)	106.37(3)
Ni(2)-Ga(2)-Ga(2)	131.45(3)	Ga(1)-Ni(1)-Ga(1)	73.63(3)
Ni(2)-Ga(2)-Ga(2)	48.55(3)	Ga(1)-Ni(1)-Ga(1)	180.00(5)
Ga(2)-Ga(2)-Ga(2)	180.0	Ga(1)-Ni(1)-Ga(1)	180.0
Ni(2)-Ga(2)-Ga(2)	48.55(3)	Ga(1)-Ni(1)-Ga(1)	115.87(5)
Ga(2)-Ga(2)-Ga(2)	90.0	Ga(1)-Ni(1)-Ga(1)	64.13(5)
Ni(1)-Ga(1)-Ni(1)	115.87(5)	Ge(1)-Ge(2)-Ga(1)	126.61(9)
Ni(1)-Ga(1)-Ge(2)	108.46(4)	Ga(1)-Ge(2)-Ga(1)	69.17(9)
Ge(2)-Ga(1)-Ge(2)	106.78(17)	Ga(1)-Ge(2)-Ga(1)	106.79(17)

Table VI.5. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for YNiGa_3Ge (1).

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Y	10(1)	10(1)	6(1)	0	0	0
Ga(2)	31(1)	31(1)	32(1)	0	0	0
Ga(1)	20(1)	8(1)	14(1)	0	0	0
Ge(1)	11(1)	11(1)	18(2)	0	0	0
Ni(2)	20(1)	20(1)	16(2)	0	0	0
Ni(1)	6(1)	6(1)	15(1)	0	0	0
Ge(2)	10(1)	10(1)	20(2)	0	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

X-ray Structure Refinement of 2.

The $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ (**2**) are structurally related to the REMGa_3Ge , and they crystallize in the tetragonal space group $P4/mmm$. Owing to this symmetry reduction, an increased number of atomic positions (a total of ten) were identified in the structure of $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$. Thus, the Gd atoms in the asymmetric unit of **2** occupy two atomic sites ($1a$ and $2h$), and the number of sites occupied by Ni and Ge increased to three ($1d$, $2g$, $2h$ and $1c$, $2g$, $2g$, respectively). The Ga atoms are found in two positions with multiplicity $4i$. Similar to REMGa_3Ge disorder is observed in the structure of $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ causing the short bond distances between Ni and Ge. Partial occupancies of 0.714(14) and 0.223(14) were found for the disordered atoms Ni(2) and Ni(2'), respectively. The occupancies of the Ge(2)/Ge(2') split site refined to 0.59(4)/0.40(3), while the Ge(1) site, although exhibiting enlarged thermal displacement parameter, did not favor the split position during the refinement. The details of the data collection and structure refinement of **2** are given in Table VI.6. The final atomic positions, the equivalent thermal displacement parameters and occupancies are presented in Table VI.7. Selected bond distances and angles are listed in Table VI.8 and VI.9, respectively. Anisotropic displacement parameters could be found in Table VI.10.

Table VI.6. X-ray single crystal data and structure refinement for Gd₃Ni₃Ga₈Ge₃ (2).

Empirical formula	Gd ₃ Ni _{2.79} Ga ₈ Ge ₃
Formula weight	1411.08
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Tetragonal
Space group	<i>P4/mmm</i> (#123)
Unit cell dimensions (Å)	<i>a</i> = 4.1809(18) <i>c</i> = 17.035(11)
Volume (Å ³)	297.8(3)
Z	1
Density (calculated) (g/cm ³)	7.869
Absorption coefficient (mm ⁻¹)	45.870
F(000)	614
Crystal size (mm ³)	0.07 × 0.06 × 0.02
θ range for data collection	11.02 to 33.27
Index ranges	-6 ≤ <i>h</i> ≤ 6; -6 ≤ <i>k</i> ≤ 6; -26 ≤ <i>l</i> ≤ 25
Reflections collected	3830
Independent reflections	391 [<i>R</i> _{int} = 0.0850]
Completeness to θ = 33.27°	92.4 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / parameters	391 / 35
Goodness-of-fit on <i>F</i> ²	1.001
Final R indices [<i>I</i> > 2σ(<i>I</i>)] [*]	<i>R</i> ₁ = 0.0360, <i>wR</i> ₂ = 0.0889
R indices (all data)	<i>R</i> ₁ = 0.0414, <i>wR</i> ₂ = 0.0909
Extinction coefficient	0.070(5)
Largest diff. peak and hole (e/Å ³)	2.744 and -4.546

^{*} $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table VI.7. Atomic coordinates, equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) and occupancies for $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ (2).

Atomic Position	Wyckoff Symbol	x	y	z	U_{eq}^*	Occupancy
Gd(1)	$1a$	0	0	0	9(1)	1
Gd(2)	$2h$	$\frac{1}{2}$	$\frac{1}{2}$	0.2862(1)	9(1)	1
Ge(1)	$1c$	$\frac{1}{2}$	$\frac{1}{2}$	0	98(4)	1
Ge(2)	$2g$	0	0	0.3307(2)	8(1)	0.59(3)
Ge(2')	$2g$	0	0	0.2939(6)	17(1)	0.40(4)
Ga(1)	$4i$	0	$\frac{1}{2}$	0.4233(1)	13(1)	1
Ga(2)	$4i$	0	$\frac{1}{2}$	0.1401(1)	23(1)	1
Ni(1)	$1d$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	10(1)	1
Ni(2)	$2g$	0	0	0.1959(2)	11(1)	0.714(14)
Ni(2')	$2h$	$\frac{1}{2}$	$\frac{1}{2}$	0.0997(4)	10(1)	0.223(14)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table VI.8. Selected bond lengths [Å] for Gd₃Ni₃Ga₈Ge₃ (2).

Bond	Distance	Multiplicity	Ga(1)-Ni(1)	2.4653(11)	× 2
Gd(1)-Ge(1)	2.9563(13)	×4	Ga(1)-Ge(2)	2.618(2)	× 2
Gd(1)-Ga(2)	3.1722(16)	× 8	Ga(1)-Ga(1)	2.9563(13)	× 4
Gd(2)-Ge(2')	2.9593(14)	× 4	Ga(1)-Gd(2)	3.1344(16)	× 1
Gd(2)-Ge(2)	3.0522(14)	× 4	Ga(2)-Ni(2')	2.200(2)	× 2
Gd(2)-Ga(1)	3.1344(16)	× 4	Ga(2)-Ni(2)	2.2967(16)	× 2
Ge(1)-Ni(2')	1.699(7)	× 2	Ga(2)-Ga(2)	2.9563(13)	× 4
Ge(1)-Gd(1)	2.9563(13)	× 3	Ga(2)-Gd(1)	3.1722(16)	× 1
Ge(2)-Ge(2')	0.628(8)	× 1	Ga(2)-Gd(2)	3.2508(17)	×
Ge(2)-Ni(2)	2.297(5)	× 1	Ni(1)-Ga(1)	2.4653(11)	× 1
Ge(2)-Ga(1)	2.618(2)	× 4	Ni(2)-Ga(2)	2.2967(16)	× 3
Ge(2)-Gd(2)	3.0522(15)	× 3	Ni(2)-Gd(2)	3.3325(18)	× 3
Ge(2')-Ni(2)	1.670(11)	× 1	Ni(2')-Ga(2)	2.200(2)	× 3
Ge(2')-Gd(2)	2.9593(14)	× 3	Ni(2')-Gd(1)	3.410(4)	× 3

Table VI.9. Selected bond angles [°] for Gd₃Ni₃Ga₈Ge₃ (2).

Bond	Angle	Bond	Angle
Ge(1)-Gd(1)-Ge(1)	180.0	Ni(1)-Ga(1)-Ge(2)	108.48(6)
Ge(1)-Gd(1)-Ge(1)	90.0	Ga(1)-Ga(1)-Ge(2)	126.71(13)
Ge(1)-Gd(1)-Ga(2)	117.776(16)	Ge(2)-Ga(1)-Ge(2)	106.6(3)
Ge(1)-Gd(1)-Ga(2)	62.225(16)	Ni(1)-Ga(1)-Ga(1)	53.160(14)
Ga(2)-Gd(1)-Ga(2)	124.45(3)	Ni(1)-Ga(1)-Ga(1)	126.839(14)
Ga(2)-Gd(1)-Ga(2)	55.55(3)	Ge(2)-Ga(1)-Ga(1)	55.47(7)
Ga(2)-Gd(1)-Ga(2)	180.0	Ge(2)-Ga(1)-Ga(1)	124.53(7)
Ga(2)-Gd(1)-Ga(2)	82.45(5)	Ga(1)-Ga(1)-Ga(1)	90.0
Ga(2)-Gd(1)-Ga(2)	97.55(5)	Ga(1)-Ga(1)-Ga(1)	180.0
Ge(2')-Gd(2)-Ge(2')	89.76(8)	Ga(1)-Ga(1)-Ga(1)	89.999(1)
Ge(2')-Gd(2)-Ge(2')	172.5(12)	Ni(2')-Ga(2)-Ni(2')	143.8(4)
Ge(2')-Gd(2)-Ge(2)	161.5(7)	Ni(2')-Ga(2)-Ni(2)	97.40(8)
Ge(2')-Gd(2)-Ge(2)	89.05(16)	Ni(2)-Ga(2)-Ni(2)	131.04(14)
Ge(2')-Gd(2)-Ge(2)	11.0(5)	Ni(2')-Ga(2)-Ga(2)	132.23(5)
Ge(2)-Gd(2)-Ge(2)	150.6(3)	Ni(2')-Ga(2)-Ga(2)	47.77(5)
Ge(2)-Gd(2)-Ge(2)	86.30(6)	Ni(2)-Ga(2)-Ga(2)	130.06(3)
Ge(2')-Gd(2)-Ga(1)	115.0(5)	Ni(2)-Ga(2)-Ga(2)	49.94(3)
Ge(2')-Gd(2)-Ga(1)	58.7(5)	Ga(2)-Ga(2)-Ga(2)	179.999(1)
Ge(2)-Gd(2)-Ga(1)	49.81(10)	Ga(2)-Ga(2)-Ga(2)	90.0
Ge(2)-Gd(2)-Ga(1)	105.49(12)	Ga(1)-Ni(1)-Ga(1)	180.0
Ga(1)-Gd(2)-Ga(1)	56.28(3)	Ga(1)-Ni(1)-Ga(1)	73.68(3)
Ga(1)-Gd(2)-Ga(1)	83.68(5)	Ga(1)-Ni(1)-Ga(1)	106.32(3)
Ni(2')-Ge(1)-Ni(2')	180.0	Ga(1)-Ni(1)-Ga(1)	115.98(6)
Ge(2')-Ge(2)-Ni(2)	0.000(4)	Ga(1)-Ni(1)-Ga(1)	64.02(6)
Ge(2')-Ge(2)-Ga(1)	126.72(13)	Ge(2')-Ni(2)-Ga(2)	114.48(7)
Ga(1)-Ge(2)-Ga(1)	69.06(13)	Ga(2)-Ni(2)-Ga(2)	80.11(6)
Ga(1)-Ge(2)-Ga(1)	106.6(3)	Ge(2')-Ni(2)-Ge(2)	0.000(1)
Ge(2)-Ge(2')-Ni(2)	180.000(1)	Ge(1)-Ni(2')-Ga(2)	108.11(18)
Ni(1)-Ga(1)-Ni(1)	115.97(6)	Ga(2)-Ni(2')-Ga(2)	84.46(11)
Ni(1)-Ga(1)-Ga(1)	57.99(3)	Ga(2)-Ni(2')-Ga(2)	143.8(4)

Table VI.10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ (2).

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Gd(1)	9(1)	9(1)	10(1)	0	0	0
Gd(2)	9(1)	9(1)	10(1)	0	0	0
Ge(1)	6(1)	6(1)	285(11)	0	0	0
Ge(2)	9(1)	9(1)	0(3)	0	0	0
Ge(2')	7(2)	7(2)	62(14)	0	0	0
Ga(1)	7(1)	15(1)	16(1)	0	0	0
Ga(2)	25(1)	19(1)	26(1)	0	0	0
Ni(1)	6(1)	6(1)	17(1)	0	0	0
Ni(2)	13(1)	13(1)	14(1)	0	0	0
Ni(2')	15(3)	15(3)	0(4)	0	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

X-ray Structure Refinement of 3.

The crystal structure of $\text{Y}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (**3**) is orthorhombic, space group *Cmcm*. To our knowledge the structure type of **3** is novel, the corresponding Pearson's symbol is oC34. The asymmetric unit of **3** contains a total of ten crystallographically distinct atomic positions, each of multiplicity $4c$. In the unit cell there are two Y, two Ni, three Ga and three Ge sites. The positions of Y and Ga are fully occupied; however, some of the Ni and Ge sites reveal partial occupancies. Thus, the site population of Ni(1), Ge(2) and Ge(2') refined close to 50% level; therefore in the final refinement cycle these occupancies were constrained to exactly $\frac{1}{2}$. It should be noted that the latter two sites Ge(2) and Ge(2') essentially represent a split Ge position with the Ge-Ge distances of ~ 0.5 Å. Hence, the structure of **3** appears disordered. The "disorder" in **3** is similar to that observed in **1** and **2** and is manifested in the unrealistically short Ge-Ni and Ge-Ge distances and partial site vacancies.

The information relevant to data collection and refinement of **3** is presented in Table VI.11. The fractional atomic coordinates, isotropic displacement parameters and site populations are given in Table VI.12. Selected bond distances and angles are listed in Tables VI.13 and VI.14, respectively. The anisotropic displacement parameters are given in Table VI.15.

Table VI.11. X-ray single crystal data and structure refinement for Y₄Ni₃Ga₆Ge₄ (**3**).

Empirical formula	Y ₄ Ni ₃ Ga ₆ Ge ₄
Formula weight	1240.45
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Cmcm</i>
Unit cell dimensions (Å)	<i>a</i> = 4.0999(19) <i>b</i> = 35.628(17) <i>c</i> = 4.0968(19)
Volume (Å ³)	598.4(5)
Z	2
Density (calculated) (g/cm ³)	6.884
Absorption coefficient (mm ⁻¹)	46.800
F(000)	1108
Crystal size (mm ³)	0.08 × 0.06 × 0.12
θ range for data collection (°)	2.29 to 28.74°.
Index ranges	-5 ≤ <i>h</i> ≤ 5; -44 ≤ <i>k</i> ≤ 46; -2 ≤ <i>l</i> ≤ 5
Reflections collected	1567
Independent reflections	470 [R(int) = 0.0398]
Completeness to θ = 28.74°	93.4 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	470 / 0 / 42
Goodness-of-fit on F ²	0.963
Final R indices [I > 2σ(I)] *	R ₁ = 0.0436, wR ₂ = 0.1101
R indices (all data)	R ₁ = 0.0624, wR ₂ = 0.1201
Extinction coefficient	0.00033(18)
Largest diff. peak and hole (e/Å ³)	2.700 and -1.874

* $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table VI.12. Atomic coordinates equivalent isotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) and occupancies for $\text{Y}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (**3**).

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)	Occ.
Y(1)	4 <i>c</i>	0	0.4530(1)	¼	2(1)	1.0
Y(2)	4 <i>c</i>	0	0.1828(1)	¼	4(1)	1.0
Ge(1)	4 <i>c</i>	0	0.0207(1)	¼	5(1)	1.0
Ge(2)	4 <i>c</i>	0	0.3214(2)	¼	8(1)	0.5
Ge(2')	4 <i>c</i>	0	0.3361(2)	¼	12(1)	0.5
Ni(1)	4 <i>c</i>	0	0.2725(1)	¼	16(1)	0.5
Ni(2)	4 <i>c</i>	0	0.0847(1)	¼	6(1)	1.0
Ga(1)	4 <i>c</i>	0	0.7495(1)	¼	27(1)	1.0
Ga(2)	4 <i>c</i>	0	0.6167(1)	¼	7(1)	1.0
Ga(3)	4 <i>c</i>	0	0.8835(1)	¼	8(1)	1.0

*U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table VI.13. Selected bond lengths [$\text{\AA}$] for $\text{Y}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (**3**).

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
Y(2)-Ge(2)	2.9019(10)	$\times 4$	Ga(1)-Ga(1)	2.8982(9)	$\times 4$
Y(2)-Ge(2')	2.9752(17)	$\times 4$	Ga(2)-Ni(2)	2.3446(17)	$\times 2$
Y(1)-Ge(1)	3.0457(12)	$\times 4$	Ga(2)-Ge(2')	2.652(4)	$\times 2$
Y(1)-Ge(1)	3.164(2)	$\times 2$	Ga(2)-Ga(3)	2.8980(9)	$\times 4$
Y(1)-Ni(2)	3.1950(15)	$\times 4$	Ga(3)-Ni(2)	2.3406(16)	$\times 2$
Y(1)-Ga(3)	3.216(2)	$\times 2$	Ga(3)-Ge(2')	2.656(4)	$\times 2$
Y(1)-Ga(2)	3.219(2)	$\times 2$	Ge(1)-Ge(1)	2.523(2)	$\times 2$
Y(2)-Ga(2)	3.124(2)	$\times 2$	Ge(2)-Ge(2')	0.522(7)	$\times 1$
Y(2)-Ga(3)	3.127(2)	$\times 2$	Ge(2)-Ni(1)	1.742(7)	$\times 1$
Y(2)-Ga(1)	3.137(2)	$\times 2$	Ge(2')-Ni(1)	2.265(7)	$\times 1$
Y(2)-Ga(1)	3.164(2)	$\times 2$	Ni(2)-Ge(1)	2.282(3)	$\times 1$
Y(2)-Ni(1)	3.306(3)	$\times 4$	Ni(2)-Ga(3)	2.3406(16)	$\times 2$
Ga(1)-Ni(1)	2.193(2)	$\times 2$	Ni(2)-Ga(2)	2.3446(17)	$\times 2$
Ga(1)-Ni(1)	2.208(2)	$\times 2$			

Table VI.14. Selected bond angles [°] for Y₄Ni₃Ga₆Ge₄ (**3**).

Bond	Angle	Bond	Angle
Ge(1)-Y(1)-Ge(1)	144.16(9)	Ge(2)-Y(2)-Ge(2)	89.89(4)
Ge(1)-Y(1)-Ge(1)	84.61(4)	Ge(2)-Y(2)-Ge(2')	10.10(13)
Ge(1)-Y(1)-Ge(1)	47.90(4)	Ge(2)-Y(2)-Ge(2')	163.9(2)
Ge(1)-Y(1)-Ge(1)	101.63(5)	Ge(2)-Y(2)-Ge(2')	89.28(5)
Ge(1)-Y(1)-Ge(1)	80.76(7)	Ge(2)-Y(2)-Ge(2')	89.37(5)
Ge(1)-Y(1)-Ni(2)	173.02(7)	Ge(2)-Y(2)-Ge(2')	163.9(2)
Ge(1)-Y(1)-Ni(2)	42.82(5)	Ge(2')-Y(2)-Ge(2')	153.8(2)
Ge(1)-Y(1)-Ni(2)	97.48(4)	Ge(2)-Y(2)-Ge(2')	163.9(2)
Ge(1)-Y(1)-Ni(2)	137.43(4)	Ge(2')-Y(2)-Ge(2')	87.02(6)
Ge(1)-Y(1)-Ni(2)	84.55(5)	Ge(2')-Y(2)-Ge(2')	87.10(6)
Ge(1)-Y(1)-Ni(2)	97.41(4)	Ge(2')-Y(2)-Ge(2')	153.8(2)
Ni(2)-Y(1)-Ni(2)	130.20(9)	Ge(2)-Y(2)-Ga(2)	59.81(10)
Ni(2)-Y(1)-Ni(2)	79.75(5)	Ge(2)-Y(2)-Ga(2)	115.10(11)
Ni(2)-Y(1)-Ni(2)	79.82(5)	Ge(2')-Y(2)-Ga(2)	51.47(10)
Ge(1)-Y(1)-Ga(3)	131.77(4)	Ge(2')-Y(2)-Ga(2)	106.34(11)
Ge(1)-Y(1)-Ga(3)	78.93(4)	Ge(2)-Y(2)-Ga(3)	59.88(10)
Ge(1)-Y(1)-Ga(3)	179.22(4)	Ge(2)-Y(2)-Ga(3)	115.03(10)
Ge(1)-Y(1)-Ga(3)	100.02(5)	Ge(2')-Y(2)-Ga(3)	51.53(10)
Ni(2)-Y(1)-Ga(3)	94.85(6)	Ge(2')-Y(2)-Ga(3)	106.26(11)
Ga(3)-Y(1)-Ga(3)	79.20(6)	Ga(2)-Y(2)-Ga(3)	55.24(3)
Ge(2)-Y(2)-Ge(2)	174.0(2)	Ge(2)-Y(2)-Ga(3)	59.88(10)
Ge(2)-Y(2)-Ge(2)	89.80(4)	Ga(3)-Y(2)-Ga(3)	81.85(7)

Table VI.14. (continued)

Bond	Angle	Bond	Angle
Ni(2)-Ge(1)-Ge(1)	125.72(7)	Ni(1)-Ga(1)-Ga(1)	130.69(9)
Ge(1)-Ge(1)-Ge(1)	108.55(14)	Ga(1)-Ga(1)-Ga(1)	178.5(2)
Ge(2')-Ge(2)-Ni(1)	180.000(1)	Ga(1)-Ga(1)-Ga(1)	90.03(4)
Ge(2)-Ge(2')-Ga(2)	129.42(11)	Ga(1)-Ga(1)-Ga(1)	89.95(4)
Ga(2)-Ge(2')-Ga(2)	101.2(2)	Ni(2)-Ga(2)-Ni(2)	121.93(13)
Ga(2)-Ge(2')-Ga(3)	66.18(11)	Ni(2)-Ga(2)-Ge(2')	107.95(5)
Ge(2)-Ge(2')-Ga(3)	129.49(11)	Ge(2')-Ga(2)-Ge(2')	101.2(2)
Ge(1)-Ni(2)-Ga(3)	118.94(6)	Ni(2)-Ga(2)-Ga(3)	128.14(5)
Ga(3)-Ni(2)-Ga(3)	122.13(12)	Ni(2)-Ga(2)-Ga(3)	51.73(3)
Ge(1)-Ni(2)-Ga(2)	119.04(6)	Ge(2')-Ga(2)-Ga(3)	56.99(7)
Ga(3)-Ni(2)-Ga(2)	76.42(5)	Ge(2')-Ga(2)-Ga(3)	123.18(8)
Ga(2)-Ni(2)-Ga(2)	121.93(13)	Ga(3)-Ga(2)-Ga(3)	179.78(10)
Ge(2)-Ni(1)-Ga(1)	110.92(13)	Ga(3)-Ga(2)-Ga(3)	90.04(4)
Ga(1)-Ni(1)-Ga(1)	138.2(3)	Ga(3)-Ga(2)-Ga(3)	89.96(4)
Ge(2)-Ni(1)-Ga(1)	111.80(14)	Ni(2)-Ga(3)-Ni(2)	122.13(12)
Ga(1)-Ni(1)-Ga(1)	82.38(8)	Ni(2)-Ga(3)-Ge(2')	107.92(5)
Ga(1)-Ni(1)-Ga(1)	136.4(3)	Ge(2')-Ga(3)-Ge(2')	101.0(2)
Ni(1)-Ga(1)-Ni(1)	97.62(8)	Ni(2)-Ga(3)-Ga(2)	51.85(4)
Ni(1)-Ga(1)-Ni(1)	136.4(3)	Ni(2)-Ga(3)-Ga(2)	128.28(5)
Ni(1)-Ga(1)-Ga(1)	131.67(8)	Ge(2')-Ga(3)-Ga(2)	123.00(8)
Ni(1)-Ga(1)-Ga(1)	49.03(5)	Ge(2')-Ga(3)-Ga(2)	56.83(6)
Ni(1)-Ga(1)-Ga(1)	48.59(5)		

Table VI.15. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Y}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (3).

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Y(1)	3(1)	2(1)	2(1)	0	0	0
Y(2)	5(1)	4(1)	4(1)	0	0	0
Ge(1)	7(1)	7(1)	3(1)	0	0	0
Ge(2)	3(2)	20(3)	2(2)	0	0	0
Ge(2')	6(2)	21(3)	9(2)	0	0	0
Ni(1)	18(3)	13(2)	18(2)	0	0	0
Ni(2)	4(1)	8(1)	5(1)	0	0	0
Ga(1)	25(1)	24(1)	33(1)	0	0	0
Ga(2)	5(1)	9(1)	7(1)	0	0	0
Ga(3)	8(1)	10(1)	5(1)	0	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

The apparent disorder observed in these three structures is evidently pointing to a possible super-cell. However, no clear indication of it could be seen from the X-ray data except for the RECoGa₃Ge (RE = Y, Sm, Gd), where the reciprocal lattice featured satellite reflections with incommensurate spacings. We observed that the supercell reflections are generally too weak to be accurately measured. To further probe for long-range ordering, we performed electron diffraction studies (see below).

Single Crystal Neutron Structure Determination of 1.

Because the X-ray scattering power of Ga and Ge is nearly identical, elemental analysis was used in combination with bond distance considerations to assign the Ga and Ge atoms positions. However, in order to accurately determine these positions, neutron diffraction was used. The neutron scattering power between Ga and Ge differs by ~10% compare to ~3% for the X-ray radiation.

Neutron diffraction data were collected from a single crystal of YCoGa₃Ge (**1**) at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. The single-crystal diffractometer (SCD) is a time-of-flight instrument with a time- and position-sensitive detector. A detailed description of the SCD instrument and data collection and analysis procedures have been published.^{15, 16} A total of 13 histograms were measured at χ and ϕ values suitable to cover a unique octant of reciprocal space. An auto-indexing algorithm¹⁷ was used to obtain an initial orientation matrix from the peaks in one histogram. Data were indexed using individual orientation matrices for each histogram to

allow for any misalignment of the sample. Bragg peaks were integrated in three dimensions about their predicted locations and corrected for the incident neutron spectrum, detector efficiency and dead-time loss. The lattice constants were refined using 299 intense peaks, corresponding to an *I*-centered tetragonal cell with $a = 4.1882(7)$ Å and $c = 23.776(9)$ Å. The intensities were corrected for absorption using a local program ANVRED and assuming a spherical crystal of radius 1.27 mm, and linear absorption coefficients of $\mu_s = 0.409$ cm⁻¹ and $\mu_a = 0.471$ cm⁻¹ ($\lambda = 1.798$ Å). The GSAS software package¹⁸ was used for structural analysis. The refinement was based on F using reflections with $|F_o| > 3\sigma(F_o)$. Initial coordinates were obtained from single crystal X-ray analysis. The information relative to neutron data collection and refinement of **1** is given in Table VI.16; the positional and thermal displacement parameters and occupancies are presented in Table VI.17. The selected interatomic distances are listed in Table VI.18.

Refinement of the neutron structure shows that the original X-ray assignment of Ga and Ge atoms (based on bond distances) was correct, *i.e.*, the Ge atoms indeed occupy $4e$ sites, while Ga was refined on the $8g$ and $4d$ sites. The neutron refinement also confirmed that the Ge atoms in **1** are in split sites with 50% occupancy on each, and the Co $4e$ position is 50 percent occupied. Thus, the unit cell composition of **1** can be formulated as YCoGa₃Ge with $Z = 4$.

Table VI.16. Neutron crystal data and structural refinement parameters for YCoGa₃Ge
(1).

Formula	YCoGa ₃ Ge
Fw	429.62
temperature, K	295
crystal system	<i>Tetragonal</i>
space group	<i>I4/mmm</i>
<i>a</i> , Å	4.1882(7)
<i>c</i> , Å	23.776(9)
<i>V</i> , Å ³	417.1(2)
<i>Z</i>	4
<i>d</i> _{calc} , g/cm ³	6.84
radiation	neutrons
data collection technique	time-of-flight Laue
$\mu(\lambda)$, cm ⁻¹	0.409 + 0.262 λ
reflns. (<i>I</i> > 3 σ (<i>I</i>)) / parameters	433 / 34
refinement method	Full-matrix least-squares on <i>F</i>
<i>R</i> indices <i>Rw(F)</i> ^a <i>R(F)</i> , ^b	0.062, 0.068

$$^a R_w(F) = \left\{ \sum [w(F_o - F_c)^2] / \sum [w(F_o)^2] \right\}^{1/2}; \quad ^b R(F) = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|$$

Table VI.17. Fractional Coordinates and Site Occupancy of YCoGa₃Ge (1).

Position	Wyckoff. Symbol	<i>x</i>	<i>y</i>	<i>z</i>	Occ.
Y	<i>4e</i>	0	0	0.14900(7)	1
Ga(1)	<i>8g</i>	0	½	0.05446(6)	1
Ga(2)	<i>4d</i>	0	½	¼	1
Co(1)	<i>2a</i>	0	0	0	1
Co(2)	<i>4e</i>	0	0	0.2777(5)	0.5
Ge(1)	<i>4e</i>	0	0	0.3562(3)	0.5
Ge(2)	<i>4e</i>	0	0	0.3754(2)	0.5

Table VI.18. Selected Interatomic Distances (Å) for YCoGa₃Ge (1).

Bond	Distance	Y—Ge(2)	3.018(1)
Y—Ga(1)	3.072(2)	Co(1)—Ga(1)	2.462(1)
Y—Ge(1)	2.9641(6)	Co(2)—Ga(2)	2.195(4)
Y—Co(2)	3.436(6)	Ga(1)—Ga(1)	2.9615(5)
Ga(1)—Ge(2)	2.677(3)	Co(2)—Ge(2)	2.323(13)
Y—Ga(2)	3.186(1)	Ga(1)—Ge(1)	2.982(5)

The transmission electron microscopy (TEM) studies were performed on TEM microscope JEOL 100CX. The electron beam was generated from the CeB₆ filament at accelerating voltage 120 kV. Both the imaging mode and the selected area electron diffraction (SAED) were used. The samples were stable under the impact of electron beam.

Sample preparation: large, often square plate-like single crystals of **1** and irregularly shaped flat single crystals of **2**, normally over 10 mm² in area and up to 600 μm in thickness were selected. The samples were hand-polished with subsequently increasing grit (1000 – 1500) sandpaper to approximately 200 – 300 μm in thickness. A core drill was then used to cut out circular shaped specimens 3 mm in diameter, suitable for use in the TEM holder. As-prepared samples were electrolytically thinned using Tenupole-3 twin-jet polishing unit equipped with an infrared detector. The electropolishing experiment was conducted in the temperature range from -35°C to -40°C with applied potential 15V using four-component acidic electrolyte¹⁹. The mean size of the resultant hole is regularly $\sim 100 \mu\text{m}$ in diameter, with the average area lucent to the electron beam on the order of $400 \mu\text{m}^2$. Due to the plate-like habit of the crystals, in most cases the [001] zone axis could be observed at zero tilt. It is only in the case of GdCoGa₃Ge when the transverse [010] zone axis was possible to observe owing to the unusual cuboid shape of the crystal. The polished specimen and the resulting hole surrounded by the thin area are shown in Figure VI.2.A and B, respectively.

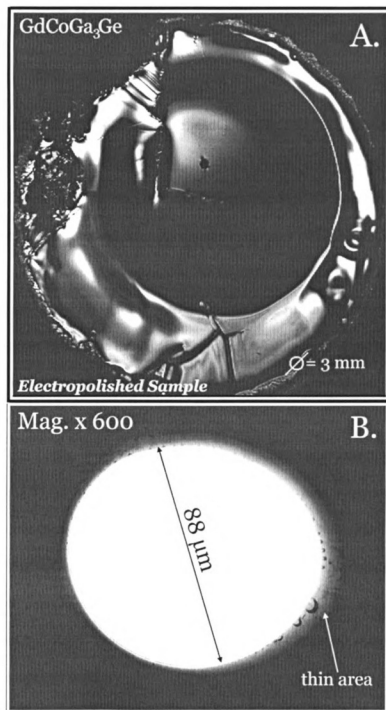


Figure VI.2. The electropolished sample of GdCoGa_3Ge . (A) The image of the bowl-shaped specimen with the hole in the center; (B) Low magnification TEM image of the thin area surrounding the hole.

Magnetic Measurements

The magnetic susceptibility was measured on single crystal and polycrystalline samples of **1** (TbNiGa₃Ge, GdCoGa₃Ge and YCoGa₃Ge) and **2** (Gd₃Ni₃Ga₈Ge₃) as a function of temperature in the range 2 – 400 K in an applied external magnetic field 500 Gauss with MPMS Quantum Design Inc. SQUID magnetometer. The magnetic properties of **3** were studied on polycrystalline samples of Tb₄Ni₃Ga₆Ge₄.

Sample preparation: the crystalline samples of **1** and **2** were picked manually and polished with sandpaper to the mirror-like finish. These special precautions were taken in order to remove the Ni (Co) or Ni-, Co-containing impurities that may have been adhered to the surface of the crystals. The crystals were subsequently sonicated in water, and dried with acetone and ether.

The field dependence of the magnetic susceptibility was determined at 2 - 3 K in the fields up to ± 5 T. The susceptibility data was corrected for the sample holder contribution. The isotropic measurements (TbNiGa₃Ge, GdCoGa₃Ge, YCoGa₃Ge and Tb₄Ni₃Ga₆Ge₄) were carried out using ground polycrystalline samples. For anisotropic measurements (GdCoGa₃Ge and Gd₃Ni₃Ga₈Ge₃) crystals with explicit plate-like morphology were placed with the *c*-axis parallel and perpendicular to the external magnetic field.

3. Results and Discussion

Reaction Chemistry

The reaction chemistry in the system RE/M/Ga/Ge (RE = rare-earth, M = nickel/cobalt) conducted in excess Ga with RE : M = 1 is one of the most complex among metal flux systems. For example, in previous studies in the related systems with Al (RE/M/Al/Ge, RE/M/Al/Si) and with Ga (RE/M/Ga/Si and RE/M/Ga/Ge with RE : M < 1) we observed that, generally, for a given set of reaction conditions a series of isotypic compounds with different RE and/or M metal could be obtained. For instance, over twenty analogs of $\text{RE}_{0.67}\text{M}_2\text{Ga}_{5-x}\text{Tt}_x$ ^{1,20} and $\text{RE}_{0.67}\text{M}_2\text{Al}_{5-x}\text{Tt}_x$ ²¹ (Tt = Si or Ge), have been obtained and nearly every heavy RE analog of $\text{RENiAl}_4\text{Ge}_2$ ⁴ grown. For the first time in the course of investigations in the RE/M/Ga/Ge system, with RE : M = 1, we observe such delicate sensitivity of the products to the reaction conditions and a tremendous variation of the crystal structure with the RE element.

Thus, for M = Ni the reaction of different lanthanide elements under otherwise identical conditions results in YNiGa_3Ge , $\text{Ce}_2\text{NiGa}_9\text{Ge}_2$, $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$, and TbNiGa_3Ge . The case is even more complicated for Sm, as up to three phases $\text{Sm}_2\text{NiGa}_9\text{Ge}_2$, SmNiGa_3Ge and $\text{Sm}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ could be found in the reaction product. The latter two possibly form an intergrowth in one isolated crystal. Furthermore, increased reaction times (3 – 6 days), with Tb and Y produced $\text{Y}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ and $\text{Tb}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (compared to YNiGa_3Ge and TbNiGa_3Ge obtained in shorter reaction times). Interestingly, if Ni is substituted for Co, the following phases form in quantitative yield: YCoGa_3Ge ,

$\text{Ce}_2\text{CoGa}_9\text{Ge}_2$, SmCoGa_3Ge , GdCoGa_3Ge and ErCoGa_5 for the RE = Y, Ce, Sm, Gd and Er, respectively. As we will describe below, these different phases share many structural components and may have similar formation energies. Also, some may be intermediates that were quenched before they had a chance to transform to more thermodynamically stable phases.

Crystal Structure of 1.

The crystal structure of REMGa_3Ge derives from the $\text{Ce}_2\text{NiGa}_{10}$ structure type²², however, no disorder has been reported for the latter. To show the relationship of these two structures, we can rewrite the formula of $\text{Ce}_2\text{NiGa}_{10}$ -type and **1** as $\text{RE}_4\text{Ni}_2[\text{Ga}'_4\text{Ga}''_{12}\text{Ga}'''_4]$ and $\text{RE}_4\text{M}_2[\text{M}_2\Box_2\text{Ga}''_{12}\text{Ge}_4]$, respectively. In this formulation the different crystal sites in their structures are clearly indicated. Thus, the relation of **1** to $\text{Ce}_2\text{NiGa}_{10}$ lies in substitution of Ga' with M and a vacancy, $\Box$, plus a substitution of Ga''' with Ge. The REMGa_3Ge compounds are the first gallium-containing analogs in this structure type. The quaternary aluminum isotype $\text{Ce}_2\text{NiAl}_{6-x}\text{Ge}_{4+y}$ has been recently reported⁵. The crystal structure of the YCoGa_3Ge , as refined using neutron diffraction data and projected onto bc plane is depicted in Figure VI.3. In this plot, no bonds were drawn to the Y atoms in order to emphasize the different types of layers participating in the construction of this structure. Sub-divided in this fashion, the structure can be represented as a consecutive stacking of the Y-Ge plane, a $[\text{CoGa}_4\text{Ge}_2]$ slab and a puckered $[\text{CoGa}]_2$ layer.

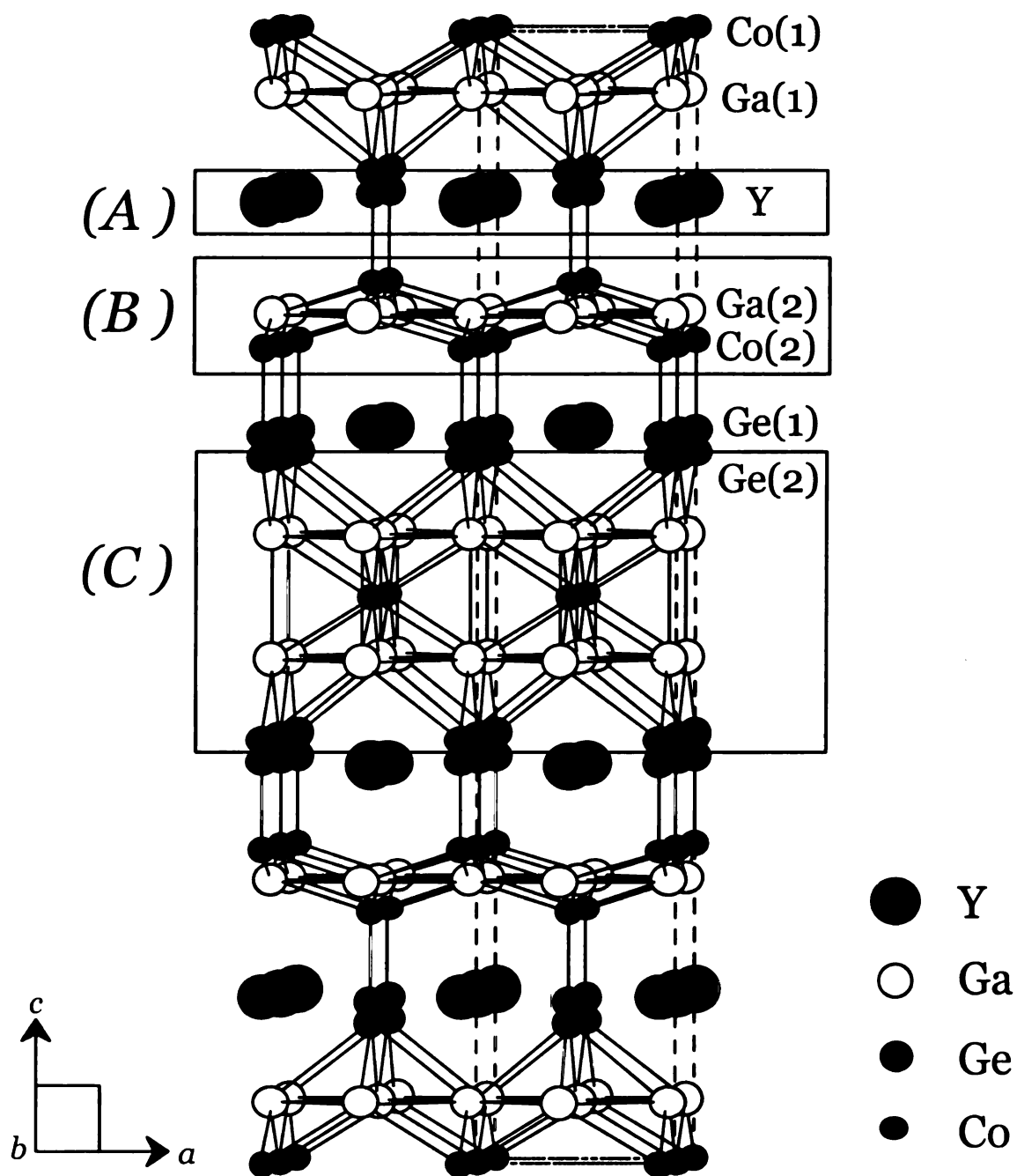


Figure VI.3. The structure of YCoGa_3Ge (1) viewed along the b -axis. No bonds are drawn to Y atoms. The unit cell is shown with dashed lines. The 2D slabs participating in structure building are contoured with solid line and marked by the letters (A), (B) and (C).

The fragment of the Y-Ge plane (*A*) viewed along the *c*-axis is shown in Figure VI.4.A. The layer is defected, with the Ge atomic site being only 50% occupied. In the ideal YGe layer, the Y and Ge atoms are arranged in square-like manner, with Ge atoms being slightly off the plane of Y atoms. The distance between the Y and Ge in the plane is normal 2.9641(6) Å, the Y–Y distance in the square net corresponds to the length of the unit cell, *a*. The [CoGa]₂ disordered puckered layer (*B*), viewed approximately down the *c*-axis is shown in the Figure VI.4.B. In this layer Ga(2) atoms form a monoatomic square net with Ga(2)-Ga(2) distance of 2.9520(7) Å. The Co atoms are located above or below every Ga(2) square in a puckered manner (note that every second Co(2) position is not occupied).

Finally, the structure contains [CoGa₄Ge₂] slab (*C*), see Figure VI.4.C. This type of layer has been previously observed in a number of ternary and quaternary intermetallic compounds such as Ce₂NiGa₁₀²², Pr₃NiGa₁₀²³, Ce₄NiGa₁₈²⁴, Sm₂NiGa₁₂⁷, Sm₂Ni(Ni_{*x*}Si_{1-*x*})Al₄Si₆¹ and Ce₂NiAl_{6-*x*}Ge_{4-*y*}⁵. The layer consists of greatly compressed Ga₈ cubes, with the lengths of the cube sides being 2.590(3) Å and 2.9615(5) Å that are condensed via face-sharing into two-dimensional Ga₄ framework. A half of the cubes in this framework are centered with Co(1) atoms, while the other half is vacant but capped with Ge atoms from above and below, Figure VI.4.C. The distance from the central Co(1) atom to the corners of Ga(1) cube is 2.462(1) Å, the bond length between the capping Ge(2) and Ga(1) atoms is 2.677(3) Å. This slab is again defected, so that every second Ge(2) atom is missing. In the structure of **1** the stacking sequence of the layers described above is *ABAC ABAC* if YGe, [CoGa]₂ and [CoGa₄Ge₂] slabs were denoted as *A*, *B* and *C*, respectively.

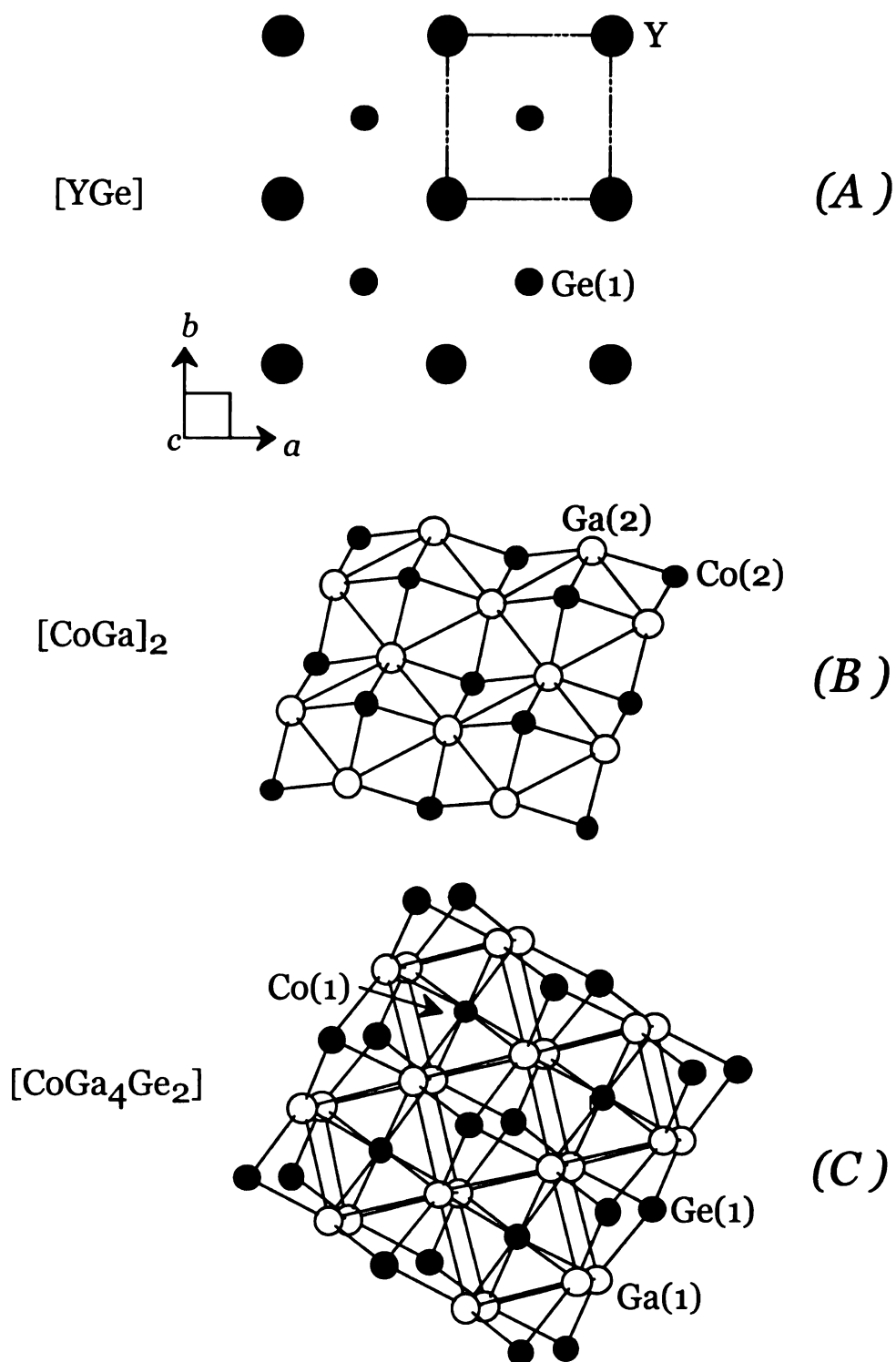


Figure VI.4. The building blocks of the structure of **1**. (A) the Y-Ge monatomic layer projected onto ab plane; (B) the $[CoGa]_2$ puckered layer; (C) the $[CoGa_4Ge_2]$ slab viewed approximately along the c -axis.

The local coordination environments of the Y atoms within 3.5 Å and of the Co, Ga and Ge atoms within 3.0 Å are presented in Figure VI.5. The Ge(1) and Ge(2) positions are regarded as one (split) Ge site. The Y atoms have four nearly in-plane contacts with Ge atoms; above and below this Y-Ge plane, the squares of Ga(1)₄ and Ga(2)₄ are located in staggered conformation to each other. The Co(1) capping the Ge(1)₄ square, and additional five Co(2) atoms from the Ga(2)Co(2) puckered layer complete the 18-coordination sphere of Y atoms. The Co(1) is in the distorted cubic environment of eight Ga(1) atoms. The Co(2) local coordination is square-pyramidal with a square base made of Ga(2) atoms and an apex of Ge atom. Similarly, the Ge atom is in the center of a Ga(1)₄Co(2) square pyramid.

The Ga(1) atom is nine-coordinate, it has slightly distorted tetrahedral environment of two Co(1) and two Ge atoms (the Co(1)-Ga(1)-Ge angle is 109.1°). The Ga(1) is additionally self bonded to four atoms in *ab* plane (Ga(1)-Ga(1) = 2.9615(5) Å) and to one out-of plane Ga(1) that caps the Co(1)-Co(1) edge of the tetrahedron. The Ga(2) is eight-coordinate, its nearest coordination is formed by a severely distorted tetrahedron of four Co(2) atoms (Co(2)-Ga(2) = 2.195(4) Å); the next four near-neighbors are four in-plane Ga(2) atoms bonded at 2.9615(5) Å.

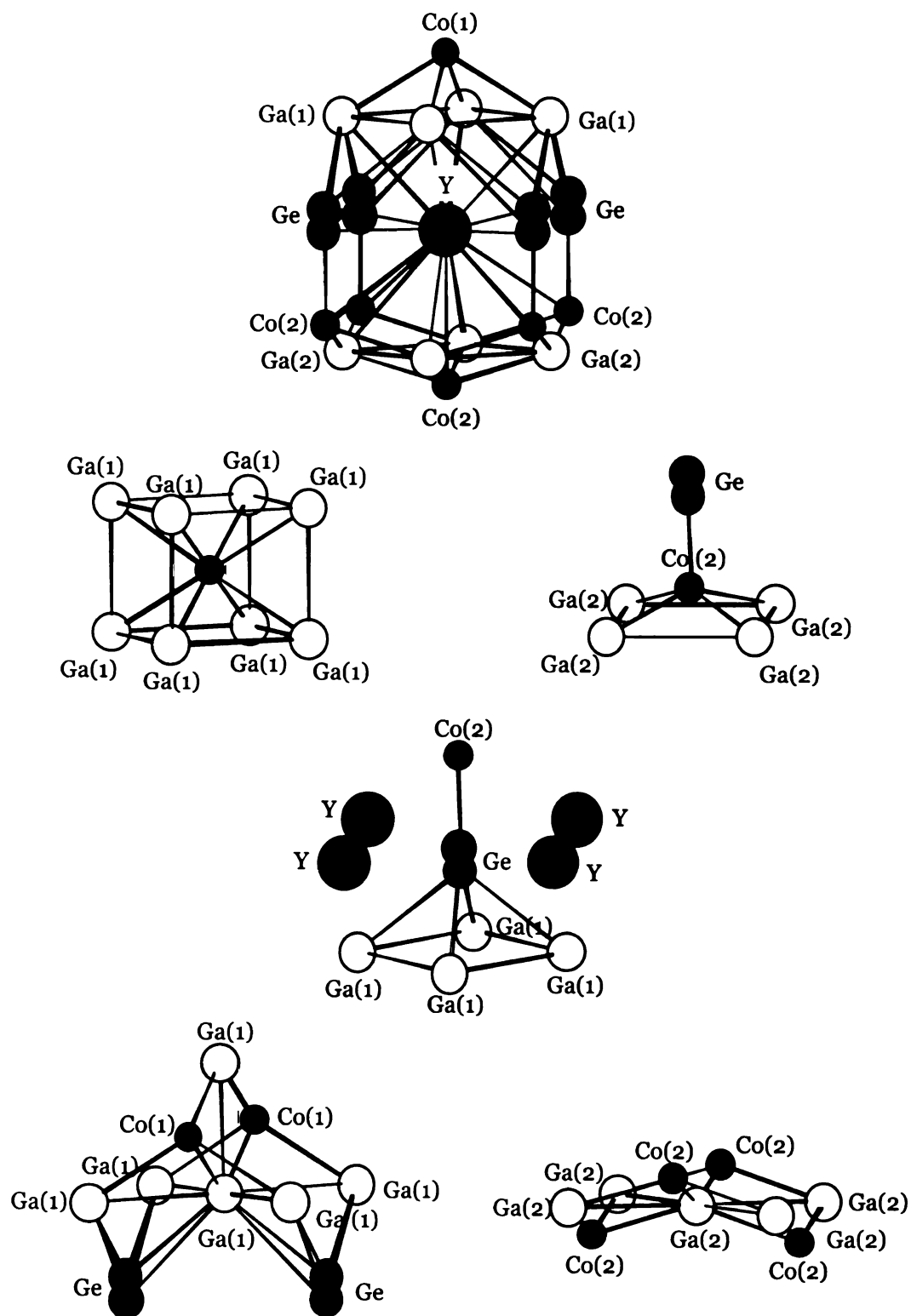


Figure VI.5. The local coordination of Y atoms within 3.5 Å and Co, Ga and Ge atoms within 3.0 Å. The Ge(1) and Ge(2) positions are depicted as one split Ge site.

Crystal Structure of 2.

The structure of **2**, to the best of our knowledge, constitutes a new structure type. The crystal structure of $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ (**2**) is shown in Figure VI.6, and is reminiscent of that of YCoGa_3Ge (**1**). Although the neutron structure refinement is not available for **2**, we are confident in assigning the Ga and Ge atoms similar to that of **1**, considering the strong structural similarities of these two compounds. Using the same analogy, the structure of **2** could be constructed of the same building motifs as **1**; however, in the $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ the stacking sequence is different. Namely, the Gd-Ge (A) plane, a $[\text{NiGa}]_2$ (B) puckered layer and $[\text{NiGa}_4\text{Ge}_2]$ (C) slab appear in the sequence: *ABACABA ABACABA*.

The local environment of the ordered atoms in **2** is identical to those found in **1** with the exception of Gd(1) which is sandwiched between two $[\text{NiGa}]_2$ B-type layers and does not have a counterpart in **1**. The local coordination of the Gd(1) atom, remarkably, includes 22 atoms within a radius of 3.5 Å, see Figure VI.7. However, because of the partial occupancies on Ni(2') site, the actual number of Gd(2) neighbors is less than 22. The environment of the Gd(2) atom contains four Ge(1) atoms lying in a plane that includes Gd(2). Additionally, two fragments of the $[\text{Ni}(2')_4\text{Ga}(2)_4\text{Ni}(2)]$ puckered layer (related to each other by mirror symmetry) are located above and below the Gd(2)/Ge(1) plane.

It is useful to view the structure of **2** in polyhedral representation, see Figure VI.8.A. The Gd(1) atoms are in ideal, and Gd(2) in distorted, cubooctahedral environment of Ga and Ge atoms (within 3.2 Å).

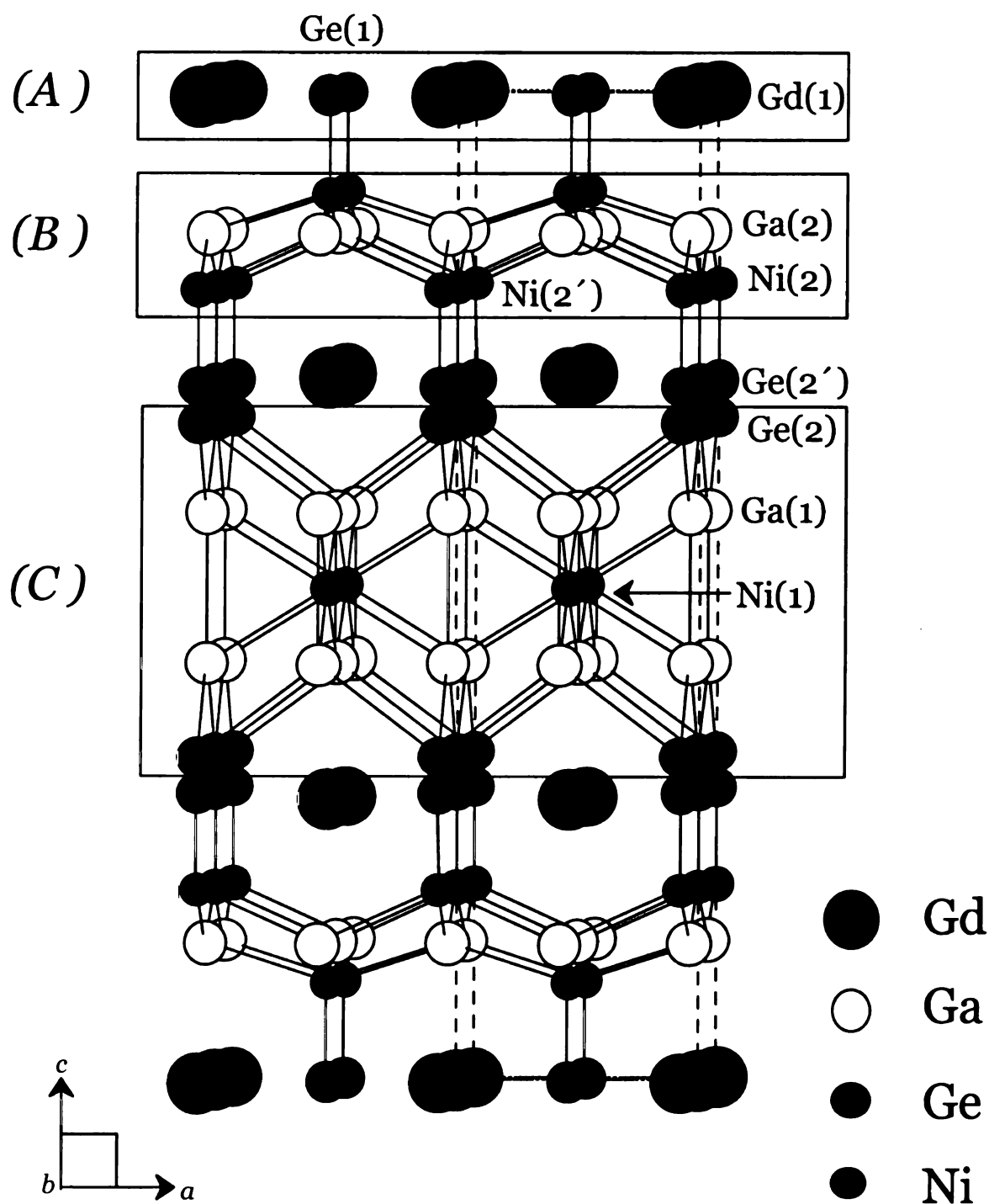


Figure VI.6. The structure of $\text{Gd}_3\text{NiGa}_8\text{Ge}_3$ (2) viewed down the b -axis. The unit cell is shown with dashed lines. The 2D slabs participating in structure building are contoured with solid line and marked by the letters (A), (B) and (C).

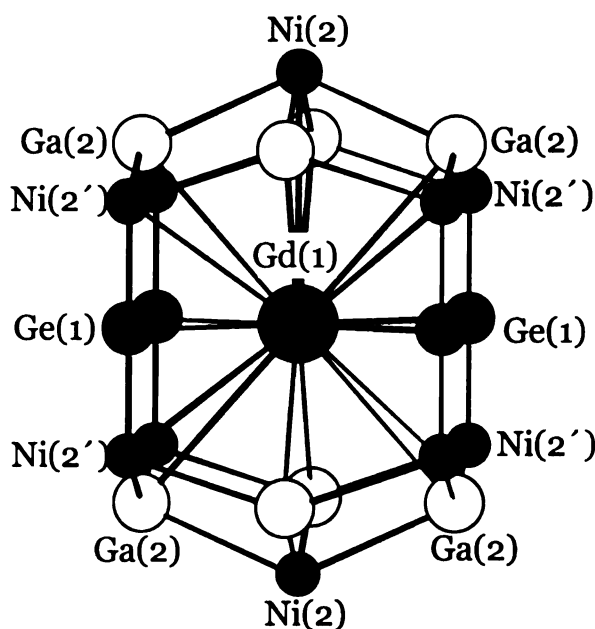
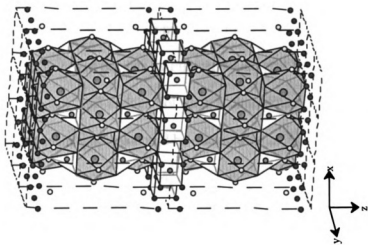


Figure VI.7. The local coordination of the Gd atoms within 3.5 Å and the Ni, Ga and Ge atoms within 3.0 Å. Only ordered atoms are shown, the Ge(2) and Ge(2') positions are depicted as one split Ge(2) site.

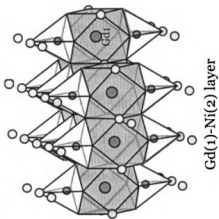
The Gd(1) cubooctahedra are condensed into a 2D layer via sharing four out of their six square faces with each other, infinitely extending in the *ab* plane, see Figure VI.8.B. Likewise, the Gd(2) polyhedra share rhombic faces forming a 2D layer, see Figure VI.8.C. In this Gd(2) layer, the pyramidal voids are occupied by Ni(2) atoms. The Ni(1) atoms are in a distorted cubic environment of Ga atoms. These cubes share edges to form a 2D Ni(1)-Ga(1) layer as shown in Figure VI.8.D. The Gd(1), Gd(2)-Ni(2) and Ni(1)-Ga(1) layers alternate along the *c*-axis and connected via face-sharing interactions between Gd and Ni polyhedra and via edge sharing between Gd(1) and Gd(2) cubooctahedra. The coordination polyhedra of the Gd(1), Gd(2), Ni(1) and Ni(2) atoms are outlined in Figure VI.8.E.

Figure VI.8. (A) The structure of $\text{Gd}_3\text{NiGa}_8\text{Ge}_3$ (**2**) in polyhedral representation. (B) The isolated layer of the Gd(1) cubooctahedra; (C) the fragment of the Gd(2)-Ni(2) layer; (D) distorted cubic layer of Ni(1); (E) coordination polyhedra of Gd and Ni atoms in **2**.

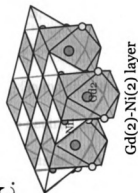
A.



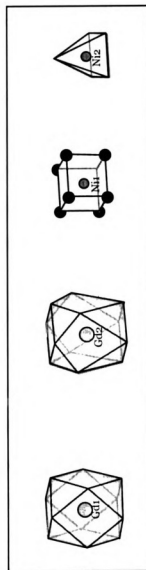
B.

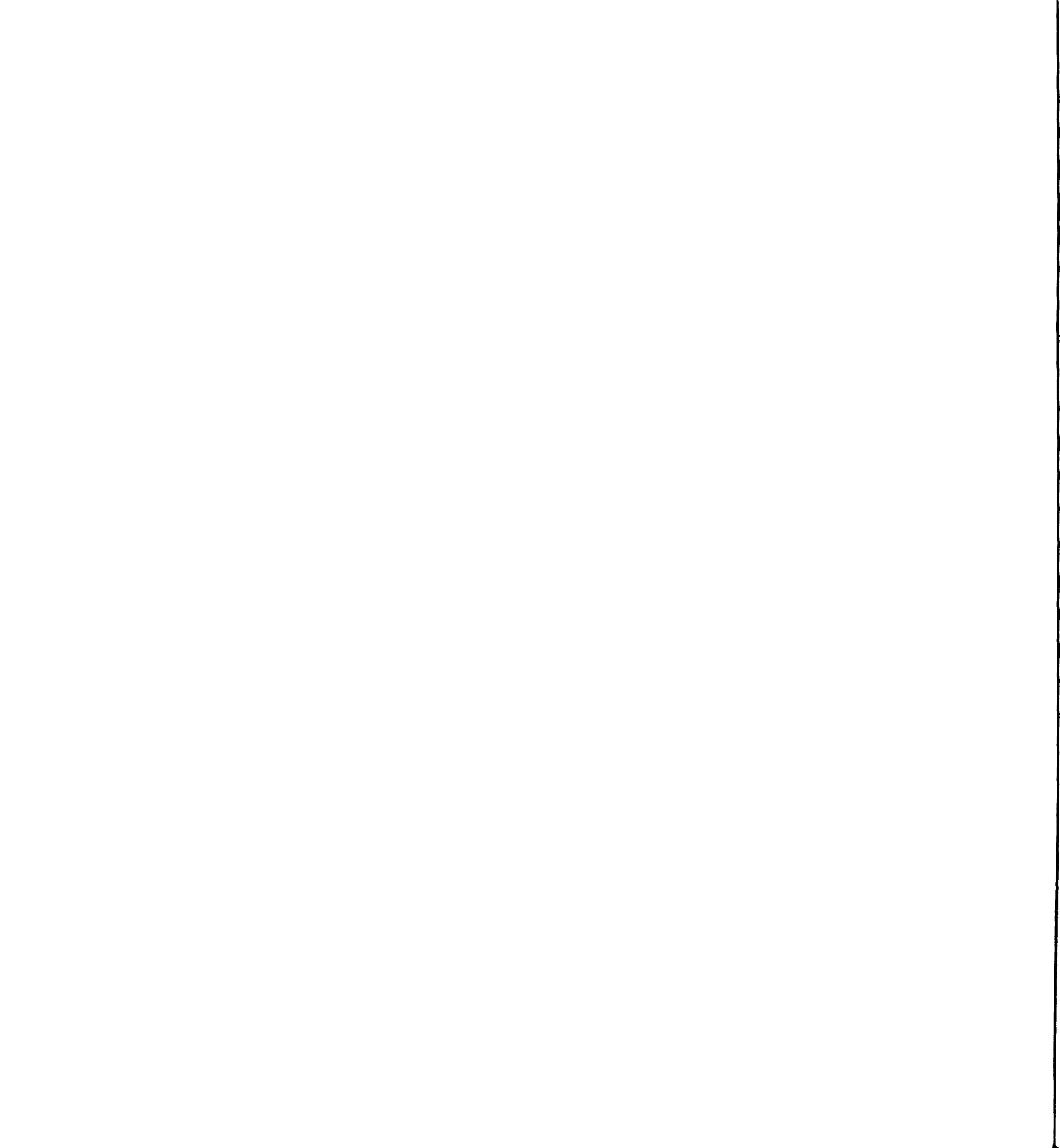


C.



D.





Crystal Structure of 3.

Although the neutron diffraction experiment was not performed on the crystals of **3** to accurately determine Ga/Ge distribution, we are confident in the correctness of current assignment based on X-ray data. For **3**, we founded our Ga/Ge assignment on the principles of connectivity, so that the shorter Y-X distances (where X could be Ga or Ge) were attributed to Y-Ge, while longer to Y-Ga interactions. The obtained assignment was then cross-checked for consistency with the neutron solution available for **1**, since both **1** and **3** have common structural units. The consistency was confirmed, thus supporting the accurateness of current assignment in **3**.

The crystal structure of $\text{Y}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (**3**) viewed along the *b*-axis is shown in Figure VI.9. Four building blocks could be identified in the structure of **3**. Two of fragments, namely [REGe] plane (*A*) and [MGa]₂ layer (*B*) are identical to those found in the structures of **1** and **2**. The next two blocks: (*A*′) and (*B*′) have geometries similar to (*A*) and (*B*), as could be seen in Figures VI.10 and VI.11. The last structural motif is a Ge zigzag chain (*C*), and it does not have a counterpart in **1** and **2**. Using these four motifs, the building principle in **3** could be outlined as ... *AB*′*A*′*CA*′*B*′*AB* ... *AB*′*A*′*CA*′*B*′*AB*.

A fragment of [YGe] (*A*) and Y (*A*′) monoatomic planes viewed down the *b*-axis is shown in Figure VI.10. The Y-only layer (*A*′) is orthorhombic and formed by Y(1) atoms. The [YGe] layer (*A*) consists of orthorhombic mesh of Y(2) and Ge(2) atoms. The Y(2) is bonded to Ge(2) at 2.9019(10) Å and to Y(2) at 4.0999(19) Å and 4.0968(19) Å (unit cell parameters *a* and *c*).

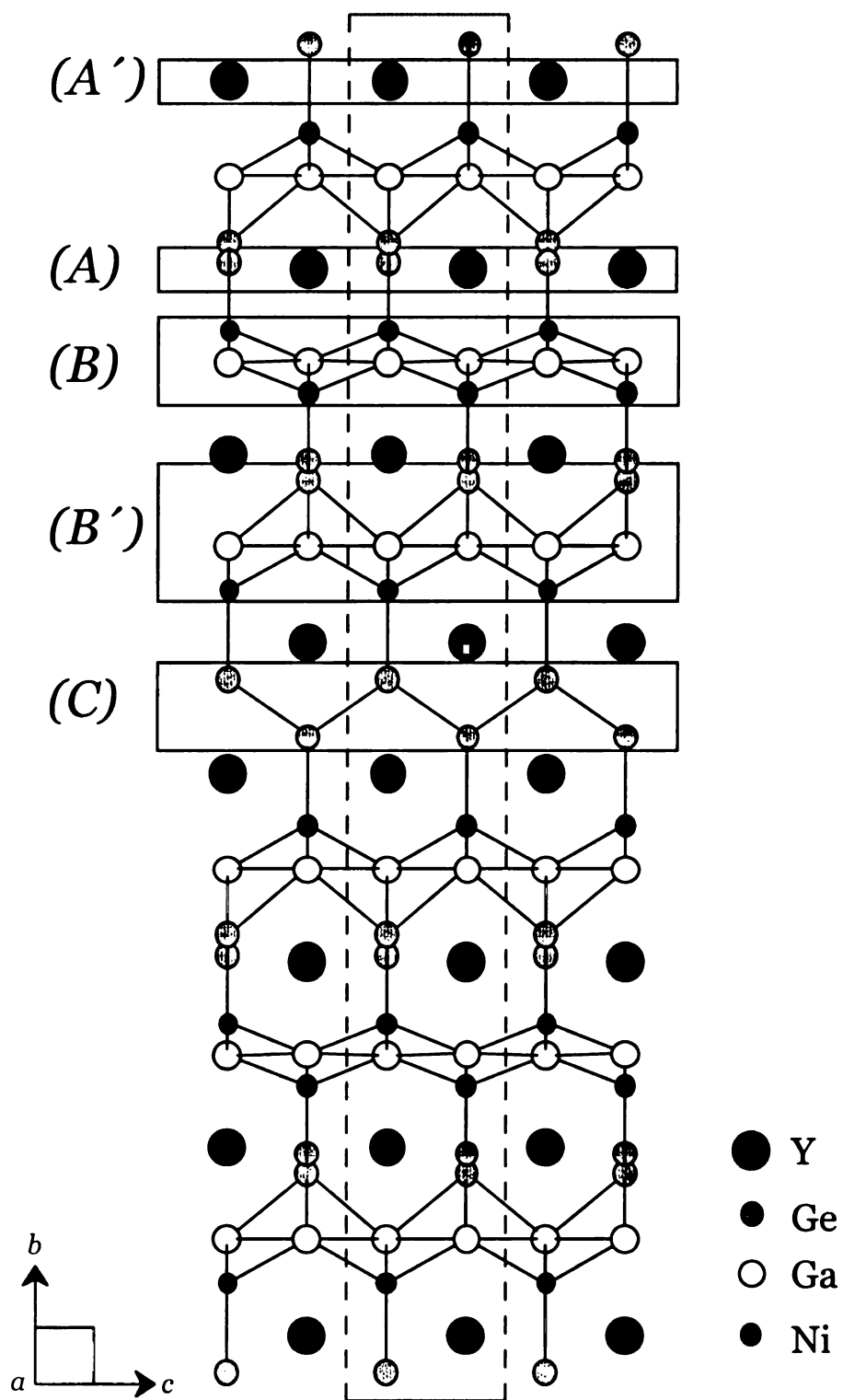


Figure VI.9. The structure of $\text{Y}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (3). The unit cell is shown in dashed lines.

The constituting structural fragments are outline in solid lines.

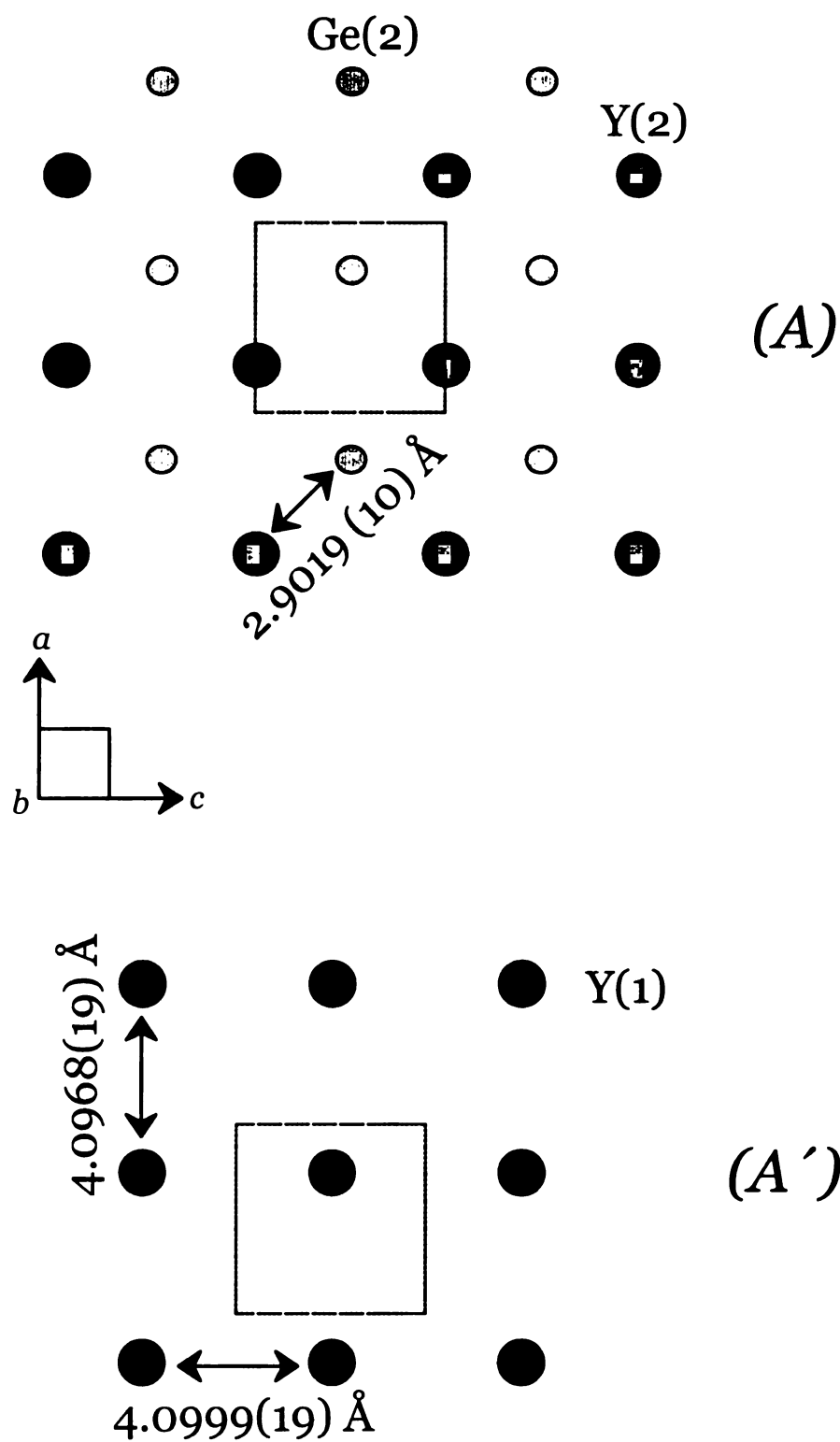


Figure VI.10. The monoatomic layers: $[\text{Y}(2)\text{Ge}(2)]$ (up) and $\text{Y}(1)$ (down). The unit cell is given with dashed lines.

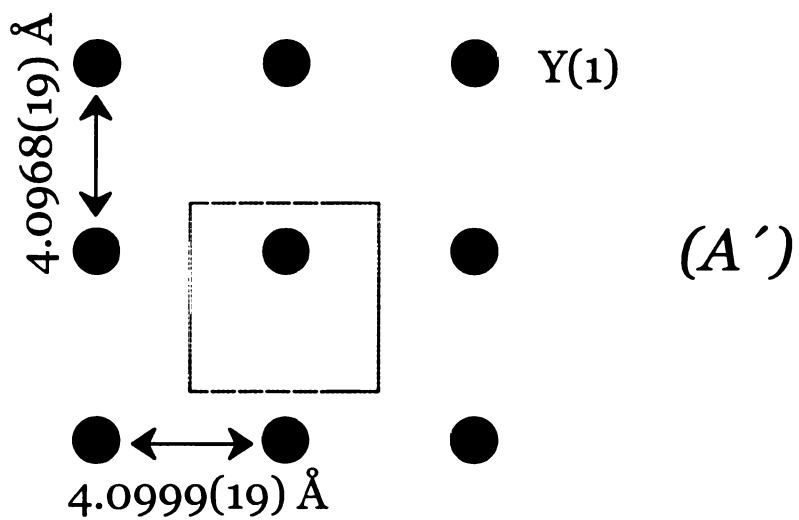
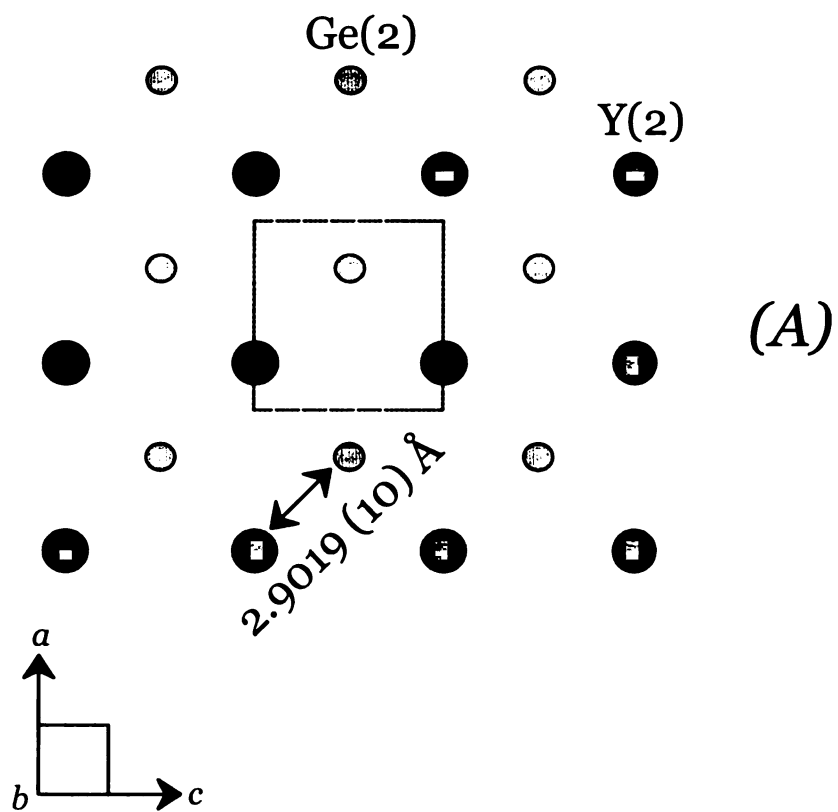


Figure VI.10. The monoatomic layers: [Y(2)Ge(2)] (up) and Y(1) (down). The unit cell is given with dashed lines.

A portion of the $[\text{NiGa}]_2$ (*B*) and $[\text{NiGa}_2\text{Ge}]$ (*B'*) slabs is shown in Figure VI.11. In layer (*B*) and (*B'*), the Ga atoms form a square lattice with Ga-Ga bond distances of 2.8982(9) Å and 2.8980(9) Å, respectively. These are significantly shorter than the corresponding Ga-Ga distances in puckered layers of **1** and **2** (Ga-Ga is 2.9520(7) Å for **1** and 2.9563(13) Å for **2**). In (*B*) layer, the squares of Ga(1) net are capped from above and from below with Ni(1) at 2.208(2) Å and 2.193(2) Å. These distances are unreasonably short for Ni-Ga connectivity, and therefore the Ni(1) site has a reduced occupancy (50%). In (*B'*) layer, the squares are formed with Ga(2) and Ga(3) and capped on the opposite sides with Ni(2) and Ge(2'). The bonding interactions in this layer are regular; those are 2.3446(17) Å and 2.3406(16) Å for Ni-Ga and 2.652(4) Å and 2.656(4) Å for Ga-Ge connectivities. In view of the sum of single-bonded metallic radii for Ni and Ga (2.46 Å), the Ni-Ga interaction in (*B'*) is very strong, with a large covalent contribution to the bonding character. The corresponding Ga-Ge interactions are comparable to the sum of single-bonded metallic radii for Ga and Ge (2.47 Å) and could be considered as bonding. Similar Ga-Ge bonding has been observed in compounds **1** and **2** (Ga-Ge = 2.600(3); **2**: Ga-Ge = 2.618(2) Å).

Alternatively (*B'*) slab could be viewed as a part of the cube layer $[\text{MGa}_4\text{Ge}_2]$ found in **1** and **2**. Thus, if two (*B'*) layers are merged together to share their Ni(2) atoms, a $[\text{NiGa}_4\text{Ge}_2]$ slab could be produced, see Figure VI.9.

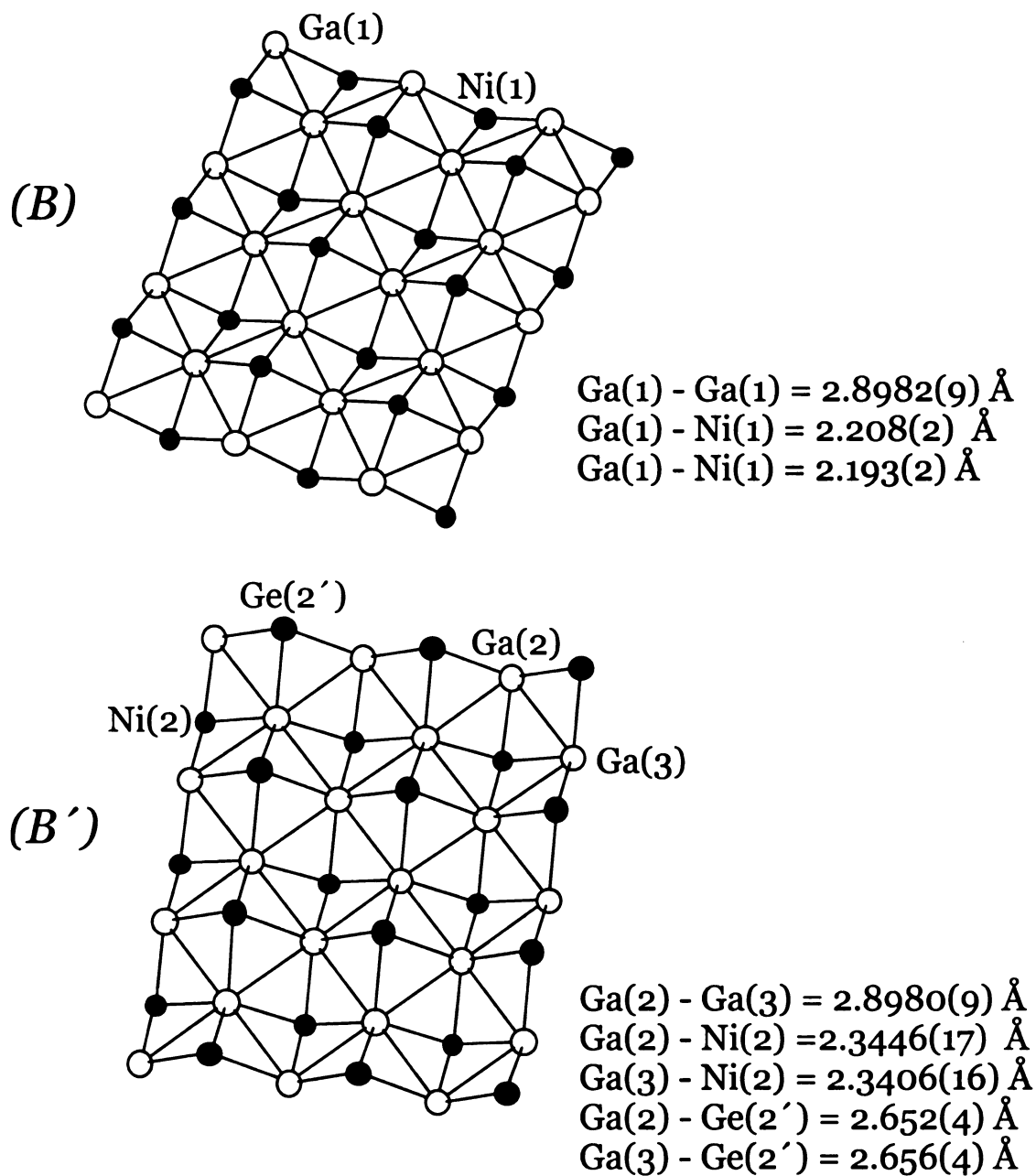


Figure VI.11. A fragment of pucker layers: $[\text{NiGa}]_2$ (up) and $[\text{NiGa}_2\text{Ge}]$ (down).

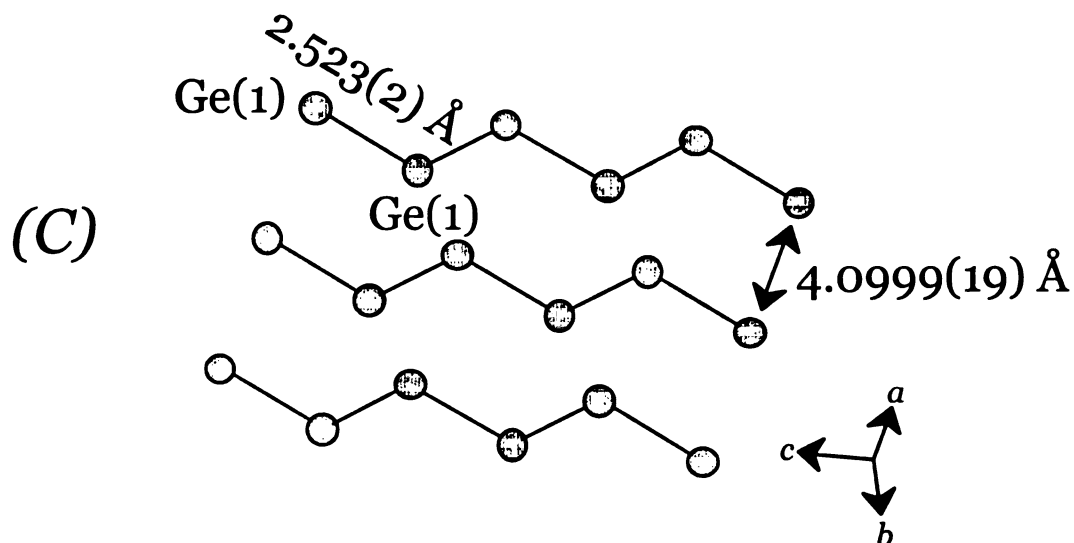


Figure VI.12. Isolated [Ge(1)] zigzag chains.

A fragment of **3** containing Ge(1) zigzag chains is given in Figure VI.12. The bond distances and angles are uniform throughout the chain and equal 2.523(2) Å and 108.55(14)°, respectively. The chain separation distance is a unit cell parameter $a = 4.0999(19)$ Å. The axis of the chain is parallel to c , and the plane of the chain is perpendicular to the a -axis. The Ge(1)-Ge(1) interactions are comparable to those found in the related Tb_4FeGe_8 (Ge zigzag chain: Ge-Ge = 2.586(3) Å; Ge-Ge-Ge = 100.94(16)°), but more strongly bonding than in the latter. This Ge(1)-Ge(1) distance is comparable to the sum of covalent radii²⁵ of Ge (2.44 Å) and the Ge-Ge distances found in elemental Ge²⁶. The Ge-Ge bonding interaction within the chain is thus of a strong covalent character.

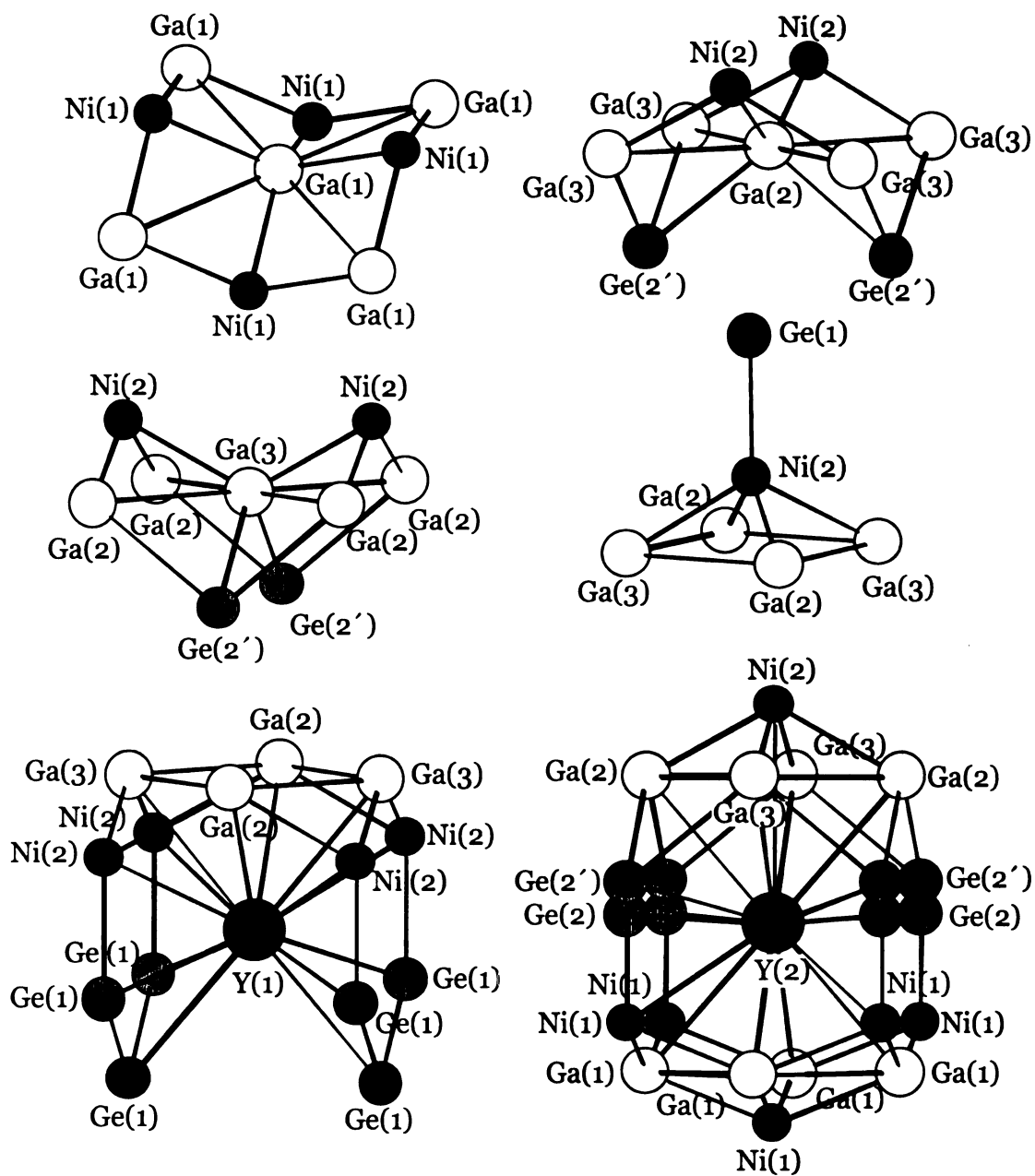


Figure VI.13. Local coordination environments of Y (within 3.5 Å), Ga, Ge and Ni (within 3.0 Å). Only coordination spheres of ordered atoms are shown.

The local coordination environments of Y atoms within cutoff radius of 3.5 Å and Ni, Ga and Ge within 3.0 Å are shown in Figure VI.13. Only the coordination spheres of the ordered atoms are considered. The Ga(1) atoms are eight-coordinate, they have a slightly distorted square planar environment of four Ga(1) atoms (the Ga(1)-Ga(1) bond distance is 2.8982(9) Å, and Ga(1)-Ga(1)-Ga(1) angles are 90.03(4)° and 89.95(4)°). Additionally, Ga(1) is bonded to four Ni(1) atoms in shape of grossly distorted tetrahedron at 2.208(2) Å and 2.193(2) Å. The Ni(1)-Ga(1)-Ni(1) angles range from 97.62(8)° to 138.2(3)°. Similarly, Ga(2) has eight neighbors; of those four in-plane contacts come from Ga(3) atoms at 2.8980(9) Å (Ga(3)-Ga(2)-Ga(3) angles are 90.03(4)° and 89.95(4)°) and another four from two Ni(2) atoms at 2.3446(17) Å and two Ge(2') at 2.652(4) Å. The latter four atoms form slightly distorted tetrahedron with the corresponding angles of 101.2(2), 107.95(5) and 121.93(13)°. The Ga(3) environment is identical to that of Ga(1) and Ga(2); the in-plane interactions come from four Ga(2) atoms, and tetrahedral surrounding is formed by two Ni(2) and two Ge(2') atoms. The central Ge(3) is bonded to Ni(2) and Ge(2') at 2.3406(16) Å and 2.656(4) Å, respectively. The Ni(2) atoms occupy a center of a square prism with a base of four Ga(2) atoms and an apex of Ge(1) atom (Ni(2)-Ge(1) = 2.282(3) Å).

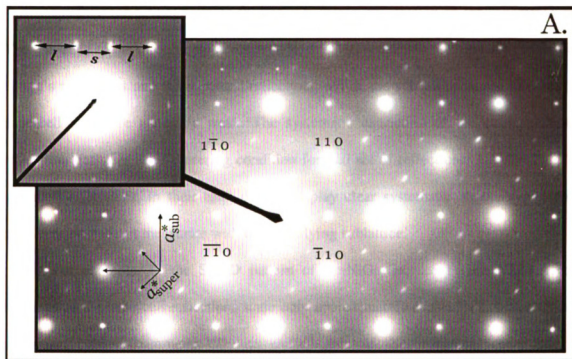
The Y(1) atoms are 14-coordinate, those are bonded to six Ge(1) atoms (from two zigzag chains) at 3.0457(12) Å and 3.164(2) Å, plus four Ni(2) atoms at 3.1950(15) Å and four Ga(2) atoms at 3.219(2) Å and 3.216(2) Å. The immediate environment of Y(2) atoms includes twenty-two Ni, Ga and Ge atoms. However, due to partial occupancy the actual number of neighbors is 16. For complete list of bond distances and angles see Table VI.14.

Probing Long-Range Order with TEM and Electron Diffraction

The apparent disorder in the sub-cells of **1** and **2** motivated us to undertake a search for possible superstructure and long range ordering with help of electron diffraction. Because the nature of interaction of matter with electron beams is conceptually different from that of X-ray and neutron diffraction, and the interaction itself is much stronger, electron diffraction studies allow detecting weak satellite reflections nearly invisible when using X-rays. Indeed, we find that the apparent disorder on the layers of REGe and [MGa]₂ is an artifact, and that these layers possess long range order.

[001] Zone Axis of 1

The [001] zone axis photographs probe the structure of these materials in the *ab*-plane. The [001] zone axis selected area diffraction patterns (SAED) taken at room temperature on single crystals of **1** (SmNiGa₃Ge, SmCoGa₃Ge and GdCoGa₃Ge) are shown in Figures VI.14.A - C with the corresponding bright-field TEM images of the thin areas given below. The inspection of the thin electron-lucent area shows no irregularities in the way the crystal has developed. The cracks, if present, are random and most probably due to the stress imposed on the crystal during the TEM sample preparation.



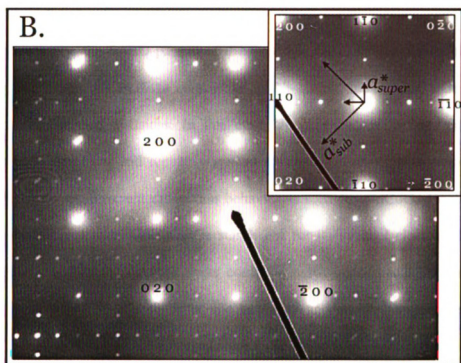
SmNiGa₃Ge [001] Zone Axis



Figure VI.14. (A) The [001] zone SAED pattern (up) and the TEM image (down) of GdNiGa₃Ge. The indexing is given for a subcell. No rotation calibration was performed.

Luckily, the SAED patterns contained valuable information on the superstructure. Thus, in each of the three studied compounds, the SAED patterns feature both the subcell Bragg's reflections and the supercell reflections. While the subcell spots are intense, the supercell spots are generally weak. The systematic extinction of the strong sub-cell reflections satisfies the *I*-centering condition for *hk0* set of reflections: $h + k = 2n$. The supercell reflections, in their turn, do not display clear systematic absences and their positions are not commensurate with the underlying sublattice.

For example, in the SAED pattern of SmNiGa₃Ge, see Figure VI.14.A, the spacings of the supercell reflections scale only approximately as $\frac{1}{3} \cdot a^* \cdot \sqrt{2}$, where a^* is a reciprocal subcell parameter. The magnified area of the reciprocal space of the SmNiGa₃Ge is shown in the inset of Figure VI.14.A. In order to describe the reciprocal supercell lattice, two unit vectors indicated by the letters “*l*” and “*s*” (which stand for “long” and “short” reciprocal lattice spacings) were used. These incommensurately spaced reflections propagate along both main axes of the reciprocal supercell (**a'**, **b'**); however, in one direction the supercell reflections seem to be stronger, suggesting the presence of an orthorhombic supercell and twinning.



SmCoGa₃Ge [001] Zone Axis

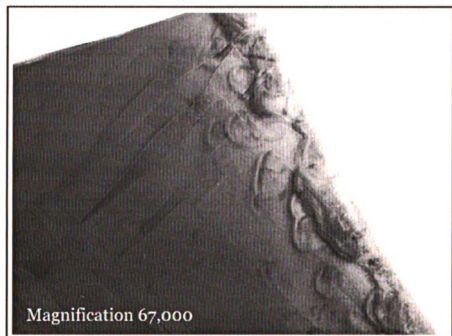
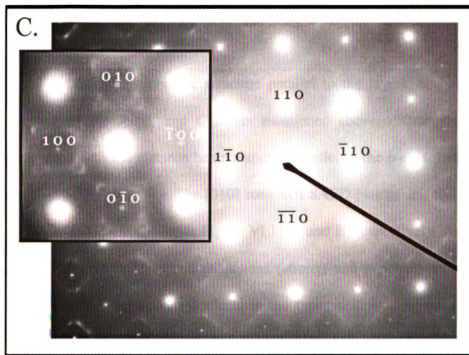


Figure VI.14. (B) The [001] zone SAED pattern (up) and the TEM image (down) of SmCoGa₃Ge. The indexing is given for a subcell. No rotation calibration was performed.

Interestingly, the SAED pattern of the SmCoGa_3Ge is different from that of the Ni-analog, see Figure VI.14.B. In contrast to its Ni-analog, the SmCoGa_3Ge does not exhibit incommensurate distances. In this case, the supercell reflections are equally intense in both directions and regularly spaced scaling as $\frac{1}{4} \cdot a^* \cdot \sqrt{2}$ with respect to the subcell a^* . However, different diffraction behavior is seen for GdCoGa_3Ge . The [001] zone axis SAED pattern of GdCoGa_3Ge stands out for its unusual electron diffraction pattern. Here, no discrete supercell spots could be easily recognized. Instead, diffuse scattering is observed in the shape of the octagons and squares appear, see Figure VI.14.C. The larger octagons are centered around the strong subcell reflections with $h + k = 2n$, while the smaller squares surround the sub-cell symmetry forbidden reflections with $h + k = 2n + 1$. Thus, using the tile of this two “unit cells”, the 2D diffraction pattern could be constructed. It should be noted, that the ED pattern featuring diffuse scattering has been repeatedly seen in a number of crystals of GdCoGa_3Ge .



GdCoGa₃Ge [001] Zone Axis

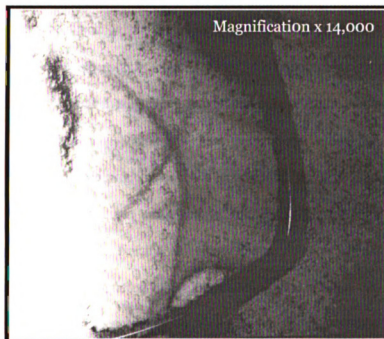
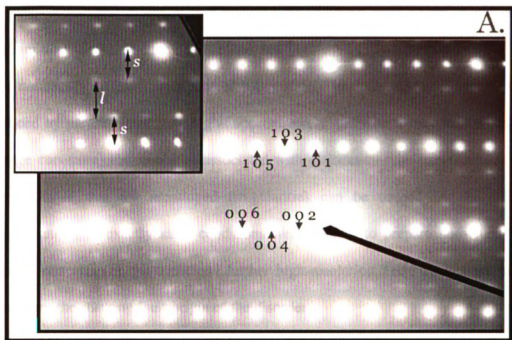


Figure VI.14. (C) The [001] zone SAED pattern (up) and the TEM image (down) of SmNiGa₃Ge. The indexing is given for a subcell. No rotation calibration was performed.

[010] Zone Axis of 1

In order to probe the structure parallel to the layers, and examine the relative stacking of the *A*, *B*, and *C* layers mentioned above, diffraction experiments were performed with the electron beam directed parallel to the *b*-axis. In this fashion, we are observing the [010] zone. The [010] zone axis SAED pattern and corresponding thin area of GdCoGa₃Ge are shown in Figure VI.15.A and B, respectively. Again, the diffraction pattern features both subcell reflections (strong) and supercell reflections (weak). The stronger subcell reflections conform to the systematic limiting conditions of *I*-centered cell for *h*0*l* set of reflections: $h + l = 2n$, consistent with *I*4/*mmm* space group of the substructure. No additional reflections corresponding to a supercell were observed along the reciprocal *c**-axis, which leads us to conclude that there is not super structure along *c**-axis. However, the supercell reflections with incommensurate periodicity of short and long spacings appear in the direction of reciprocal *a**-axis. An interesting feature of these supercell reflections is their slightly elongated shape, along the *c**-direction. This could be attributed to stacking faults (not severe) of the *ab* planes. A similar but more exacerbated situation was observed in the RE_{0.67}M₂Ga_{5-x}Ge_x¹ and RE_{0.67}M₂Ga_{6-x}Ge_x¹ families of compounds. For the latter two, the model was proposed where the structure is considered to be constructed of the 2D building blocks fully ordered in the *ab* plane, but stacked irregularly along the *c*-axis. Considering the similarities by which the disorder is expressed (streaking along the *c**-axis) in both RE_{0.67}M₂Ga_{5+n-x}Ge_x (*n* = 0, 1)¹ and 1, it is reasonable to adopt a similar model also in the case of 1.



GdCoGa₃Ge [010] Zone Axis



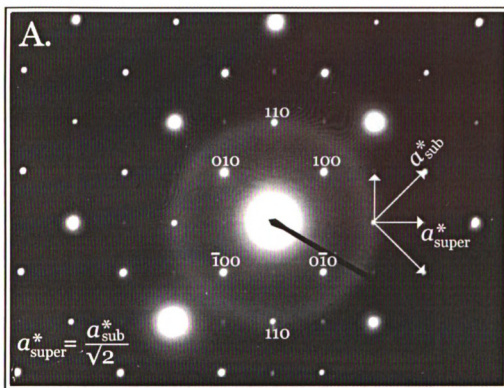
Figure VI.15. The [010] zone axis SAED pattern (A) and the TEM image (B) of GdCoGa₃Ge. The indexing is given for a subcell. No rotation calibration was performed.

Additional evidence that supports the stacking fault model might be found in examining the [010] zone TEM image, see Figure VI.15.B. The thin area for [010] zone is noticeably different from that of [001] zone. Thus, the thin area around the edge is sliced by parallel lines (running at approximately 45° with respect to the tangent of the edge curvature) that could be associated with dislocation-type irregularities. It is rather improbable that the mentioned irregularities can be caused by the TEM sample preparation, as exactly same conditions were applied to prepare both [001] and [010] zone axis samples. Nevertheless, further high-resolution TEM studies are necessary to confirm the stacking fault origin of the disorder.

To summarize, the superstructures found in **1** take place in the *ab* plane only, whereas the direction of the *c*-axis is not modulated. The in-plane modulation varies from analog to analog and reaches up to 8-fold supercell in volume (SmCoGa_3Ge). In some instances the period of modulation scales incommensurately with underlying sub-lattice. The investigation of incommensuration observed in a number of Co analogs of **1** is currently in progress²⁷ and will be discussed later in this Chapter. It is yet unclear what causes the variety of complex ordering in the *ab* plane to occur in different analogs of **1**. However a size effect has to be ruled out, as different superstructures were obtained for the analogs with the elements of similar radii (compare SmMGa_3Ge ($\text{M} = \text{Ni}$ and Co) and RECoGa_3Ge ($\text{RE} = \text{Sm}$ and Gd)).

[001] Zone Axis of 2

The [001] zone axis SAED pattern and the thin area of $\text{Sm}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ and $\text{Sm}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ (**2**) are presented in Figure VI.16. Similar to **1**, the [001] zone electron diffraction patterns of **2** contain the information on the supercell. The electron diffraction pattern of Sm analog of **2** is shown in Figure VI.16.A. The subcell reflections reveal no systematic absences, in accord with a primitive Bravais lattice. In addition to the subcell reflections, the ED pattern features very weak supercell reflections. The supercell parameters in the *ab* plane were found to be $\frac{1}{2} a^* \sqrt{2} \times \frac{1}{2} a^* \sqrt{2}$. Likewise, the ED pattern obtained for Gd analog, see Figure VI.16.B, also exhibits a $\frac{1}{2} a^* \sqrt{2} \times \frac{1}{2} a^* \sqrt{2}$ supercell. Thus, in contrast to **1**, consistent supercell parameters were obtained for Gd and Sm analogs of **2**. Assuming no modulation takes place along the *c*-axis (as it is in case of **1**), the supercell of **2** is 2-fold ($a\sqrt{2} \times a\sqrt{2}$). Because the supercell reflections were extremely weak, no X-ray data supporting the supercell could be obtained for either **1** or **2** compounds.



Sm₃Ni₃Ga₈Ge₃ [001] Zone Axis



Figure VI.16. (A) The [001] zone axis of **2**: SAED pattern (up) and the TEM image of Sm₃Ni₃Ga₈Ge₃ (down). The indexing is given for a subcell. No rotation calibration was performed.

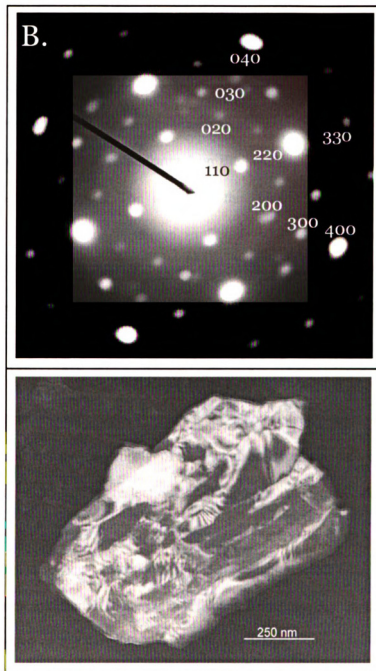


Figure VI.16. (B) The [001] zone axis of **2**: SAED pattern (up) and the TEM image (down) of $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$. The indexing is given for a subcell. No rotation calibration was performed.

[010] Zone Axis of **3**

Because of the difficulty to grow sufficiently large ($\sim 10 \text{ mm}^2$) single crystals of **3** and to adjust the parameters of the electrochemical thinning experiment, the TEM and electron diffraction studies were performed on the samples of **3** prepared via specimen pulverization and suspension. The image of the micro-crystallite of $\text{Tb}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ viewed along the [010] zone is shown in Figure VI.17.A. In Figures VI.17.B and VI.17.C, the corresponding SAED patterns at different camera lengths are given. All reflections present in the patterns could be indexed using a subcell. However, the multiple violations of the extinction conditions associated with *Cmcm* space group are observed. That is, the symmetry forbidden reflections with $h + l = 2n + 1$ are present in the SAED patterns; the reflections intensities are also relatively high. Although without the tilting experiment the possibility of double diffraction can not be ruled out, the appearance of these additional reflections could, on the other hand, be associated with presence of a $(a^2 + c^2)^{1/2} \times (a^2 + c^2)^{1/2}$ supercell.

Interestingly, the view of reciprocal lattice points obtained using X-ray diffraction data also features additional (supercell) reflections that appear in the center of the orthorhombic lattice of the (a^*c^*) -plane, see Figure VI.18. Hence, both electron and X-ray diffraction contain an indication on the existence of a 2-fold supercell with the modulation most likely taking place along the [101] diagonal relative to a subcell.

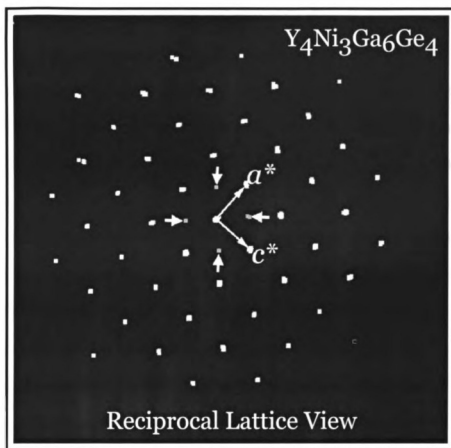


Figure VI.18. Lattice view of a hemisphere of X-ray reciprocal data for $\text{Y}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ (3). The white reflections correspond to a subcell ($a = 4.0999(19) \text{ \AA}$, $b = 35.628(17) \text{ \AA}$, $c = 4.0968(19) \text{ \AA}$), the grey reflections (marked with arrows) are of supercell.

Incommensurately Modulated Structure of GdCoGa₃Ge (I)

Besides the appearance of regular (or commensurate) supercell spots in the reciprocal lattice, as discussed above, some analogs of **1** exhibited incommensurate spacings of the supercell reflections. For example, in the case of YCoGa₃Ge, SmCoGa₃Ge and GdCoGa₃Ge unequal intervals between satellite spots were observed in the reciprocal a^*b^* -plane of the X-ray intensity data. The underlying sublattice belongs to an average structure of **1** ($a \sim 4 \text{ \AA}$, $b \sim 4 \text{ \AA}$, $c \sim 23 \text{ \AA}$). In some instances, such as SmNiGa₃Ge, the incommensurate satellite spots were detected in the electron diffraction patterns only, possibly due to their weak intensity.

Incommensurate structures belong to a class of aperiodically modulated structures. There exist three kinds of aperiodic structures: incommensurate structures, composite crystals and quasicrystals. Despite the notion of “aperiodicity”, the modulated structures are not disordered. The sharp Bragg diffraction spots are indicative of the presence of long range order in these structures. At the same time, their true (ordered) structures cannot be described within the framework of conventional 3D crystallography²⁸. Instead, the basis for understanding such a peculiar structure lies in higher-dimensional crystallography. Thus, the location of the Bragg spots in the modulated structure is related to a n -dimensional lattice (where n is > 3). In such n D superspace the modulated structure is periodic. The 3D space, in its turn, could be regarded as a projection of the n D reciprocal lattice points onto 3D space or intersection of n D with 3D space. If the gradient of intersection of n D with 3D space is irrational, such cut of the periodic electron density leads to an aperiodic structure at the intersection.

Practically, in the diffraction pattern of incommensurate and composite structures we can easily recognize prominent reflections constructing a 3D lattice. These so-called main reflections are accompanied by weak satellite reflections. This means that there exists an average structure* with 3D periodicity and a weak perturbation from it. In the incommensurate structures, there are two kinds of modulations that could cause perturbation and give rise to the appearance of satellites: (a) a displacive modulation, where a periodic displacement of the atomic coordinates belonging to the basic structure occurs, (b) an occupational modulation, where the atomic positions of the basic structure are occupied with periodic probability function.

The substructure of **1**, as shown in Table VI.1 and Figure VI.3 represents an average structure without perturbation. When incommensurate satellite reflections of higher dimensions are taken into account, a perturbed structure results. Thus, in case of GdCoGa₃Ge, a 20-fold supercell with modulation occurring along the *a*-axis resulted (cell parameters: $a' = 83.47 \text{ \AA}$, $b = 4.1735$, $c = 23.8028 \text{ \AA}$). The corresponding structure refinement in the 4D orthorhombic superspace group *Immm*($\alpha 00$)00s (see Appendix A for the details of data collection and refinement) revealed an interesting *displacive* perturbation from the original substructure. In Figure VI.19, a single unit cell of the GdCoGa₃Ge 20-fold superstructure is presented. The atoms are labeled in the same manner as for a substructure, for clarity. The unit cell of the substructure is drawn in dashed line for comparison. The [Gd] plane, [CoGa₂] puckered layer and [CoGa₄Ge₂]

* This restricts the possible incommensurate space groups within the crystallographic ones. For quasicrystals, there are no prominent reflections constructing a 3D sublattice, and their diffraction pattern show non-crystallographic symmetry (5-fold, 7-fold, 8-fold, 10-fold, 12-fold). This constitutes a major difference between the quasicrystals and IC structures.

slab are also outlined. It could be seen from Figure VI.19 that in the superstructure of **1**, the [CoGa₂] puckered layer underwent the major changes, while [CoGa₄Ge₂] and [Gd] slabs had adjusted to the latter perturbation by shifting the Ge atoms toward or away from the [Gd] plane.

The fragment of the [CoGa₂] slab viewed approximately down the *c*-axis is shown in Figure VI.20.A. The underlying net of Ga atoms (what used to be a square lattice in the substructure of **1**) had not only lost its tetragonal symmetry, but also the integrity of a 2D framework. This could be clearly seen if the Ga-only sub-unit of [CoGa₂] slab is considered, as shown in Figure VI.21. Evidently, the extent of distortion from square lattice is so immense that the stretching of the square lattice along the *a*-axis produced ripping of the “tapestry” of 2D net, yielding a number of 1D chains (C), 1D ribbons (R) and even isolated Ga monomers (M). A total of eleven different chains (C^I – C^{XI}) and three kinds of ribbons (R^I – R^{III}), varying in the Ga-Ga bond lengths and Ga-Ga-Ga bond angles, could be identified*. Table VI.19 summarizes the connectivity and bond angle data for 1D Ga entities found in [CoGa₂] layer. While the Ga-Ga bonding is changing from chain to chain and from ribbon to ribbon, the bonding between the monomers is constant. Those form a straight line (Ga-Ga-Ga = 180°) and are 4.174 Å apart from each other (length of *b*-axis).

* The cutoff distance of 3.0 Å was used for Ga-Ga bonding interactions.

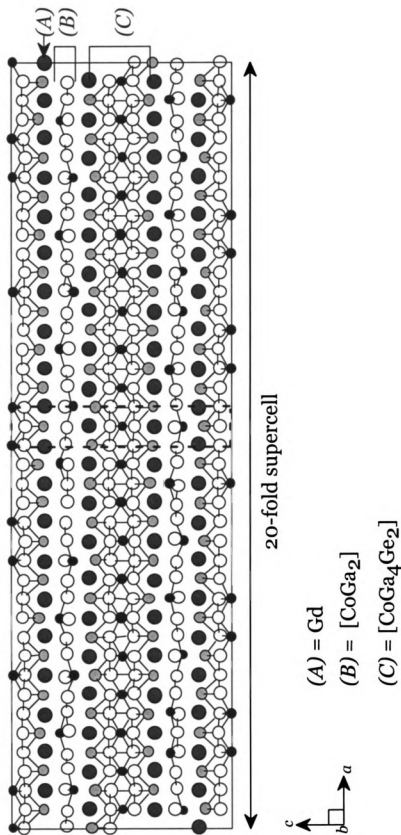


Figure VI.19. A single unit cell of the 20-fold superstructure of GdCoGa_3Ge (1) obtained from higher-dimensional crystallography. The atoms are labeled in the same way as for substructure. The subcell is shown with dashed line for comparison.

Table VI.19. A summary on Ga-Ga bond lengths (Å) and Ga-Ga-Ga bond angles (°) for 1D Ga entities found in the [CoGa]₂ layer in the 20-fold superstructure of **1**.

1D Ga entity	Ga-Ga bond (Å)	Ga-Ga bond (Å)	Ga-Ga-Ga angle (°)
C ^I	2.612		106.040
C ^{II}	2.636		104.671
C ^{III}	2.692		101.642
C ^{IV}	2.780		97.312
C ^V	2.735		99.457
C ^{VI}	2.662		103.245
C ^{VII}	2.621		105.542
C ^{VIII}	2.637		104.642
C ^{IX}	2.693		101.587
C ^X	2.781		97.234
C ^{XI}	2.734		99.511
R ^I	2.838	2.966	87.765 – 94.680
R ^{II}	2.612	2.976	82.242 – 106.040
R ^{III}	2.836	2.968	87.762 – 94.755

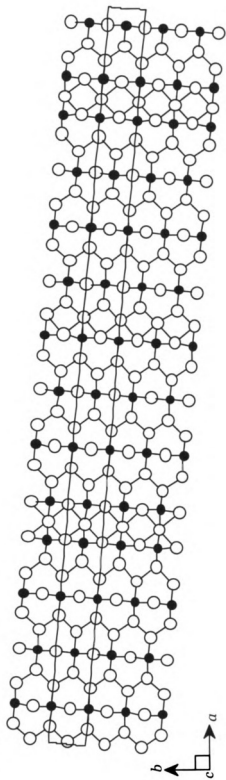
Returning to the $[\text{CoGa}_2]$ layer in Figure VI.20.A, we see that Co atoms assume the positions along the lines parallel to the b -axis, whereas in substructure those were spread out uniformly within the plane (compare $[\text{CoGa}_2]$ to the puckered layer in Figure VI.4). In the superstructure, the Co atoms are located either in the row together with Ga monomers, or alongside the ribbons, see Figure VII.20.B. As positioned, Co serves as bridging atom linking one- and zero-dimensional Ga units into 2D $[\text{CoGa}_2]$ puckered layer.

In the $[\text{CoGa}_4\text{Ge}_2]$ layer of 20-fold superstructure, the $[\text{CoGa}_4]$ cube fragment remained factually unchanged, whereas the Ge atoms in capping positions underwent substantial displacement, see Figure VII.20.B. This displacement, in fact, occurs in unison with the one that takes place in neighboring $[\text{CoGa}_2]$ layer. As was mentioned above, the Co atoms of the $[\text{CoGa}_2]$ layer are not distributed uniformly throughout the slab, but form rows parallel to b . The Ge atoms of the $[\text{CoGa}_4\text{Ge}_2]$ layer arrange accordingly, situating closer to the $[\text{CoGa}_2]$ if the Co row is empty, and away from it if the row is occupied, see Figure VI.19.

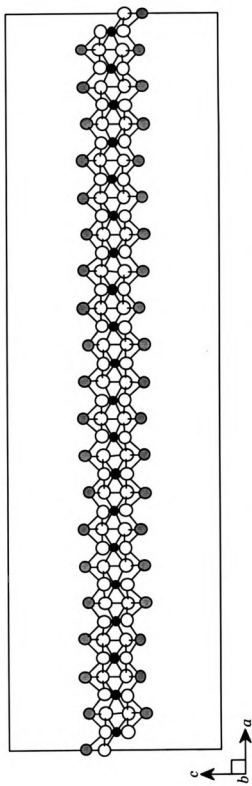
The complexity of the superstructure obtained on the basis of the structure solution in 4D space is striking. Yet, even more remarkable is to unfold the mystery of the apparently disordered class of compounds such as REMGa_3Ge that had troubled us through years of research. In view of this accomplishment, it is worthwhile to reconsider the other cases where similar “disorder” is observed.

Figure VI.20. Fragments of a 20-fold superstructure of GdCoGa_3Ge (**1**). (A) a $[\text{CoGa}]_2$ layer viewed down the c -axis and (B) a $[\text{CoGa}_4\text{Ge}_2]$ slab viewed down the b -axis. The Ga-Ga, Ga-Co and Ga-Ge bonding interactions are shown within 3.0 Å. The unit cell is drawn with a solid line.

A.



B.



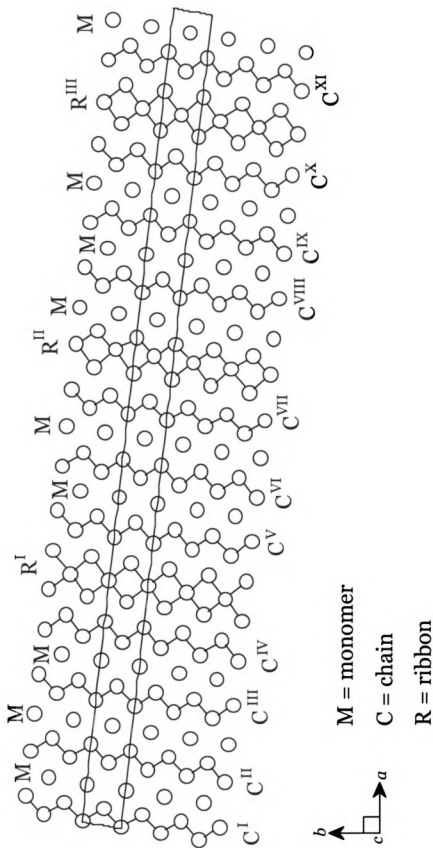


Figure VI.21. A Ga-only fragment of the $[\text{CoGa}]_2$ layer of a 20-fold superstructure of GdCoGa_3Ge (1). The Ga-Ga bonding is shown within 3.0 Å. The unit cell is drawn with a solid line. Three types of Ga entities are identified: chains (C), ribbons (R) and isolated Ga atoms or monomers (M).

Magnetic Properties

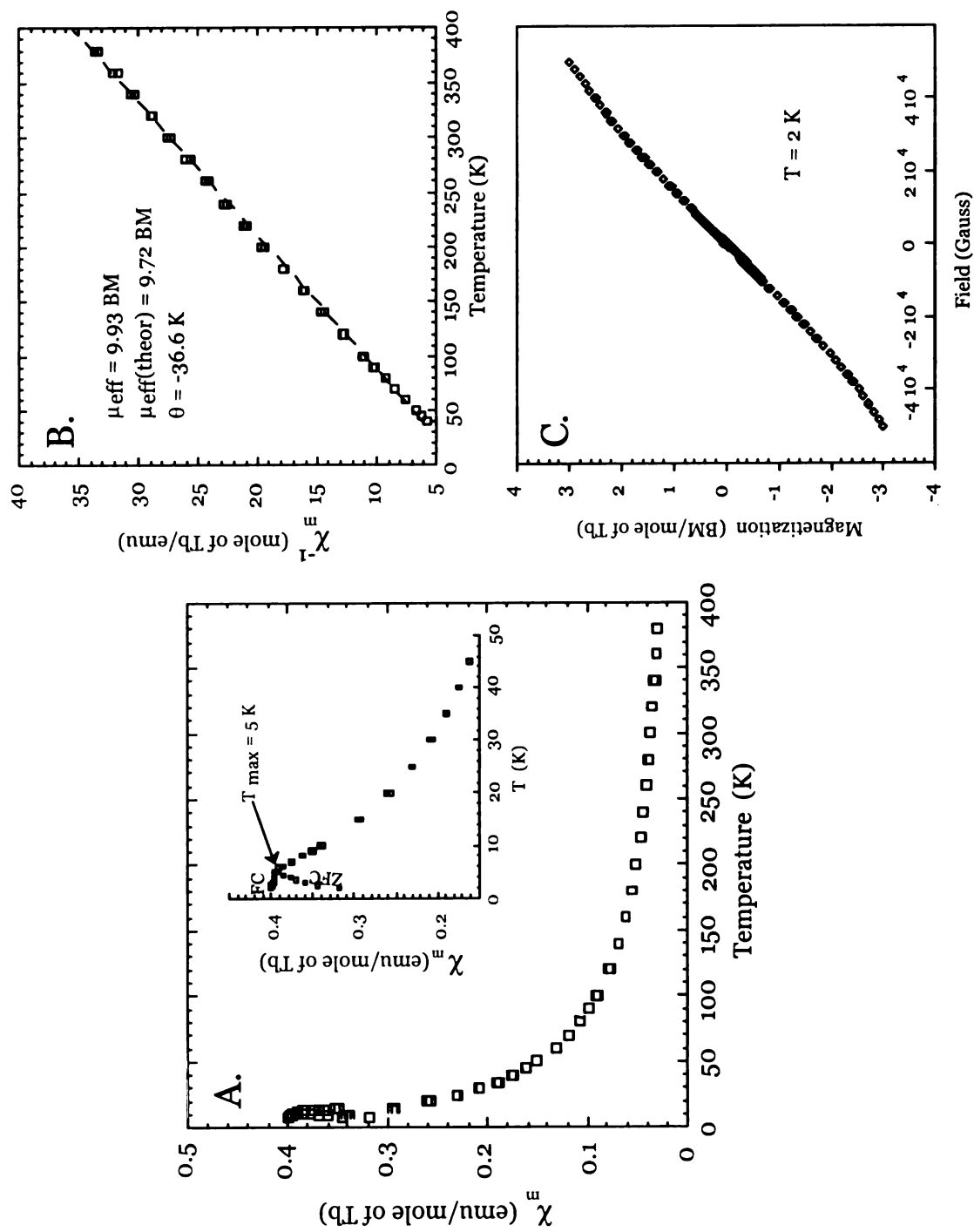
Magnetism of 1: (TbNiGa₃Ge, GdCoGa₃Ge and YCoGa₃Ge)

(a) Tb-analog

The magnetic properties were studied for three analogs of **1** (RE = Tb, Gd and Y). The temperature dependence of susceptibility of a polycrystalline sample of the TbNiGa₃Ge calculated per mole of Tb is shown in Figure VI.22.A. The temperature of the maximum susceptibility (T_{max}) is ~ 5 K. Below that temperature the zero-field cooled (ZFC) and field cooled (FC) parts of susceptibility diverge, see inset in Figure VI.22.A. Above 30 K the reciprocal susceptibility increases linearly with temperature, indicating Curie-Weiss behavior, see Figure VI.22.B. The effective magnetic moment (μ_{eff}) calculated from the linear part of the plot is 9.93 BM, in agreement with the free-ion value for Tb³⁺ (9.72 BM). The Weiss constant is negative, $\theta = -36.6$ K, in accord with proposed antiferromagnetic ordering.

The magnetization in fields up to ± 5 T is nearly linear and shows no saturation, with maximal moment of ~ 3 BM developed in the field 5 T that corresponds to only 30% of the full saturation value, see Figure VI.22.C.

Figure VI.22. The magnetization data for the TbNiGa₃Ge polycrystalline sample. (A) Temperature dependence of molar magnetic susceptibility; *Inset*: low temperature region of magnetic susceptibility; (B) inverse susceptibility; (C) The molar magnetization in fields up to ± 5 Tesla.

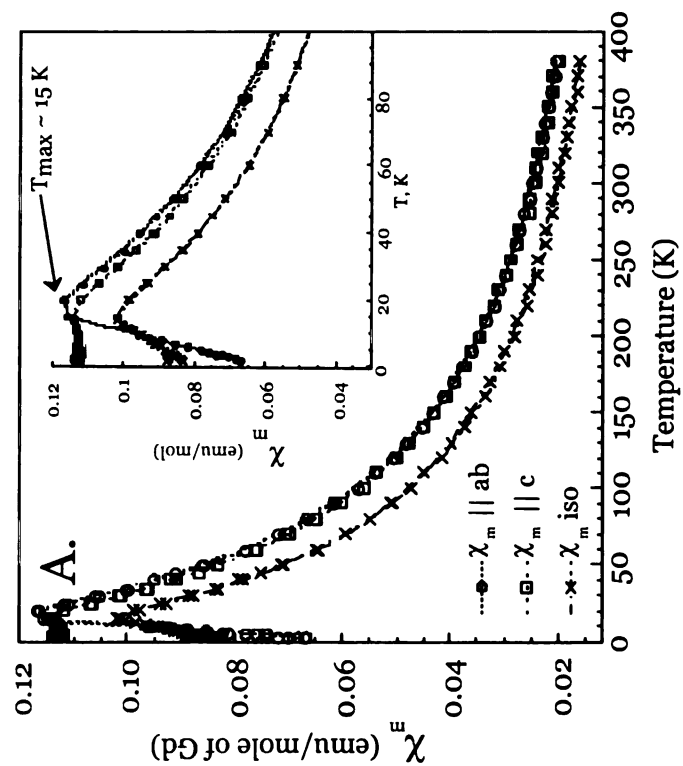
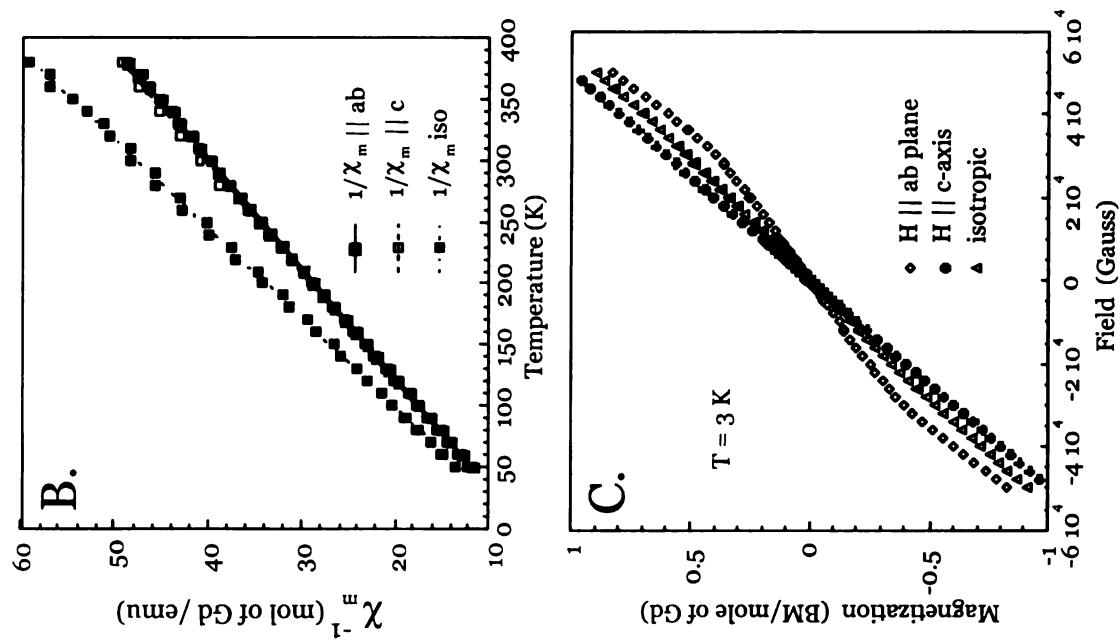


(b) *Gd-analog*

The magnetic properties of the GdCoGa₃Ge analog were studied in both isotropic (polycrystalline) and anisotropic (single crystal) type measurements. The molar susceptibility data *vs* temperature is plotted in Figure VI.23.A. For the Gd analog, the T_{max} occurs at higher temperature compared to the Tb, analog at ~15 K, as shown in the inset in Figure VI.23.A. At the temperature 50 K and higher, the inverse magnetic susceptibility obeys Curie-Weiss law, see Figure VI.23.B, with the average $\mu_{\text{eff}} = 8.15$ BM close to the free-ion value for Gd³⁺ (7.94 BM). The exact values for μ_{eff} and θ for different orientations are $\mu^{\parallel} = 8.42$ BM; $\mu^{\perp} = 8.43$ BM; $\mu^{\text{iso}} = 7.62$ BM and $\theta^{\parallel} = -56$ K; $\theta^{\perp} = -54$ K; $\theta^{\text{iso}} = -47$ K. The negative sign of the Weiss constants is again in favor of the antiferromagnetic moments ordering on the Gd atoms. The subsequent determination of the Néel temperature from the set of isofield plots of χ_m *vs* T yielded $T_N = 15$ K, see Figure VI.24.

The field dependence of magnetization for all orientations is shown in Figure VI.23.C. The maximum moment developed in the field of ± 5 Tesla does not exceed 1 BM, which is only 14% of the full saturation value. From both temperature- and field-dependence measurements it is evident that the relative crystal to field orientation does not produce any impact on magnetization and susceptibility. Thus, the effect of crystal field in GdCoGa₃Ge is obviously negligible. Such isotropic behavior of magnetization is consistent with S-state of the Gd³⁺ atoms²⁹ and has been previously observed in a number of Gd-containing intermetallic compounds including RE_{0.67}Ni₂Ga_{5-x}Ge_x¹ and Gd₃Ga₉Ge³⁰, as well as in pure Gd metal.

Figure VI.23. (A) Temperature dependence of molar magnetic susceptibility and (B) inverse susceptibility of GdCoGa₃Ge single crystal oriented with [100] axis parallel, perpendicular to the external magnetic field (H_{ex}) and isotropic. *Inset:* magnetic susceptibility in the proximity of an antiferromagnetic transition temperature. (C) The molar magnetization in fields up to ± 5 Tesla.



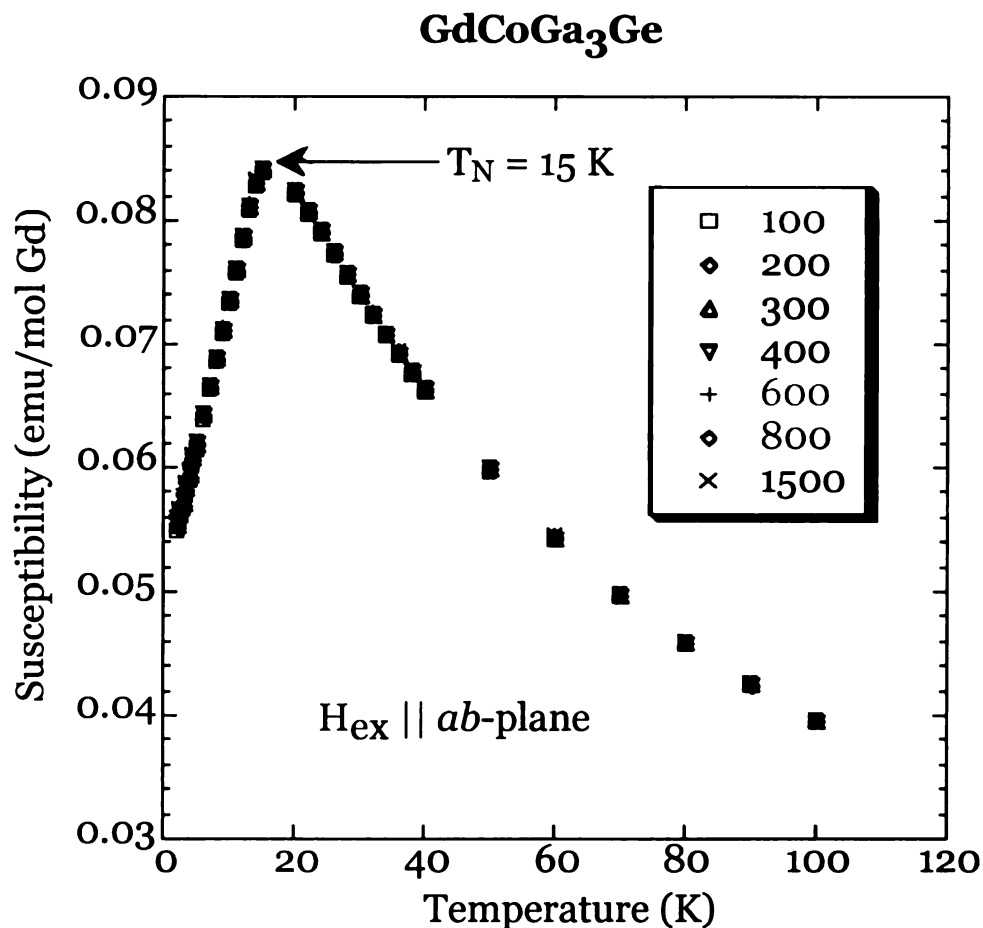


Figure VI.24. Isofield plots of molar magnetic susceptibility of GdCoGa₃Ge measured at various fields (100 – 1500 Gauss).

(c) Y-analog

The effective magnetic moments obtained for the analogs of **1** with Gd and Tb indicate that the magnetic moments are carried solely by the rare-earth ions, while the transition metals are in diamagnetic state. However, in order to reconfirm the non-magnetic nature of the transition metal atoms (Ni and Co), magnetic measurements were performed using the Y analogs. As a result, the susceptibility of YCoGa₃Ge was

determined to be very low ($0.6 \cdot 10^{-3}$ emu/mol or $0.6 \cdot 10^{-9}$ m³/mol) and nearly temperature independent, which is characteristic of Pauli paramagnetism, see Figure VI.25. Thus, in 1 the magnetic moments indeed originate only from rare-earth atoms, whereas the Ni and Co atoms are in diamagnetic states. This situation is now a recurring theme in this type of intermetallic chemistry since diamagnetic behavior of the transition metal atoms was observed in $\text{Sm}_2\text{NiGa}_{12}$ ⁷, $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Ge}_x$ ¹, RENiSi_3 ^{Error! Bookmark not defined.}, $\text{RENiAl}_4\text{Ge}_2$ ⁴, $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Si}_{1-x})\text{Al}_4\text{Si}_6$ ³, $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ and many other related intermetallic compounds.

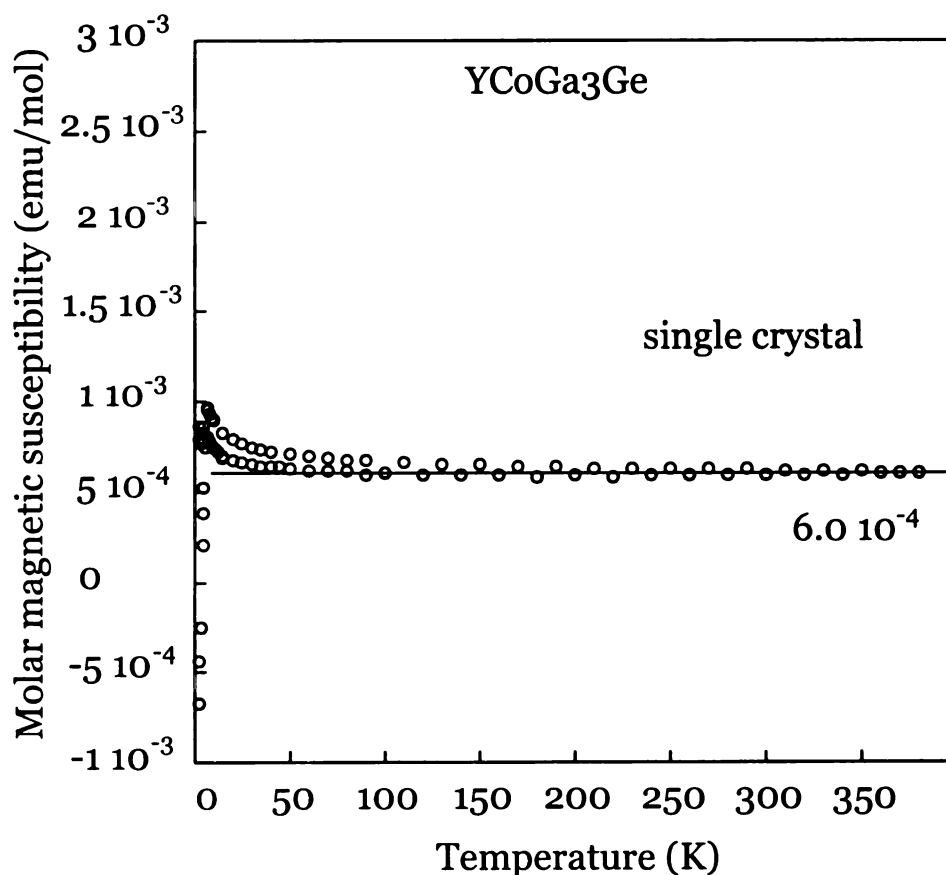


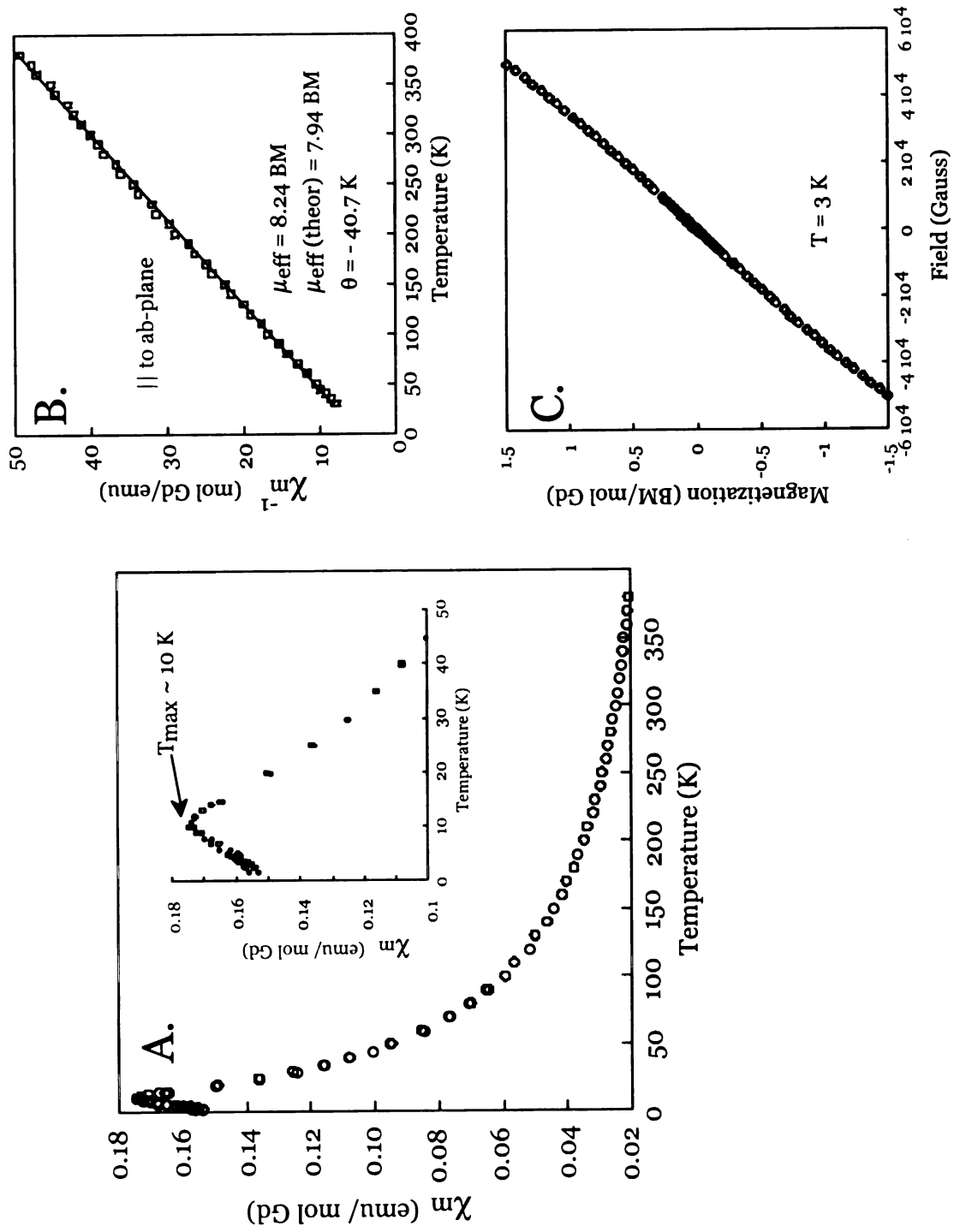
Figure VI.25. Molar magnetic susceptibility of the crystalline sample of YCoGa₃Ge.

Magnetism of 2: Gd₃Ni₃Ga₈Ge₃

The temperature dependence of the susceptibility of single crystal of **2** (Gd₃Ni₃Ga₈Ge₃) is presented in Figure VI.26.A. The maximum of the magnetic susceptibility occurs at ~ 10 K. Slight variation of the ZFC–FC parts is observed below that temperature. In Figure VI.26.B the inverse magnetic susceptibility (χ_m^{-1}) is plotted against the temperature. The linear increase in χ_m^{-1} with temperature and non-zero intercept with temperature axis indicate Curie-Weiss behavior; the Weiss constant and the effective magnetic moment were determined to be –40.7 K and 8.24 BM, respectively. Both the sign and the maximum on χ_m indicate the antiferromagnetic ordering below $T_{\max}$. The Néel temperature $T_N = 10$ K was determined from the set of the isofield χ_m – T plot by extrapolating the maximal temperature to the zero field, see Figure VI.27. The μ_{eff} found for Gd₃Ni₃Ga₈Ge₃ is in agreement with the free-ion value for Gd³⁺ ion. Similar to **1**, the Ni atoms in **2** are in non-magnetic state.

The field dependence of magnetization in **2** does not show any saturation. The value of μ_{eff} reaches only the value of 1.5 BM in the fields of ± 5 Tesla, see Figure VI.26.C. A similar situation was observed in field dependence of Gd-analog of **1** and in a number of other intermetallic compounds.

Figure VI.26. (A) Temperature dependence of molar magnetic susceptibility and (B) inverse susceptibility of $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ single crystal; *Inset*: magnetic susceptibility in the proximity of an antiferromagnetic transition temperature. (C) The molar magnetization in fields up to ± 5 Tesla.



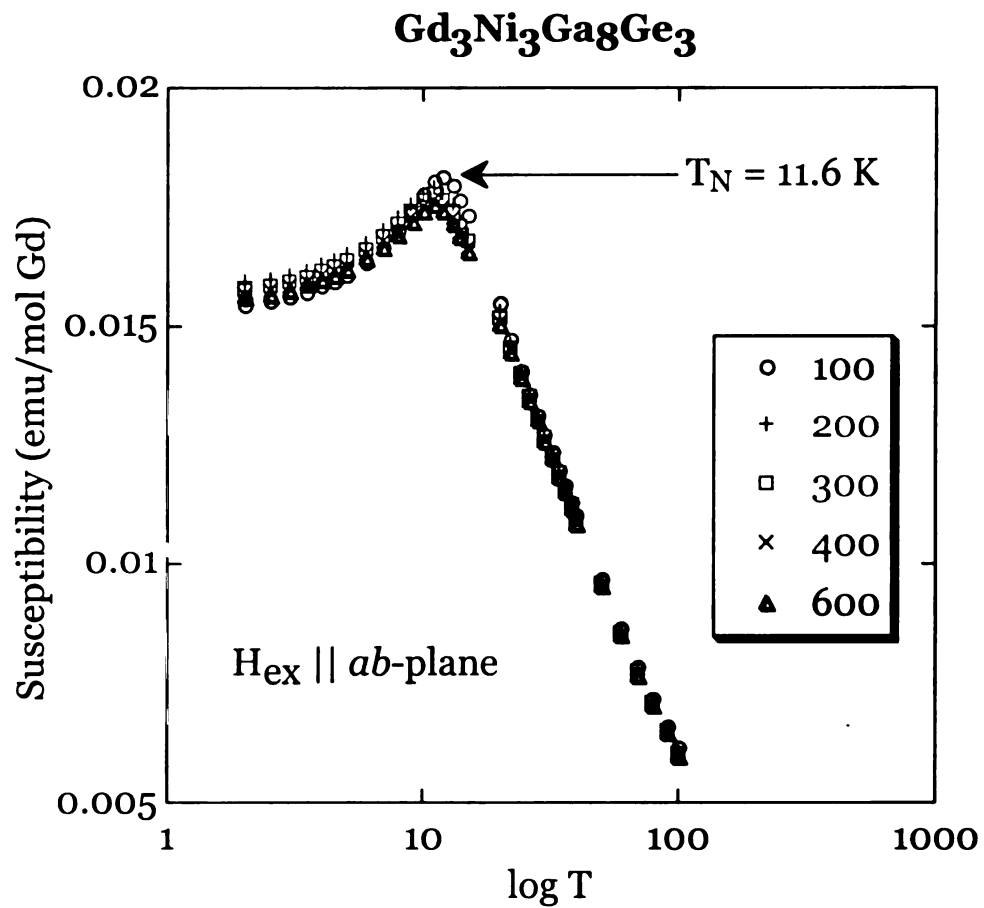
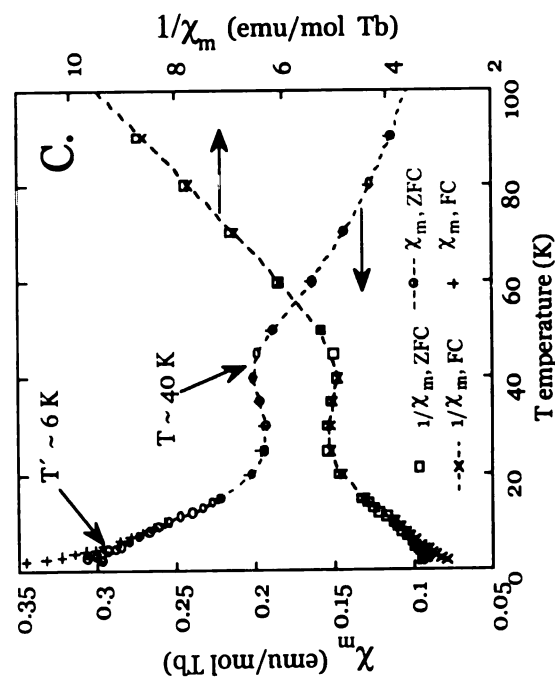
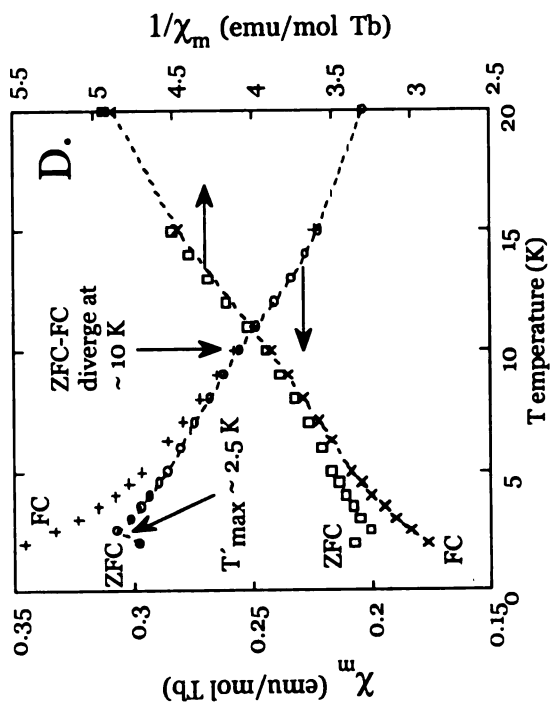
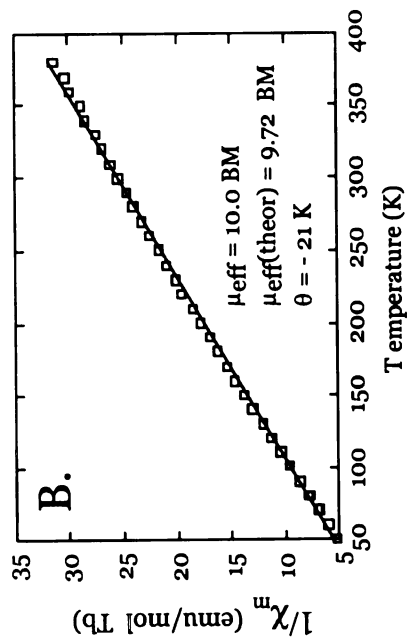
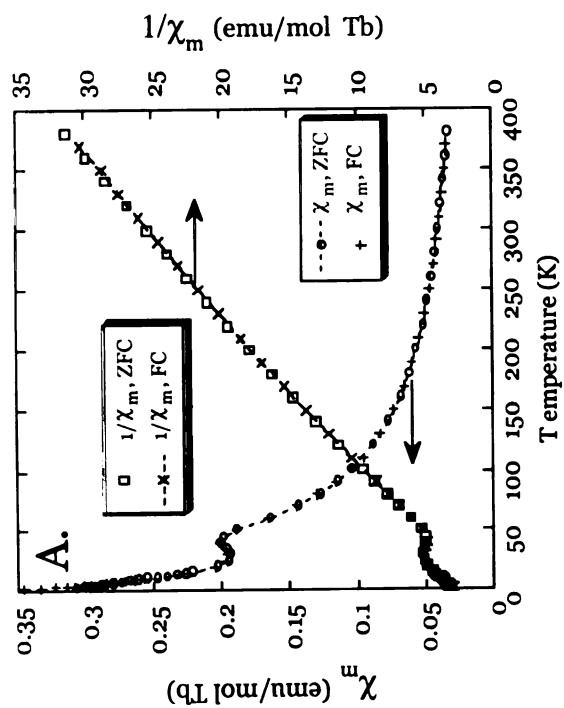


Figure VI.27. Isofield plots of molar magnetic susceptibility of Gd₃Ni₃Ga₈Ge₃ measured at various fields (100 – 600 Gauss).

The results of the susceptibility measurements performed on polycrystalline sample of **3** with the external magnetic field 500 G are given in Figure VI.28. The low-temperature data indicate the presence of short-range magnetic ordering, while at higher temperature Curie-Weiss behavior is observed, see Figure VI.28.A. The effective magnetic moment calculated from the slope of χ_m -T plot is 10.0 BM, in agreement with Tb³⁺ free-ion value (9.72 BM), see Figure VI.28.B. The Weiss constant is negative ($\theta = -21$ K), suggesting antiferromagnetic-type ordering. An expanded low-temperature region of χ_m and χ_m^{-1} is shown in Figure VI.28.B. Below 50 K, the molar magnetic susceptibility undergoes an antiferromagnetic transition with a broad maximum centered at $T_{\max} \sim 40$ K. However, the susceptibility continues to rise even below $T_{\max}$. The onset of yet an additional transition is observed at temperatures below 10 K. The temperature dependence of χ_m and χ_m^{-1} in the proximity of this ordering transition is given in Figure VI.28.C. It could be seen that the zero-field-cooled (ZFC) and field-cooled (FC) parts of susceptibility start to diverge at ~ 10 K. Below that temperature, the ZFC part decreases, whereas FC continues to rise. The maximum in the ZFC part of χ_m , $T'_{\max}$, is observed at ~ 2.5 K. At present, it is difficult to judge about the nature of this transition, as it occurs very close to the lowest measured temperature (2 K). Yet, the behavior of the ZFC vs FC susceptibility curves suggests a ferromagnetic-type transition. Additionally, the field dependence measurements show hysteretic behavior that is also indicative of a ferromagnetic coupling interaction, see Figure VI.29.

Figure VI.28. The magnetization data for the $\text{Tb}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ polycrystalline sample. (A) Temperature dependence of molar and reciprocal molar magnetic susceptibility; (B) Linear part of the reciprocal susceptibility; (C) Low temperature region of magnetic susceptibility; (D) Susceptibility in the vicinity of the 10 K ordering temperature.



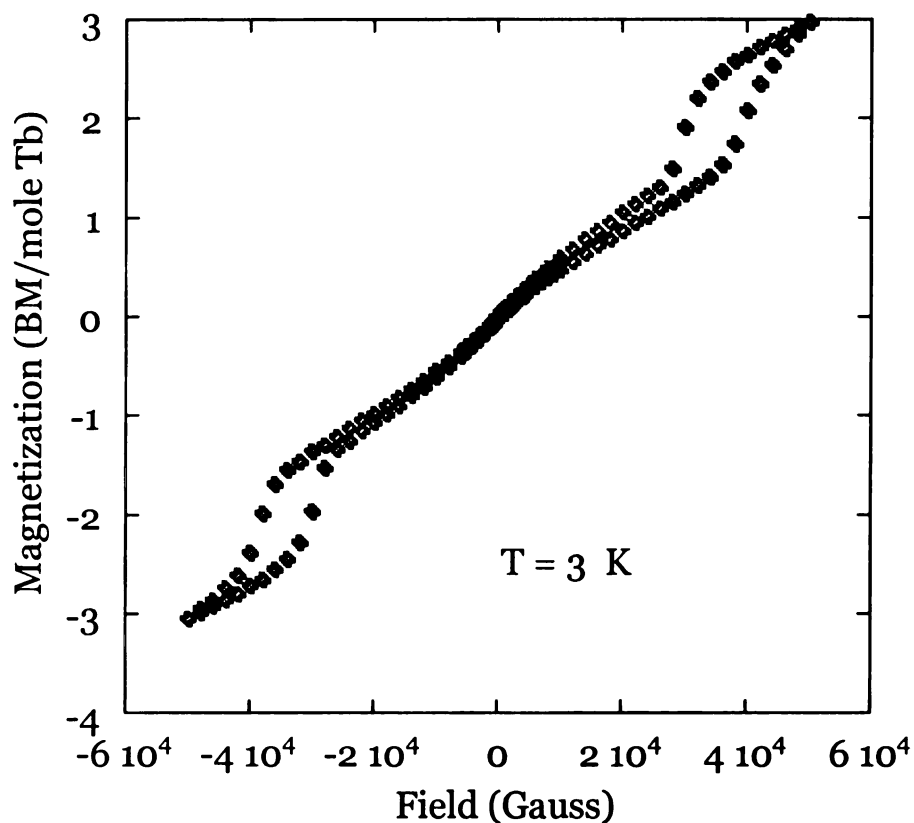


Figure VI. 29. Magnetization of Tb₄Ni₃Ga₆Ge₄ (**3**) calculated in Bohr magnetons per mole of Tb as a function of external magnetic field.

The appearance of the two ordering transitions in **3** is reminiscent of the magnetic behavior of Tb₄FeGe₈. When the Tb sublattice in **3** is compared to that in Tb₄FeGe₈, it reveals further similarities. Thus, the RE atoms in **3** form a sequence of monoatomic planes of RE(2) atoms and thick 2D layer of trigonal prisms of RE(1) stacked along the *b*-axis, see Figure VI.30. The common feature of Tb₄FeGe₈ and **3** RE sublattices is the trigonal prism layer. As was shown for Tb₄FeGe₈, the comparable RE-RE distances in the direction parallel and perpendicular to the *b*-axis could cause possible frustration and

onset of two magnetic ordering. In case of **3**, the RE-RE distances within the prism layer (3.924 Å, 4.097 Å and 4.100 Å) are also very similar indicating that the interactions within the prism layer could be responsible for the appearance of two magnetic ordering transitions in **3** as well.

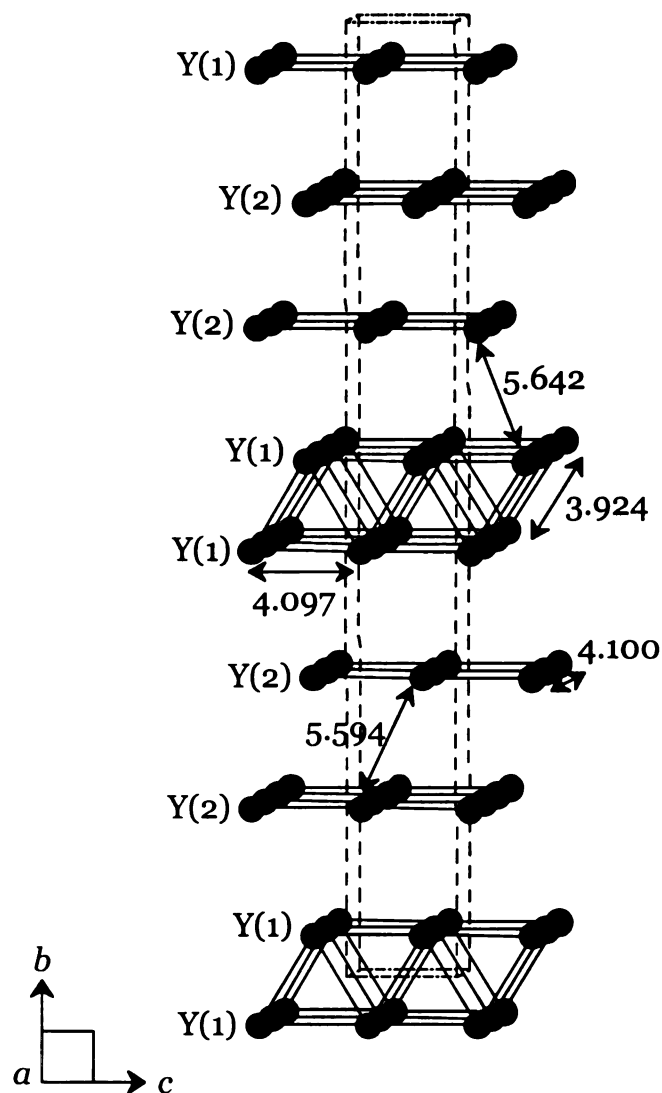


Figure VI.30. The RE-only framework in **3** (RE = Y is shown). The distances are given in Å. The unit cell is indicated with dashed lines.

4. Conclusion

As a result of the exploratory synthesis in the system RE/M/Ga/Ge with RE : M = 1 conducted in liquid Ga, three families of new quaternary compounds REMGa₃Ge (M = Ni, Co), RE₃Ni₃Ga₈Ge₃, RE₄Ni₃Ga₆Ge₄ were obtained. The flux method proves an excellent tool for discovering and growing large single crystals of new quaternary intermetallic compounds. In compounds containing Ga and Ge (just as for those containing Al and Si), it is often difficult to assign with a high degree of confidence the corresponding sites, requiring neutron diffraction analysis in some representative cases. The single crystal neutron diffraction performed on YCoGa₃Ge shows the position of Ge on the 4e site, while Ga atoms occupy 4d and 8g crystallographic sites.

Both the X-ray and neutron diffraction structural refinements evidence that a “disorder” taking place in the REGe and [MGa]₂ slabs is actually an artifact of the small unit cell. Investigations performed with electron diffraction indicate that in REMGa₃Ge a complex long range ordering occurs in the *ab* plane, that varies in nature with the RE element. The various superstructures up to 8-fold in volume ($2a\sqrt{2} \times 2a\sqrt{2}$) were found for the analogs of REMGa₃Ge. Additionally some analogs of REMGa₃Ge show incommensurate modulation relative to the underlying sublattice. The structure solution in 4-dimensional space lead to a 20-fold superstructure and revealed displacive modulations of Ga atoms from their average positions in the square lattice of [CoGa]₂ layer. For the RE₃Ni₃Ga₈Ge₃ and RE₄Ni₃Ga₆Ge₄ the superstructure was determined to be 2-fold ($a\sqrt{2} \times a\sqrt{2}$) taking place in the *ab*- and *ac*-plane, respectively.

The magnetic moments in these materials are localized on the RE atoms while the transition metal atoms are in non-magnetic state. Antiferromagnetic ordering transitions are observed in for GdCoGa_3Ge , $\text{Gd}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ and TbNiGa_3Ge at Néel temperatures of 15 K, 10 K and 5 K, respectively. The $\text{Tb}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4$ exhibit two ordering transitions: an antiferromagnetic at ~ 40 K and weak ferromagnetic at ~ 10 K associated with competing Tb-Tb interactions in the Tb prism layer. The Gd analogs of RECoGa_3Ge and $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ show no magnetic anisotropy in accord with S-ground state of Gd^{3+} ion.

5. References

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Chapter VII

Flux Synthesis and Characterization of the Novel Ternary Orthorhombic $\text{RE}_2\text{Ga}_2\text{Ge}_5$ (RE = Sm, Tb, La) and $\text{La}_3\text{Ga}_2\text{Ge}$ and the Quaternary Tetragonal $\text{RE}_2\text{MGa}_9\text{Ge}_2$ (RE = Ce, Sm; M = Ni, Co).

1. Introduction

The far reaching implications of the molten metal flux technique for the synthesis of complex intermetallic phases including rare-earth (RE), transition metal (M), and the main group III and IV elements such as Ga, Al and Si, Ge is now evident. In the explorations using molten Ga as a solvent, we have already described the systems with M = Fe, Ni and Co. In case of Fe, we have discovered two new phases Tb_4FeGe_8 and $\text{RE}_4\text{FeGa}_{12-x}\text{Ge}_x$ that form at RE : Fe > 1. For the systems with M = Ni and Co, we thus far mostly regarded the cases with the RE : M ratios less than or to equal unity. From

these reactions, a large number of new ternary and quaternary intermetallic compounds have been synthesized. Examples include RENiSi_3 ¹, $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ², $\text{RE}_{0.67}\text{M}_2\text{Ga}_{5+n-x}\text{Ge}_x$ ³, REMGa_3Ge ⁴ and $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ ⁵. Although in the Si-containing system RE/Ni/Ga/Si the compositions with RE : Ni > 1 were previously studied, similar investigations in the related RE/M/Ga/Ge system with RE : M > 1 have not yet been performed. For these reasons, we proceeded to probe the reactivity in the RE/M/Ga/Ge systems with RE : M > 1 employing molten Ga as a flux. It is fascinating that these reactions yield predominantly quaternary compounds, whereas in the analogous RE/Ni/Ga/Si system mostly ternary $\text{RE}_2\text{NiGa}_{12}$ and pseudo-ternary $\text{RE}_2\text{NiGa}_{12-x}\text{Si}_x$ ⁶ intermetallic compounds were produced. This discrepancy in Si versus Ge chemistry is captivating, since Ge is isoelectronic to Si. Similar behavior was seen for instance in the RE/M/Ga/Si and RE/M/Ga/Ge systems with M = Ni, Co and RE : M ≤ 1.

Herein we present the results of the exploratory synthesis in the RE/M/Ga/Ge system with RE : M > 1 (M = Fe, Ni and Co) employing molten Ga as a solvent. The synthesis, structure and magnetic properties of novel intermetallides $\text{RE}_2\text{MGa}_9\text{Ge}_2$ (RE = Ce, Sm; M = Co, Ni), $\text{RE}_2\text{Ga}_2\text{Ge}_5$ (La, Sm, Tb) and $\text{La}_3\text{Ga}_2\text{Ge}$ are reported.

2. Experimental

(a) Synthesis of $RE_2MGa_9Ge_2$ ($RE = Ce, Sm$; $M = Ni, Co$)

First representatives of the $RE_2MGa_9Ge_2$ family were obtained from the exploratory reactions containing a 4 : 1 : 30 : 4 ratio of RE : M : Ga : Ge. For the rational synthesis of $RE_2MGa_9Ge_2$, elemental RE (Ce, Sm 2.26 mmol), M (Co, Ni 1.13 mmol), and Ge (3.4 mmol) of typical purity 99.9% and higher (CERAC Inc.) were combined in the molar ratio 2 : 1 : 3 with 30 equivalents of Ga (33 mmol) and placed in alumina crucibles. The metals were handled in the dry box under nitrogen atmosphere. The crucibles were then sealed in a quartz ampoule under high vacuum ($\sim 1 \cdot 10^{-4}$ Torr). The reaction mixtures were heated to 1000°C in 15 hours, left at 1000°C for a short period of time (5 h) to allow proper homogenization of the melt, cooled in 2 hours to 850°C and kept there isothermally for 6 days, then cooled to $\sim 250^\circ\text{C}$ at the rate $8^\circ/\text{h}$ and next taken out for hot-filtration of liquid Ga.

The filtration was carried out at $\sim 250^\circ\text{C}$ via centrifuging unused liquid Ga through a specially designed quartz filter with coarse frit. Further isolation was done in a 3 – 5 molar solution of iodine in dimethylformamide (DMF) over 12 – 24 hours at room temperature. The product was rinsed with hot water and DMF and dried with acetone and ether. The crystals of $RE_2MGa_9Ge_2$ are large, plate-like, often with phylломorphous character. The crystals of this phase occasionally grow as agglomerates. The $RE_2MGa_9Ge_2$ phase was recovered in high yield ($> 90\%$) from the Ce/M/Ga/Ge reactions. However, attempts to synthesize the Sm analog of $RE_2NiGa_9Ge_2$ in pure form

were hampered by the formation of the $\text{Sm}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3$ side phase. It was found that in flux conditions the growth of these two phases is closely interrelated. The enhanced yield (~80%) of the $\text{Sm}_2\text{NiGa}_9\text{Ge}_2$ phase was observed on the initial stages of the reaction upon heating for only 5 hours at 1000°C. Additionally, needle-like crystals of $\text{Ce}_3\text{Ga}_9\text{Ge}$ and $\text{Sm}_3\text{Ga}_9\text{Ge}$ together with recrystallized Ge were observed in minor quantities, as by-products.

(b) Synthesis of $\text{RE}_2\text{Ga}_2\text{Ge}_5$ ($\text{RE} = \text{Sm}, \text{Tb}, \text{La}$) and $\text{La}_3\text{Ga}_2\text{Ge}$

Although $\text{RE}_2\text{Ga}_2\text{Ge}_5$ and $\text{La}_3\text{Ga}_2\text{Ge}$ compounds were originally discovered in the reactions containing Fe, the latter is not needed for their synthesis. The $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ compound was obtained in quite low yield (~ 15%) from the reactions containing Sm, Fe, Ga and Ge combined in the atomic ratios 4 : 1 : 30 : 6. The reaction conditions for the synthesis of this phase in pure form have not yet been optimized. The temperature variation profile and isolation technique used in this reaction is identical to that given for $\text{RE}_2\text{MGa}_9\text{Ge}_2$. The crystals of $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ grow as poorly formed thick plates, occasionally featuring right angles. Besides the $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ phase, additional products of the Sm/Fe/Ga/Ge reaction included cubic $\text{Sm}_4\text{FeGa}_{12-x}\text{Ge}_x$ ⁷, orthorhombic $\text{Sm}_3\text{Ga}_9\text{Ge}$ ⁸ and $\text{FeGa}_{3-x}\text{Ge}_x$, a pseudo-binary derivative of FeGa_3 ⁹.

The $\text{La}_3\text{Ga}_2\text{Ge}$ phase was detected as a side product in the reaction involving La, Fe, Ga and Ge taken in the ratio: 5 : 2 : 8 : 8, respectively. The heating profile included heating (60°/hour) up to 1000°C, a short (5 hours) isothermal step at 1000°C to obtain proper melt, quick cooling to 850°C followed by 3 days isothermal step at 850°C, then

slow cooling (16°/hour) to ~250°C. The excess of Ga was removed in two-step process: first by hot-temperature span-filtration forcing liquid Ga through specially designed filters by centrifuging at high speed (> 3000 rpm) for approximately 30 seconds, and second by treating the product with ~3 M solution of I₂ in DMF for 12 - 24 hours. The product was subsequently rinsed in DMF, hot water and dried with acetone and ether.

Elemental Analysis and X-Ray Powder Diffraction

The elemental composition was studied by Energy Dispersive Spectroscopy (EDS) semi-quantitative analysis on a SEM equipped with a NORAN Inc. EDS detector. The routine data acquisition was done at an acceleration voltage 20 kV and collection time of 30 seconds. An extensive averaging of the results obtained on the different crystals was carried out in order to attain accurate values of the atomic ratios. As a result, averaged compositions for Ce₂CoGa₉Ge₂, Sm₂Ga₂Ge₅ and La₃Ga₂Ge were determined to be: “Ce₂Co_{1.3}Ga_{6.1}Ge_{4.0}” (normalized to the amount of Ce), “Sm_{1.8}Ga_{3.2}Ge_{5.0}” (normalized to the amount of Ge) and “La₃Ga_{3.7}Ge_{0.9}” (normalized per amount of La), respectively. These formulas are in agreement with the results of single crystal X-ray refinement.

The X-ray powder diffraction (XRD) patterns of products were taken at room temperature on a CPS 120 INEL X-ray diffractometer (Cu K α radiation) equipped with position-sensitive detector. Experimental XRD patterns were then compared to that calculated from a single crystal data using the CERIUS² software package¹⁰.

Single Crystal X-Ray Crystallography

The intensity data was collected on single crystals of $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ ($\text{Sm}_2\text{NiGa}_9\text{Ge}_2$), $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ and $\text{La}_3\text{Ga}_2\text{Ge}$ with a Siemens Platform SMART¹¹ CCD X-ray diffractometer. The crystals of suitable size $0.02 \times 0.06 \times 0.10 \text{ mm}^3$ for $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$, $0.05 \times 0.05 \times 0.02 \text{ mm}^3$ for $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ and $0.16 \times 0.12 \times 0.07 \text{ mm}^3$ for $\text{La}_3\text{Ga}_2\text{Ge}$ were cut off from larger crystals and mounted on glass fibers. A full sphere of reciprocal data (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, the X-ray radiation was generated at 34 kV/40 mA) was acquired up to 46° in 2θ for $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ using an exposure time of 50 s per frame. For $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ and $\text{La}_3\text{Ga}_2\text{Ge}$ data were acquired up to 56° in 2θ , covering a hemisphere of reciprocal space (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$, X-ray radiation was generated at 50 kV/40 mA for $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ and at 34 kV/40 mA for $\text{La}_3\text{Ga}_2\text{Ge}$). The individual frames were measured using the ω -steps of 0.30° and an exposure time 40 s and 30 s per frame for $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ and $\text{La}_3\text{Ga}_2\text{Ge}$, respectively.

The data collection and acquisition was performed with the SMART¹¹ software package and the SAINTPLUS¹² program was used for data reduction. The analytical absorption corrections were done using a face-indexing routine, and an empirical correction for absorption based on symmetry equivalent reflections was consequently applied with the SADABS¹³ software package. The crystal structure was solved with direct methods using the SHELXTL¹⁴ program. All atomic positions were refined anisotropically. The setting of the cell was standardized with the STRUCTURE TIDY program¹⁵.

Structure Refinement of Ce₂CoGa₉Ge₂ (1)

The Ce₂CoGa₉Ge₂ (1) crystallizes in tetragonal space group *P4/nmm* in a structure type related to that of Sm₂Ni(Si_{1-x}Ni_x)Al₄Si₆¹⁶. The variation of the Ga/Ge versus Al/Si assignment underlies the differences in 1 and its structure type. In the structure of 1, a total of seven atomic positions were identified; of those, site with multiplicity *4f* was assigned to Ce and *2a* was assigned to the Co atoms. The Ge atoms are found on two sites with multiplicity *2c*. Contrarily to Sm₂Ni(Si_{1-x}Ni_x)Al₄Si₆¹⁶, the substitution of Ge at *2c* with Co was not favorable during the structure refinement of 1. The Ga atoms in 1 occupy three atomic sites: two at *8j* and one at *2c*. Even though the Ga and Ge atoms were given particular atomic positions in this structure, accurate determination of the Ga and Ge distribution is very difficult, if relying on X-ray diffraction data solely. In this particular case, the assignment of Ga and Ge was made on the basis of elemental analysis and connectivity data. Because Ge has slightly smaller covalent radii than Ga, the shorter Ce-X distances (where X could be Ga or Ge) were assigned to Ge. Previous Ga/Ge and Al/Si assignments based on this approach was shown to be accurate^{17,18,4}. Further investigation of the Ga/Ge distribution is currently being carried out with powder neutron diffraction. The information relevant to the data collection structure refinement of Ce₂CoGa₉Ge₂ is given in the Table VII.1a and for Sm₂NiGa₉Ge₂ in Table VII.1b. The final atomic positions and the equivalent thermal displacement parameters for the Ce₂CoGa₉Ge₂ and Sm₂NiGa₉Ge₂ are listed in Table VII.2a and VII.2b, respectively. Selected interatomic distances (up to 3.5 Å), bond angles and anisotropic displacement parameters refined for Ce₂CoGa₉Ge₂ are presented in Tables VII.3, VII.4 and VII.5.

Table VII.1. Crystal data and structure refinement for 1: (a) Ce₂CoGa₉Ge₂ and (b) Sm₂NiGa₉Ge₂.

Empirical formula	(a) Ce ₂ CoGa ₉ Ge ₂	(b) Sm ₂ NiGa ₉ Ge ₂
Formula weight	1111.83	1132.07
Temperature (K)	173(2)	298(2) K
Wavelength (Å)	0.71073	0.71073 Å
Crystal system	Tetragonal	Tetragonal
Space group	<i>P4/nmm</i>	<i>P4/nmm</i>
Unit cell dimensions (Å)	<i>a</i> = 5.9582(5) <i>b</i> = 5.9582(5) <i>c</i> = 15.0137(18)	<i>a</i> = 5.9082(17) <i>b</i> = 5.9082(17) <i>c</i> = 14.919(6)
Volume (Å ³)	532.99(9)	520.8(3)
Z	2	2
Density (calculated) (g/cm ³)	6.928	7.220
Absorption coefficient (mm ⁻¹)	37.663	41.297
F(000)	972	990
Crystal size (mm ³)	0.02 × 0.06 × 0.10	0.20 × 0.16 × 0.04
θ range for data collection	2.71 to 23.23°	1.36 to 23.13°
Index ranges	-6 ≤ <i>h</i> ≤ 6, -6 ≤ <i>k</i> ≤ 6, -16 ≤ <i>l</i> ≤ 16	-4 ≤ <i>h</i> ≤ 6, -4 ≤ <i>k</i> ≤ 6, -16 ≤ <i>l</i> ≤ 13
Reflections collected	3197	1946
Independent reflections	270 [<i>R</i> _{int} = 0.0338]	267 [<i>R</i> _{int} = 0.0593]
Completeness to θ	99.6 %	100.0 %
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	270 / 0 / 29	267 / 0 / 29
Goodness-of-fit on <i>F</i> ²	1.426	1.603
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] *	<i>R</i> ₁ = 0.0194, <i>wR</i> ₂ = 0.0506	<i>R</i> ₁ = 0.0397, <i>wR</i> ₂ = 0.1210
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0221, <i>wR</i> ₂ = 0.0514	<i>R</i> ₁ = 0.0406, <i>wR</i> ₂ = 0.1214
Extinction coefficient	0.00243(16)	0.0019(3)
Largest diff. peak and hole (e ⁻ Å ⁻³)	0.630 and -0.996	1.977 and -1.874

* $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2\{|F_o|\}$.

Table VII.2. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1: (a) $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ and (b) $\text{Sm}_2\text{NiGa}_9\text{Ge}_2$.

(a)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*
Ce	4 <i>f</i>	$\frac{3}{4}$	$\frac{1}{4}$	0.2529(1)	6(1)
Co	2 <i>a</i>	$\frac{3}{4}$	$\frac{1}{4}$	0	6(1)
Ga(1)	8 <i>j</i>	0.0103(1)	0.0103(1)	0.0851(1)	7(1)
Ga(2)	8 <i>j</i>	0.0362(2)	0.0362(2)	0.4190(1)	9(1)
Ga(3)	2 <i>c</i>	$\frac{1}{4}$	$\frac{1}{4}$	0.6471(2)	8(1)
Ge(1)	2 <i>c</i>	$\frac{1}{4}$	$\frac{1}{4}$	0.8130(2)	8(1)
Ge(2)	2 <i>c</i>	$\frac{1}{4}$	$\frac{1}{4}$	0.2115(2)	7(1)

(b)

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*
Sm	4 <i>f</i>	$\frac{3}{4}$	$\frac{1}{4}$	0.2548(1)	2(1)
Ni	2 <i>a</i>	$\frac{3}{4}$	$\frac{1}{4}$	0	3(1)
Ga(1)	8 <i>j</i>	0.0110(3)	0.0110(3)	0.0877(2)	4(1)
Ga(2)	8 <i>j</i>	0.0333(4)	0.0333(4)	0.4179(2)	8(1)
Ga(3)	2 <i>c</i>	$\frac{1}{4}$	$\frac{1}{4}$	0.6513(3)	6(1)
Ge(1)	2 <i>c</i>	$\frac{1}{4}$	$\frac{1}{4}$	0.8157(3)	6(1)
Ge(2)	2 <i>c</i>	$\frac{1}{4}$	$\frac{1}{4}$	0.2151(4)	7(1)

* U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table VII.3. Selected bond lengths [$\text{\AA}$] for $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ (1).

Bond	Distance	Multiplicity
Ce-Ge(2)	3.0430(6)	$\times 2$
Ce-Ge(1)	3.1387(8)	$\times 2$
Ce-Ga(2)	3.2789(11)	$\times 4$
Ce-Ga(1)	3.2843(11)	$\times 4$
Ce-Ga(3)	3.3362(12)	$\times 2$
Co-Ga(1)	2.4655(6)	$\times 8$
Ga(1)-Ga(1)	2.562(2)	$\times 1$
Ga(1)-Ge(1)	2.6743(18)	$\times 1$
Ga(1)-Ge(2)	2.772(2)	$\times 1$
Ga(1)-Ga(1)	2.8566(17)	$\times 2$
Ga(2)-Ga(2)	2.508(2)	$\times 1$
Ga(2)-Ga(2)	2.5482(18)	$\times 2$
Ga(2)-Ga(3)	2.6075(16)	$\times 1$
Ga(3)-Ge(1)	2.490(3)	$\times 1$

Table VII.4. Selected bond angles [°] for Ce₂CoGa₉Ge₂ (1).

Bond	Angle	Bond	Angle
Ge(2)-Ce-Ge(2)	156.47(9)	Ga(1)-Co-Ga(1)	105.59(2)
Ge(2)-Ce-Ge(1)	86.320(17)	Ga(1)-Co-Ga(1)	77.95(5)
Ge(1)-Ce-Ge(1)	143.30(9)	Co-Ga(1)-Co	117.39(4)
Ge(2)-Ce-Ga(2)	131.62(5)	Co-Ga(1)-Ga(1)	58.70(2)
Ge(2)-Ce-Ga(2)	69.27(4)	Co-Ga(1)-Ge(1)	105.53(4)
Ge(1)-Ce-Ga(2)	127.46(4)	Ga(1)-Ga(1)-Ge(1)	121.03(8)
Ge(1)-Ce-Ga(2)	82.57(4)	Co-Ga(1)-Ge(2)	112.37(3)
Ga(2)-Ce-Ga(2)	45.73(4)	Ga(1)-Ga(1)-Ge(2)	137.09(8)
Ga(2)-Ce-Ga(2)	80.95(3)	Ge(1)-Ga(1)-Ge(2)	101.88(7)
Ga(2)-Ce-Ga(2)	62.66(4)	Co-Ga(1)-Ga(1)	128.98(3)
Ga(2)-Ce-Ga(2)	45.73(4)	Co-Ga(1)-Ga(1)	54.60(3)
Ge(2)-Ce-Ga(1)	51.79(4)	Ga(1)-Ga(1)-Ga(1)	92.74(4)
Ge(2)-Ce-Ga(1)	107.81(5)	Ge(1)-Ga(1)-Ga(1)	125.44(2)
Ge(1)-Ce-Ga(1)	49.15(4)	Ga(1)-Ga(1)-Ga(1)	90.0
Ge(1)-Ce-Ga(1)	99.87(4)	Ga(2)-Ga(2)-Ga(2)	99.89(4)
Ga(2)-Ce-Ga(1)	176.17(3)	Ga(2)-Ga(2)-Ga(2)	90.0
Ga(2)-Ce-Ga(1)	131.28(3)	Ga(2)-Ga(2)-Ga(3)	98.31(9)
Ga(2)-Ce-Ga(1)	99.71(2)	Ga(2)-Ga(2)-Ga(3)	130.83(2)
Ga(2)-Ce-Ga(1)	120.45(3)	Ge(1)-Ga(3)-Ga(2)	112.37(6)
Ga(2)-Ce-Ga(1)	99.71(2)	Ga(2)-Ga(3)-Ga(2)	81.67(4)
Ga(1)-Ce-Ga(1)	51.56(4)	Ga(2)-Ga(3)-Ga(2)	135.25(11)
Ga(1)-Ce-Ga(1)	56.35(4)	Ga(3)-Ge(1)-Ga(1)	124.91(5)
Ga(1)-Ce-Ga(1)	79.87(3)	Ga(1)-Ge(1)-Ga(1)	110.19(10)
Ga(1)-Co-Ga(1)	175.97(6)	Ga(1)-Ge(1)-Ga(1)	70.89(5)
Ga(1)-Co-Ga(1)	62.61(4)	Ga(1)-Ge(2)-Ga(1)	62.04(5)
Ga(1)-Co-Ga(1)	117.55(4)	Ga(1)-Ge(2)-Ga(1)	93.57(9)
Ga(1)-Co-Ga(1)	70.81(5)	Ge(2)-Ga(1)-Ga(1)	58.98(2)

Table VII.5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ (1).

Atomic Position	U11	U22	U33	U23	U13	U12
Ce	4(1)	4(1)	8(1)	0	0	0
Co	4(1)	4(1)	8(1)	0	0	0
Ga(1)	6(1)	6(1)	9(1)	0(1)	0(1)	1(1)
Ga(2)	7(1)	7(1)	12(1)	-2(1)	-2(1)	-1(1)
Ga(3)	7(1)	7(1)	10(1)	0	0	0
Ge(1)	7(1)	7(1)	10(1)	0	0	0
Ge(2)	6(1)	6(1)	10(1)	0	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Structure Refinement of Sm₂Ga₂Ge₅ (2)

The Sm₂Ga₂Ge₅ (**2**) adopts a *C*-centered orthorhombic crystal lattice, space group *Cmca*. The crystal structure of **2** belongs to Ce₂GaGe₆¹⁹ structure type, which was previously determined from single crystal X-ray diffraction. There are a total of seven atomic positions in **2**. The Sm atoms occupy the highest multiplicity *16g* site, the two *8f* sites were assigned to Ga atoms, and the remaining four sites (*16g*, *8f*, *8f*, *8f*) to Ge atoms. As it is in case of **1**, the Ga/Ge distribution in **2** was made using a combination of elemental analysis and connectivity statistics. However, in this case, shorter bond distances were attributed to Ge-Ge and longer distances to Ga-Ga contacts. Detailed description of the Ga/Ge assignment is given in the section devoted to crystal structure of **2**.

Details of the data collection and structure refinement for the Sm₂Ga₂Ge₅ are listed in Table VII.6. The final atomic positions and equivalent thermal displacement parameters are given in Table VII.7. The interatomic distances (up to 3.5 Å) and selected bond angles are listed in Tables VII.8 and VII.9, respectively. Anisotropic displacement parameters for all atoms are presented in Tables VII.10

Table VII.6. Crystal data and structure refinement for Sm₂Ga₂Ge₅ (2).

Empirical formula	Sm ₂ Ga ₂ Ge ₅
Formula weight	803.09
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Cmca</i>
Unit cell dimensions (Å)	<i>a</i> = 8.448(2) <i>b</i> = 8.192(2) <i>c</i> = 21.286(5)
Volume (Å ³)	1473.3(6)
Z	8
Density (calculated) (g/cm ³)	7.241
Absorption coefficient (mm ⁻¹)	42.843
F(000)	2768
Crystal size (mm ³)	0.05 × 0.05 × 20
θ range for data collection	1.91 to 28.40°
Index ranges	-11 ≤ <i>h</i> ≤ 9, -9 ≤ <i>k</i> ≤ 10, -27 ≤ <i>l</i> ≤ 27
Reflections collected	4408
Independent reflections	943 [<i>R</i> _{int} = 0.0598]
Completeness to θ	95.2 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	943 / 0 / 50
Goodness-of-fit on <i>F</i> ²	1.018
Final <i>R</i> indices [<i>I</i> > σ(<i>I</i>)] [*]	<i>R</i> ₁ = 0.0451, <i>wR</i> ₂ = 0.1151
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0702, <i>wR</i> ₂ = 0.1288
Extinction coefficient	0.00010(3)
Largest diff. peak and hole (e·Å ⁻³)	2.882 and -4.254

^{*}*R*₁ = Σ|*F*_o - *F*_c| / Σ|*F*_o|; *wR*₂ = [Σ*w*{|*F*_o - *F*_c||² / Σ*w*|*F*_o|²]^{1/2}, *w* = 1/σ²{|*F*_o|}.

Table VII.7. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ (**2**).

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*
Sm	<i>16g</i>	0.2501(1)	0.3747(4)	0.0815(1)	7(1)
Ge(1)	<i>8f</i>	0	0.1313(7)	0.0282(1)	9(1)
Ge(2)	<i>8f</i>	0	0.3375(3)	0.3066(1)	13(1)
Ge(3)	<i>16g</i>	0.2831(2)	0.1248(4)	0.1932(1)	13(1)
Ge(4)	<i>8f</i>	0	0.4105(3)	0.1928(1)	13(1)
Ga(1)	<i>8f</i>	0	0.1189(7)	0.4585(1)	7(1)
Ga(2)	<i>8f</i>	0	0.1233(3)	0.1445(1)	10(1)

* U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table VII.8. Selected bond lengths [$\text{\AA}$] for $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ (2).

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
Sm-Ga(1)	3.032(5)	$\times 1$	Ge(1)-Ge(1)	2.463(11)	$\times 1$
Sm-Ga(1)	3.094(5)	$\times 1$	Ge(1)-Ga(2)	2.476(3)	$\times 1$
Sm-Ge(1)	3.119(5)	$\times 1$	Ge(1)-Ga(1)	2.528(9)	$\times 1$
Sm-Ge(1)	3.1476(16)	$\times 1$	Ge(2)-Ge(4)	2.495(3)	$\times 1$
Sm-Ge(3)	3.151(3)	$\times 2$	Ge(2)-Ge(3)	2.529(3)	$\times 2$
Sm-Ge(1)	3.188(5)	$\times 1$	Ge(2)-Ga(2)	2.563(3)	$\times 1$
Sm-Ge(4)	3.1890(17)	$\times 1$	Ge(3)-Ge(3)	2.481(3)	$\times 1$
Sm-Ge(2)	3.1978(18)	$\times 1$	Ge(3)-Ge(4)	2.538(3)	$\times 1$
Sm-Ga(2)	3.225(3)	$\times 1$	Ge(3)-Ga(2)	2.6075(17)	$\times 1$
Sm-Ga(2)	3.241(3)	$\times 1$	Ge(4)-Ga(2)	2.568(3)	$\times 1$
Sm-Ga(1)	3.3639(17)	$\times 1$	Ga(1)-Ga(1)	2.629(10)	$\times 1$

Table VII.9. Selected bond and angles [°] for Sm₂Ga₂Ge₅ (**2**).

Bond	Angle	Bond	Angle
Ga(1)-Sm-Ga(1)	147.70(8)	Ge(4)-Sm-Ge(2)	83.82(4)
Ga(1)-Sm-Ge(1)	81.23(5)	Ga(1)-Sm-Ga(2)	98.99(14)
Ga(1)-Sm-Ge(1)	85.93(16)	Ga(1)-Sm-Ga(2)	95.48(8)
Ga(1)-Sm-Ge(1)	105.64(9)	Ge(1)-Sm-Ga(2)	176.70(5)
Ga(1)-Sm-Ge(1)	47.76(16)	Ge(1)-Sm-Ga(2)	83.06(9)
Ge(1)-Sm-Ge(1)	100.07(8)	Ge(3)-Sm-Ga(2)	92.22(6)
Ga(1)-Sm-Ge(3)	134.62(5)	Ge(3)-Sm-Ga(2)	48.25(5)
Ga(1)-Sm-Ge(3)	72.97(9)	Ge(1)-Sm-Ga(2)	45.41(6)
Ge(1)-Sm-Ge(3)	85.35(11)	Ge(4)-Sm-Ga(2)	93.83(6)
Ge(1)-Sm-Ge(3)	119.36(11)	Ge(2)-Sm-Ga(2)	47.03(6)
Ga(1)-Sm-Ge(3)	73.81(10)	Ga(1)-Sm-Ga(2)	94.64(8)
Ga(1)-Sm-Ge(3)	135.12(6)	Ga(1)-Sm-Ga(2)	97.37(13)
Ge(1)-Sm-Ge(3)	129.02(13)	Ge(1)-Sm-Ga(2)	45.76(6)
Ge(3)-Sm-Ge(3)	81.97(4)	Ge(1)-Sm-Ga(2)	137.23(15)
Ga(1)-Sm-Ge(1)	85.80(15)	Ge(3)-Sm-Ga(2)	48.12(5)
Ga(1)-Sm-Ge(1)	84.08(5)	Ge(3)-Sm-Ga(2)	92.44(6)
Ge(1)-Sm-Ge(1)	137.82(7)	Ge(1)-Sm-Ga(2)	176.36(9)
Ge(1)-Sm-Ge(1)	45.76(18)	Ge(4)-Sm-Ga(2)	47.07(6)
Ge(3)-Sm-Ge(1)	129.68(5)	Ge(2)-Sm-Ga(2)	93.54(6)
Ge(3)-Sm-Ge(1)	84.20(11)	Ga(2)-Sm-Ga(2)	131.00(7)
Ga(1)-Sm-Ge(4)	71.71(6)	Ga(1)-Sm-Ga(1)	48.19(17)
Ga(1)-Sm-Ge(4)	135.96(12)	Ga(1)-Sm-Ga(1)	103.01(7)

Table VII.9. (continued)

Bond	Angle	Bond	Angle
Ge(1)-Sm-Ge(4)	83.11(6)	Ge(1)-Sm-Ga(1)	45.70(16)
Ge(1)-Sm-Ge(4)	175.60(17)	Ge(1)-Sm-Ga(1)	81.07(4)
Ge(3)-Sm-Ge(4)	63.71(6)	Ge(3)-Sm-Ga(1)	130.77(12)
Ge(3)-Sm-Ge(4)	47.18(6)	Ge(3)-Sm-Ga(1)	121.40(11)
Ge(1)-Sm-Ge(4)	129.99(13)	Ge(1)-Sm-Ga(1)	97.41(8)
Ga(1)-Sm-Ge(2)	137.07(12)	Ge(4)-Sm-Ga(1)	99.24(4)
Ga(1)-Sm-Ge(2)	71.94(6)	Ge(2)-Sm-Ga(1)	174.73(14)
Ge(1)-Sm-Ge(2)	131.09(13)	Ga(2)-Sm-Ga(1)	136.44(14)
Ge(1)-Sm-Ge(2)	96.21(4)	Ga(2)-Sm-Ga(1)	85.53(8)
Ge(3)-Sm-Ge(2)	46.94(6)	Ge(1)-Sm-Ge(2)	83.72(6)
Ge(3)-Sm-Ge(2)	63.79(6)	Ge(4)-Ge(3)-Ga(2)	131.14(13)
Ge(2)-Ge(4)-Ge(3)	99.34(8)	Ge(3)-Ge(4)-Ge(3)	92.46(14)
Ge(1)-Ge(1)-Ga(2)	117.7(3)	Ge(2)-Ge(4)-Ga(2)	99.78(10)
Ge(1)-Ge(1)-Ga(1)	114.92(14)	Ge(3)-Ge(4)-Ga(2)	129.43(7)
Ga(2)-Ge(1)-Ga(1)	127.4(3)	Ge(1)-Ga(2)-Ge(2)	115.49(18)
Ge(4)-Ge(2)-Ge(3)	99.58(8)	Ge(1)-Ga(2)-Ge(4)	112.13(17)
Ge(3)-Ge(2)-Ge(3)	92.86(14)	Ge(2)-Ga(2)-Ge(4)	132.38(11)
Ge(4)-Ge(2)-Ga(2)	100.12(10)	Ge(1)-Ga(2)-Ge(3)	113.45(5)
Ge(3)-Ge(2)-Ga(2)	128.99(7)	Ge(2)-Ga(2)-Ge(3)	80.92(9)
Ge(3)-Ge(3)-Ge(2)	99.33(8)	Ge(4)-Ga(2)-Ge(3)	80.58(9)
Ge(2)-Ge(3)-Ge(4)	87.34(7)	Ge(3)-Ga(2)-Ge(3)	133.06(10)
Ge(3)-Ge(3)-Ga(2)	100.44(9)	Ge(1)-Ga(1)-Ga(1)	101.89(12)
Ge(2)-Ge(3)-Ga(2)	131.93(13)		

Table VII.10. Anisotropic displacement parameters* ($\text{\AA}^2 \times 10^3$) for $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ (2).

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Sm	6(1)	8(1)	6(1)	0(1)	0(1)	0(1)
Ge(1)	12(1)	9(1)	8(1)	2(1)	0	0
Ge(2)	13(1)	11(2)	15(1)	-2(1)	0	0
Ge(3)	14(1)	13(1)	12(1)	0(1)	-3(1)	-1(1)
Ge(4)	13(1)	11(2)	14(1)	-2(1)	0	0
Ga(1)	10(1)	11(1)	8(1)	0(1)	0	0
Ga(2)	5(1)	6(1)	10(1)	-3(1)	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Structure Refinement of La₃Ga₂Ge (3)

The La₃Ga₂Ge (**3**) compound crystallizes in the orthorhombic space group *Cmcm*. To our knowledge, the structure of **3** is novel and belongs to a new structure type, Pearson symbol oC24. Among the compounds **1**, **2** and **3**, the structure of **3** is the most RE-rich. The La atoms occupy two out of four atomic positions in the asymmetric unit of **3**: *8f* and *4c*. The Ga and Ge atoms are found at *8f* and *4c* sites, respectively. The assignment of Ga and Ge was made based on the elemental analysis data that indicated higher Ga content compared to that of Ge.

Details of the data collection and structure refinement for La₃Ga₂Ge are listed in Table VII.11. The final atomic positions and equivalent thermal displacement parameters are given in Table VII.12. The interatomic distances (up to 3.5 Å) and selected bond angles are listed in Tables VII.13 and VII.14. Anisotropic displacement parameters for all atoms are presented in Table VII.15.

Table VII.11. Crystal data and structure refinement for La₃Ga₂Ge (3).

Empirical formula	La ₃ Ga ₂ Ge
Formula weight	628.76
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Cmcm</i> (#63)
Unit cell dimensions (Å)	<i>a</i> = 4.4628(11) <i>b</i> = 11.703(3) <i>c</i> = 12.739(3)
Volume (Å ³)	665.4(3)
Z	4
Density (calculated) (g/cm ³)	6.277
Absorption coefficient (mm ⁻¹)	31.129
F(000)	1060
Crystal size (mm ³)	0.16 × 0.12 × 0.07
θ range for data collection	3.20 to 28.40°
Index ranges	-5 ≤ <i>h</i> ≤ 5, -14 ≤ <i>k</i> ≤ 15, -16 ≤ <i>l</i> ≤ 10
Reflections collected	2055
Independent reflections	471 [<i>R</i> _{int} = 0.0268]
Completeness to θ	96.9 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	471 / 0 / 22
Goodness-of-fit on <i>F</i> ²	1.299
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] *	<i>R</i> ₁ = 0.0266, <i>wR</i> ₂ = 0.0831
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0290, <i>wR</i> ₂ = 0.0842
Extinction coefficient	0.00094(14)
Largest diff. peak and hole (e/Å ³)	1.214 and -1.694

$$^*R_1 = \sum |F_o| - |F_c| / \sum |F_o|; wR_2 = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}, w = 1/\sigma^2\{|F_o|\}.$$

Table VII.12. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{La}_3\text{Ga}_2\text{Ge}$ (**3**).

Atomic Position	Wyckoff Symbol	<i>x</i>	<i>y</i>	<i>z</i>	U(eq)*
La(1)	4 <i>c</i>	0	0.3468(1)	¼	13(1)
La(2)	8 <i>f</i>	0	0.6408(1)	0.0904(1)	12(1)
Ga	8 <i>f</i>	0	0.0702(1)	0.5794(1)	14(1)
Ge	4 <i>c</i>	0	0.0546(1)	¼	16(1)

* U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table VII.13. Selected bond lengths [$\text{\AA}$] for $\text{La}_3\text{Ga}_2\text{Ge}$ (**3**).

Bond	Distance	Multiplicity	Bond	Distance	Multiplicity
La(1)-Ga	3.2626(8)	× 4	La(2)-Ga	3.2159(8)	× 2
La(1)-Ge	3.2999(13)	× 2	La(2)-Ga	3.3312(12)	× 2
La(1)-Ge	3.4204(18)	× 1	La(2)-Ga	3.3849(16)	× 1
La(1)-La(2)	3.8635(9)	× 4	La(2)-La(2)	4.0209(13)	× 1
La(1)-La(2)	3.9964(12)	× 1	La(2)-La(2)	4.0666(14)	× 1
La(2)-Ge	3.1831(7)	× 2	Ga-Ga	2.606(2)	× 1
			Ga-Ge	2.6182(14)	× 1

Table VII.14. Selected bond angles [°] for La₃Ga₂Ge (3).

Bond	Angle	Bond	Angle
Ga-La(1)-Ga	145.37(4)	Ga-La(2)-Ga	87.87(3)
Ga-La(1)-Ga	83.53(3)	Ge-La(2)-Ga	105.15(3)
Ga-La(1)-Ga	86.30(3)	Ge-La(2)-Ga	47.33(2)
Ga-La(1)-Ge	47.02(2)	Ga-La(2)-Ga	46.88(3)
Ga-La(1)-Ge	104.08(3)	Ga-La(2)-Ga	104.24(2)
Ge-La(1)-Ge	85.09(4)	Ga-La(2)-Ga	84.11(4)
Ga-La(1)-Ge	107.31(2)	Ge-La(2)-Ga	110.07(3)
Ge-La(1)-Ge	137.45(2)	Ga-La(2)-Ga	103.24(3)
Ge-La(2)-Ge	89.02(3)	Ga-La(2)-Ga	137.642(19)
Ge-La(2)-Ga	146.58(4)	Ga-Ga-Ge	107.02(8)
Ge-La(2)-Ga	82.06(2)	Ga-Ge-Ga	112.21(8)

Table VII.15. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for La₃Ga₂Ge (3).

Atomic Position	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
La(1)	11(1)	13(1)	14(1)	0	0	0
La(2)	11(1)	14(1)	13(1)	-1(1)	0	0
Ga	15(1)	16(1)	11(1)	0(1)	0	0
Ge	16(1)	18(1)	14(1)	0	0	0

*The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

Magnetic Measurements

The magnetic susceptibilities were measured on single crystal and polycrystalline samples of $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ and $\text{Ce}_2\text{NiGa}_9\text{Ge}_2$ in the temperature range 1.8 – 400 K using a MPMS SQUID magnetometer (Quantum Design, Inc.) with a magnetic field of 500 Gauss. *Sample preparation:* the crystals of **1** were picked manually and polished with sandpaper (1500 grit) to eliminate the risk of contamination with Co or Co-containing phases. As-obtained samples were further treated with 30% solution of HCl for approximately one minute under sonication, then rinsed with water and dried with acetone and ether.

The anisotropic measurements were performed using single crystal samples by positioning them with the *c*-axis parallel and perpendicular to the external magnetic field (H_{ex}). For isotropic measurements ground polycrystalline samples were used. The field dependence of magnetization was studied at 2 – 3 K in fields up to ± 5 T. The susceptibility data was corrected for the sample holder contribution.

3. Results and Discussions

Reaction Chemistry

In employing Ga flux as a synthetic route for the exploratory synthesis in the RE/M/Ga/Ge (RE = rare-earth, M = Fe, Ni, Co) system with RE : M > 1, we find that

depending on the transition metal M, the reaction may result in the formation of either M-containing quaternary phases, or other ternary phases like RE/M/Ga, RE/M/Ge and RE/Ga/Ge. Thus, for M = Fe, the yield of ternary phases such as $\text{RE}_3\text{Ga}_9\text{Ge}^8$, $\text{Tb}_4\text{FeGe}_8^{20}$, $\text{RE}_2\text{Ga}_2\text{Ge}_5$ and $\text{La}_3\text{Ga}_2\text{Ge}$, is rather high. Although in some instances the quaternary phases with Fe could also be produced, for instance cubic $\text{Tb}_4\text{FeGa}_{12-x}\text{Ga}_x^7$, their occurrence is not as high as that of ternary phases. When using the compositions with RE : Fe < 1, the Fe-rich ternary $\text{YFe}_{4+x}\text{Ga}_{8-x}^{21}$ and quaternary $\text{YFe}_4\text{Ga}_2\text{Ge}_6^{22}$ variants of ThMn_{12} -type²³ form. The main factors contributing to the shift of the reaction equilibrium toward the formation of ternary versus quaternary phases seem to be connected with the heating/cooling scheme, as well as the type of RE. For example, if RE = Y, Ce, Sm and Gd, the reaction RE/Fe/Ga/Ge results in the phase separation yielding ternary $\text{RE}_3\text{Ga}_9\text{Ge}^8$ and $\text{FeGa}_{3-x}\text{Ge}_x$. For RE = Tb and Sm, the kinetic product of the reaction is quaternary $\text{RE}_4\text{FeGa}_{12-x}\text{Ga}_x^7$ phase, whereas the thermodynamic product includes Fe-free and Ga-free phases $\text{RE}_2\text{Ga}_2\text{Ge}_5$ and $\text{Tb}_4\text{FeGe}_8^{20}$. For RE = La, an admixture of phases including $\text{La}_3\text{Ga}_2\text{Ge}$, $\text{La}_2\text{Ga}_2\text{Ge}_5$, $\text{LaGa}_{1-x}\text{Ge}_x^{24}$ and $\text{FeGa}_{3-x}\text{Ge}_x$ could be obtained.

In contrast, if M = Ni and Co were used, the formation of the quaternary phases is extremely favorable. This tendency has already been seen in the systems with RE : M = 1, where the quaternary phases $\text{REMGa}_3\text{Ge}^4$, $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3^4$ and $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4^5$ were produced in high yield. The identity of the rare-earth and the length of the temperature variation profile also appear to play a role in the phase formation in RE/M/Ga/Ge system with M = Ni, Co. For example, the growth of the $\text{RE}_2\text{MGa}_9\text{Ge}_2$ phase was observed only with the lighter RE elements such as Ce and Sm, whilst for the rest of rare-earth other structures ($\text{REMGa}_3\text{Ge}^4$, $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3^4$ and $\text{RE}_4\text{Ni}_3\text{Ga}_6\text{Ge}_4^5$) are preferential. Of those

REMGa₃Ge is especially stable. Interestingly, for RE = Sm, the Sm₂NiGa₉Ge₂ and Sm₃Ni₃Ga₈Ge₃ phases are equally favorable, with Sm₂NiGa₉Ge₂ forming in the early stages of the reaction, and Sm₃Ni₃Ga₈Ge₃ growing upon further heating. The crystals of Sm₂NiGa₉Ge₂ phase occasionally form an outgrowth on the bulk of Sm₃Ni₃Ga₈Ge₃ phase. Coincidentally, the separation of these two phases was possible owing to the variation in adhesive properties of these two compounds. Thus, during high-temperature filtration using glass wool as a filter, the crystals of Sm₃Ni₃Ga₈Ge₃ phase were found at the filter, while crystals of the Sm₂NiGa₉Ge₂ settled down at the bottom of the container. Yet, the occurrence of intergrowth makes the separation of the products of the Sm/Ni/Ga/Ge reaction an even more challenging task.

Crystal Structure of 1

The structure of Ce₂CoGa₉Ge₂ (**1**) projected onto *ac*-plane is depicted in Figure VII.1. The bonds to Ce atoms were omitted for clarity. In this view, the lighter atoms Co, Ga and Ge form a three-dimensional [CoGa₉Ge₂] framework, where Ce atoms are filling in the voids. The [CoGa₉Ge₂] sub-structural could be further broken down to a pair of 2D fragments, namely a [CoGa₄Ge₂] layer and a Ga-only slab. These layers alternate along the *c*-axis while extending infinitely in the *ab*-plane.

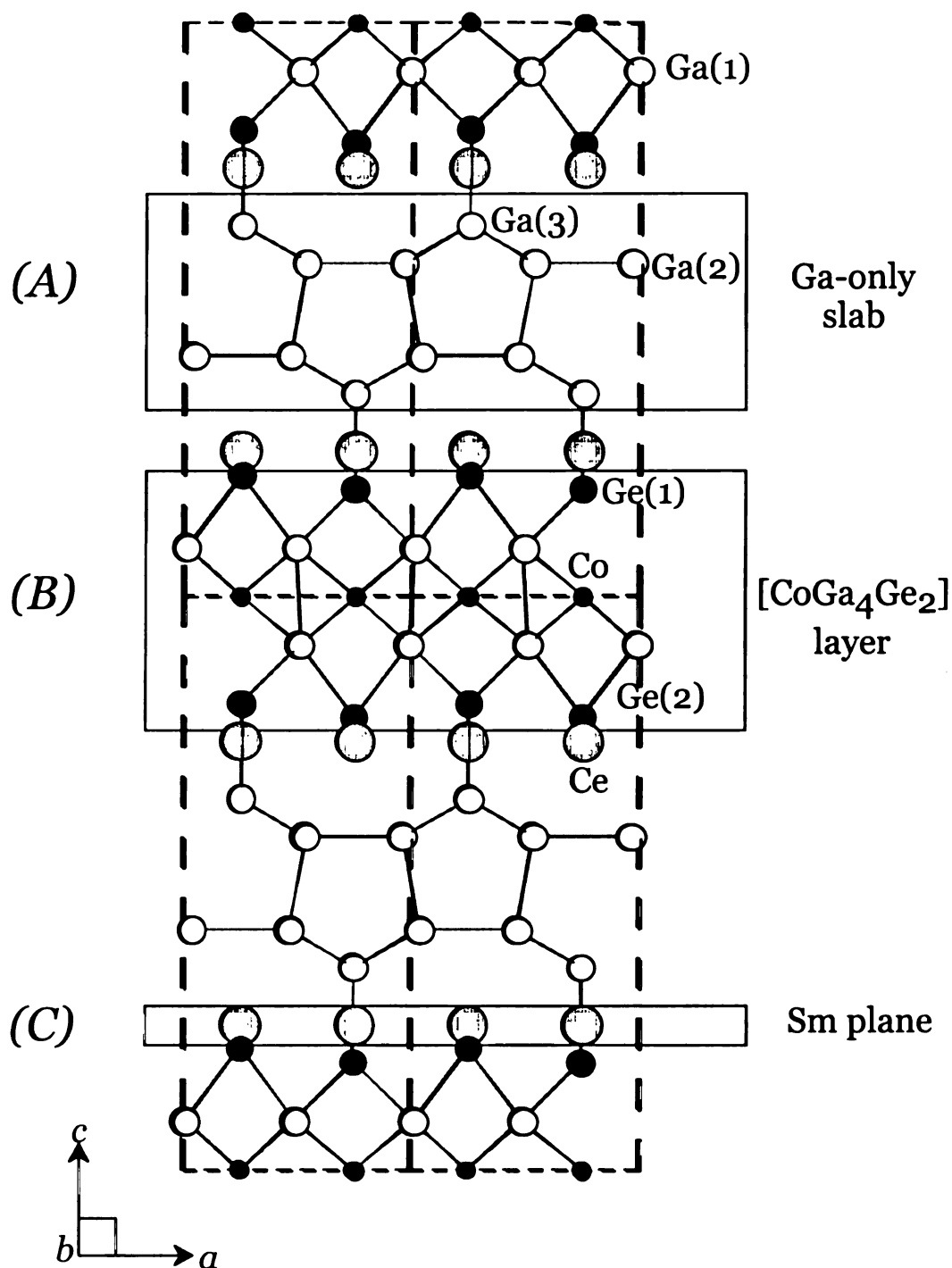
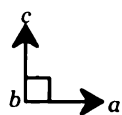
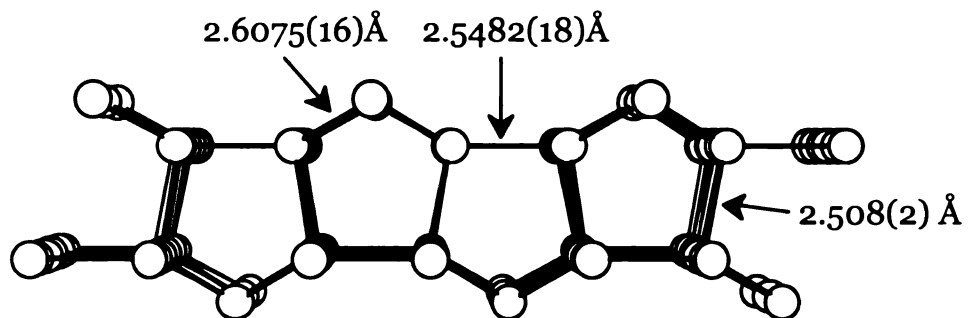


Figure VII.1. The structure of $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ (1). The Ce atoms are shown in larger and Ge in smaller grey spheres. The Ga atoms are drawn in open and Co in filled black circles. The unit cell is shown with dashed line. Three main structural fragments are contoured with a solid line and marked with letters (A), (B) and (C) indicating $[\text{Ga}]_5$; $[\text{CoGa}_4\text{Ge}_2]$ and Ce slabs, respectively.

The $[\text{Ga}_5]$ two-dimensional network (A) is shown in Figure VII.2. When viewed along the b -axis, as shown in Figure VII.2.A, this Ga-only slab features pentagonal tunnels (the axis of the tunnels is parallel to b). The $[\text{Ga}_5]$ fragment could be further subdivided into two 2D corrugated Ga sheets; one of these is depicted in Figure VII.2.B. Here, the Ga atoms are arranged with a tetragonal symmetry. The Ga-Ga contacts within $[\text{Ga}(2)_4]$ squares are 2.5482(18) Å and are strongly bonding, whereas the distance between the squares exceeds 3.4 Å and is non-bonding. A half of the larger hollows of the Ga(2) square net is mono-capped with Ga(3) atoms at 2.6075(16) Å. The two corrugated Ga sheets are arranged in a staggered conformation to each other and bonded via Ga(2)-Ga(2) interactions at 2.508(2) Å. This Ga(2)-Ga(2) interaction is the shortest Ga-Ga distance found in this structure. The $[\text{CoGa}_4\text{Ge}_2]$ and $[\text{Ga}_5]$ sub-structural fragments alternate along the c -axis and linked to each other through Ga(3)-Ge(1) interaction at 2.490(3) Å, which is, in its turn, the shortest Ga-Ge bonding distance in 1.

A.



B.

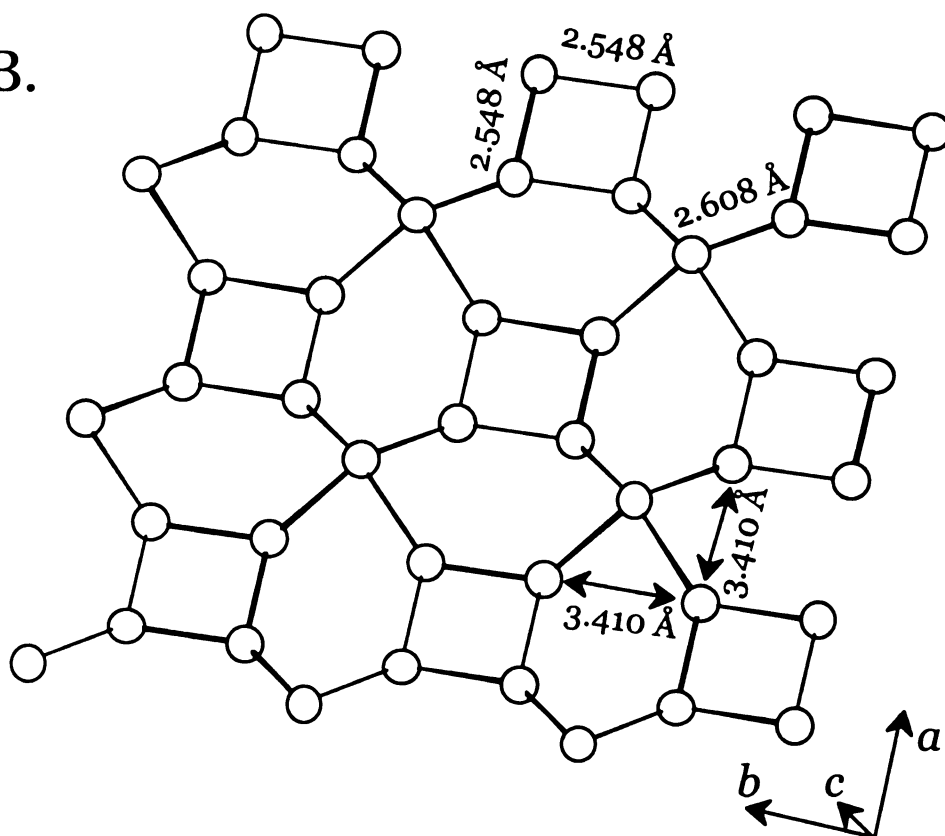


Figure VII.2. The Ga-only substructural unit. (A) view along the *b*-axis; (B) a single sheet of $[\text{Ga}]_5$ layer viewed approximately down the *c*-axis.

The next fragment participating in the construction of $[\text{CoGa}_9\text{Ge}_2]$ network is a $[\text{CoGa}_4\text{Ge}_2]$ layer (*B*), see Figure VII.3. In this layer, the Ga(1) atoms form a distorted cubic arrangement. The distortion is severe, as the Ga(1)-Ga(1) distances range from 2.562(2) Å to 3.102 Å, and it is even more pronounced than in the related YCoGa_3Ge , where Ga-Ga distances varied within the cubes from 2.615(3) Å to 2.9615(5) Å. Considering such a big divergence in the Ga-Ga bonding in the Ga “cube” layer, it is perhaps more appropriate to view the latter as a collection of $[\text{Ga}_2]$ dimers, (Ga-Ga = 2.562(2) Å). Yet, for the sake of clearness, we will continue to refer to the Ga arrangement as “cubic”, but only in the description of the $[\text{CoGa}_4\text{Ge}_2]$ layer.

The Co atoms occupy centers of a half of $[\text{Ga}_8]$ “cubes” in a checker manner, while the remaining half are bi-capped with Ge atoms, see Figure VII.3.B. The distance from the central Co atom to the corners of Ga “cubes” is 2.4655(6) Å, comparable to that found in YCoGa_3Ge (Co-Ga = 2.462(1) Å). The capping Ge(1) and Ge(2) atoms are bonded to Ga(1) network at 2.6743(18) Å and 2.772(2) Å, respectively, which also agrees well with the Ga-Ge distances found in the related YCoGa_3Ge (Ga-Ge = 2.667(3) Å). The same type of layer, although defected, has been observed in the $\text{REMGa}_3\text{Ge}^4$ and $\text{RE}_3\text{Ni}_3\text{Ga}_8\text{Ge}_3^4$, $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Si}_{1-x})\text{Al}_4\text{Si}_6^{16}$ and $\text{Ce}_2\text{NiAl}_{6-x}\text{Ge}_{4-y}^{25}$ compounds. Similar arrangements have been previously seen in a number of ternary polygallides such as $\text{Ce}_2\text{NiGa}_{10}^{26}$, $\text{Pr}_3\text{NiGa}_{10}^{27}$, $\text{Ce}_4\text{NiGa}_{18}^{28}$, $\text{Sm}_2\text{NiGa}_{12}^6$ as well.

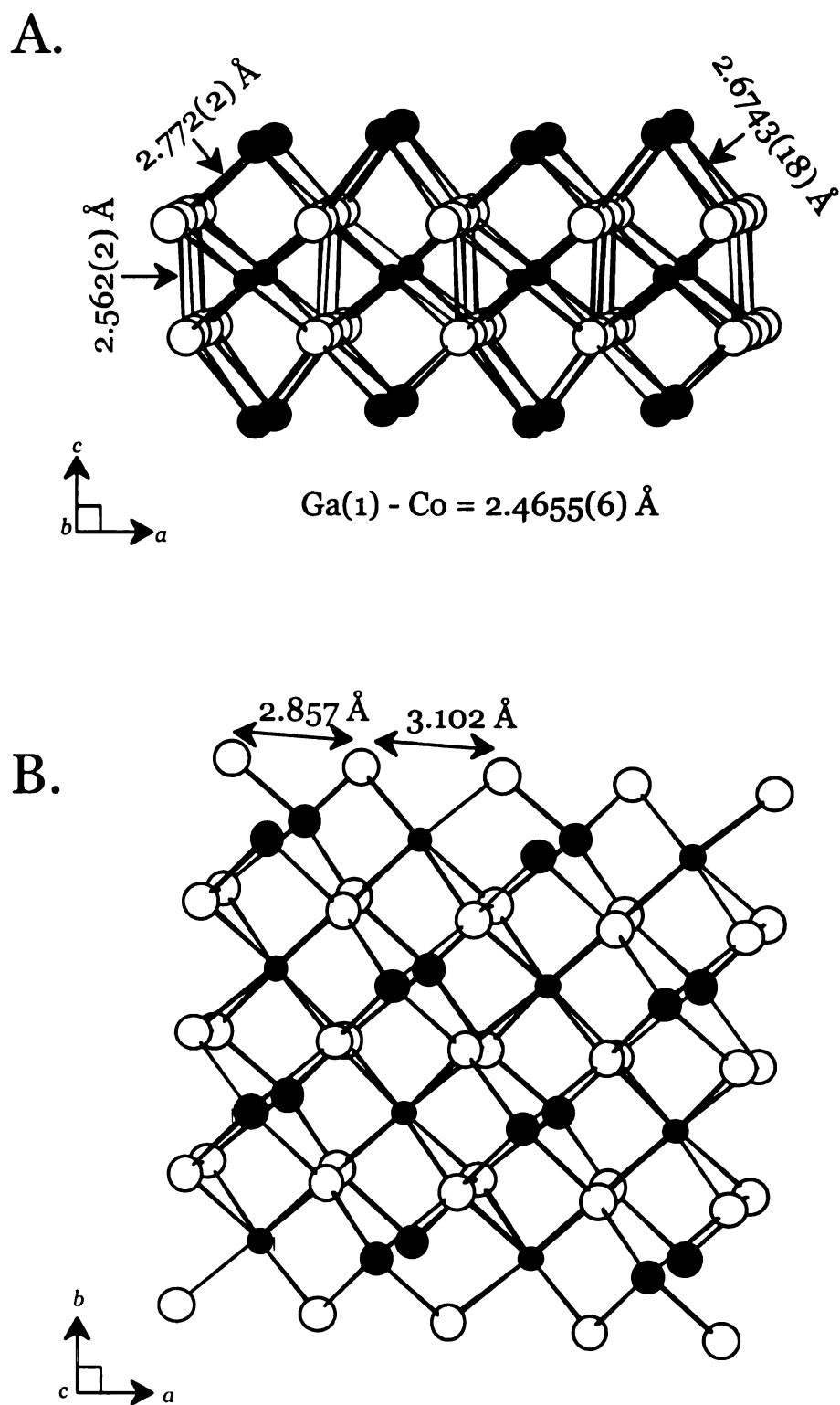


Figure VII.3. The $[\text{CoGa}_4\text{Ge}_2]$ substructural unit. (A) view along the b -axis; (B) view approximately down the c -axis.

The last structural fragment found in **1** is a Ce monoatomic plane (C), see Figure VII.4. In it, Ce atoms form a square pattern with intraatomic distances of 4.213 Å. This Ce-Ce interaction is quite typical and have been observed in a number of Ce-containing intermetallic compounds^{25,8,29,30}. The next closest Ce-Ce interaction occurs at 5.9582(5) Å (unit cell parameter a).

Using these three structural motifs, namely cubic [CoGa₄Ge₂] layer (A), Ga-only slab (B) and Ce monoatomic plane (C), the structure of **1** could be constructed via their consequent stacking along the (long) c -axis in the sequence: *ACBC ACBC* ... etc.

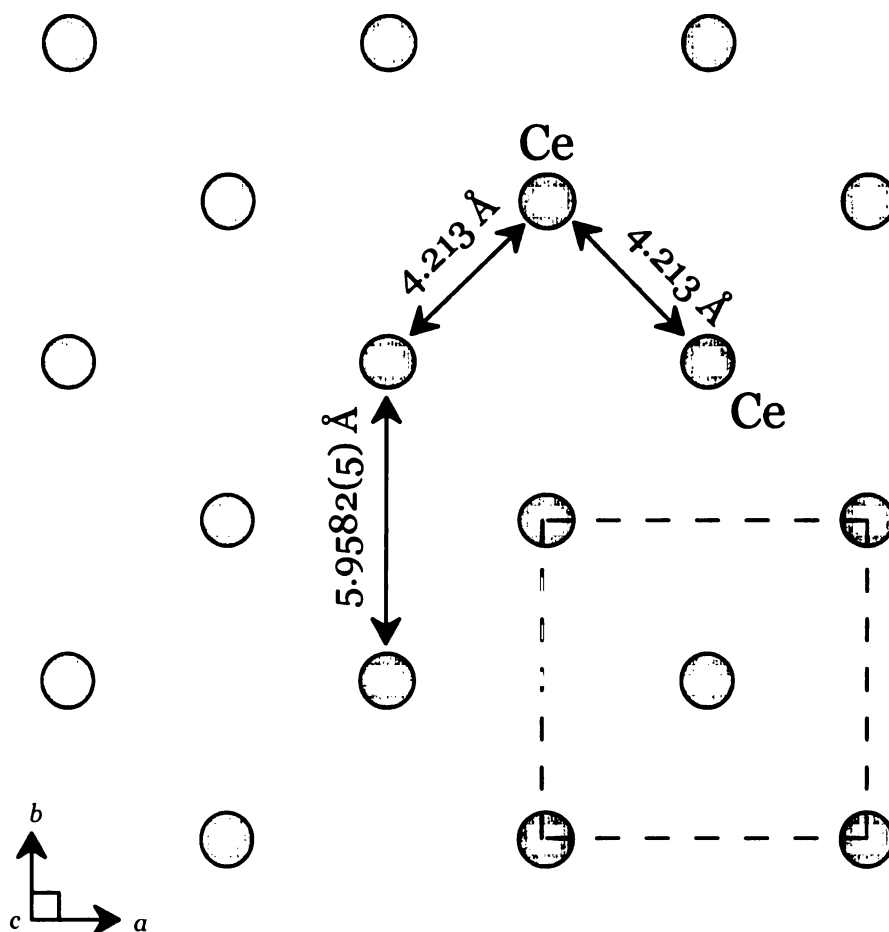


Figure VII.4. The Ce-only square net viewed along the c -axis. The dashed line outlines the unit cell.

The local coordination of all atoms is shown in Figure VII.5. The immediate coordination sphere of Ce atom is limited to 3.5 Å, whereas for the Co, Ga and Ge atoms it is 3.0 Å. The Ga(1) atoms are seven-coordinate; their environment includes six atoms {Ga(1)₃Ge(2)Co₂} in the form of a hexagon in chair conformation and an additional Ge(1) atom in the apex position. The distance from the central Ga(1) atom to the Ga(1) atoms of the hexagon are 2.562(2) Å and 2.8566(17) Å. The Ge(2) and Co atoms are bonded to the central Ga(1) at 2.772(2) Å and 2.4655(6) Å, respectively. The Ga(2) is bonded to three Ga(2) atoms at 2.508(2) Å and 2.5482(18) Å and one Ga(3) at 2.6075(16) Å in the shape of severely distorted tetrahedron. The departure from the tetrahedral angles is reflected in the Ga(2)-Ga(2)-Ga(2) and Ga(2)-Ga(2)-Ga(3) angles of 90° - 99.89(4)° and 130.83(2)° - 98.31(9)°, respectively. The Ga(3) atoms are located in the center of the square pyramid with the base of four Ga(2) atoms and an apex of an Ge(1) atom (Ga(3)-Ge(1) = 2.490(3) Å). The Ge(1)-Ga(3)-Ga(2) angle is 112.37(6)°.

Analogously, the Ge(1) atom has a square pyramidal environment that consists of four Ga(1) atoms (Ge(1)-Ga(1) = 2.67443(18) Å) and Ga(3) atom in the apex position. The Ga(3)-Ge(1)-Ga(1) angle is 124.91(5)°. The Ge(2) atoms are four-coordinate, they are bonded equidistantly to four Ga(1) atoms with a Ge(2)-Ga(1)-Ga(1) bond angle of 58.98(2). The Co atoms are in the center of the distorted cube of eight Ga(1) atoms; the Co-Ga(1) bond is 2.4655(6) Å, and the Ga(1)-Co-Ga(1) bond angles are 62.61(4)° 70.81(5)°, 77.95(5)°, 105.59(2)°, 117.55(4) and 175.97(6)°.

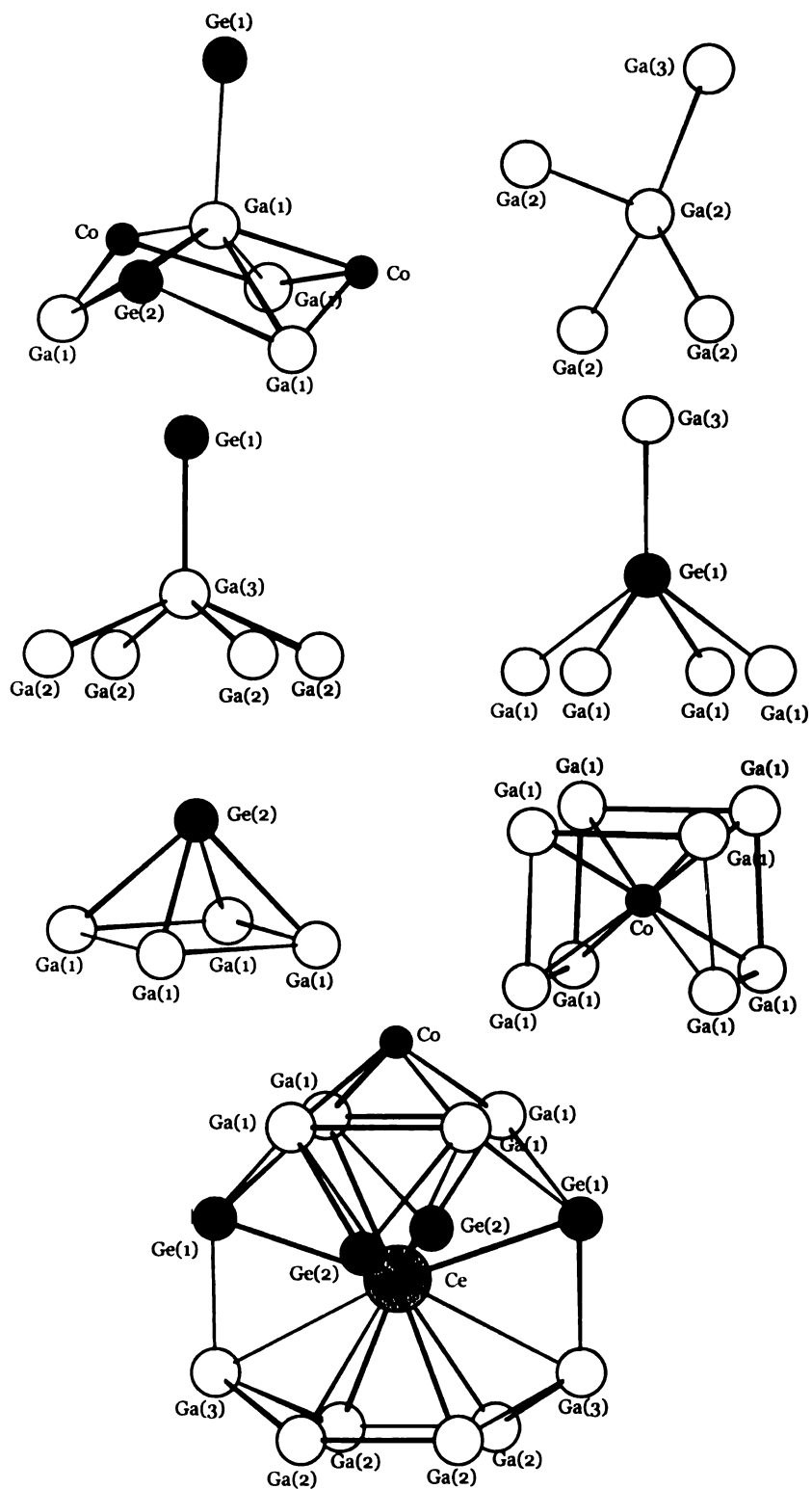


Figure VII.5. The local coordination environments of Ga, Ge and Co atoms (shown within the sphere of radius 3.0 Å) and Ce atoms (within 3.5 Å).

The 14-atom coordination polyhedron of the Ce atoms include ten Ga atoms (Ce-Ga(1) = 3.2843(11) Å; Ce-Ga(2) = 3.2789(11) Å; Ce-Ga(3) = 3.3362(12) Å) and four Ge atoms (Ce-Ge(1) = 3.1387(8) Å; Ce-Ge(2) = 3.0430(6) Å). The next closest bond occurs to the Co atom at 3.796 Å. For a more complete list of bond distances and bond angles see Tables VII.3 and VII.4.

Crystal Chemistry and Chemical Bonding in 1

Although $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ is a Ga-rich compound, the Ga atoms do not form a network on their own. A Ga-only sub-structural unit bears zero- and two-dimensional character. As could be seen from Figure VII.6.A, the Ga(1) atoms form dimers, while Ga(2) and Ga(3) are assembled into 2D layers with pentagonal channels (discussed above). The dimers and the layers with pentagonal channels are not connected to each other as the separation between these two fragments is over 5 Å. The average Ga-Ga bond distance (for all interactions up to 3.0 Å) is 2.641 Å, which is comparable to the sum of single-bonded metallic radii³¹ (2.50 Å) and is quite shorter than the average Ga-Ga distance of 2.70 Å found in metallic Ga³². The bonding within the Ga framework is thus reasonably strong. Similar Ga-Ga bonding interactions were observed in the $\text{Ce}_3\text{Ga}_9\text{Ge}$ polygallide with an average distance of 2.64 Å. The connection between 1D and 2D fragments within the Ga-only network occurs via bridging Ge(1) atoms that link Ga(1) to Ge(1) at 2.6743(18) Å and Ge(1) to Ga(3) at 2.490(3) Å. The latter bonding Ge(1)-Ga(3) contact is the shortest one in the structure, and in view of the sum of

covalent radii of Ga and Ge (2.47 Å) reflects considerable covalent character. The average Ga-Ge bond distance found in **1** is 2.694 Å.

The Ce-Ga connectivity interactions cover the range from 3.2789(11) Å to 3.3362(12) Å with an average Ce-Ga bond distance of 3.293 Å. Allowing for the sum of single-bonded metallic radii³¹ of Ce (1.818 Å for CN = 12) and Ga (1.25 Å), these interactions could be regarded moderately to weakly bonding. The Ce-Ga bond distances found in **1** fall in the same range as those found in other Ce-containing gallides such as Ce₃Ga₉Ge⁸ (3.1139(16) Å - 3.4342(9) Å) and CeRu₂Ga₈³³ (3.135 Å - 3.387 Å). The Ce-Ge distances are substantially shorter than the corresponding Ce-Ga bonds with an average Ce-Ge connectivity of 3.091 Å, in accord with the original Ga/Ge assignment. Judging by the sum of single-bonded metallic radii for Ce and Ge (3.04 Å), the Ce-Ge interactions in **1** are bonding, with a sensible covalent contribution to the bonding character. Oppositely, the Ce-Ce interactions could be thought of as only weakly bonding to non-bonding, taking into account the sum of single-bonded radii for Ce (3.64 Å). In the Ce-only monoatomic plane the closest Ce-Ce contacts occur at 4.121 Å; the next nearest Ce neighbor is at 5.96 Å.

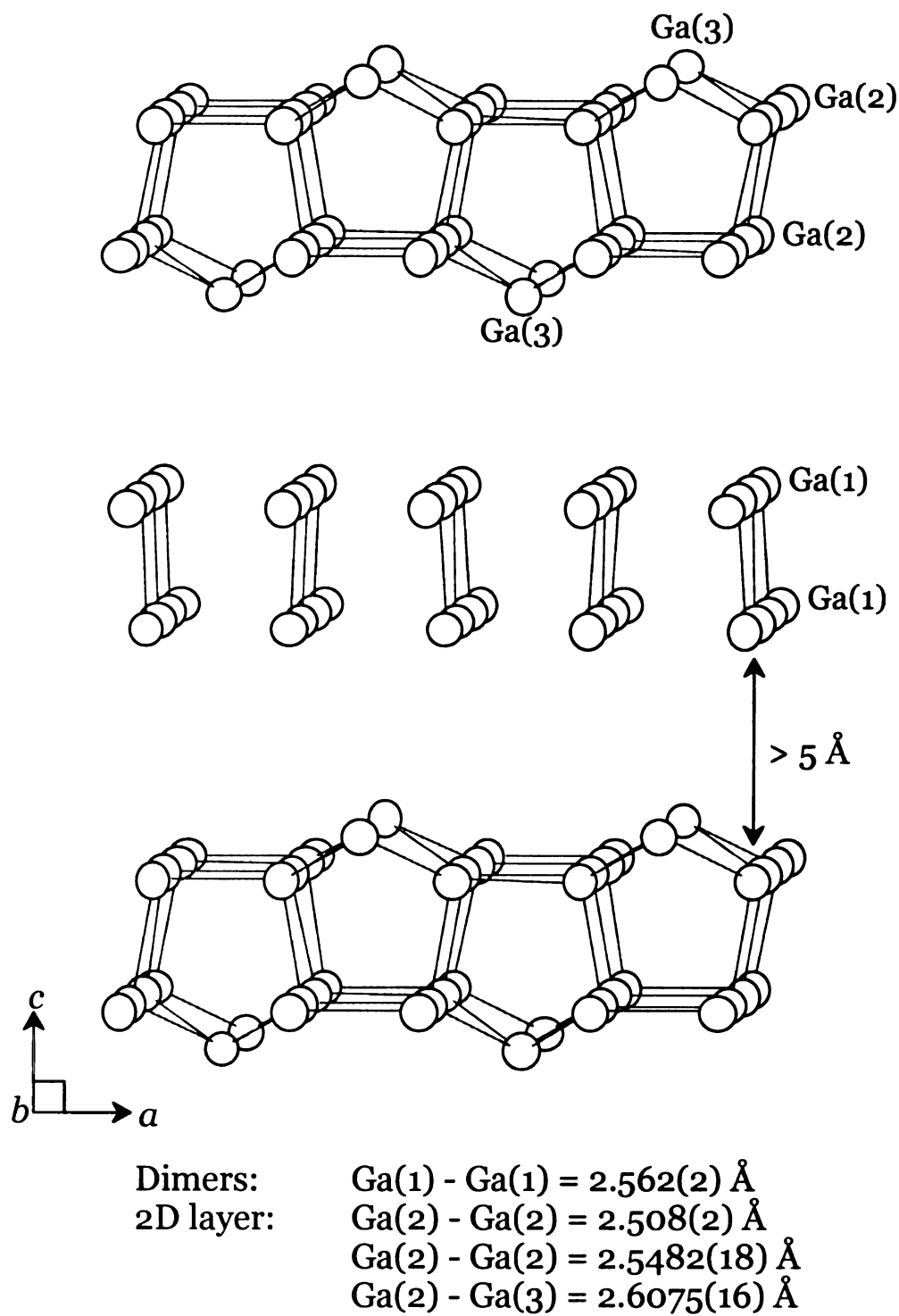


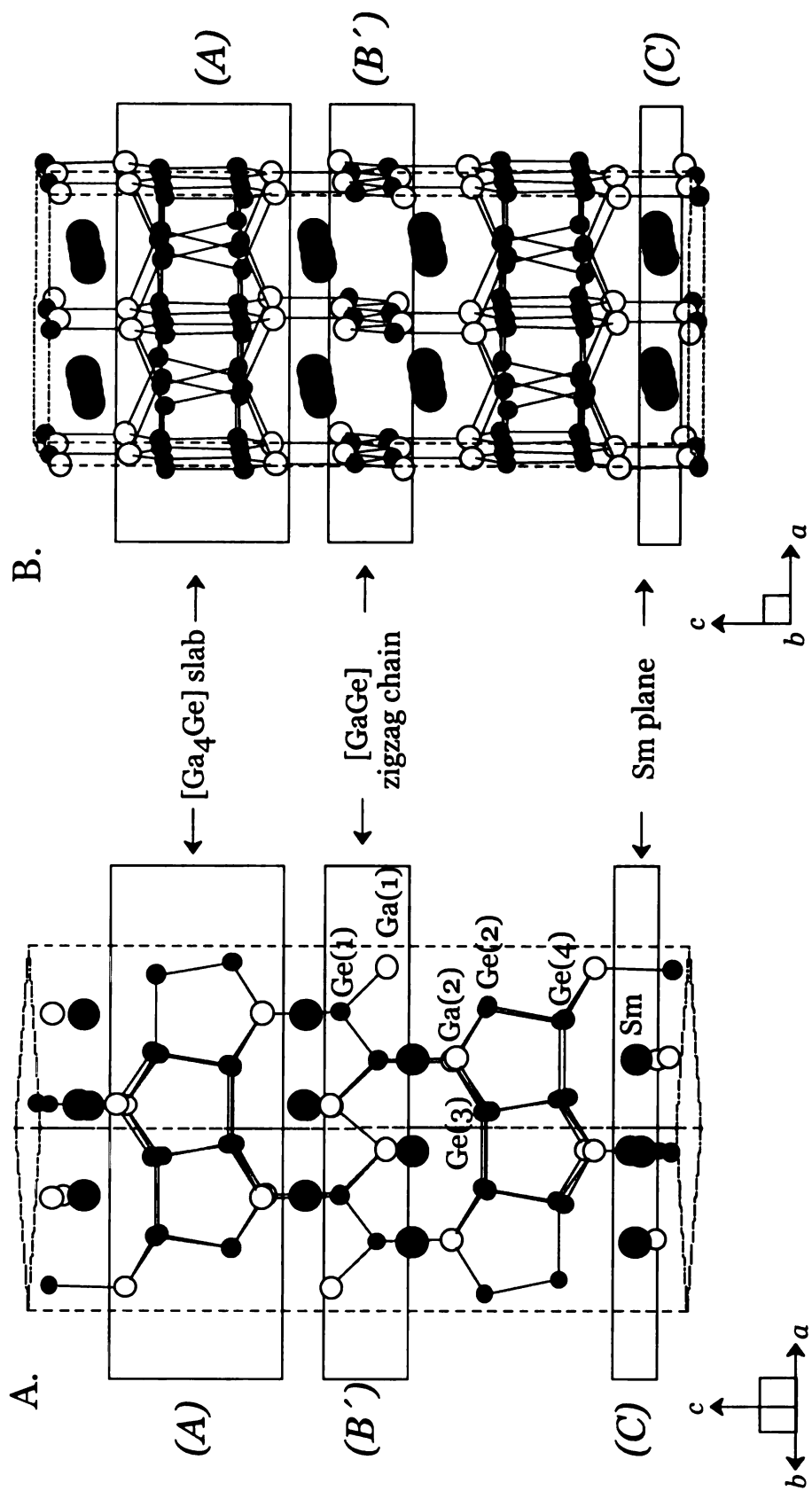
Figure VII.6. Ga-only substructural unit featuring $[\text{Ga}(1)]_2$ dimers and $[\text{Ga}(2)_4\text{Ga}(3)]$ slab with pentagonal channels.

Crystal Structure of 2

The structure of $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ (**2**) is very similar to that of **1**, as the building blocks comprising this structure are reminiscent of those found in **1**. In order to easier recognize the similarities between **1** and **2**, the projection of **2** onto (110) plane is given in Figure VII.7.A; the view along the *b*-axis is shown in Figure VII.7.B. One of the ways to represent the structure of **2** is to view it as a combination of two interpenetrating sublattices: a $[\text{Ga}_2\text{Ge}_5]$ framework and a Sm substructure. In Figure VII.7, no bonds were drawn to the Sm atoms to outline the $[\text{Ga}_2\text{Ge}_5]$ 3D network. The 3D $[\text{Ga}_2\text{Ge}_5]$ network in **2** features large straight tunnels that infinitely extend in the direction of *b*-axis. Each of the tunnels is occupied with a pair of Sm atoms, see Figure VII.7.B.

Another way to view the structure of **2** is to break it down into three major building blocks. The first two, namely the $[\text{Ga}_4\text{Ge}]$ slab with pentagonal channels (*A*) and the RE square plane (*B*) are similar to those found in **1**. Note that the layers (*A*) and (*B*) are denoted in the same way as for **1**, for consistency. The third building block does not have a counterpart in **1** and represents a $[\text{GaGe}]$ zigzag chain (*C'*). These three types of layers alternate along the *c*-axis in the following manner: *ACB'C ACB'C*, thus constructing the whole structure.

Figure VII.7. The structure of $\text{Sm}_2\text{Ga}_2\text{Ge}_5$ (**2**). (A) view along the $[110]$ diagonal; (B) projection of **2** onto ac -plane. Grey circles represent Sm atoms, open circles are Ga atoms and black filled circles are Ge atoms. The unit cell is shown with dashed lines, the $[\text{Ge}_4\text{Ge}]$, $[\text{GaGe}]$ and Sm structural fragments are contoured with solid lines and denoted with letters (A), (B) and (C), respectively.

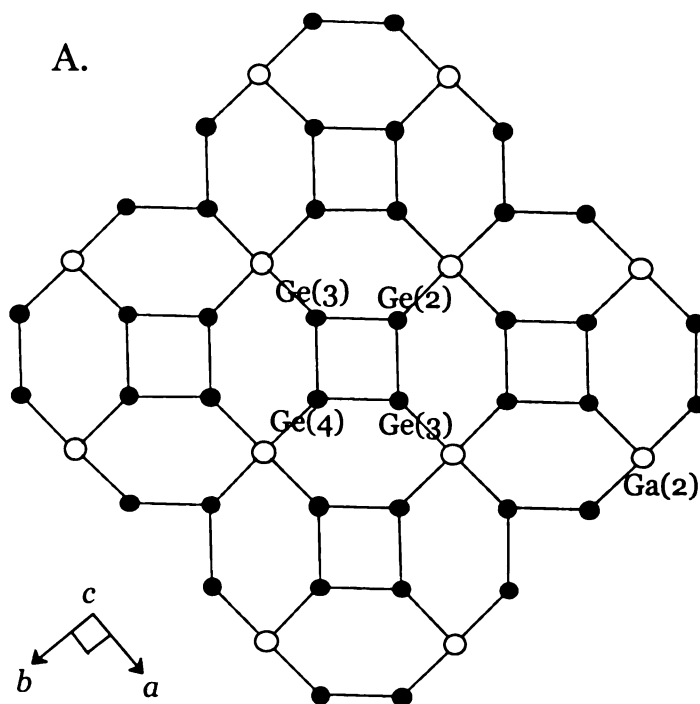


A portion of the $[\text{Ge}_4\text{Ga}]$ 2D layer (A) with pentagonal channels is outlined in Figure VII.7.A. The axis of the channels coincides with the $[110]$ direction; the plane of the $[\text{Ge}_4\text{Ga}]$ layer extends infinitely in the ab -plane. As it is in case of **1**, the $[\text{Ge}_4\text{Ga}]$ slab can be sub-divided into two corrugated planes, one of which, viewed along the c -axis, is depicted in Figure VII.8.A. In this plane, the Ge atoms (Ge(2), Ge(3), Ge(4)) form a slightly distorted square net (Ge-Ge distances vary from 2.529(3) Å to 2.538(3) Å). The larger hollows of the square net (Ge-Ge > 3 Å) are capped with Ga(2) atoms at 2.563(3) Å and 2.568(3) Å and 2.6075(17) Å.

The fragment containing a $[\text{GaGe}]$ zigzag chain (B) is shown in Figure VII.8.B. The bc crystallographic plane contains the plane of the chain, and the direction of chain propagation coincides with the b -axis. The Ge(1)-Ge(1), Ga(1)-Ga(1) and Ga(1)-Ge(1) distances within the chain are 2.463(11) Å, 2.629(10) Å and 2.528(9) Å, respectively. The Ge(1)-Ga(1)-Ga(1) and Ge(1)-Ge(1)-Ga(1) angles are respectively 101.89(12)° and 114.92(14)°. The $[\text{GaGe}]$ units are one-dimensional, as the neighboring chains are separated by the considerable distance of 4.235 Å. A similar chain, although consisting of Tt atoms only (Tt = Si, Ge) was observed for Tb_4FeGe_8 ²⁰, LaNiGe_2 ³⁴, RENiSi_3 ¹, $\text{RE}_4\text{Ni}_3\text{Ga}_7\text{Ge}_3$ ⁵ and many other intermetallides. The distinct feature of the zigzag chain in **2**, which differentiates it from the Tt chains mentioned above, is a quite large bond length variation within the chain (2.463(11) Å – 2.629(10) Å). Because Ge has a slightly smaller covalent radius than Ga, it appears that the chain might consist of two kinds of atoms: Ga and Ge. If so, the shorter bond lengths could be assigned to Ge-Ge contacts, longer ones to Ga-Ga, and medium ones to the Ga-Ge contacts. Thus, in assigning the

Ga/Ge distribution we were guided by the principle of shorter Ge-Ge vs Ga-Ga bond distance in the chain. Yet, there is a chance that the zigzag chain contains Ge atoms only, since the Sm-Ga(1) bond distance in **2** emerges as a typical Sm-Ge connectivity. However, from the standpoint of convergence factors the current Ga/Ge assignment is slightly more favorable than that with a pure Ge chain. Further investigation of the Ga/Ge distribution ought to be performed with the methods capable of distinguishing these atoms in a crystalline sample.

The last structural motif found in **2** is a Sm monoatomic plane (C). In this plane, the Sm atoms are arranged with an orthorhombic symmetry with the bond distances of 4.096 Å and 4.226 Å, see Figure VII.9.A. The monoatomic planes are stacked along the *c*-axis and linked to each other at the distances of 4.025 Å and 4.030 Å to form a sheet of condensed trigonal prisms, see Figure VII.9.B. A similar RE arrangement has been observed in the Tb-only framework of Tb₄FeGe₈, as described in Chapter II.B. The prism layers in **2** are separated from each other (along the *c*-axis) by a large distances of ~ 7 Å. Each Sm prism is additionally centered with Ga (Ge) atoms, so that the [GaGe] zigzag chain is woven through the inside of the Sm prism layer, see Figure VII.10.A and B. At the same time, the sufficiently large gap between the prism sheets hosts the [Ga₄Ge] slab, see Figure VII.10.C.



$$2.529(3) \text{ \AA} < \text{Ge} - \text{Ge} < 2.538(3) \text{ \AA}$$

$$2.563(3) \text{ \AA} < \text{Ga} - \text{Ge} < 2.6075(17) \text{ \AA}$$

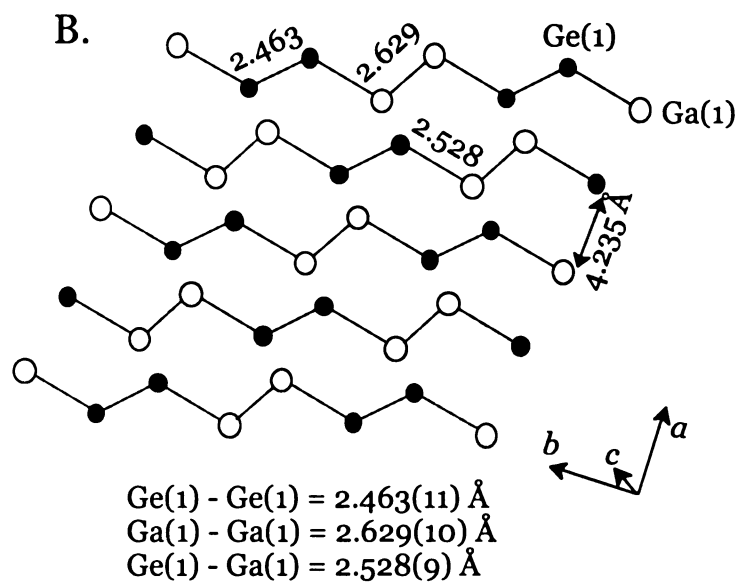
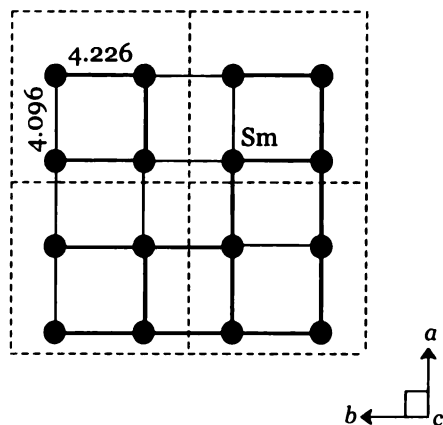


Figure VII.8. The structural motifs of **2**. (A) a single sheet of $[\text{Ge}_4\text{Ga}]$ slab projected onto the ab -plane; (B) $[\text{GaGe}]$ zigzag chains. The bond distances are given in \AA.

A.



B.

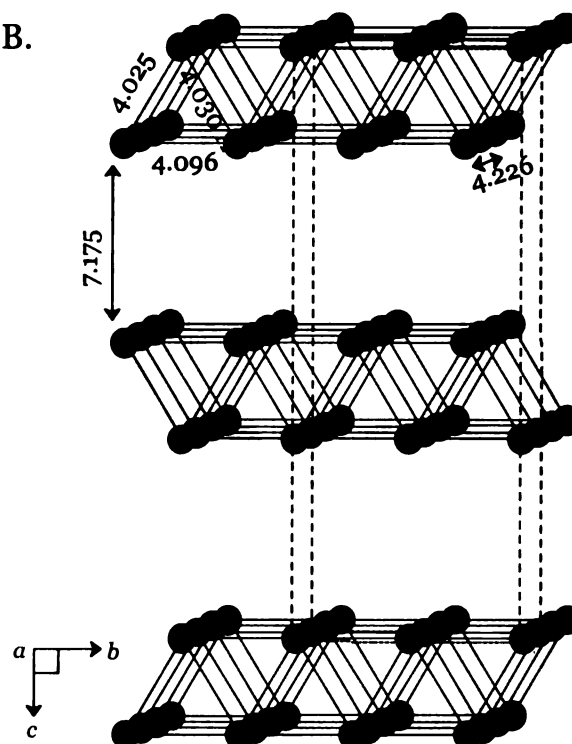


Figure VII.9. The Sm sublattice of **2**. The unit cell is indicated with dashed lines, the Sm-Sm bond distances are given in Å. (A) The Sm square lattice viewed along the *c*-axis; (B) Stacking of the Sm square planes along the *c*-axis produces sheets of Sm trigonal prisms separated by the distance > 7 Å.

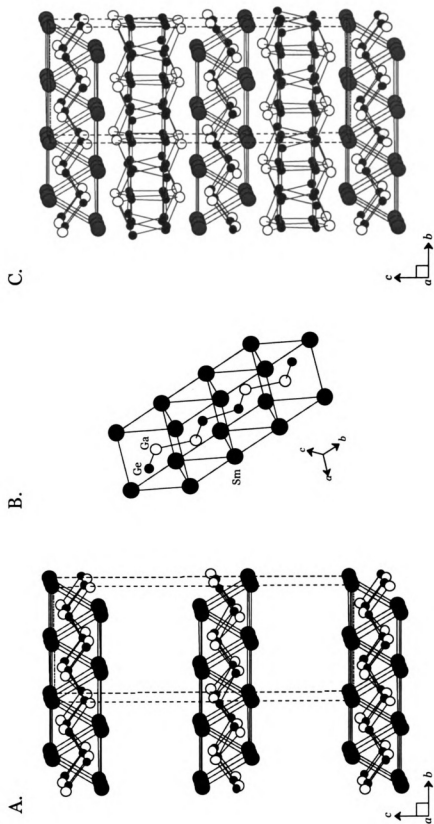


Figure VII.10. The structure evolution of **2**. (A) The Sm prism layers filled with [GaGe] chains; (B) A [Sm₂GaGe] fragment depicting six Sm prisms centered with Ga and Ge; (C) The gap between the Sm prism layers accommodating the [Ge₄Ga] slabs.

The local coordination of the Sm, Ga and Ge atoms with a cutoff radius of 3.5 Å for Sm and 3.0 Å for Ga and Ge is presented in Figure VII.11. The Ga(1) atoms (zigzag chain) occupy a very low-coordination site. They are bonded to Ge(1) at 2.463(11) Å and self-bonded at 2.629(10) Å. All three atoms lie in *bc*-plane with a Ga(1)-Ga(1)-Ge(1) angle of 101.89(12)°. The five-coordinate Ga(2) atoms are positioned in the center of a square pyramid consisting of five Ge atoms (Ge(1) – Ge(4)). The bonding of the central Ga(2) atom and the base of the pyramid occurs at 2.563(3) Å (Ga(2)-Ge(2)), 2.568(3) Å (Ga(2)-Ge(4)) and 2.6075(17) Å (Ga(2)-Ge(3)). The Ge(1) in the apex position is bonded to Ga(2) at 2.476(3) Å. The Ge(1) atoms have trigonal planar environment of Ga(1), Ga(2) and Ge(1) atoms. The Ge(1)-Ge(1)-Ga(1), Ge(1)-Ge(1)-Ga(2) and Ga(2)-Ge(1)-Ga(1) angles are slightly distorted from the ideal trigonal and equal 114.92(14)°, 117.7(3)° and 127.4(3)°, respectively. The bonding interactions of Ge(1) with the atoms in the triangle are quite strong: the Ge(1)-Ge(1) bond is 2.463(3) Å, the Ge(1)-Ga(1) and Ge(1)-Ga(2) bond distances are 2.528(9) Å and 2.476(3) Å, respectively. The Ge(2), Ge(3) and Ge(4) atoms have four atoms in their immediate coordination environments. Those include three Ge and one Ga(2) atom. The central Ge atom is located in the center of a grossly compressed tetrahedron, the corresponding tetrahedral angles vary from 92.86° to 128.99(7)° for the central Ge(2) atom; from 87.34(7)° to 131.93(13)° for central Ge(3) and from 92.46(14)° to 129.43(7)° for the central Ge(3) atom. The Sm atoms are 12-coordinate; they are bonded to six Ga and Ge atoms that form a {Ge₂Ge(3)₂Ge(4)Ga(2)₂} hexagon in a boat conformation. Six additional atoms (3 × Ga(1) and 3 × Ge(1)) are located on the opposite side from the hexagon. For more complete information on bond distances and angles refer to Tables VII.7 – VII.9.

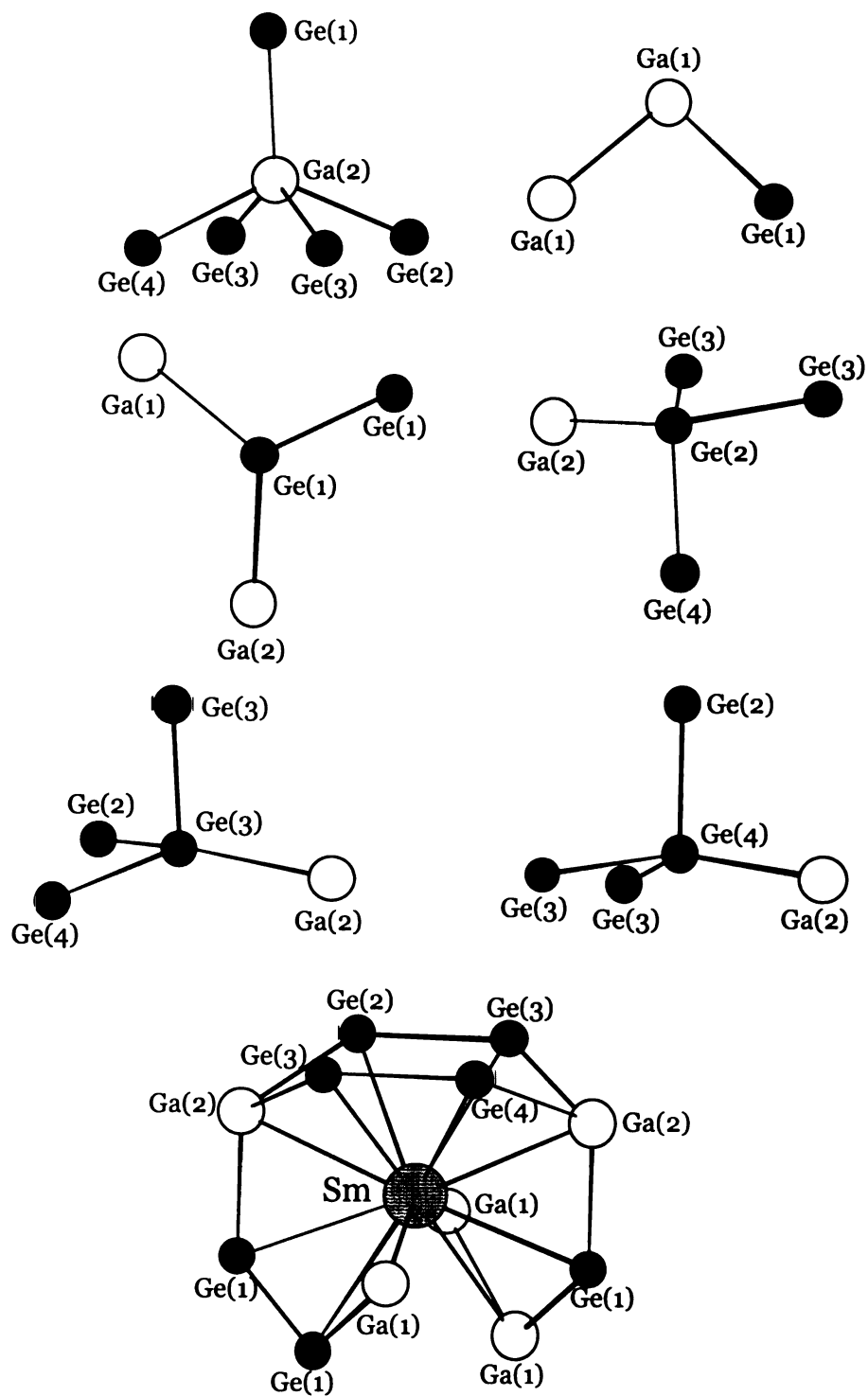


Figure VII.11. The local coordination environments of Ga and Ge atoms (shown within the sphere of radius 3.0 Å) and Sm atoms (within 3.5 Å).

Crystal Structure of **3**

The structure of $\text{La}_3\text{Ga}_2\text{Ge}$ (**3**) projected onto the *bc*- and *ab*-plane is presented in Figures VII.12.A and VII.12.B, respectively. The atoms are depicted in the same way as for **2**. The structure of **3** closely resembles the structure of **2**, although it is far less complex than the latter. Following the same analogy, the structure of **3** could be easily represented using a single building block found in **2**, namely the 2D sheets of La trigonal prisms filled with [GaGe] zigzag chains. Such prism layers alternate along the *b*-axis and are connected to each other via La-La interactions at 3.863 Å and 4.01 Å. Alternatively, the structure of **3** could be broken down to two structural motifs: a [Ga₂Ge] zigzag chain (*B'*) and La monoatomic square plane (*C*). For consistency, the layers were denoted in the same manner as it was done for **1** and **2**. The stacking order of these layers in **2** is *CB'C* *CB'C*, and the direction of stacking coincides with the *b*-axis. Interestingly, using such representation, the structure of **3** could be easily related to the well-known AlB_2 structure type³⁵. In the AlB_2 , the *C* and *B'*-type layers alternate along the [120] direction of the hexagonal cell in the *CB'CB'...* manner.

Figure VII.13 gives the structure of **3** in comparison with the structural fragment of **2** containing only the [GaGe] stuffed Sm prism layer. In Figure VII.12.A no bonds were drawn between the sheets to emphasize the structural similarities between **3** and **2**. It could be easily seen that the layer separation of over 7 Å which existed in **2** has been reduced to ~ 2.5 Å (in projection) in the structure of **3**. While in **2** an additional [Ga₄Ge] slab could be accommodated between the prism layers, in **3** an intralayer separation is small, and therefore the space between the layers is vacant.

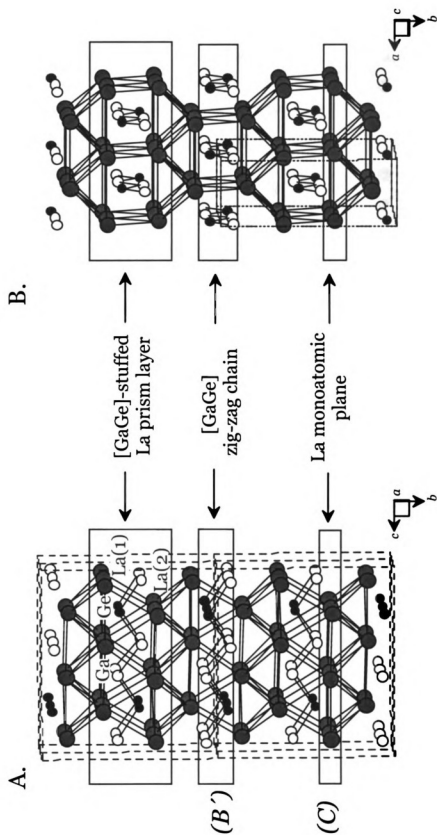


Figure VII.12. The structure of $\text{La}_3\text{Ga}_5\text{Ge}$ (3) viewed (A) along the a -axis; (B) along the c -axis. The dashed line defines the unit cell, the bold lines depict major structural fragments. For clarity, no bonds were drawn between La and $[\text{Ga}_2\text{Ge}]$ sublayers.

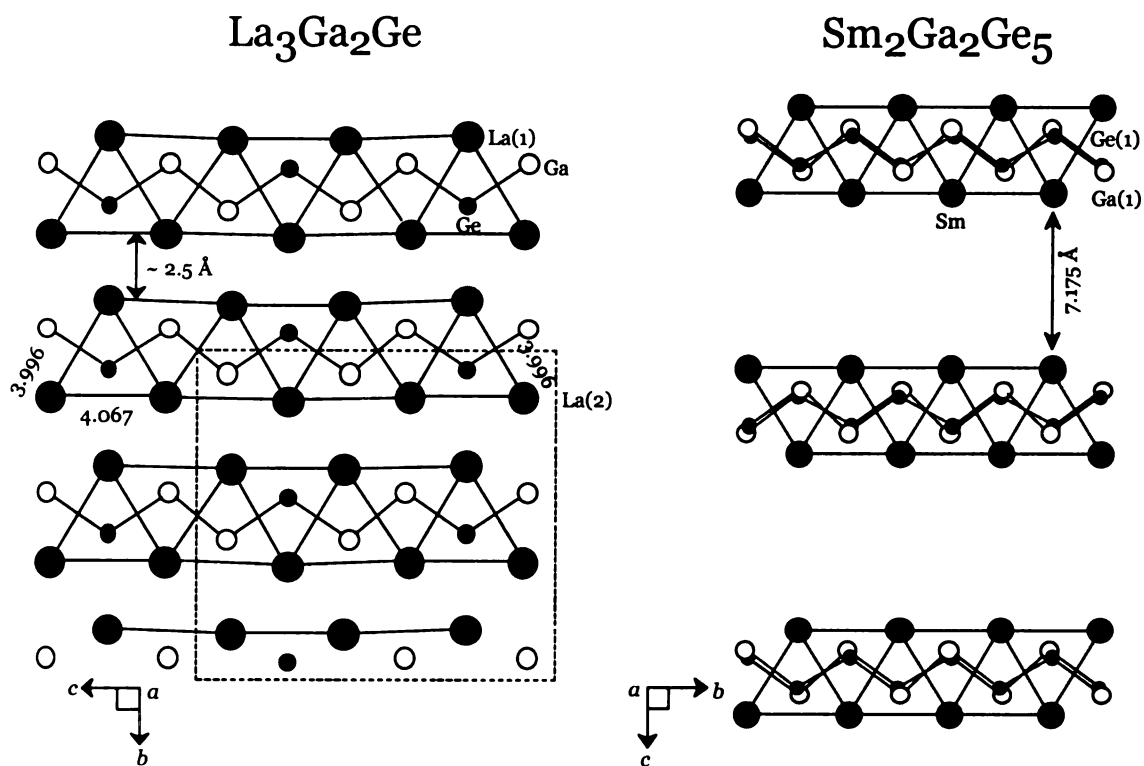


Figure VII.13. A comparative depiction of the La₃Ga₂Ge (3) and Sm₂Ga₂Ge₅ (2) structures. For 2, only the Sm₂[GaGe] fragment consisting of Sm prism layer filled with [GaGe] chains is shown. For 3, no La-La bonds between the prism layers were drawn, for clarity. The distances are given in Å, the intralayer separation indicated with arrows is given in projection.

The fragment of the [GaGe] zigzag chain is shown in Figure VII.14.A. The chain lies in the *bc*-plane and propagates along the *c*-axis. Again, the chains are well-separated from each other with the intrachain distance of ~ 4.5 Å. The [Ga₂Ge] sub-structural unit is thus one dimensional. The bond lengths in this chain are 2.606(2) Å and 2.6182(14) Å, which are quite typical for Ga-Ga interactions. However, in view of the fact that EDS elemental analysis indicated presence of Ge, one of the positions (with lowest multiplicity) was assigned to Ge. Still, these Ga-Ga and Ga-Ge bond distances are certainly realistic. The examples of similar Ga-Ge bonding interactions can be found in the compounds REMGa₃Ge, where the accurate Ga/Ge assignment was done on the basis of single crystal neutron diffraction.

The La atoms in **3** form monoatomic sheets parallel to the *ac*-plane, see Figure VII.14.B. The sheets are assembled into thick 2D layers of trigonal prisms. The neighboring sheets are connected to each other via La-La interactions. Thus, the La sublattice in **3** is three-dimensional, which effectively reflects the La-rich composition of this compound. It is useful to compare and contrast the RE-only sublattices found in the structure of **1**, **2** and **3** to survey the gradual change in their dimensionality as the RE : (M + Ga + Ge) ratio increases. That is, in the case of **1**, the ratio is 2 : 12 and the RE sublattice represents a set of single sheets of RE atoms separated by a large distance of ~ 7.5 Å (*c*/2). In **2**, the ratio increases to 2 : 7; as a result, the RE monoatomic planes condense to form 2D thick prism layers. The separation between the layers in **2** is still non-bonding (> 7 Å). Finally, in **3**, the ratio is further increased to 1 : 1 (or 2 : 2), at which point the prism layers are joined together to give a 3D RE-only framework.

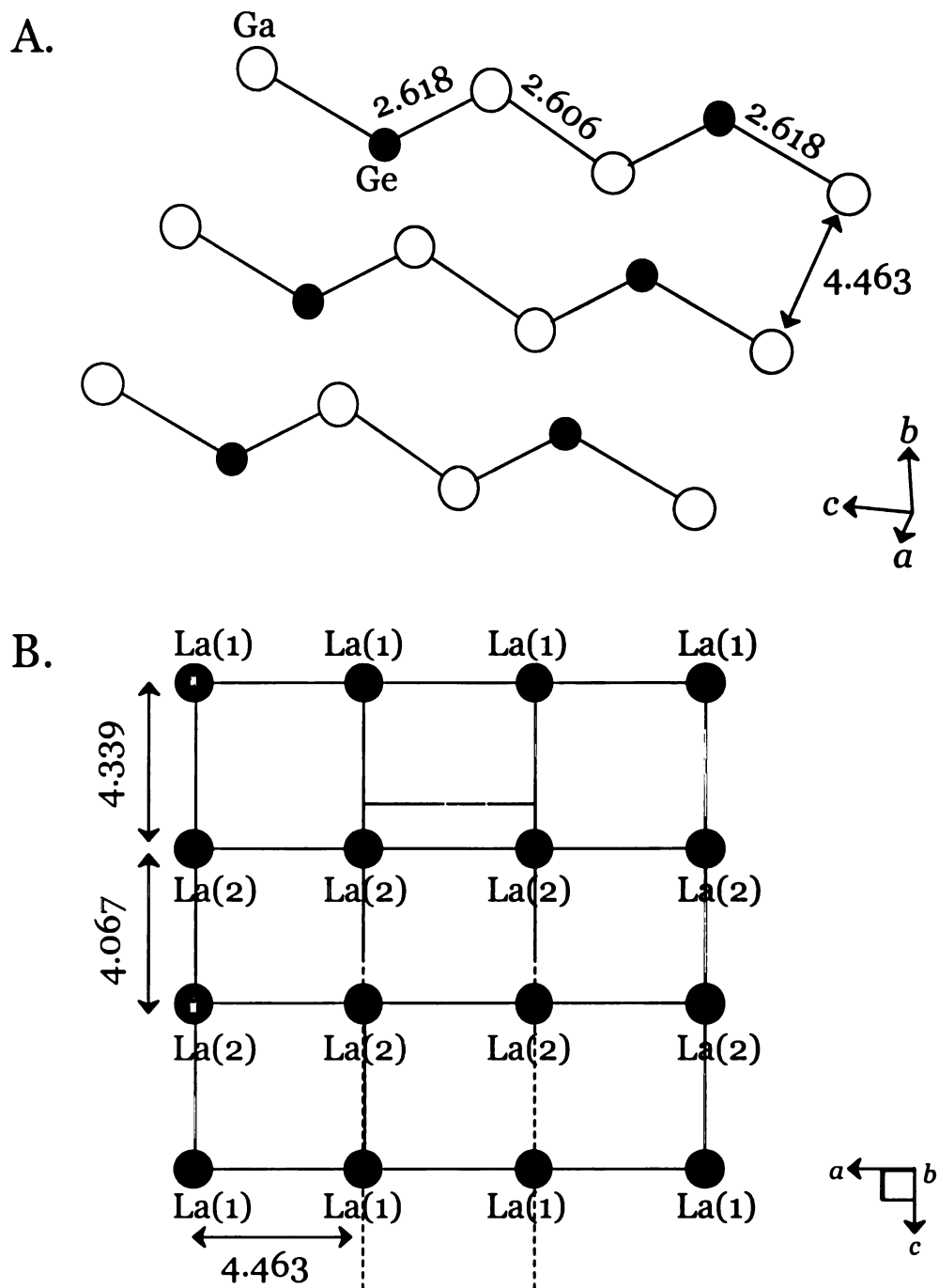


Figure VII.14. (A) The fragment of the $[\text{Ga}_2\text{Ge}]$ zigzag chain; (B) The La orthorhombic net. The distances are given in Å. The unit cell is shown with dashed lines.

The local coordination of the La, Ga and Ge atoms is shown in Figure VII.15. The Ga and Ge atoms are two-coordinate with planar geometry. The Ga-Ga and Ga-Ge bond distances are 2.606(2) Å and 2.6182(14) Å, respectively. The La(1) and La(2) atoms have similar coordination geometries consisting of four Ga and two Ge atoms of a zigzag chain, and one apex Ga (Ge) atoms from the neighboring chain. The central La(1) atom is bonded to four Ga atoms at 3.2626(8) Å and to a Ge atom at 3.4204(18) Å. The La(2) is bonded to two Ge atoms at 3.1831(7) Å and to five Ga atoms at 3.2159(8) Å, 3.3312(12) Å and 3.3849(16) Å.

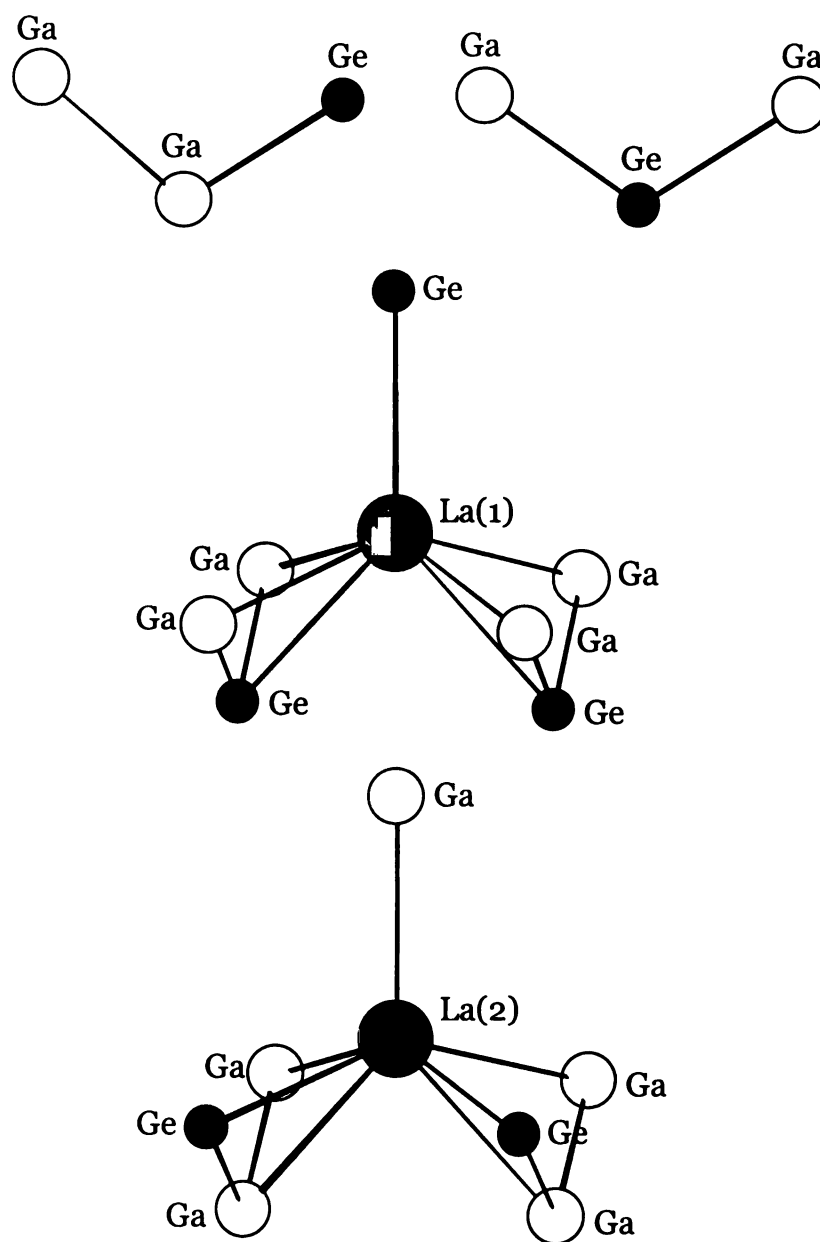


Figure VII.15. The local coordination spheres of Ga and Ge atoms (within 3.0 Å) and La atoms (within 3.5 Å).

Magnetic Properties

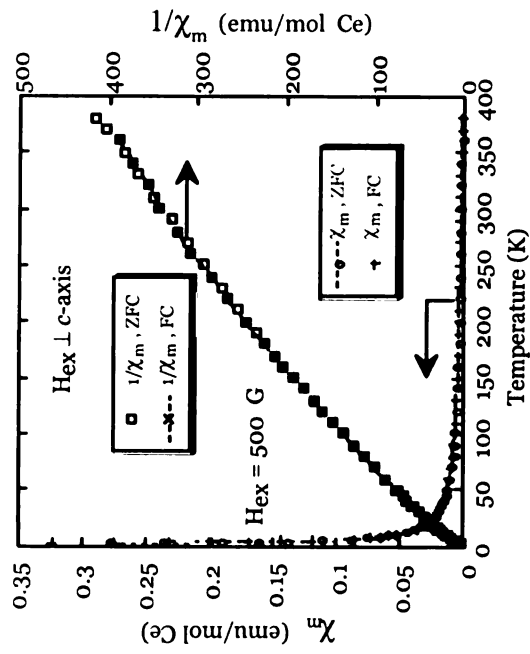
(a) Ce₂NiGa₉Ge₂ (1)

The magnetic susceptibility of Ce₂NiGa₉Ge₂ (1) was measured anisotropically by positioning the single crystal with the crystallographic *c*-axis parallel and perpendicular to the external magnetic field (H_{ex}). The plot of the molar magnetic susceptibility ($\chi_{\text{m}}^{\perp}$) and reciprocal molar magnetic susceptibility ($(\chi_{\text{m}}^{\perp})^{-1}$) of Ce₂NiGa₉Ge₂ versus temperature measured with H_{ex} perpendicular to the *c*-axis is presented in Figures VII.16 A–C. The $\chi_{\text{m}}^{\perp}$ is inversely proportional to *T* in the entire region of measured temperatures (2 – 400 K), see Figure VII.16.A. The expanded low-temperature region of $\chi_{\text{m}}^{\perp}$ vs *T* is also featureless, as evident from Figure VII.6.B. Consequently, no upturn or ZFC – FC (zero-field-cooled – field-cooled) history dependence is observed up to the lowest measured temperature of 2 K. The inverse molar susceptibility in the high temperature region (50 – 400 K) is linear and could be fitted within the Curie-Weiss law with the effective magnetic moment (μ_{eff}) of 2.80 BM and the Weiss constant (θ) of -33 K. The obtained μ_{eff} is in a good agreement with the theoretical value (2.56 BM) given by the formula $\mu_{\text{eff}} = g_J[J(J + 1)]^{1/2}$, where g_J is a Landé factor³⁶, and *J* is a total angular momentum of the Ce³⁺ ion³⁷.

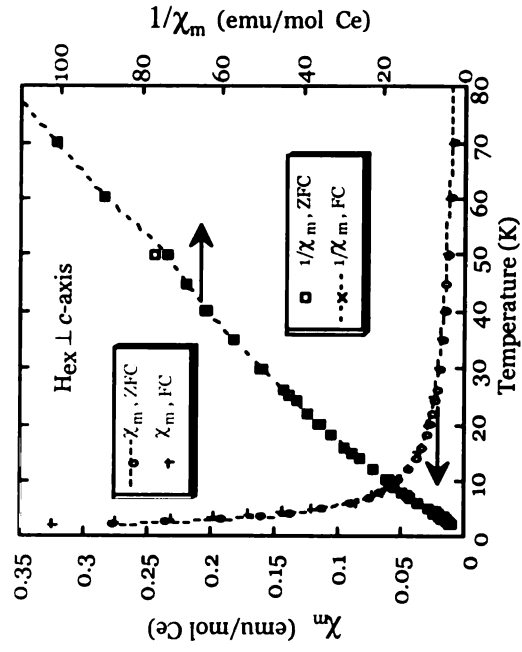
The field dependence of magnetization measured in the fields up to ± 5 Tesla and calculated in Bohr magnetons per mole of Ce is given in Figure VII.16.D. The onset of saturation of the magnetic moments is observed at 5 Tesla with the total moment of ~ 0.8 BM.

Figure VII.16. (A) Temperature dependence of molar magnetic susceptibility ($\chi_m^\perp$) and inverse susceptibility ($(\chi_m^\perp)^{-1}$) of a $\text{Ce}_2\text{NiGa}_9\text{Ge}_2$ single crystal oriented with c -axis perpendicular to the external magnetic field (H_{ex}); (B) Low temperature region of $\chi_m^\perp$ and $(\chi_m^\perp)^{-1}$; (C) Linear part of molar magnetic susceptibility; (D) The magnetization data for a single crystal of $\text{Ce}_2\text{NiGa}_9\text{Ge}_2$ oriented with c -axis perpendicular to H_{ex} in fields up to ± 5 Tesla.

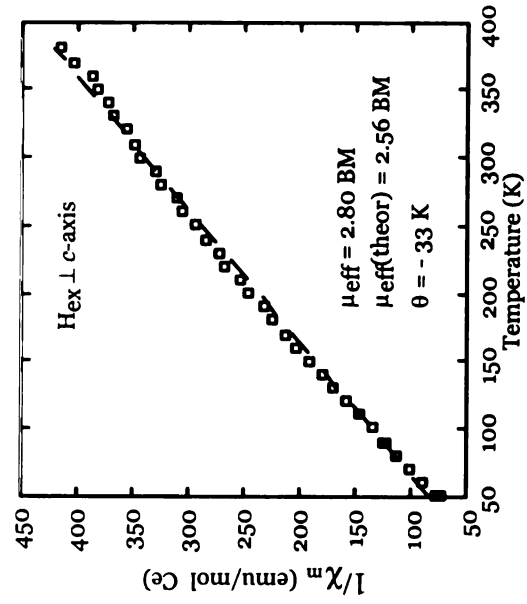
A.



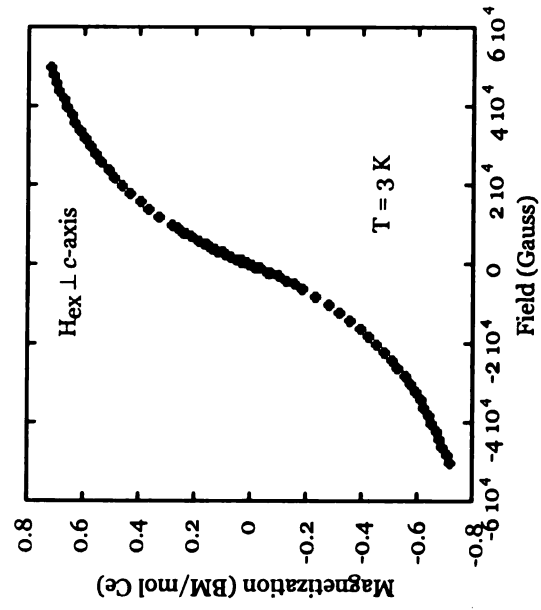
B.



C.



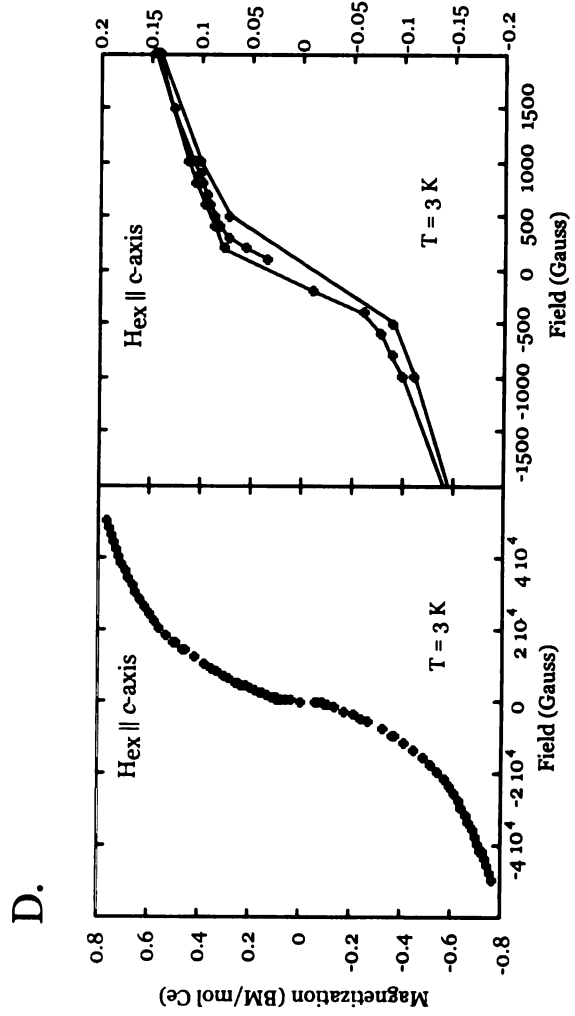
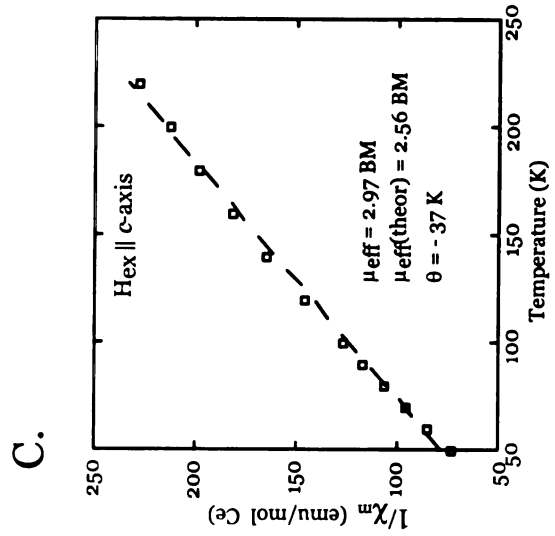
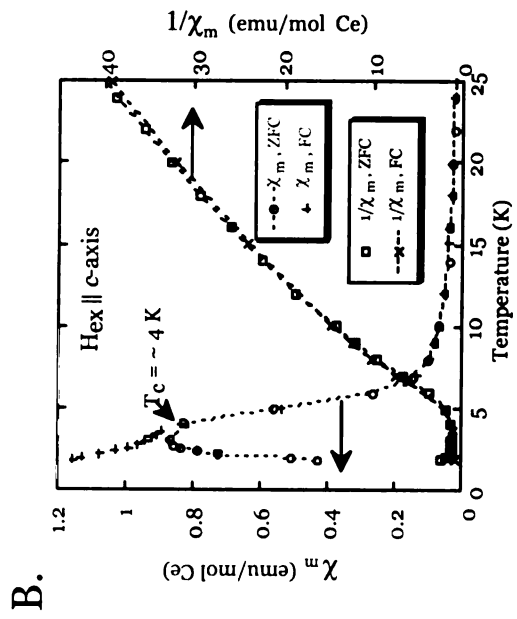
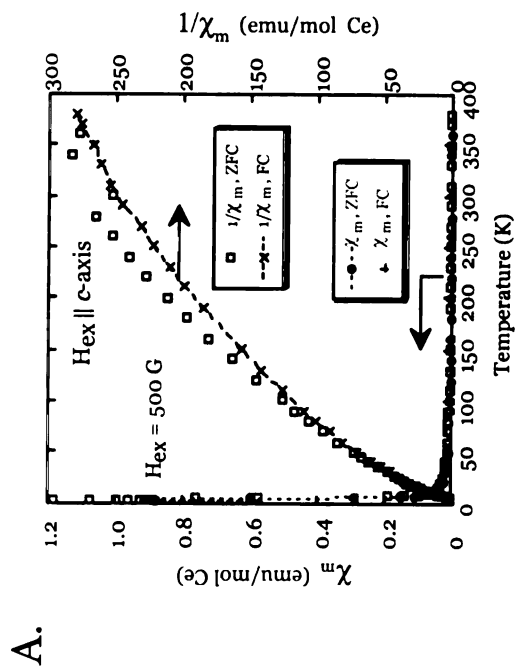
D.



The lower value of μ^{sat} compared to the theoretical value of (2.14 BM) that could be obtained using the formula $\mu^{\text{sat}} = g_J J$ is indicative of the lifting degeneracy of the $J = 5/2$ ground multiplet of the Ce^{3+} ion due to the crystal field^{38,39}. Similar experimental values of μ^{sat} (0.8 – 1.2) have been previously observed in a number of Ce-containing intermetallic compounds^{29a,40,41}.

In the perpendicular direction, when the external magnetic field is directed parallel to the c -axis, the magnetic response changes quite drastically. The temperature dependence of $\chi_m^{\parallel}$ and $(\chi_m^{\parallel})^{-1}$ is shown in Figures VII.17.A - C. First of all, in the parallel direction the magnetic response is nearly four times greater than that in perpendicular direction (1.2 emu/mol for $\chi_m^{\parallel}$ versus 0.33 emu/mol for $\chi_m^{\perp}$), see Figure VII.17.A. Additionally, at low temperatures, ferromagnetic ordering transition is observed, see Figure VII.17.B. Characteristic to the ferromagnetic system below critical temperature (T_c), under ~ 4 K the zero-field-cooled (ZFC) part of $\chi_m^{\parallel}$ rapidly decreases, whereas its field-cooled (FC) part continues to rise. The value of T_c for $\text{Ce}_2\text{NiGa}_9\text{Ge}_2$ is thus estimated to be 4 K. Above the critical temperature, the system behaves as a regular paramagnet, as evident from the linear part of $(\chi_m^{\parallel})^{-1}$, see Figure VII.17.A. However, an irreversibility in the ZFC – FC branches of $(\chi_m^{\parallel})^{-1}$ was detected. Nevertheless, the calculation of $\mu_{\text{eff}} = 2.97$ BM from the high-temperature data of $(\chi_m^{\parallel})^{-1}$ vs T yielded reasonably good agreement with the theoretical value (2.56 BM). The Weiss constant is negative, $\theta = -37$ K, despite the ferromagnetic ordering of the moments.

Figure VII.17. (A) Temperature dependence of molar magnetic susceptibility ($\chi_m^{\parallel}$) and inverse susceptibility ($(\chi_m^{\parallel})^{-1}$) of a $\text{Ce}_2\text{NiGa}_9\text{Ge}_2$ single crystal oriented with c -axis parallel to the external magnetic field (H_{ex}); (B) Low temperature region of $\chi_m^{\parallel}$ and $\chi_m^{\parallel -1}$; (C) Linear part of molar magnetic susceptibility; (D) The magnetization data for a single crystal of $\text{Ce}_2\text{NiGa}_9\text{Ge}_2$ oriented with the c -axis parallel to H_{ex} in fields up to ± 5 Tesla.



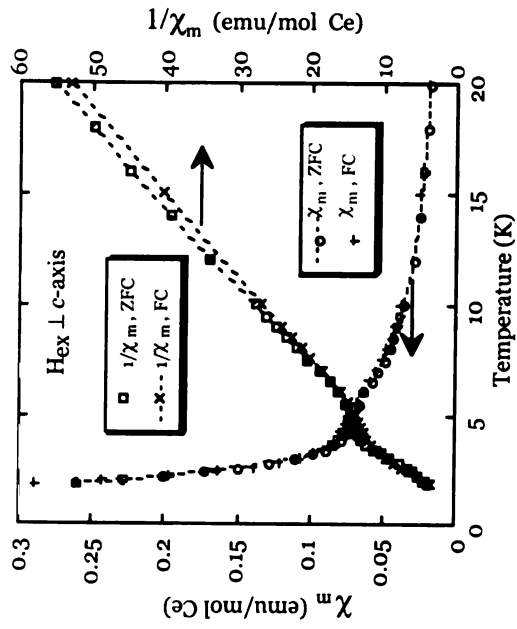
The field dependence of magnetization for $H_{ex}||c$ is similar to that of $H_{ex}\perp c$, see Figure VII.17.D (left). That is, the magnetization is practically saturated at 5 Tesla, yielding the value of only 0.8 BM, same as in case of $H_{ex}\perp c$. However, because of the fact that for $H_{ex}||c$ the magnetization measurements were performed below the ordering temperature (in contrast to $H_{ex}\perp c$, where T_c was not detected up to 2 K), a weak hysteresis loop is observed in the $M(H)$ characterized with a very small remnant magnetization, see Figure VII.17.D (right). The history dependence of magnetization is an additional evidence supporting proposed ferromagnetic ordering taking place below 4 K.

(b) $Ce_2CoGa_9Ge_2(1)$

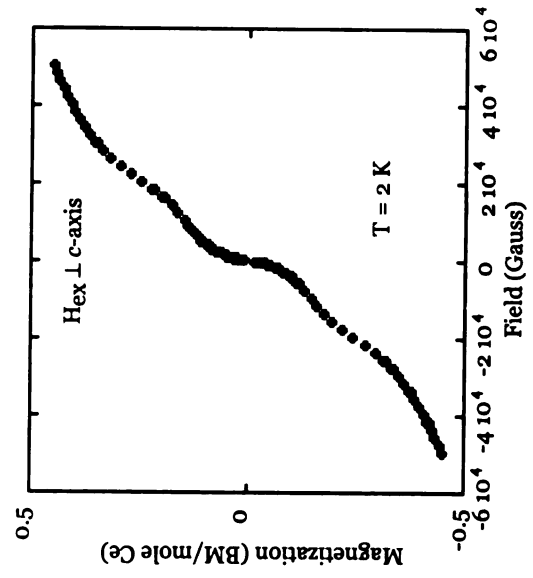
Magnetic properties were further studied on the Co-analog, $Ce_2CoGa_9Ge_2$. As with the Ni compound, anisotropic measurements were performed where the crystal was positioned with c -axis parallel and perpendicular to the external magnetic field. The susceptibility data for the Co analog, $\chi_m^\perp$ and $(\chi_m^\perp)^{-1}$, shown in Figures VII.18.A – C, is reminiscent of that found for $Ce_2NiGa_9Ge_2$. For example in the Co analog, the maximal magnetic response at 2 K ($\chi_m^\perp = 0.30$ emu/mol) is very close to that observed for the Ni analog ($\chi_m^\perp = 0.33$ emu/mol), see Figure VII.18.A. The low temperature area of the $\chi_m^\perp - T$ plot is again featureless, except for the broad shoulder centered around 4 K, see Figure VII.18.B. The temperature dependence of $(\chi_m^\perp)^{-1}$ above 50 K is linear, obeying the Curie-Weiss law, as shown in Figure VII.18.C.

Figure VII.18. (A) Temperature dependence of molar magnetic susceptibility ($\chi_m^\perp$) and inverse susceptibility ($(\chi_m^\perp)^{-1}$) of a $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ single crystal oriented with the c -axis perpendicular to the external magnetic field (H_{ex}); (B) Low temperature region of $(\chi_m^\perp)$ and $(\chi_m^\perp)^{-1}$; (C) Linear part of molar magnetic susceptibility; (D) (left) The magnetization data for a single crystal of $\text{Ce}_2\text{CoGa}_9\text{Ge}_2$ oriented with the c -axis perpendicular to H_{ex} in fields up to ± 5 Tesla (right) An expanded region of low-field magnetization data.

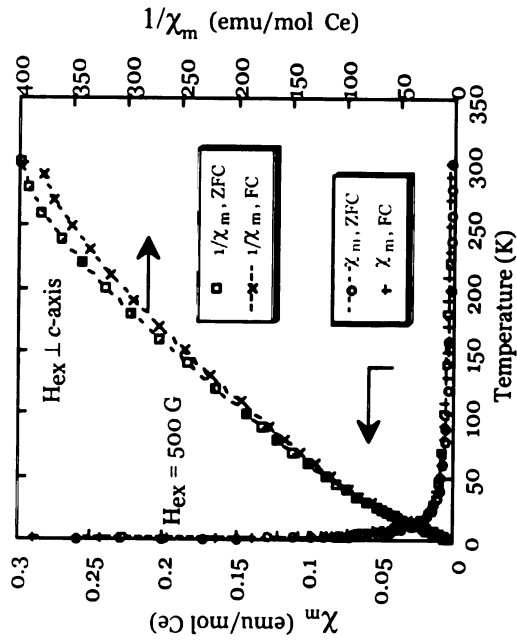
B.



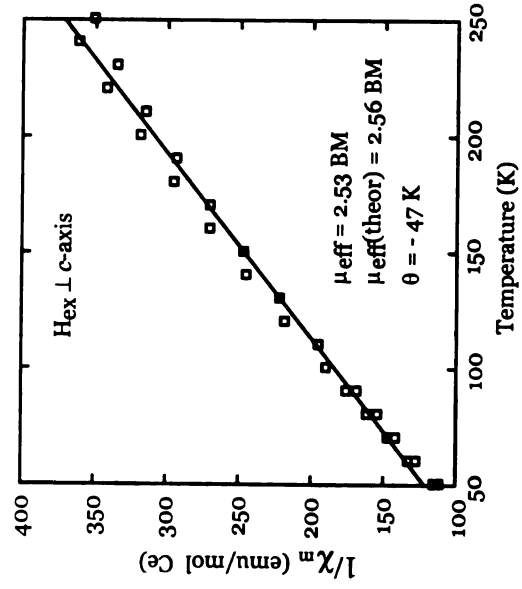
D.



A.



C.



The experimental $\mu_{\text{eff}} = 2.53$ BM is in excellent agreement with the theoretical value of 2.56 BM. The Weiss constant has an even larger negative value than in the case of Ni analog, $\theta = -47$ K. The field dependence of magnetization $M(H)$ for perpendicular orientation is depicted in Figure VII.18.D. Here, a maximal moment developed in field of 5 Tesla is only 0.5 BM, which is only $\sim 25\%$ of the full saturation value. No history dependence was observed for $M(H)$ in perpendicular orientation.

The anisotropy effects studied in the Ce_2MGe_2 samples of **1** with $M = \text{Ni}$ and Co have shown quite fascinating results. Because T_c in these compounds occurs at quite low temperatures, the direction of the magnetic field with respect to the easy axis of the crystal may obstruct the detection of the ferromagnetic transition or even bring about the effect of “appearance” and “vanishing” of the latter. In the isostructural $\text{Sm}_2\text{Ni}(\text{Si}_{1-x}\text{Ni}_x)\text{Al}_4\text{Si}_6$ ¹⁶ compound grown from Al flux, the ferromagnetic transition was observed at much higher temperature $T_c = 17.5$ K compared to the analogs of **1**. Although the effects of the crystal field on the ferromagnetic transition have not been studied in the case of $\text{Sm}_2\text{Ni}(\text{Si}_{1-x}\text{Ni}_x)\text{Al}_4\text{Si}_6$, the difficulty in reproducing the ferromagnetic transition from batch to batch has been noted. If the crystal field anisotropy does take place in $\text{Sm}_2\text{Ni}(\text{Si}_{1-x}\text{Ni}_x)\text{Al}_4\text{Si}_6$, it could, to some extent, explain the difficulty in the reproducibility of the ferromagnetic transition. That is, if the crystals were occasionally placed with the easy axis parallel or perpendicular to the H_{ex} , the transition to ferromagnetic state may randomly be “switched on” and “off”.

4. Concluding Remarks

The reaction chemistry in the RE/M/Ga/Ge system ($M = \text{Fe, Ni, Co}$) was studied at $\text{RE} : M > 1$ under Ga flux conditions. It was shown, that in the case of $M = \text{Ni/Co}$, quaternary phases are predominantly produced while for $M = \text{Fe}$, a variety of ternary phases form (where Fe itself is often excluded). It has been also noted that the reaction outcome is affected by the identity of the RE metal and the heating conditions. Three new families of intermetallic compounds $\text{RE}_2\text{MGa}_9\text{Ge}_2$ ($\text{RE} = \text{Ce, Sm; } M = \text{Ni, Co}$), $\text{RE}_2\text{Ga}_2\text{Ge}_5$ ($\text{RE} = \text{La, Sm, Tb}$) and $\text{La}_3\text{Ga}_2\text{Ge}$ were discovered in the course of these investigations, and their structures were studied with single crystal X-ray diffraction. The structures of these three compounds could be described using four structural fragments: a Ga-rich slab with pentagonal channels (*A*), a $[\text{CoGa}_4\text{Ge}_2]$ cube layer (*B*), a $[\text{GaGe}]$ zigzag chain (*B'*) and a RE monoatomic plane (*C*). The stacking sequence of the layers is *ACBC ACBC ...* for $\text{RE}_2\text{MGa}_9\text{Ge}_2$, *ACB'C ACB'C ...* for $\text{RE}_2\text{Ga}_2\text{Ge}_5$ and *CB'C CB'C ...* for $\text{La}_3\text{Ga}_2\text{Ge}$. The increasing RE : ($M + \text{Ga} + \text{Ge}$) ratio in progressing from $\text{RE}_2\text{MGa}_9\text{Ge}_2$ to $\text{RE}_2\text{Ga}_2\text{Ge}_5$ to $\text{La}_3\text{Ga}_2\text{Ge}$ results in a gradual change in the dimensionality of the RE sublattice from monoatomic plane to 2D prism layer to 3D framework, respectively.

The magnetic measurements conducted on $\text{Ce}_2\text{MGa}_9\text{Ge}_2$ ($M = \text{Ni, Co}$) show that the magnetic moments of the Ce sublattice undergo ferromagnetic transition at low temperatures ($T_c = 4 \text{ K}$), while at higher temperatures Curie-Weiss behavior is observed. Strong crystal field anisotropy in **1** directs the moments parallel to the *c*-axis, making it the magnetically easy axis. The value of the effective magnetic moment is consistent with the Ce^{3+} free ion value, whereas Ni (Co) atoms are in a non-magnetic state.

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³⁵ A number of rare-earth di-gallides (REGa₂) crystallizes in the AlB₂ structure type.

³⁶ For the systems with strong spin-orbit coupling the gyromagnetic ratio g_J (or Landé factor) differs from the spin-only value 2.0 and can be calculated using the formula $g_J = 1 + \{[S(S + 1) - L(L + 1) + J(J + 1)]/[2J(J + 1)]\}$, where S is spin momentum, L is orbital momentum and J is total angular momentum.

³⁷ The total angular momentum (J) of the ion with unfilled 4f shell is determined by the Hund's rules. $J = L + S$, $|L - S|$ for shells greater or less than half full, respectively.

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APPENDIX A

Table A.I - Crystallographic Data for Incommensurate GdCo_{0.869}Ga₃Ge.

1 - Physical, crystallographic, and analytical data.

Formula	GdCo _{0.869} Ga ₃ Ge
Crystal color	dark grey
Molecular weight (g.mol ⁻¹)	490.21
Crystal system	orthorhombic
Superspace group	<i>Immm</i> (α 00)00s
Temperature (K)	293
Cell parameters (from 980 reflections):	
<i>a</i> (Å)	4.1641(8)
<i>b</i> (Å)	4.1641(8)
<i>c</i> (Å)	23.774(14)
q = 0.3043(12) a *	
<i>V</i> (Å ³)	412.2(4)
Z	4
Density (calc., g.cm ⁻³)	7.8960
Crystal description	block
Crystal size (mm ³)	~ 0.14 × 0.10 × 0.08

2 - Data collection

Diffractometer	Bruker-Nonius Kappa CCD
Monochromator	oriented graphite (002)
Radiation	MoK-L _{2,3} ($\lambda = 0.71073 \text{ \AA}$)
Scan mode	φ / ω
No. of measured reflections	91236
hkl range	$-7 \leq h \leq 7$ $-7 \leq k \leq 7$ $-41 \leq l \leq 41$ $-2 \leq m \leq 2$
$\sin(\theta)/\lambda$ range	0.157 - 0.869
twin matrices	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
twin fractions	0.5268(9), 0.4732

3 - Data reduction

Linear absorption coeff. (mm ⁻¹)	45.57
Absorption correction	analytical (Gaussian integration)
T _{min} /T _{max}	0.041/0.138
Number of reflections	91263
No. of independent reflections	5649 (687 main + 2435 1 st + 2517 2 nd)
Criteria for observed reflections	I > 2σ(I)
R _{int} (obs)	0.0678
Average redundancy	16.2
No. of observed reflections	2766 (680 main + 1677 1 st + 409 2 nd)

4 - Refinement

Refinement	F ²
F(000)	850
No. of reflections used in the refinement	5649
R [†] (obs) / R [†] (all)	0.0388 / 0.0948
R _w [†] (obs) / R _w [†] (all)	0.0834 / 0.1003
S (obs) / S (all)	1.32 / 1.10
No. of refined parameters	84
Weighting scheme	w = 1/(σ ² F ₀ + (0.04 F ₀) ²)
Secondary extinction coeff.	0.094(6)
Difference Fourier residues	[-4.1, +5.6] e ⁻ / Å ³

[†]

$$R = \sum |F_o| - |F_c| / \sum |F_o|$$
$$R_w = [\sum w (|F_o|^2 - |F_c|^2)^2 / \sum w (|F_o|^4)]^{1/2}$$

Table A.II - Final residual factors for GdCo_{0.869}Ga₃Ge.

	N (obs)	R (obs)	R _w (obs)
Main	680	0.0222	0.0643
First order	1677	0.0429	0.0801
Second order	409	0.246	0.360
overall	2766	0.0388	0.0834

Table A.III - Fractional atomic coordinates, their Fourier series modulation terms*, equivalent isotropic displacement parameters ($\text{\AA}^2$) and s.u.'s for GdCo_{0.869}Ga₃Ge.

Atom	wave	x	y	z	U _{eq}
Gd	0	0	0	0.149047(7)	0.00714(6)
	s,1	0	0	0.000109(9)	
	c,1	0.02882(7)	0	0	
	s,2	0.00112(10)	0	0	
	c,2	0	0	-0.00048(2)	
Ga1	0	0	0.5	0.05409(3)	0.00960(14)
	s,1	0	0	-0.00299(2)	
	c,1	-0.01603(13)	0	0	
	s,2	-0.0016(2)	0	0	
	c,2	0	0	-0.00003(5)	
Ga2	0	0.5	0	0.05410(3)	0.00927(14)
	s,1	0	0	-0.00486(3)	
	c,1	0.00916(11)	0	0	
	s,2	-0.0009(2)	0	0	
	c,2	0	0	0.00022(5)	

Table A.III. (continued)

Ga3	0	0	0.5	0.24626(6)	0.01734(18)
	s,1	0	0	0.00418(4)	
	c,1	-0.0439(3)	0	0	
	s,2	-0.0126(3)	0	0	
	c,2	0	0	-0.00022(6)	
Co1	0	0	1	0	0.00628(19)
	s,1	0	0	-0.00392(3)	
	c,1	0	0	0	
	s,2	-0.0027(3)	0	0	
	c,2	0	0	0	
Co2	0	0.5	0.5	0.2204(8)	0.00763(18)
	s,1	0	0	-0.0014(14)	
	c,1	-0.0289(11)	0	0	
	s,2	0.0092(12)	0	0	
	c,2	0	0	-0.0004(8)	
Ge1	0	0.5	0.5	0.1205(9)	0.00627(13)
	s,1	0	0	0.0034(15)	
	c,1	0.0083(9)	0	0	
	s,2	-0.0012(10)	0	0	
	c,2	0	0	0.0023(9)	
Ge2	0	0.5	0.5	0.14115(11)	0.01212(17)
	s,1	0	0	-0.00285(17)	
	c,1	0.0189(3)	0	0	
	s,2	0.0037(5)	0	0	
	c,2	0	0	0.00024(15)	

* s,1 = Sin term, first order; s,2 = Sin term, second order;
c,1 = Cos term, first order; c,2 = Cos term, second order.

Table A.IV – Occupation factors, their Fourier series modulation terms*, and s.u.'s for $\text{GdCo}_{0.869}\text{Ga}_3\text{Ge}$.

Atom	wave	Occupation
Co2	0	0.369(2)
	s,1	0.462(2)
	c,1	0
	s,2	0
	c,2	-0.079(3)
Ge1	0	0.369(2)
	s,1	0.462(2)
	c,1	0
	s,2	0
	c,2	-0.079(3)
Ge2	0	0.631(2)
	s,1	-0.462(2)
	c,1	0
	s,2	0
	c,2	0.079(3)

* s,1 = Sin term, first order; s,2 = Sin term, second order;
c,1 = Cos term, first order; c,2 = Cos term, second order.

Table A.V – Anisotropic displacement parameters U^{ij} [†] ($\text{\AA}^2$), their Fourier series modulation terms*, and s.u.'s for $\text{GdCo}_{0.869}\text{Ga}_3\text{Ge}$.

Atom	wave	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Gd	0	0.00882(10)	0.00699(10)	0.00562(8)	0	0	0
	s,1	0.00144(8)	0.00006(7)	0.00086(7)	0	0	0
	c,1	0	0	0	0	0.00021(6)	0
	s,2	0	0	0	0	0.00025(12)	0
	c,2	-0.00328(15)	0.0006(2)	-0.00102(17)	0	0	0
Ga1	0	0.0130(3)	0.0070(2)	0.0088(2)	0	0	0
Ga2	0	0.0057(2)	0.0144(3)	0.0077(2)	0	0	0
Ga3	0	0.0229(3)	0.0128(3)	0.0164(3)	0	0	0
	s,1	-0.0048(4)	0.0024(3)	0.0062(4)	0	0	0
	c,1	0	0	0	0	0.0004(4)	0
Co1	0	0.0043(4)	0.0072(4)	0.0073(2)	0	0	0
Ge2	0	0.0072(2)	0.0093(3)	0.0198(4)	0	0	0

* s,1 = Sin term, first order; s,2 = Sin term, second order;
c,1 = Cos term, first order; c,2 = Cos term, second order.

[†] U^{ij} coefficient are multiplied by 10^3

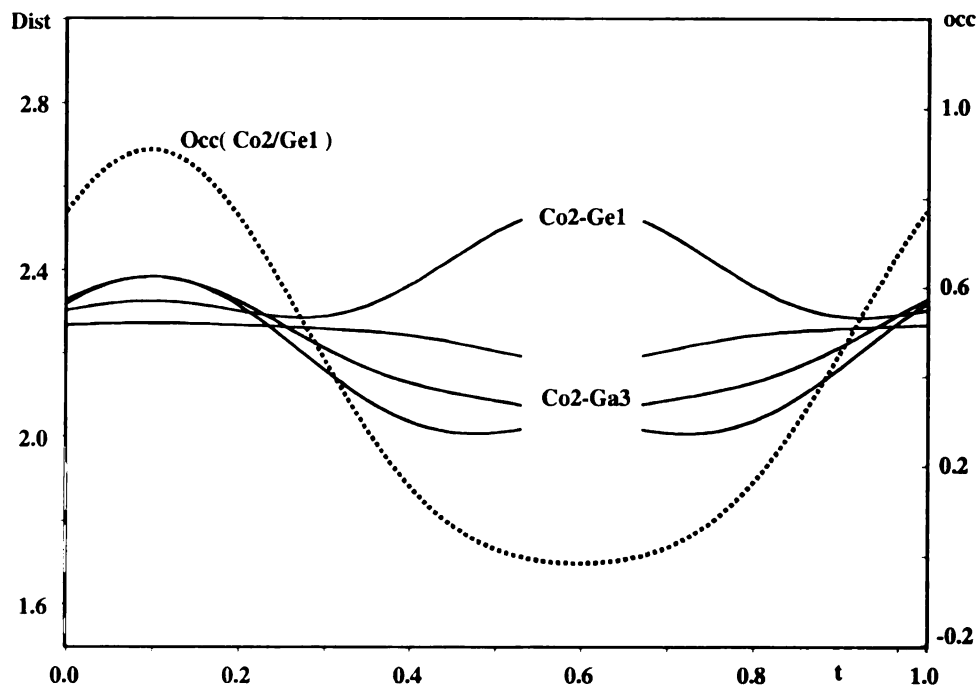
Table A.VI – Gram-Charlier non-harmonic Debye-Waller parameters C^{ijk} [†], their Fourier series modulation terms, and s.u.'s for GdCo_{0.869}Ga₃Ge.

Atom	wave	C^{111}	C^{112}	C^{113}	C^{122}	C^{123}
Ga3	0	0	0	-0.0031(2)	0	0
	s,1	0	0	-0.0077(3)	0	0
	c,1	0.055(4)	0	0	-0.0074(16)	0

Atom	wave	C^{133}	C^{222}	C^{223}	C^{233}	C^{333}
Ga3	0	0	0	0.00083(18)	0	-0.000056(13)
	s,1	0	0	-0.0012(2)	0	-0.000076(16)
	c,1	0.00066(5)	0	0	0	0

[†] C^{ijk} coefficient are multiplied by 10^3

A.



B.

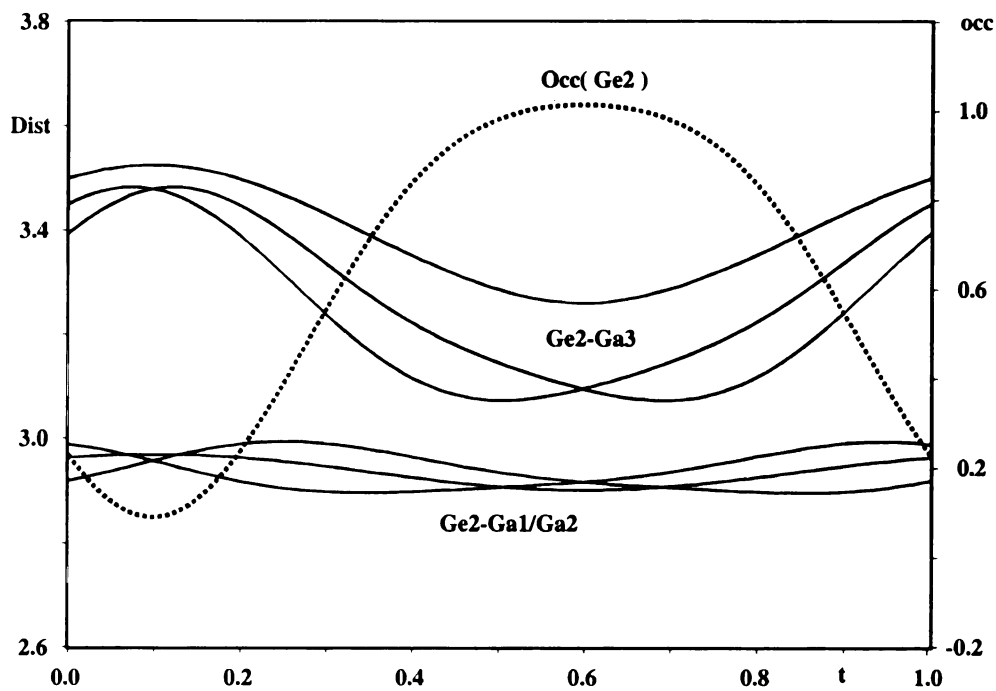


Figure A.1. (A) The occupational modulation of Co(2)/Ge(1) (dotted line) and Co(2)-Ge(1) and Co(2)-Ga(3) distances (in Å, solid line) as a function of internal coordinate t . (B) The occupational modulation of Ge(2) (dotted line) and Ge(2)-Ga(1)/Ga(2) and Ge(2)-Ga(3) distances (in Å, solid line) as a function of internal coordinate t for incommensurately modulated structure of $\text{GdCo}_{0.869}\text{Ga}_3\text{Ge}$.

APPENDIX B

Table B.1. Crystal data and structure refinement for $\text{YFe}_{4+x}\text{Ga}_{8-x}$.

Empirical formula	$\text{YFe}_{4+x}\text{Ga}_{8-x}$	
x	0.4	
Formula weight	864.52	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	TETRAGONAL	
Space group	I4/mmm (#139)	
Unit cell dimensions	$a = 8.6781(8)$ Å	$\alpha = 90^\circ$.
	$b = 8.6781(8)$ Å	$\beta = 90^\circ$.
	$c = 5.0939(7)$ Å	$\gamma = 90^\circ$.
Volume	$383.62(7)$ Å ³	
Z	2	
Density (calculated)	7.484 Mg/m ³	
Absorption coefficient	41.612 mm ⁻¹	
F(000)	778	
Crystal size	0.12 x 0.08 x 0.06 mm ³	
Theta range for data collection	3.32 to 29.43°.	
Index ranges	-12 ≤ h ≤ 11, -9 ≤ k ≤ 11, -6 ≤ l ≤ 5	
Reflections collected	1111	
Independent reflections	173 [R(int) = 0.0455]	
Completeness to theta = 29.43°	97.2 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	173 / 1 / 18	
Goodness-of-fit on F ²	1.175	
Final R indices [I > 2σ(I)]	R1 = 0.0332, wR2 = 0.0903	
R indices (all data)	R1 = 0.0339, wR2 = 0.0909	
Extinction coefficient	0.0049(10)	
Largest diff. peak and hole	2.218 and -1.633 e.Å ⁻³	

Table B.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{YFe}_{4+x}\text{Ga}_{8-x}$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Y(1)	0	0	0	3(1)
Fe(1)	2500	2500	2500	2(1)
Ga(1)	3401(1)	0	0	5(1)
Ga(2)	2800(2)	5000	0	11(1)
Fe(2)	2800(2)	5000	0	11(1)

Table B.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\text{YFe}_{4+x}\text{Ga}_{8-x}$.

Y(1)-Ga(1)#1	2.9510(11)
Y(1)-Ga(1)	2.9510(11)
Y(1)-Ga(1)#2	2.9510(11)
Y(1)-Ga(1)#3	2.9510(11)
Y(1)-Fe(2)#4	3.1833(10)
Y(1)-Fe(2)#5	3.1833(10)
Y(1)-Ga(2)#4	3.1833(10)
Y(1)-Ga(2)#5	3.1833(10)
Y(1)-Fe(2)#6	3.1833(10)
Y(1)-Fe(2)#7	3.1833(10)
Y(1)-Ga(2)#6	3.1833(10)
Y(1)-Ga(2)#7	3.1833(10)
Fe(1)-Ga(2)	2.5291(2)
Fe(1)-Fe(2)#4	2.5291(2)
Fe(1)-Fe(2)#8	2.5291(2)
Fe(1)-Fe(2)#5	2.5291(2)
Fe(1)-Ga(2)#4	2.5291(2)
Fe(1)-Ga(2)#8	2.5291(2)
Fe(1)-Ga(2)#5	2.5291(2)
Fe(1)-Fe(1)#9	2.5469(4)
Fe(1)-Fe(1)#10	2.5469(4)
Fe(1)-Ga(1)	2.6343(4)
Fe(1)-Ga(1)#5	2.6343(4)
Ga(1)-Fe(1)#6	2.6343(4)
Ga(1)-Fe(1)#11	2.6343(4)
Ga(1)-Fe(1)#9	2.6343(4)
Ga(1)-Fe(2)#12	2.7517(8)
Ga(1)-Ga(2)#12	2.7517(8)
Ga(1)-Fe(2)#5	2.7517(8)
Ga(1)-Ga(2)#5	2.7517(8)
Ga(1)-Ga(1)#13	2.776(2)
Ga(1)-Fe(2)#8	2.7981(14)
Ga(1)-Ga(2)#8	2.7981(14)
Ga(1)-Fe(2)#2	2.7981(14)
Ga(2)-Fe(1)#9	2.5291(2)
Ga(2)-Fe(1)#14	2.5291(2)
Ga(2)-Fe(1)#15	2.5291(3)
Ga(2)-Fe(2)#16	2.700(2)
Ga(2)-Ga(2)#16	2.700(2)
Ga(2)-Fe(2)#8	2.700(2)
Ga(2)-Ga(2)#8	2.700(2)
Ga(2)-Ga(1)#12	2.7517(8)
Ga(2)-Ga(1)#5	2.7517(8)
Ga(2)-Ga(1)#1	2.7981(14)
Ga(2)-Ga(1)#16	2.7981(14)
Ga(1)#1-Y(1)-Ga(1)	90.0
Ga(1)#1-Y(1)-Ga(1)#2	180.0
Ga(1)-Y(1)-Ga(1)#2	90.0
Ga(1)#1-Y(1)-Ga(1)#3	90.0
Ga(1)-Y(1)-Ga(1)#3	180.0
Ga(1)#2-Y(1)-Ga(1)#3	90.0
Ga(1)#1-Y(1)-Fe(2)#4	53.14(2)

Ga(1)-Y(1)-Fe(2)#4	90.0
Ga(1)#2-Y(1)-Fe(2)#4	126.86(2)
Ga(1)#3-Y(1)-Fe(2)#4	90.0
Ga(1)#1-Y(1)-Fe(2)#5	90.0
Ga(1)-Y(1)-Fe(2)#5	53.14(2)
Ga(1)#2-Y(1)-Fe(2)#5	90.0
Ga(1)#3-Y(1)-Fe(2)#5	126.86(2)
Fe(2)#4-Y(1)-Fe(2)#5	50.20(3)
Ga(1)#1-Y(1)-Ga(2)#4	53.14(2)
Ga(1)-Y(1)-Ga(2)#4	90.0
Ga(1)#2-Y(1)-Ga(2)#4	126.86(2)
Ga(1)#3-Y(1)-Ga(2)#4	90.0
Fe(2)#4-Y(1)-Ga(2)#4	0.0
Fe(2)#5-Y(1)-Ga(2)#4	50.20(3)
Ga(1)#1-Y(1)-Ga(2)#5	90.0
Ga(1)-Y(1)-Ga(2)#5	53.14(2)
Ga(1)#2-Y(1)-Ga(2)#5	90.0
Ga(1)#3-Y(1)-Ga(2)#5	126.86(2)
Fe(2)#4-Y(1)-Ga(2)#5	50.20(3)
Fe(2)#5-Y(1)-Ga(2)#5	0.0
Ga(2)#4-Y(1)-Ga(2)#5	50.20(3)
Ga(1)#1-Y(1)-Fe(2)#6	126.86(2)
Ga(1)-Y(1)-Fe(2)#6	90.0
Ga(1)#2-Y(1)-Fe(2)#6	53.14(2)
Ga(1)#3-Y(1)-Fe(2)#6	90.0
Fe(2)#4-Y(1)-Fe(2)#6	180.0
Fe(2)#5-Y(1)-Fe(2)#6	129.80(3)
Ga(2)#4-Y(1)-Fe(2)#6	180.0
Ga(2)#5-Y(1)-Fe(2)#6	129.80(3)
Ga(1)#1-Y(1)-Fe(2)#7	90.0
Ga(1)-Y(1)-Fe(2)#7	126.86(2)
Ga(1)#2-Y(1)-Fe(2)#7	90.0
Ga(1)#3-Y(1)-Fe(2)#7	53.14(2)
Fe(2)#4-Y(1)-Fe(2)#7	129.80(3)
Fe(2)#5-Y(1)-Fe(2)#7	180.0
Ga(2)#4-Y(1)-Fe(2)#7	129.80(3)
Ga(2)#5-Y(1)-Fe(2)#7	180.0
Fe(2)#6-Y(1)-Fe(2)#7	50.20(3)
Ga(1)#1-Y(1)-Ga(2)#6	126.86(2)
Ga(1)-Y(1)-Ga(2)#6	90.0
Ga(1)#2-Y(1)-Ga(2)#6	53.14(2)
Ga(1)#3-Y(1)-Ga(2)#6	90.0
Fe(2)#4-Y(1)-Ga(2)#6	180.0
Fe(2)#5-Y(1)-Ga(2)#6	129.80(3)
Ga(2)#4-Y(1)-Ga(2)#6	180.0
Ga(2)#5-Y(1)-Ga(2)#6	129.80(3)
Fe(2)#6-Y(1)-Ga(2)#6	0.0
Fe(2)#7-Y(1)-Ga(2)#6	50.20(3)
Ga(1)#1-Y(1)-Ga(2)#7	90.0
Ga(1)-Y(1)-Ga(2)#7	126.86(2)
Ga(1)#2-Y(1)-Ga(2)#7	90.0
Ga(1)#3-Y(1)-Ga(2)#7	53.14(2)
Fe(2)#4-Y(1)-Ga(2)#7	129.80(3)
Fe(2)#5-Y(1)-Ga(2)#7	180.0
Ga(2)#4-Y(1)-Ga(2)#7	129.80(3)
Ga(2)#5-Y(1)-Ga(2)#7	180.0

Fe(2)#6-Y(1)-Ga(2)#7	50.20(3)
Fe(2)#7-Y(1)-Ga(2)#7	0.0
Ga(2)#6-Y(1)-Ga(2)#7	50.20(3)
Ga(2)-Fe(1)-Fe(2)#4	115.46(6)
Fe(2)#4-Fe(1)-Fe(2)#8	180.0
Ga(2)-Fe(1)-Fe(2)#5	180.0
Fe(2)#8-Fe(1)-Fe(2)#5	115.46(6)
Fe(2)#4-Fe(1)-Ga(2)#4	0.00(7)
Fe(2)#8-Fe(1)-Ga(2)#4	180.0
Fe(2)#4-Fe(1)-Ga(2)#8	180.0
Fe(2)#8-Fe(1)-Ga(2)#8	0.00(7)
Fe(2)#5-Fe(1)-Ga(2)#8	115.46(6)
Ga(2)#4-Fe(1)-Ga(2)#8	180.0
Ga(2)-Fe(1)-Ga(2)#5	180.0
Fe(2)#4-Fe(1)-Ga(2)#5	64.54(6)
Fe(2)#8-Fe(1)-Ga(2)#5	115.46(6)
Fe(2)#5-Fe(1)-Ga(2)#5	0.00(7)
Ga(2)#8-Fe(1)-Ga(2)#5	115.46(6)
Ga(2)-Fe(1)-Fe(1)#9	59.766(5)
Fe(2)#4-Fe(1)-Fe(1)#9	120.234(5)
Fe(1)#9-Fe(1)-Fe(1)#10	180.0
Ga(2)-Fe(1)-Ga(1)	115.631(16)
Fe(2)#4-Fe(1)-Ga(1)	114.41(4)
Fe(2)#5-Fe(1)-Ga(1)	64.369(16)
Ga(2)#4-Fe(1)-Ga(1)	114.41(4)
Ga(2)#8-Fe(1)-Ga(1)	65.59(4)
Ga(2)#5-Fe(1)-Ga(1)	64.369(16)
Fe(1)#9-Fe(1)-Ga(1)	61.090(6)
Fe(1)#10-Fe(1)-Ga(1)	118.910(6)
Fe(2)#8-Fe(1)-Ga(1)#5	114.41(4)
Fe(2)#5-Fe(1)-Ga(1)#5	115.631(16)
Ga(2)#5-Fe(1)-Ga(1)#5	115.631(16)
Fe(1)#9-Fe(1)-Ga(1)#5	118.910(6)
Fe(1)#10-Fe(1)-Ga(1)#5	61.090(6)
Ga(1)-Fe(1)-Ga(1)#5	180.0
Fe(1)#6-Ga(1)-Fe(1)	145.49(5)
Fe(1)#6-Ga(1)-Fe(1)#11	57.819(11)
Fe(1)-Ga(1)-Fe(1)#11	110.89(2)
Fe(1)-Ga(1)-Fe(1)#9	57.819(11)
Fe(1)#11-Ga(1)-Fe(1)#9	145.49(5)
Fe(1)#6-Ga(1)-Fe(2)#12	55.962(10)
Fe(1)-Ga(1)-Fe(2)#12	109.58(3)
Fe(1)#9-Ga(1)-Fe(2)#12	55.962(10)
Fe(2)#12-Ga(1)-Ga(2)#12	0.0
Fe(1)#6-Ga(1)-Fe(2)#5	109.58(3)
Fe(2)#12-Ga(1)-Fe(2)#5	135.52(7)
Fe(1)#6-Ga(1)-Ga(2)#5	109.58(3)
Fe(1)-Ga(1)-Ga(2)#5	55.962(10)
Fe(1)#9-Ga(1)-Ga(2)#5	109.58(3)
Fe(2)#12-Ga(1)-Ga(2)#5	135.52(7)
Fe(2)#5-Ga(1)-Ga(2)#5	0.00(6)
Fe(1)#9-Ga(1)-Ga(1)#13	107.26(2)
Fe(2)#12-Ga(1)-Ga(1)#13	112.24(4)
Fe(1)#6-Ga(1)-Fe(2)#8	149.572(18)
Fe(1)-Ga(1)-Fe(2)#8	55.393(13)
Fe(2)#12-Ga(1)-Fe(2)#8	100.822(9)

Ga(1)#13-Ga(1)-Fe(2)#8	60.26(3)
Fe(1)#6-Ga(1)-Ga(2)#8	149.572(18)
Fe(2)#8-Ga(1)-Ga(2)#8	0.00(3)
Fe(2)#8-Ga(1)-Fe(2)#2	120.52(5)
Fe(1)#9-Ga(2)-Fe(1)#14	168.20(7)
Fe(1)#9-Ga(2)-Fe(1)	60.468(9)
Fe(1)#9-Ga(2)-Fe(1)#15	118.149(14)
Fe(1)-Ga(2)-Fe(1)#15	168.20(7)
Fe(1)#9-Ga(2)-Fe(2)#16	132.79(3)
Fe(1)#15-Ga(2)-Fe(2)#16	57.73(3)
Fe(2)#16-Ga(2)-Ga(2)#16	0.00(5)
Fe(2)#16-Ga(2)-Fe(2)#8	90.0
Ga(2)#16-Ga(2)-Fe(2)#8	90.0
Fe(1)-Ga(2)-Ga(2)#8	57.73(3)
Fe(2)#16-Ga(2)-Ga(2)#8	90.0
Ga(2)#16-Ga(2)-Ga(2)#8	90.0
Fe(2)#8-Ga(2)-Ga(2)#8	0.00(5)
Fe(1)#9-Ga(2)-Ga(1)#12	59.669(11)
Fe(1)-Ga(2)-Ga(1)#12	115.29(3)
Fe(1)#15-Ga(2)-Ga(1)#12	59.669(11)
Fe(2)#16-Ga(2)-Ga(1)#12	105.52(2)
Fe(1)#9-Ga(2)-Ga(1)#5	115.29(3)
Fe(1)#14-Ga(2)-Ga(1)#5	59.669(11)
Ga(1)#12-Ga(2)-Ga(1)#5	135.52(7)
Fe(1)#9-Ga(2)-Ga(1)#1	59.01(3)
Fe(1)#14-Ga(2)-Ga(1)#1	109.65(5)
Ga(2)#16-Ga(2)-Ga(1)#1	164.74(3)
Fe(2)#8-Ga(2)-Ga(1)#1	105.26(3)
Ga(1)#12-Ga(2)-Ga(1)#1	70.81(4)
Fe(1)#9-Ga(2)-Ga(1)#16	109.65(5)
Fe(1)#15-Ga(2)-Ga(1)#16	59.01(3)
Fe(2)#16-Ga(2)-Ga(1)#16	105.26(3)
Ga(2)#8-Ga(2)-Ga(1)#16	164.74(3)
Ga(1)#5-Ga(2)-Ga(1)#16	70.81(4)
Ga(1)#1-Ga(2)-Ga(1)#16	59.48(5)

Symmetry transformations used to generate equivalent atoms:

#1 -y,x,z #2 y,-x,-z #3 -x,-y,-z #4 y-1/2,-x+1/2,-z+1/2
#5 -x+1/2,-y+1/2,-z+1/2 #6 -y+1/2,x-1/2,z-1/2
#7 x-1/2,y-1/2,z-1/2 #8 -y+1,x,z #9 -x+1/2,-y+1/2,z-1/2
#10 -x+1/2,-y+1/2,z+1/2 #11 y,-x,z #12 -x+1/2,-y+1/2,-z-1/2
#13 -x+1,-y,-z #14 y,-x+1,z #15 -y+1/2,x+1/2,z-1/2
#16 y,-x+1,-z

Table B.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{YFe}_{4+x}\text{Ga}_{8-x}$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	2(1)	2(1)	5(1)	0	0	0
Fe(1)	1(1)	1(1)	4(1)	0(1)	0(1)	-1(1)
Ga(1)	3(1)	2(1)	10(1)	0	0	0
Ga(2)	24(1)	3(1)	5(1)	0	0	0
Fe(2)	24(1)	3(1)	5(1)	0	0	0

APPENDIX C

Table C.1. Crystal data and structure refinement for $\text{YFe}_6\text{Ga}_2\text{Ge}_4$.

Empirical formula	$\text{YFe}_6\text{Ga}_2\text{Ge}_4$	
Formula weight	853.81	
Temperature	571(2) K	
Wavelength	0.71073 Å	
Crystal system	ORTHORHOMBIC	
Space group	Cmc2(1)	
Unit cell dimensions	$a = 8.2572(14)$ Å	$\alpha = 90^\circ$.
	$b = 17.578(3)$ Å	$\beta = 90^\circ$.
	$c = 5.0911(9)$ Å	$\gamma = 90^\circ$.
Volume	739.0(2) Å ³	
Z	4	
Density (calculated)	7.674 Mg/m ³	
Absorption coefficient	42.199 mm ⁻¹	
F(000)	1540	
Crystal size	0.14 x 0.12 x 0.08 mm ³	
Theta range for data collection	2.73 to 29.28°.	
Index ranges	$-11 \leq h \leq 11$, $-20 \leq k \leq 23$, $-6 \leq l \leq 6$	
Reflections collected	2526	
Independent reflections	962 [R(int) = 0.0342]	
Completeness to theta = 29.28°	96.1 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	962 / 1 / 69	
Goodness-of-fit on F ²	1.035	
Final R indices [I > 2sigma(I)]	R1 = 0.0283, wR2 = 0.0739	
R indices (all data)	R1 = 0.0370, wR2 = 0.0814	
Absolute structure parameter	0.01(10)	
Extinction coefficient	0.00182(12)	
Largest diff. peak and hole	1.365 and -1.612 e.Å ⁻³	

Table C.2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{YFe}_6\text{Ga}_2\text{Ge}_4$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Y(1)	0	1286(1)	7091(5)	5(1)
Fe(1)	2467(1)	1250(1)	12119(5)	4(1)
Fe(2)	2503(4)	2501(2)	4613(6)	5(1)
Fe(3)	2460(1)	4(2)	9624(6)	5(1)
Ga(1)	0	421(1)	12122(5)	3(1)
Ga(2)	5000	-399(1)	7117(6)	6(1)
Ge(1)	3475(1)	1234(1)	7120(4)	7(1)
Ge(2)	0	2135(1)	12117(5)	6(1)
Ge(3)	0	2980(1)	7114(5)	8(1)

Table C.3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\text{YFe}_6\text{Ga}_2\text{Ge}_4$.

Y(1)-Ge(1)	2.8711(7)
Y(1)-Ge(1)#1	2.8711(7)
Y(1)-Ge(2)#2	2.939(3)
Y(1)-Ga(1)#2	2.952(3)
Y(1)-Ge(2)	2.962(3)
Y(1)-Ge(3)	2.9781(11)
Y(1)-Ga(1)	2.979(3)
Y(1)-Ga(1)#3	3.0008(10)
Y(1)-Fe(2)	3.228(3)
Y(1)-Fe(2)#1	3.228(3)
Y(1)-Fe(2)#4	3.232(3)
Y(1)-Fe(2)#5	3.232(3)
Fe(1)-Ge(3)#4	2.4909(7)
Fe(1)-Ga(1)	2.5050(7)
Fe(1)-Fe(2)#4	2.539(3)
Fe(1)-Fe(3)	2.533(3)
Fe(1)-Fe(2)#6	2.539(3)
Fe(1)-Fe(3)#7	2.547(3)
Fe(1)-Ge(2)	2.5626(7)
Fe(1)-Ga(2)#8	2.5727(7)
Fe(1)-Ge(1)	2.678(4)
Fe(1)-Ge(1)#6	2.679(4)
Fe(1)-Y(1)#6	3.249(3)
Fe(2)-Ge(2)#9	2.507(3)
Fe(2)-Ge(2)#2	2.510(3)
Fe(2)-Fe(1)#9	2.539(3)
Fe(2)-Fe(1)#2	2.539(3)
Fe(2)-Fe(2)#9	2.5456(5)
Fe(2)-Fe(2)#4	2.5456(5)
Fe(2)-Ge(3)	2.570(3)
Fe(2)-Ge(3)#9	2.566(3)
Fe(2)-Ge(1)#9	2.684(3)
Fe(2)-Ge(1)	2.689(3)
Fe(2)-Y(1)#9	3.232(3)
Fe(3)-Ga(1)#3	2.511(2)
Fe(3)-Ga(1)	2.506(2)
Fe(3)-Fe(1)#10	2.547(3)
Fe(3)-Fe(3)#10	2.5456(5)
Fe(3)-Fe(3)#7	2.5456(4)
Fe(3)-Ga(2)#8	2.548(2)
Fe(3)-Ga(2)	2.555(2)
Fe(3)-Ge(1)	2.647(3)
Fe(3)-Ge(1)#7	2.656(3)
Fe(3)-Y(1)#11	3.293(3)
Ga(1)-Fe(1)#1	2.5050(7)
Ga(1)-Fe(3)#11	2.511(2)
Ga(1)-Fe(3)#7	2.511(2)
Ga(1)-Fe(3)#1	2.506(2)
Ga(1)-Ga(1)#3	2.9441(8)
Ga(1)-Ga(1)#11	2.9441(8)
Ga(1)-Y(1)#6	2.952(3)
Ga(1)-Y(1)#11	3.0008(10)
Ga(2)-Fe(3)#10	2.548(2)
Ga(2)-Fe(3)#12	2.548(2)



Ga(2)-Fe(3)#13	2.555(2)
Ga(2)-Fe(1)#10	2.5727(7)
Ga(2)-Fe(1)#12	2.5727(7)
Ga(2)-Ge(3)#14	2.8496(12)
Ga(2)-Ga(2)#8	2.9055(8)
Ga(2)-Ga(2)#12	2.9055(8)
Ge(1)-Ge(1)#13	2.5181(11)
Ge(1)-Fe(3)#10	2.656(3)
Ge(1)-Fe(1)#2	2.679(4)
Ge(1)-Fe(2)#4	2.684(3)
Ge(2)-Fe(2)#4	2.507(3)
Ge(2)-Fe(2)#5	2.507(3)
Ge(2)-Fe(2)#6	2.510(3)
Ge(2)-Fe(2)#15	2.510(3)
Ge(2)-Fe(1)#1	2.5626(7)
Ge(2)-Y(1)#6	2.939(3)
Ge(3)-Fe(1)#9	2.4909(7)
Ge(3)-Fe(1)#16	2.4909(7)
Ge(3)-Fe(2)#1	2.570(3)
Ge(3)-Fe(2)#4	2.566(3)
Ge(3)-Fe(2)#5	2.566(3)
Ge(3)-Ga(2)#17	2.8496(12)

Ge(1)-Y(1)-Ge(1)#1	176.31(3)
Ge(1)-Y(1)-Ge(2)#2	91.18(5)
Ge(1)#1-Y(1)-Ge(2)#2	91.18(5)
Ge(1)-Y(1)-Ga(1)#2	89.31(4)
Ge(1)#1-Y(1)-Ga(1)#2	89.31(4)
Ge(2)#2-Y(1)-Ga(1)#2	61.54(7)
Ge(1)-Y(1)-Ge(2)	90.66(5)
Ge(1)#1-Y(1)-Ge(2)	90.66(5)
Ge(2)#2-Y(1)-Ge(2)	119.24(3)
Ga(1)#2-Y(1)-Ge(2)	179.22(7)
Ge(1)-Y(1)-Ge(3)	91.821(14)
Ge(1)#1-Y(1)-Ge(3)	91.821(14)
Ge(2)#2-Y(1)-Ge(3)	59.72(5)
Ga(1)#2-Y(1)-Ge(3)	121.26(10)
Ge(2)-Y(1)-Ge(3)	59.52(5)
Ge(1)-Y(1)-Ga(1)	88.81(5)
Ge(1)#1-Y(1)-Ga(1)	88.81(5)
Ge(2)#2-Y(1)-Ga(1)	179.80(7)
Ga(1)#2-Y(1)-Ga(1)	118.26(3)
Ge(2)-Y(1)-Ga(1)	60.96(7)
Ge(3)-Y(1)-Ga(1)	120.48(10)
Ge(1)-Y(1)-Ga(1)#3	88.176(14)
Ge(1)#1-Y(1)-Ga(1)#3	88.176(14)
Ge(2)#2-Y(1)-Ga(1)#3	120.81(10)
Ga(1)#2-Y(1)-Ga(1)#3	59.27(4)
Ge(2)-Y(1)-Ga(1)#3	119.95(10)
Ge(3)-Y(1)-Ga(1)#3	179.47(13)
Ga(1)-Y(1)-Ga(1)#3	58.99(4)
Ge(1)-Y(1)-Fe(2)	51.92(6)
Ge(1)#1-Y(1)-Fe(2)	131.52(7)
Ge(2)#2-Y(1)-Fe(2)	47.74(7)
Ga(1)#2-Y(1)-Fe(2)	90.35(9)
Ge(2)-Y(1)-Fe(2)	90.25(7)

Ge(3)-Y(1)-Fe(2)	48.71(6)
Ga(1)-Y(1)-Fe(2)	132.36(9)
Ga(1)#3-Y(1)-Fe(2)	131.57(8)
Ge(1)-Y(1)-Fe(2)#1	131.52(7)
Ge(1)#1-Y(1)-Fe(2)#1	51.92(6)
Ge(2)#2-Y(1)-Fe(2)#1	47.74(7)
Ga(1)#2-Y(1)-Fe(2)#1	90.35(9)
Ge(2)-Y(1)-Fe(2)#1	90.25(7)
Ge(3)-Y(1)-Fe(2)#1	48.71(6)
Ga(1)-Y(1)-Fe(2)#1	132.36(9)
Ga(1)#3-Y(1)-Fe(2)#1	131.57(8)
Fe(2)-Y(1)-Fe(2)#1	79.61(12)
Ge(1)-Y(1)-Fe(2)#4	51.78(6)
Ge(1)#1-Y(1)-Fe(2)#4	131.04(7)
Ge(2)#2-Y(1)-Fe(2)#4	90.43(7)
Ga(1)#2-Y(1)-Fe(2)#4	132.88(9)
Ge(2)-Y(1)-Fe(2)#4	47.51(7)
Ge(3)-Y(1)-Fe(2)#4	48.61(6)
Ga(1)-Y(1)-Fe(2)#4	89.73(9)
Ga(1)#3-Y(1)-Fe(2)#4	131.11(8)
Fe(2)-Y(1)-Fe(2)#4	46.413(11)
Fe(2)#1-Y(1)-Fe(2)#4	97.32(2)
Ge(1)-Y(1)-Fe(2)#5	131.04(7)
Ge(1)#1-Y(1)-Fe(2)#5	51.78(6)
Ge(2)#2-Y(1)-Fe(2)#5	90.43(7)
Ga(1)#2-Y(1)-Fe(2)#5	132.88(9)
Ge(2)-Y(1)-Fe(2)#5	47.51(7)
Ge(3)-Y(1)-Fe(2)#5	48.61(6)
Ga(1)-Y(1)-Fe(2)#5	89.73(9)
Ga(1)#3-Y(1)-Fe(2)#5	131.11(8)
Fe(2)-Y(1)-Fe(2)#5	97.32(2)
Fe(2)#1-Y(1)-Fe(2)#5	46.413(11)
Fe(2)#4-Y(1)-Fe(2)#5	79.29(12)
Ge(3)#4-Fe(1)-Ga(1)	177.27(3)
Ge(3)#4-Fe(1)-Fe(2)#4	61.43(8)
Ga(1)-Fe(1)-Fe(2)#4	120.77(10)
Ge(3)#4-Fe(1)-Fe(3)	118.09(7)
Ga(1)-Fe(1)-Fe(3)	59.66(5)
Fe(2)#4-Fe(1)-Fe(3)	119.73(14)
Ge(3)#4-Fe(1)-Fe(2)#6	61.35(8)
Ga(1)-Fe(1)-Fe(2)#6	120.90(10)
Fe(2)#4-Fe(1)-Fe(2)#6	60.173(16)
Fe(3)-Fe(1)-Fe(2)#6	179.43(8)
Ge(3)#4-Fe(1)-Fe(3)#7	118.17(7)
Ga(1)-Fe(1)-Fe(3)#7	59.62(5)
Fe(2)#4-Fe(1)-Fe(3)#7	179.53(8)
Fe(3)-Fe(1)-Fe(3)#7	60.148(16)
Fe(2)#6-Fe(1)-Fe(3)#7	119.94(14)
Ge(3)#4-Fe(1)-Ge(2)	109.76(3)
Ga(1)-Fe(1)-Ge(2)	72.97(3)
Fe(2)#4-Fe(1)-Ge(2)	58.87(8)
Fe(3)-Fe(1)-Ge(2)	121.55(7)
Fe(2)#6-Fe(1)-Ge(2)	58.94(8)
Fe(3)#7-Fe(1)-Ge(2)	121.60(7)
Ge(3)#4-Fe(1)-Ga(2)#8	68.47(3)
Ga(1)-Fe(1)-Ga(2)#8	108.80(3)

Fe(2)#4-Fe(1)-Ga(2)#8	119.66(10)
Fe(3)-Fe(1)-Ga(2)#8	59.86(5)
Fe(2)#6-Fe(1)-Ga(2)#8	119.65(10)
Fe(3)#7-Fe(1)-Ga(2)#8	59.87(5)
Ge(2)-Fe(1)-Ga(2)#8	178.23(3)
Ge(3)#4-Fe(1)-Ge(1)	75.14(7)
Ga(1)-Fe(1)-Ge(1)	104.31(9)
Fe(2)#4-Fe(1)-Ge(1)	61.86(9)
Fe(3)-Fe(1)-Ge(1)	60.99(8)
Fe(2)#6-Fe(1)-Ge(1)	118.73(9)
Fe(3)#7-Fe(1)-Ge(1)	117.87(8)
Ge(2)-Fe(1)-Ge(1)	104.66(9)
Ga(2)#8-Fe(1)-Ge(1)	74.97(8)
Ge(3)#4-Fe(1)-Ge(1)#6	75.26(8)
Ga(1)-Fe(1)-Ge(1)#6	104.26(9)
Fe(2)#4-Fe(1)-Ge(1)#6	118.92(9)
Fe(3)-Fe(1)-Ge(1)#6	117.91(8)
Fe(2)#6-Fe(1)-Ge(1)#6	61.98(9)
Fe(3)#7-Fe(1)-Ge(1)#6	61.03(8)
Ge(2)-Fe(1)-Ge(1)#6	104.71(9)
Ga(2)#8-Fe(1)-Ge(1)#6	75.02(8)
Ge(1)-Fe(1)-Ge(1)#6	143.74(3)
Ge(3)#4-Fe(1)-Y(1)#6	121.11(10)
Ga(1)-Fe(1)-Y(1)#6	60.09(7)
Fe(2)#4-Fe(1)-Y(1)#6	112.39(8)
Fe(3)-Fe(1)-Y(1)#6	113.96(6)
Fe(2)#6-Fe(1)-Y(1)#6	66.48(9)
Fe(3)#7-Fe(1)-Y(1)#6	68.01(7)
Ge(2)-Fe(1)-Y(1)#6	59.36(6)
Ga(2)#8-Fe(1)-Y(1)#6	121.42(10)
Ge(1)-Fe(1)-Y(1)#6	159.29(7)
Ge(1)#6-Fe(1)-Y(1)#6	56.96(7)
Ge(3)#4-Fe(1)-Y(1)	120.76(10)
Ga(1)-Fe(1)-Y(1)	60.36(7)
Fe(2)#4-Fe(1)-Y(1)	66.19(9)
Fe(3)-Fe(1)-Y(1)	67.86(7)
Fe(2)#6-Fe(1)-Y(1)	112.45(8)
Fe(3)#7-Fe(1)-Y(1)	114.03(6)
Ge(2)-Fe(1)-Y(1)	59.55(6)
Ga(2)#8-Fe(1)-Y(1)	121.13(10)
Ge(1)-Fe(1)-Y(1)	56.65(7)
Ge(1)#6-Fe(1)-Y(1)	159.61(7)
Y(1)#6-Fe(1)-Y(1)	102.65(2)
Ge(2)#9-Fe(2)-Ge(2)#2	179.85(18)
Ge(2)#9-Fe(2)-Fe(1)#9	61.03(7)
Ge(2)#2-Fe(2)-Fe(1)#9	118.96(13)
Ge(2)#9-Fe(2)-Fe(1)#2	119.00(13)
Ge(2)#2-Fe(2)-Fe(1)#2	61.00(8)
Fe(1)#9-Fe(2)-Fe(1)#2	179.81(18)
Ge(2)#9-Fe(2)-Fe(2)#9	120.68(19)
Ge(2)#2-Fe(2)-Fe(2)#9	59.46(13)
Fe(1)#9-Fe(2)-Fe(2)#9	120.24(19)
Fe(1)#2-Fe(2)-Fe(2)#9	59.92(12)
Ge(2)#9-Fe(2)-Fe(2)#4	59.56(13)
Ge(2)#2-Fe(2)-Fe(2)#4	120.30(19)
Fe(1)#9-Fe(2)-Fe(2)#4	59.91(12)

Fe(1)#2-Fe(2)-Fe(2)#4	119.93(19)
Fe(2)#9-Fe(2)-Fe(2)#4	179.7(3)
Ge(2)#9-Fe(2)-Ge(3)	109.02(13)
Ge(2)#2-Fe(2)-Ge(3)	70.90(9)
Fe(1)#9-Fe(2)-Ge(3)	58.36(7)
Fe(1)#2-Fe(2)-Ge(3)	121.49(13)
Fe(2)#9-Fe(2)-Ge(3)	119.64(19)
Fe(2)#4-Fe(2)-Ge(3)	60.23(13)
Ge(2)#9-Fe(2)-Ge(3)#9	71.06(9)
Ge(2)#2-Fe(2)-Ge(3)#9	109.03(13)
Fe(1)#9-Fe(2)-Ge(3)#9	121.74(13)
Fe(1)#2-Fe(2)-Ge(3)#9	58.40(7)
Fe(2)#9-Fe(2)-Ge(3)#9	60.35(13)
Fe(2)#4-Fe(2)-Ge(3)#9	119.78(19)
Ge(3)-Fe(2)-Ge(3)#9	179.89(15)
Ge(2)#9-Fe(2)-Ge(1)#9	106.06(11)
Ge(2)#2-Fe(2)-Ge(1)#9	74.04(9)
Fe(1)#9-Fe(2)-Ge(1)#9	61.62(10)
Fe(1)#2-Fe(2)-Ge(1)#9	118.49(14)
Fe(2)#9-Fe(2)-Ge(1)#9	61.81(13)
Fe(2)#4-Fe(2)-Ge(1)#9	118.26(18)
Ge(3)-Fe(2)-Ge(1)#9	73.78(9)
Ge(3)#9-Fe(2)-Ge(1)#9	106.28(12)
Ge(2)#9-Fe(2)-Ge(1)	74.00(9)
Ge(2)#2-Fe(2)-Ge(1)	105.91(11)
Fe(1)#9-Fe(2)-Ge(1)	118.32(14)
Fe(1)#2-Fe(2)-Ge(1)	61.57(10)
Fe(2)#9-Fe(2)-Ge(1)	118.30(18)
Fe(2)#4-Fe(2)-Ge(1)	61.63(13)
Ge(3)-Fe(2)-Ge(1)	106.06(12)
Ge(3)#9-Fe(2)-Ge(1)	73.88(9)
Ge(1)#9-Fe(2)-Ge(1)	179.84(16)
Ge(2)#9-Fe(2)-Y(1)	119.78(13)
Ge(2)#2-Fe(2)-Y(1)	60.08(8)
Fe(1)#9-Fe(2)-Y(1)	112.45(12)
Fe(1)#2-Fe(2)-Y(1)	67.36(9)
Fe(2)#9-Fe(2)-Y(1)	112.87(17)
Fe(2)#4-Fe(2)-Y(1)	66.88(14)
Ge(3)-Fe(2)-Y(1)	60.56(7)
Ge(3)#9-Fe(2)-Y(1)	119.34(10)
Ge(1)#9-Fe(2)-Y(1)	122.68(11)
Ge(1)-Fe(2)-Y(1)	57.19(6)
Ge(2)#9-Fe(2)-Y(1)#9	60.60(9)
Ge(2)#2-Fe(2)-Y(1)#9	119.55(13)
Fe(1)#9-Fe(2)-Y(1)#9	67.86(9)
Fe(1)#2-Fe(2)-Y(1)#9	112.33(12)
Fe(2)#9-Fe(2)-Y(1)#9	66.71(14)
Fe(2)#4-Fe(2)-Y(1)#9	113.54(17)
Ge(3)-Fe(2)-Y(1)#9	119.58(10)
Ge(3)#9-Fe(2)-Y(1)#9	60.52(7)
Ge(1)#9-Fe(2)-Y(1)#9	57.16(7)
Ge(1)-Fe(2)-Y(1)#9	122.97(11)
Y(1)-Fe(2)-Y(1)#9	179.59(16)
Ga(1)#3-Fe(3)-Ga(1)	71.85(2)
Ga(1)#3-Fe(3)-Fe(1)	120.87(8)
Ga(1)-Fe(3)-Fe(1)	59.61(7)

Ga(1)#3-Fe(3)-Fe(1)#10	59.37(7)
Ga(1)-Fe(3)-Fe(1)#10	120.59(8)
Fe(1)-Fe(3)-Fe(1)#10	179.76(6)
Ga(1)#3-Fe(3)-Fe(3)#10	59.41(9)
Ga(1)-Fe(3)-Fe(3)#10	120.58(9)
Fe(1)-Fe(3)-Fe(3)#10	120.39(19)
Fe(1)#10-Fe(3)-Fe(3)#10	59.66(12)
Ga(1)#3-Fe(3)-Fe(3)#7	120.39(9)
Ga(1)-Fe(3)-Fe(3)#7	59.61(9)
Fe(1)-Fe(3)-Fe(3)#7	60.19(12)
Fe(1)#10-Fe(3)-Fe(3)#7	119.76(18)
Fe(3)#10-Fe(3)-Fe(3)#7	179.4(3)
Ga(1)#3-Fe(3)-Ga(2)#8	178.29(13)
Ga(1)-Fe(3)-Ga(2)#8	109.56(13)
Fe(1)-Fe(3)-Ga(2)#8	60.84(7)
Fe(1)#10-Fe(3)-Ga(2)#8	118.92(8)
Fe(3)#10-Fe(3)-Ga(2)#8	119.97(9)
Fe(3)#7-Fe(3)-Ga(2)#8	60.21(9)
Ga(1)#3-Fe(3)-Ga(2)	109.17(13)
Ga(1)-Fe(3)-Ga(2)	178.83(13)
Fe(1)-Fe(3)-Ga(2)	119.23(8)
Fe(1)#10-Fe(3)-Ga(2)	60.57(7)
Fe(3)#10-Fe(3)-Ga(2)	59.93(9)
Fe(3)#7-Fe(3)-Ga(2)	119.88(9)
Ga(2)#8-Fe(3)-Ga(2)	69.42(2)
Ga(1)#3-Fe(3)-Ge(1)	104.74(11)
Ga(1)-Fe(3)-Ge(1)	105.18(10)
Fe(1)-Fe(3)-Ge(1)	62.22(10)
Fe(1)#10-Fe(3)-Ge(1)	117.75(13)
Fe(3)#10-Fe(3)-Ge(1)	61.48(12)
Fe(3)#7-Fe(3)-Ge(1)	119.06(17)
Ga(2)#8-Fe(3)-Ge(1)	75.92(8)
Ga(2)-Fe(3)-Ge(1)	74.08(7)
Ga(1)#3-Fe(3)-Ge(1)#7	104.75(10)
Ga(1)-Fe(3)-Ge(1)#7	104.64(11)
Fe(1)-Fe(3)-Ge(1)#7	117.93(13)
Fe(1)#10-Fe(3)-Ge(1)#7	61.94(10)
Fe(3)#10-Fe(3)-Ge(1)#7	118.31(17)
Fe(3)#7-Fe(3)-Ge(1)#7	61.15(12)
Ga(2)#8-Fe(3)-Ge(1)#7	74.05(7)
Ga(2)-Fe(3)-Ge(1)#7	75.71(8)
Ge(1)-Fe(3)-Ge(1)#7	143.15(3)
Ga(1)#3-Fe(3)-Y(1)#11	59.33(7)
Ga(1)-Fe(3)-Y(1)#11	60.53(5)
Fe(1)-Fe(3)-Y(1)#11	113.94(10)
Fe(1)#10-Fe(3)-Y(1)#11	66.18(8)
Fe(3)#10-Fe(3)-Y(1)#11	112.20(13)
Fe(3)#7-Fe(3)-Y(1)#11	67.37(11)
Ga(2)#8-Fe(3)-Y(1)#11	120.36(12)
Ga(2)-Fe(3)-Y(1)#11	120.42(10)
Ge(1)-Fe(3)-Y(1)#11	160.32(6)
Ge(1)#7-Fe(3)-Y(1)#11	56.50(6)
Ga(1)#3-Fe(3)-Y(1)	60.42(5)
Ga(1)-Fe(3)-Y(1)	59.94(7)
Fe(1)-Fe(3)-Y(1)	66.79(8)
Fe(1)#10-Fe(3)-Y(1)	113.40(10)

Fe(3)#10-Fe(3)-Y(1)	67.19(11)
Fe(3)#7-Fe(3)-Y(1)	113.24(13)
Ga(2)#8-Fe(3)-Y(1)	121.05(10)
Ga(2)-Fe(3)-Y(1)	119.96(12)
Ge(1)-Fe(3)-Y(1)	56.49(6)
Ge(1)#7-Fe(3)-Y(1)	160.36(6)
Y(1)#11-Fe(3)-Y(1)	103.88(2)
Fe(1)-Ga(1)-Fe(1)#1	108.79(4)
Fe(1)-Ga(1)-Fe(3)#11	146.19(13)
Fe(1)#1-Ga(1)-Fe(3)#11	61.02(7)
Fe(1)-Ga(1)-Fe(3)#7	61.02(7)
Fe(1)#1-Ga(1)-Fe(3)#7	146.19(13)
Fe(3)#11-Ga(1)-Fe(3)#7	107.98(14)
Fe(1)-Ga(1)-Fe(3)#1	146.01(13)
Fe(1)#1-Ga(1)-Fe(3)#1	60.73(7)
Fe(3)#11-Ga(1)-Fe(3)#1	60.973(17)
Fe(3)#7-Ga(1)-Fe(3)#1	145.71(3)
Fe(1)-Ga(1)-Fe(3)	60.73(7)
Fe(1)#1-Ga(1)-Fe(3)	146.01(13)
Fe(3)#11-Ga(1)-Fe(3)	145.71(3)
Fe(3)#7-Ga(1)-Fe(3)	60.973(17)
Fe(3)#1-Ga(1)-Fe(3)	108.31(14)
Fe(1)-Ga(1)-Ga(1)#3	106.98(8)
Fe(3)#7-Ga(1)-Ga(1)#3	106.82(8)
Fe(3)#1-Ga(1)-Ga(1)#3	54.16(7)
Fe(3)-Ga(1)-Ga(1)#3	54.16(7)
Fe(1)-Ga(1)-Ga(1)#11	107.03(8)
Fe(3)#11-Ga(1)-Ga(1)#11	53.99(7)
Fe(3)#7-Ga(1)-Ga(1)#11	53.99(7)
Fe(3)-Ga(1)-Ga(1)#11	106.96(8)
Ga(1)#3-Ga(1)-Ga(1)#11	119.68(5)
Fe(1)#1-Ga(1)-Y(1)#6	72.56(7)
Fe(3)#7-Ga(1)-Y(1)#6	73.64(8)
Fe(3)-Ga(1)-Y(1)#6	125.84(7)
Ga(1)#3-Ga(1)-Y(1)#6	179.13(5)
Ga(1)#11-Ga(1)-Y(1)#6	61.18(4)
Fe(1)#1-Ga(1)-Y(1)	72.68(7)
Fe(3)#7-Ga(1)-Y(1)	126.01(7)
Fe(3)#1-Ga(1)-Y(1)	73.34(9)
Ga(1)#3-Ga(1)-Y(1)	60.87(4)
Ga(1)#11-Ga(1)-Y(1)	179.45(5)
Y(1)#6-Ga(1)-Y(1)	118.26(3)
Fe(1)#1-Ga(1)-Y(1)#11	125.605(18)
Fe(3)#7-Ga(1)-Y(1)#11	72.88(8)
Fe(3)#1-Ga(1)-Y(1)#11	72.83(8)
Ga(1)#3-Ga(1)-Y(1)#11	59.54(8)
Ga(1)#11-Ga(1)-Y(1)#11	60.14(8)
Y(1)#6-Ga(1)-Y(1)#11	121.33(11)
Y(1)-Ga(1)-Y(1)#11	120.41(12)
Fe(3)#10-Ga(2)-Fe(3)#12	110.81(15)
Fe(3)#10-Ga(2)-Fe(3)#13	148.13(3)
Fe(3)#12-Ga(2)-Fe(3)#13	59.856(17)
Fe(3)#12-Ga(2)-Fe(3)	148.13(3)
Fe(3)#13-Ga(2)-Fe(3)	110.34(14)
Fe(3)#10-Ga(2)-Fe(1)#10	59.30(7)
Fe(3)#12-Ga(2)-Fe(1)#10	145.91(12)

Fe(3)#13-Ga(2)-Fe(1)#10	145.93(12)
Fe(3)-Ga(2)-Fe(1)#10	59.56(7)
Fe(3)#10-Ga(2)-Fe(1)#12	145.91(12)
Fe(3)#12-Ga(2)-Fe(1)#12	59.30(7)
Fe(3)#13-Ga(2)-Fe(1)#12	59.56(7)
Fe(1)#10-Ga(2)-Fe(1)#12	108.81(4)
Fe(3)#12-Ga(2)-Ge(3)#14	105.79(8)
Fe(3)#13-Ga(2)-Ge(3)#14	106.08(8)
Fe(1)#12-Ga(2)-Ge(3)#14	54.403(18)
Fe(3)#12-Ga(2)-Ga(2)#8	107.77(8)
Fe(3)#13-Ga(2)-Ga(2)#8	55.17(7)
Fe(3)-Ga(2)-Ga(2)#8	55.17(7)
Fe(1)#12-Ga(2)-Ga(2)#8	106.28(8)
Ge(3)#14-Ga(2)-Ga(2)#8	118.86(9)
Fe(3)#12-Ga(2)-Ga(2)#12	55.40(7)
Fe(3)-Ga(2)-Ga(2)#12	107.72(8)
Fe(1)#10-Ga(2)-Ga(2)#12	106.32(8)
Ge(3)#14-Ga(2)-Ga(2)#12	118.79(9)
Ga(2)#8-Ga(2)-Ga(2)#12	122.35(5)
Ge(1)#13-Ge(1)-Fe(3)	108.46(3)
Ge(1)#13-Ge(1)-Fe(3)#10	108.39(3)
Fe(3)-Ge(1)-Fe(3)#10	57.374(15)
Ge(1)#13-Ge(1)-Fe(1)	108.12(3)
Fe(3)-Ge(1)-Fe(1)	56.80(8)
Fe(3)#10-Ge(1)-Fe(1)	111.42(8)
Ge(1)#13-Ge(1)-Fe(1)#2	108.12(3)
Fe(3)-Ge(1)-Fe(1)#2	111.58(7)
Fe(3)#10-Ge(1)-Fe(1)#2	57.03(8)
Fe(1)-Ge(1)-Fe(1)#2	143.74(3)
Ge(1)#13-Ge(1)-Fe(2)#4	107.51(7)
Fe(3)-Ge(1)-Fe(2)#4	110.72(12)
Fe(3)#10-Ge(1)-Fe(2)#4	144.09(8)
Fe(1)-Ge(1)-Fe(2)#4	56.52(8)
Fe(1)#2-Ge(1)-Fe(2)#4	110.32(8)
Ge(1)#13-Ge(1)-Fe(2)	107.38(7)
Fe(3)-Ge(1)-Fe(2)	144.16(8)
Fe(3)#10-Ge(1)-Fe(2)	110.93(12)
Fe(1)-Ge(1)-Fe(2)	110.45(8)
Fe(1)#2-Ge(1)-Fe(2)	56.46(8)
Fe(2)#4-Ge(1)-Fe(2)	56.555(15)
Ge(1)#13-Ge(1)-Y(1)	178.153(17)
Fe(3)-Ge(1)-Y(1)	73.27(4)
Fe(3)#10-Ge(1)-Y(1)	73.03(4)
Fe(1)-Ge(1)-Y(1)	72.17(6)
Fe(1)#2-Ge(1)-Y(1)	71.58(6)
Fe(2)#4-Ge(1)-Y(1)	71.06(7)
Fe(2)-Ge(1)-Y(1)	70.90(7)
Fe(2)#4-Ge(2)-Fe(2)#5	110.66(16)
Fe(2)#4-Ge(2)-Fe(2)#6	60.980(13)
Fe(2)#5-Ge(2)-Fe(2)#6	150.37(3)
Fe(2)#4-Ge(2)-Fe(2)#15	150.37(3)
Fe(2)#5-Ge(2)-Fe(2)#15	60.980(13)
Fe(2)#6-Ge(2)-Fe(2)#15	110.85(16)
Fe(2)#4-Ge(2)-Fe(1)#1	143.97(12)
Fe(2)#5-Ge(2)-Fe(1)#1	60.09(8)
Fe(2)#6-Ge(2)-Fe(1)#1	144.06(11)

Fe(2)#15-Ge(2)-Fe(1)#1	60.06(7)
Fe(2)#5-Ge(2)-Fe(1)	143.97(12)
Fe(2)#6-Ge(2)-Fe(1)	60.06(7)
Fe(2)#15-Ge(2)-Fe(1)	144.06(11)
Fe(1)#1-Ge(2)-Fe(1)	105.26(4)
Fe(2)#4-Ge(2)-Y(1)#6	124.58(8)
Fe(2)#6-Ge(2)-Y(1)#6	72.17(8)
Fe(1)#1-Ge(2)-Y(1)#6	72.03(7)
Fe(2)#4-Ge(2)-Y(1)	71.90(8)
Fe(2)#6-Ge(2)-Y(1)	124.50(8)
Fe(1)-Ge(2)-Y(1)	72.22(7)
Y(1)#6-Ge(2)-Y(1)	119.24(3)
Fe(1)#9-Ge(3)-Fe(1)#16	114.25(4)
Fe(1)#9-Ge(3)-Fe(2)#1	148.65(13)
Fe(1)#16-Ge(3)-Fe(2)#1	60.21(7)
Fe(1)#16-Ge(3)-Fe(2)	148.65(13)
Fe(2)#1-Ge(3)-Fe(2)	107.08(16)
Fe(1)#9-Ge(3)-Fe(2)#4	60.24(7)
Fe(1)#16-Ge(3)-Fe(2)#4	148.57(13)
Fe(2)#1-Ge(3)-Fe(2)#4	141.60(3)
Fe(2)-Ge(3)-Fe(2)#4	59.423(13)
Fe(1)#9-Ge(3)-Fe(2)#5	148.57(13)
Fe(1)#16-Ge(3)-Fe(2)#5	60.24(7)
Fe(2)#1-Ge(3)-Fe(2)#5	59.423(13)
Fe(2)-Ge(3)-Fe(2)#5	141.60(3)
Fe(2)#4-Ge(3)-Fe(2)#5	106.92(16)
Fe(1)#16-Ge(3)-Ga(2)#17	57.124(19)
Fe(2)-Ge(3)-Ga(2)#17	109.17(8)
Fe(2)#5-Ge(3)-Ga(2)#17	109.24(8)
Fe(1)#9-Ge(3)-Y(1)	122.876(19)
Fe(1)#16-Ge(3)-Y(1)	122.88(2)
Fe(2)#1-Ge(3)-Y(1)	70.73(8)
Fe(2)#5-Ge(3)-Y(1)	70.87(8)
Ga(2)#17-Ge(3)-Y(1)	179.80(14)

Symmetry transformations used to generate equivalent atoms:

#1 -x,y,z #2 x,y,z-1 #3 -x,-y,z-1/2 #4 -x+1/2,-y+1/2,z+1/2
#5 x-1/2,-y+1/2,z+1/2 #6 x,y,z+1 #7 x,-y,z+1/2
#8 -x+1,-y,z+1/2 #9 -x+1/2,-y+1/2,z-1/2 #10 x,-y,z-1/2
#11 -x,-y,z+1/2 #12 -x+1,-y,z-1/2 #13 -x+1,y,z
#14 x+1/2,y-1/2,z #15 -x,y,z+1 #16 x-1/2,-y+1/2,z-1/2
#17 x-1/2,y+1/2,z

Table C.4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{YFe}_6\text{Ga}_2\text{Ge}_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Y(1)	4(1)	4(1)	7(1)	2(1)	0	0
Fe(1)	4(1)	1(1)	8(1)	0(1)	1(1)	0(1)
Fe(2)	4(1)	3(1)	7(1)	-1(1)	0(1)	0(1)
Fe(3)	4(1)	3(1)	7(1)	-1(1)	-2(1)	1(1)
Ga(1)	1(1)	2(1)	6(1)	1(1)	0	0
Ga(2)	2(1)	6(1)	9(1)	1(1)	0	0
Ge(1)	3(1)	6(1)	11(1)	0(1)	2(1)	0(1)
Ge(2)	4(1)	6(1)	9(1)	2(1)	0	0
Ge(3)	5(1)	5(1)	13(1)	3(2)	0	0

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