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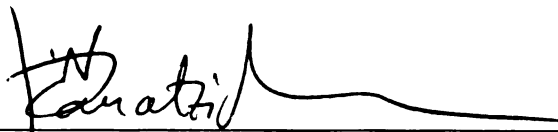
Molten Metal Flux Synthesis and Crystal Growth of
Intermetallic Silicides, Germanides, and Indides

presented by

James R. Salvador

has been accepted towards fulfillment
of the requirements for the

Ph.D. degree in Chemistry



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**MOLTEN METAL FLUX SYNTHESIS AND CRYSTAL GROWTH OF
INTERMETALLIC SILICIDES GERMANIDES AND INDIDES.**

By

James R. Salvador

A DISSERTATION

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

2004

Professor Mercouri Kanatzidis

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ABSTRACT

MOLTEN METAL FLUX SYNTHESIS AND CRYSTAL GROWTH OF INTERMETALLIC SILICIDES GERMANIDES AND INDIDES.

By

James R. Salvador

Molten metal fluxes have shown themselves to be powerful tools for both crystal growth of known intermetallic compounds, and in the exploratory synthesis of systems containing rare earth metals, transition metals, and a metalloid such as Si B or Ge. Our group has recently launched a research project to explore molten Al and Ga as media to carry out exploratory synthesis of intermetallics of the type RE/TM/Al/Si or Ge when Al is used as a solvent and RE/TM/Ga/Si or Ge when Ga is used. In each case RE is a rare earth metal and TM is some, generally late transition metal. This work has been extremely lucrative producing dozens of new compounds, some of which possess new structure types. It was found that in several cases that the new compounds could only be synthesized by metal flux reactions.

In the present work these concepts are expanded upon and the work with molten Ga is continued. The new boron rich compounds $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE = Tb and Er) and $\beta\text{-SiB}_3$ were synthesized by the use of liquid Ga, and both crystallize as new structure

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types. Both compounds are semiconductors and are quite refractory. 2 Intermetallic compounds RENiSi_3 ($\text{RE} = \text{Tb-Er, Yb and Lu}$) and $\text{RE}_5\text{Co}_4\text{Si}_{14}$ ($\text{Dy, Ho, Er, and Tm}$) were also grown from a Ga flux and their crystal size made characterization of their physical properties possible.

The work was also expanded to include molten indium as a solvent. Using this we were able to trap a new form of RENiGe_2 , which was determined to be kinetically stable. The near Zintl phase intermetallic $\text{RE}_2\text{Zn}_3\text{Ge}_6$, and the new ordered quaternary variant of the Mg_5Si_6 structure $\text{RE}_4\text{Ni}_2\text{InGe}_4$ were also produced from the In flux. In addition 2 new indium rich ternary compounds REAu_2In_4 ($\text{RE} = \text{La-Nd}$) and YbAu_2In_4 were also synthesized. YbAu_2In_4 shows evidence of a first order valence transition. The crystal structures of these compounds will be discussed as well as selected physical properties.

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LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Chapter 1 Introduction

1.1

1.2

Chapter 2 Review of Literature

2.1

2.2

2.3

Chapter 3

TABLE OF CONTENTS

	Page
LIST OF TABLES.....	x
LIST OF FIGURES.....	xiv
LIST OF ABBREVIATIONS.....	xxiv
 Chapter 1	
Introduction.....	1
1. Introduction to Intermetallics and Their Selected Properties.....	1
2. The Use of Liquid Al, Ga and In for the Exploratory Synthesis of Rare Earth Transition Metal and Tetral Containing Intermetallics.....	5
 Chapter 2	
RE _{3-x} C ₂ Si ₈ (B ₁₂) ₃ (RE = Tb, Er) Synthesis and Characterization of New Boron Rich Phases Grown from Ga Flux.....	17
1. Introduction.....	17
2. Experimental Section.....	18
Reagents.....	18
Synthesis.....	19
X-ray Crystallography.....	19
Elemental Analysis.....	21
U.V.-Vis Spectroscopy.....	25
Magnetic Measurements.....	25
Band Structure Calculations.....	25
3. Results and Discussion.....	26
Synthesis.....	26
Structure.....	28
Band Structure and Spectroscopy.....	33
Magnetic Measurements.....	34
4. Conclusions.....	39
 Chapter 3	
β-SiB ₃ A New Refractory Si-B Binary Phase Grown from a Ga Flux.	42
1. Introduction.....	42
2. Experimental Section.....	43
Reagents and Synthesis.....	43
X-ray Crystallography.....	44
Elemental Analysis.....	45
CHN analysis.....	48
Differential thermal analysis.....	48

	Thermal Gravimetric Analysis.....	48
	Spectroscopy.....	49
	Refractory Testing.....	49
	Band Structure Calculations.....	50
	3. Results and Discussion.....	51
	4. Conclusions.....	64
Chapter 4	Gallium Flux Synthesis and Crystal Growth of RENiSi_3 (RE = Tb, Dy, Ho, Er, Yb, Lu) Intermetallics Displaying Anisotropic Magnetic Behavior.	67
	1. Introduction.....	67
	2. Experimental Sections.....	69
	Reagents.....	69
	Synthesis.....	70
	Method A.....	70
	Method B.....	70
	Elemental Analysis.....	77
	X-ray Crystallography.....	71
	Magnetic Characterization.....	72
	3. Results and Discussion.....	80
	Synthesis.....	80
	Structural Description.....	81
	Magnetic Measurements.....	86
	TbNiSi_3	90
	DyNiSi_3	96
	HoNiSi_3	101
	ErNiSi_3	107
	YbNiSi_3	110
	LuNiSi_3	114
	Magnetic Measurement Discussion.....	114
	4. Conclusions.....	118
Chapter 5	$\text{RE}_5\text{Co}_4\text{Si}_{14}$ (RE = Ho, Er, Tm and Yb) Intermetallic Phases Grown from Ga Flux Showing Exceptional Resistance to Chemical and Thermal Attack.	123
	1. Introduction.....	123
	2. Experimental Section.....	125
	Reagents.....	125
	Synthesis.....	125

	Elemental Analysis.....	126
	X-ray Crystallography.....	127
	Other Physical Methods.....	129
	3. Results and Discussion.....	134
	Flux Reaction versus Direct Combination.....	134
	Structure.....	136
	Oxidation.....	142
	Magnetic Measurements.....	148
	4. Conclusions.....	155
Chapter 6	β -RENiGe ₂ (RE = Dy, Er, Yb and Lu) a New Form of RENiGe ₂ Stabilized by Indium Flux.	158
	1. Introduction.....	158
	2. Experimental Section.....	160
	Reagents.....	160
	Synthesis.....	161
	Elemental Analysis.....	161
	X-ray crystallography.....	162
	Differential Thermal Analysis.....	163
	Magnetic Measurements.....	163
	Band Structure Calculations.....	168
	3. Results and Discussion.....	169
	Structure.....	169
	Synthesis and Thermal Stability.....	174
	Band Structure Calculations.....	176
	Magnetic Properties.....	181
	4. Conclusions.....	184
Chapter 7	RE ₂ Zn ₃ Ge ₆ (RE = La, Ce, Pr, and Nd) Intermetallic Phases with Near Zintl Phase Behavior Grown from Liquid Indium.	188
	1. Introduction.....	188
	2. Experimental Section.....	190
	Reagents.....	190
	Synthesis.....	190
	Method A.....	190
	Method B.....	191
	X-ray Crystallography.....	191
	Elemental Analysis.....	193
	Differential Thermal Analysis.....	193
	Magnetic Measurements.....	194

Diffuse Reflectance Infrared Spectroscopy.....	194
Band Structure calculations.....	201
3. Results and Discussion.....	201
Structure.....	201
Synthesis and Stability.....	203
Band Structure Calculations.....	210
Magnetic Properties.....	213
La ₂ Zn ₃ Ge ₆	214
Ce ₂ Zn ₃ Ge ₆	214
Pr ₂ Zn ₃ Ge ₆	215
Nd ₂ Zn ₃ Ge ₆	216
4. Conclusions.....	221

Chapter 8	RE ₄ Ni ₂ InGe ₄ A New Quaternary Intermetallic Grown from Molten Indium: The First Bulk Representative of the Mg ₅ Si ₆ Structure Type.	225
	1. Introduction.....	225
	2. Experimental Section.....	227
	Reagents.....	227
	Synthesis.....	227
	Elemental Analysis.....	229
	X-ray Crystallography.....	230
	Magnetic Measurements.....	231
	Differential Thermal Analysis.....	232
	3. Results and Discussion.....	239
	Structure.....	239
	Synthesis.....	246
	Magnetic Properties.....	248
	Dy ₄ Ni ₂ InGe ₄	249
	Ho ₄ Ni ₂ InGe ₄	252
	Er ₄ Ni ₂ InGe ₄	253
	Tm ₄ Ni ₂ InGe ₄	256
	Summary.....	259
	4. Conclusions.....	262

Chapter 9	Indium Flux Synthesis of REAu ₂ In ₄ (RE = La, Ce, Pr, Nd) a New Indium Rich Ternary Intermetallic Phase.	265
	1. Introduction.....	265
	2. Experimental Section.....	267

	Reagents.....	267
	Synthesis.....	267
	Method A.....	267
	Method B.....	268
	X-ray Crystallography.....	268
	Elemental Analysis.....	270
	Differential Thermal Analysis.....	270
	Magnetic Measurements.....	271
3. Results and Discussion.....		278
	Structure.....	278
	Synthesis.....	287
	Magnetization Measurements.....	288
	LaAu ₂ In ₄	288
	CeAu ₂ In ₄	289
	PrAu ₂ In ₄	290
	NdAu ₂ In ₄	291
	Summary.....	295
4. Conclusions.....		296
Chapter 10	YbAu ₂ In ₄ A New Indium Rich Intermetallic Exhibiting a Novel	
	First Order Valence Transition.....	300
	1. Introduction.....	300
	2. Experimental Section.....	301
	Reagents.....	301
	Synthesis.....	302
	X-ray Crystallography.....	303
	Elemental Analysis.....	304
	Differential Thermal Analysis.....	307
	Magnetic Measurements.....	307
	3. Results and Discussion.....	308
	Structure.....	308
	Synthesis.....	312
	Magnetic Measurements.....	314
	4. Conclusions and Future Work.....	317
Chapter 11	Conclusions and Future Work.....	321

LIST OF TABLES

	Page
Table 2-1 Crystal data and structure refinement for $\text{RE}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE=Tb, Er).	22
Table 2-2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE = Tb and Er).	23
Table 2-3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE = Tb and Er).	24
Table 2-4 Bond lengths [$\text{\AA}$] for $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE = Tb and Er).	32
Table 3-1 Crystal data and structure refinement for $\beta\text{-SiB}_3$	46
Table 3-2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\beta\text{-SiB}_3$	47
Table 3-3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\beta\text{-SiB}_3$	47
Table 3-4 Bond lengths [$\text{\AA}$] for $\beta\text{-SiB}_3$	54
Table 3-5 Bond angles [deg] for $\beta\text{-SiB}_3$	55
Table 4-1 Crystal data and structure refinement for RENiSi_3 (RE=Tb, Dy). ...	73
Table 4-2 Crystal data and structure refinement for RENiSi_3 (RE = Ho, Er). ...	74
Table 4-3 Crystal data and structure refinement for RENiSi_3 (RE=Yb, Lu). ...	75
Table 4-4 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiSi_3 (RE = Tb, Dy, Ho, Er).	76

Table 4-5	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiSi_3 (RE = Yb and Lu).	77
Table 4-6	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiSi_3 (RE = Tb, Dy, Ho, Er).	79
Table 4-7	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiSi_3 (RE = Yb, Lu).	77
Table 4-8	Bond lengths [$\text{\AA}$] for RENiSi_3 (RE = Tb, Dy, Ho).	88
Table 4-9	Bond lengths [$\text{\AA}$] for RENiSi_3 (RE = Er, Yb, Lu).	86
Table 4-10	Polycrystalline magnetic data for RENiSi_3	88
Table 5-1	Crystal data and structure refinement for $\text{RE}_5\text{Co}_4\text{Si}_{14}$ (RE = Ho, Tm).	131
Table 5-2	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters $\text{\AA}^2 \times 10^3$ for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ and $\text{Ho}_5\text{Co}_4\text{Si}_{14}$	132
Table 5-3	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ and $\text{Ho}_5\text{Co}_4\text{Si}_{14}$	133
Table 5-4	Bond lengths [$\text{\AA}$] for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$	140
Table 5-5	Bond lengths [$\text{\AA}$] for $\text{Ho}_5\text{Co}_4\text{Si}_{14}$	141
Table 6-1	Crystal data and structure refinement for RENiGe_2 (RE=Dy, Er). ...	164
Table 6-2	Crystal data and structure refinement for RENiGe_2 (RE=Yb, Lu). ...	165
Table 6-3	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiGe_2 (RE =Dy, Er, Yb, Lu).	166

Table 6-4	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiGe_2 (RE = Dy, Er, Yb, Lu).	167
Table 6-5	Bond lengths [$\text{\AA}$] for RENiGe_2 (RE=Dy, Er, Yb, Lu).	172
Table 7-1	Crystal data and structure refinement for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE=La, Ce). .	195
Table 7-2	Crystal data and structure refinement for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE=Pr, Nd). .	196
Table 7-3	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = La, Ce).	197
Table 7-4	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = Pr, Nd).	198
Table 7-5	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = La, Ce).	199
Table 7-6	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = Pr, Nd).	200
Table 7-7	Bond distances ($\text{\AA}$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = La, Ce, Pr, Nd).	206
Table 8-1	Crystal data and structure refinement for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE=Dy, Ho).	233
Table 8-2	Crystal data and structure refinement for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE=Tm, Er).	234
Table 8-3	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Dy, Ho).	235
Table 8-4	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Er, Tm).	236

Table 8-5	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_4\text{Ni}_5\text{InGe}_4$ (RE = Dy, Ho).	237
Table 8-6	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Er and Tm).	238
Table 8-7	Bond lengths [$\text{\AA}$] for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Dy, Ho, Er, Tm).	245
Table 9-1	Crystal data and structure refinement for REAu_2In_4 (RE=La, Ce).	272
Table 9-2	Crystal data and structure refinement for REAu_2In_4 (RE=Pr, Nd).	273
Table 9-3	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for REAu_2In_4 (RE = La, Ce).	274
Table 9-4	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for REAu_2In_4 (RE = Pr, Nd).	275
Table 9-5	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for REAu_2In_4 (RE = La, Ce).	276
Table 9-6	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for REAu_2In_4 (RE = Pr, Nd).	277
Table 9-7	Bond distances ($\text{\AA}$) for REAu_2In_4 (RE = La, Ce, Pr, Nd).	282
Table 10-1	Crystal data and structure refinement for YbAu_2In_4	305
Table 10-2	Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for YbAu_2In_4	306
Table 10-3	Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for YbAu_2In_4	306

LIST OF FIGURES

		Page
Figure 2-1	View of the total structure of $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ as viewed along the ab plane diagonal axis.	30
Figure 2-2	((A) Coordination environment of Si(2) showing the 3 bonds to 3 separate B_{12} cages, 1 to B(4) and 2 to B(1). (B) Coordination environment around the C dimer showing the C atom bonding to 3 different B_{12} cages at B(2). (C) View of a layer of B_{12} cages showing their connectivity to the Si and carbon sub-lattices.	31
Figure 2-3	(A) Total density of states for $\text{La}_3\text{C}_2\text{Si}_8(\text{B}_{12})_3$. The region between 0.5 eV and the fermi level integrates to yield 3.2 electrons. (B) Solid State U.V. / Vis absorption spectrum for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ showing a band gap of 0.96 eV.	35
Figure 2-4	(A) Magnetic susceptibility for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ which shows no magnetic ordering and obeys Curie/Weiss law from 300 to ∞ K. (B) Magnetization curve for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$	37
Figure 2-5	(A) Magnetic susceptibility for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ which shows no magnetic ordering and obeys Curie/Weiss law from 300 to 2 K. (B) Magnetization curve for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$	38
Figure 3-1	(A) View of the Si chain which propagates along the a -axis. (B) View of a B_{12} layer as it is arranged in the ac plane. The connectivity results in a rectangular array of cages.	52
Figure 3-2	The overall view of $\beta\text{-SiB}_3$ as seen along the c -axis.	53
Figure 3-3	The band structure of $\beta\text{-SiB}_3$ showing an indirect band gap of 1.2 eV.	58
Figure 3-4	(A) The polycrystalline Raman spectrum of $\beta\text{-SiB}_3$. (B) A comparative plot of optical absorbance as a function of energy for α and $\beta\text{-SiB}_3$, the solid line is the spectrum of $\alpha\text{-SiB}_3$, which has a band gap of about 0.2 eV, the broken line is the spectrum of $\beta\text{-SiB}_3$, which has a band gap of 2.0 eV.	59

Figure 3-5	A comparative plot of the thermal gravimetric analysis (TGA) of α and β SiB_3 , the solid line is the TGA curve of α SiB_3 with an ignition point at about 600 °C. The broken line is β SiB_3 , which has no evident ignition point.	60
Figure 3-6	(A) Scanning electron micrograph of a β - SiB_3 single crystal before annealing. (B) Scanning electron micrograph of a β - SiB_3 single crystal after annealing under an ambient atmosphere at 700 °C for 24 hrs.	62
Figure 3-7	(A) Scanning electron micrograph of a β - SiB_3 single crystal before annealing. (B) Scanning electron micrograph of a β - SiB_3 single crystal after annealing under an ambient atmosphere at 1000 °C for 24 hrs.	63
Figure 4-1	SEM micrograph of a HoNiSi_3 single crystal.	81
Figure 4-2	(A) This is a depiction of the staggered pseudo square net that defines the rare earth sub lattice. (B) This is a representation of the NiSi_3 structure with the rare earth ions removed for clarity. This shows the si zig-zag chains and the NiSi_2 cages.	83
Figure 4-3	(A) A view of the Si zig-zag chains and their connectivity to the Ni atoms. (B) A portion of the NiSi_2 cages that are composed of disilicide bonds with capping by Ni atoms.	84
Figure 4-4	Coordination environment of the one crystallographically distinct rare earth ion.	85
Figure 4-5	(A) The susceptibility data for a polycrystalline sample of DyNiSi_3 . (B) The magnetization curve for a polycrystalline sample of DyNiSi_3 . This sample undergoes 2 meta-magnetic transitions at 25 and 45 kOe. (C) The susceptibility data for a polycrystalline sample of HoNiSi_3 . (D) The magnetization curve for a polycrystalline sample of HoNiSi_3	89

Figure 4-6	The magnetic susceptibility as a function of rotation angle about the basal plane, the data were collected at 5 K. The maxima and minima are located at 180° intervals.	91
Figure 4-7	(A) The molar susceptibility and inverse susceptibility for the <i>c</i> -axis of TbNiSi ₃ . (B) The magnetization curve for TbNiSi ₃ with the field parallel to the <i>c</i> -axis. (C) Susceptibility and inverse susceptibility for the <i>a</i> -axis of TbNiSi ₃ . (D) The magnetization curve for the <i>a</i> -axis of TbNiSi ₃ . (E) Magnetic susceptibility measurements performed along the <i>b</i> -axis of TbNiSi ₃ . (F) Magnetization curve for the field applied along the <i>b</i> -axis.	95
Figure 4-8	(A) The molar susceptibility and inverse susceptibility for the <i>c</i> -axis of DyNiSi ₃ . (B) The magnetization curve for the <i>c</i> -axis of DyNiSi ₃ . (C) The molar susceptibility and inverse susceptibility for the <i>a</i> -axis of DyNiSi ₃ . (D) Magnetization curve for <i>a</i> -axis of DyNiSi ₃ . (E) The molar susceptibility and inverse susceptibility for the basal plane diagonal for DyNiSi ₃ . (F) The magnetization curve of the basal plane diagonal of DyNiSi ₃	102
Figure 4-9	(A) The susceptibility and inverse susceptibility data collected with the applied field perpendicular to the basal plane. (B) The magnetization curve collected perpendicular to the basal plane.	103
Figure 4-10	(A) The molar susceptibility and inverse susceptibility for the <i>c</i> -axis of HoNiSi ₃ . (B) Magnetization data with the field oriented along the <i>c</i> -axis. (C) The molar susceptibility and inverse susceptibility for the <i>a</i> -axis of HoNiSi ₃ . (D) Magnetization curve for HoNiSi ₃ with the field oriented parallel to the <i>a</i> -axis.	106
Figure 4-11	(A) Molar susceptibility and inverse susceptibility for the <i>c</i> -axis of ErNiSi ₃ . (B) Magnetization curve with the field oriented parallel to the <i>c</i> -axis. (C) Molar susceptibility and inverse susceptibility for the <i>a</i> -axis of ErNiSi ₃ . (D) Magnetization curve with the field oriented with the <i>a</i> -axis parallel to the <i>a</i> -axis.	110

V

R

Fig

Fig

Fig

F

A

F

Figure 4-12	(A) Molar susceptibility and inverse susceptibility for the <i>c</i> -axis of YbNiSi ₃ . (B) Magnetization curve for YbNiSi ₃ with the field parallel to the <i>c</i> -axis. (C) Molar susceptibility and inverse susceptibility for the <i>a</i> -axis of YbNiSi ₃ . (D) Magnetization curve for YbNiSi ₃ with the field parallel to the <i>a</i> -axis.	113
Figure 4-13	Plot of the Néel temperature as a function of the de Gennes factor. Near linear behavior is expected for a metal as the magnitude of magnetic coupling in RKKY systems is proportional to the moment, of which the de Gennes factor is a measure.	116
Figure 5-1	Scanning electron micrograph of Tm ₅ Co ₄ Si ₁₄ crystal clusters. This figure shows the crystal habit and plate stack twinning typical of these compounds.	136
Figure 5-2	(A) View of a Co ₂ Si ₁₀ cage. (B) Structure of RE ₅ Co ₄ Si ₁₄ as viewed down the <i>a</i> -axis showing the interconnectivity of the Co ₂ Si ₁₀ cages in the <i>bc</i> plane. (C) View of the Si zig-zag chains which connect the cages along the <i>a</i> -axis rare earth atoms omitted for clarity.	138
Figure 5-3	The overall structure of RE ₅ Co ₄ Si ₁₄ as viewed down the <i>b</i> -axis.	139
Figure 5-4	(A) Coordination environment of Tm(1). (B) Coordination environment of Tm(2). (C) Coordination environment of Tm(3). ...	143
Figure 5-5	(A) Differential thermal analysis of Tm ₅ Co ₄ Si ₁₄ performed under vacuum, from room temperature to 1000 °C. (B) Thermal gravimetric analysis of Tm ₅ Co ₄ Si ₁₄ under flowing air.	144
Figure 5-6	(A) Scanning electron micrograph of Tm ₅ Co ₄ Si ₁₄ after annealing at 1000 °C in an ambient atmosphere for 24 hours. (B) Close up view of crystal face 1. (C) Close up view of crystal face 2.	146
Figure 5-7	(A) Magnetic susceptibility data for Ho ₅ Co ₄ Si ₁₄ . (B) Magnetization curve for Ho ₅ Co ₄ Si ₁₄ . (C) Magnetic susceptibility data for Er ₅ Co ₄ Si ₁₄ . (D) Magnetization curve for Er ₅ Co ₄ Si ₁₄	153

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure 5-8	(A) Magnetic susceptibility data for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$. (B) Magnetization curve for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$. (C) Magnetic susceptibility data for $\text{Yb}_5\text{Co}_4\text{Si}_{14}$. (D) Magnetization curve for $\text{Yb}_5\text{Co}_4\text{Si}_{14}$	154
Figure 6-1	The structure of $\beta\text{-RENiGe}_2$ as viewed down the a -axis. (B) The overall structure of $\alpha\text{-RENiGe}_2$ a perspective view along the a -axis.	170
Figure 6-2	(A) The structure of $\beta\text{-RENiGe}_2$ as viewed down the b -axis. (B) The structure of $\alpha\text{-RENiGe}_2$ as viewed along the c -axis. This figures helps illustrate the structural similarities between the α and β -forms.	171
Figure 6-3	Conceptual stepwise scheme for the interconversion of the $\beta\text{-RENiGe}_2$ structure to the α -form (CeNiSi_2 type structure). The shaded ovals after step (b) need to be rotated to break the Ge(3)-Ge(3) bond and form the PbO-type layer.	174
Figure 6-4	(A) Powder pattern of ErNiGe_2 after annealing without In, as it compares to the calculated pattern of $\beta\text{-ErNiGe}_2$. (B) Powder pattern of ErNiGe_2 after annealing in indium as it compares to the calculated pattern of $\alpha\text{-ErNiGe}_2$	178
Figure 6-5	(A) Total (DOS) for $\beta\text{-LuNiGe}_2$ (B) Ni d DOS for $\beta\text{-LuNiGe}_2$. (C) Lu(1) d and Lu(2) d DOS for $\beta\text{-LuNiGe}_2$. (D) Ge(1) s, Ge(2) s, and Ge(3) s DOS for $\beta\text{-LuNiGe}_2$. (E) LuNiGe ₂ . Ge(1) p , Ge(2) p , and Ge(3) p DOS for $\beta\text{-LuNiGe}_2$	180
Figure 6-6	(Magnetic susceptibility (χ_m and $1/\chi_m$) for $\beta\text{-DyNiGe}_2$. The inset shows the antiferromagnetic ordering at low temperatures. (B) Magnetization curve for $\beta\text{-DyNiGe}_2$ (C) Magnetic susceptibility (χ_m and $1/\chi_m$) for $\beta\text{-ErNiGe}_2$. The inset shows the antiferromagnetic ordering. (D) Magnetization curve for $\beta\text{-ErNiGe}_2$	183

Figure 7-1	(A) View of the pentagonal ZnGe_4 cages structure which extends in the ac plane and are similar to $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Si}_{1-x})\text{Al}_4\text{Si}_{6-y}$. (B) Perspective view of the Ge^{-1} fragment. (C) View of the ZnGe layer showing the PbO structure, which extend in the ac plane. The layer is similar to those in the ThCrSi_2 structure type.	204
Figure 7-2	Overall structure of $\text{RE}_2\text{Zn}_3\text{Ge}_6$ as viewed down the c -axis showing the interconnections between the two Zn/Ge layers along the b -axis.	205
Figure 7-3	(A) Initial heating for a mixture of La/Zn/Ge in the differential thermal analysis. There are 3 exothermic peaks in the first heating cycle at 360 °C, 530 °C, and 755 °C. The endotherm at 790 °C is thought to correspond to the reaction to form $\text{La}_2\text{Zn}_3\text{Ge}_6$, and the endothermic peak at 820 °C is its melting point. (B) The second heating cycle of the now reacted elements. The endotherm at 775 °C is the melting point of an impurity due to the incongruent melting of $\text{La}_2\text{Zn}_3\text{Ge}_6$ in the first heating cycle.	209
Figure 7-4	(A) The total Density of States (DOS) for $\text{La}_2\text{Zn}_3\text{Ge}_6$. The Inset shows a close up view illustrating the low DOS at the Fermi level characteristic of a semi-metal. (B) The DOS for the $\text{Zn } d$ electrons showing them well below the Fermi level. (C) The DOS for the $\text{Zn } s$ electrons distributed above and below the Fermi level. (D) The DOS for the $\text{La } d$ electrons showing them mainly above the fermi level.	212
Figure 7-5	(A) Sections of the band structure of $\text{La}_2\text{Zn}_3\text{Ge}_6$. It shows the semimetallic nature of the compound i.e. the negative band gap near the Γ point and elsewhere in the Brillouin zone. (B) The Brillouin zone for a face centered orthorhombic unit cell...	213
Figure 7-6	(A) Magnetic susceptibility data for $\text{Ce}_2\text{Zn}_3\text{Ge}_6$ collected from 2 to 300K in both field cooled and zero field cooled modes. (B) Magnetization curve for $\text{Ce}_2\text{Zn}_3\text{Ge}_6$ collected at 2 K.	217

Figure 7-7	(A) Magnetic susceptibility data for $\text{Pr}_2\text{Zn}_3\text{Ge}_6$. The data show an antiferromagnetic transition at 7K. (B) The magnetization curve for $\text{Pr}_2\text{Zn}_3\text{Ge}_6$. The data show a transition at 3.6 kOe, the μ_{sat} ($3.1\mu_{\text{B}}$) is approximately 65% of the calculated value of $4.8\mu_{\text{B}}$	218
Figure 7-8	(A) Magnetic susceptibility data for $\text{Nd}_2\text{Zn}_3\text{Ge}_6$ exhibiting antiferromagnetic ordering at 4 K and Curie/Weiss behavior above this temperature. (B) Magnetization curve for $\text{Nd}_2\text{Zn}_3\text{Ge}_6$ showing a transition at 8 kOe.	219
Figure 8-1	Overall structure of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ as viewed along the b -axis.	240
Figure 8-2	(A) The view of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ along the b -axis. (B) The view of $\beta\text{-RENiGe}_2$ as viewed along the a -axis and also along the b -axis. The light shaded circles in (A) and (B) view of $\beta\text{-RENiGe}_2$ show the Ni_2Ge_2 structure common to both phases. The darker circles show the Ge dimers common to both phases. (C) The view of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ along the ac plane diagonal. (D) The view of $\beta\text{-RENiGe}_2$ along the b -axis. The projections of the 2 structures in (C) and (D) show the similarity in the channels containing the rare earth ions.	241
Figure 8-3	The Ni-Ge(1) ribbon which runs along the b -axis.	243
Figure 8-4	(A) The coordination environment of $\text{RE}^{3+}(1)$ ion (B) The coordination environment of $\text{RE}^{3+}(2)$ ion.	244
Figure 8-5	(A) Susceptibility and inverse susceptibility data for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ collected with an applied field of 2000 Oe (B) Magnetization curve for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ collected at 2 K.	251
Figure 8-6	(A) Susceptibility and inverse susceptibility data for $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ collected with an applied field of 500 Oe. (B) Magnetization curve for $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ collected at 2K.	254

Fig.

F

Fig.

Figure

Figure

Figure

Fig

Figure 8-7	(A) Susceptibility and inverse susceptibility data for $\text{Er}_4\text{Ni}_2\text{InGe}_4$ collected with an applied field of 1000 Oe. (B) Magnetization data for $\text{Er}_4\text{Ni}_2\text{InGe}_4$ collected at 2 K.	255
Figure 8-8	(A) Susceptibility and inverse susceptibility for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$ collected with an applied field of 1000 Oe. (B) Magnetization curve for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$ collected at 2 K.	258
Figure 8-9	(A) The higher temperature susceptibility maximum as a function of the de Gennes factor. (B) The lower temperature susceptibility maximum as a function of the de Gennes factor.	262
Figure 9-1	Overall structure of REAu_2In_4 as viewed along the <i>b</i> -axis.	279
Figure 9-2	(A) REAu_2In_4 as viewed along the <i>b</i> axis. The Au atoms have been removed to show the In tetramers. (B) The coordination sphere of Au(1) out to 3.3 Å bond distances listed are for LaAu_2In_4 . (C) The coordination sphere of Au(2) out to 3.3 Å bond distances listed are for LaAu_2In_4 . (D) Segment of the Au_2In_4 polyanionic network as viewed along the <i>b</i> axis.	280
Figure 9-3	The coordination environment of the one crystallographically unique rare earth site in REAu_2In_4	281
Figure 9-4	(A) Wire frame structure of $\text{RE}_2\text{Au}_3\text{In}_4$ as viewed along the <i>c</i> -axis. Shaded regions highlight Au_2In_2 units. Look closely. See the frog? (B) Wire frame structure of $\text{RE}_2\text{Au}_3\text{In}_5$ as viewed along the <i>a</i> -axis showing the connectivity of the Au_2In_2 units. (C) Wire frame structure of REAu_2In_4 as viewed along the <i>b</i> -axis shading regions are the Au_2In_2 parallelograms which are interconnected by common Au atoms.	284

Figure 8

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure

Figure 9-5	(A) The overall crystal structure of UNi_5Ge_3 as viewed along the b -axis. (B) A view of the overall structure of LaAu_2In_4 along the b -axis. (C) The wire frame structure of UNi_5Ge_3 as viewed along the b -axis. The shaded regions are Ni_2Ge_2 parallelogram. (D) Wire frame structure of LaAu_2In_4 as viewed along the b -axis to compare the connectivity of the Au_2In_2 units of this structure to the Ni_2Ge_2 units.	286
Figure 9-6	Scanning electron micrograph of a LaAu_2In_4 crystal showing that the length of the needle is in excess of 2.5 mm.	288
Figure 9-7	Magnetic susceptibility data for LaAu_2In_4 . The diamagnetic response at high temperatures is indicative of semi-metallic behavior. The upturn in the data in the low temperature regions is likely due to a paramagnetic impurity.	286
Figure 9-8	(A) Magnetic susceptibility for CeAu_2In_4 collected with an applied field of 500 Oe. (B) Magnetization data for CeAu_2In_4 collected at 2 K.	292
Figure 9-9	(A) Magnetic susceptibility data for PrAu_2In_4 collected with an applied field of 2000 Oe. (B) Magnetization data for PrAu_2In_4 collected at 2 K.	293
Figure 9-10	(A) Magnetic susceptibility data for NdAu_2In_4 collected with an applied field of 2000 Oe. Magnetization curve for NdAu_2In_4 , data collected at 2 K.	294
Figure 10-1	The overall structure of YbAu_2In_4 as viewed along the b -axis.	309
Figure 10-2	(A) Coordination environment for Au(1) out to 3.5 Å. (B) Coordination environment for Au(2) out to 3.5 Å. (C) Coordination environment for Yb out to 4.0 Å. No atoms are shown that have bond distances longer than 3.5 Å as they are too long to be considered bonding.	311

Figure 10-3 Wire frame view of YbAu_2In_4 with shading of the Au_2In_2 parallelograms. YbAu_2In_4 is composed of edge sharing parallelograms propagating along the c axis and interconnected by corner sharing parallelograms in the a direction with common Au atoms. 313

Figure 10-4 (A) Magnetic susceptibility for YbAu_2In_4 showing the first order valence transition at 16 K. (B) The inverse susceptibility plot of YbAu_2In_4 for data below 16 K. (C) Magnetization curve for YbAu_2In_4 at 3 K displaying normal paramagnetic behavior. 312

LIST OF **ABBREVIATIONS**

CCD	Charge Couple Devise
SQUID	Superconducting Quantum I nterference Device
SEM	Scanning Electron Microsc o pe

Chapter 1

1-1 Introduction to Intermetallics and Their Selected Properties.

Intermetallic compounds play an indispensable role in modern technology, with broad applications in fields ranging from microelectronics, and biomedical materials to aerospace materials. Many of the intermetallics that find themselves in wide use are relatively simple binary compounds or solid solutions with a third component, or are otherwise doped to optimize properties. The method of physical property optimization of old systems can only be carried out for so long, and at some point the old material or method must be abandoned, and the investment of time and resources must be made to introduce new materials for next generation technology. This includes new refractory coatings and materials for power plants and propulsion systems to allow for greater efficiency. There is a need for superconducting materials that can both withstand high magnetic field fluxes and current densities, yet require liquid nitrogen as a cryogen instead of non-renewable helium. Materials exhibiting magnetoresistance for improved magnetic memory devices in order to further reduce the size and energy consumption of computer hard drives. New catalysts need to be developed for the electrochemical

processes required for fuel cells. This is but a short list of demands the world faces as technology advances, and the requirements for material performance increase. These new materials will come from the exploratory synthesis conducted at the basic research level. This research is an indispensable portion of the material science process, at the heart of which is an interdependence of engineering, physics, and of course chemistry.

Intermetallic compounds have been used since antiquity, but their systematic study was not really undertaken until the 1830's. It was during this time that the first scientific paper emerged on the topic, and it was not until 1900 that the first review of the state of research was undertaken.¹ Since that time this area of research has experienced explosive growth. To date literally tens of thousands of intermetallic compounds have been described adopting hundreds of different structure types.² Indeed the inorganic crystallographic data service (ICSD) lists over 2300 silicon containing intermetallics and over 2000 germanides.³ This research has been driven by the desire to discover new compounds whose chemical and physical properties are superior to the alloys that are currently in use in a broad range of applications.⁴ The other driving force is the basic curiosity to explore the reactivity of transition metals with main group metalloids such as Al, Ga, Si and Ge and electropositive elements like alkaline and rare earth metals.

Over the years this exploration has been greatly rewarded by the discovery of an unbelievably diverse structural collection of intermetallics. This structural diversity is matched only by the variety of physical properties these compounds have been found to

display. There is no better example in the intermetallic literature than the discovery of the superconducting boro-carbides,⁵ which have been hailed as a "Toy box for Physicists."⁶ These intriguing systems display a wide variety of physical phenomena, some of which were once thought to be mutually exclusive by the conventional superconductivity theory of Bardeen, Cooper and Schreiffer (BCS).⁷ Specifically, the coexistence of large magnetic moments, magnetic ordering and the superconducting state was thought impossible because the magnetic portion of the lattice would disrupt the formation of cooper pairs, the charge carriers in superconductors.⁸

The phenomenon of mixed and intermediate valence⁹ and the related heavy fermion¹⁰ and Kondo insulator behavior^{11,12} is another result of the investigation of intermetallic compounds containing rare earth elements such as Ce, Sm Tm and Yb. A great deal of work has focused on systems such as $\text{YbCu}_{2-x}\text{In}_x$ ¹³ and $\text{Ce}_3\text{Pt}_3\text{Bi}_4$ ¹⁴ to better understand the nature of interaction between the highly correlated f electrons of the rare earth ion and the s and d conduction electrons.

Also discovered in rare earth containing intermetallics is the rich magnetic behavior they display. Of particular interest is the exotic long range magnetic ordering that has been found. These diverse magnetic structures were first found by neutron diffraction of the rare earth metals themselves.¹⁵ And through the study of intermetallic compounds with lattice symmetries other than hexagonal, a generalized theory of magnetic interactions could be established that works for other symmetries and elemental

compositions as well. Systems of the type RETMGe_2 (RE is a late rare earth metal and TM is a second or third row transition metal) which adopt the body centered orthorhombic YIrGe_2 structure¹⁶ have been intensely studied. The work has focused on the magnetic structure of REIrGe_2 , REPtGe_2 , REPdGe_2 , which are very complex and include canted antiferromagnetism, and incommensurately modulated antiferromagnetism to name a few.¹⁷ Another example is the variety of behavior exhibited by the body centered tetragonal RETM_2Tt_2 , where RE is a late rare earth metal, TM is first row transition metal and Tt is either Si or Ge.^{18, 11}

Intermetallics containing elements such as Al and Si have been investigated intensively for applications in extreme environments such as structural components for turbines, heating elements, and coating to be used in pipes for electric power generating plants.¹⁹ A large portion of this research has centered on Ni_3Al , Fe_3Si , MoSi_2 .²⁰ These compounds have shown themselves to possess superior corrosion resistance as compared to the Ni based super alloys, which are found almost ubiquitously in aerospace applications. The Achilles heel of these intermetallics has always been the fact that they are very brittle especially at low temperatures.²¹ It is ironic that the very property that gives them the superior corrosion resistance, the strong amount of covalent bonding, is likely at the root of their inferior mechanical properties. Despite this, intense research continues with intermetallics to improve their mechanical properties while preserving the chemical properties²² and to explore new systems.²³

It has only been through the meticulous exploratory synthesis of these systems and the concomitant property evaluations that these discoveries have been made. New products have been brought to market because of this research, and it is in the spirit of this tradition that this work is presented. In this dissertation I will present the extension of the work started by the Kanatzidis, Jitschko and Stucky groups who have begun using molten metal reaction techniques to grow new and complex intermetallic and Zintl phases. The Literature concerning this will be reviewed in the following section.

1-2 The Use of Liquid Al Ga and In for the Exploratory Synthesis of Rare Earth Transition Metal and Tantalum Containing Intermetallics.

Inspection of the physical properties of the reactants involved in intermetallic compounds specifically the melting points reveals that transition metals melt between 960 °C for Ag and 3422 °C for W with the exception of Zn, Cd and Hg. Rare earth metals with the exception of Yb, Ce, Pr, La and Eu melt in excess of 1000°C. In the main group elements the melting points are even higher. For example Si and B melt at 1414 °C and 2075 °C respectively. It is well understood that many solid state reactions are diffusion limited.²⁴ This means for reactions to take place at a reasonable rate the reactants need to be highly mobile, which generally means molten. With the melting points listed above one can see that this is a hard proposition, and will generally require

specialized equipment and techniques such as melting by arc welding or reactions carried out in a radio frequency induction furnace. Molten metals that dissolve elements such as those listed above allow them to be highly mobile at much lower temperatures. Using lower temperatures can allow for the trapping of kinetically stable phases that cannot be formed in higher temperature reactions. These products may be stable in the flux, but could not otherwise be formed in its absence either by virtue of these temperature or the chemical environment that is provided by the melt.

The use of molten metals has also been shown to greatly facilitate the growth of high quality single crystals. This rarely happens when arc melting and induction furnaces are used to carry out the reaction because they involve rapid cooling conditions, which are generally not conducive to crystal growth. The enhanced crystal growth is due to the solvent like properties provided by the excess molten metal. These metal solutions behave in much the same way as any conventional solvent would. That is when the solution becomes saturated the product begins to crystallize in the melt. The size and quality of the crystals is dependent on the kinetics of crystal growth and conditions used. The availability of single crystals greatly aids structural elucidation and the determination of physical properties, especially if they are anisotropic in nature.

Over the course of the past few years several research groups have undertaken the investigation of the reactivity of rare earth (RE) and transition metals TM with and without Si or Ge in liquid aluminum to produce ternary and quaternary phases of the type

RE/TM/Al²⁵ or RE/TM/Al/Si or Ge.²⁶ These studies have produced dozens of new compounds as well as new structure types.²⁷ In addition the chemistry that has emerged from this work is fairly remarkable. It has been shown that molten Al, when used as a reactive flux, can reduce rare earth oxides to the metallic form making it possible to use these oxides as starting materials to produce compounds of the type RE/TM/Al/Si or Ge.²⁸ It has even been shown recently, that stable oxides such as perovskites can be used as starting materials to yield fully reduced intermetallics containing the corresponding alkaline earth metal and early transition metal.²⁹

This research served two basic purposes; first and most importantly from a chemical standpoint, was to explore what products could be obtained by combining electropositive rare earth metals with relatively highly electronegative transition metals and main group metalloids like Si and Ge in a molten aluminum matrix. The other variable that was tested was the effect of using drastically reduced temperatures in the synthesis of intermetallics. The molten Al reactions were generally run below 1000 °C (melting point of Al is 660 °C). This is a fraction of the temperature generally used to synthesize intermetallics, which are typically carried out at temperatures in excess of 2000 °C to 3500 °C. The second purpose of this research was to determine the kinds of intermetallic phases that form in an aluminum matrix when small amounts of metals are added to increase tensile strength.³⁰ Often small amount of Mg and Si are added to elemental Al in order to harden it.

Given the tremendous success of this research the concept was extended to Ga.

Ga possesses many of the same properties that makes Al attractive for use as a reaction medium. Specifically its low melting point of 29 °C and its high boiling point which is in excess of 2200 °C. It also has the ability to dissolve both Ge and Si without forming binary phases, and its ability to dissolve a host of other transition and rare earth metals.³¹ The products from these reactions are easily isolable by a combination of mechanical and chemical means. Ga is however unique from Al in that its reducing power is much lower than that of Al and so reaction run with rare earth oxides do not form reduced intermetallics as they do with Al.³² Secondly, it has been found that quaternary phases of the type RE/TM/Ga/Si do not form readily. Instead reactions of this type carried out in molten Ga generally form ternary phases, as in the case of RENiSi_3 ($\text{RE} = \text{Sm}$ and Y)³³ and $\text{RE}_2\text{Ni}_{3+x}\text{Si}_{5-x}$ ($\text{RE} = \text{Sm}, \text{Gd}, \text{Tb}$).³⁴ There has not been a reported instance of the exclusion of Al from the final products of RE/TM/Ge or Si when it is used as a flux. Ga on the other hand readily plays the part of a non-reactive medium and is in these cases acting like a conventional solvent.

Others have used Ga to grow large single crystals for the characterization of clathrates and Zintl phases.³⁵ Molten Ga has also recently found a new role as a medium in which to grow highly ordered nanotubes of silica.³⁶ Prior to these reports and those cited above Ga was used mainly as a means of crystal growth.³⁷

In this present work these concepts are expanded upon to include B in the reactions. The focus of this work is to generate new B/Si containing intermetallic phases by molten metal synthesis. The idea being to explore the heavier analogs of the RE/TM/C/B systems, specifically $\text{RETM}_2\text{C}_2\text{B}$ which display superconductivity. Also B containing compounds have seen resurgence in interest due to the discovery of superconductivity in MgB_2 .³⁸ Ga is an ideal choice for this work, as both B and Si are soluble in it and do not form binary phases, and as was mentioned previously, Ga/Si containing phases are difficult to form and so competing phases of this type are not anticipated. There are quite a few examples of B rich Si containing compounds in the literature, but many of them have been produced by direct combination reactions and include: $\text{REB}_{41}\text{Si}_{1.2}$ (RE=Y, Tb), $\text{Sc}_{0.83-x}\text{B}_{10.0-y}\text{C}_{0.17+y}\text{Si}_{0.083-z}$,³⁹ SiB_4 and SiB_6 ⁴⁰ to name a few. There has been extensive work on the growth of single crystals of borides from molten Al⁴¹ solutions and to a lesser extent Cu⁴² and Sn.⁴³ The bulk of this work concentrates on the growth of known thermodynamic phases for structural or advanced property characterization, and little has been done to use flux methods for exploratory synthesis.

The other part of this research will focus on growth of ternary phases such as RE/TM/Si from molten Ga. Si containing intermetallics are a technologically important class of compounds and exploration into these systems is worthwhile if only to explore the chemistry of these systems.

The final portion of this work will include the use of indium as a molten metal reaction medium. This is also a logical extension of the work done using Al and Ga, as In has many of the same physical and chemical properties that make them attractive for use in exploratory synthesis, which are again the low melting point of 156 °C, and its ability to dissolve Ge and Si and a host of transition and rare earth metals. As was the case with Al and Ga, In does not form binary phases with Ge or Si so it can dissolve the Si and Ge into the flux making them highly reactive at temperatures far below their melting points. The objective of this study was to explore the heavier analogs of the RE/TM/Al/Si or Ge and the RE/TM/Ga/ Ge or Si (RE is a rare earth metal and TM is a first row transition metal). As stated previously, the reactions carried out in Al always formed quaternary phases of the type RE/TM/Al/Si or Ge while reactions carried out in Ga, quaternary phases containing RE/TM/Ga/Si formed only reluctantly, though quaternary phases like RE/TM/Ga/Ge formed with few exceptions.⁴⁴ We predict that the same trend will be continued with indium in that RE/TM/In/Ge phases will be very difficult to form. A thorough search of the literature found no reports of quaternary phases of the type RE/TM/In/Ge, though many papers have been published where indium has been used as a flux to grow large single crystals of the type RE/TM/Ge.⁴⁵ Often in these cases the phases that were grown were known stable phases that could be produced by arc welding or heating with a radio frequency induction furnace, and then simply recrystallized in the melt. In addition there are very few reports of the use of In as a

medium to conduct exploratory synthesis, and in these cases report ternary compounds such as RE/TM/In (TM is a late transition metal).⁴⁶

Whenever one is faced with a situation where there is little to no literature precedence in an area of research one must consider two possibilities. First, is this truly an unexplored phase space? Or is it a fact that phases simply do not form when these particular elements are combined. If indeed quaternary phases of the type RE/TM/In/Ge do not form, the fact that these reactions will be run at a fraction of the temperature usually used for these systems may stabilize kinetically stable ternary phases that could not be formed otherwise. This work intends to explore these possibilities and to expand the use of In as a medium for the synthesis of intermetallic compounds.

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Chapter 2

$\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE = Tb, Er) Synthesis and Characterization of New

Boron Rich Phases Grown from Ga Flux.

2-1 Introduction.

Aluminum, gallium and indium fluxes provide a substantial advantage in the exploratory synthesis of a large class of both quaternary and ternary silicides and germanides.¹ We have demonstrated that flux chemistry is a powerful tool for the stabilization of complex aluminum/silicide intermetallic phases of the type RE/M/Si/Al where RE is La–Yb and M is a transition metal.² Complex intermetallics can have useful properties such as exceptionally high melting points, hardness, chemical inertness, and high temperature thermoelectric energy conversion to name a few.^{3,4} In an attempt to extend this chemistry into the RE/M/Si/B systems, as lighter analogs of the Al-based compounds, we have explored the use of liquid gallium in the synthesis of complex silicon borides. We selected gallium because our studies of the RE/Ni/Si/Ga showed that it was exceptionally difficult to form corresponding quaternary phases.⁵ Therefore competing phases of this type were not expected. Liquid Ga may be an ideal solvent for

such systems because it has a low melting point of 29.6 °C, and does not react with silicon or boron, though both are soluble in it especially at elevated temperatures. The solubility of the elements results in highly reactive boron and silicon dissolved in the flux.⁶

In this chapter we describe the discovery of $\text{RE}_{3-x}\text{Si}_8\text{C}_2(\text{B}_{12})_3$ ($x = 1.2$ and $\text{RE} = \text{Tb}$ and Er), which was initially found as a minor phase of a reaction between Tb, B, Ni, and Si in a 1:6:1:1 mole ratio respectively with a 10 fold mole excess of gallium. Similar reactions with early rare earth metals, B, Ni, Si in a 1:6:1:1 ratio with a 10 fold excess of gallium yielded mainly REB_6 , REB_{12} , re-crystallized silicon and $\text{Ni}_5\text{Ga}_3\text{Si}_2$.⁷ Quaternary boron-rich systems are quite rare; a thorough review of the literature reveals but a handful reported having compositions such as: $\text{REB}_{22}\text{C}_2\text{N}$ with $\text{RE} = \text{Y}$, Ho, Er, Tm, and Lu, and $\text{CrSi}_3(\text{B}_{12})\text{Se}_{12}(\text{B}_2\text{Se}_3)_{1.33}$.⁸

2-2 Experimental Section.

Reagents:

All reagents were used as received without further purification: Boron (sub-micron amorphous 99.9 % Aldrich, Milwaukee, WI) Silicon (~500 mesh amorphous 99.999% Cerac, Milwaukee, WI), Carbon (submicron graphitic 99.5% Fischer Scientific, Danvers, MA), Tb metal(50 mesh 99.9% Cerac, Milwaukee, WI), Ga metal (3-5 m shot

99.999% plasmaterials, Livermore, CA) and Er metal (powder ground from an ingot 99.9% Chinese rare earth information center Inner Mongolia China).

Synthesis:

1.80 mmol B, 0.4 mmol Si, 0.2 mmol C, 0.09 mmol rare earth metal, and 21 mmol Ga metal were combined in an Al_2O_3 crucible which was flame sealed in a fused silica tube under a vacuum of 7.0×10^{-5} mbar. The materials were heated to 1000°C over 12 h, held at 1000°C for 96 h, and then cooled to 500°C over 60 h. The final reaction product was isolated by a warm centrifugation to remove excess gallium, and further isolation was effected by etching with a 5 M I_2 dimethylformamide solution. Total yield after isolation was generally 90% with approximately 80% purity.

X-ray crystallography:

Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART CCD diffractometer with graphite monochromatized Mo $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Unit cell refinement and data merging were done with the SAINT program, and an empirical absorption correction was applied using the program SADABS.⁹ The original cell for the Tb analog determined by SMART was the rhombohedral P cell with lattice parameters $a = 8.001 \text{ \AA}$ and $\alpha = 78.46^\circ$. This cell was converted to the rhombohedral R centered cell with the hexagonal lattice parameters $a =$

10.1203 Å and $c = 16.339$ Å. After the empirical absorption correction was applied the space group was determined using XPREP. The systematic absences yielded 5 possible space groups: $R\bar{3}$, $R3$, $R\bar{3}m$, $R32$, and $R\bar{3}m$, all of which had comparable combined figures of merit. The mean value of $|E^2 - 1|$ was 0.881 indicating that the structure was likely centrosymmetric. The only choices of space groups with centers of symmetry were $R\bar{3}$ and $R\bar{3}m$. The higher symmetry $R\bar{3}m$ was chosen, and proved to be correct upon refinement of the final structure. The structure for $Tb_{3-x}C_2Si_8(B_{12})_3$ was solved by direct methods using SHELXS, and the final structure was refined using SHELXL. The data collection and refinement details for $Tb_{3-x}C_2Si_8(B_{12})_3$, and $Er_{3-x}C_2Si_8(B_{12})_3$ can be found in Table 2-1. The structural solution for $Er_{3-x}C_2Si_8(B_{12})_3$ was obtained by using the Tb analog solution as a starting point. During the structural refinement process R values below 20% could not be obtained, and high residual electron density persisted until the occupancies of each of the atoms was refined. The occupancy of the rare earth site refined to approximately 60%. The rest of the sites refined to full occupancy, with the exception of the C site (Wyckoff position 6c), which was originally thought to be a Si atom, this site refined to about 50% occupancy when this assignment was made. Inspection of bond distances and coordination environment led to the conclusion that the site was occupied by carbon, and then refined to full occupancy. The resulting stoichiometry for these two analogs after the vacancy at the rare-earth site is taken into consideration is $RE_{1.8}C_2Si_8(B_{12})_3$.

Phase identity and purity of products were determined by powder x-ray diffraction, which was carried out on an Inel diffractometer using Cu K α radiation. Experimental powder patterns were compared to patterns calculated from the structural refinement using the Cerius² modeling software.

Elemental Analysis:

Electron microprobe energy dispersive spectroscopy (EDS) was performed on several crystals of the compounds and indicated that boron silicon and the rare earth were present in the black trigonal anti-prismatic crystals. Data were collected using 20KV accelerating voltages and 120 s acquisition times. The ratio of terbium to silicon was 1 to 4. EDS data were also acquired at a low accelerating voltage of 8 kV and high magnification of 2500X to quantify boron and carbon. High magnification was used to ensure exclusion of carbon tape. It was found that boron and carbon were present in an approximate ratio of 17 to 1, which is in good agreement with the expected ratio of 18 to 1. EDS analyses were performed with a JEOL JSM-35C scanning electron microscope equipped with a Noran Vantage energy dispersive spectrometer with a (Si:Li) detector and NorvarTM window suitable for the standardless quantitation of light elements (Z $\geq$ 4).

Table 2-1. Crystal data and structure refinement for $RE_{1.8}C_2Si_8(B_{12})_3$ (RE=Tb, Er).

	Tb _{1.8} C ₂ Si ₈ (B ₁₂) ₃	Er _{1.8} C ₂ Si ₈ (B ₁₂) ₃
Formula	Tb _{1.8} C ₂ Si ₈ (B ₁₂) ₃	Er _{1.8} C ₂ Si ₈ (B ₁₂) ₃
Formula weight	925.00	940.03
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Rhombohedral	Rhombohedral
Space group	R -3m (#166)	R -3m (#166)
Unit cell dimensions	a = 10.1203(14) Å	a = 10.0994(9) Å
	b = 10.1203(14) Å	b = 10.0994(9) Å
	c = 16.399(3) Å	c = 16.354(2) Å
	1454.6(3) Å ³	1444.6(3) Å ³
Volume	1454.6(3) Å ³	1444.6(3) Å ³
Z, Density(calculated)	3, 3.168 g/cm ³	3, 3.230 g/cm ³
Absorption coefficient	7.049 mm ⁻¹	8.250 mm ⁻¹
F(000)	1264	1276
Theta range for data collection	2.64 to 27.22°.	2.64 to 27.03°.
Index ranges	-13<=h<=11	-12<=h<=12
	-13<=k<=13	-11<=k<12
	-13<=l<=21	-20<=l<=20
Reflections collected / unique	3967 / 431	3807 / 413
R(int)	0.0250	0.0351
Completeness to θ_{max}	100 %	100%
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	431 / 0 / 49	413 / 0 / 49
Goodness-of-fit on F ²	1.296	1.135
Final R indices [I>2 σ (I)]	R1 = 0.0252,	R1 = 0.0210
	wR2 = 0.0587	wR2 = 0.0523
R indices (all data)	R1 = 0.0259,	R1 = 0.0236
	wR2 = 0.0590	wR2 = 0.0531
Extinction coefficient	0.00031(18)	0.0047(3)
Largest diff. peak and hole	0.924 / -1.44 e/Å ³	0.773 / -0.724 e/Å ³

$$R1 = \frac{\sum |F_o|}{\sum |F_c|} \text{ and } wR2 = \left[\frac{\sum (F_o^2 - F_c^2)^2}{\sum (w F_o^2)^2} \right]^{1/2}$$

Table 2-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE = Tb and Er).

Atom	Wyckoff Position	x	y	z	U(eq)*
Tb	9e	5/6	1/6	1/6	14(1)
Si(1)	18h	0	0	710(1)	12(1)
Si(2)	6c	1305(1)	2611(2)	1063(1)	13(1)
C	6c	1/3	2/3	1153(5)	9(2)
B(1)	36i	6278(4)	-322(4)	516(2)	11(1)
B(2)	18h	4265(3)	5735(3)	661(3)	14(1)
B(3)	36i	6701(4)	1594(4)	299(2)	12(1)
B(4)	18h	5235(3)	469(6)	1028(3)	11(1)
Er	9e	5/6	1/6	1/6	12(1)
Si(2)	18h	1301(1)	2602(2)	1066(1)	10(1)
Si(1)	6c	0	0	712(1)	9(1)
C(1)	6c	1/3	2/3	1147(4)	4(1)
B(1)	36i	6281(4)	-323(4)	521(2)	8(1)
B(2)	18h	4268(3)	5732(3)	661(3)	10(1)
B(3)	36i	6700(4)	1593(4)	300(2)	8(1)
B(4)	18h	5236(3)	472(6)	1029(3)	8(1)

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

Table 2-3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE = Tb and Er).

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Tb	14(1)	14(1)	13(1)	1(1)	-1(1)	6(1)
Si(1)	13(1)	13(1)	12(1)	0	0	6(1)
Si(2)	14(1)	13(1)	12(1)	0(1)	0(1)	6(1)
C	9(2)	9(2)	8(4)	0	0	4(1)
B(1)	10(2)	10(2)	12(2)	-1(1)	-1(1)	5(2)
B(2)	14(2)	14(2)	15(2)	-1(1)	1(1)	7(2)
B(3)	9(2)	11(2)	14(2)	0(1)	1(1)	5(1)
B(4)	10(2)	12(3)	11(2)	0(2)	0(1)	6(1)
Er	13(1)	13(1)	9(1)	2(1)	-2(1)	5(1)
Si(2)	11(1)	10(1)	9(1)	0(1)	0(1)	5(1)
Si(1)	10(1)	10(1)	6(1)	0	0	5(1)
C	4(2)	4(2)	4(3)	0	0	2(1)
B(1)	6(2)	8(2)	9(2)	-1(1)	0(1)	2(1)
B(2)	9(2)	9(2)	10(2)	0(1)	0(1)	2(2)
B(3)	7(2)	7(2)	8(2)	-1(1)	0(1)	3(1)
B(4)	8(2)	8(2)	9(2)	-2(2)	-1(1)	4(1)

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.V.-Vis. Spectroscopy:

Spectroscopic data for $\text{Tb}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ were collected on a Shimadzu UV-3101 scanning UV-Vis. Spectrophotometer, equipped with solid state sample measurement geometry. The measurements were made in reflectance mode with BaSO_4 as the standard reference. The reflectance signal was converted to absorption using the Kubelka-Munk equation.

Magnetic Measurements:

Magnetic measurements were made on hand selected single crystals of $\text{RE}_3\text{-}_x\text{C}_2\text{Si}_8(\text{B}_{12})_3$ ($\text{RE} = \text{Tb}$ and Er), which were placed in an envelop of Kapton tape. Temperature dependant susceptibility measurements were made in both the field cooled and zero field cooled modes with an applied field of 500 Oe between 2 and 300 K. Magnetization data were collected at 5K with field sweeps from - 55 kOe to 55 kOe. All measurements were performed on a Quantum Design MPMS SQUID magnetometer.

Band Structure Calculations:

Band structure calculations were performed on the hypothetical compound $\text{La}_3\text{C}_2\text{Si}_8(\text{B}_{12})_3$ using the self-consistent full-potential linearized augmented plane wave method (LAPW)¹⁰ within density functional theory (DFT) with a generalized gradient approximation (GGA) for the exchange and correlation potential within the Perdew-

Burke-Emzerhof model.¹¹ Scalar relativistic corrections were *added and spin-orbit interactions* (SOI) were incorporated using a second variational procedure.¹² *The calculations* were performed with the WIEN97 program.¹³ Self-consistent iterations *were performed* with 27 k points in the reduced Brillouin zone with a cutoff between valence and core *states* of -6.0 Ry; convergence was assumed when the total energy difference *between cycle* was within 0.0001 Ry. These calculations were performed on the fully occupied La analog due to the inability of DFT to accurately model the highly correlated *f electrons*, and because vacancies are very difficult to model without introducing large *super cells*, which considerably increase calculation time.

2-3 Results and Discussion.

Synthesis:

The initial formation of $\text{RE}_{1.8}\text{Si}_8\text{C}_2(\text{B}_{12})_3$ was truly surprising since we started with a *quinary* system of boron, gallium, silicon, terbium and nickel; yet both the Ni and Ga were excluded from the final product despite the large excess of Ga. Adventitious carbon *on the other hand*, presumably present in one of the starting materials (most likely Ni or B), was *drawn* into the structure to stabilize the new quaternary boron-rich compound. $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ could only be produced by reactions carried out in Ga flux. Several *unsuccessful* attempts to make them by direct combination of the elements were made. The direct *combination* reactions were carried out by arc melt alloying and by heating in

a radio frequency (rf) induction furnace. The reactions carried out in the rf furnace failed to attain a sufficient temperature to react as the products consisted mainly of unreacted boron and a rare earth / Si binary phase. Reactions were run at a variety of time scales ranging from 5 minutes to several hours. Tanaka et. al. report the existence of a compound closely related to $\text{RE}_{1.8}\text{Si}_8\text{C}_2(\text{B}_{12})_3$. In their report the site we assign as carbon was claimed to be partially occupied Si.¹⁴ The compounds $\text{RE}_{3-x}\text{Si}_{10-y}\text{B}_{36}$ (RE = Tb-Lu) were produced by a direct combination of the elements, and grown as ingots using an induction furnace. We have up to this point been unable to reproduce these results.

Reactions carried out by arc welding phase separated forming mainly recrystallized Si and REB_{12} , and a small amount of rhombohedral SiB_3 . There was no evidence for the formation of $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ as determined by powder x-ray diffraction. Annealing of the arc welded pellets for a week at 1000 °C also did not form the target phase. Reactions carried out by combining the reactants in their stoichiometric ratios, and heating to 1000 °C for one week likewise yielded unreacted B and a small amount of rare earth / Si binary phase.

Inspection of the Ga/Si, and Ga/B binary phase diagrams show that no binary phases are expected for these components. On the other hand, the Tb/Ga, Si/B, and Tb/Si phase diagrams have rather rich chemistry and form several intermetallic phases each. It is a testament to the stability of $\text{RE}_{1.8}\text{Si}_8\text{C}_2(\text{B}_{12})_3$ that it forms at all, given the number of other phases which can form.

Structure:

The compounds $\text{RE}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ ($\text{RE} = \text{Tb}$ and Er) presented here represent a new structure type, and is shown in Figure 2-1. There are three salient building blocks to this structure: first the B_{12} icosahedral cages themselves, second a Si_8 ethane-like cluster, and third their mode of connectivity. There are four crystallographically distinct boron atoms all of which are contained in the B_{12} cluster. The B_{12} cluster itself is distorted from the ideal, and has boron-boron bond distances that range from 1.785(7) Å to 1.831(8) Å for the Tb analog, and 1.781(5) Å to 1.826(5) Å for the Er analog, with the average bond distance being 1.803 Å for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ and 1.807 Å for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$. These are reasonable distances for the electron deficient bonding found in the B_{12} icosahedron. The structure contains two crystallographically distinct silicon atoms. The eight Si atoms are clustered together to define a staggered ethane-like configuration with a central Si(1)-Si(1) bond of 2.329(5) Å for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ and 2.328(4) Å for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$. Each Si(1) atom is bound to three Si(2) atoms, at 2.360(2) Å for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ and 2.3486(14) Å for the Er analog. The Si(2) atom then forms three bonds to B_{12} clusters. The Si(1) tetrahedral structure is compressed along the Si(1)-Si(1) bond axis resulting in Si(2)-Si(1)-Si(2) bond angles of 114.25(2)° for the Tb compound and 114.12(4)° for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$, which deviates from the ideal tetrahedral angle of 109.5°. The remaining Si(2) bonds are to boron atoms of three separate B_{12} cages at B(1) and B(4) Figure 2-2(A). The carbon atom also forms C-C bonds to a symmetry equivalent atom

resulting in a C-C bond of 1.695(1) Å for the Tb analog and 1.700(14) Å for Er, with a similarly compressed staggered ethane unit with sp^3 hybridization. The carbon atom forms an additional 3 bonds at 1.822(7) Å to three separate boron cages at B(2) with a B(2)-C-C bond angle of 115.5(2)° for $Tb_{1.8}C_2Si_8(B_{12})_3$ and a B-C distance of 1.818(6) Å and B(2)-C-C bond angle of 115.9(2)° for $Er_{1.8}C_2Si_8(B_{12})_3$, Figure 2-2(B). The B_{12} cages are linked to each other through symmetry generated B(3)-B(3) bonds at a distance of 1.726(8) Å for the Tb compound and 1.724(7) for Er, and are arranged in a trigonal layer extending over the *ab* plane, Figure 2-2(C). The one crystallographically distinct Tb site refined to 60% occupancy, which is in good agreement with the measured atomic ratios from EDS. The Tb ion is situated on a 3d Wyckoff site, and is coordinated by 4 Si(2) atoms at 2.8400(7) Å for the Tb analog and 2.8302(7) for Er, 2 Si(1) atoms at 3.315 Å and 3.3075(10) for $Tb_{3-x}C_2Si_8(B_{12})_3$ and $Er_{3-x}C_2Si_8(B_{12})_3$ respectively, and 12 boron atoms with distances between 2.764(4) Å and 2.930(4) Å for $Tb_{3-x}C_2Si_8(B_{12})_3$ and between 2.757(3) and 3.038(5) for $Er_{3-x}C_2Si_8(B_{12})_3$. A complete list of bond distances can be found in Table 2-4.

The structure presented here while unique is similar to other boron rich compounds such as B_6P .¹⁵ B_6P is composed of a phosphorus dimer, which in turn is bound to 6 B_{12} cages again in a staggered ethane configuration. This arrangement is closely related to the Si_8 cluster of $RE_{3-x}C_2Si_8(B_{12})_3$ though there is a larger degree of homo-atomic Si bonding in the title compound. Additionally the carbon dimer, which

forms bonds to 6 B_{12} cages, is reminiscent of rhombohedral elemental boron. The connectivity of the B_{12} cages in both B_6P and rhombohedral boron are similar in that they interconnect along the c axis in order to form connectivity along this axis though they are in fact isolated from one another in the ab plane. The title compounds on the other hand have B_{12} cage connectivity exclusively in the ab plane where they form a trigonal array around the carbon atom and are isolated from one another along the c axis where their bonding is via the Si_8 clusters.

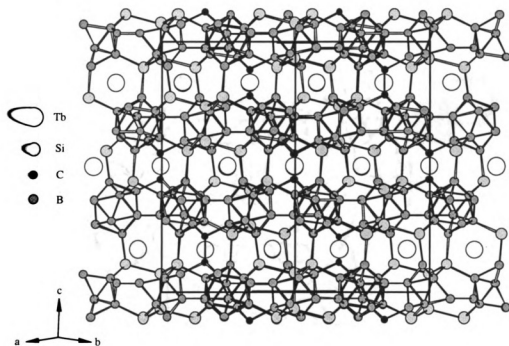


Figure 2-1 View of the total structure of $RE_{1.5}C_2Si_8(B_{12})_3$ as viewed along the ab plane diagonal axis.

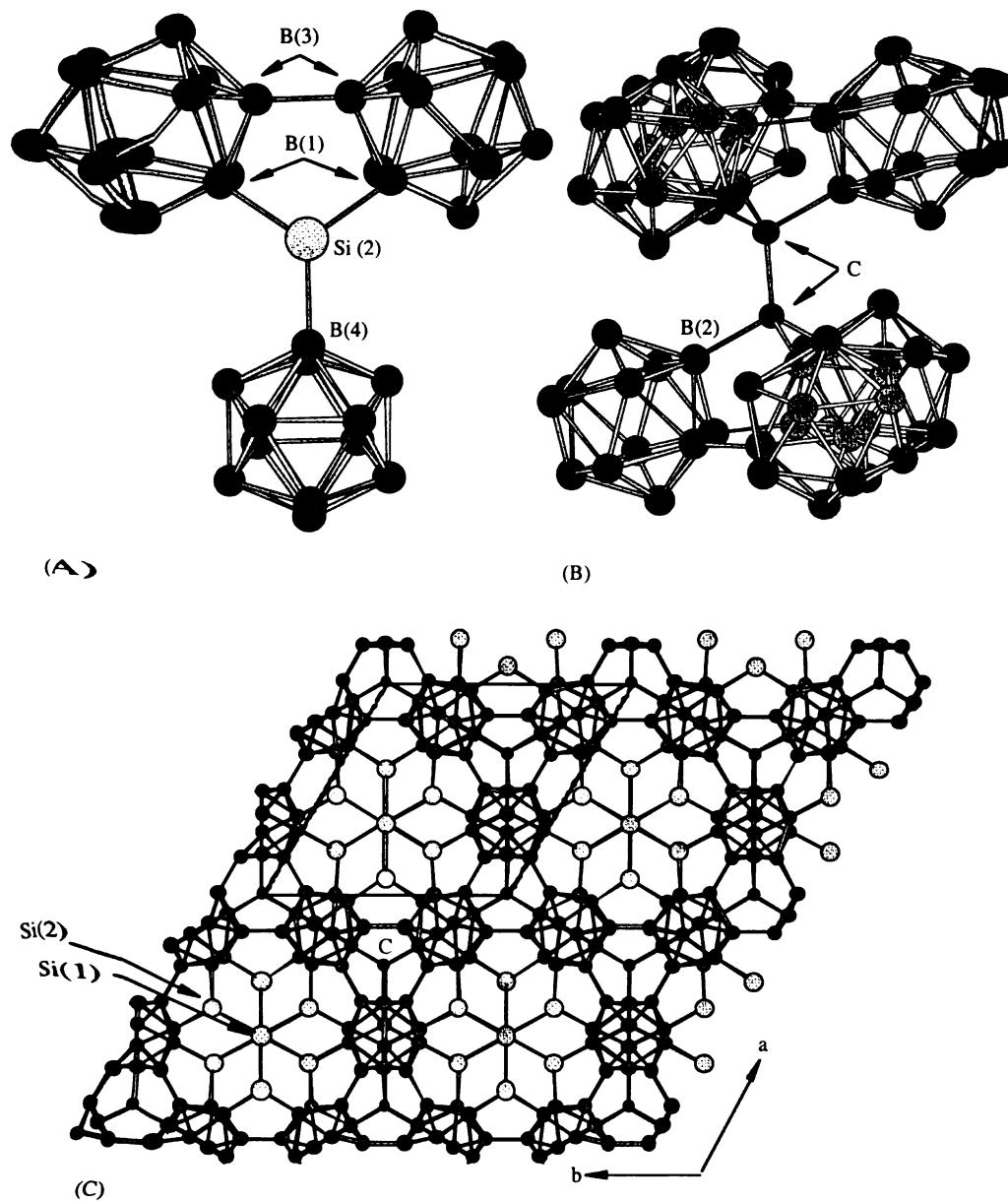


Figure 2-2 (A) Coordination environment of Si(2) showing the 3 bonds to 3 separate B₁₂ cages, 1 to B(4) and 2 to B(1). (B) Coordination environment around the C dimer showing the C atom bonding to 3 different B₁₂ cages at B(2). (C) View of a layer of B₁₂ cages showing their connectivity to the Si and carbon sub-lattices.

Table 2-4 Bond lengths [Å] for $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ (RE = Tb and Er).

	Tb	Er	
Tb(1)-B(3)	2.764(4)	2.757(3)	x4
Tb(1)-B(1)	2.784(4)	2.771(3)	x4
Tb(1)-Si(2)	2.8400(7)	2.8302(7)	x4
Tb(1)-B(4)	2.932(3)	3.038(5)	
Si(1)-Si(1)	2.329(5)	2.328(4)	
Si(1)-Si(2)	2.3601(16)	2.3486(14)	x3
Si(1)-Tb(1)	3.3159(12)	3.3075(10)	x2
Si(2)-B(1)	2.044(4)	2.039(3)	x2
Si(2)-B(4)	2.049(5)	2.038(5)	
B(1)-B(1)	1.785(7)	1.795(7)	
B(1)-B(2)	1.786(5)	1.781(5)	x2
B(1)-B(3)	1.800(5)	1.798(5)	
B(1)-B(4)	1.818(5)	1.816(4)	
B(1)-B(3)	1.823(5)	1.825(5)	
C-C	1.685(15)	1.700(14)	
C-B(2)	1.822(7)	1.818(6)	x3
B(2)-B(4)	1.803(8)	1.797(7)	
B(2)-B(3)	1.825(6)	1.821(5)	x2
B(3)-B(3)	1.726(8)	1.724(7)	
B(3)-B(4)	1.799(6)	1.793(5)	
B(3)-B(3)	1.831(8)	1.825(7)	

Band structure and Spectroscopy:

To determine the reason for the rare earth vacancy in $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ *ab-initio* band structure calculations were performed. Due to the inability of density functional theory to accurately treat the highly correlated electrons in the *f* levels the system was modeled using La as the rare earth metal. Also because it is difficult to treat vacancies without introducing large super cells, the model assumes the rare earth site is fully occupied. If the system happens to be valence precise with the vacancy, the fully occupied model will likely show metallic or semimetallic character with a gap in the vicinity of the fermi level. Figure 2-3(A) shows the total density of states for the hypothetical compound $\text{La}_3\text{C}_2\text{Si}_8(\text{B}_{12})_3$. The main feature of this plot is the fact that there is electron density at the fermi-level with a gap appearing below it, indicating metallic or semimetallic behavior as predicted. Integration of the total density of states from -0.5 eV to the fermi level in Figure 2-3(A) results in 3.2 electrons. This corresponds to the removal of slightly more than one atom per formula unit from the rare earth sub-lattice, since each rare earth ion presumably contributes 3 electrons to the conduction band due to the ionization of the 6s and 5d electrons.

The density of states suggests that the driving force for the rare earth ion vacancy is for the compound to be valence precise by removing electronic states from the conduction band. This valence precision should result in a band gap. Infact the band gap predicted by calculations is approximately 1.0 eV. Figure 2-3(B) shows the UV-Vis.

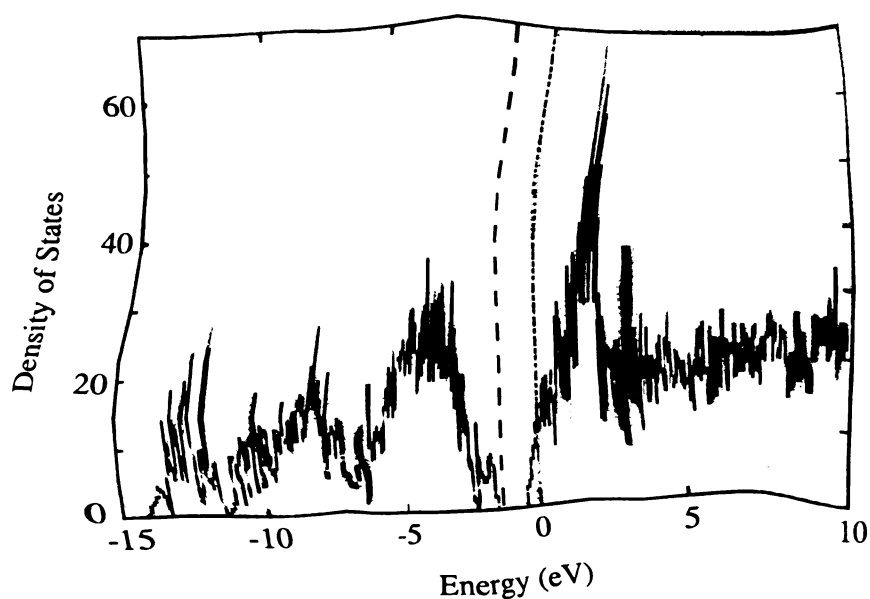
spectrum for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$. The measured band gap was found to be about 0.9 eV . This finding strongly suggests that the driving force for the rare-earth vacancy is for valence precision, which in turn results in the formation of a band gap by removal of electron density for the Fermi level.

Magnetic Measurements:

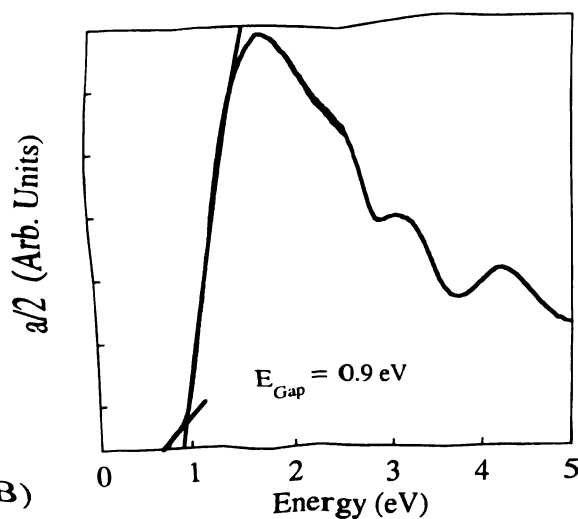
Magnetic susceptibility measurements performed on both $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ and $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ found that they are paramagnetic and obey the Curie Weiss law from 300 K to 2 K. There was no evidence of magnetic ordering in either compound which is to be expected as the distance between the ions of a fully occupied rare earth sub-lattice is about $5 \text{ \AA}$ for both compounds making direct exchange between them very weak. Additionally indirect exchange mechanisms such as RKKY where exchange is mediated by conduction electrons is not viable, as we have demonstrated this compound to be a rather large band gap semiconductor. Exchange mediated by bonding electrons is not likely here either as the f electrons of the late rare earth ions are not very involved in bonding as their energy lies too far below the frontier orbitals of the systems and their spatial extent is very limited.

Figure 2-4 (A) shows the temperature dependent susceptibility for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$. The resulting effective magnetic moment, as determined from Curie Weiss law, is $12.9 \mu_B$ per formula unit with a Weiss constant of -4 K indicating weak

antiferromagnetic interactions between the ions. The effective magnetic moment obtained from the susceptibility is in good agreement with the moment calculated for 1.8 isolated Tb ion which is $13.1 \mu_B$.



(A)



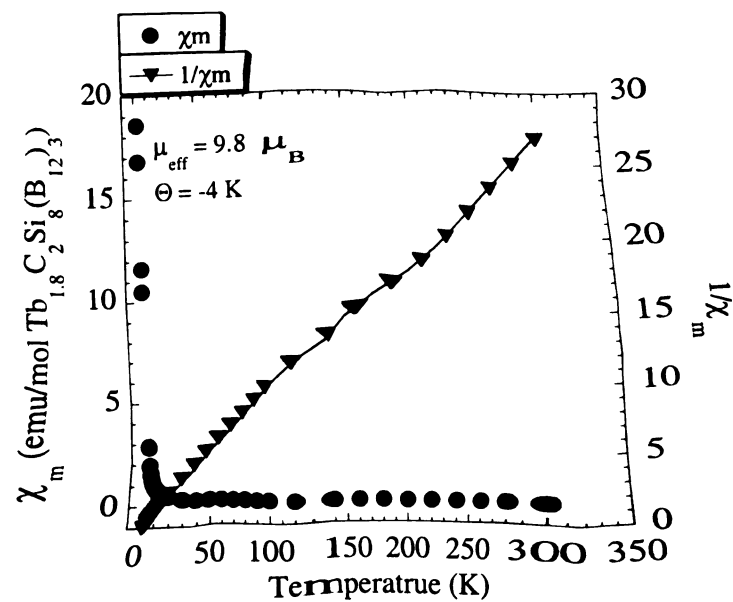
(B)

Figure 3 (A) Total density of states for $\text{La}_3\text{C}_2\text{Si}_8(\text{B}_{12})_3$. The region between 0.5 eV and the fermi level integrates to yield 3.2 electrons. (B) Solid State U.V. / Vis absorption spectrum for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ showing a band gap of 0.96 eV.

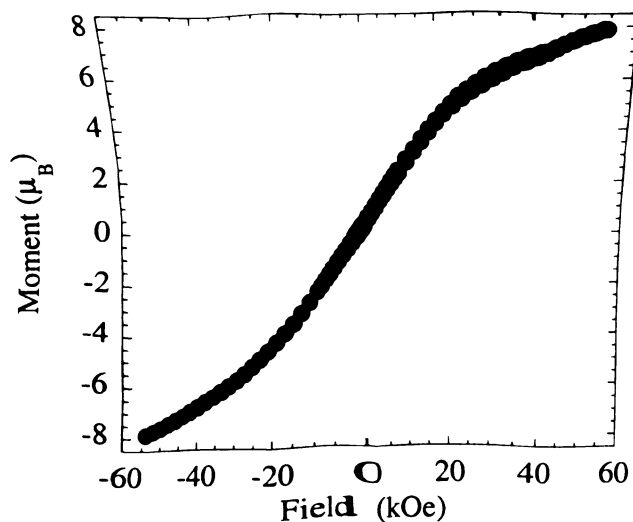
The magnetization curve for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ can be seen in Figure 2-4 (B). The magnetization is linear up to an applied field of about 20 kOe. There is a change in slope at this point and then continues its linear behavior up to 55 kOe with no signs of saturation. The expected saturated moment is approximately $12.5 \mu_B$ and the magnetization curve reaches only 75% of this value.

The magnetic susceptibility for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ can be seen in Figure 2-5 (A). As was the case with the Tb analog $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ exhibits Curie / Weiss behavior over the entire temperature range investigated. The resulting effective magnetic moment derived from this data is $12.8 \mu_B$, which is in excellent agreement with the theoretical value of $12.9 \mu_B$. The Weiss constant is small and positive with a value of 3 K indicating weak ferromagnetic interactions between the Er^{3+} moments.

The magnetization curve for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ can be found in Figure 2-5 (B). The behavior displayed here is somewhat different from the Tb analog which had a linear response with increasing field up to 20 kOe where the slope then changed and linear behavior was observed out to 55 kOe. The moment of the Er analog has a very strong dependence on field up to about 2 kOe, at which point the dependence falls off substantially and saturation behavior begins. The magnitude of the moment at the highest applied field however is less than half of the value predicted.

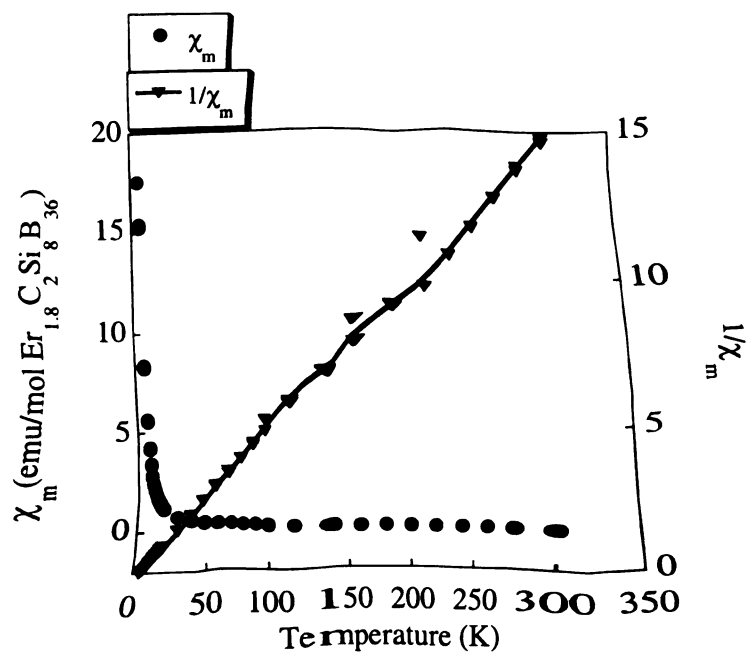


(A)

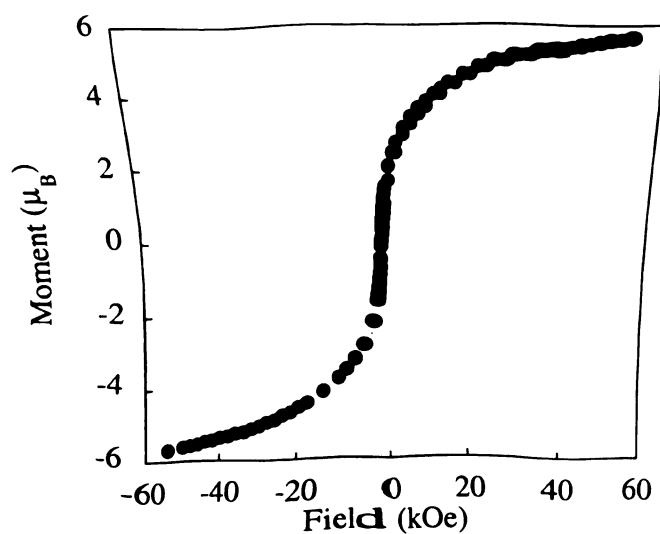


(B)

Figure 2-4 (A) Magnetic susceptibility for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ which shows no magnetic ordering and obeys Curie/Weiss law from 300 to 2 K. (B) Magnetization curve for $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$.



(A)



(B)

Figure 2-5 (A) Magnetic susceptibility for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ which shows no magnetic ordering and obeys Curie/Weiss law from 300 to 2 K. (B) Magnetization curve for $\text{Er}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$.

2-4 Conclusions-

Presented here are the new boron rich quaternary silicides $RE_{3-x}C_2Si_8(B_{12})_3$ ($RE = Tb$ and Er) representing a new structure type. Both analogs have a vacancy in the rare earth sub lattice of about 40 %. Ab-initio band structure calculations performed on the hypothetical compound $La_3C_2Si_8(B_{12})_3$ found the compound to be metallic as there was significant electron density at the fermi level. Just below the fermi level there is an energy gap that is about 1 eV wide. We found that by integrating the density of states from -0.5 eV to the fermi level we obtained 3.2 electrons corresponding to the removal of a little more than 1 rare earth atom per formula unit. Therefore the driving force for the vacancy is for valence precision by the removal of electron density from the conduction band. This notion was lent further credence by determining that $Tb_{3-x}C_2Si_8(B_{12})_3$ did in fact have a band gap equal to 0.96 eV.

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Chapter 3

β -SiB₃ A New Refractory Si-B Binary Phase Grown from a Ga Flux.

3-1 Introduction.

Liquid metals can be powerful solvents for the exploration of novel refractory solid state materials ranging from intermetallic compounds to silicides, carbides and borides. Recently we have discovered, from liquid Al and Ga, a large variety of ternary and quaternary phases of the type: RE/TM/Si or Ge, RE/TM/Al or Ga, RE/TM/Al/Si or Ge, and RE/TM/Ga/Ge or Si (RE=rare earth La-Lu, and TM = 1st, 2nd, or 3rd row transition metal).^{1,2} Many of these phases cannot be formed by conventional high temperature solid-state synthetic techniques such as direct combination reactions with arc melting or radio frequency (rf) induction furnace heating.³ We have extended the flux methodology to include RE/TM/B/Si (borosilicides) in an attempt to produce lighter analogs of the RE/TM/Al/Si compounds, and we chose liquid gallium as the reaction medium because both Si and B are soluble in it and do not form binaries.⁴ Also from previous work we learned that RE/TM/Ga/Si phases do not form readily, and so competing phases of this type are not anticipated.¹ Boron containing solids have acquired

renewed interest because of the superconducting quaternary borocarbides⁵ and MgB_2 a high temperature, non-oxidic superconductor.⁶

Borosilicides are an unfamiliar class of compounds. Specifically boron-rich borosilicides are rare with only a handful of examples present in the literature, which include: $\text{CrSi}_3(\text{B}_{12})\text{Se}_{12}(\text{B}_2\text{Se}_3)_{1.33}$, $\text{REB}_{41}\text{Si}_{1.2}$ ($\text{RE}=\text{Y}, \text{Tb}$), $\text{Sc}_{0.83-x}\text{B}_{10.0-y}\text{Co}_{1.17+y}\text{Si}_{0.083-z}$ ⁷, SiB_4 and SiB_6 ⁸. We report here the discovery of a new boron-rich binary phase SiB_3 . This is the first new Si-B binary phase reported in over 40 years, and is the first to date that is crystallographically ordered. The title compound has a similar stoichiometry to a phase reported previously, $\text{SiB}_{2.89}$, which crystallizes as the B_6P structure type. $\text{SiB}_{2.89}$ is, in actuality, a member of a solid solution of Si-B where their ratios are varied by substituting more Si atoms into the B_{12} cages resulting in a disordered structure. Members of this solid solution can take on compositions ranging from $\text{SiB}_{2.8}$ to SiB_4 and will henceforth be referred to as $\alpha\text{-SiB}_3$. The title compound, referred to as $\beta\text{-SiB}_3$, on the other hand does not form a solid solution as it is not a disordered compound, and crystallizes in the orthorhombic space group Imma , as a new structure type.

3-2 Experimental Section.

Reagents and Synthesis:

All reagents were used as received without further purification, and were handled under a N_2 atmosphere in a dry box. 1 mmol of Si (~500 mesh amorphous, 99.99%

Cerac, Milwaukee, WI), 4 mmol B (submicron, amorphous, 99.9%, Cerac, Milwaukee, WI), 40 mmol Ga (3-5 mm shot, 99.999% Plasmaterials, Livermore, CA) and 0.5 mmol Cu (1-2 mm pieces 99.9% Research chemical, Phoenix, AZ) were combined into an alumina (Al_2O_3) reaction crucible. The crucible and reactants were then flame sealed under a reduced atmosphere of approximately 1.0×10^{-4} mbar in a fused silica tube. The system was then heated to 1000 °C over a 12 h period then held for an additional 96 h. Finally the reaction was cooled to 150 °C over the course of 48 h.

The product was isolated from the excess Ga by centrifugation, and a subsequent chemical etch in a 5M I_2 /dimethyl formamide (DMF) solution. The reaction yields were approximately 40 to 60%, and about 60 to 80% purity. Side products included: recrystallized Si, an unidentified Cu/Si binary and some unreacted B. A small amount of Cu was added to the reaction as it was found to increase yields of $\beta\text{-SiB}_3$, presumably by increasing the solubility of the B in the flux. The compound crystallizes as small hexagonal plates that were amber in color.

X-ray crystallography:

Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART CCD diffractometer with graphite monochromatized $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Unit cell refinement and data merging were done with the SAINT program, and an empirical absorption correction was applied using the program

SADABS.⁹ Inspection of the systematic absences immediately found the structure to be centered. The condition $h+k+l = 2n$ was present. In addition the $hk0$, $h=2n$ was also present resulting in the space group *Imma* (no. 74).¹⁰ A structural solution was obtained by direct methods using the program **SHELXS**, and the final structural refinement was completed with the **SHELXL** suite of programs.¹¹ The crystal structure refinement data for β -SiB₃ can be found in Table 3-1. The atomic coordinates and isotropic displacement parameters are found in Table 3-2, and anisotropic temperature parameters are in Table 3-3.

Elemental Analysis:

Semi-quantitative microprobe analysis was performed with a **JEOL JSM-35C** scanning electron microscope (SEM) equipped with a **Noran Vantage** energy dispersive spectrometer (EDS) with a Si / Li detector, and a **Norvar™** window suitable for the standardless quantitation of light elements ($Z \geq 4$). Spectra were obtained with an accelerating voltage of 8 kV and 120 s acquisition times in order to accurately determine the boron content. To minimize the possibility of carbon contamination in the EDS spectra, all samples were mounted with silver paste on an aluminum stub. The ratio of boron to Si was determined to be 2.4 to 1 after extensive averaging. There was no clear carbon peak detected in the EDS spectra.

Table 3-1. Crystal data and structure refinement for β -SiB₃.

Empirical formula	SiB ₃	
Formula weight	69.17	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system / Space group	Orthorhombic / <i>I mma</i> (#74)	
Unit cell dimensions	a = 8.3812(9) Å	α = 90°.
	b = 12.5530(14) Å	β = 90°.
	c = 6.2056(7) Å	γ = 90°.
Volume	652.89(13) Å ³	
Z	16	
Density (calculated)	2.463 g/cm ³	
Absorption coefficient	0.808 mm ⁻¹	
F(000)	464	
Theta range for data collection	3.25 to 27.11°.	
Index ranges	-10 ≤ h ≤ 10, -16 ≤ k ≤ 15, -7 ≤ l ≤ 7	
Reflections collected / Unique	2863 / 406 [R(int) = 0.0161]	
Completeness to theta = 27.11°	99.5 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	406 / 0 / 43	
Goodness-of-fit on F ²	1.235	
Final R indices [I > 2σ(I)]	R1 = 0.0167, wR2 = 0.0497	
R indices (all data)	R1 = 0.0168, wR2 = 0.0498	
Largest diff. peak and hole	0.405 and -0.180 e.Å ⁻³	
R1 = $\sum F_o - F_c / \sum F_o $ and wR2 = $[\sum (F_o ^2 - F_c ^2)^2 / \sum (w F_o^2)^2]^{1/2}$		

Table 3-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for β -SiB₃.

Atom	Wyckoff Position	x	y	z	U(eq)
Si(1)	8i	2700(1)	1/4	642(1)	7(1)
Si(2)	8h	0	3454(1)	-26(1)	7(1)
B(1)	16j	3888(2)	3871(1)	25(2)	7(1)
B(2)	8h	0	4306(2)	2708(3)	7(1)
B(4)	16j	3248(2)	5016(1)	1554(2)	7(1)
B(3)	8h	0	4253(2)	-2759(3)	7(1)

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

Table 3-3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for β -SiB₃.

	U11	U22	U33	U23	U13	U12
Si(1)	8(1)	6(1)	8(1)	0	0(1)	0
Si(2)	10(1)	6(1)	5(1)	0(1)	0	0
B(1)	8(1)	7(1)	6(1)	0(1)	0(1)	0(1)
B(2)	8(1)	7(1)	6(1)	0(1)	0	0
B(4)	7(1)	7(1)	7(1)	0(1)	0(1)	0(1)
B(3)	8(1)	7(1)	6(1)	0(1)	0	0

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

CHN Analysis:

Carbon, hydrogen and nitrogen combustion analysis was performed on hand selected single crystals with a Perkin / Elmer Series II CHNS/O analyzer 2400. Prior to analysis the crystals were washed in aqua regia, and Piranha solution (75 vol% H_2SO_4 and 25 vol%) in order to minimize surface carbon contamination. The analysis showed no trace of hydrogen nor nitrogen and the carbon content was 0.3% by weight, a value that is near the detection limit of the instrument.

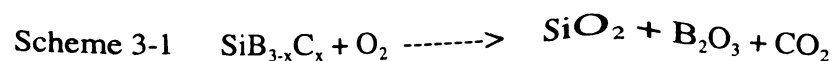
Differential Thermal Analysis:

Differential thermal analysis was performed with a Shimadzu DTA-50 analyzer. 35 mg of single crystals were hand picked and flame sealed under a reduced atmosphere of 1.0×10^{-4} mbar in a fused silica ampoule. The analysis was run with α -alumina as a standard reference. No phase transitions were detected up to 1000 °C for the title compound. The β - SiB_3 crystals were unchanged by heating to 1000 °C by visual inspection.

Thermal Gravimetric Analysis:

Thermal gravimetric analysis was performed on several batches of hand picked single crystals of β - SiB_3 with masses ranging from 5 to 15 mg with a Shimadzu TGA 50

analyzer. The analysis was originally carried out to roughly determine the carbon content through the reaction seen in Scheme 3-1. Carbon was not found in this phase, and the TGA was then used to screen the thermal oxidative resistance.



Spectroscopy:

A solid state UV/ Vis spectrum of $\beta\text{-SiB}_3$ was collected on a Shimadzu UV-3101PC UV-Vis-NIR solid state spectrophotometer in order to determine the optical band gap. Measurements were made in %reflectance mode from a BaSO_4 standard reference. The spectrum was converted to absorbance using the Kubelka-Munk equation.

Raman Spectroscopy was performed with a Bio-Rad FT Raman spectrometer. The spectra were taken in order to investigate possible structural disorder by the substitution of silicon or carbon into the B_{12} cages. The spectra were taken of hand picked single crystals, which were finely ground under acetone.

Refractory Testing:

$\beta\text{-SiB}_3$ was subjected to several different tests to determine its inertness to chemical attack and thermal oxidation. Several single crystals were picked and submerged in concentrated H_2SO_4 , HNO_3 , HCl , HF , aqua regia, piranha solution (75 vol% H_2SO_4 and 25 vol% 30% H_2O_2) and 5 M NaOH to see if any of them dissolved or

etched them. The crystals were left submerged for 2 weeks. This required replacing the aqua-regia and piranha solution every couple of days over this period of time.

To test thermal oxidation resistance several single crystals were picked and placed in open ended fused silica tubes and heated to 600 °C and held for 24 hrs. This process was repeated with other crystals using 700, 850, and 1000 °C isothermal steps as well.

Band Structure Calculations:

Band structure calculations were performed on β -SiB₃. The system was modeled as the binary phase with the notion that if carbon were required to stabilize the phase it would be manifested as an electronic deficiency detectable by the calculation. The calculations were carried out using the self-consistent full-potential linearized augmented plane wave method (LAPW)¹² within density functional theory (DFT) with a generalized gradient approximation (GGA) for the exchange and correlation potential within the Perdew-Burke-Ernzerhof model.¹³ Scalar relativistic corrections were added and spin-orbit interaction (SOI) was incorporated using a second variational procedure.¹⁴ The calculations were performed with the WIEN97 program.¹⁵ Self-consistent iterations were performed with 27 k points in the reduced Brillouin zone with a cutoff between valence and core states of -6.0 Ry; convergence was assumed when the total energy difference between cycle was within 0.0001 Ry.

3-3 Results and Discussion.

The structure of β -SiB₃ is composed of two building blocks: infinite Si₄ chains and B₁₂ cages, see Figure 3-1(A) and (B) respectively. The B₁₂ cages are linked together forming a layer, Figure 3-1(B). The Si₄ chains contain two base-fused triangle units forming a rhombus. The rhombi are linked to one another to form a sinusoidal chain that propagates along the *a*-axis, Figure 3-1 (A). There are two crystallographically distinct Si atoms, one at the apex of the fused triangles (Si(1)), and one that forms the base with its symmetry equivalent (Si(2)). The Si(1)-Si(1) bond from apex to apex is 2.3336(8) Å. The other Si-Si bonds in the structure are substantially longer with Si(1)-Si(2) being 2.5967(4) Å long and Si(2)-Si(2) (base of the triangle) at 2.3970(8) Å. To the best of our knowledge the infinite Si₄ chain is a novel structural feature. There is a slight similarity to the (Ge₄)⁴⁻ chains of BaGe₂, but in the latter compound the (Ge₄)⁴⁻ chains are anionic, and are well rationalized via the Zintl concept.¹⁶ In contrast, the Si₄ chains of β -SiB₃ are not anionic, and are not regarded as Zintl species.

The four crystallographically distinct boron atoms are arranged in B₁₂ cages that form a two-dimensional sheet structure that extends over the *ac* plane resulting in a regular 4-sided ring of cages Figure 3-1 (B). The cages are bound through symmetry-generated B(4)-B(4) bonds at 1.717(2) Å. Intra-cage bond distances range from 1.934(2) Å for B(4)-B(4) to 1.756(2) Å for B(1)-B(3) with an average of 1.792 Å. The Si zigzag chains insert between the B₁₂ icosahedral sheets forming B-Si bonds and a three-

dimensional framework along the *b*-axis, as seen in Figure 3-2. The B-Si bond distances are 2.027(1) Å for Si(1)-B(1), 1.973(2) Å between Si(2) and B(3), and 2.009(2) for Si(2)-B(2). Table 2-4 gives a complete list of the bond distances for β -SiB₃ and Table 3-5 gives the complete list of bond angles.

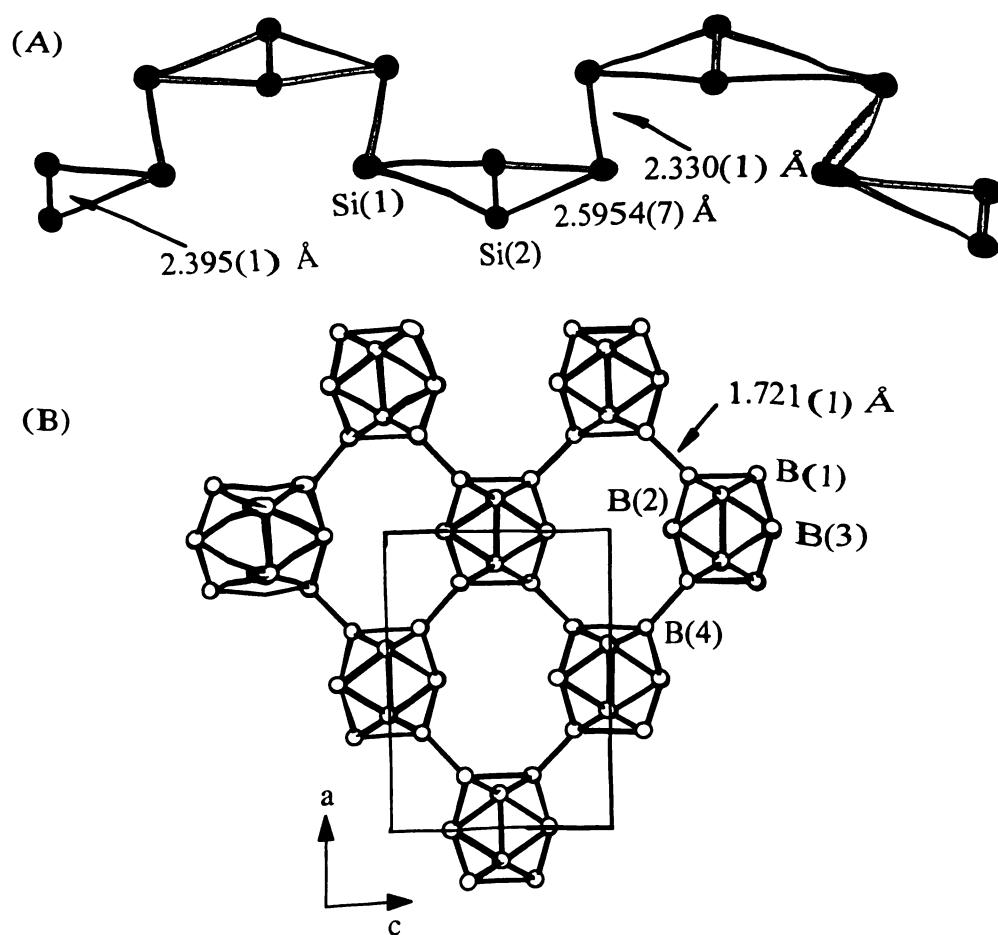


Figure 3-1 (A) View of the Si chain which propagates along the *a*-axis. (B) View of a B₁₂ layer as it is arranged in the *ac* plane. The connectivity results in a rectangular array of cages.

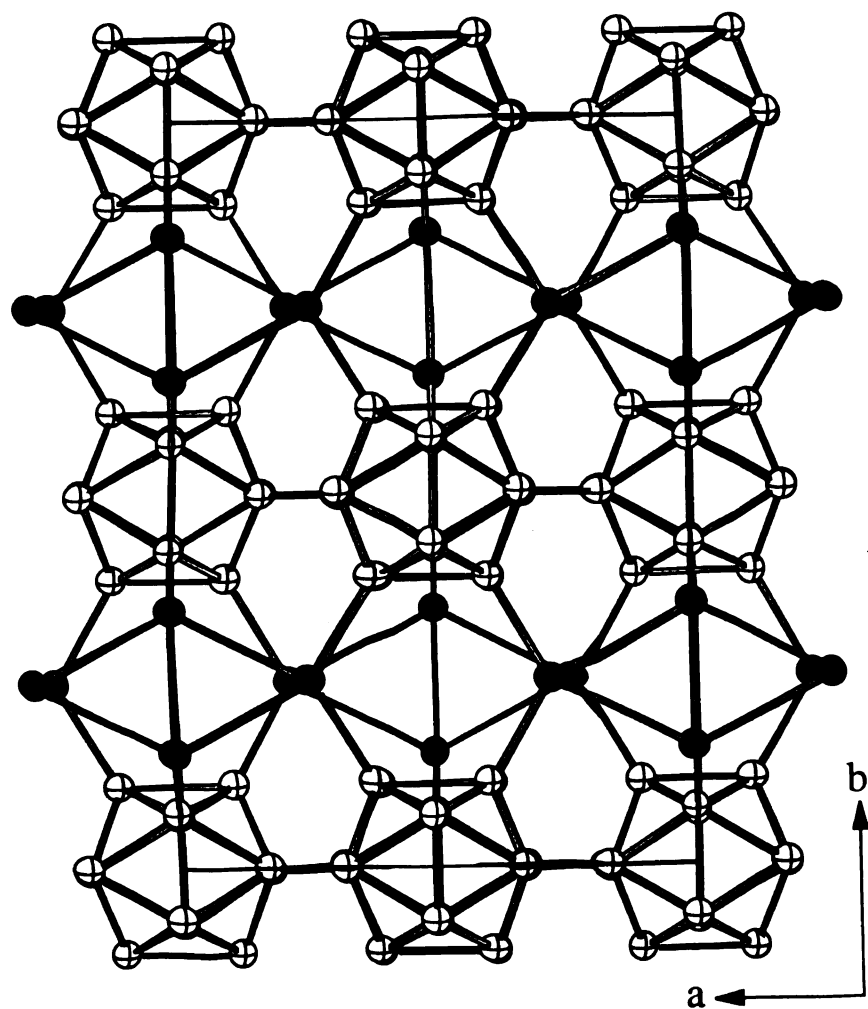


Figure 3-2 The overall view of β -SiB₃ as seen along the *c*-axis.

Table 3-4. Bond lengths [Å] for β -SiB₃.

Si(1)-B(1)	2.0251(15)	B(4)-B(4)	1.929(3)
Si(1)-Si(1)	2.3304(10)	B(3)-B(4)	1.7837(18)
Si(1)-Si(2)	2.5934(5)	B(1)-B(4)	1.804(2)
Si(2)-B(3)	1.970(2)	B(1)-B(1)	1.863(3)
Si(2)-B(2)	2.005(2)	B(2)-B(4)	1.7785(18)
Si(2)-Si(2)	2.3943(10)	B(2)-B(3)	1.810(3)
B(1)-B(3)	1.754(2)	B(4)-B(4)	1.717(3)
B(1)-B(2)	1.773(2)	B(4)-B(1)	1.789(2)
B(1)-B(4)	1.789(2)		

Table 3-5. Bond angles [deg] for β -SiB₃.

B(1)-Si(1)-B(1)	116.41(8)	B(1)-B(2)-B(3)	107.07(11)
B(1)-Si(1)-Si(1)	104.94(4)	B(1)-B(2)-Si(2)	120.48(10)
B(1)-Si(1)-Si(2)	142.31(4)	B(4)-B(2)-Si(2)	119.04(8)
B(1)-Si(1)-Si(2)	90.38(4)	B(3)-B(2)-Si(2)	123.23(12)
Si(1)-Si(1)-Si(2)	91.86(3)	B(4)-B(4)-B(2)	115.25(12)
Si(2)-Si(1)-Si(2)	54.98(2)	B(4)-B(4)-B(3)	115.94(12)
B(3)-Si(2)-B(2)	117.17(9)	B(2)-B(4)-B(3)	61.08(9)
B(3)-Si(2)-Si(2)	120.60(6)	B(4)-B(4)-B(1)	126.42(7)
B(2)-Si(2)-Si(2)	122.23(6)	B(2)-B(4)-B(1)	106.55(10)
B(3)-Si(2)-Si(1)	111.87(2)	B(3)-B(4)-B(1)	58.80(9)
B(2)-Si(2)-Si(1)	96.38(3)	B(4)-B(4)-B(1)	125.23(7)
Si(2)-Si(2)-Si(1)	62.508(11)	B(2)-B(4)-B(1)	59.33(9)
B(1)-B(3)-B(4)	112.71(12)	B(3)-B(4)-B(1)	106.89(10)
Si(1)-Si(2)-Si(1)	121.52(2)	B(1)-B(4)-B(1)	104.16(10)
B(3)-B(1)-B(2)	105.86(10)	B(4)-B(4)-B(4)	133.12(10)
B(3)-B(1)-B(4)	60.45(8)	B(2)-B(4)-B(4)	104.30(9)
B(2)-B(1)-B(4)	110.63(10)	B(3)-B(4)-B(4)	104.47(9)
B(3)-B(1)-B(4)	111.24(11)	B(1)-B(4)-B(4)	57.90(8)
B(2)-B(1)-B(4)	59.62(8)	B(1)-B(4)-B(4)	57.15(8)
B(4)-B(1)-B(4)	64.95(9)	B(1)-B(3)-B(1)	64.17(12)
B(3)-B(1)-B(1)	57.91(6)	B(1)-B(3)-B(4)	112.71(12)
B(2)-B(1)-B(1)	58.31(6)	B(1)-B(3)-B(4)	60.75(8)
B(4)-B(1)-B(1)	107.47(6)	B(4)-B(3)-B(4)	110.86(13)
B(4)-B(1)-B(1)	107.32(6)	B(1)-B(3)-B(2)	106.68(11)
B(3)-B(1)-Si(1)	130.16(10)	B(4)-B(3)-B(2)	59.32(7)
B(2)-B(1)-Si(1)	111.71(9)	B(1)-B(3)-Si(2)	123.46(10)
B(4)-B(1)-Si(1)	128.27(9)	B(4)-B(3)-Si(2)	117.89(8)
B(4)-B(1)-Si(1)	115.56(8)	B(2)-B(3)-Si(2)	119.60(12)
B(1)-B(1)-Si(1)	119.46(4)		
B(1)-B(2)-B(1)	63.39(11)		
B(1)-B(2)-B(4)	61.05(8)		
B(1)-B(2)-B(4)	112.57(12)		
B(1)-B(2)-B(4)	61.05(8)		
B(4)-B(2)-B(4)	111.35(13)		

The issue of whether carbon was required to stabilize this phase, or if it was a true binary phase was one that was approached from several perspectives. It was found that the addition of a small amount of carbon (0.5 mmol) did increase the yields of the β phase by as much as 10-20%. If carbon were to be included in the compound, presumably it would substitute at the boron sites to compensate for some electronic deficiencies, as has been observed previously in other systems such as KB_3C .¹⁷ The substitution of carbon for boron would be undetectable by x-ray crystallography, and it was quite clear from the crystallographic results that carbon was not making an isoelectronic substitution for Si, as both Si sites refine to 99% occupancy.

To determine if there was an electronic requirement for carbon substitution into the B_{12} cages, ab-initio band structure calculations were performed on $\beta\text{-SiB}_3$. The results showed that the binary composition formed a valence precise compound with a resulting band gap of 1.2 eV. Figure 3-3 shows the band structure of $\beta\text{-SiB}_3$. This finding indicates that there is no electron deficiency in the system, and therefore carbon is not required for stabilization.

Extensive efforts were made to detect carbon in the system by different forms of elemental analysis. Several single crystals were picked and washed in aqua-regia, and then mounted in silver paste for energy dispersive spectroscopy. This was done to avoid using carbon tape and introducing it into the background of the spectrum. A small

shouldering on the boron K α peak was observed consistent with carbon being present in the crystals. Combustion carbon, hydrogen and nitrogen (CHN) analysis was also performed on chemically cleaned single crystals. It was found that carbon was present at the 0.3% by weight level. This amount is very close to the detection limit of the instrument. We have therefore concluded on the basis of calculations, CHN analysis and the fact that the phase can form without the addition of carbon, that carbon is not required to stabilize the phase and that β -SiB₃ is in fact a true binary. The fact that the addition of carbon does increase yields could be rationalized by it increasing the solubility of one of the reaction components, or that it inhibits the formation of the Cu/Si side product making Si more available to form β -SiB₃.

Finally we used spectroscopy to investigate the issue of Si/B and B/C disorder in the system because Raman spectroscopy can be diagnostic for this. It has been found that disorder within the B₁₂ cages leads to extensive line broadening in the Raman active modes of up to several hundred wavenumbers.¹⁸ Inspection of the Raman bands associated with the B₁₂ cages (700 to 1100 cm⁻¹) showed no substantial broadening and therefore it is unlikely that Si/B, or C/B disorder exists in this compound Figure 3-4 (A). This is consistent with our findings from calculations, and combustion elemental analysis, that this compound is a true binary phase.

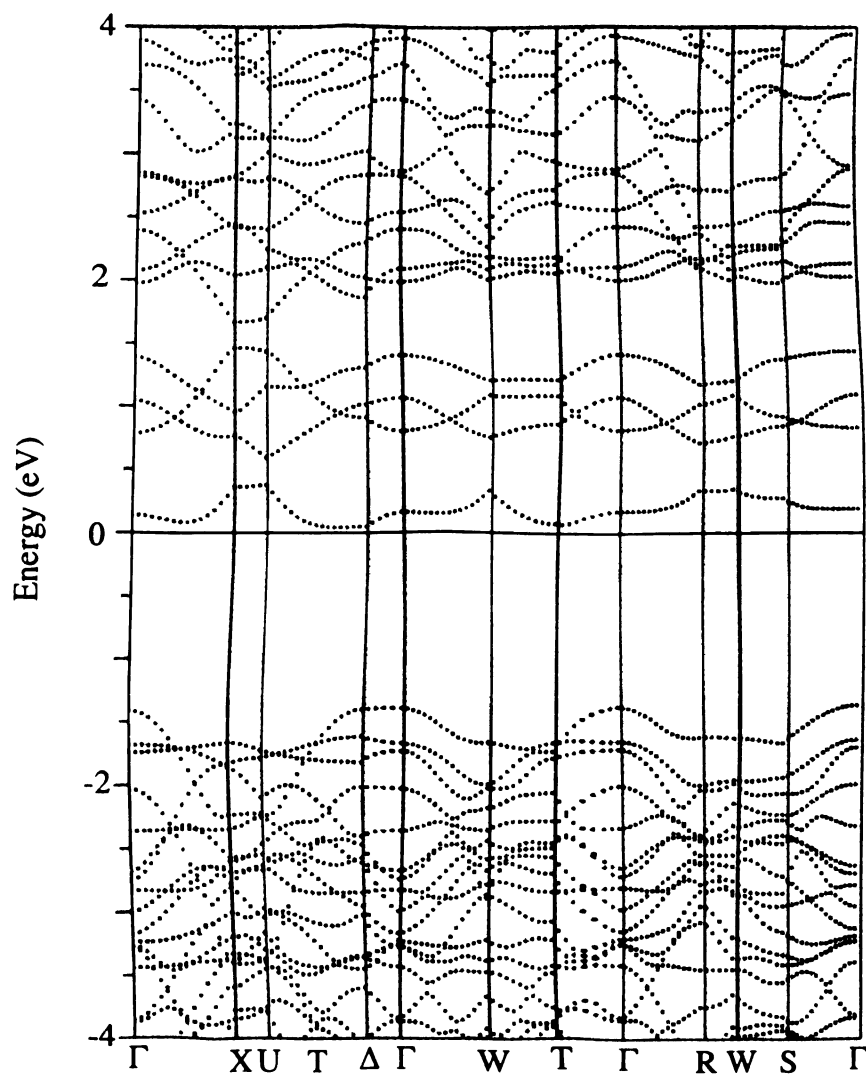


Figure 3-3 The band structure of β -SiB₃ showing an indirect band gap of 1.2 eV.

β -SiB₃ possesses a moderately wide band gap of 2.07 eV, which is quite large when compared to that of α -SiB₃ which is approximately 0.3 eV, Figure 3-4 (B). This band gap is substantially larger than the band gap predicted by the calculations, but is consistent with the amber color of the crystals.

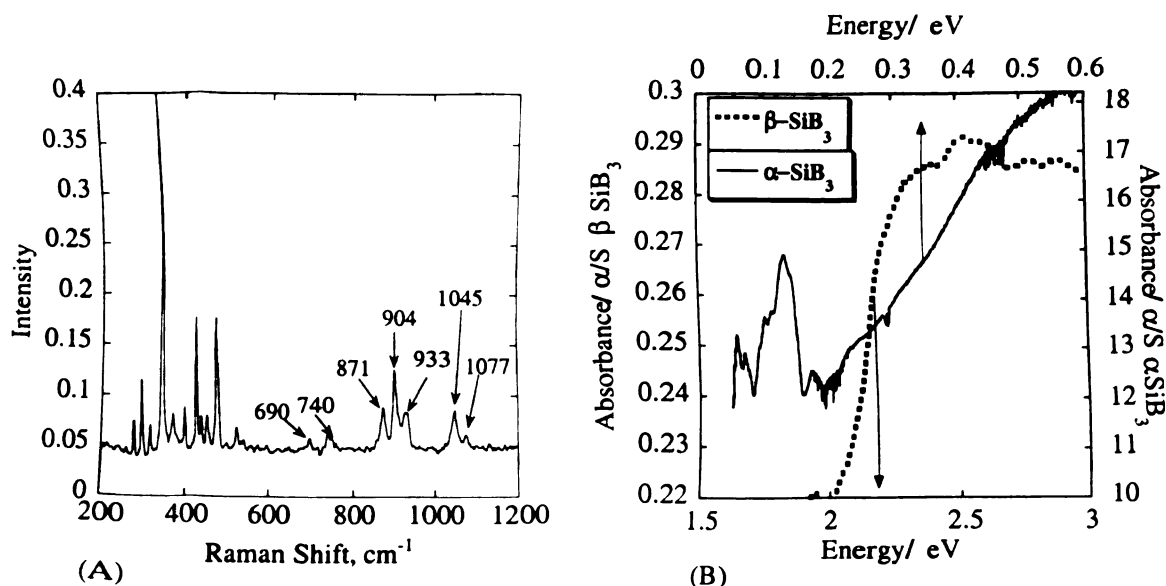


Figure 3-4 (A) The polycrystalline Raman spectrum of $\beta\text{-SiB}_3$. (B) A comparative plot of optical absorbance as a function of energy for α and $\beta\text{-SiB}_3$, the solid line is the spectrum of $\alpha\text{-SiB}_3$, which has a band gap of about 0.2 eV, the broken line is the spectrum of $\beta\text{-SiB}_3$, which has a band gap of 2.0 eV.

As mentioned previously, $\beta\text{-SiB}_3$ is the first crystallographically ordered Si-B binary phase discovered. The α form on the other hand has ordered Si sites which form as dimers, and disordered B/Si sites within the icosahedra. This disorder has a profound effect on the physical stability of the system. $\beta\text{-SiB}_3$ was found to be inert to most forms of chemical attack. It was not dissolved nor etched in concentrated H_2SO_4 , HNO_3 , HCl , boiling aqua-regia, and room temperature aqua-regia, piranha solution (75 vol% H_2SO_4 and 25 vol% 30% H_2O_2) and 5M NaOH solutions, however it dissolved in concentrated HF. The α form was similarly resistant to chemical attack, but was badly etched by boiling aqua-regia, and HF.

The difference in the stability of the two forms is most evident when it comes to thermal oxidation resistance. Thermal gravimetric analysis (TGA) was performed on both phases by heating them up to 1000 °C under flowing air, and observing the amount of weight they gained. This weight gain would be proportional to the extent of oxidation. Figure 3-5 shows a comparative TGA plot of the α and β forms of SiB_3 . At 600 °C the mass of the α form begins to increase rapidly, indicating combustion, and continues to do so up to 1000 °C. The mass of the β form remains more or less constant up to 1000 °C indicating resistance to oxidation.

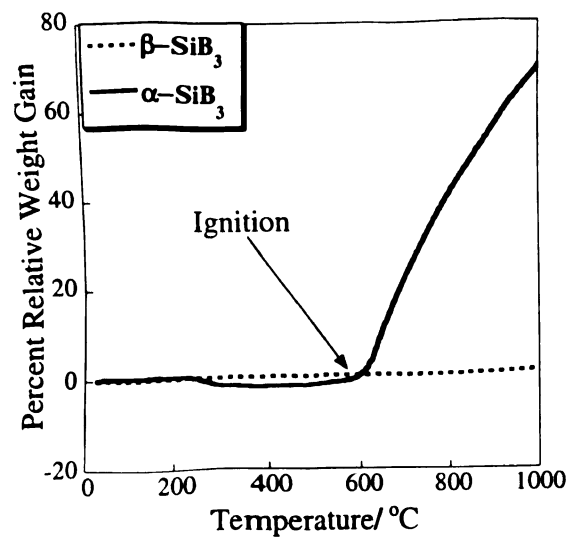


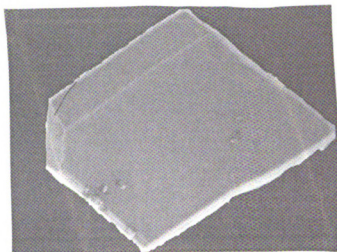
Figure 3-5 A comparative plot of the thermal gravimetric analysis (TGA) of α and β SiB_3 , the solid line is the TGA curve of α SiB_3 with an ignition point at about 600 °C. The broken line is β SiB_3 , which has no evident ignition point.

To more realistically test the resistance to thermal oxidation, several single crystals were picked and placed in open fused silica tubes, and heated under an ambient

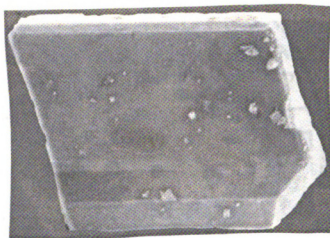
atmosphere at 700, 850 and 1000 °C for 24 hours. Scanning electron micrographs of the crystals, before and after heating at 700 °C can be seen in Figures 3-6 (A) and (B), respectively. β -SiB₃ was somewhat oxidized by being annealed at 700 °C under an ambient atmosphere for 24 hours, but the crystal was still quite intact as the crystal faces are still evident. Upon heating β -SiB₃ at still higher temperatures, the compound is badly damaged, Figures 3-7(A) and (B) show a single crystal of β -SiB₃ before and after annealing at 1000 °C respectively. The crystal faces of this sample have been badly rounded indicating that the protective oxide coating began to melt or otherwise deteriorate allowing the attack of freshly exposed crystal faces. The very bright white region in Figure 3-7(B) is composed principally of SiO₂ as determined by EDS.

Presumably the protective oxide coating is composed of both SiO₂ and B₂O₃. SiO₂ scales can provide excellent protection against further oxidation if the scale is reasonably well bound to the substrate.¹⁹ B₂O₃ on the other hand has a rather low melting point of approximately 700-800 °C, depending on the partial pressure of O₂,²⁰ and is probably the reason why β -SiB₃ is not more resistant to oxidation at elevated temperatures. The binary oxide, SiO₂ and B₂O₃, may melt or react at a higher temperature than the B₂O₃ alone, and this break down is evident at temperatures above 700 °C.

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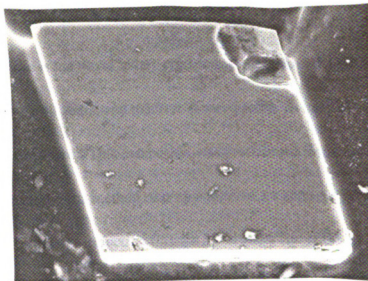
(A)



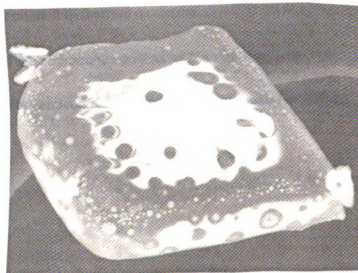
(B)

Figure 3-6 (A) Scanning electron micrograph of a β -SiB₃ single crystal before annealing. (B) Scanning electron micrograph of a β -SiB₃ single crystal after annealing under an ambient atmosphere at 700 °C for 24 hrs.

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Figure 3-7 (A) Scanning electron micrograph of a β -SiB₃ single crystal before annealing. (B) Scanning electron micrograph of a β -SiB₃ single crystal after annealing under an ambient atmosphere at 1000 °C for 24 hrs.

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3-4 Conclusions.

Presented here is the novel binary compound SiB_3 . It is the first new Si-B binary phase reported in over 40 years, and the first binary phase in the Si/B system that is crystallographically ordered. This compound was produced from a molten metal flux, and is in fact exclusive to this method of preparation as reactions run by arc melting, or heating by a radio frequency induction furnace yield only the α form. It should also be emphasized that the metal flux reaction completely bypasses the α form.

The fact that the β form has no Si-B disorder seems to effect its stability making it significantly more resistant to thermal oxidation as compared to the α form. The refractory nature of the compound coupled with its moderately wide band gap makes it a suitable candidate for semiconductor applications in extreme environments.

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Chapter 4

Gallium Flux Synthesis and Crystal Growth of RENiSi_3

(RE = Tb, Dy, Ho, Er, Yb, Lu) Intermetallics Displaying Anisotropic

Magnetic Behavior

4-1 Introduction

Ga flux reactions are an excellent route to a wide variety of intermetallic compounds.^{1, 2} This method has several advantages over more traditional methods of intermetallic synthesis, e.g. arc melting or the use of a radio frequency (rf) induction furnace, namely the products can often be grown as large high quality single crystals which aids in the characterization of the phase. Structural elucidation is particularly accelerated by the availability of high quality single crystals. In addition, measurements performed on single crystals can reveal unexpected anisotropic phenomena. The anisotropic behavior of certain physical properties is interesting from an intellectual standpoint, and is often of practical importance as well. This is particularly true for magnetoresistance compounds,³ superconducting materials,⁴ compounds exhibiting magnetic transitions, like DyCo_2Si_2 and ErRu_2Ge_2 ⁵ and thermoelectric materials.⁶

Molten metals have long been used to grow single crystal samples for the

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investigation of magnetic properties,⁷ structure investigations of quasi-crystals⁸, heavy fermion behavior⁹ and superconductivity¹⁰. A wide variety of low-melting metals have been used extensively to produce a variety of compounds including Al, which has been used to produce $\text{RE}_2\text{Al}_3\text{Si}_2$.¹¹ The heavy fermion compounds $\text{Ce}_3\text{Pt}_3\text{Bi}_4$ and CeBi_2 , have been grown from a Bi flux. Other compounds displaying heavy fermion behavior like YbCu_2Si_2 , and CeCu_2Ge_2 have been grown from In,¹² and the Kondo insulator CePtPb was grown from Pb¹³. Ga¹⁴ has been used to synthesize compounds such as SmNiSi_3 , YNiSi_3 and $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Tt}_x$ (RE = Sm-Tm, Y, Tt = Ge or Si and $n = 0,1$). Sn¹⁵ has been used to grow the narrow band gap half Huesler compounds TiNiSn and MnNiSn , and Sb¹⁶ can be used to produce the meta-magnetic compound CeSb and the Zintl phase REGaSb_2 .

In this chapter we expand on the previous work that used molten Ga to synthesize YNiSi_3 and SmNiSi_3 ¹⁴ to include the other late rare earth metals. Large, high quality, single crystals of RENiSi_3 (RE = Tb, Dy, Ho, Er, Yb, and Lu) have been grown by using a Ga flux. These compounds grow as plates with typical dimensions $2 \times 2 \times 0.2$ mm. They adopt the SmNiGe_3 structure type¹⁷ in the orthorhombic $Cmmm$ space group. Compounds with the composition RENiSi_3 (RE = late rare earth metal) have been reported previously, but these crystallize in the tetragonal BaNiSn_3 ¹⁸ structure type and do not order magnetically.¹⁹ It is likely the BaNiSn_3 structure type is accessible by annealing the arc-welded product at an appropriate temperature. Reactions carried out in

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molten Ga by-pass this product as do reactions carried out by arc melt alloying the elements. In this chapter we will describe the crystal growth, structural characterization and magnetic properties of RENiSi_3 , which adopts the SmNiGe_3 structure type and orders antiferromagnetically. These compounds have been found to undergo multi step, field induced meta-magnetic transitions that are highly anisotropic in nature. It was only after the investigation of these properties with single crystal techniques that the nature of these transitions became clear.

4-2. Experimental Section.

Reagents:

All of the following reagents were used as received without further purification. Tb metal (99.9% 25 mesh, Cerac, Milwaukee WI), Ho metal (99.9% 325 mesh powder, Cerac, Milwaukee, WI), Dy metal (99% sponge Research Chemicals, Phoenix, AZ), Er metal (99% ingot, Chinese Rare Earth Information Center, Inner Mongolia, China), Yb metal (99% ingot, Chinese Rare Earth Information Center, Inner Mongolia, China), Lu metal (99.9% 25 mesh turnings, Cerac, Milwaukee, WI), Ni metal (99.9% -325 mesh powder Cerac, Milwaukee, W), Si (99.99% -325 mesh amorphouse powder, Cerac, Milwaukee, WI) and Ga metal (99.99%, 2-5mm shot, Plasmaterials, Livermore, CA).

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Synthesis:

Method A: Large high quality single crystals of RENiSi_3 were produced by combining RE, Ni, Si, and Ga in a 1 : 1 : 3 : 10 ratio in an Al_2O_3 reaction crucible, which was then flame sealed under a reduced atmosphere of 10^{-5} mbar. The reactants were heated to 1000 °C over the course of 10 h and held there for 4 h before being cooled to 850 °C over the course of 2 h and held there for an additional 96 h. The system was then cooled to 50 °C in 48 h. The excess Ga was immediately decanted by centrifugation, and further isolation was completed by soaking the product in a 5 M I_2 dimethyl formamide (DMF) solution for 30 min. The resulting product was composed of plate-like single crystals, ranging in size from a few tenths of a mm to several mm on a side.

Method B: Pellets of RENiSi_3 were prepared by combining the elements in their stoichiometric ratios and cold pressing them into a pellet. The pellets were then placed on a water cooled copper plate, and arc melted under an Ar atmosphere that was gettered by Zr. The pellets were flipped and re-melted 3 times to ensure complete melting and homogenous distribution of all reactants. The resulting melts were annealed for 1 week at 850 °C and yielded single phases of the desired compounds as determined by powder X-ray diffraction.

Elemental Analysis:

Semi-quantitative microprobe analysis was performed on single crystals with a JEOL JSM-35C Scanning Electron Microscope (SEM) equipped with a Tracor Noran energy dispersive spectrometer (EDS) capable of standardless analysis of elements with $Z \geq 4$. Data were collected with an accelerating voltage of 25 kV and 60 s acquisition times. The approximate atomic ratios were found to be 1 : 1: 3 for RE, Ni and Si respectively, and are in excellent agreement with the those obtained from the crystallographic refinements.

X-ray Crystallography:

Single crystal x-ray diffraction data for RENiSi_3 (RE=Tb, Dy, Ho, Er, Yb and Lu) were collected at room temperature on a Bruker SMART CCD diffractometer with graphite monochromitized $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data integration and cell parameter refinement were carried out using the program SAINT, and an absorption correction was applied to the data empirically using SADABS.²⁰ The structure of DyNiSi_3 was solved by direct methods using the program SHELXS, and the final refinement of the structure by least squares on F^2 was carried out by SHELXL.²¹ For the other analogs, the atomic coordinates of DyNiSi_3 were used as a solution, and structural refinement with SHELXL was used to obtain final solutions. Data collection parameters and refinement details for TbNiSi_3 and DyNiSi_3 can be found in Table 4-1. The

refinement details for HoNiSi_3 and ErNiSi_3 are listed in Table 4-2 and the Lu and Yb analog information can be found in Table 4-3. Atomic positions and displacement parameters for RENiSi_3 (RE = Tb, Dy, Ho, and Er) are listed in Table 4-4 and the positions and displacement parameters for the Yb and Lu analogs are listed in Table 4-5. The anisotropic displacement parameters for RENiSi_3 (RE = Tb, Dy, Ho, and Er) are listed in Table 4-6 and the displacement parameters for the Yb and Lu analogs are found in Table 4-7.

Magnetic Characterization:

Magnetic susceptibility measurements were made on both powder and single crystal samples using a Quantum Design MPMS SQUID magnetometer. Finely ground poly-crystalline samples were placed in a polyethylene bag for the magnetic measurements. Single crystals were mounted on a rotating stage. In order to orient the crystals properly they were placed in a small spot of Apiezon grease, which solidifies at lower temperatures, (below 20 K) thus preventing the crystal from moving during the experiment. Temperature dependent susceptibility measurements were made with an applied field of 200 Oe from 2 to 300K with both field cooled and zero field cooled modes, and isothermal magnetization measurements were performed at 5 K with field sweeps from -55 kOe to 55 kOe.

Table 4.1. Crystal data and structure refinement for RENiSi₃ (RE=Tb, Dy).

Formula	TbNiSi ₃	DyNiSi ₃
Formula weight	301.90	305.48
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Space group	Cmmm (#65)	Cmmm(#65)
Unit cell dimensions	a = 3.9308(6) Å	a = 3.9155(11) Å
	b = 21.013(3) Å	b = 20.968(6) Å
	c = 3.9589(6) Å	c = 3.9427(11) Å
	326.99(9) Å ³	323.70(16) Å ³
Volume	4, 6.133 g/cm ³	4, 6.268 g/cm ³
Z, Density (calculated)	28.013 mm ⁻¹	29.533 mm ⁻¹
Absorption coefficient	540	544
F(000)	0.1 x 0.07 x 0.05 mm ³	0.3x0.3x0.09 mm ³
Crystal size	1.94 to 26.99°	1.94 to 27.01°
Theta range for data collection	-4<=h<=4	-4<=h<=5
	-22<=k<=26	-26<=k<=26
	-5<=l<=3	-4<=l<=4
Index ranges	1392 / 239	1282 / 233
Reflections collected / unique	0.0400	0.0673
R(int)	99.6 %	98.3
Completeness to θ_{max}	Full-matrix least-squares on F ²	
Refinement method	239 / 0 / 22	233 / 0 / 22
Data / restraints / parameters	1.249	1.156
Goodness-of-fit on F ²	R1 = 0.0372,	R1 = 0.0533
Final R indices [I>2σ(I)]	wR2 = 0.1032	wR2 = 0.1283
	R1 = 0.0372,	R1 = 0.0533
R indices (all data)	wR2 = 0.1032	wR2 = 0.1283
Extinction coefficient	0.048(5)	0.026(4)
Largest diff. peak and hole	2.270 / -2.303 e/Å ³	5.737 / -2.695 e/Å ³
R1 = $\sum F_o - F_c / \sum F_o $ and wR2 = $[\sum (F_o ^2 - F_c ^2)^2 / \sum (w F_o^2)^2]^{1/2}$		

Table 4.2. Crystal data and structure refinement for RENiSi₃ (RE = Ho, Er).

Formula	HoNiSi ₃	ErNiSi ₃
Formula weight	307.91	310.21
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system/ Space group	Cmmm (#65)	Cmmm (#65)
Unit cell dimensions	a = 3.9166(8) Å b = 20.982(5) Å c = 3.9386(9) Å	a = 3.9006(13) Å b = 20.886(7) Å c = 3.9209(13) Å
Volume	323.67(12) Å ³	319.42(18) Å ³
Z, density (calculated)	4, 6.319 g/cm ³	4/6.451 g/cm ³
Absorption coefficient	30.896 mm ⁻¹	32.809 mm ⁻¹
F(000)	548	552
Crystal size	0.4x0.3x0.2 mm ³	0.5x0.3x0.07 mm ³
Theta range for data collection	3.88 to 27.00°	1.95 to 26.25°
Index ranges	-5 ≤ h ≤ 4 -26 ≤ k ≤ 19 -4 ≤ l ≤ 4	-4 ≤ h ≤ 4 -22 ≤ k ≤ 21 -4 ≤ l ≤ 3
Reflections collected/unique	1522/234	849/163
R(int)	0.0880	0.0785
Completeness to θ_{max}	98.7 %	100%
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	234 / 0 / 22	163 / 0 / 22
Goodness-of-fit on F ²	1.129	1.113
Final R indices [I > 2σ(I)]	R1 = 0.0417 wR2 = 0.1098	R1 = 0.0578 wR2 = 0.1340
R indices (all data)	R1 = 0.0417 wR2 = 0.1098	R1 = 0.0578 wR2 = 0.1340
Extinction coefficient	0.041(5)	0.044(7)
Largest diff. peak / hole	3.592/-2.961 e/Å ³	2.657/-3.777 e/Å ³
R1 = $\sum F_o - F_c / \sum F_o $ and wR2 = $[\sum (F_o^2 - F_c^2)^2 / \sum (w F_o^2)^2]^{1/2}$		

Table 4.3. Crystal data and structure refinement for RENiSi₃ (RE = Yb, Lu)

Formula	YbNiSi ₃	LuNiSi ₃
Formula weight	316.02	317.95
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system/ Space group	Cmmm (#65)	Cmmm (#65)
Unit cell dimensions	a = 3.8927(8) Å b = 20.917(4) Å c = 3.9064(8) Å	a = 3.892(3) Å b = 20.910(18) Å c = 3.898(3) Å
Volume	318.08(11) Å ³	317.3(5) Å ³
Z, density (calculated)	4, 6.599 g/cm ³	4, 6.657 g/cm ³
Absorption coefficient	35.966 mm ⁻¹	37.698 mm ⁻¹
F(000)	560	564
Crystal size	0.2x0.07x0.05mm ³	0.2x0.1x0.05 mm ³
Theta range for data collection	3.90 to 27.00°	1.95 to 27.90°
Index ranges	-4 ≤ h ≤ 2 -22 ≤ k ≤ 26 -4 ≤ l ≤ 4	-5 ≤ h ≤ 3 -27 ≤ k ≤ 24 -4 ≤ l ≤ 5
Reflections collected/Unique	1320/220	1294/247
R(int)	0.0400	0.0258
Completeness to theta = 27.00°	96.9 %	96.5 %
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	220 / 0 / 22	247 / 0 / 22
Goodness-of-fit on F ²	1.112	1.139
Final R indices [I > 2σ(I)]	R1 = 0.0323 wR2 = 0.0829	R1 = 0.0266, wR2 = 0.0676
R indices (all data)	R1 = 0.0323, wR2 = 0.0829	R1 = 0.0269, wR2 = 0.0677
Extinction coefficient	0.030(3)	0.0068(8)
Largest difference peak and hole	2.652 / -1.847 e/Å ³	2.761 / -2.164 e/Å ³
R1 = $\sum F_o - F_c / \sum F_o $ and wR2 = $[\sum (F_o ^2 - F_c ^2)^2 / \sum (w F_o^2)^2]^{1/2}$		

Tabl 44. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiSi_3 (RE = Tb, Dy, Ho, Er).

Atom	Wyckoff Position	x	y	z	U(eq)*
Tb					
	4i	0	3314(1)	0	13(1)
Ni	4I	5000	6099(1)	5000	14(1)
Si(1)	4j	5000	5557(1)	0	14(1)
Si(2)	4j	0	4441(2)	5000	15(1)
Si(3)	4j	0	2179(2)	5000	14(1)
Dy	4i	0	3313(1)	0	7(1)
Ni	4i	5000	6104(1)	5000	8(1)
Si(1)	4j	5000	5561(2)	0	7(1)
Si(2)	4j	0	4443(3)	5000	7(1)
Si(3)	4j	0	2179(3)	5000	7(1)
Ho	4i	0	3312(1)	0	12(1)
Ni	4i	5000	6106(1)	5000	8(1)
Si(1)	4j	5000	5555(2)	0	12(1)
Si(2)	4j	0	4441(3)	5000	14(1)
Si(3)	4j	0	2185(2)	5000	13(1)
Er(1)	4i	0	3312(1)	0	16(1)
Ni	4i	5000	6108(2)	5000	17(1)
Si(1)	4j	5000	5556(3)	0	18(2)
Si(2)	4j	0	4440(5)	5000	19(2)
Si(3)	4j	0	2183(5)	-5000	17(2)

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

Table 4.5 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiSi_3 (RE = Yb and Lu).

Atom	Wyckoff Position	x	y	z	U(eq)
Yb					
	4i	0	3312(1)	0	12(1)
Ni	4i	5000	6115(1)	5000	12(1)
Si(1)	4j	5000	5559(2)	0	13(1)
Si(2)	4j	0	4443(2)	5000	12(1)
Si(3)	4j	0	2180(2)	5000	11(1)
Lu					
	4i	0	3312(1)	0	4(1)
Ni	4i	5000	6115(1)	5000	6(1)
Si(1)	4j	5000	5557(2)	0	7(1)
Si(2)	4j	0	4437(2)	5000	5(1)
Si(3)	4j	0	2180(2)	5000	5(1)

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

Table 46 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiSi_3 (RE = Tb, Dy, Ho, Er)

	U11	U22	U33	U23	U13	U12
Tb	12(1)	10(1)	15(1)	0	0	0
Ni	15(1)	9(1)	18(1)	0	0	0
Si(1)	20(2)	5(2)	18(2)	0	0	0
Si(2)	13(2)	10(2)	22(2)	0	0	0
Si(3)	14(2)	10(2)	18(2)	0	0	0
Dy	9(1)	5(1)	7(1)	0	0	0
Ni	10(2)	4(1)	10(2)	0	0	0
Si(1)	13(2)	2(2)	6(2)	0	0	0
Si(2)	6(2)	2(3)	13(2)	0	0	0
Si(3)	9(2)	4(3)	8(3)	0	0	0
Ho	16(1)	6(1)	15(1)	0	0	0
Ni	18(1)	5(1)	17(1)	0	0	0
Si(1)	19(2)	3(2)	15(2)	0	0	0
Si(2)	16(2)	2(2)	22(2)	0	0	0
Si(3)	16(2)	5(2)	19(2)	0	0	0
Er	18(1)	12(2)	20(1)	0	0	0
Ni	18(1)	12(2)	20(1)	0	0	0
Si(1)	26(4)	8(4)	20(4)	0	0	0
Si(2)	18(4)	10(5)	28(4)	0	0	0
Si(3)	19(4)	9(5)	23(4)	0	0	0

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

Table 4.7 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiSi_3 (RE = Yb, Lu).

	U11	U22	U33	U23	U13	U12
Yb	15(1)	11(1)	12(1)	0	0	0
Ni	16(1)	8(1)	14(1)	0	0	0
Si(1)	23(2)	5(2)	12(2)	0	0	0
Si(2)	15(2)	5(2)	17(2)	0	0	0
Si(3)	14(2)	4(2)	16(2)	0	0	0
Lu(1)	2(1)	3(1)	8(1)	0	0	0
Ni	4(1)	2(1)	11(1)	0	0	0
Si(1)	8(2)	3(1)	9(1)	0	0	0
Si(2)	2(2)	2(2)	11(2)	0	0	0
Si(3)	2(2)	1(2)	11(2)	0	0	0

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

4-3 Results and Discussion.

Synthesis:

There are several methods to obtain RENiSi_3 ($\text{RE}=\text{Tb, Dy, Ho, Er, Yb, Lu}$) in relatively pure form. Since the purpose of this particular study was to determine anisotropic magnetic properties large single crystals were required. We know from this and previous work that lanthanide and transition metals are soluble in Ga as are a host of main group elements in particular Si. We also know that quaternary phases of the type RE/Ni/Si/Ga do not form easily, making Ga an ideal medium for the synthesis and crystallization of silicides. Figure 4-1 shows a SEM micrograph of a HoNiSi_3 single crystal formed from a Ga flux reaction. Differential thermal analysis of RENiSi_3 (specifically DyNiSi_3) showed no phase change up to 1000 °C, meaning the Ga flux reaction allows the formation, and crystal growth of this phase at temperatures well below its melting point.

Large polycrystalline pellets of RENiSi_3 can be produced from arc melting reactions as well. This indicates that RENiSi_3 is most likely a thermodynamically stable phase, and that its formation in the Ga flux is not a result of trapping a kinetically stable phase as we have seen in other systems.²² Polycrystalline samples were also used to investigate the magnetic properties of these compounds. It is curious that the BaNiSn_3 structure of RENiSi_3 was not observed in the products prepared by arc melting, as similar conditions were used to produce this phase.¹⁸

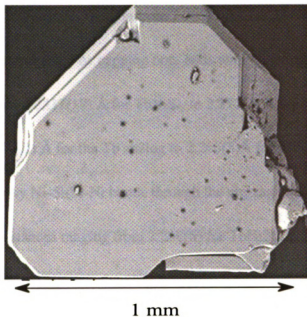


Figure 4-1 SEM micrograph of a HoNiSi_3 single crystal.

Structural Description:

RENiSi_3 is composed of 2 building blocks. The first is a stack of staggered pseudo-square nets of rare earth ions like that shown in Figure 4-2(A). The distances between the rare earth ions in the ac plane are equal to the a and c lattice parameters. The second is a NiSi_3 network, Figure 4-2(B). The NiSi_3 network can be further decomposed into a Si(3) zig-zag chain propagating along the a -axis with bond distances that range from 2.358(5) Å for TbNiSi_3 to 2.362(4) for LuNiSi_3 , Figure 4-3(A), and NiSi_2 cages like those seen in Figure 4-3(B). The cage is formed by disilicide bonds made through Si(1) and Si(2) forming bonds with their symmetry generated equivalent with Si(1)-Si(1) distances ranging from 2.342(6) Å for TbNiSi_3 to 2.331(7) Å for the Lu

analog, and Si(2)-Si(2) distances ranging from 2.349(10) Å for TbNiSi₃ to 2.355(7) Å for LuNiSi₃. The cage is completed by capping both ends with Ni atoms, with Ni-Si(1) bond distances ranging from 2.2837(18) Å for TbNiSi₃ to 2.272(2) Å for LuNiSi₃ and the Ni-Si(2) range from 2.270(3) Å for the Tb analog to 2.263(3) Å for LuNiSi₃. The cages are linked to one another by Ni-Si(3)-Ni bonds through the zig-zag chain with stacking along the *b*-axis. Ni Si(3) distances ranging from 2.268(5) for TbNiSi₃ to 2.226(4) Å for LuNiSi₃.

The rare earth ions that define the pseudo-square net lie in the *ac* plane, which defines the basal plane of the structure. As mentioned before the rare earth ion separation within this plane is equal to the *a* and *c* lattice parameters of the particular compound. The distance between rare-earth ions along the *b*-axis is comparable to the separation of those in the plane. The one crystallographically distinct rare earth atom is in a highly symmetric 14 coordinate environment of 6 Si(3) atoms 4 Ni atoms 2 Si(1) atoms and 2 Si(2) atoms as can be seen in Figure 4-4. A complete list of the bond distances for RENiSi₃ (RE = Tb, Dy and Ho) can be found in Table 4-8, and the distances for RE = Er, Yb and Lu are listed in Table 4-9.

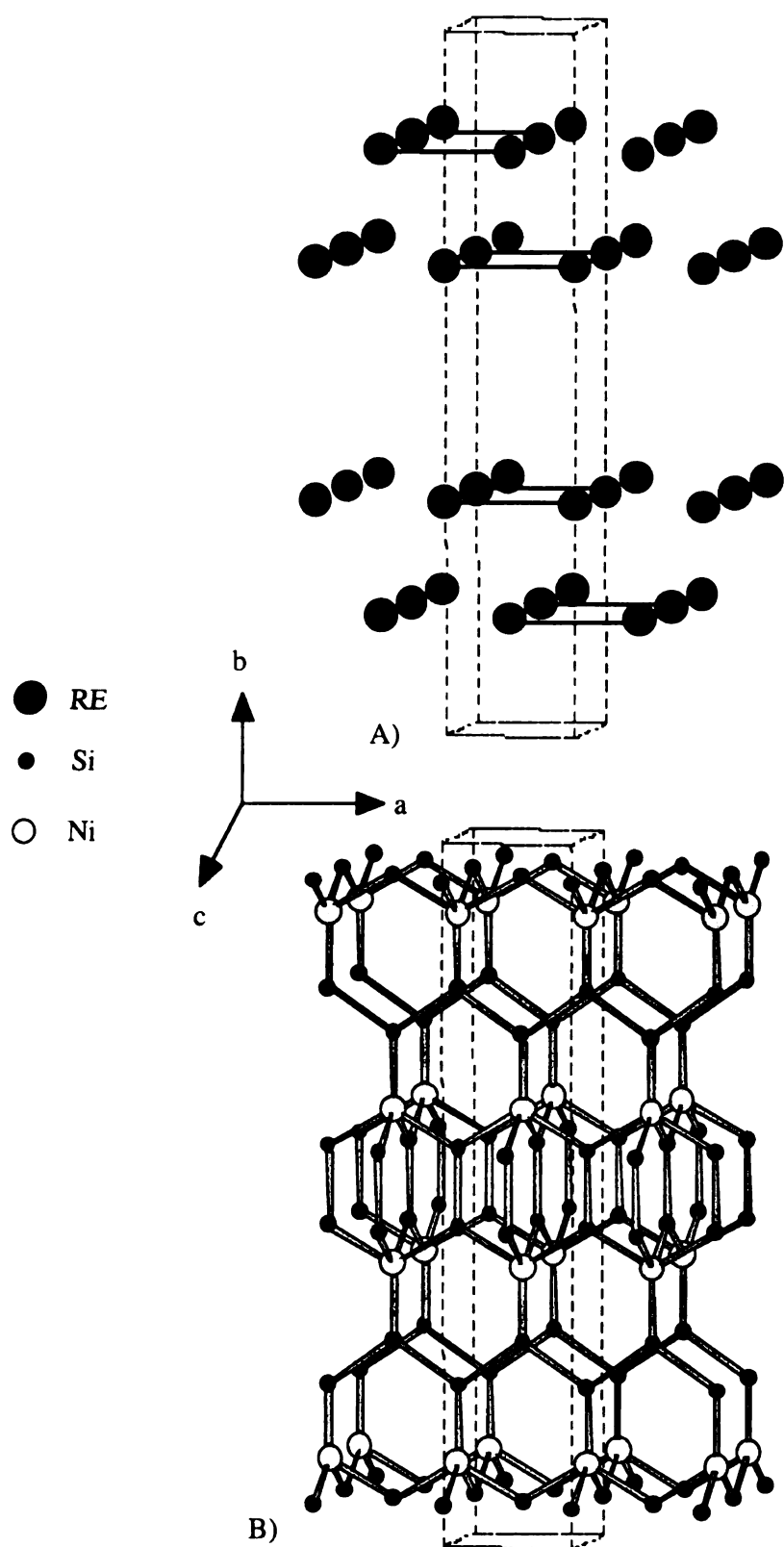
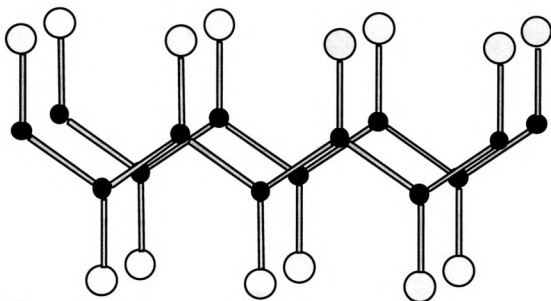
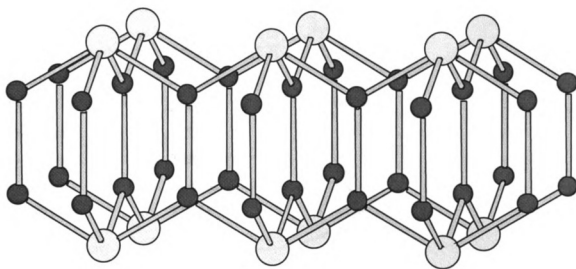


Figure 4-2 (A) View of the staggered pseudo square net that defines the rare earth sub lattice. (B) Representation of the NiSi_3 structure with the rare earth ions removed for clarity. This shows the Si zig-zag chains and the NiSi_2 cages.



A)



B)

Figure 4-3 (A) A view of the Si zig-zag chains and their connectivity to the Ni atoms.
(B) A portion of the NiSi_2 cages that are composed of disilicide bonds with capping by Ni atoms.

Figure 4-4 Co
ion.

Table 4-8. Bo

RE(1)-Si(3) x 4

RE(1)-Ni(1) x 4

RE(1)-Si(1) x 4

RE(1)-Si(2) x 4

RE(1)-Si(3)

Ni(1)-Si(3)

Ni(1)-Si(2) x 2

Ni(1)-Si(1) x 2

Si(1)-Si(1)

Si(1)-Si(2) x 4

Si(2)-Si(2)

Si(2)-Si(1) x 4

Si(3)-Si(3) x 2

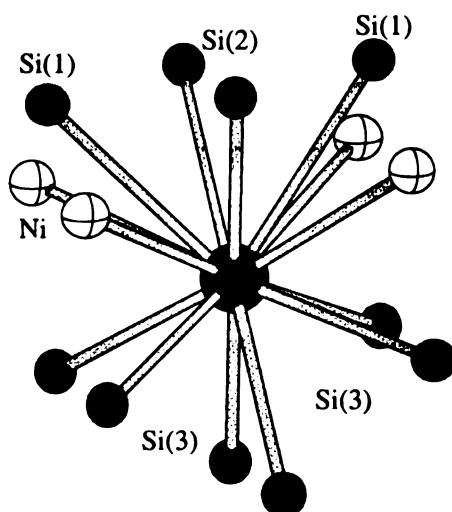


Figure 4-4 Coordination environment of the one crystallographically distinct rare earth ion.

Table 4-8. Bond lengths [$\text{\AA}$] for RENiSi_3 (RE = Tb, Dy, Ho).

	TbNiSi ₃	DyNiSi ₃	HoNiSi ₃
RE(1)-Si(3) x 4	2.9754(16)	2.964(2)	2.9660(18)
RE(1)-Ni(1) x 4	3.0496(9)	3.0352(13)	3.0342(11)
RE(1)-Si(1) x 2	3.080(2)	3.068(3)	3.077(4)
RE(1)-Si(2) x 2	3.086(4)	3.083(5)	3.080(3)
RE(1)-Si(3)	3.100(4)	3.088(5)	3.077(4)
Ni(1)-Si(3)	2.268(5)	2.254(7)	2.263(6)
Ni(1)-Si(2) x 2	2.270(3)	2.270(4)	2.269(3)
Ni(1)-Si(1) x 2	2.2837(18)	2.277(2)	2.283(2)
Si(1)-Si(1)	2.342(6)	2.351(8)	2.330(7)
Si(1)-Si(2) x 4	2.7894(3)	2.7783(6)	2.7773(4)
Si(2)-Si(2)	2.349(10)	2.334(12)	2.270(3)
Si(2)-Si(1) x 4	2.7895(3)	2.7783(5)	2.7773(4)
Si(3)-Si(3) x 2	2.385(5)	2.375(7)	2.363(6)

Table 4-9. Bond

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Table 4-9. Bond lengths [$\text{\AA}$] for RENiSi_3 (RE = Er, Yb, Lu).

	ErNiSi ₃	YbNiSi ₃	LuNiSi ₃
RE(1)-Si(3) x 4	2.952(4)	2.9433(15)	2.940(2)
RE(1)-Ni(1) x 4	3.019(2)	3.0070(9)	3.0039(17)
RE(1)-Si(1) x 2	3.066(5)	3.068(3)	3.063(3)
RE(1)-Si(2) x 2	3.066(9)	3.060(3)	3.080(3)
RE(1)-Si(3)	3.100(4)	3.068(3)	3.055(3)
Ni(1)-Si(3)	2.244(13)	2.229(5)	2.226(4)
Ni(1)-Si(2) x 2	2.262(7)	2.269(3)	2.263(3)
Ni(1)-Si(1) x 2	2.275(4)	2.2725(19)	2.271(2)
Si(1)-Si(1)	2.321(12)	2.340(6)	2.331(7)
Si(1)-Si(2) x 4	2.7653(7)	2.7574(4)	2.7544(17)
Si(2)-Si(2)	2.34(2)	2.331(9)	2.355(7)
Si(2)-Si(1) x 4	2.7653(6)	2.7574(4)	2.7544(17)
Si(3)-Si(3) x 2	2.358(12)	2.362(5)	2.362(4)

Magnetic Measurements:

Susceptibility and magnetization measurements were made on single crystal as well as polycrystalline samples for each of the analogs. For each single crystal, measurements were made on each of the 3 principle crystallographic axes, and in the case of DyNiSi_3 , magnetic measurements of the basal plane diagonal were made as well. As is often found with intermetallics containing electropositive elements, such as rare earths, the Ni does not contribute to the paramagnetic susceptibility of these compounds. It is therefore anticipated to have a diamagnetic d^{10} configuration.²³ Ab-initio band structure

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calculations, previously run on YNiSi_3 , found that the Ni d states were far below the fermi-level and therefore filled. Indeed susceptibility measurements made on YNiSi_3 found only Pauli paramagnetism.¹⁴ This behavior was found for the title compounds as well. The only contribution to the paramagnetic susceptibility is from the rare-earth ions, which are all in the 3+oxidation state. TbNiSi_3 , DyNiSi_3 , HoNiSi_3 , ErNiSi_3 and YbNiSi_3 all order antiferromagnetically. Above the antiferromagnetic ordering temperature all the compounds (with the exception of LuNiSi_3) follow the Curie/Weiss law with effective magnetic moments that are in excellent agreement with the calculated value of the corresponding isolated ions. The experimentally determined moment from polycrystalline samples, and the calculated moments are compared in Table 4-10. Figures 4-5 (A) and (B) show the susceptibility and magnetization data for a polycrystalline sample of DyNiSi_3 . The compound orders antiferromagnetically with a Néel temperature of 20 K. The magnetization data shows a 2 step meta-magnetic transition, with one step at 25 kOe, and the second at 45 kOe. Figures 4-5 (C) and (D) show the susceptibility and magnetization curve, respectively for a polycrystalline sample of HoNiSi_3 . This compound was also found to order antiferromagnetically, and possess a field induced meta-magnetic transition. In addition pronounced hysteresis was also found in the magnetization curve of the HoNiSi_3 . It is the two step meta-magnetic transition found in DyNiSi_3 and the meta-magnetic and hysteresis behavior found in HoNiSi_3 that inspired the growth of single crystals for further investigation of the magnetic properties

of this series of compounds. In the following sections the single crystal magnetic measurements of each of the compounds will be presented, then compared and summarized in the subsequent section.

Table 4-10 Polycrystalline magnetic data for RENiSi_3 .

	TbNiSi_3	DyNiSi_3	HoNiSi_3	ErNiSi_3	YbNiSi_3	LuNiSi_3
$\mu_{\text{eff}} (\mu_{\text{B}})$	9.5	10.6	10.4	9.3	4.5	0
$T_{\text{N}} (\text{K})$	35	20	11	4	3	0
$\Theta (\text{K})$	-30	-25	-3	-2	-130	

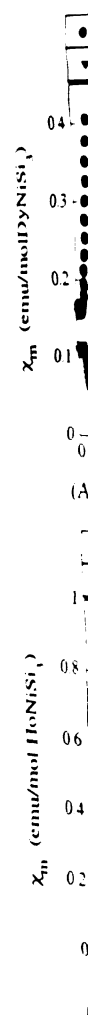


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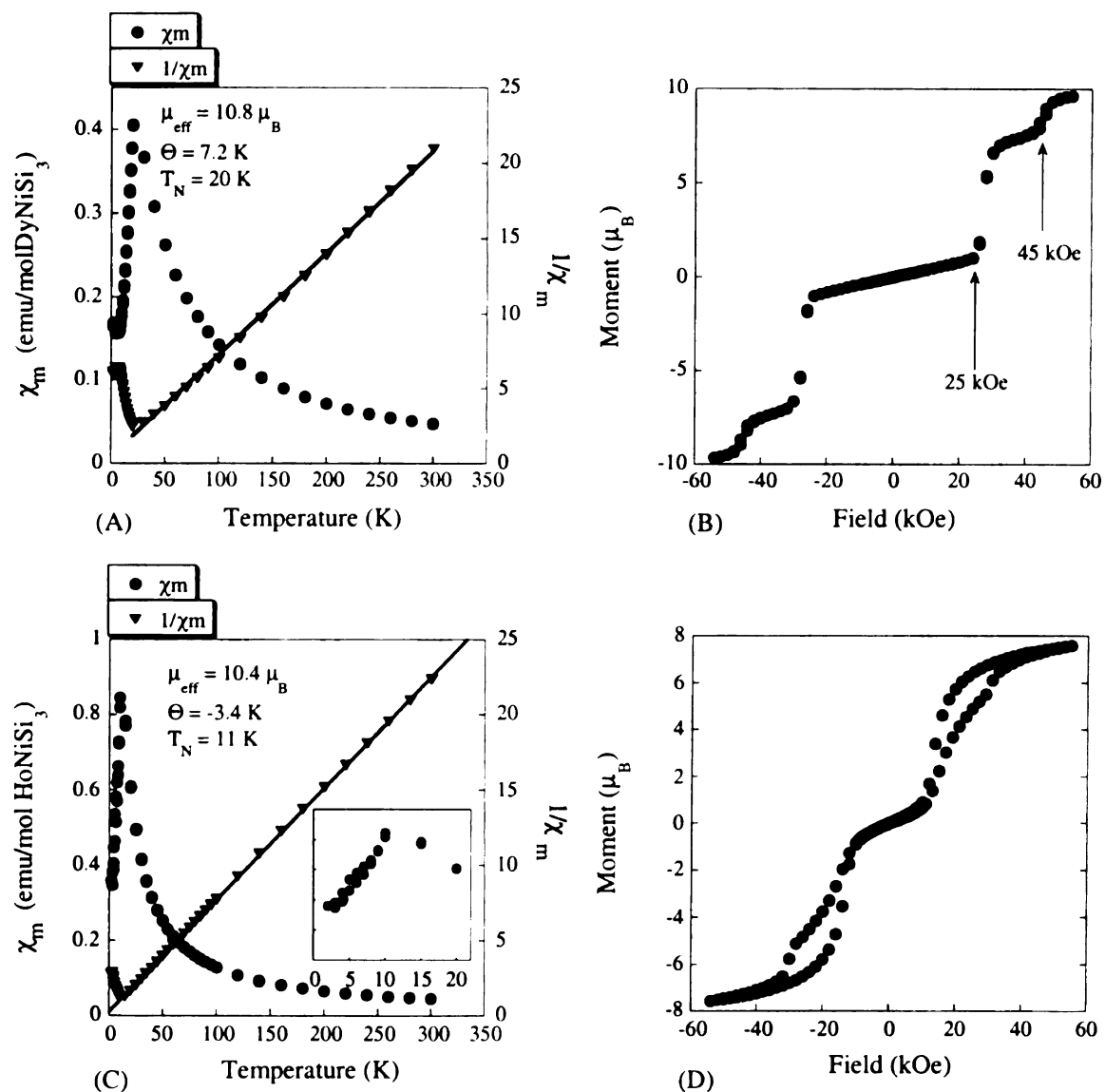


Figure 4-5 (A) The susceptibility data for a polycrystalline sample of DyNiSi₃. (B) The magnetization curve for a polycrystalline sample of DyNiSi₃. This sample undergoes 2 meta-magnetic transitions at 25 and 45 kOe. (C) The susceptibility data for a polycrystalline sample of HoNiSi₃. (D) The magnetization curve for a polycrystalline sample of HoNiSi₃.

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TbNiSi₃: Tb is the earliest rare earth metal that will form this phase, and several attempts to make GdNiSi₃ were unsuccessful. TbNiSi₃ also has the highest Néel temperature of the compounds presented, at 35 K for the polycrystalline sample. A single crystal with dimensions of 2 x 1.5 mm x 0.3mm was picked and screened by single crystal x-ray diffraction to ensure quality, and that is was composed of a single crystallographic domain. This crystal was found to be single and face indexing determined that the 2 mm edge coincided with the *c*-axis and the 1.5 mm side with the *a*-axis. The crystal was mounted on the single crystal stage of the SQUID magnetometer with the basal plane oriented parallel with the applied field. A field of 200 Oe was applied, and the susceptibility was measured as a function of the rotation angle through the basal plane. The results are shown in Figure 4-6. There are maxima and minima in the susceptibility that appear as the crystal is rotated. These maxima and minima are separated by 180 ° as would be expected for a crystal with orthorhombic symmetry. It was found that the *a*-axis coincided with the maximum and the *c*-axis with the minimum.

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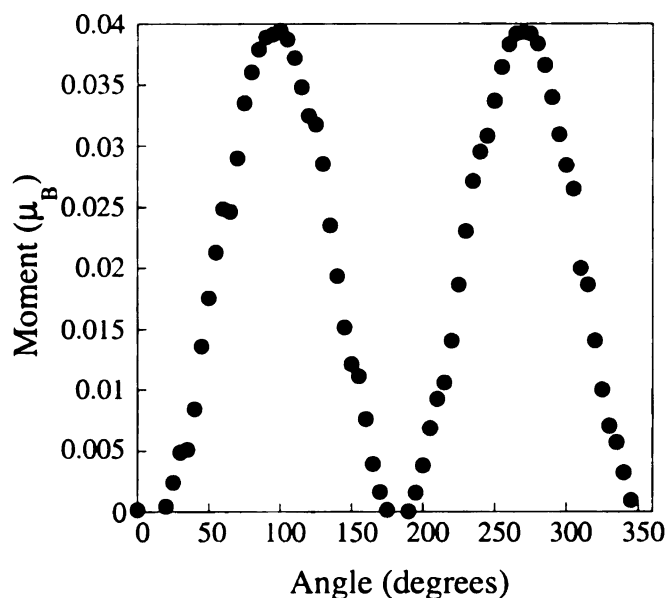


Figure 4-6 The magnetic susceptibility as a function of rotation angle about the basal plane, the data were collected at 5 K. The maxima and minima are located at 180° intervals.

The crystal was oriented with the applied field parallel to the c -axis (susceptibility minimum), and susceptibility and magnetization measurements were performed. The results of these measurements can be seen in Figures 4-7 (A) and (B) respectively.

There is a maximum in the zero field cooled susceptibility, indicating the onset of antiferromagnetic order at approximately 35 K. Below this temperature the susceptibility drops quickly to nearly 0 at 10 K. There is a small upturn in the data below this temperature, which is most likely due to a paramagnetic impurity. Upon closer inspection of the susceptibility minima a hysteresis was found between the zero field cooled and field cooled data. There are several possible explanations for this hysteresis, one being that the system is a spin glass, and that as the system is cooled in the absence

of a field the moments align antiferromagnetically and the susceptibility falls to 0.

However, when the system is field cooled the moments tend to align with the field, and may get "frozen" into place below the ordering temperature with a component of the magnetic dipole along the applied field axis, resulting in a higher susceptibility.

The moment, in the magnetization curve, is weakly dependant on the applied field up to approximately 47 kOe, Figure 4-7 (B). At this point an abrupt field induced transition takes place, and the moments begin to align with the applied field, forming a ferromagnetic state. The maximum field attainable by this magnetometer was insufficient to saturate the spins, but it is thought that if larger fields were applied a complete alignment of the moments could occur resulting in saturation.

The crystal was rotated 90° so the applied field was coincident with a maximum in the rotational scan and the susceptibility and magnetization measurements were repeated. These data are found in Figures 4-7 (C) and (D) respectively. There are several differences that are evident between the susceptibility and magnetization data when compared to the previous set of data. First the magnitude of the molar susceptibility near the Néel temperature along the *a*-axis is approximately 1/4 of that measured along the *c*-axis. As was the case with measurements made along the *c*-axis there is a minimum in the susceptibility at about 10K before the susceptibility increases. Again this is attributed to a small paramagnetic impurity. What is also evident here is the same hysteresis behavior

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In the case of the magnetization experiments, no magnetic transition was observed when the field was applied along the *a*-axis. Instead a linear increase in the moment with the applied field was observed, with the magnitude of the moment being quite comparable to the *c*-axis moment in low fields. At higher fields along the *c*-axis a metamagnetic transition was observed. No such transition was observed in the *a*-axis and so the magnitude of the moment is rather modest as compared to the high field moment along the *c*-axis.

Finally, the crystal was oriented with the applied field parallel to the *b*-axis (perpendicular to the basal plane), and the experiments were repeated. The susceptibility and magnetization data for this orientation can be found in Figures 4-7(E) and (F) respectively. What is immediately evident upon inspection of the susceptibility data is that no antiferromagnetic ordering is found. Instead, the susceptibility data increases continuously down to 2 K. When looking at the inverse susceptibility data a departure from Curie/Weiss behavior is found below 15 K, however the data above this temperature, follow Curie/Weiss law with an effective magnetic moment of $9.6 \mu_B$. This is in good agreement with the calculated moment of a free Tb^{3+} ion. The Weiss constant is 0.6 K indicating very weak ferromagnetic interactions of the ions along the *b*-axis. These

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findings indicate that the magnetic moments of the Tb^{3+} ion, below the Néel temperature, are confined to the basal plane. Since no ordering was observed perpendicular to this plane we can infer that no vector component of the magnetic moment is out of the plane.

The behavior of the magnetization data along the b -axis is similar to the a -axis behavior in that there is a linear dependence between the moment and the applied field. Even the magnitude of the moment between the a and b -axis are comparable, and again there is no observation of a magnetic transition.

These results can be rationalized by thinking of a plane of antiferromagnetically ordered spins. The nature of the antiferromagnetic ordering is not important, only that that they are confined to a plane. If a magnetic field is applied perpendicular to these ordered spins (i.e. along the b -axis of the present structure) they will begin to bend out of the plane in response to the force of the applied field. The stronger the field, the more the moments are bent out of the plane. A similar scenario can be envisioned for the a -axis moments as well. If the moments order with the majority of the vector component aligned with the c -axis a similar mechanism will arise where the moments are bent away from the c -axis as a field is applied perpendicular to this direction. Again the extent of the bending will be proportional to the strength of the field applied. The nature of the crystalline electric field and its consequences will be revisited in the discussion section.

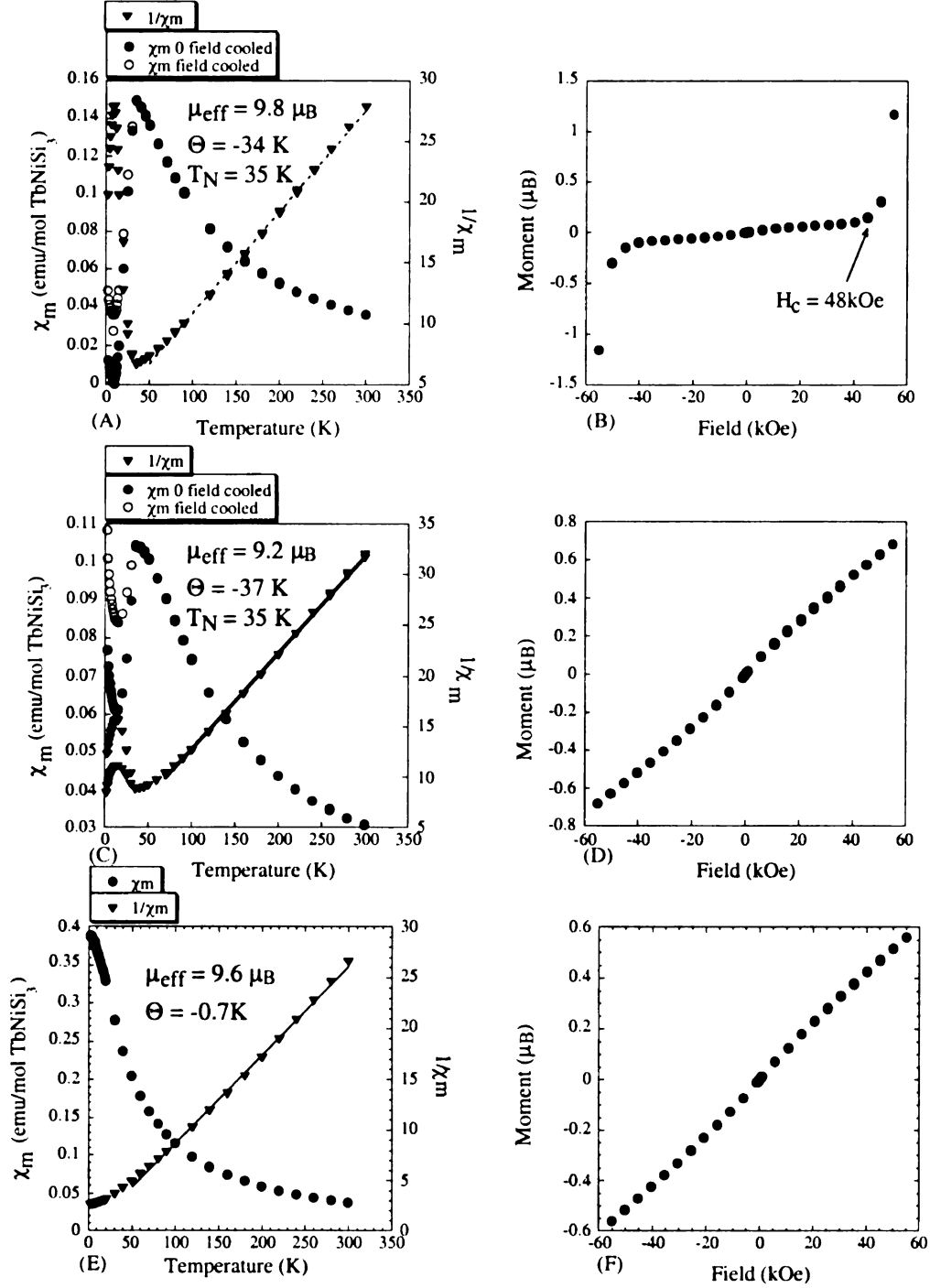


Figure 4-7 (A) The molar susceptibility and inverse susceptibility for the *c*-axis of TbNiSi₃. (B) The magnetization curve for TbNiSi₃ with the field parallel to the *c*-axis. (C) Susceptibility and inverse susceptibility for the *a*-axis of TbNiSi₃. (D) The magnetization curve for the *a*-axis of TbNiSi₃. (E) Magnetic susceptibility measurements performed along the *b*-axis of TbNiSi₃. (F) Magnetization curve for the field applied along the *b*-axis.

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DyNiSi₃: The crystal picked for these magnetic measurements was approximately 1mm x 1.2 mm x 0.2mm. It was screened for elemental composition to ensure it was purely DyNiSi₃, and then mounted for single crystal x-ray diffraction to check for quality and to assign the crystallographic axes. It was found that the *c*-axis was parallel with the 1mm edge, the *a*-axis with 1.2 mm edge, and the *b*-axis perpendicular to the plate, and that the crystals was composed of a single crystallographic domain. The crystal was mounted on the single crystal stage, again with the basal plane parallel to the applied field. The rotational susceptibility about the *b*-axis was collected at 5 K with an applied field of 200 Oe. Qualitatively similar behavior was found for the DyNiSi₃ rotational susceptibility as was found for TbNiSi₃. The difference being, the susceptibility of DyNiSi₃ did not go to 0 for any orientation of the basal plane. There were still maxima and minima in the data with a period of 180 ° consistent with the orthorhombic symmetry of the system, and the minima were again coincident with the *c*-axis and the maxima with the *a*-axis.

The crystal was oriented with the *c*-axis parallel to the applied field, and susceptibility and magnetization data were collected. The results of these measurements can be seen in Figures 4-8 (A) and (B) respectively. The susceptibility data shows a maximum at 20 K corresponding to the onset of antiferromagnetic order. Below the Néel temperature, the susceptibility decreases to its minimum value of 0.1 emu/mol at 6K. At even lower temperatures there is an upturn in the susceptibility, which is again likely due

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to a small paramagnetic impurity. Unlike TbNiSi₃, the susceptibility never goes to zero and there is little hysteresis between the field cooled and zero-field cooled data. The fact that the susceptibility does not go to zero indicates that the magnetic moments do not completely cancel along the *c*-axis as they do in TbNiSi₃.

The magnetization data, Figure 4-8 (B), shows a field induced magnetic transition at about 25 kOe. At this field there is a dramatic increase in the moment from 0.5 μ_B to 7.3 μ_B . The Dy³⁺ ion moments are nearly saturated above this point, as evidenced by the magnitude of the moment becoming nearly independent of the applied field. The experimentally determined moment is about 7.5 μ_B at the highest attainable field, a value that is considerably smaller than the calculated μ_{sat} for a Dy³⁺ ion, which is 10.0 μ_B . This implies that the field induced magnetic transition does not fully align the magnetic moments of the rare earth ions along the *c*-axis.

The crystal was rotated 90° so the applied field was parallel to the *a*-axis, and the experiments were repeated. The results of the susceptibility and magnetization measurements can be seen in Figures 4-8 (C) and (D) respectively. Surprisingly there was no maximum found in the susceptibility data along this axis, instead only a small discontinuity was observed in the susceptibility at about 20 K. Despite this small deviation, the susceptibility data can be fit to the Curie/Weiss law over the entire temperature range investigated. The resulting effective magnetic moment of 10.5 μ_B

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compares well with the calculated value of 10.63 and the Weiss constant (θ) of -32 K indicates strong antiferromagnetic interaction of the ions along this axis.

The magnetization curve, Figure 4-8 (D), shows no magnetic transitions when the field is applied along the a -axis, but instead behaves much like the a -axis magnetization curve of TbNiSi₃, with the moment increasing linearly with field. The moment obtained at 55 kOe for DyNiSi₃ is substantially larger than the corresponding value in the Tb analog.

Several other measurements were made at angles intermediate to the maxima and minima to look for the second transition that we observed at 45 kOe in the polycrystalline sample. It was found that when the crystal was oriented with the basal plane diagonal parallel to the applied field the second transition was observed. The susceptibility and magnetization for the basal plane diagonal can be seen in Figures 4-8 (E) and (F) respectively. Along this direction antiferromagnetic ordering was observed in the susceptibility data with a Néel temperature of 20 K. Above this temperature the data follow a Curie/Weiss law with an extremely small Weiss constant of 0.14K meaning only weak interactions are taking place between the ions in this direction.

In the magnetization curve there is a linear dependence of moment on field up to 45 kOe. The slope of this curve, and the magnitude of the moment are similar to those

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measured along the a -axis. Above 45 kOe the moment is nearly independent of the applied field. The experimentally determined saturation moment is $9.5 \mu_B$, which is quite close to the calculated value of $10.0 \mu_B$

There are several possible reasons why the moments do not saturate fully along the diagonal. One is an insufficient field, as can be seen in Figure 4-7 (F) there is still a small slope to the magnetization curves at high fields, and perhaps with a stronger field the moments would saturate fully. Another possibility is there exists a small component of the magnetic moment that lies outside the basal plane, and there is no way to orient the sample as to align this small component with the field.

To investigate this possibility the crystal was oriented with the b -axis parallel with the field and susceptibility and magnetization data were re-collect. These data can be seen in Figure 4-9 (A) and (B) respectively. It is immediately apparent by inspection that an antiferromagnetic transition occurred with a Néel temperature of 20K. The Weiss constant (θ) extracted from the data above the transition is quite small and negative indicating weakly antiferromagnetically coupled moments along the b -axis. The magnetization curve is linear with a magnitude and field dependence that is similar to that observed for the a -axis. The fact that ordering is observed perpendicular to the plane suggests that there is at least a small component of the rare earth magnetic moment vector that lies outside of the basal plane. In the case of TbNiSi_3 no ordering was observed

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The magnetic behavior of DyNiSi₃ is different from TbNiSi₃ in several respects. The first being that a crystallographic orientation could not be found with the single axis crystal stage in which the moments canceled fully below the Néel temperature, as they did along the *c*-axis of TbNiSi₃. Secondly, two magnetic transitions were observed along two crystallographic axes, which were not mutually orthogonal. The magnetic transition which occurred at 25 kOe along the *c*-axis for DyNiSi₃, is analogous to that found in the TbNiSi₃ case, though it is not a complete field induced meta-magnetic transition as only 75 % of the moments are accounted for. When the crystal is re-oriented with the applied field parallel to the *a*-axis there is only a small bump in the susceptibility data at 20 K, Figure 4-8 (C). This indicates that there is only a small vector component of the magnetic dipole along the *a*-axis as only a weak response in the susceptibility was observed. This is further supported by the results of the magnetization data, which shows no meta-magnetic transition when the field is applied along this axis, Figure 4-8 (D). When the crystal was oriented with the basal plane diagonal parallel to the field there is again a maximum in the susceptibility data at 20 K that corresponds to the Néel temperature, Figure 4-8 (E). The magnetization of DyNiSi₃ along the basal plane diagonal is nearly linear with applied field up to 40 kOe at which point there is a meta-magnetic transition

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that takes place, Figure 4-7(F). We found that this crystal orientation allowed the magnetic moments to nearly completely align with the applied field. This higher field transition could be caused by a quasi-stable arrangement of spins when the field is applied to the *c*-axis that causes either part of the magnetic sub-lattice to orient along the *c*-axis or a component of the moment to become aligned along this direction. It is curious that when the field is applied to the basal plane diagonal the transition that occurs in the *c*-axis is not seen at all even though the field is not orthogonal to this axis.

HoNiSi₃: A single crystal with approximate dimensions 0.9 x 1.2 x 0.3 mm³ was picked from the Ga flux reaction of the elements. Microprobe elemental analysis was carried out to confirm the composition, and it was determined that the crystal was composed of Ho, Ni and Si. Single crystal face indexing determined that the *a*-axis was 0.9mm, the *c* axis was 1.2 mm and *b* was 0.3 mm. The crystal was mounted on the single crystal stage as before, and the rotational susceptibility data was found to be similar to those found for TbNiSi₃ and DyNiSi₃. As was the case with the two previous systems maxima and minima were observed with a period of 180°, and the minima were coincident with the *c*-axis and the maxima to the *a*-axis. As was the case with DyNiSi₃ there was no orientation of the basal plane that coincides with a complete cancellation of the HoNiSi₃ moments.

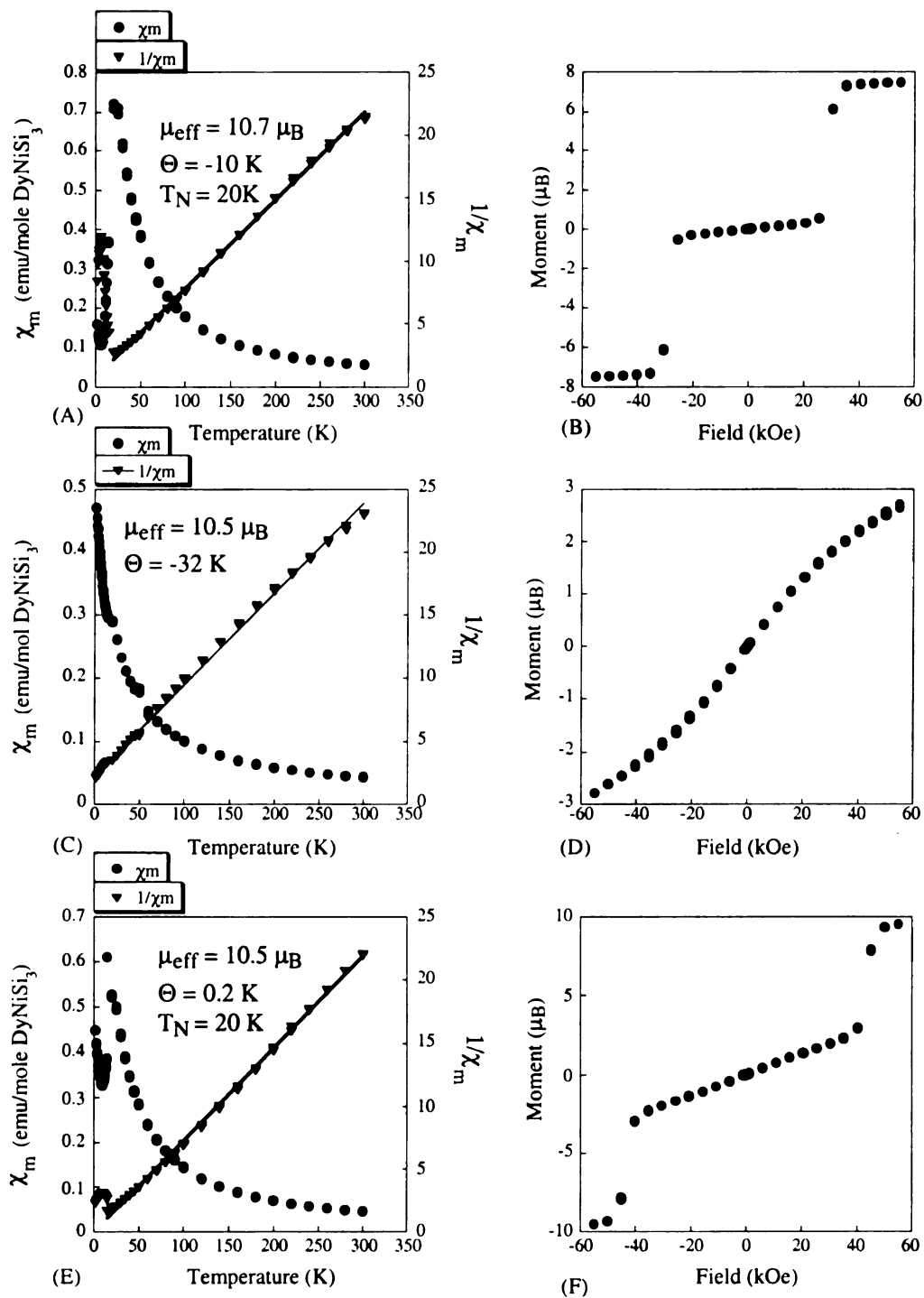


Figure 4-8 (A) The molar susceptibility and inverse susceptibility for the *c*-axis of DyNiSi₃. (B) The magnetization curve for the *c*-axis of DyNiSi₃. (C) The molar susceptibility and inverse susceptibility for the *a*-axis of DyNiSi₃. (D) Magnetization curve for *a*-axis of DyNiSi₃. (E) The molar susceptibility and inverse susceptibility for the basal plane diagonal for DyNiSi₃. (F) The magnetization curve of the basal plane diagonal of DyNiSi₃.

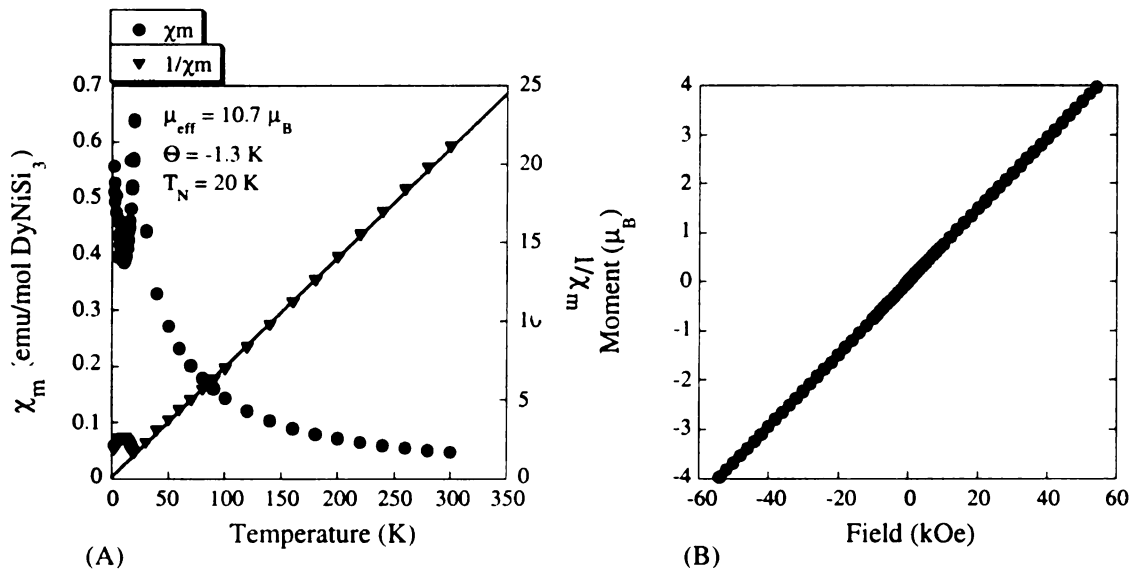


Figure 4-9 (A) The susceptibility and inverse susceptibility data collected with the applied field perpendicular to the basal plane. (B) The magnetization curve collected perpendicular to the basal plane.

The susceptibility and magnetization data collected with the applied field parallel to the *c*-axis (minimum) can be seen in Figures 4-10 (A) and (B) respectively. HoNiSi₃ orders antiferromagnetically with a Néel temperature of 10 K, as evidenced by the maximum in the susceptibility at this temperature. Below the ordering temperature the susceptibility drops to a minimum at 2 K with no upturn in the susceptibility found. Above the ordering temperature the data follow the Curie/Weiss law with an effective moment of $10 \mu_B$, and a Weiss constant of -11 K indicating moderate antiferromagnetic interactions between the ions. The effective moment is lower than the calculated moment of a free Ho³⁺ ion, which is $10.4 \mu_B$, but is still in reasonably good agreement. The

magnetization curve, Figure 4-10 (B), shows a sharp meta-magnetic transition at 11 kOe where the moments begin to align ferromagnetically along the *c*-axis. By 15 kOe the magnitude of the moment becomes nearly independent of the applied field, with a value of $7.5 \mu_B$. This behavior mirrors that of DyNiSi_3 when the field was applied along the *c*-axis, in that a single transition was observed which aligns approximately 75 % of the magnetic moments.

When the crystal was rotated 90° and the experiment was repeated antiferromagnetic ordering was again found in the susceptibility data, and a field induced meta-magnetic transition was found at a higher field in the magnetization curve, Figures 4-10 (C) and (D), respectively. Several difference in the susceptibility data between the *a* and *c*-axis are immediately evident. First, and most significantly, along the *a*-axis there is a small bump in the susceptibility data at 11 K (The Néel temperature observed along the *c*-axis) and then a maximum at 6 K, well below the temperature found along the *c* - axis. This is shown more clearly in the inset of Figure 4-10 (C). This indicates that a second magnetic ordering event is taking place along this axis. It is curious that this transition was not observed in the polycrystalline data seen in Figure 4-5 (C). As was the case with the *c*-axis susceptibility, the *a*-axis susceptibility data also follow the Curie/Weiss law above the Néel temperature. The resulting effective moment of $10.3 \mu_B$

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is in excellent agreement with calculated value for a Ho^{3+} ion, and a Weiss constant of -16 K indicates antiferromagnetic interactions.

In the magnetization curve, again there is no evidence of the transition at 11 kOe instead the moment has a nearly linear dependence on the field until a meta-magnetic transition takes place at 45 kOe. In the magnetization curve of the polycrystalline sample we observed a hysteresis loop in the high field region, Figure 4-5 (D). This behavior is mirrored in the single crystal case as well, though in the single crystal case it is confined to a narrower field region between 30 and 55 kOe. The polycrystalline sample exhibited the hysteresis between 20 and 45 kOe. In Figure 4-10(D) arrows have been inserted to guide the eye in the direction of the events. The first transition takes place at about 45 kOe where it reaches its maximum value of $9.5 \mu_B$. This value is quite close to the calculated saturation moment of $10.0 \mu_B$ for a Ho^{3+} ion. As the field is decreased the moment remains almost constant at $9.5 \mu_B$ until about 30 kOe when the value drops to $5.7 \mu_B$. As the field is decreased further the hysteresis behavior disappears, and the data follows the same, nearly linear, curve as when the field was being increased. When the field orientation is reversed the same behavior is observed, and the hysteresis is fully reversible.

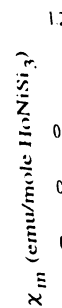
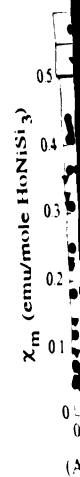


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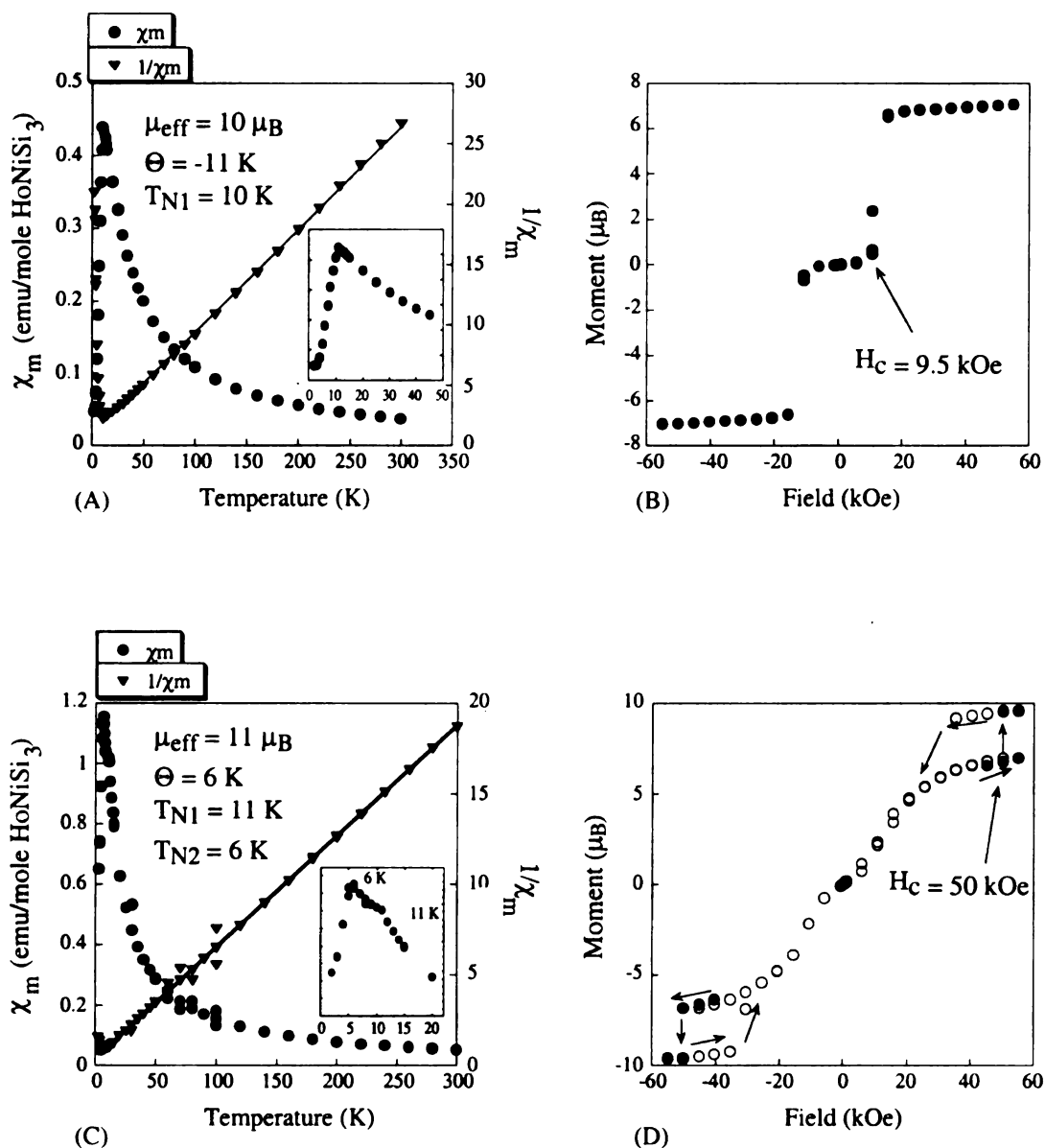


Figure 4-10 (A) The molar susceptibility and inverse susceptibility for the c -axis of HoNiSi_3 . (B) Magnetization data with the field oriented along the c -axis. (C) The molar susceptibility and inverse susceptibility for the a -axis of HoNiSi_3 . (D) Magnetization curve for HoNiSi_3 with the field oriented parallel to the a -axis.

Some of the magnetic behavior of the HoNiSi_3 is analogous to that of DyNiSi_3 in

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antiferromagnetic ordering was observed (near cancellation of the magnetic moment inferred from susceptibility data). A field induced transition also occurred at a low field in this direction, which was only able to align 75 % of the total moment. When the crystal was oriented along a different axis in the basal plane a second meta-magnetic transition was found at a higher field, which aligned 95+% of the moments. The main differences being, that the two transitions that take place in HoNiSi₃ occur along orthogonal axes in the basal plane, and the magnetization curve parallel to the *a*-axis shows hysteresis while the Dy analog is fully reversible. It is also evident that the moments in HoNiSi₃ are more easily bent away from the *c*-axis. The slope of the moment versus applied field in the low field region of the *a*-axis data is substantially steeper when compare to the basal plane diagonal magnetization data for DyNiSi₃, or the *a*-axis magnetization for TbNiSi₃.

ErNiSi₃: A single crystal with dimensions 0.7x0.6x0.2 mm³ was picked and microprobe elemental analysis was done to ensure the crystal was composed exclusively of Er, Ni and Si. The crystal was also screened by x-ray diffraction to ensure it was composed of a single domain, and to face index it. It was determined that the 0.6 mm edge coincided with the *a*- axis, the *c*-axis with the 0.7 mm edge, and the 0.2 mm axis with the *b*-axis. The single crystal was once again oriented with the basal plane parallel with the applied magnetic field. The rotational susceptibility data for ErNiSi₃ was qualitatively identical to those previously discussed. The difference being that the relative difference between the

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maximum and minimum in the susceptibility, for ErNiSi_3 is about 1/2 that of the Dy or Ho analogs. The minimum susceptibility was again found to coincide with the c -axis, as it has with the other samples.

The crystal was oriented with the c -axis parallel to the applied field, and collection of susceptibility and magnetization data proceeded. These data can be seen in Figures 4-11 (A) and (B) respectively. ErNiSi_3 also orders antiferromagnetically with a Néel temperature of about 4 K. Above this temperature ErNiSi_3 follows the Curie/Weiss law with a resulting effective magnetic moment of $9.4 \mu_B$ and a very small Weiss constant of -0.7 K. The measured effective moment is in good agreement with the calculated value of an Er^{3+} ion, which is $9.6 \mu_B$. The magnetization curve for the c -axis shows one transition at approximately 2 kOe. At this field the moment rises from $1 \mu_B$ to $6.5 \mu_B$ by 16 kOe. Above 16 kOe the moment does not increase substantially, and reaches a value of $7.2 \mu_B$, which is considerably smaller than the theoretical μ_{sat} value of $9.0 \mu_B$. The field induced meta-magnetic transition seen here is not nearly as sharp as those observed in the previous systems, and is likely due to the fact that the magnetization curve was measured at a temperature that was quite close to the ordering temperature.

The ErNiSi_3 crystal was rotated 90° , and the measurements were repeated. In this case antiferromagnetic order was also observed at 4 K, Figure 4-11 (C). Upon inspection

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of the inverse susceptibility data, there is a second inflection at approximately 20 K, again this inflection at 20 K was not observed in the polycrystalline data. The inverse susceptibility data between 2 and 20 K do not follow a Curie/Weiss law, though above 20 K it does with an effective magnetic moment of $9.3 \mu_B$ and a Weiss constant (θ) of -1.4 K indicating weakly antiferromagnetically coupled moments.

The magnetization curve with the field oriented along the a -axis can be seen in Figure 4-11 (D). Its behavior is similar to the c -axis magnetization curve, in that there is an increase in the moment between 2 kOe and 16 kOe, before the slope becomes shallower. This is likely due to the fact that a component of the magnetic dipole vector lies along the a -axis, and the meta-magnetic transition is induced at the same field as it was along the c -axis. However, above this field the moments are not aligned along the a -axis and so no saturation is observed, as was found in the c -axis data. Instead the moments feel a torque by the field applied nearly perpendicular to them, and they respond by bending along the field. This bending will be proportional to the applied field strength giving the linear behavior in the high field region that we see in Figure 4-11 (D).

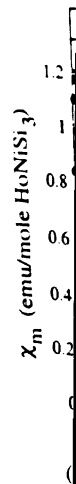


Figure
(B) Magnetic susceptibility
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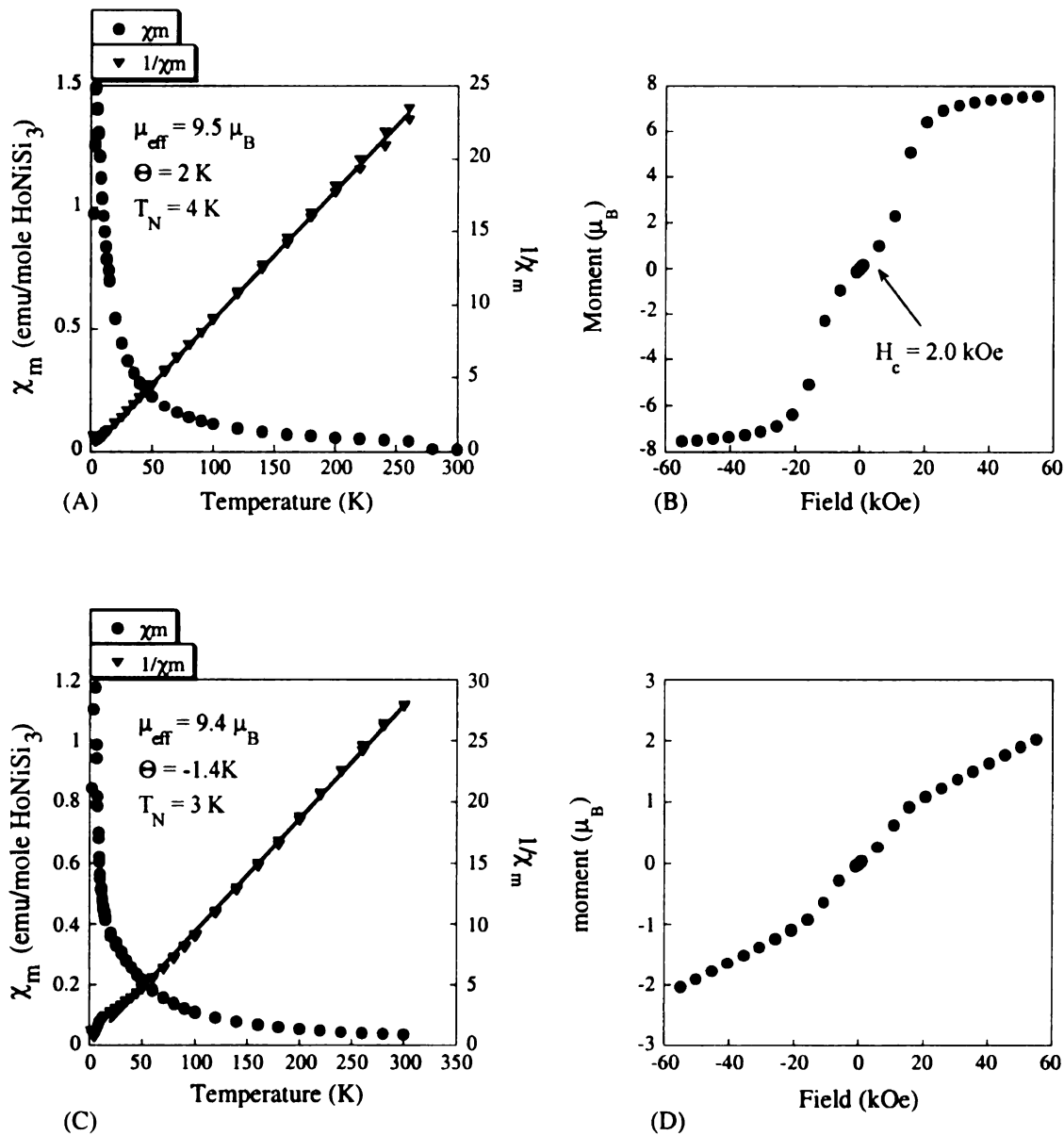


Figure 4-11 (A) Molar susceptibility and inverse susceptibility for the *c*-axis of ErNiSi₃. (B) Magnetization curve with the field oriented parallel to the *c*-axis. (C) Molar susceptibility and inverse susceptibility for the *a*-axis of ErNiSi₃. (D) Magnetization curve with the field oriented with the *a*-axis parallel to the *a*-axis.

YbNiSi₃: A polycrystalline sample of YbNiSi₃ found evidence of antiferromagnetic ordering with a Néel temperature of 4 K, but there was no sign of a meta-magnetic

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transition. A single crystal with dimensions 0.3 x 0.4 x 0.02 mm was picked and screened by microprobe elemental analysis to ensure elemental content, and was found to be composed only of Yb Ni and Si. The single crystal was mounted for x-ray diffraction to verify that it was composed of a single crystallographic domain and to determine axis orientation. It was found that the 0.3 mm edge was the *c*-axis, and the 0.4 mm edge was coincident with the *a*-axis. The rotational susceptibility measurements found the susceptibility to be nearly independent of crystallographic orientation when rotated about the basal plane. The crystal was oriented in the magnetic field with the *c*-axis parallel to the applied field, and susceptibility and magnetization measurements were conducted. Figures 4-12 (A) and (B) show the susceptibility and magnetization of the *c*-axis, respectively. There is a small drop in the susceptibility below 3 K indicating the onset of antiferromagnetic order. The inverse susceptibility data show a non-linearity in the low temperature region up to about 50 K. This is likely due to crystal field splitting of the $\text{Yb}^{3+} 7/2$ ground state.²⁴ Above 50 K the data follow a Curie/Weiss law with a resulting effective magnetic moment of $4.6 \mu_B$, and a Weiss constant of -14 K. The effective magnetic moment measured here is in excellent agreement with the theoretical value of $4.56 \mu_B$.

No meta-magnetic transition was observed when the field was aligned with the *c*-axis instead the moment varied linearly with the applied field, behavior that is characteristic of a paramagnetic system.

The crystal was reoriented with the *a*-axis parallel to the applied field, and the measurements were repeated. Figures 4-12 (C) and (D) show the susceptibility and magnetization data respectively for YbNiSi₃. There is no maximum observed in the susceptibility data along this direction, and therefore no antiferromagnetic ordering. This is in contrast to the *c*-axis susceptibility. The non-linearity observed in the *c*-axis data is again observed along the *a*-axis, although it is over a larger temperature range from 2 to 100K. The data above 100 K obey the Curie /Weiss law, with an effective magnetic moment that was determined to be $4.5 \mu_B$, and a Weiss constant of -138 K. The effective magnetic moment agrees well with the theoretical value of $4.56 \mu_B$.

The magnetization data, shown in Figure 4-12 (D), is again linear with no field induced transitions taking place. The moment obtained at the highest attainable field is $0.75 \mu_B$, and is significantly smaller than the moment measured along the *c*-axis. This indicates that once again the moments tend to favor aligning along the *c*-axis.

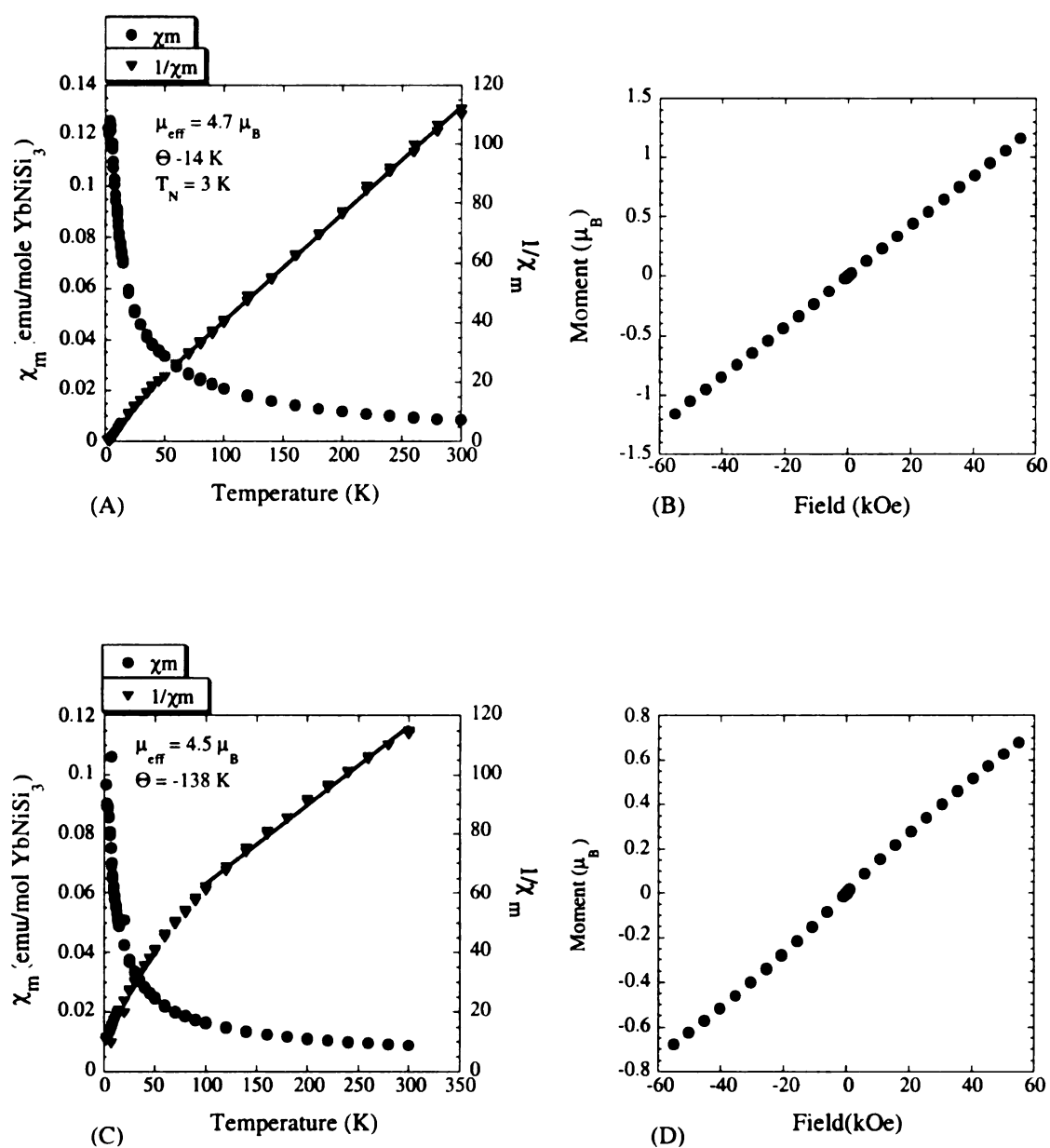


Figure 4-12 (A) Molar susceptibility and inverse susceptibility for the *c*-axis of YbNiSi₃. (B) Magnetization curve for YbNiSi₃ with the field parallel to the *c*-axis. (C) Molar susceptibility and inverse susceptibility for the *a*-axis of YbNiSi₃. (D) Magnetization curve for YbNiSi₃ with the field parallel to the *a*-axis.

LuNiSi₃: Unlike other compounds presented previously, LuNiSi₃ displays temperature independent Pauli paramagnetism. This is an anticipated result as the other example had paramagnetic contributions exclusively from the rare earth ions, due to the fact that the Ni *d* bands lie low in energy below the fermi-level and are filled. Consequently Ni is diamagnetic. Lu has a filled *f* shell, and is therefore also diamagnetic. The temperature independent paramagnetic susceptibility arises from the polarization of the itinerant electrons by the applied field. The field tends to align them giving the paramagnetic response.

Magnetic Measurement Discussion:

As has been shown by band structure calculations performed on YNiSi₃ presented previously,¹⁴ and given the nature of the paramagnetic susceptibility of LuNiSi₃ the compounds presented here are metallic. As such, we expect the dominant mechanism for magnetic exchange to be via the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism,²⁵ especially given that the rare earth ions are too far apart for direct exchange to be effective. RKKY is indirect magnetic exchange that is mediated by the conduction electrons. The conduction electrons "feel" the moment of the rare earth ion, and then the electrons impart that perturbation on to adjacent rare earth ions in the lattice. The magnitude of this type of exchange depends on two factors: the size and nature of the isolated magnetic moment and the topology of the fermi surface. The nature of the

exchange, be it antiferromagnetic or ferromagnetic, is strongly dependent upon the distance between the ions.

The topology of the fermi surface will be a constant of the system, as the only variable between the various analogs is the rare earth ion. The f orbitals of these ions are compact and do not contribute to the DOS near the fermi level. We can thus expect there to be a correlation between the ordering temperatures (strength of the antiferromagnetic exchange) and the nature of the moment of the rare earth ion, expressed as the de Gennes factor Equation 1.²⁶ Where λ is Lande's factor, defined in Equation 2, and J is the total angular momentum quantum number.

$$\text{Equation 1. } G = (\lambda - 1)^2 J(J + 1)$$

$$\text{Equation 2 } \lambda = 1 + \left(\frac{J(J + 1) - L(L + 1) + S(S + 1)}{2J(J + 1)} \right)$$

We find that indeed the Néel temperatures do scale approximately linearly with the de Gennes factor, Figure 4-13. This behavior has been observed in intermetallic compounds such as REM_2Si_2 , (RE is a late rare-earth and M is Ni or Co) and RENiSi_2 (RE is a late rare earth metal).²⁷

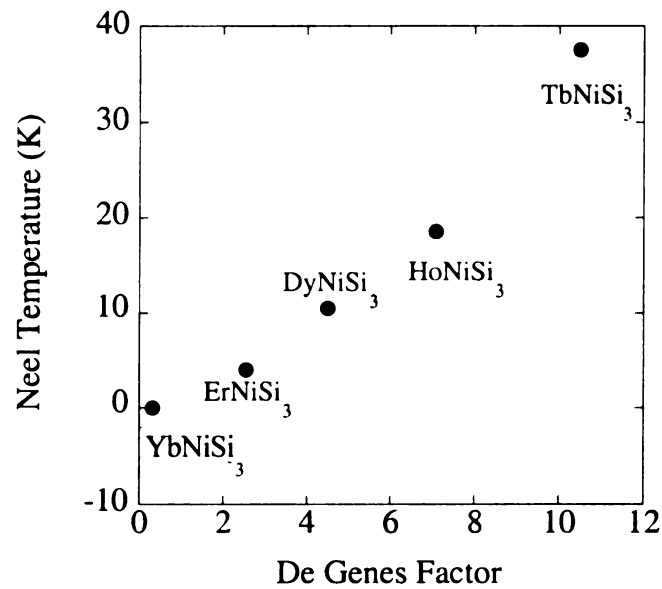


Figure 4-13 Plot of the Néel temperature as a function of the de Gennes factor. Near linear behavior is expected for a metal as the magnitude of magnetic coupling in RKKY systems is proportional to the moment, of which the de Gennes factor is a measure.

The anisotropic behavior of the meta-magnetic transitions is the result of anisotropic crystal field effects. That is to say that the non-spherical 4f electron cloud (and consequently the magnetic moments) of the rare earth ions interact with the crystal field, which adopts the symmetry of the system under investigation, in this case orthorhombic. The general crystal field Hamiltonian has the form of Equation 3. Where B_k^q denotes the crystalline electric field parameters determined from experiments, and are dependent on the sub-lattice the rare earth ions find themselves in. O are the Stevens operators, which replace the polynomials of xyz with the angular momentum products of

the rare earth ions.²⁸ For an orthorhombic system with C_{2v} symmetry the crystal field Hamiltonian is expressed as in Equation 4.²⁹

$$\text{Equation 3 } H = \sum_{kq} B_k^q O_k^q(xyz)$$

$$\text{Equation 4 } H_{CEF} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6$$

In the case of the $RENiSi_3$ phases, the crystalline electric field remains more or less constant for each of the analogs. What is changing is the charge distribution of the rare earth ion as it is progressively filled from the $f^8 Tb^{3+}$ ion to the $f^{14} Lu^{3+}$. We have found that as we proceed from $TbNiSi_3$ to $DyNiSi_3$, the spins are not as strictly confined to the basal plane, and that in the susceptibility of $DyNiSi_3$, a maximum (ordering) is found perpendicular to the basal plane, though it was not found in $TbNiSi_3$. Maxima are observed in the susceptibility data perpendicular to the basal for other analogs as well. This is because the forces aligning the moments into the plane, and along the c -axis are weaker for the later rare earth analogs. This is due to the angular momentum of the f electrons decreasing (as a consequence the magnitude of the Stevens operators also decreases), and thereby lowering the crystal field anisotropy energy. As the anisotropy energy is decreased the moments have a greater range of motion due to thermal agitation, and weak inter layer exchange effects. This allows components of the magnetic moment

to be out of the basal plane. This is indeed the trend we observe, as we move to later rare earth analogs. The ability to bend the rare-earth moments away from their preferred axis does tend to increase indicating weaker anisotropic forces.

4-4 Conclusions:

We have presented here a series of isostructural Si rich intermetallic compounds, which crystallize in the Orthorhombic $Cmmm$ space group with the SmNiGe_3 structure type. They were grown from a Ga flux, and large high quality single crystals were routinely produced. All compounds with the exception of LuNiSi_3 order antiferromagnetically with Néel temperatures that scale linearly with the de Gennes factor of the rare earth ions, and exhibit highly anisotropic magnetic behavior. The behavior manifests as field induced meta-magnetic transitions with a critical field that is dependent on the orientation of the crystal in a magnetic field. The anisotropy is thought to be due to crystalline electric field effects, which tend to align the moments along the c -axis. In the cases of the Tb, Dy, and Ho analogs it was found that when the crystal was oriented with the applied field parallel to the c -axis a field induced meta-magnetic transition took place. In the case of TbNiSi_3 this was the only observed transition, for Dy a second transition, at higher fields, was found when the crystal was oriented along the basal plane diagonal relative to the applied field. HoNiSi_3 behaved similarly, though it showed a second meta-magnetic transition when the field was applied parallel to the a -axis. All of these

phenomena can be understood by considering a crystalline electric field with orthorhombic symmetry applying a Coulombic potential on the non-spherical charge cloud of the rare earth ions (and as a result the magnetic moment). This field forces the moments to be confined to the basal plane and aligned predominantly with the c -axis.

Future work with this system should include single crystal neutron diffraction in order to determine the nature of the antiferromagnetic ordering. It may then become clear why in the case of HoNiSi_2 and DyNiSi_3 the meta-magnetic transition along the c -axis only aligns 75% of the moments that are present. Crystals of appropriate size can easily be grown from liquid Ga using the methods explained here. It has been found that larger crystals grow from reactions that are scaled up, and so the limiting factor appears to be reactor size.¹

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Chapter 5

RE₅Co₄Si₁₄ (RE = Ho, Er, Tm, Yb) Intermetallic Phases Grown from Ga Flux Showing Exceptional Resistance to Chemical and Thermal Attack.

5-1 Introduction.

Intermetallic silicides comprise a technologically important class of compounds with wide spread use in semiconductor applications, refractory coatings, and in thermal processing applications such as heating elements.^{1,2} The source of the refractory character in silicides is the formation of a protective SiO₂ layer,³ which can be stable at elevated temperatures since crystalline SiO₂ does not melt until 1750 °C.⁴ Although, often the oxide layers break down at considerably lower temperatures.³

One of the leading silicides for refractory applications is MoSi₂, which is used extensively in heating elements for high temperature furnaces. It suffers from several major drawbacks, as do many intermetallic compounds, which limit its applications. Namely its extreme brittleness especially at room temperature³, its tendency for pesting in low temperature and low moisture regimes,⁵ and its susceptibility to attack by Na₂SO₄, and NaCO₃ in melts and hot burner gasses⁶. Other binary silicides of transition metals such as Fe₃Si, Ni₃Si,⁷ and TMSi_x (TM = transition metal and x = 2-3) have also been

investigated for refractory applications,⁸ and it has been found that these compounds suffer from the same drawback, namely their brittleness at room and elevated temperatures.

We have been interested new Si containing intermetallics of the type RE/TM/Si (RE = rare-earth metal, TM = 1st or 2nd row transition metal) in hopes of discovering new silicides with interesting physical properties ,including resistance to thermal oxidation. Si based intermetallics are desirable, because they will likely be less dense than the Ni super alloys currently used in the bulk of aerospace propulsion components.

We have used Ga flux with a great deal of success to synthesize a large class of complex silicides and germanides of the type RE/TM/Si,⁹ RE/TM/Ga/Si,¹⁰ RE/TM/Ga/Ge, and borosilicides such as $\text{Tb}_{1.8}\text{Si}_8\text{C}_2(\text{B}_{12})_3$ ¹¹ and $\beta\text{-SiB}_3$.¹² We have found from this research that quaternary Ga silicides do not form readily. In these cases Ga plays the role of a non-reactive solvent, and is therefore an excellent medium from which to grow crystals of intermetallic silicides. This approach can greatly facilitate structural and physiochemical characterization by producing large high quality crystals and pure samples.

We present here a series of rare-earth cobalt silicides, $\text{RE}_5\text{Co}_4\text{Si}_{14}$ (RE = Ho, Er, Tm and Yb), synthesized from a Ga flux all of which crystallize with the $\text{Lu}_5\text{Co}_4\text{Si}_{14}$ structure type.¹³ These compounds can also be obtained by direct combination of the elements with arc melting, though not as pure phases. These compounds, produced from

a Ga flux, have excellent corrosion resistance at temperatures exceeding 900 °C. The crystal structure, corrosion resistance, and magnetic properties of $\text{RE}_5\text{Co}_4\text{Si}_{14}$ are described here.

5-2 Experimental Section.

Reagents:

All reagents were used as received without further purification and reactions were prepared under an inert N_2 atmosphere in a dry box: Ho metal(-40 mesh powder, 99.9%, Cerac, Milwaukee, WI), Er metal(powder ground from metal chunk, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), Tm metal(powder ground from metal chunk, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), Yb metal(powder ground from metal chunk, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China) Co metal (-325 mesh, 99.9%, Cerac, Milwaukee, WI) and 3.0 mmol Si(-325 mesh amorphous powder, 99.999%, Cerac, Milwaukee, WI) and 10.0 mmol Ga (3-5 mm pieces 99.999% Plasmaterials, Livermore, CA).

Synthesis:

1 mmole of the corresponding rare earth metal, 1 mmole of Co, 3 mmole Si, and 10 mmole Ga were combined in an Al_2O_3 (alumina) crucible. The crucible and reactants were flames sealed in a fused silica tube under a reduced atmosphere of 10^{-4} mbar. The

reaction was carried out by first heating to 850°C over the course of 8 h, and holding at 850 °C for 72 h, before cooling to room temperature over 48 h. The product was isolated by gently warming the crucible, and decanting the excess liquid Ga. Ga, in general, wets the surface of the product, and isolation was completed by soaking in a 5M I₂ dimethyl formamide (DMF) solution. Yields were generally greater than 80% based the rare earth with purities that were greatly dependent on the rare earth metal used.

This phase was also formed by direct combination of the elements with arc melting, by combining and cold pressing the elements in their stoichiometric ratios on the mmole scale under a N₂ atmosphere in a glove box. Reactions were run under a gettered Ar atmosphere on a water-cooled copper plate. Reaction melts were flipped, and re-melted three times in order to ensure a homogenous distribution of reactants. Yields were nearly quantitative though pure samples of the title compounds could not be prepared by this method. Purity was not significantly improved by a week of annealing at 950 °C.

Elemental Analysis:

Semiquantitative microprobe elemental analysis was performed with a JEOL JSM-35C scanning electron microscope (SEM), equipped with the Noran energy dispersive spectrometer (EDS). Data were acquired using an accelerating voltage of 20 kV and 100 s acquisition times. Several crystals from each reaction were analyzed, and the resulting approximate atomic ratios of 1.2 : 1 : 2.2 RE : Co : Si were found. A SmNiSi₃ single

crystal⁹ was used as a standard reference and after a correction factor was applied the ratios were approximately 1.3 : 1 : 3.6 RE:Co:Si. These results agree well with the atomic ratios that were derived from the crystallographic refinement of the structure.

X-ray Crystallography:

Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART CCD diffractometer with graphite monochromatized Mo K α (λ = 0.71073 Å) radiation. Unit cell refinement and data merging were done with the SAINT program, and an empirical absorption correction was applied using the program SADABS.¹⁴ The original cell indexed by SMART was $a = 7.705$ Å, $b = 7.778$ Å, and $c = 12.314$ Å in a monoclinic C Bravais lattice. Inspection of the remaining systematic absences gave the possible space groups: C 2, C m , and C 2/ m . C2/ m was the only centrosymmetric space group, and was therefore chosen.¹⁵ A satisfactory solution could not be obtained with this space group, or any C centered space group, and lead to a structure containing mixed and partially occupied sites, with high residual electron density and atomic ratios that were at odds with elemental analysis. The reason for the mistaken assignment of C centering was due to the $h+k = 2n$ reflections being systematically weak, but not absent. If these reflections are taken into account a primitive lattice is obtained with systematic absences consistent with the space group P2₁/ a . A simple transformation matrix was applied to interchange the a and c -axes

yielding the reported lattice parameters: $a = 12.314 \text{ \AA}$, $b = 7.778 \text{ \AA}$, and $c = 7.705 \text{ \AA}$, and the conventional space group setting $P 2_1/c$.¹³ The crystal solution obtained in this space group gave a structure that was ordered, and each site was fully occupied. Further the atomic ratios obtained from this solution agree well with those obtained from EDS. The single crystal data collection parameters, and refinement details for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ and $\text{Ho}_5\text{Co}_4\text{Si}_{14}$ can be found in Table 5-1. The atomic coordinates and the isotropic displacement parameters for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ and $\text{Ho}_5\text{Co}_4\text{Si}_{14}$ are listed in Table 5-2 and the anisotropic displacement parameters can be found in Table 5-3.

Crystal twinning was a major difficulty in elucidating the structures of these compounds. In fact acceptable crystallographic solutions could only be obtained for the Tm and Ho analogs. Data sets on several crystals of $\text{Er}_5\text{Co}_4\text{Si}_{14}$ and $\text{Yb}_5\text{Co}_4\text{Si}_{14}$ were collected but could not be refined as large residual electron densities remained. The space group and atomic positions from the Tm analog were used as starting solution, and after refinement still the residual peaks did not fall below $30 \text{ e/\AA}^3$ and R_1 and wR_2 would not fall below 20% and 35% respectively. The application of several twin laws, including rotational twinning, was not successful in refining the structure, and inspection of the reciprocal lattice found no obvious evidence of twinning. Crystals whose structures could not be refined were originally found to be C centered when determining the unit cell with the SMART software, as well as by XPREP even after the data were integrated using a primitive cell setting. This observation may be tied to the kind of twinning that is

taking place. There is, perhaps a translational or rotational shifting of the atoms during crystal growth caused by the nature of the structure that brings about this subtle yet very intimate twinning of the crystal domains. Thus one would suspect the crystals to stack along the c axis and the translational defect to be in the ab plane.

Phase identity and purity was evaluated by powder x-ray diffraction carried out on a Rigaku rotating Cu anode powder diffractometer. The diffractometer has post diffraction monochromatization of the Cu $K\alpha$ line, which was required to cut out the fluorescence of Co. The target phases were identified by comparing the experimental powder patterns to powder patterns calculated from the single crystal structure solutions. Single crystals of sufficient quality could not be found for $\text{Er}_5\text{Co}_4\text{Si}_{14}$ and $\text{Yb}_5\text{Co}_4\text{Si}_{14}$, and so these compounds were identified by powder x-ray diffraction. Their structures were not refined, but all peaks in the powder pattern could be indexed to the monoclinic cell found for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ and $\text{Ho}_5\text{Co}_4\text{Si}_{14}$, and are therefore isostructural.

Other Physical Methods:

Differential thermal analysis (DTA) was performed on a Shimadzu DTA-50 differential thermal analyzer with an $\alpha\text{-Al}_2\text{O}_3$ standard reference. The samples were heated to 1000 °C at a rate of 10 °C/min then cooled to 150 °C at the same rate. The cycle was then repeated to determine if the compound melted congruently.

Thermal gravimetric analysis (TGA) was performed on a Shimadzu TGA-50 thermal gravimetric analyzer. The sample was heated to 1000 °C at a rate of 10 °C/min. under flowing air, and held at 1000 °C for 5 min.

Magnetic susceptibility measurements were made on selected crystals that were ground and screened by powder x-ray diffraction for phase identity and purity. The samples were cleaned prior to measurement by submersion in concentrated HCl for 20 minutes to remove Co containing impurities. Measurements were performed with a Quantum Design MPMS SQUID magnetometer in both field cooled and zero field cooled settings at temperatures between 2K and 300K. Magnetization data were also collected at 5K with fields sweeping from 55 kOe to -55 kOe.

Table 5-1. Crystal data and structure refinement for RE₅Co₄Si₁₄ (RE = Ho, Tm).

Empirical formula	Tm ₅ Co ₄ Si ₁₄	Ho ₅ Co ₄ Si ₁₄
Formula weight	1473.60	1453.44
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c (#14)	P2 ₁ /c (#14)
Unit cell dimensions	a = 12.3140(16) α = 90°. b = 7.7780(10) β = 98.815(2)° c = 7.7053(10) γ = 90°.	a = 12.3765(15) α = 90°. b = 7.8142(9) β = 98.867(2)° c = 7.7330(9) γ = 90°.
Volume	729.28(16) Å ³	738.94(15) Å ³
Z	2	2
Density (calculated)	6.711 g/cm ³	6.533 g/cm ³
Absorption coefficient	35.619 mm ⁻¹	31.905 mm ⁻¹
F(000)	1298	1278
Theta range for data	1.67 to 27.06°	5.2 to 32.14°
Crystal Size (mm ³)	0.02x0.02x0.01	0.03x0.02x0.01
Index ranges	-15 ≤ h ≤ 15, -9 ≤ k ≤ 9, -9 ≤ l ≤ 3	-18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -9 ≤ l ≤ 9,
Reflections collected	4826	10500
Independent reflections	1565 [R(int) = 0.0375]	2436 [R(int) = 0.0810]
Completeness to theta	98.2 %	93.8%
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1565 / 0 / 107	2436 / 0 / 106
Goodness-of-fit on F ²	1.144	0.960
Final R indices [I > 2σ(I)]	R1 = 0.0427, wR2 = 0.1257	R1 = 0.0415, wR2 = 0.0926
R indices (all data)	R1 = 0.0474, wR2 = 0.1302	R1 = 0.1150, wR2 = 0.1225
Extinction coefficient	0.0033(3)	none
Largest diff. peak and hole	3.483 and -3.509 e.Å ⁻³	3.450 and -3.108 e.Å ⁻³
R1 = Σ F _o - F _c / Σ F _o and wR2 = [Σ(F _o ² - F _c ²) ² / Σ(wF _o ²) ²] ^{1/2}		

Table 5-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters $\text{\AA}^2 \times 10^3$) for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ and $\text{Ho}_5\text{Co}_4\text{Si}_{14}$.

Atom	Wyckoff Position	x	y	z	U(eq)*
Tm(1)	2b	5000	0	0	7(1)
Tm(2)	4e	8650(1)	2518(1)	-1576(1)	8(1)
Tm(3)	4e	1348(1)	2489(1)	1602(1)	8(1)
Co(1)	4e	4998(1)	3741(2)	1272(2)	7(1)
Co(2)	4e	7501(1)	-2(1)	611(2)	8(1)
Si(1)	4e	4994(2)	-3338(3)	1661(4)	9(1)
Si(2)	4e	9401(3)	4999(3)	1106(5)	10(1)
Si(3)	4e	3215(3)	-54(3)	2314(5)	7(1)
Si(4)	4e	6789(3)	-55(3)	3187(5)	7(1)
Si(5)	4e	6786(3)	2738(4)	500(5)	7(1)
Si(6)	4e	6788(2)	-2741(4)	389(5)	7(1)
Si(7)	4e	9406(3)	8(3)	1092(5)	8(1)
Ho(1)	2b	5000	0	0	7(1)
Ho(2)	4e	8643(1)	2517(1)	-1577(1)	3(1)
Ho(3)	4e	1355(1)	2490(1)	1605(1)	2(1)
Co(1)	4e	4997(2)	3746(3)	1276(3)	8(1)
Co(2)	4e	7491(1)	-4(3)	608(2)	4(1)
Si(1)	4e	5001(4)	-3359(5)	1621(6)	7(1)
Si(2)	4e	9411(3)	4990(7)	1123(5)	6(1)
Si(3)	4e	6785(3)	58(7)	-2328(5)	5(1)
Si(4)	4e	6788(3)	-51(7)	3200(5)	6(1)
Si(5)	4e	6775(4)	2749(6)	505(6)	5(1)
Si(6)	4e	6770(4)	-2748(6)	383(6)	4(1)
Si(7)	4e	9399(3)	4(7)	1094(5)	4(1)

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

Table 5-3 Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ and $\text{Ho}_5\text{Co}_4\text{Si}_{14}$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Tm(1)	4(1)	6(1)	12(1)	0(1)	4(1)	0(1)
Tm(2)	4(1)	6(1)	14(1)	0(1)	3(1)	0(1)
Tm(3)	4(1)	6(1)	14(1)	0(1)	4(1)	0(1)
Co(1)	5(1)	6(1)	10(1)	3(1)	3(1)	0(1)
Co(2)	3(1)	7(1)	16(1)	0(1)	4(1)	0(1)
Si(1)	9(1)	7(1)	13(1)	-1(1)	3(1)	2(1)
Si(2)	7(2)	9(2)	14(2)	0(1)	4(1)	0(1)
Si(3)	2(1)	6(2)	14(2)	1(1)	3(1)	0(1)
Si(4)	2(1)	6(2)	13(2)	0(1)	4(1)	0(1)
Si(5)	2(1)	6(1)	12(2)	0(1)	3(1)	-1(1)
Si(6)	2(1)	6(1)	12(2)	0(1)	4(1)	1(1)
Si(7)	2(2)	8(2)	15(2)	1(1)	3(1)	1(1)
Ho(1)	4(1)	4(1)	4(1)	1(1)	1(1)	0(1)
Ho(2)	3(1)	3(1)	3(1)	0(1)	1(1)	0(1)
Ho(3)	2(1)	3(1)	3(1)	-1(1)	0(1)	0(1)
Co(1)	8(1)	7(1)	9(1)	-4(1)	1(1)	0(1)
Co(2)	3(1)	5(1)	4(1)	0(1)	0(1)	1(1)
Si(1)	3(2)	10(2)	11(2)	8(2)	1(2)	1(2)
Si(2)	9(2)	7(2)	4(2)	0(2)	1(1)	1(3)
Si(3)	7(2)	4(2)	5(2)	-1(2)	1(1)	-2(2)
Si(4)	8(2)	4(2)	6(2)	0(2)	1(1)	-2(3)
Si(5)	4(3)	4(2)	7(2)	-2(2)	4(2)	4(2)
Si(6)	6(3)	5(2)	1(2)	-2(2)	1(2)	-2(2)
Si(7)	1(2)	7(2)	5(2)	-2(2)	1(1)	1(2)

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

5-3 Results and Discussion.

Flux Reaction vs. Direct Combination:

In the previous report of this structure only the Lu compound was presented.¹³ In that paper $\text{Lu}_5\text{Co}_4\text{Si}_{14}$ was produced by arc melt alloying of the elements in their stoichiometric ratios. In this work we repeated the arc melting synthesis with other rare earth metals (Ho, Er, Tm, and Yb), and found that the "as cast" pellets did produce the target phase as the major component, but a large amounts of an unidentified impurities were also present. Annealing did not eliminate these impurities. Several attempts with different temperatures (950 °C and 850°C) and soaking times (1 and 2 weeks) were attempted without greatly improving the purity of the sample. In fact the longer annealing step at 950 °C introduced more reflections into the powder pattern, which could not be indexed to $\text{RE}_5\text{Co}_4\text{Si}_{14}$, or the original impurity, and the target compound no longer appeared to be the majority phase. Presumably, a reaction occurred between $\text{RE}_5\text{Co}_4\text{Si}_{14}$ and the impurity phase to yield another, as yet, unidentified phase.

Impure samples prohibit the accurate characterization of these compounds, and so an alternative synthetic route employing Ga flux was devised. The flux reactions were optimized for time and temperature to yield the largest fraction of $\text{RE}_5\text{Co}_4\text{Si}_{14}$, which was a balance between letting reactions run to completion while trying to minimize the presence of quaternary Ga containing phases, which tended to form over time. The yields of these reactions are typically 80%. The fully isolated product consisted of 2 main

phases: the target phase, and the Co analog of the hexagonal $\text{RE}_{0.67}\text{Ni}_2\text{Ga}_{5+n-x}\text{Si}_x$, which has been reported previously.¹⁶ The exact ratio of the two products depended on the rare earth metal used, but the target phase was generally 60 to 80% of the product. If longer reaction times or higher temperatures are used, the product distribution favored the quaternary hexagonal phase for every rare earth analog tried. The Ho and Er system favored the formation of the hexagonal $\text{RE}_{0.67}\text{Co}_2\text{Ga}_{5-x}\text{Si}_x$ phase compared to the Tm and Yb, and it is suspect that this maybe due to size effects. The crystal habits of these two phases are sufficiently different to easily separate them mechanically, and thereby obtain pure samples for physical characterization.

$\text{RE}_5\text{Co}_4\text{Si}_{14}$ grows as stacks of plates which stagger along the stacking axis, which appears to be the *c*-axis. A typical crystal of $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ is shown in Figure 5-1. It is this twinned stacking that has prohibited the single structural analysis of the Er and Yb analogs.



Figure 5-1 Scanning electron micrograph of $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ crystal clusters. This figure shows the crystal habit and plate stack twinning typical of these compounds.

Structure:

The crystal structure of this phase will be described for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$. The structure is quite complex when viewed in its entirety, but it is composed of several simpler units.

The first of these units is a $\text{Co}_2\text{Si}_{10}$ cage, Figure 5-2(A). This cage has a center of

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symmetry and is composed of two face-sharing anti-square prisms. It has one crystallographically distinct Co atom (Co(1)) and 5 different Si atoms (Si(1), Si(3), Si(4), Si(5), and Si(6)). The Co(1) Si distances range from 2.283(3) and 2.292(3) Å for Si(1), to about 2.49 Å for the remaining Si atoms. These cages are connected to one another in the *bc* plane through two types of bonds. One bond is between Co(1) and Si(1) at a distance of 2.269(3) Å, the other is between Co(2) and one of the four crystallographically distinct Si atoms, which comprise the top and the bottom of the Co₂Si₁₀ cage (Si(3), Si(4), Si(5), and Si(6)). These distances are approximately 2.3 Å, Figure 5-2 (B). The rare earth atoms are omitted from these figures for clarity. This arrangement of Co₂Si₁₀ cages forms a slab that extends over the *bc* plane.

The slabs are interconnected via Co(2) bonding to a Si zigzag chain propagating along the *c*-axis, which then bonds to the slabs below it. Figure 5-2 (C) is a perspective view, along the diagonal bisecting the *b* and *c*-axes, of the zigzag chain showing that Si(2) forms bonds only to other Si atoms, with a distance of 2.419(8) Å for Si(2)-Si(2) and Si(2)-Si(7), and that Si(7) forms the bond between the chain, and the Co(2) atoms with a distance of 2.318(4) Å. These Si-Si distances compare well with other Si rich intermetallics such as SmNiSi₃, whose Si-Si distances range from 2.344 to 2.409 Å. This bonding results in an alternating stack of slabs and zigzag chains along the *a*-axis, Figure 5-3. A complete list of bond distances for Tm₅Co₄Si₁₄ and Ho₅Co₄Si₁₄ can be found in Tables 5-4 and 5-5, respectively.

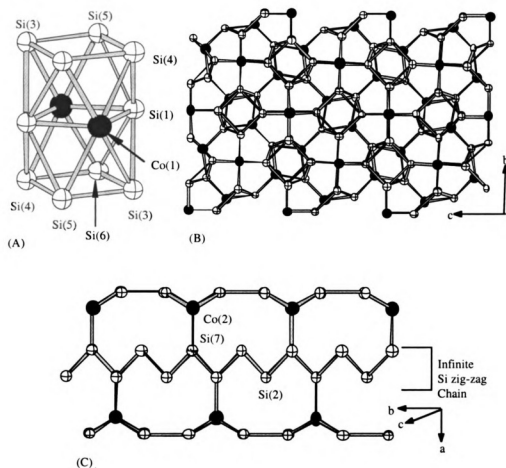


Figure 5-2 (A) View of a $\text{Co}_2\text{Si}_{10}$ cage. (B) Structure of $\text{RE}_3\text{Co}_2\text{Si}_{14}$ as viewed down the a -axis showing the interconnectivity of the $\text{Co}_2\text{Si}_{10}$ cages in the bc plane. (C) View of the Si zig-zag chains which connect the cages along the a -axis rare earth atoms omitted for clarity.

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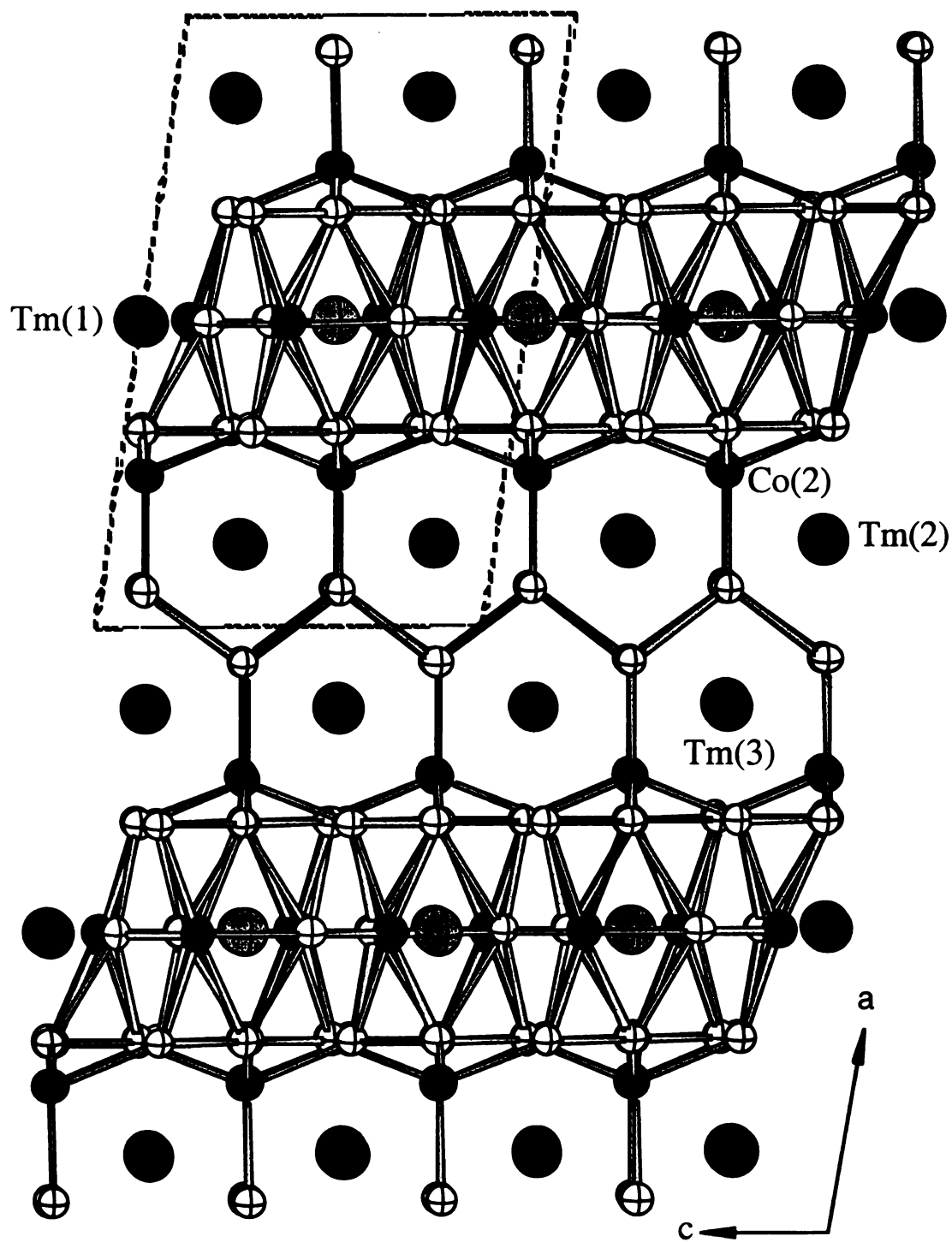


Figure 5-3 The overall structure of $\text{RE}_5\text{Co}_4\text{Si}_{14}$ as viewed down the b -axis.

Table

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Table 5-4. Bond lengths [Å] for Tm₅Co₄Si₁₄.

Tm(1)-Si(1)x2	2.878(3)	Co(1)-Si(1)	2.269(3)
Tm(1)-Si(1)x2	2.895(3)	Co(1)-Si(1)	2.283(3)
Tm(1)-Co(1)x2	3.0347(14)	Co(1)-Si(1)	2.292(3)
Tm(1)-Si(3)x2	3.035(4)	Co(1)-Si(3)	2.484(4)
Tm(1)-Si(4)x2	3.038(4)	Co(1)-Si(4)	2.485(3)
Tm(1)-Si(5)x2	3.043(3)	Co(1)-Si(5)	2.491(3)
Tm(2)-Si(2)	2.875(3)	Co(1)-Si(6)	2.493(3)
Tm(2)-Si(7)x2	2.883(3))	Co(1)-Co(1)	2.771(3)
Tm(2)-Si(2)	2.896(3)	Co(2)-Si(4)	2.290(4)
Tm(2)-Si(5)	2.967(3)	Co(2)-Si(3)	2.291(4)
Tm(2)-Si(3)	2.979(3)	Co(2)-Si(6)	2.301(3)
Tm(2)-Si(5)	2.997(3)	Co(2)-Si(5)	2.303(3)
Tm(2)-Si(4)	3.008(3)	Co(2)-Si(7)	2.318(4)
Tm(2)-Si(2)	3.058(3)	Si(1)-Si(5)	2.584(4)
Tm(2)-Co(2)	3.0681(15)	Si(1)-Si(4)	2.589(4)
Tm(2)-Si(7)	3.076(3)	Si(1)-Si(6)	2.591(4)
Tm(2)-Co(2)	3.0810(16)	Si(2)-Si(7)	2.419(7)
Tm(3)-Si(2)	2.867(3)	Si(2)-Si(2)	2.419(8)
Tm(3)-Si(7) x2	2.890(3)	Si(3)-Si(5)	2.405(5)
Tm(3)-Si(2)	2.904(3)	Si(3)-Si(1)	2.594(4)
Tm(3)-Si(6)	2.957(3)	Si(4)-Si(6)	2.412(5)
Tm(3)-Si(4)	2.970(3)	Si(4)-Si(5)	2.535(5)
Tm(3)-Si(6)	3.008(3)	Si(6)-Si(3)	2.524(5)
Tm(3)-Si(3)	3.019(3)	Si(7)-Si(7)	2.393(5)
Tm(3)-Si(3)	3.019(3)		
Tm(3)-Si(3)	3.019(3)		
Tm(3)-Co(2)	3.0660(15)		
Tm(3)-Si(2)	3.070(3)		
Tm(3)-Co(2)	3.0816(16)		

Table 5

Ho(1)-5

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Table 5-5. Bond lengths [Å] for Ho₅Co₄Si₁₄.

Ho(1)-Si(1)x2	2.909(4)	Co(1)-Si(1)	2.261(5)
Ho(1)-Si(1)x2	2.911(4)	Co(1)-Si(1)	2.278(5)
Ho (1)-Co(1)x2	3.042(2)	Co(1)-Si(1)	2.313(6)
Ho (1)-Co(2)x2	3.0466(14)	Co(1)-Si(3)	2.490(5)
Ho (1)-Si(6)x2	3.049(5)	Co(1)-Si(4)	2.491(5)
Ho (1)-Si(5)x2	3.055(5)	Co(1)-Si(5)	2.492(5)
Ho (2)-Si(2)	2.896(4)	Co(1)-Si(6)	2.484(5)
Ho (2)-Si(7)x2	2.897(4)	Co(1)-Co(1)	2.782(5)
Ho (2)-Si(2)	2.902(5)	Co(2)-Si(4)	2.305(4)
Ho (2)-Si(5) x2	2.902(5)	Co(2)-Si(3)	2.304(4)
Ho (2)-Si(3)	2.902(5)	Co(2)-Si(6)	2.319(5)
Ho (2)-Si(4)	3.016(5)	Co(2)-Si(7)	2.333(4)
Ho (2)-Si(2)	3.016(5)	Si(1)-Si(5)	2.579(7)
Ho (2)-Co(2)	3.084(2)	Si(1)-Si(4)	2.601(6)
Ho (2)-Si(7)	3.101(4)	Si(1)-Si(6)	2.566(7)
Ho (2)-Co(2)	3.097(2)	Si(2)-Si(7)	2.413(5)
Ho (3)-Si(2)	2.883(4)	Si(2)-Si(2)	2.435(7)
Ho (3)-Si(7) x2	2.903(4)	Si(3)-Si(5)	2.396(7)
Ho (3)-Si(2)	2.935(4)	Si(3)-Si(1)	2.597(6)
Ho (3)-Si(6)	2.982(5)	Si(4)-Si(6)	2.413(7)
Ho (3)-Si(4)	2.982(5)	Si(4)-Si(5)	2.534(7)
Ho (3)-Si(6)	3.030(5)	Si(6)-Si(3)	2.527(7)
Ho (3)-Si(2)	3.077(5)	Si(7)-Si(7)	2.419(7)
Ho (3)-Co(2)	3.081(2)		
Ho (3)-Si(7)	3.081(4)		
Ho (3)-Co(2)	3.094(2)		

The coordination environments for the three crystallographically distinct Tm atoms can be seen in Figures 5-4 (A), (B), and (C) for Tm(1), Tm(2), and Tm(3) respectively. Tm(1) is in an irregular 12 coordinate environment of Si and Co atoms with the following distances: 2 different Tm(1)-Si(1) distances at 2.878(3)Å and 2.895(3)Å,

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Tm(1)-Si(3) at 3.035 Å, Tm(1)-Si(4) at 3.038(4)Å, Tm(1)-Si(5) at 3.043(3)Å, and Tm(1)-Co(1) at 3.0348(14)Å. Tm(2) and Tm(3) are in almost identical coordination environments, surrounded by 10 Si atoms and 2 Co with the following distances: Tm(2)-Si(2) has three different distances of 2.875(3)Å, 2.896(3)Å, and 3.058(3)Å the Tm(2)-Si(7) distances are 2.883(3)Å and 3.076(3)Å, Tm(2)-Si(5) has two different distances at: 2.967(3) Å, and 2.997(3)Å, Tm(2)-Si(3) has a distance of 2.979(3)Å, Tm(2)-Si(4) is 3.008(3)Å, and Tm(2)-Co(2) are 3.0681(16)Å and 3.0810(16)Å. The Tm(3) distances are 2.867(3)Å, 2.904(3)Å 3.070(3)Å for Si(2). For Si(7) the distances are 2.890(3)Å and 3.052(3)Å, for Si(6) it is 2.957(3)Å and 3.008(3)Å, for Si(3) it is 3.019(3)Å, and for Co(2) the distances are 3.0660(15)Å and 3.0816(16)Å.

Oxidation:

A remarkable feature of these materials is their extreme inertness to both chemical and thermal attack. Crystals of the title compounds were exposed to concentrated HCl, HNO₃, H₂SO₄, aqua-regia (HCl and HNO₃ in a 3:1 ratio) and a 5M NaOH solution, and were found to be completely intact after 2 weeks. The compounds were, however, etched by concentrated HF.

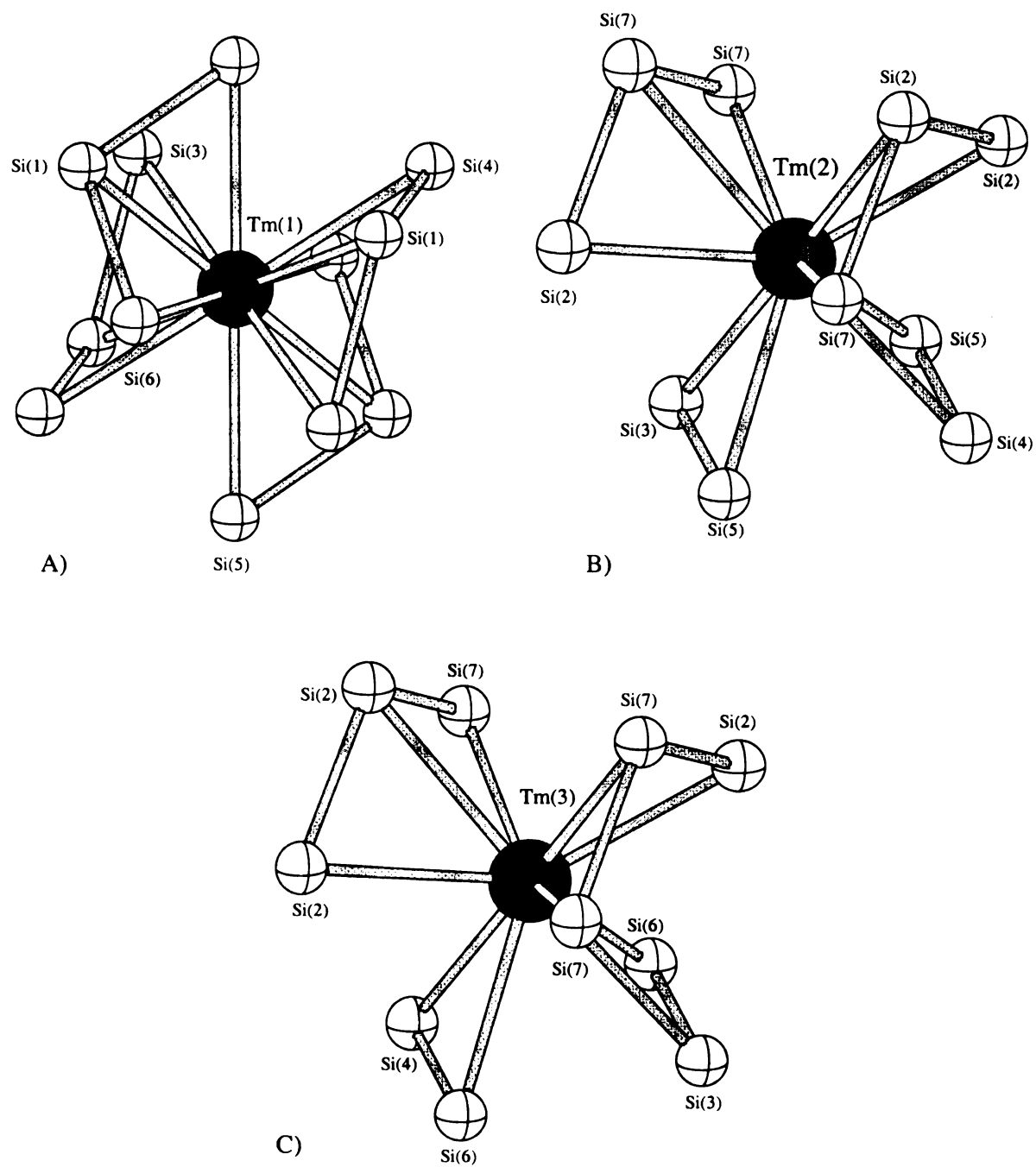


Figure 5-4 (A) Coordination environment of Tm(1). (B) Coordination environment of Tm(2). (C) Coordination environment of Tm(3).

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$\text{RE}_5\text{Co}_4\text{Si}_{14}$ is also quite resistant to thermal oxidation. Differential thermal analysis performed under a reduced pressure of 10^{-4} mbar showed no evidence of a phase change up to 1000°C , Figure 5-5(A). After the DTA experiment visual inspection of the crystals found that the surface was slightly etched, but otherwise completely intact. Thermal gravimetric analysis was performed on crystals of $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ to determine the extent to which they oxidize when heated under normal atmospheric conditions. The material was found to undergo a very small weight gain of 1%, indicating that this compound does not oxidize appreciably when heated in the atmosphere, Figure 5-5(B). The slight weight gain upon heating indicates that whatever oxide is formed during the heating process is not volatile, and adheres to the surface of the sample presumably forming a protective layer.

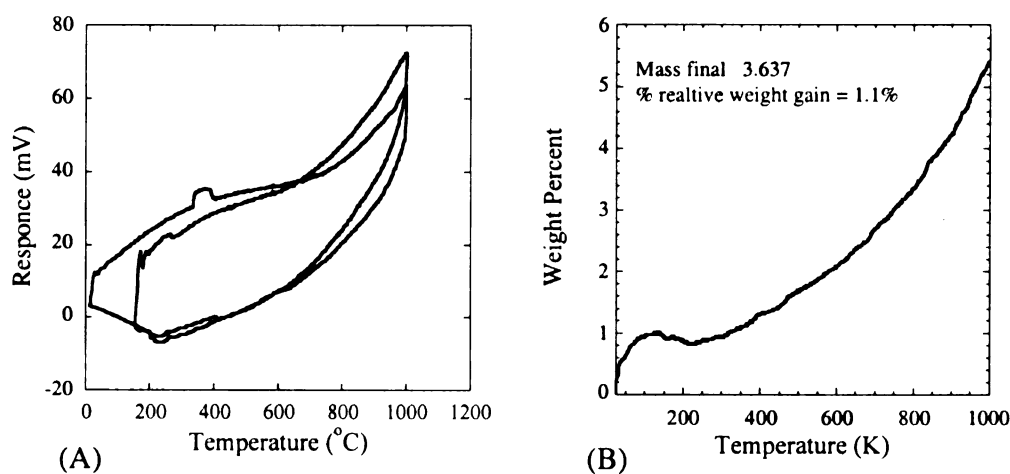


Figure 5-5 (A) Differential thermal analysis of $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ performed under vacuum, from room temperature to 1000°C . (B) Thermal gravimetric analysis of $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ under flowing air.

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To more realistically test the resistance to atmospheric corrosion several crystals were selected and loaded into open ended fused silica tubes and, annealed in air at 1000 °C for 24 h. Remarkably this annealing process did not compromise the structural integrity of the compound. Crystal facets were still evident as seen in the SEM micrograph in Figure 5-6(A). It is apparent by visual inspection, and elemental analysis that an oxide layer formed on the surface of the crystals as a result of the annealing. Semi-quantitative microprobe elemental analysis of the annealed samples revealed elevated levels of Si on the surface as compared to those of the un-annealed crystal, also the oxygen K α line was present in the spectrum, a feature not present in the spectrum of the pristine sample. These findings support the notion of a protective SiO₂ coating being formed on the surface of the material, thereby preventing further oxidation below the oxide surface.

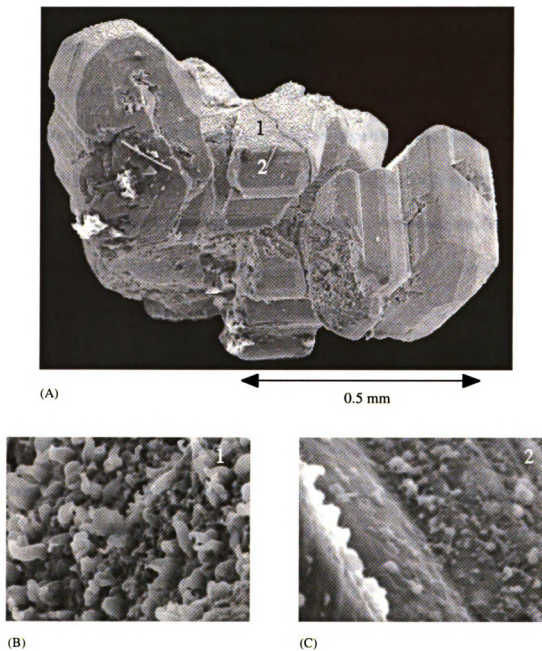


Figure 5-6 (A) Scanning electron micrograph of $\text{Tm}_5\text{Co}_5\text{Si}_{14}$ after annealing at 1000 °C in an ambient atmosphere for 24 hours. (B) Close up view of crystal face 1. (C) Close up view of crystal face 2.

It is apparent by inspection of Figure 5-6 that different crystal faces have different scale formations. The single crystal whose faces are numbered in Figure 5-6(A) was separated from the annealed cluster, and the crystal faces were indexed by single crystal x-ray diffraction. The crystal face labeled 1 was determined to be the (100) face and 2 indexed as the (101) face. The (100) face forms an oxide that resembles the hooks found in Velcro™, and showed a larger elevation of Si content as compared to the (101) surface. This would indicate that the silicon oxide layer is thicker in the former. The (101) surface, face 2, showed an increase in the atomic ratios of both Si and Co (15% and 13% respectively) and is smoother in appearance. This suggests that the oxide layer on this face is composed of Si and Co oxide.

The fact that different scales form on different faces upon heating in the presence of oxygen can be understood by considering the species that would likely be present in each of them based on the crystal structure. The (100) faces are likely to have larger amounts of Si present, and thus have a coating that is composed of almost pure SiO₂. Based on the crystal structure the (101) crystal plane may contain larger amounts of Co and rare earth ions, and while the protective coating still exists on these faces, it is probably not as thick or may be mixed with a metal oxide. These metal oxide surfaces do not appear to be as bright in the micrographs because they are better conductors and therefor do not charge as much as SiO₂ surfaces do.¹⁷

The protective layer formed by these compounds is a passivating SiO_2 layer, which does not allow transport of oxygen below the surface, thus preventing more extensive corrosion. This suggests that the kinetics of oxide formation in this particular compound are diffusion controlled, and the rate of oxide layer formation, the thickness of the layer, slows as the oxide layer thickens, and is effectively halted after a certain critical thickness is obtained.¹⁸

Reactive metals such as rare earths, and some transition metals have been found to enhance the refractory nature of materials by forming barriers between the SiO_2 layer and the bulk which can both decrease the rate of oxide formation and enhance the adhesion of the oxide layer.¹⁹ This is known as the reactive element effect, and it is likely the fact that $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ is rich in rare earth and transition metal that makes it such a refractory material. This may imply that more complex ternary or quaternary intermetallics will show superior oxide resistance compared to binaries.

Magnetic Measurements:

Magnetic susceptibility measurements performed on washed polycrystalline samples of $\text{Ho}_5\text{Co}_4\text{Si}_{14}$, $\text{Er}_5\text{Co}_4\text{Si}_{14}$, $\text{Tm}_5\text{Co}_4\text{Si}_{14}$ and $\text{Yb}_5\text{Co}_4\text{Si}_{14}$ are shown in Figures 5-7 (A)(B), Figures 5-7 (C)(D), Figure 5-8 (A)(B), and Figure 5-8 (C)(D), respectively. Temperature dependent magnetic susceptibility of $\text{Ho}_5\text{Co}_4\text{Si}_{14}$ (Figure 5-7 (A)) obeys the Curie/Weiss law from 300K to 2K with a resulting effective moment of $22.6 \mu_B$ and a

Weiss constant (θ) of 5.8 K indicating weak ferromagnetic interactions.²⁰ The measured magnetic moment is in reasonably good agreement with that calculated for 5 Ho^{3+} ions which is $23.7 \mu_B$.

The magnetization data for $\text{Ho}_5\text{Co}_4\text{Si}_{14}$ shows a sharp jump in the magnitude of the moment with the application of a small field. Above 500 Oe the moment increases nearly linearly up to 22 kOe. At this point the moment begins to saturate and slowly increases up to the maximum field of 55 kOe to a value of $21 \mu_B$. This is also in good agreement with the expected μ_{sat} value for 5 Ho^{3+} ions, which is $20.5 \mu_B$. As the field is decreased there is a small hysteresis in the moment between 20 and 10 kOe. This can be rationalized by imagining the Ho^{3+} ion moments being aligned by the application of the magnetic field, then as the field is decreased ferromagnetic interactions keep the moments aligned below the field needed to align them resulting in the hysteresis. As the field is decreased further the ordering is no longer stable, and a more random arrangement of spins is adopted resulting in a decrease in the moment. This model is consistent with the susceptibility data that showed ferromagnetic interactions between the Ho ions to be present ($\theta = 5.8$ K), though no ferromagnetic ordering was observed down to 2 K.

The susceptibility data for $\text{Er}_5\text{Co}_4\text{Si}_{14}$ shows a maximum in the susceptibility at 4 K, Figure 5-7(C). Above this temperature the data follow Curie/Weiss behavior with a

resulting effective magnetic moment of $20 \mu_B$ and Weiss constant $\Theta = -12K$ indicating antiferromagnetic interactions, consistent with the probable antiferromagnetic ordering observed at low temperatures. The measured effective magnetic moment for $Er_5Co_4Si_{14}$, $21.4 \mu_B$ agrees very well with the moment calculated for 5 isolated Er^{3+} ions which is $21.4 \mu_B$.

The magnetization data for $Er_5Co_4Si_{14}$ Figure 5-7 (D) displays a transition at about 600 Oe followed by a steep increase in the moment with field up to about 15 kOe. Above this field the moments begin to saturate, and the field dependence decreases greatly. The moment continues to increase up to 55 kOe reaching a maximum value of $20 \mu_B$, which is larger than the calculated μ_{sat} value of $19.0 \mu_B$. The transition observed in the magnetization data could likely correspond to the applied field breaking antiferromagnetic ordering causing the moments to align with the field. This would result in a ferromagnetic arrangement of the moments, which saturates at high fields. There was no hysteresis found in the magnetization curve.

The susceptibility data for $Tm_5Co_4Si_{14}$ does not show any magnetic ordering, and obeys the Curie/Weiss law over a limited temperature range from 2 to 150 K, Figure 5-8 (A). The effective magnetic moment obtained from the data in this range was $16.1 \mu_B$, which compares to the calculated moment for 5 Tm^{3+} ions of $17 \mu_B$. The Weiss constant was very small with a value $\theta = 0.18 K$. The extremely small Weiss constant suggests

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that there are no significant interactions between the ions. Above 150 K the inverse susceptibility negatively diverges, which could be caused by crystal field splitting of the 3H_6 ground state multiplet.

The magnetization data shows no transitions and no hysteresis. The moment shows a strong linear field dependence up to 10 kOe. Above this point the moments begin to saturate with a magnitude of $16 \mu_B$ at 55 kOe. This moment equals the calculated saturation moment for 5 Tm^{3+} ions indicating that $Tm_5Co_4Si_{14}$ saturates completely.

The susceptibility data for $Yb_5Co_4Si_{14}$, Figure 5-8(C), also shows no magnetic ordering down to 2K. Similarly to the Tm analog the data also followed the Curie/Weiss law over a limited temperature range of 50 to 300 K. These result in an effective magnetic moment of $10.7 \mu_B$ and a large Weiss constant of $\theta = -41$ K. The effective magnetic moment obtained from the susceptibility measurements agrees well with the value calculated for 5 Yb^{3+} ions which is $10.2 \mu_B$. Below 70K the inverse susceptibility diverges from linearity, and may be due either to crystal field splitting of the $^2F_{7/2}$ multiplet,²¹ or a temperature induced valence transition between Yb^{3+} and Yb^{2+} . The magnetization was measured only up to 1000 Oe, and there was a linear dependence of the moment on field up to 1000 Oe.

Each of the compounds investigated obeyed the Curie or Curie/Weiss law in the major part of the temperature range where measurements were made. The measured

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effective magnetic moments were in good agreement with the moments calculated for isolated 3+ ions of the corresponding rare earth. In all cases the Co ion was diamagnetic which is suggestive of a filled d^{10} electron configuration. It is common in compounds, such as these, with highly electropositive elements like rare earth metals to have late transition metals such as Co and Ni display filled shell paramagnetic behavior.²²

Given the electropositive nature of the rare earth elements, and the results of the magnetic measurements, these compounds can be thought of as polar intermetallics with a charge distribution $(\text{RE}^{3+})_5^{15+}(\text{Co}_4\text{Si}_{14})^{15-}$. It is clear from the magnetic measurements that the only paramagnetic contribution to the susceptibility is from the unpaired 4f electrons of the rare earth ions. This indicates that the rare earth ions are in a 3+ oxidation state.

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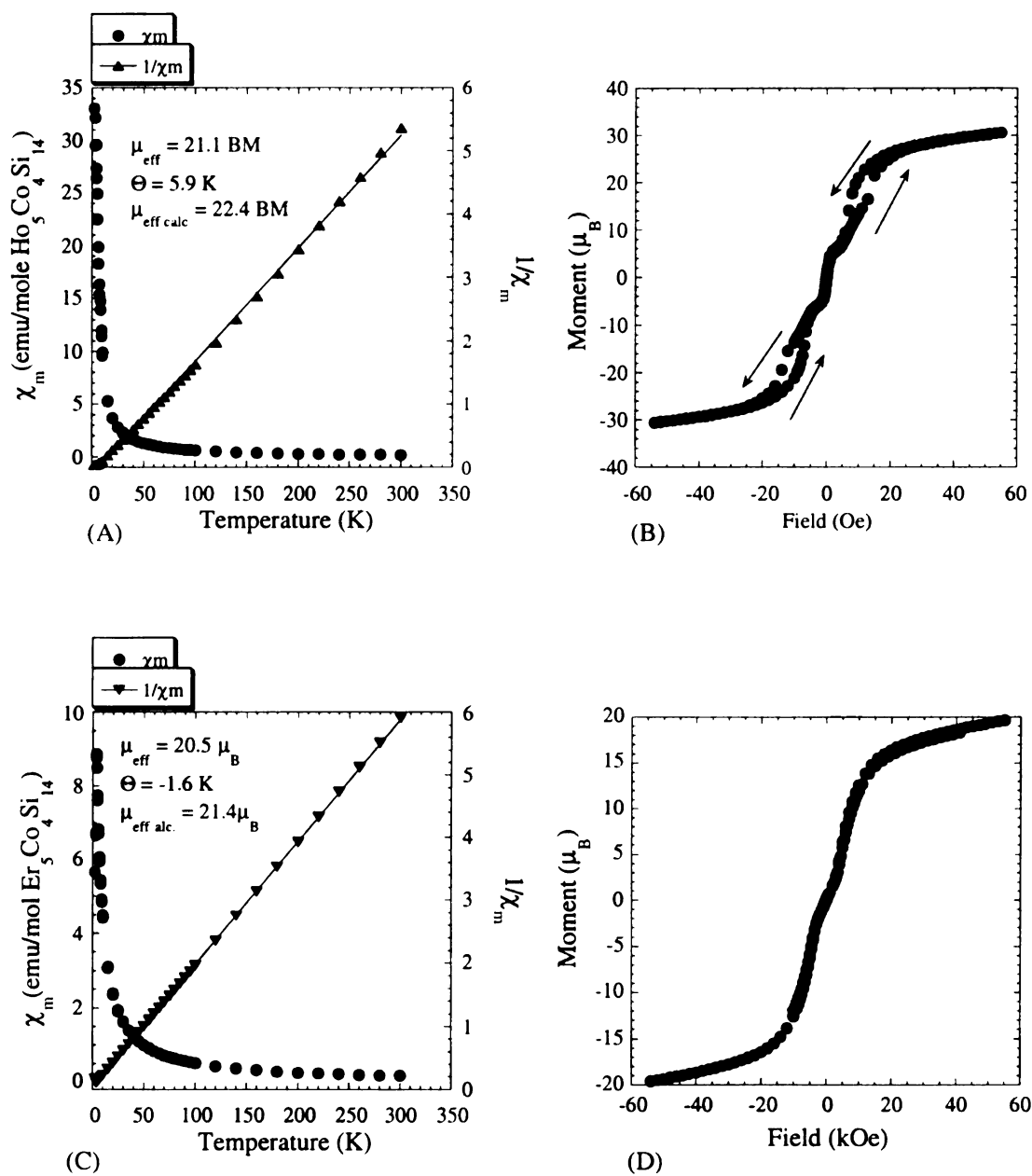


Figure 5-7 (A) Magnetic susceptibility data for $\text{Ho}_5\text{Co}_4\text{Si}_{14}$. (B) Magnetization curve for $\text{Ho}_5\text{Co}_4\text{Si}_{14}$. (C) Magnetic susceptibility data for $\text{Er}_5\text{Co}_4\text{Si}_{14}$. (D) Magnetization curve for $\text{Er}_5\text{Co}_4\text{Si}_{14}$.

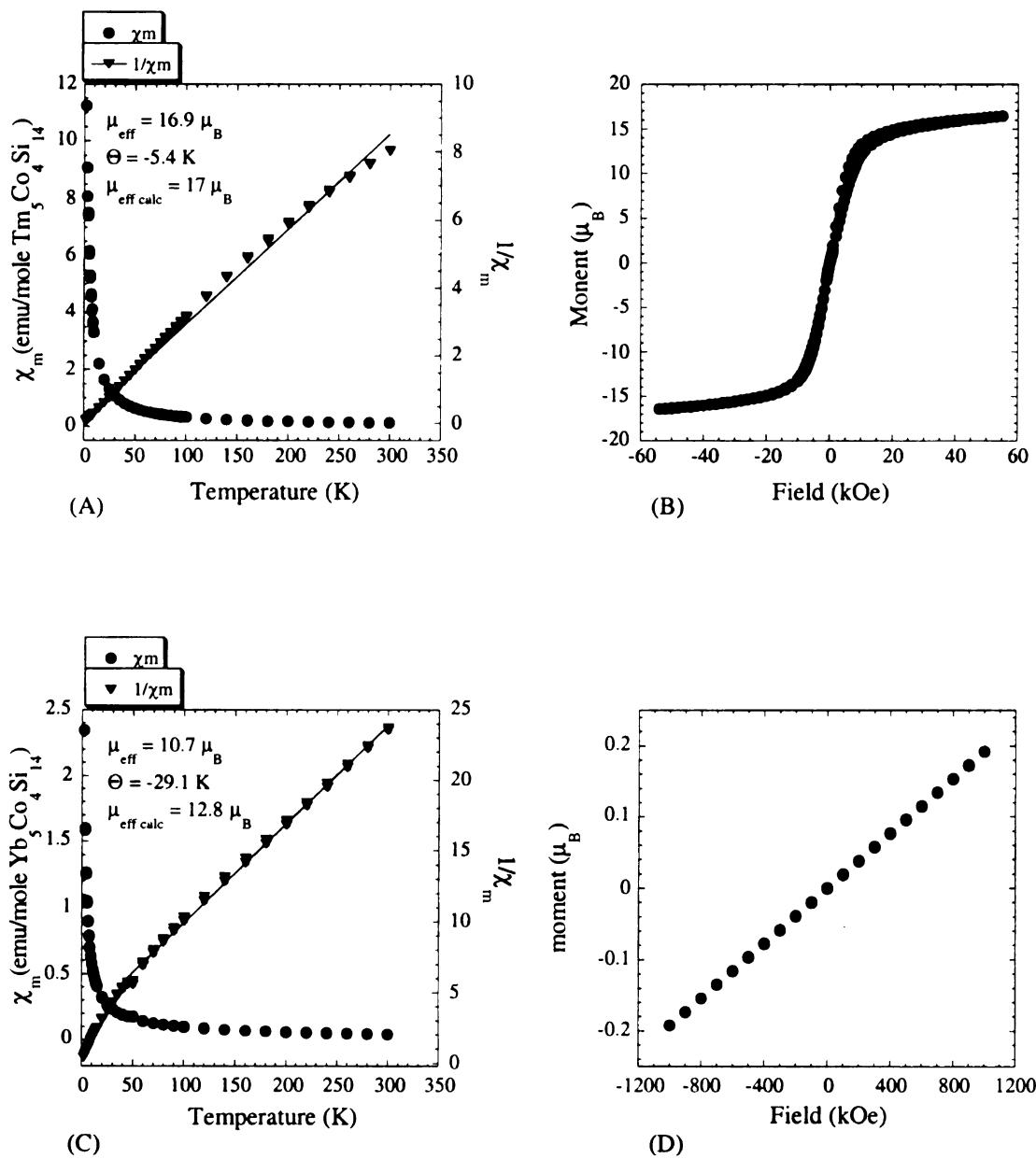


Figure 5-8 (A) Magnetic susceptibility data for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$. (B) Magnetization curve for $\text{Tm}_5\text{Co}_4\text{Si}_{14}$. (C) Magnetic susceptibility data for $\text{Yb}_5\text{Co}_4\text{Si}_{14}$. (D) Magnetization curve for $\text{Yb}_5\text{Co}_4\text{Si}_{14}$.

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5-4 Conclusions.

We have presented here the compounds $\text{RE}_5\text{Co}_4\text{Si}_{14}$ ($\text{RE} = \text{Ho, Er, Tm and Yb}$) which were synthesized by molten Ga. Ga flux has proven to be an excellent route to ternary silicide intermetallics such as these, and is in this particular case superior to more conventional techniques such as arc melting as pure phases could be obtained.

$\text{RE}_5\text{Co}_4\text{Si}_{14}$ appears to be remarkably resistant to attack in high temperature oxidizing environments, as well as harsh chemical conditions such as concentrated acids and bases due the formation of a protective SiO_2 layer. The fact that $\text{RE}_5\text{Co}_4\text{Si}_{14}$ can be produced by high temperature reactions may make possible the growth of thin films of these via a variety of vapor deposition techniques for surface coatings and related applications. Further work should be done in order to assess possible use of this system for refractory metal applications.

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17. The different levels of brightness are from charging effects from the electron beam striking the thicker oxide layer on the (100) face. The (101) face (as well as other crystal faces) having a thinner oxide coating and different chemical make up does not charge as much and is therefore not as bright.
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Chapter 6

β -RENiGe₂ (RE = Dy, Er, Yb, Lu) a New Form of RENiGe₂ Stabilized by Indium Flux.

6-1 Introduction.

In recent years our group and others have used molten metal fluxes for the exploratory synthesis of intermetallic compounds with a great deal of success. Specifically molten Al and Ga fluxes have shown themselves to be excellent routes to complex ternary and quaternary intermetallic phases of the type RE/M/Al¹ and RE/M/Al/Si,Ge² when Al is used as the solvent, and RE/M/Ga³, RE/M/Si,⁴ RE/M/Ga/Si, or Ge,⁵ and RE/Ga/Ge⁶ when Ga is used as the solvent (where RE = Y, La-Lu, M = is a transition metal). One of the advantages of using these fluxes is that the products often form as large high quality crystals, which facilitates the structural and physical characterization of these new compounds.

Given the success of molten Al and Ga in forming new compounds it seems the next logical step would be to employ indium as a flux for the synthesis of intermetallic compounds, since it has many of the characteristics that make Al and Ga excellent candidates for such applications. Particularly attractive is the capacity to dissolve Si, Ge

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and a host of lanthanide and transition metals, which results in highly reactive forms of the elements. Further, indium does not form binaries with Ge or Si and possesses a low melting point of 156 °C.⁷ A quick review of the literature shows only a handful of examples of In being used as a flux for exploratory work, and so this area is relatively unexplored.⁸

One of the most important findings from the exploration of molten metals as solvents was that some compounds can only be formed via flux synthesis. They either could not be, or were very difficult to obtain by more conventional intermetallic solid state reaction techniques such as arc-melt alloying or radio frequency (rf) induction heating of the elements.⁹ That is to say that certain compounds are stabilized by the flux, either by virtue of the chemical environment provided by the molten metal or simply because the reactions are being carried out in a lower temperature regime, making it possible to trap phases that are kinetically stable.

We report here the stabilization of a new form of the compounds RENiGe_2 (RE = Dy, Er, Yb, Lu), which crystallize in the orthorhombic *Immm* space group with the YIrGe_2 structure type.¹⁰ There have been many reported members of this structure type with compositions REMGe_2 (RE = Tb-Lu, Y, M = Ir, Pd, Pt), and many of these have been characterized by magnetic neutron diffraction and possess complex magnetically ordered structures.¹¹ All of these phases, however, contain second row transition metals, and were produced by arc melting of the elements. If, on the other hand, one arc-melts Er,

Dy, Yb, or Lu, with a first row transition metals such as Ni, and Ge in 1:1:2 ratio a different structure is obtained, namely compounds with the CeNiSi₂ structure type.¹² The title compounds contain first row transition metals, but adopt the YIrGe₂ structure type. They can only be produced by an indium flux reaction of the elements, which suggests that this new form (henceforth referred to as the β -form) of RENiGe₂ is a kinetically stable phase. Here we show that the CeNiSi₂-type form (henceforth referred to as the α -form) is the thermodynamically stable form.

6-2 Experimental Section.

Reagents:

The following reagents were used as received without further purification: Er metal (5-10 mm ribbons, 99.6%, Research Chemicals, Phoenix, AZ), Dy metal (sponge, 99.6%, Research Chemicals, Phoenix, AZ), Yb metal (chunk, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), and Lu metal (-40 mesh, 99.9, Cerac, Milwaukee, WI), Ni metal (-325 mesh, 99.9%, Cerac, Milwaukee, WI), Ge (2-5 mm pieces, 99.99%, Plasma Materials, Livermore, CA), and In, tear drops 99.9 Cerac Milwaukee, WI).

Synthesis:

1 mmol rare earth metal, 1 mmol Ni, 2 mmol, Ge and 10 mmol In were combined in alumina tubes under an inert N₂ atmosphere in a dry box. The alumina tubes and reactants were then flame-sealed in fused silica tubes under a reduced atmosphere to prevent oxidation during heating. The samples were heated to 1000 °C over 10 h and held for 4 h. The temperature was then ramped down to 850 °C, and held for an additional 48 h, then cooled to room temperature over the course of another 48 h. Product isolation from the excess indium was accomplished by centrifugation, where a coarse frit was placed in the open end of the reaction vessel and then re-sealed under a reduced atmosphere in a Pyrex tube. This was heated to 300 °C to ensure the excess indium was molten, then the sample was centrifuged for 5 min. This process removed almost all excess indium. Further purification was carried out by a 15 min submersion and sonication in 6 M aqueous HCl. Longer exposure to, or use of higher concentrations of HCl had a deleterious effect on product crystal quality.

Elemental Analysis:

Semi-quantitative microprobe elemental analysis was performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with the Noran energy dispersive spectrometer (EDS). Data were acquired using an accelerating voltage of 20 kV and 100 s acquisition times. Several crystals from each reaction were analyzed with

the resulting approximate atomic ratios of 1 : 1 : 2 for RE : Ni : Ge. These results agree quite well with the atomic ratios that were derived from the crystallographic refinement of the structure.

X-ray Crystallography:

Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART CCD diffractometer with graphite monochromatized Mo K α ($\lambda = 0.71073$ Å) radiation. Unit cell refinement and data merging were done with the SAINT program, and an empirical absorption correction was applied using the program SADABS.¹³ Inspection of the systematic absences immediately found the structure to be I centered. The condition $h+k+l = 2n$ was the only independent condition found, which lead to 4 possible space groups I222, I2₁2₁2₁, Imm2 and Immm. Immm (no.71) was the only centro-symmetric choice available and so was chosen.¹⁴ A structural solution was obtained by direct methods using the program SHELXS, and the final structural refinement was completed with the SHELXL suite of programs.¹⁵ The structure of ErNiGe₂ was solved first, and these atomic coordinates were used as a starting point for the other analogs. The crystal structure refinement data for DyNiGe₂, and ErNiGe₂, are listed in Table 6-1, the data for YbNiGe₂ and LuNiGe₂ are given in Table 6-2. The atomic positions and isotropic displacement parameters for RENiGe₂ (RE=Dy, Er, Yb, Lu) are listed in Table 6-3. The structural solutions for these compounds indicate fully occupied

sites and no disorder, The anisotropic temperature parameters for all compounds can be found in Table 6-4.

Phase identity and purity was confirmed by powder x-ray diffraction carried out on an INEL diffractometer with Cu K α radiation. The experimental powder patterns were compared to the calculated powder patterns generated from the single crystal structural refinements. Powder patterns were calculated using CERIUS².¹⁶

Differential Thermal Analysis:

Differential thermal analysis (DTA) was performed on a Shimadzu DTA-50 differential thermal analyzer. Samples were heated at a rate of 10 °C/min up to 1000 °C then cooled at the same rate to 100 °C; α -Al₂O₃ was used as a standard reference as it is stable over the entire range of the experiment.

Magnetic Measurements:

Magnetic susceptibility measurements were made on hand picked crystals, which were ground and screened by powder x-ray diffraction for phase identity and purity. Measurements were performed with a Quantum Design MPMS SQUID magnetometer in both field cooled and 0 field cooled settings at temperatures between 2K and 300K with an applied field of 500 Oe. Additionally isothermal field dependent susceptibility measurements were made from -55 kOe to 55 kOe at 2K.

Table 6-1. Crystal data and structure refinement for RENiGe₂ (RE=Dy, Er).

Formula	DyNiGe ₂	ErNiGe ₂
Formula weight	366.39	371.15
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal System	Orthorhombic	Orthorhombic
Space group	Immm (#71)	Immm(#71)
Unit cell dimensions	a = 4.1784(9) Å b = 8.865(2) Å c = 15.745(3) Å	a = 4.114(1) Å b = 8.430(5) Å c = 15.741(19) Å
Volume	583.2(2) Å ³	564.0(5) Å ³
Z, Density(calculated)	8, 8.346 g/cm ³	8, 9.031 g/cm ³
Absorption coefficient	51.756 mm ⁻¹	58.656 mm ⁻¹
F(000)	1264	1280
Theta range for data collection	2.59 to 27.01°.	2.59 to 27.06°.
Index ranges	-5<=h<=5 -11<=k<=9 -19<=l<=20	-5<=h<=2 -10<=k<10 -20<=l<=19
Reflections collected / unique	2522 / 401	1845/378
R(int)	0.0517	0.0324
Completeness to $\theta_{\max}$	99.8 %	99.7
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	401 / 0 / 30	378 / 0 / 30
Goodness-of-fit on F ²	1.266	0.763
Final R indices [I>2σ(I)]	R1 = 0.0421, wR2 = 0.1174	R1 = 0.0253 wR2 = 0.0855
R indices (all data)	R1 = 0.0429, wR2 = 0.1181	R1 = 0.0266 wR2 = 0.0871
Extinction coefficient	0.0038(3)	0.0047(3)
Largest diff. peak and hole	3.984 / -4.443 e/Å ³	2.080 / -1.942 e/Å ³

$$R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \text{ and } wR2 = [\sum (|F_o^2 - F_c^2|)^2 / \sum (w F_o^2)^2]^{1/2}$$

Table 6-2 Crystal data and structure refinement for RENiGe₂ (RE=Yb, Lu).

Formula	YbNiGe ₂	LuNiGe ₂
Formula weight	376.93	378.86
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal System	Orthorhombic	Orthorhombic
Space group	Immm (#71)	Immm(#71)
Unit cell dimensions	a = 4.0935(6) Å b = 8.4277(13) Å c = 15.751(2) Å	a = 4.0924(14) Å b = 8.418(5) Å c = 15.742(5) Å
Volume	543.40(14) Å ³	543.3(3) Å ³
Z, Density(calculated)	8, 9.215 g/cm ³	8, 9.281 g/cm ³
Absorption coefficient	62.466 mm ⁻¹	64.511 mm ⁻¹
F(000)	1296	1304
Theta range for data collection	2.59 to 27.15°.	4.558 to 29.58°.
Index ranges	-5<=h<=5 -10<=k<=10 -20<=l<=19	-5<=h<=5 -11<=k<11 -21<=l<=19
Reflections collected / unique	2432 / 377	2261/450
R(int)	0.0602	0.0304
Completeness to $\theta_{\max}$	99.2 %	94.7 %
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	377 / 0 / 30	450 / 0 / 30
Goodness-of-fit on F ²	1.183	1.060
Final R indices [I>2σ(I)]	R1 = 0.0443, wR2 = 0.1018	R1 = 0.0231 wR2 = 0.0592
R indices (all data)	R1 = 0.0454, wR2 = 0.1033	R1 = 0.0271 wR2 = 0.0605
Extinction coefficient	0.0055(3)	0.00224(15)
Largest diff. peak and hole	7.009 / -4.913 e/Å ³	3.063 / -2.043 e/Å ³

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ and } wR2 = [\frac{\sum (|F_o|^2 - |F_c|^2)^2}{\sum (w F_o^2)^2}]^{1/2}$$

Table 6-3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiGe_2 (RE =Dy, Er, Yb, Lu).

Atom	Wyckoff Position	x	y	z	U(eq)*
Dy(1)	4j	0	5000	2081(1)	5(1)
Dy(2)	4g	0	2831(1)	0	7(1)
Ge(1)	4i	0	5000	4143(1)	11(1)
Ge(2)	4i	5000	5000	786(2)	6(1)
Ge(3)	8l	0	1591(2)	1907(1)	7(1)
Ni	8l	0	2352(3)	3466(1)	7(1)
Er(1)	4j	0	5000	2040(1)	5(1)
Er(2)	4g	0	2602(1)	0	7(1)
Ge(1)	4i	0	5000	4204(1)	10(1)
Ge(2)	4i	5000	5000	770(1)	5(1)
Ge(3)	8l	0	1568(2)	1958(1)	6(1)
Ni	8l	0	2490(2)	3522(1)	6(1)
Yb(1)	4j	0	5000	2033(1)	6(1)
Yb(2)	4g	0	2388(1)	0	9(1)
Ge(1)	4i	0	5000	4231(1)	7(1)
Ge(2)	4i	5000	5000	794(1)	14(1)
Ge(3)	8l	0	1570(2)	1966(1)	9(1)
Ni	8l	0	2512(2)	3525(1)	8(1)
Lu(1)	4j	0	5000	2034(1)	5(1)
Lu(2)	4g	0	2615(1)	0	7(1)
Ge(1)	4i	0	5000	4228(1)	5(1)
Ge(2)	4i	5000	5000	795(1)	11(1)
Ge(3)	8l	0	1572(1)	1966(1)	6(1)
Ni	8l	0	2428(1)	3526(1)	6(1)

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

Ta
YU

—
D
D
G
G
G
N

E
E
G
G
G
N

Y
Y
C
C
C
M

L
L
C
C
C
M

T
k

Table 6-4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for RENiGe_2 (RE = Dy, Er, Yb, Lu).

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Dy(1)	6(1)	5(1)	6(1)	0	0	0
Dy(2)	8(1)	5(1)	7(1)	0	0	0
Ge(1)	22(1)	4(1)	8(1)	0	0	0
Ge(2)	9(1)	5(1)	4(1)	0	0	0
Ge(3)	8(1)	5(1)	9(1)	3(1)	0	0
Ni	9(1)	5(1)	8(1)	-1(1)	0	0
Er(1)	8(1)	4(1)	2(1)	0	0	0
Er(2)	10(1)	6(1)	4(1)	0	0	0
Ge(1)	24(1)	3(1)	4(1)	0	0	0
Ge(2)	10(1)	4(1)	2(1)	0	0	0
Ge(3)	9(1)	4(1)	6(1)	1(1)	0	0
Ni	9(1)	4(1)	5(1)	2(1)	0	0
Yb(1)	12(1)	2(1)	5(1)	0	0	0
Yb(2)	14(1)	6(1)	6(1)	0	0	0
Ge(1)	16(1)	2(1)	5(1)	0	0	0
Ge(2)	32(1)	3(1)	9(1)	0	0	0
Ge(3)	14(1)	3(1)	10(1)	2(1)	0	0
Ni	14(1)	3(1)	8(1)	0	0	0
Lu(1)	6(1)	4(1)	4(1)	0	0	0
Lu(2)	8(1)	8(1)	6(1)	0	0	0
Ge(1)	9(2)	5(1)	2(1)	0	0	0
Ge(2)	25(1)	4(1)	6(1)	0	0	0
Ge(3)	7(1)	5(1)	8(1)	-2(1)	0	0
Ni	8(1)	3(1)	6(1)	-2(1)	0	0

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

Band Structure Calculations:

Band structure calculations were performed on both α - and β -LuNiGe₂ using the self-consistent full-potential linearized augmented plane wave method (LAPW)¹⁷ within density functional theory (DFT) with a generalized gradient approximation (GGA) for the exchange and correlation potential within the Perdew-Burke-Ernzerhof model.¹⁸ Scalar relativistic corrections were added and spin-orbit interactions (SOI) were incorporated using a second variational procedure.¹⁹ Calculations were carried out on the Lu system due to the inability of DFT to accurately model the highly correlated electrons found in partially filled *f* levels. The calculations were performed with the WIEN97 program.²⁰ The atomic radii values (in atomic units 1a.u. = 0.529 Å) used in the calculation are as follows 2.4 for Lu, 2.15 for Ni and 2.25 for Ge. Self-consistent iterations were performed with 27 k points in the reduced Brillouin zone with a cutoff between valence and core states of -6.0 Ry; convergence was assumed when the total energy difference between cycles was within 0.0001 Ry. Total energy was computed for both α and β forms of the structure by a full volume relaxation method in which the structure is allowed to minimize its energy by relaxing the cell volume and atomic positions.

6-3 Results and Discussion.

Structure:

Despite their stoichiometric equivalence the structure of the title compounds are distinct from that of the α -form. Figure 6-1 (A) shows the overall structure of β -RENiGe₂ as viewed down the a -axis, and Figure 6-1 (B) shows the structure of the α -form for comparison. Figure 6-2 (A) shows the structure of the β -phase as viewed down the b -axis, and Figure 6-2 (B) shows the c -axis view of the α -phase. The main difference between the two phases is in the distribution of the Ge species. The α -form exists as single Ge atoms and infinite Ge chains, whereas the β -form contains only Ge dimers. A list of the selected bond distances for β -RENiGe₂ is found in Table 6-5.

The title compounds are composed of two sets of Ge dimers that are formed by the bonding of symmetry equivalent atoms, Ge(1)–Ge(1), with lengths of 2.698(4)Å, 2.507(4)Å, 2.423(4)Å, 2.558(4)Å for the Er, Dy, Yb, and Lu compound respectively, and Ge(2)-Ge(2) with lengths 2.476(5)Å, 2.423(4)Å, 2.500(4)Å, 2.453(4)Å for Dy, Er, Yb, and Lu respectively. These Ge dimers then bond to Ni atoms with Ge(1)-Ni distances of 2.578(2)Å, 2.373(2)Å, 2.3713(19)Å, 2.3949(18)Å and Ge(2)-Ni distances of 2.394(3)Å, 2.394(3)Å, 2.3762(18)Å, 2.3992(19)Å for Dy, Er, Yb and Lu respectively. This arrangement forms distorted Ni₂Ge₄ hexagons, with both Ge(1) and Ge(2) in trigonal planar bonding arrangements. The Ni atom forms an additional 3 bonds to Ge(3) atoms at a distances of 2.3637(14)Å, 2.3313(14)Å, 2.328(1)Å, 2.550(2)Å for Dy, Er, Yb and Lu

making for a 5 coordinate square pyramidal geometry. The Ge(3) atoms form another kind of dimer where each Ge(3) atom is tetrahedrally surrounded by 3 Ni atoms with distances of 2.3637(14)Å, 2.3313(14)Å, 2.328(1)Å, 2.550(2)Å for the Dy, Er, Yb and Lu analogs respectively, the fourth bond is to another Ge(3) atom. Therefore the Ge(3)-Ge(3) dimer is an ethane-like unit with an eclipsed geometry. The result is a three-dimensional [NiGe₂] network with channels extending down the *b*-axis (Figure 6-2(A)), and cages encapsulating the rare earth atoms.

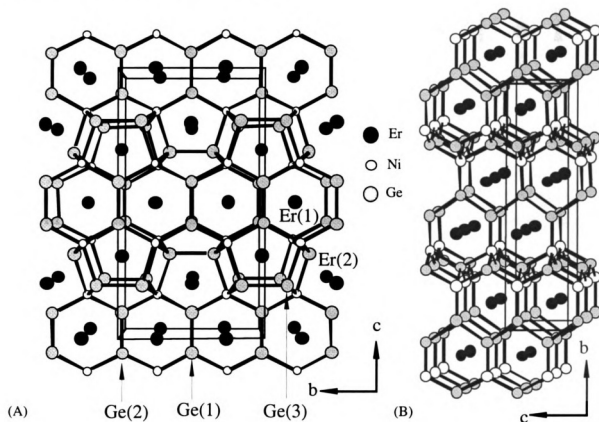


Figure 6-1 (A) The structure of β -RENiGe₂ as viewed down the *a*-axis. (B) The overall structure of α -RENiGe₂ a perspective view along the *a*-axis.

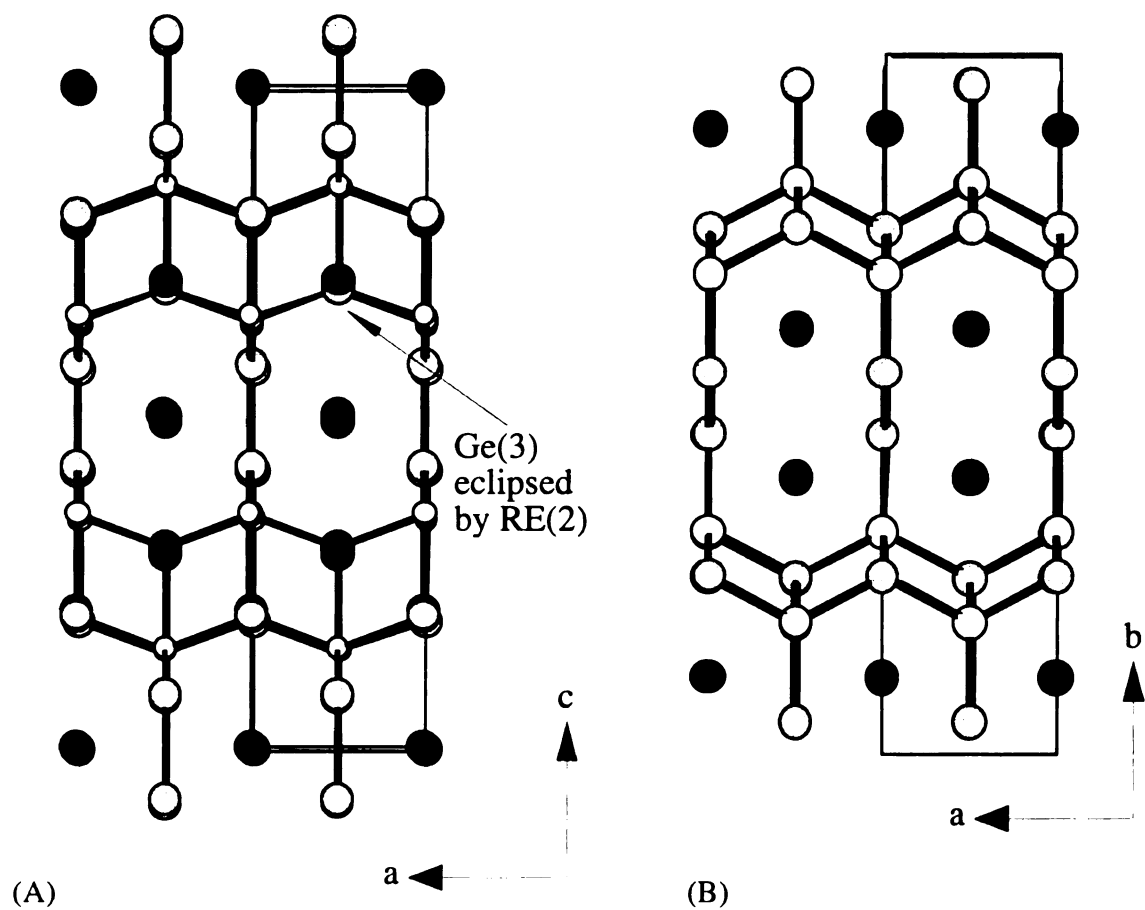


Figure 6-2 (A) The structure of β -RENiGe₂ as viewed down the b -axis. (B) The structure of α -RENiGe₂ as viewed along the c -axis. This figures helps illustrate the structural similarities between the α and β -forms.

Table 6-5 Bond lengths [$\text{\AA}$] for RENiGe_2 (RE=Dy, Er, Yb, Lu).

	RE = Dy	RE = Er	RE=Yb	RE=Lu
RE(1)-Ge(2)	2.9193(19)	2.8684(18)	2.8554(14)	2.8518(12) x2
RE(1)-Ge(3)	2.9821(13)	2.9099(14)	2.903(1)	2.8880(14) x4
RE(1)-Ge(3)	3.0340(19)	2.896(2)	2.8924(14)	2.9013(10) x2
RE(1)-Ni	3.0746(18)	3.0688(16)	3.0573(12)	3.0554(11) x4
RE(2)-Ge(1)	3.0340(19)	3.1282(13)	3.1159(9)	3.1139(9) x4
RE(2)-Ge(2)	3.0975(12)	3.2581(14)	3.255(1)	3.2551(9) x2
RE(2)-Ge(3)	3.1971(18)	3.204(2)	3.2179(3)	3.2162(14) x2
RE(2)-Ni	3.1976(18)	3.1068(18)	3.0979(15)	3.0948(12) x4
Ge(1)-Ni	2.578(2)	2.373(2)	2.3713(19)	2.3647(14) x2
Ge(1)-Ge(1)	2.698(4)	2.507(4)	2.423(4)	2.431(3)
Ge(2)-Ni	2.394(3)	2.394(3)	2.3762(18)	2.3728(14) x2
Ge(2)-Ge(2)	2.476(5)	2.423(4)	2.500(4)	2.502(3)
Ge(3)-Ni(1)	2.3637(14)	2.3313(14)	2.328(1)	2.3276(9) x3
Ge(3)-Ge(3)	2.821(4)	2.643(3)	2.647(3)	2.646(2)

In contrast to the β -form the structure of α - RENiGe_2 is composed of PbO type layers containing Ni and Ge(2) atoms. These layers are connected through Ni-Ge(1) bonds, to zigzag chains of Ge atoms, which run along the c -axis. As a result the Ni atoms are 5 coordinate with square pyramidal geometry, and the Ge(2) atoms within the layer are tetrahedrally coordinated, Figure 6-1(B). This structure also contains channels of RE ions, which run parallel to the c axis, Figure 6-2(B).

While the two phases are distinct from one another a simple scheme to inter-convert the two structures can be envisioned in the following way. If one of the Ge(1)-Ni and Ge(2)-Ni bonds is broken, and the hexagonal slab is sheered along the *b*-axis this will cause the Ge dimers to tilt until Ge(1) and Ge(2) can form a bond. This results in a Ge zigzag chain that propagates along the *b*-axis, see Figure 6-3 (A) and (B). Then if the Ge(3)-Ge(3) bond is broken and new Ge-Ni bonds form with adjacent Ni atoms (by an appropriate rotation of the fragment shown in the shaded areas in Figure 6-3) this will lead to the compression of the cage layer. This rearrangement will bring about the formation of a new NiGe, PbO-type layer, which could then connect to the zigzag Ge chains to form the CeNiSi₂ structure type. The inter-conversion thus requires the breaking of 2 Ni-Ge bonds and 1 Ge-Ge bond, and a substantial amount of atomic re-organization in order to take place. This would suggest a large reorganization barrier, and one may predict, based on this, that the kinetics of inter-conversion would be slow.

The first hint that the α -form was the thermodynamically stable form came from inspecting the cell volumes of the α - and β -phases. For α -ErNiGe₂ the volume of 2 unit cells is 503.6(3) Å³, while the unit cell volume of the β -form is 546.0(2) Å³. Since these volumes contain the same number and type of atoms, it is apparent that the atoms are more closely packed in the α -form indicating stronger bonding and presumably a more energetically favorable arrangement.

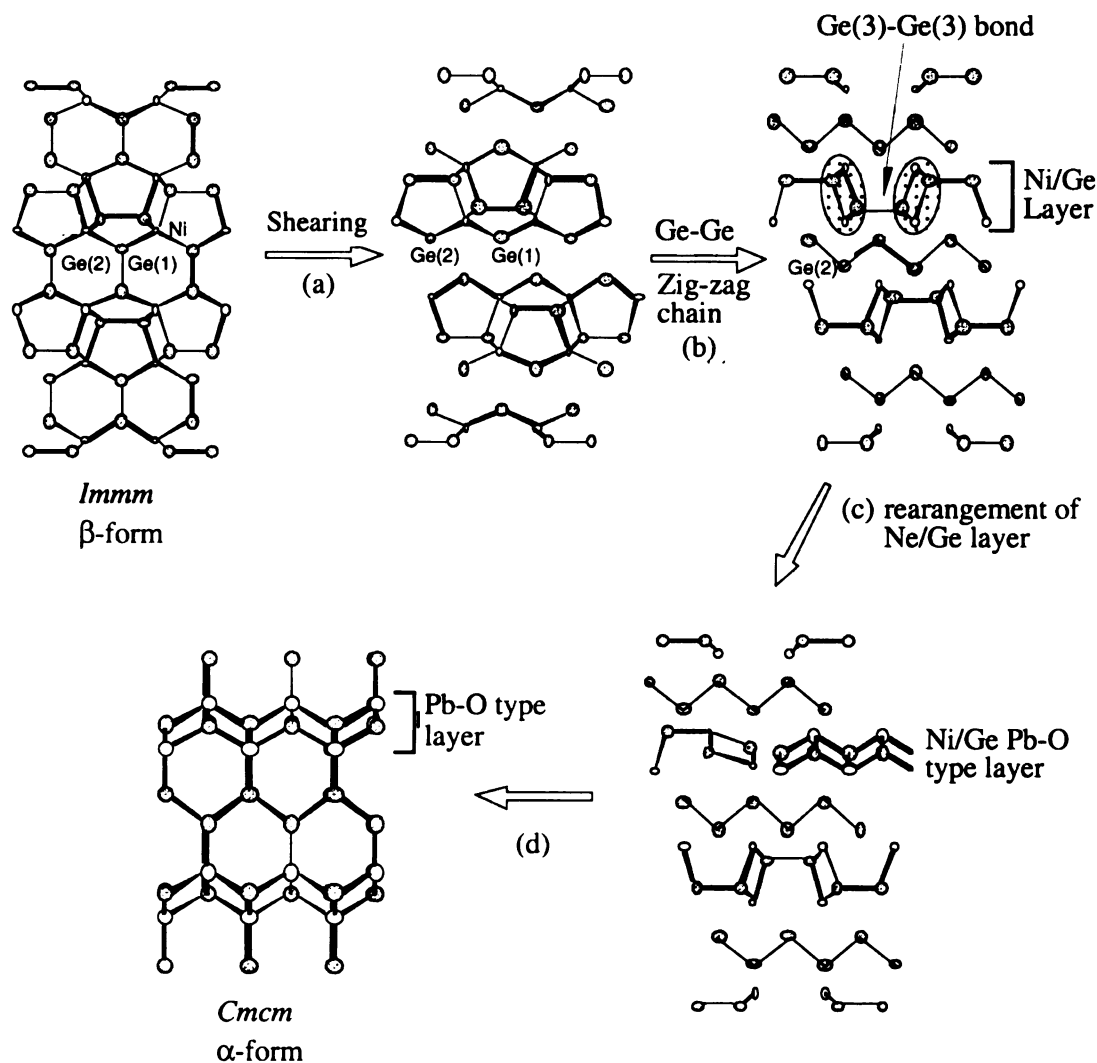


Figure 6-3 Conceptual stepwise scheme for the interconversion of the $\beta\text{-R-NiGe}_2$ structure to the α -form (CeNiSi_2 type structure). The shaded ovals after step (b) need to be rotated to break the $\text{Ge}(3)\text{-Ge}(3)$ bond and form the PbO -type layer.

Synthesis and Thermal Stability:

It is interesting to note that the formation of $\beta\text{-R-NiGe}_2$ is exclusive to the indium flux synthetic technique. The yields from these reactions range from 60 to 70%, based on the lanthanide metal, with $\sim 70\%$ purity. The main impurities were the α -phase

and recrystallized Ge. When other methods such as arc-melting or rf furnace heating were used to synthesize RENiGe_2 they led only to the α -form. Furthermore, if the length of the reactions were increased from 48 to 96 h the α -phase was the dominant fraction, approximately 65%. Likewise, if the isotherm temperature for the reactions were increased from 850 °C to 1000 °C, a larger fraction of the reaction product, approximately 50% to 60%, crystallized as the α -form. Two other experiments were also conducted where the elements (Dy or Er, Ni Ge and In) were combined in a 1:1:2:10 ratio, and then were arc-melted for 3 min, or heated with a rf furnace for 1 h. Both of these methods, which employ much higher temperatures than the flux reaction described in the experimental section, yielded practically pure α -form despite using excess indium. All of these results suggest that the α -phase is the more thermodynamically stable form, and the β -form is likely a kinetically stable phase.

Differential thermal analysis was performed on the title compounds to see if a β - to α -phase transition could be observed. Both β - ErNiGe_2 and β - DyNiGe_2 were stable up to 1000 °C.²¹ Likewise annealing samples of pure β - ErNiGe_2 at 950 °C for 2 weeks also failed to bring about a change to the α -form. X-ray powder patterns of the annealed product were compared to those taken prior to annealing, and no significant changes were observed. The resistance to convert likely indicates a high barrier to phase transformation. This is consistent with the large amount of bond breaking and reforming

required for the two phases to inter-convert, which was discussed above. One final experiment was attempted where the α - and β -forms of the compound were placed in separate alumina tubes and were combined with a 10-fold molar excess of indium and annealed at 950 °C for 2 weeks. This technique proved successful in interconverting a substantial amount (~50%) of the β -form to the α -form. The α -form was simply re-crystallized by the indium to form larger single crystals. This demonstrates that indium indeed acts as a solvent to lower the barrier of activation for inter-conversion by dissolving the β -phase and re-crystallizing it in the α -form. Powder patterns comparing the products of the indium free annealing and indium annealing with the calculated patterns of the β and α -forms are shown in Figures 6-4 (A) and (B) respectively. Figure 6-4 (A) shows that the powder pattern of β -ErNiGe₂ after annealing in the absence of In as it compares to the calculated powder pattern of β -ErNiGe₂. Figure 6-4(B) shows the powder pattern of β -ErNiGe₂ after annealing in excess indium as it compares to the calculated powder pattern for α -ErNiGe₂.

Band Structure Calculations:

Band structure calculations were performed on both the α and β -form of LuNiGe₂ in order to better understand the bonding within the system, and to calculate the total energy of each phase. The band structure of the α -form will not be discussed here, rather

we will compare its total energy to that of the β -phase. The calculations suggest that the α -LuNiGe₂ is more thermodynamically stable than the β -form by approximately 89 kJ/(mol LuNiGe₂). This result is consistent with our experimental findings described above. The α and β forms of RENiGe₂ differ by 2 key structural features, the Ge-Ge zigzag chain and the Pb-O type layers which are both part of the α -phase, but not the β -phase. Both of these units are very common in intermetallic structures particularly the Pb-O layer, the main structural component of the BaAl₄ structure, one of the most common intermetallic structure types.²² Its nearly ubiquitous presence is most likely a reflection of the stability of this structural unit. Inspection of the density of states (DOS) for both the α and β -forms found that all the corresponding bands in these two compounds all fell within comparable energy ranges with the exception of the p bands of Ge(2) in the α phase, which reside 3 eV lower in energy. The Ge(2) atoms resides in the Pb-O layer and is tetrahedrally coordinated to 4 Ni atoms, a feature exclusive to α -RENiGe₂. The Ge(1) bands of the zigzag chains are of comparable energy to those of all the corresponding Ge bands found in β -RENiGe₂. Based on these results we can infer that the stability of the α -form is due to the presence of the Pb-O layer which lowers the energy of the Ge bands, and as a result lowers the energy of the entire structure below that of β -RENiGe₂.

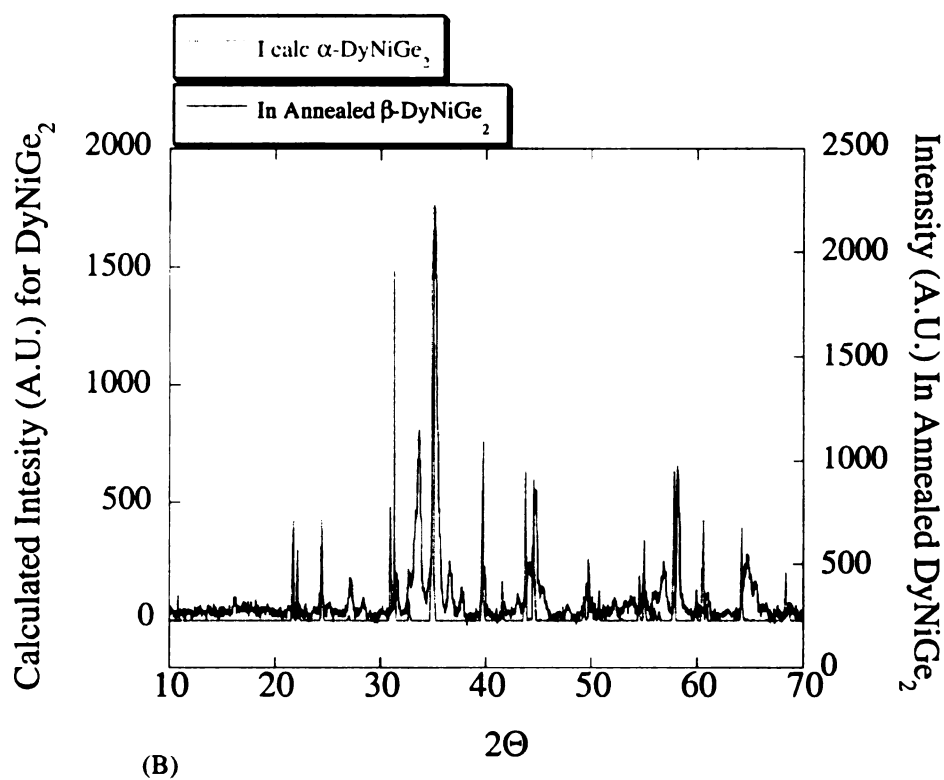
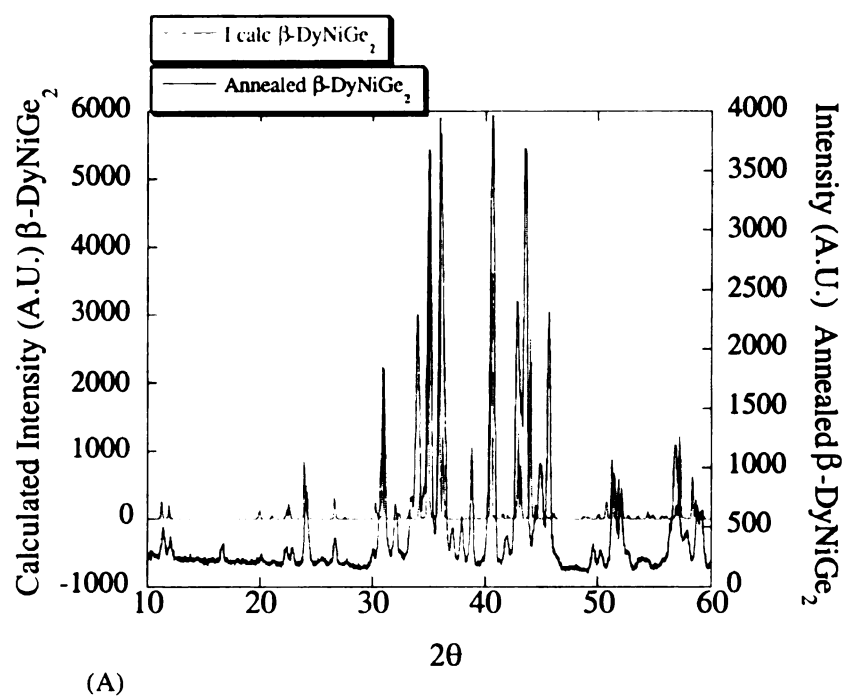


Figure 6-4 (A) Powder pattern of ErNiGe_2 after annealing without In, as it compares to the calculated pattern of β - ErNiGe_2 . (B) Powder pattern of ErNiGe_2 after annealing in indium as it compares to the calculated pattern of α - ErNiGe_2 .

The total calculated DOS for β -LuNiGe₂ is shown in Figure 6-5 (A). Two main features dominate the DOS. First is the non-dispersed *f* orbital based states of the two crystallographically distinct rare earth sites, which are located between -6 eV and -4eV. Secondly the Ni *d* states centered at -3 eV. A total of four large narrow *f* bands appear because each of the two rare earth ion bands are split in two by spin orbit coupling. These bands are quite low in energy, and are therefore not expected to play a role in conduction.

The Ni *d* bands are also located well below the Fermi level, and suggest that the Ni atoms have a filled *d*¹⁰ electronic configuration, Figure 6-5(B). Therefore the Ni is essentially reduced to a diamagnetic species. Filled *d* bands of late transition metals are a common feature in intermetallic compounds containing more electropositive elements.²³

Also evident from the total DOS plot is that the β -LuNiGe₂ is metallic as there are 8 states/eV at the Fermi level. Bands derived from Lu *d* orbitals lie between 7 and -2 eV indicating that the Lu ions are in a 3+ oxidation state as these bands are empty, Figure 6-5(C). The *s* bands of the Ge atoms are located at very low energies, between -11 and -6 eV, Figure 6-5(D). The Ge contribution to the density of states is rather small. There are *p* bands present in all three Ge atoms between -5 and 0 eV allowing for effective overlap between these bands with the *d* bands of Ni and Lu Figure 6-5(E)

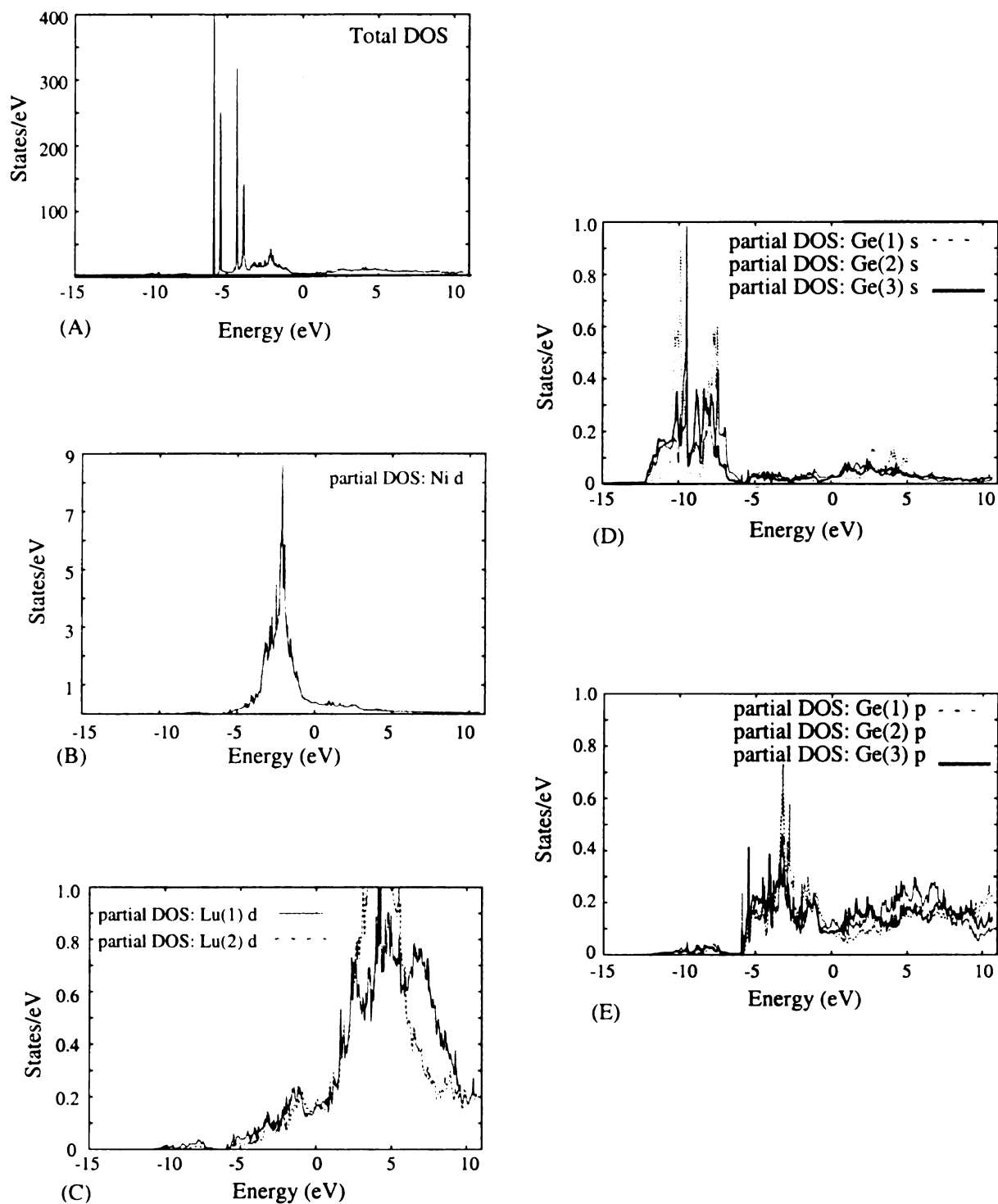


Figure 6-5 (A) Total (DOS) for β -LuNiGe₂ (B) Ni d DOS for β -LuNiGe₂. (C) Lu(1) *d* and Lu(2) *d* DOS for β -LuNiGe₂. (D) Ge(1) *s*, Ge(2) *s*, and Ge(3) *s* DOS for β -LuNiGe₂. (E) LuNiGe₂-Ge(1) *p*, Ge(2) *p*, and Ge(3) *p* DOS for β -LuNiGe₂.

Magnetic Properties:

Magnetic measurements performed on β -DyNiGe₂ and β -ErNiGe₂ show antiferromagnetic ordering with Néel temperatures of 4 K and 5 K respectively, Figures 6-6 (A) and (C). Above these temperatures the compounds obey the Curie/Weiss law. β -YbNiGe₂ and β -LuNiGe₂ show no indication of magnetic ordering. The measured effective magnetic moment of β -DyNiGe₂ is 10.0 μ_B , which in complete agreement with the value calculated for a Dy³⁺ ion which is 10.0 μ_B .²⁴ The measured magnetic moment of β -ErNiGe₂ was 9.0 μ_B , which is in good agreement with the calculated value of an Er³⁺ ion, which is 9.6 μ_B . Likewise β -YbNiGe₂ has an effective magnetic moment of 4.65 μ_B , which compares to the theoretical value of 4.56 μ_B .²¹ β -LuNiGe₂ on the other hand exhibits temperature independent Pauli paramagnetism. These findings are consistent with those predicted from the band structure calculations, which showed Ni to be a d^{10} diamagnetic species, and therefore the only contribution to the paramagnetic susceptibility would be from the lanthanide ions. Given these results we may write the compounds as RE³⁺[NiGe₂]³⁻.

The magnetization curves for β -DyNiGe₂ and β -ErNiGe₂ can be seen in Figure 6-6 (B) and (D) respectively. Both compounds undergo field induced metamagnetic transitions with small applied fields. There is a strong field dependence on the moment up to about 15 kOe for β -DyNiGe₂ and 12 kOe for β -ErNiGe₂ above these points there is

still a nearly linear dependence to the susceptibility but the slope is much shallower than at the lower fields as, presumably, the moments begin to saturate. β -DyNiGe₂ reaches a value of 8.1 μ_B which is about 90 % of the anticipated μ_{sat} value. β -ErNiGe₂ reaches a value of 7.7 μ_B at the maximum applied field which is about 80% of the anticipated value.

A great deal of work has been done characterizing the magnetic structure of the REIrGe₂ REPtGe₂, REPdGe₂.¹¹ Many of these compounds have very complex structures including canted antiferromagnetism, and incommensurately modulated antiferromagnetism to name a few. Therefore, the magnetic ordering phenomena observed in β -DyNiGe₂ and β -ErNiGe₂ are also of interest to search similar effects or even as model compounds for comparative purposes to see what effect a first row transition metal would have on magnetic properties.

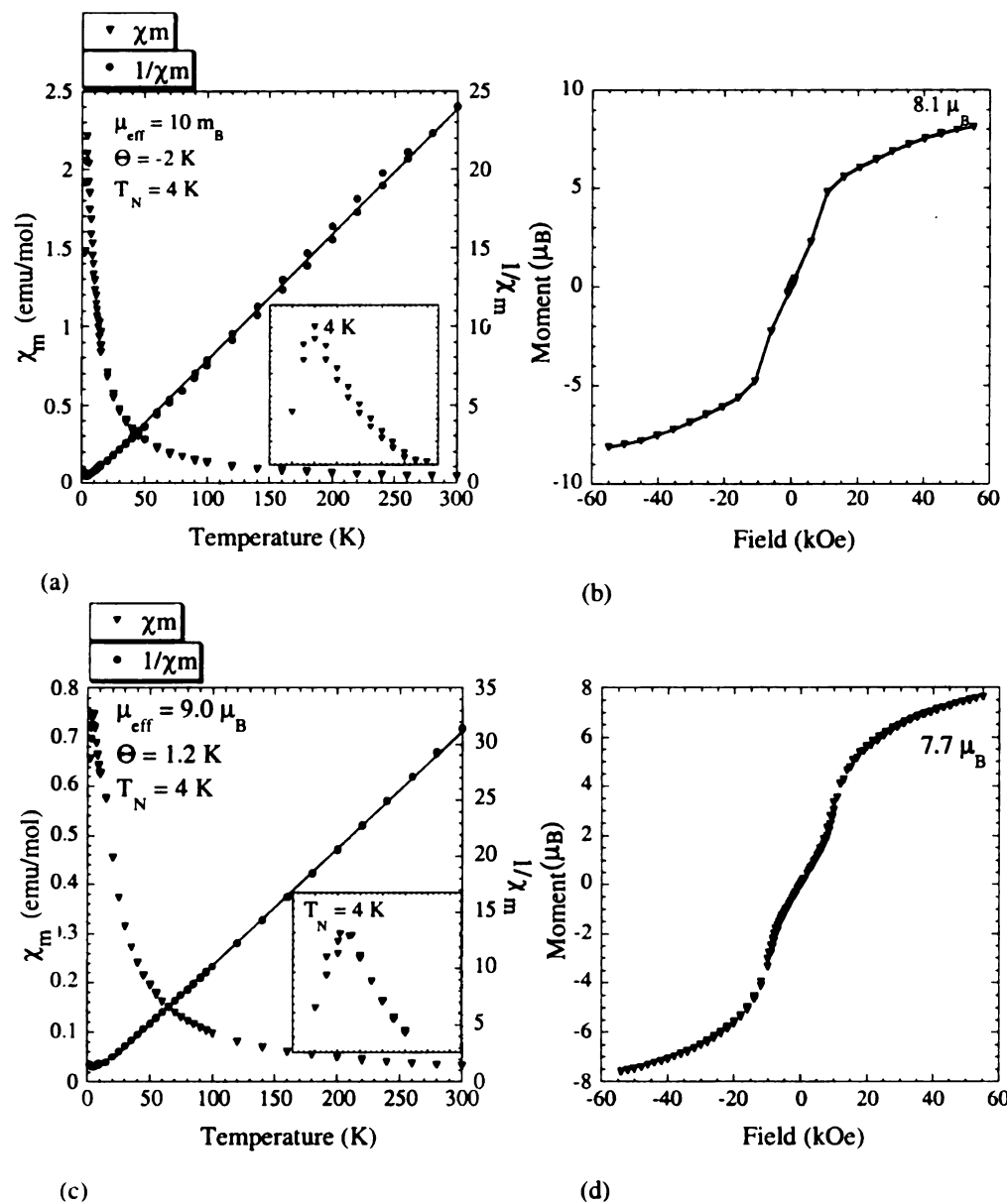


Figure 6-6 (A) Magnetic susceptibility (χ_m and $1/\chi_m$) for β -DyNiGe₂. The inset shows the antiferromagnetic ordering at low temperatures. (B) Magnetization curve for β -DyNiGe₂ (C) Magnetic susceptibility (χ_m and $1/\chi_m$) for β -ErNiGe₂. The inset shows the antiferromagnetic ordering. (D) Magnetization curve for β -ErNiGe₂.

6-4 Conclusions.

In conclusion we have presented here new forms of the compound RENiGe_2 ($\text{RE}=\text{Er, Dy, Yb, Lu}$) which crystallize as the YIrGe_2 structure type grown from an indium flux. These phases are an intriguing discovery for other phases with the same composition (RENiGe_2) have been known for sometime, but crystallize in the CeNiSi_2 structure type. What is more, many REMGe_2 compounds with $\text{RE}=\text{Tb-Lu, Y}$ and $\text{M} = \text{Pd, Pt, Ir}$, with the YIrGe_2 structure type are known, but phases containing first row transition metals have not been reported until now. The discovery of these compounds is an excellent example of how a metal flux coupled with the right conditions of temperature and time can alter the reaction outcome and stabilize kinetic phases.

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Chapter 7

RE₂Zn₃Ge₆ (RE = La, Ce, Pr, and Nd) Intermetallic Phases with Near Zintl Phase Behavior Grown from liquid Indium.

7-1 Introduction.

The remarkable utility of Al and Ga as solvents to explore new intermetallic phases in the systems RE/TM/Al/Si, Ge,¹ and RE/TM/Ga/Si or Ge² (RE = is a rare earth metal and TM is a transition metal), raises the question as to how indium would perform. Indium possesses many of the same qualities that make Al and Ga attractive for exploratory synthesis. Namely its low melting point, its inability to form binaries with Ge or Si, and the solubility of Ge, Si and a host of transition and lanthanide metals in it.³ It is therefore a logical candidate to use in the extension of the work listed above to systems of the type RE/TM/Ge/In. Indeed several groups have used molten In as a method to grow large single crystals of RE/TM/Ge compounds, and investigate their physical properties more carefully.⁴

We have recently demonstrated the ability of liquid indium to stabilize a new form of the compound RENiGe₂ (RE = Dy, Er, Tm, Yb and Lu) which could not be made by direct combination of the elements, but was exclusive to the In flux.⁵ Here we extend

this research to include other transition metals, and describe the new phases $\text{RE}_2\text{Zn}_3\text{Ge}_6$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{and Nd}$). $\text{RE}/\text{Zn}/\text{Ge}$ compounds are quite rare with only a handful of example previously reported in the literature including: $\text{RE}_4\text{Zn}_5\text{Ge}_6$,⁶ ($\text{RE} = \text{Nd and Ce}$) EuZnGe ,⁷ $\text{Nd}_2\text{Zn}_{15}\text{Ge}_2$,⁸ $\text{GdZn}_{1.6}\text{Ge}_{0.4}$, and $\text{Gd}_4\text{Zn}_8\text{Ge}_{10.82}$.⁹ There have been several examples of alkali and alkaline earth metal Zn/Ge ternary compounds, which include: Cs_6ZnGe_8 ,¹⁰ the trigonal Li_2ZnGe ¹¹ and cubic Li_2ZnGe ,¹² LiZnGe ,¹³ and SrZnGe ,¹⁴ both of which have the AlB_2 structure. Several alkaline earth/ Zn/Ge ternaries which crystallize with the ThCr_2Si_2 structure type specifically SrZn_2Ge_2 ¹⁵, and CaZn_2Ge_2 ¹⁶ have been reported as well as $\text{Ba}_8\text{Zn}_8\text{Ge}_{38}$ ¹⁷ which adopts the cubic clathrate structure. The bonding of many of these compounds can be rationalized using the Zintl concept by assuming complete electron transfer from the s orbitals of the alkali or alkaline earth metal and Zn to the Ge atoms. In $\text{RE}_4\text{Zn}_5\text{Ge}_6$ the structure is composed of 4 Ge atoms which are tetrahedrally coordinated by Zn and a pair of Ge dimers giving the charge balancing $(\text{RE}^{3+})_4(\text{Zn}^{2+})_5(\text{Ge}^{3-})_2(\text{Ge}^{4-})_4$. Cs_6ZnGe_8 is composed of 2 deltahedra (Ge_4^{4-}) linked by a central Zn^{2+} ion resulting in isolated $(\text{ZnGe}_8)^{6-}$ anions. The other examples listed above such as SrZn_2Ge_2 , CaZn_2Ge_2 and LiZnGe cannot be charge-balanced by these simple ideals, and are considered strictly intermetallic compounds.

The title compounds add to the rather short list of $\text{RE}/\text{Zn}/\text{Ge}$ borderline compounds whose bonding can be rationalized with the Zintl concept. Presented here is a series of RE analogs $\text{RE}_2\text{Zn}_3\text{Ge}_6$, whose bonding and physical properties are intermediate

between classical Zintl phases and intermetallic compounds. The crystal structure, band structure calculations, magnetic, and spectroscopic measurements are presented to better understand the nature of these compounds.

7-2 Experimental Section.

Reagents:

The following reagents were used without further purification: La metal(~40 mesh powder, 99.9%, Cerac, Milwaukee, WI), Ce metal(~250 mesh powder, 99.9%, Research Chemicals, Phoenix, AZ), Pr metal(~250 mesh powder, 99.9%, Research Chemicals, Phoenix, AZ), Nd metal(~250 mesh powder 99.9% Research Chemicals, Phoenix, AZ), Zn metal(~30 mesh granular, 99.8%, J.T. Baker Chemicals, Phillipsburg, NJ), Ge (3-5 mm shards, 99.999%, Plasmaterials, Livermore, CA), and In (3-5 mm teardrops, 99.5%, Cerac, Milwaukee, WI).

Synthesis:

Method A: $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = La, Ce, Pr, Nd) was produced by combining 2mmol of the rare earth, 3 mmol of Zn, 6 mmol of Ge and 20 mmol of In in an alumina tube which was then flame sealed under a reduced atmosphere of 10^{-4} mbar. The reactants were then heated to 1000 °C over 12 h held for 4 h, then ramped down to 850 °C over 2 h. The reaction was then soaked at this temperature for 48 h before cooling to room temperature

over 24 h. The majority of the In flux was removed by centrifuging the sample, and filtering the molten In through a coarse filter. Indium metal tended to wet the product so further purification was carried out by chemically etching away the In with acetic acid. The yields from these reactions were rather poor at about 30 % based on the rare earth. Purity and crystal quality were also quite poor.

Method B: $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = La, Ce, Pr, Nd) was synthesized by combining 2 mmol of the rare-earth, 3 mmol of Zn and 6 mmol of Ge, and cold pressing them into a pellet. The pellet was then flame sealed in a 13mm fused silica tube, with a carbon coated interior, under a reduced atmosphere of 10^{-4} mbar. The reactants were then heated to 790 °C for the La analog 785°C for $\text{Ce}_2\text{Zn}_3\text{Ge}_6$, 770 °C for the Pr and Nd compounds over the course of 8 h. The reactants were held at their respective temperatures for 72 h then quickly cooled to room temperature over 8 h. It was found that the reactions could also be quenched from the isotherm without effecting purity or crystal quality. All of the compounds could be made as single phases in quantitative yields by this method.

X-ray Crystallography:

Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART CCD diffractometer with graphite monochromatized $\text{Mo K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Unit cell refinement and data merging were done with the SAINT

program, and an empirical absorption correction was applied using the program SADABS.¹⁸ Inspection of the systematic absences immediately found the structure to be C centered. The (hkl) condition $h+k = 2n$ and $(h0l)$ $h,l = 2n$ were the only independent conditions found, which lead to 2 possible space groups $Cmc2_1$ (#36), and $Cmcm$ (#63).¹⁹ The mean $|E^2-1|$ value of 0.912 pointed to the likelihood of a centrosymmetric space group as the estimated $|E^2-1|$ value for a non-centrosymmetric space group is 0.736 and for a centrosymmetric group it is 0.968. A structural solution in the $Cmcm$ space group was obtained for $La_2Zn_3Ge_6$ by direct methods using the program SHELXS, and the final structural refinement was completed with the SHELXL suite of programs.²⁰ Structural refinements of the Ce, Pr, and Nd analogs were obtained by using the solution of $La_2Zn_3Ge_6$ as a starting point.

Data collection and refinement details for $La_2Zn_3Ge_6$ and $Ce_2Zn_3Ge_6$ can be found in Table 7-1, and information for $Pr_2Zn_3Ge_6$ and $Nd_2Zn_3Ge_6$ is listed in Table 7-2.

Atomic coordinates and isotropic displacement parameters for $La_2Zn_3Ge_6$, $Ce_2Zn_3Ge_6$, and $Pr_2Zn_3Ge_6$ and $Nd_2Zn_3Ge_6$ can be found in Table 7-3 and 7-4 respectively. The anisotropic displacement parameters for $La_2Zn_3Ge_6$, $Ce_2Zn_3Ge_6$, and $Pr_2Zn_3Ge_6$, $Nd_2Zn_3Ge_6$ are given in Tables 7-5 and 7-6 respectively. All compounds solved with atomic positions fully occupied, and without the introduction of disorder.

Phase identity and purity was confirmed by powder x-ray diffraction carried out on an INEL diffractometer with Cu $K\alpha$ radiation. The experimental powder patterns

were compared to the calculated powder patterns generated from the single crystal structural refinements. Powder patterns were calculated using the CERius² software package.²¹

Elemental Analysis:

Semi-quantitative microprobe elemental analysis was performed on several single crystals of each of the analogs including the crystals used for single crystal x-ray diffraction experiments. Spectra were collected on a JEOL JSM 35C scanning electron microscope equipped with a Tracor Noran energy dispersive spectrometer (EDS) with the NorvarTM window. Spectra were collected with an accelerating voltage of 20 kV and 200 s acquisition times. Standardless quantitation of these compounds led to the following atomic ratios: 1: 1.25 : 2.75 for La, Zn and Ge respectively. These ratios are in reasonably good agreement with the stoichiometric ratios obtained from the crystallographic refinement. Similar stoichiometric ratios were determined for the other analogs as well.

Differential Thermal Analysis:

Differential thermal analysis (DTA) was carried out with a Shimadzu DTA 50. Samples were placed in a fused silica ampoule that was carbon coated in order to prevent glass attack upon melting of the product, and flame sealed under a reduced atmosphere.

An α - Al_2O_3 standard was used as a reference. Melting point determination was done by heating the sample at a rate of 10°C per minute up to 1000°C then cooling to 150°C at the same rate, then the cycle was repeated. To determine an appropriate reaction temperature for $\text{RE}_2\text{Zn}_3\text{Ge}_6$, 0.1 mmol scale reactions were carried out in the DTA instrument. Reactants were combined in their stoichiometric ratios and heated to 1000°C at 10°C per minute, then cooled to 150°C at the same rate in an attempt to determine, at what temperature the reaction was taking place.

Magnetic Measurements:

The magnetic measurements were carried out on a Quantum Design MPMS SQUID magnetometer. Measurements were performed on polycrystalline samples, which were placed in an envelope made of Kapton tape. Temperature dependant susceptibility data were collected in both field cooled and zero field cooled modes with an applied field of 500 Oe. Magnetization data were also collected at 2K with field sweeping from - 55 kOe to 55 kOe.

Diffuse Reflectance Infrared Spectroscopy:

Band gap energy measurements were carried out by diffuse reflectance infrared spectroscopy. The measurements were performed on a Nicolet Magna750 Fourier Transform infrared spectrometer.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	8												

Table 7-1. Crystal data and structure refinement for RE₂Zn₃Ge₆ (RE = La, Ce).

Formula	La ₂ Zn ₃ Ge ₆	Ce ₂ Zn ₃ Ge ₆
Formula weight	909.48	911.89
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal System	Orthorhombic	Orthorhombic
Space group	<i>Cmcm</i> (#63)	<i>Cmcm</i> (#63)
Unit cell dimensions	a = 5.9691(9) Å b = 24.987(4) Å c = 5.9575(9) Å	a = 5.9503(5) Å b = 24.761(2) Å c = 5.9477(5) Å
Volume	888.6(2) Å ³	876.31(13) Å ³
Z, Density(calculated)	4, 6.798 g/cm ³	4, 6.921 g/cm ³
Absorption coefficient	37.208 mm ⁻¹	38.370 mm ⁻¹
F(000)	1584	1592
Theta range for data collection	1.63 to 27.13°.	1.64 to 27.88°.
Index ranges	-7<= <i>h</i> <=7 -31<= <i>k</i> <=32 -7<= <i>l</i> <=7	-7<= <i>h</i> <=7 -32<= <i>k</i> <31 -7<= <i>l</i> <=7
Crystal Dimension (mm)	0.1 x 0.2 x 0.05	0.15x0.2 x 0. 01
Reflections collected / unique	4233 / 591	4141/612
R(int)	0.0601	0.0367
Completeness to $\theta_{\max}$	99.5 %	97.6
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	591 / 0 / 36	612 / 0 / 36
Goodness-of-fit on F ²	1.183	1.343
Final R indices [<i>I</i> >2σ(<i>I</i>)]	R1 = 0.0257, wR2 = 0.0741	R1 = 0.0254 wR2 = 0.0719
R indices (all data)	R1 = 0.0270, wR2 = 0.0748	R1 = 0.0261 wR2 = 0.0723
Extinction coefficient	0.00122(11)	0.0043(2)
Largest diff. peak and hole	1.704 / -1.800 e/Å ³	1.748 / -1.240 e/Å ³

$$R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \text{ and } wR2 = [\sum (|F_o^2 - F_c^2|)^2 / \sum (w F_o^2)^2]^{1/2}$$

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Table 7-2. Crystal data and structure refinement for RE₂Zn₃Ge₆ (RE = Pr, Nd).

Formula	Pr ₂ Zn ₃ Ge ₆	Nd ₂ Zn ₃ Ge ₆
Formula weight	913.47	920.36
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal System	Orthorhombic	Orthorhombic
Space group	<i>Cmcm</i> (#63)	<i>Cmcm</i> (#63)
Unit cell dimensions	a = 5.938(2) Å b = 24.708(8) Å c = 5.936(2) Å	a = 5.9094(7) Å b = 24.619(3) Å c = 5.9063(5) Å
Volume	870.9(5) Å ³	859.28(17) Å ³
Z, Density(calculated)	4, 6.966 g/cm ³	4, 7.113 g/cm ³
Absorption coefficient	39.341 mm ⁻¹	40.620 mm ⁻¹
F(000)	1600	1608
Theta range for data collection	1.65 to 27.89°.	1.65 to 27.86°.
Index ranges	-7<= <i>h</i> <=7 -31<= <i>k</i> <=32 -7<= <i>l</i> <=7	-7<= <i>h</i> <=7 -31<= <i>k</i> <31 -7<= <i>l</i> <=7
Crystal dimensions (mm)	0.1 x 0.15 x 0.05	0.07x0.05x0.02
Reflections collected / unique	4187 / 614	3786 / 605
R(int)	0.0379	0.0753
Completeness to $\theta_{\max}$	98.4 %	97.9%
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	614 / 0 / 36	605 / 0 / 36
Goodness-of-fit on F ²	1.307	1.171
Final R indices [<i>I</i> >2σ(<i>I</i>)]	R1 = 0.0266, wR2 = 0.0697	R1 = 0.0481 wR2 = 0.1277
R indices (all data)	R1 = 0.0281, wR2 = 0.0703	R1 = 0.0492 wR2 = 0.1287
Extinction coefficient	0.00289(11)	0.0017(2)
Largest diff. peak and hole	1.794 / -2.669 e/Å ³	2.229/ -3.288 e/Å ³

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ and } wR2 = \frac{[\sum (|F_o^2 - F_c^2|)^2 / \sum (w F_o^2)^2]^{1/2}}$$

Table 7-3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = La, Ce).

Atom	Wyckoff Position	x	y	z	U(eq)*
La(1)	4c	5000	1062(1)	2500	7(1)
La(2)	4c	0	1063(1)	7500	7(1)
Ge(1)	16h	2146(1)	2021(1)	356(1)	12(1)
Ge(2)	4c	0	664(1)	2500	9(1)
Ge(3)	4c	5000	595(1)	7500	8(1)
Zn(1)	4c	5000	1616(1)	7500	12(1)
Zn(2)	8e	2407(2)	0	0	9(1)
Ce(1)	4c	5000	1065(1)	2500	6(1)
Ce(2)	4c	0	1067(1)	7500	6(1)
Ge(1)	16h	2139(1)	2016(1)	360(1)	9(1)
Ge(2)	4c	0	683(1)	2500	8(1)
Ge(3)	4c	5000	590(1)	7500	7(1)
Zn(1)	4c	5000	1612(1)	7500	11(1)
Zn(2)	8e	2381(2)	0	0	10(1)

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

Table 7-4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = Pr, Nd).

Atom	Wyckoff Position	x	y	z	U(eq)*
Pr(1)	4c	5000	3935(1)	2500	6(1)
Pr(2)	4c	0	3933(1)	7500	6(1)
Ge(1)	16h	2142(1)	2986(1)	357(1)	9(1)
Ge(2)	4c	0	4307(1)	2500	8(1)
Ge(3)	4c	5000	4410(1)	7500	7(1)
Zn(1)	4c	5000	3394(1)	7500	10(1)
Zn(2)	8e	7629(2)	5000	0	10(1)
Nd(1)	4c	0	1066(1)	2500	6(1)
Nd(2)	4c	-5000	1068(1)	7500	6(1)
Ge(1)	16h	2852(2)	2013(1)	351(2)	9(1)
Ge(2)	4c	-5000	699(1)	2500	7(1)
Ge(3)	4c	0	593(1)	7500	7(1)
Zn(1)	4c	0	1604(1)	7500	10(1)
Zn(2)	8e	-2629(2)	0	0	9(1)

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

Table 7-5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = La, Ce).

	U11	U22	U33	U23	U13	U12
La(1)	10(1)	5(1)	6(1)	0	0	0
La(2)	10(1)	5(1)	7(1)	0	0	0
Ge(1)	16(1)	6(1)	13(1)	-1(1)	-2(1)	-1(1)
Ge(2)	10(1)	10(1)	6(1)	0	0	0
Ge(3)	11(1)	6(1)	8(1)	0	0	0
Zn(1)	14(1)	10(1)	11(1)	0	0	0
Zn(2)	14(1)	7(1)	10(1)	0(1)	0	0
Ce(1)	9(1)	5(1)	5(1)	0	0	0
Ce(2)	9(1)	5(1)	6(1)	0	0	0
Ge(1)	12(1)	6(1)	9(1)	0(1)	0(1)	0(1)
Ge(2)	9(1)	10(1)	6(1)	0	0	0
Ge(3)	9(1)	6(1)	6(1)	0	0	0
Zn(1)	14(1)	9(1)	10(1)	0	0	0
Zn(2)	13(1)	8(1)	10(1)	1(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 7-6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = Pr, Nd).

	U11	U22	U33	U23	U13	U12
Pr(1)	7(1)	6(1)	6(1)	0	0	0
Pr(2)	7(1)	6(1)	6(1)	0	0	0
Ge(1)	10(1)	7(1)	9(1)	0(1)	0(1)	-1(1)
Ge(2)	8(1)	10(1)	6(1)	0	0	0
Ge(3)	8(1)	7(1)	7(1)	0	0	0
Zn(1)	11(1)	10(1)	10(1)	0	0	0
Zn(2)	11(1)	9(1)	10(1)	-1(1)	0	0
Nd(1)	7(1)	0(1)	9(1)	0	0	0
Nd(2)	8(1)	1(1)	9(1)	0	0	0
Ge(1)	11(1)	2(1)	13(1)	0(1)	0(1)	-1(1)
Ge(2)	8(1)	5(1)	9(1)	0	0	0
Ge(3)	8(1)	2(1)	9(1)	0	0	0
Zn(1)	12(1)	5(1)	14(1)	0	0	0
Zn(2)	11(1)	3(1)	13(1)	1(1)	0	0

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

Band Structure calculations:

Band structure calculations were performed on $\text{La}_2\text{Zn}_3\text{Ge}_6$ using the self-consistent full-potential linearized augmented plane wave method (LAPW)²² within density functional theory (DFT), with a generalized gradient approximation (GGA) for the exchange and correlation potential within the Perdew-Burke-Ernzerhof model.²³ Scalar relativistic corrections were added and spin-orbit interactions (SOI) were incorporated using a second variational procedure.²⁴ Calculations were carried out on the La system due to the inability of DFT to accurately model the highly correlated electrons found in partially filled *f* levels. The calculations were performed with the WIEN97 program.²⁵ The atomic radii values (in atomic units 1a.u. = 0.529 Å) used in the calculation are as follows 2.4 for La, 2.15 for Zn and 2.25 for Ge. Self-consistent iterations were performed with 27 k points in the reduced Brillouin zone with a cutoff between valence and core states of -6.0 Ry; convergence was assumed when the energy difference between cycles was less than 0.0001 Ry.

7-3 Results and Discussion:

Structure:

$\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE=La, Ce, Pr, and Nd) crystallizes in the orthorhombic *Cmcm* space group composed of known building blocks, but the connectivity of the units is unique making the title compounds new structure type members. The first is a ZnGe_4 layer

Figure 7-1 (A). If Zn is removed the remaining Ge fragment is composed of 2 layers of staggered nearly square nets which are interconnected. This is an unusual arrangement of Ge atoms with only one previous report of its occurrence in the tetragonal structure $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Ge}_{1-x})\text{Al}_4\text{Ge}_6$.²⁶ Which is the Ge analog of the previously reported Si containing compound.²⁷ Using the Zintl concept this fragment can be thought of as being composed of Ge^{1-} atoms, as each Ge is bound to three other Ge atoms and requires 1 extra electron to fill its octet (i.e. isoelectronic to phosphorous), Figure 7-1(B).

In the ZnGe_4 layer Ge (1) is tetrahedrally coordinated by 3 of its symmetry generated equivalents, Figure 7-1(C), and to 1 Zn(1). The result is a layer of intersecting pentagonal channels which run along the *a* and *c*-axis. The Zn(1) atom forms the bridging units which join the distorted square nets Figure 7-1(A). The other building unit is a PbO like layer composed of ZnGe with Zn occupying the O sites and Ge the Pb sites, Figure 7-1(C). These layers extend in the *ac* plane, and are interconnected along the *b*-axis through a Ge(3)-Zn(1) bond as shown in Figure 7-2. The ZnGe layer is composed of 2 crystallographically distinct Ge atoms and a Zn atom. The Zn atoms are tetrahedrally coordinated by 2 Ge(2) atoms and 2 Ge(3) atoms. A full list of bond distances for $\text{RE}_2\text{Zn}_3\text{Ge}_6$ (RE = La, Ce, Pr, and Nd) are listed in Table 7-7.

The resulting structure can be charge balanced as follows: $(\text{La}^{3+})_2(\text{Zn}^{2+})_3(\text{Ge}^{1-})_4(\text{Ge}^4)_2$. Care was taken in the assignment of the Zn and Ge atoms in the crystal structure as their scattering factors differ by only 10%.¹⁸ The structure we propose here

minimizes R1, wR2 and the residual electron density. It also gives the most reasonable bond lengths, and agrees quite well with elemental analysis.

Synthesis and Stability:

The title compounds were originally found in an indium flux reaction of the elements with the stoichiometric ratios 1:1:3 for La: Zn : Ge respectively, which was heated at 850 °C. Indium was present in a 20-fold excess relative to La. The crystals of $\text{La}_2\text{Zn}_3\text{Ge}_6$ were stable in glacial acetic, water and acetone. The crystals were of very poor quality and even when reactants were combined in their stoichiometric ratios for the In flux reactions, yields were generally poor. The crystals grew as stacks of very thin plates that could not be mechanically separated. A crystal from this method was used for single crystal x-ray diffraction but the quality of data was poor, with very large standard deviations in the lattice parameters, and large residual electron densities. The refinement was not improved by the application of several different twin laws. The best crystals for x-ray diffraction came from direct combination reactions.

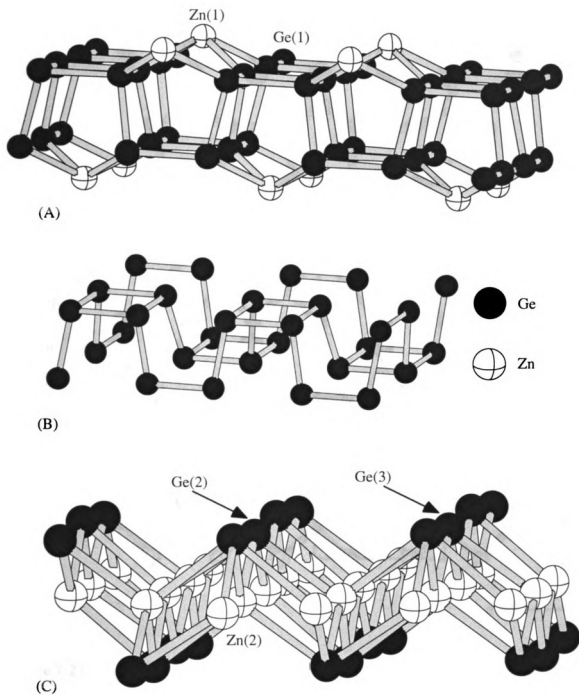


Figure 7-1 (A) View of the pentagonal ZnGe_4 cages structure which extends in the ac plane and are similar to $\text{Sm}_2\text{Ni}(\text{Ni}_x\text{Si}_{1-x})\text{Al}_4\text{Si}_{6-y}$. (B) Perspective view of the Ge^{I} fragment. (C) View of the ZnGe layer showing the PbO structure, which extend in the ac plane. The layer is similar to those in the ThCrSi_2 structure type.

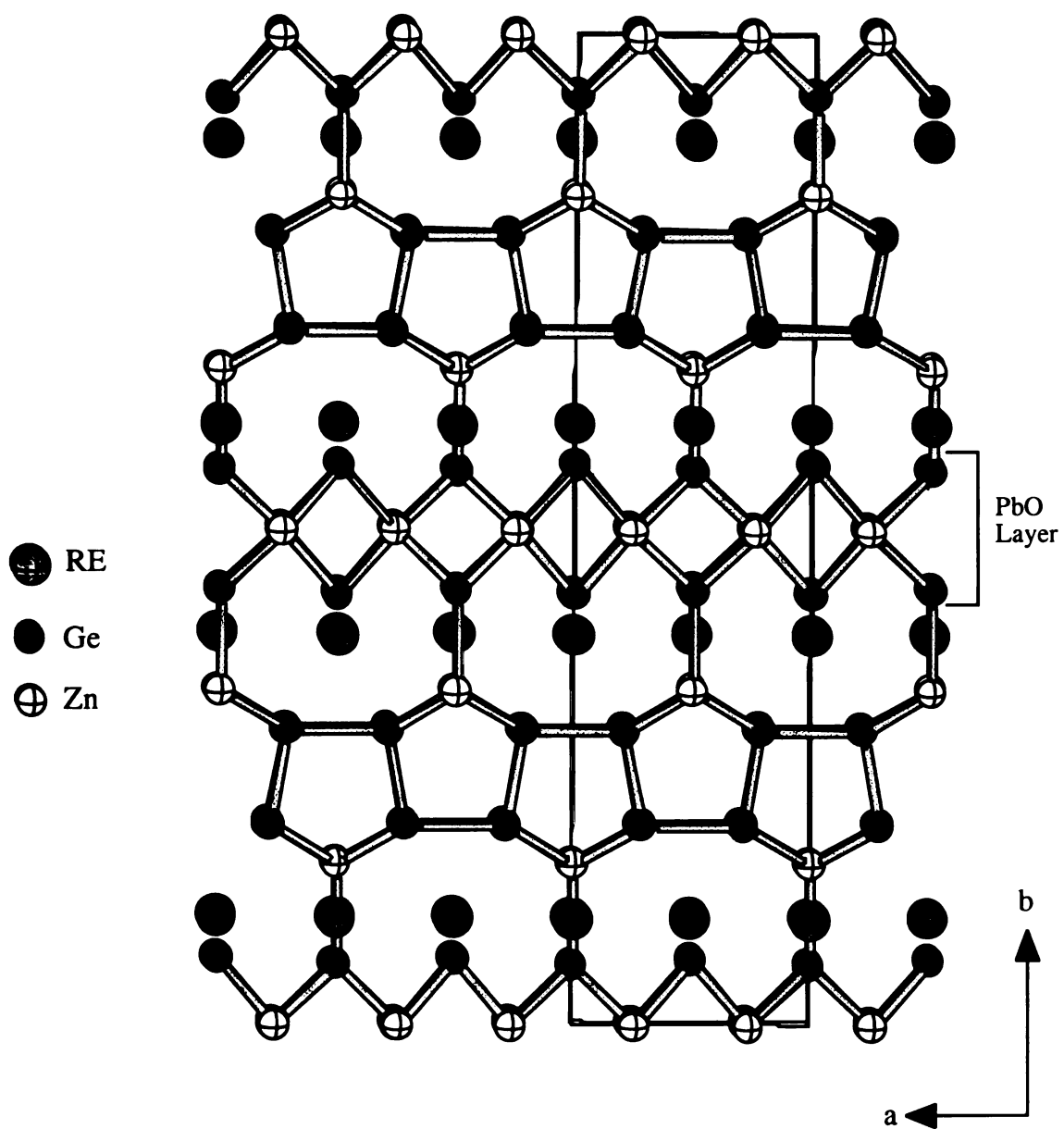


Figure 7-2 Overall structure of $\text{RE}_2\text{Zn}_3\text{Ge}_6$ as viewed down the c -axis showing the interconnections between the two Zn/Ge layers along the b -axis.

Table 7-7 Bond distances (Å) for RE₂Zn₃Ge₆ (RE = La, Ce, Pr, Nd).

	RE = La	RE = Ce	RE=Pr	RE=Nd
RE(1)-Ge(2)	3.1461(6)	3.1216(5)	3.108(1)	3.0900(7)
RE(1)-Ge(3)	3.1995(6)	3.1975(6)	3.1920(11)	3.1745(8)
RE(1)-Ge(1)	3.2047(8)	3.1727(8)	3.162(1)	3.1441(12)
RE(1)-Zn(1)	3.2842(7)	3.2673(7)	3.2555(11)	3.237(1)
RE(1)-Zn(2)	3.4147(7)	3.4050(7)	3.401(1)	3.389(1)
RE(2)-Ge(2)	3.1412(6)	3.1220(5)	3.109(1)	3.0902(7)
RE(2)-Ge(1)	3.2036(8)	3.1678(8)	3.158(1)	3.1393(12)
RE(2)-Ge(3)	3.2052(6)	3.2007(6)	3.1944(11)	3.1781(8)
RE(2)-Zn(1)	3..2888(7)	3.2662(7)	3.2542(11)	3.236(1)
RE(2)-Zn(2)	3..3671(7)	3.3468(7)	3.337(1)	3.326(11)
Ge(1)-Ge(1)	2.4691(19)	2.4689(13)	2.4713(12)	2.4733(14)
Ge(1)-Ge(1)	2.5551(14)	2.5456(15)	2.5440(16)	2.538(2)
Ge(1)-Ge(1)	2.5613(13)	2.5458(14)	2.35442(17)	2.539(2)
Ge(1)-Zn(1)	2.6119(9)	26068(9)	2.603(1)	2.5863(14)
Ge(2)-Zn(2)	2.6528(9)	2.661 (1)	2.6668(11)	2.6650(15)
Ge(3)-Zn(1)	2.5502(18)	2.5281(19)	2.511(2)	2.490(3)
Ge(3)-Zn(2)	2.6124(9)	2.6034(9)	2.601(1)	2.5933(14)

Several attempts to make this compound by direct combination of the elements with arc melting and radio frequency induction furnace heating techniques did not work due to the large vapor pressure of molten Zn. Reactions were also carried out in conventional furnaces by heating the reactants to 1000 °C and holding for 72 h, before quenching the reactions to room temperature. These reactions were successful in producing the target phase, but the product was multi-phasic. Shorter heating times of 24 to 48 h tended to improve phase purity. Lower reaction temperatures of 850 °C and 750 °C with reaction times of 72 h, produced a multi-phasic sample, and for reactions run at 850 °C the target phase dominates the mixture. The reactions carried out at 750 °C yielded a RE/Ge binary and interestingly enough recrystallized Zn.

To find a temperature that was appropriate for running these reactions, the elements were combined in their stoichiometric ratio, on the 0.1mmol scale, and flame-sealed under a reduced atmosphere of 10^{-4} mbar in a carbon coated differential thermal analysis tube. The reactants were then heated to 1000 °C at a rate of 10 °C / min. The reaction DTA for La/Zn/Ge can be seen in Figure 7-3 (A). There were 3 exothermic events in the first heating cycle at 360 °C, 530 °C and 775 °C followed by 2 endothermic event at 790 °C and 820 °C. When the sample was heated again from room temperature to 1000 °C, two melting peaks were found at 775 and 820 °C, and two re-crystallization peaks at 790°C and 760 °C were also found, Figure 7-3 (B). Powder patterns taken after

the initial heating and after the second heating cycle were both multi-phasic with $\text{La}_2\text{Zn}_3\text{Ge}_6$ being the dominant phase. Similar results were obtained for other rare earth metals. The endothermic peak at 790 °C does not reappear in the second cycle of heating neither do any of the exothermic peaks which were found upon heating. We therefore assumed that the reaction was taking place at 790 °C since the reaction did not yield the target when heated at 750 °C. As a result all $\text{RE}_2\text{Zn}_3\text{Ge}_6$ can be made as pure phases in quantitative yield by pressing a pellet of the reactants in their stoichiometric ratios and heating them at 790 °C for La, 780 °C for Ce, and 770 °C for Nd and Pr for 72 h. The DTA experiments provided insight as to why the other reaction conditions could not yield a pure phase. The reaction was being carried out above the melting point of the product, and because it melts incongruently, impurity phases formed.

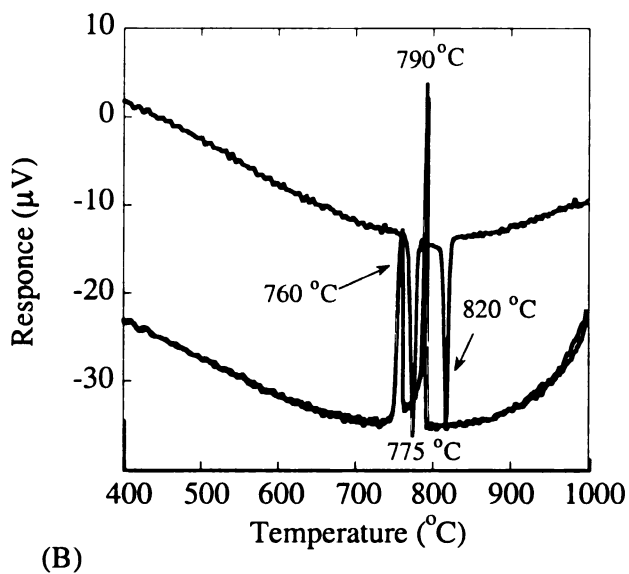
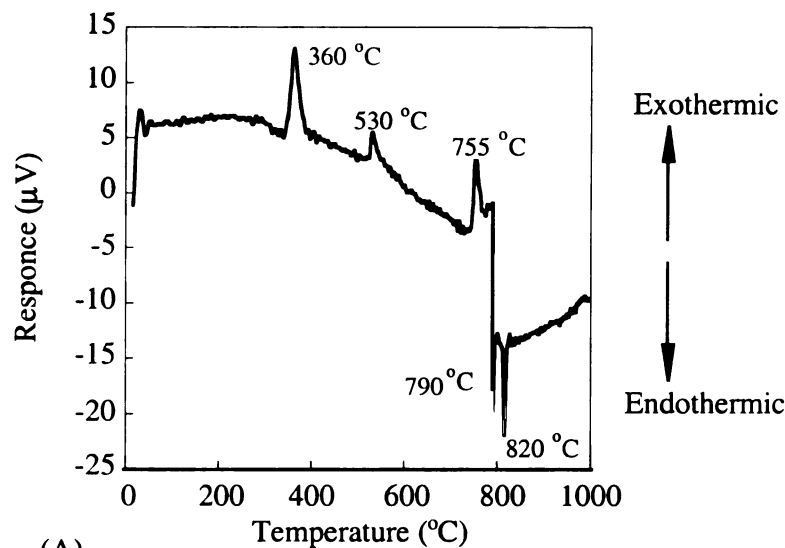


Figure 7-3 (A) Initial heating for a mixture of La/Zn/Ge in the differential thermal analysis. There are 3 exothermic peaks in the first heating cycle at 360 °C, 530 °C, and 755 °C. The endotherm at 790 °C is thought to correspond to the reaction to form $\text{La}_2\text{Zn}_3\text{Ge}_6$, and the endothermic peak at 820 °C is its melting point. (B) The second heating cycle of the now reacted elements. The endotherm at 775 °C is the melting point of an impurity due to the incongruent melting of $\text{La}_2\text{Zn}_3\text{Ge}_6$ in the first heating cycle.

Band Structure calculations:

The bonding of this compound can be rationalized by using the Zintl concept in the following manner. The rare earth ions are assumed to be in the 3+ oxidation state while the Zn ions have a filled *d* shell and the 3*s* orbitals are vacant resulting in 2+ cations. The Ge atoms thus fulfil their octet requirements by forming bonds and by formal reduction. Ge(1) which is tetrahedrally coordinated by 3 Ge atoms and 1 Zn would have a formal charge of –1 while the remaining Ge atoms are isolated from other Ge atoms requiring them to adopt a –4 charge. The overall structure is then charge balanced as $(\text{RE}^{3+})_2(\text{Zn}^{2+})_3(\text{Ge}^{-1})_4(\text{Ge}^{-4})_2$. This would lead us to anticipate semiconducting behavior from this compound.

To better understand the nature of the bonding in these compounds, and to see if the predicted band gap could be computed, band structure calculations were carried out. The total density of states (DOS) as computed for $\text{La}_2\text{Zn}_3\text{Ge}_6$ can be seen in Figure 7-4 (A). There are three main features in this figure. The first is the large narrow band located between –8 and –7 eV, corresponding to the *d* levels of Zn. The second large band, between 1 and 3 eV are due to the 5*d* electrons of La. Finally the DOS at the Fermi level is very small at less than 5 states/eV indicating semimetallic behavior. We expect a semiconductor based on the charge-balancing scheme put forth, but likely due to incomplete electron transfer from the Zn to the Ge sub-lattice there is enhanced covalent

character to the bonding in the Zn_2Ge_2 layer. The covalent bonding will likely lower the energy of the p bands of Ge and the s and p band of Zn, result in the creation of a negative gap. Figure 7-4 (B) shows Zn(1) and Zn(2) d orbital DOS. As was mentioned above they are centered at -7.5 eV indicating a d^{10} configuration for both atoms. Figure 7-4(C) shows the s contribution of Zn(1) and Zn(2). For a Zn atom in the formally 2+ oxidation state we would expect these orbitals to be above the fermi level as they should be empty, though they are not. This may be caused by the incomplete electron transfer mentioned above. Figure 7-4 (D) shows the La(1) and La(2) d band contribution to the DOS. The majority of the states lie above the fermi level indicating that they are vacant, though there is a small DOS (0.2 states/eV) at the fermi level which may suggest incomplete electron transfer from the rare earth ion to the Zn_3Ge_6 sub-lattice.

Mentioned previously was the possible existence of a negative band gap due to the hybridization of the Zn and Ge bands in the PbO layer. This is a consequence of the incomplete electron transfer, and would result in the lowering of the empty s,p orbitals of Zn,. The negative gap can be seen explicitly in the band structure plot in Figure 7-5 (A). Figure 7-5 (B) shows the first Brillouin zone for a C centered unit cell. The bands, which otherwise might have been empty conduction bands, drop below and cross the fermi level around the Λ , Σ and Γ points in the Brillouin zone thus becoming partially filled, giving semimetallic character.

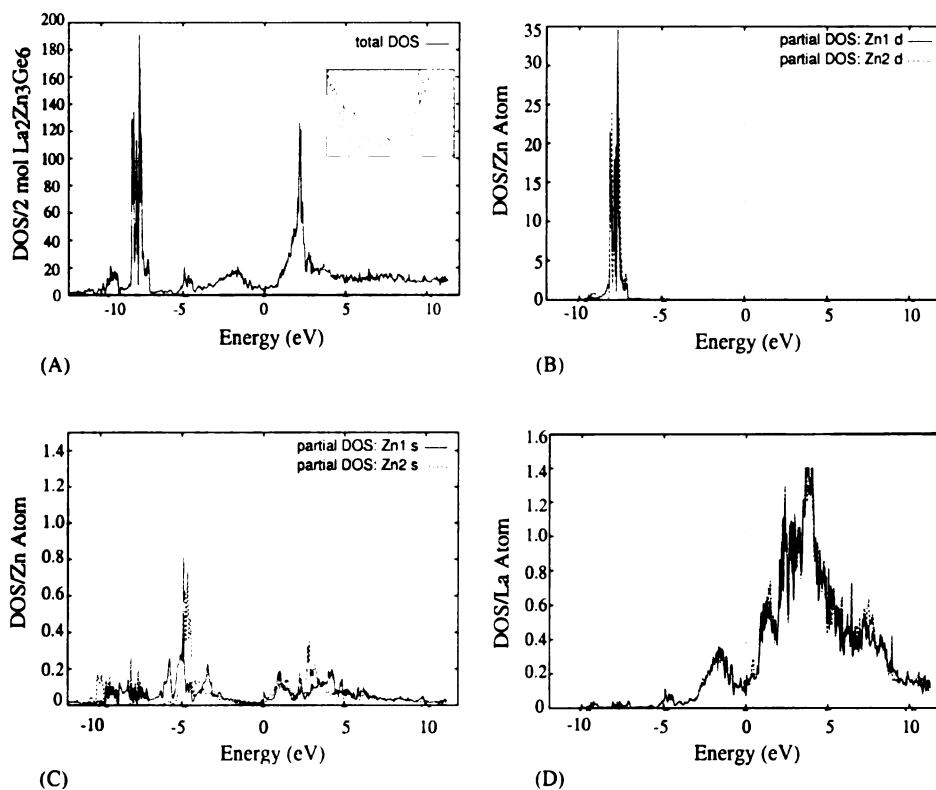


Figure 7-4 (A) The total Density of States (DOS) for $\text{La}_2\text{Zn}_3\text{Ge}_6$. The inset shows a close up view illustrating the low DOS at the Fermi level characteristic of a semi-metal. (B) The DOS for the Zn *d* electrons showing them well below the fermi level. (C) The DOS for the Zn *s* electrons distributed above and below the fermi level. (D) The DOS for the La *d* electrons showing them mainly above the fermi level.

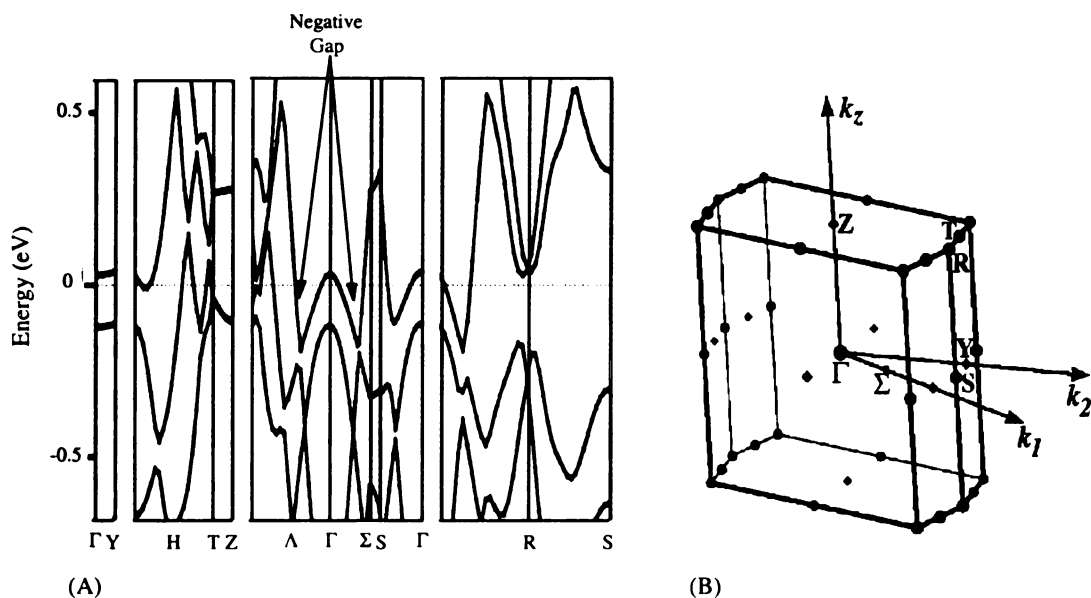


Figure 7-5 (A) Sections of the band structure of $\text{La}_2\text{Zn}_3\text{Ge}_6$. It shows the semimetallic nature of the compound i.e. the negative band gap near the Γ point and elsewhere in the Brillouin zone. (B) The Brillouin zone for a face centered orthorhombic unit cell.

Diffuse reflectance infrared spectra were collected in the range of 0.1 to 0.5 eV for each of the analogs, and in each case no bang gap was detected. If there is a gap it is likely to be <0.1 eV which is beyond the capability of our instrument.

Magnetic Measurements:

As there are two crystallographically distinct rare earth ions per formula unit, $\text{RE}_2\text{Zn}_3\text{Ge}_6$ will have an effective magnetic moment that is calculated by (1), where μ_{total} is the effective magnetic moment per formula unit and $\mu_{\text{eff}}(\text{a})$ or $\mu_{\text{eff}}(\text{b})$ are the calculated

effective magnetic moments of the rare earth (3+) ion per formula unit.

$$(1) \quad \mu_{total} = \sqrt{\mu_{eff}^2(a) + \mu_{eff}^2(b)}$$

La₂Zn₃Ge₆: The susceptibility for La₂Zn₃Ge₆ displays temperature independent diamagnetism. This is in agreement with what we expect as the *d* shell for Zn is filled, and so are the bands for Ge. So the only paramagnetic contribution would be expected to come from the rare earth ion, but as La is *f⁰* it has no magnetic moment either. The fact that the susceptibility is negative implies that the charge carrier concentration is small, as systems with large DOS at the fermi level display Pauli paramagnetism. The paramagnetism is due to the polarization of the conduction electrons of a metal by the applied field. If this effect is small, as in semimetals, then the core diamagnetism will dominate giving a negative susceptibility.

Ce₂Zn₃Ge₆: The susceptibility data for Ce₂Zn₃Ge₆ obey the Curie/ Weiss law over a rather small temperature range from 5 to 200 K. Above this temperature the susceptibility diverges. The region where Curie/ Weiss law is followed results in an effective magnetic moment of 3.71 μ_B which is in good agreement with the value calculated for 2 independent Ce³⁺ ions, which is 3.5 μ_B .²⁸ The Weiss constant is small with a value of -1.8 K. The negative sign indicates weak antiferromagnetic interactions this is consistent with the fact that Ce₂Zn₃Ge₆ orders antiferromagnetically at 3K. The

molar susceptibility and inverse susceptibility for $\text{Ce}_2\text{Zn}_3\text{Ge}_6$ can be seen in Figure 7-6(A). The divergence in the susceptibility above 200 K is likely due to the crystal field splitting of the Ce^{3+} 5/2 multiplet.²⁹

The magnetization curve for $\text{Ce}_2\text{Zn}_3\text{Ge}_6$ can be seen in Figure 7-6(B). As the field is increased there is a drastic increase in the moment. It is likely that the antiferromagnetic order is disrupted by the application of a very small field. The moment has a linear dependence on the field up to approximately 15 kOe. At which point it begins to saturate. Linear behavior returns above 20 kOe, but the slope is much shallower. This trend continues up to the maximum field without fully saturating. The resulting moment at the maximum field is $\sim 2.1 \mu_B$ which is about 60% of the value expected.²⁴ The trends described are also seen in the negative field sweeps, and there is very little hysteresis in the magnetization data.

$\text{Pr}_2\text{Zn}_3\text{Ge}_6$: The susceptibility data for $\text{Pr}_2\text{Zn}_3\text{Ge}_6$ are shown in Figure 7-7 (A). This compound orders antiferromagnetically with a Néel temperature of about 7K. Above this temperature the data obey a Curie/Weiss law with a measured effective magnetic moment of $4.8 \mu_B$, which is in reasonably good agreement with the value calculated for 2 Pr^{3+} , which is $5.0 \mu_B$.²⁴ The Pr^{3+} ion is, again, the only species that makes a paramagnetic contribution to the susceptibility, indicating that the rest of the species are closed shelled. The Weiss constant was determined to be 4.5 K indicating weak ferromagnetic

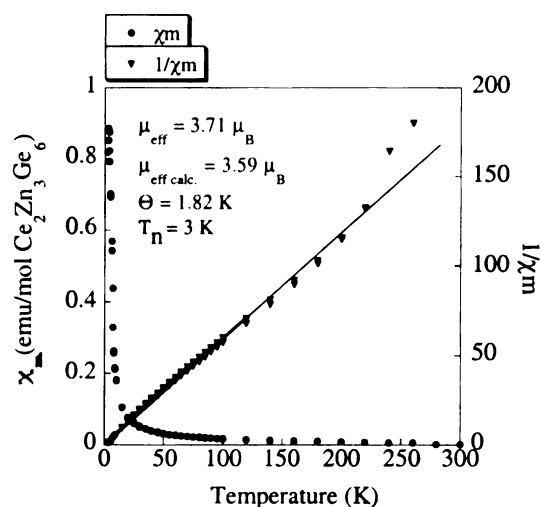
interactions between the rare-earth ions. This finding is at odds with the low temperature antiferromagnetic behavior of $\text{Pr}_2\text{Zn}_3\text{Ge}_6$.

The magnetization curve for $\text{Pr}_2\text{Zn}_3\text{Ge}_6$ is seen in Figure 7-7(B). In the low field region from 0 to 3.6 kOe the moment has very weak field dependence, however above this point it undergoes a transition, and there is a substantial increase in the moment over a narrow field range. Above 20 kOe the moments begin to saturate and the moment increases linearly with field with a shallow slope, reaching a value of $3.1 \mu_B$ at 55 kOe. This is about 65% of the value expected for μ_{sat} .

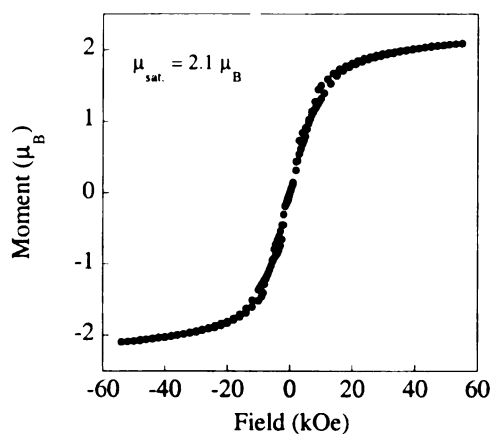
$\text{Nd}_2\text{Zn}_3\text{Ge}_6$: The magnetic susceptibility data for $\text{Nd}_2\text{Zn}_3\text{Ge}_6$ can be found in Figure 7-8 (A). This compound undergoes an antiferromagnetic transition at about 4 K. Above this temperature $\text{Nd}_2\text{Zn}_3\text{Ge}_6$ displays Curie/ Weiss behavior with a measured effective magnetic moment of $4.9 \mu_B$ which agrees well with the calculated value of $5.1 \mu_B$.²⁴ The Weiss constant is -2.0 K indicating weak antiferromagnetic coupling between the ions. As was the case with the other analogs the Nd ion is the only species that contributes to the paramagnetic susceptibility, therefore again the rest of the atoms in the compound are closed shell and diamagnetic.

Figure 7-8 (B) shows the magnetization data for $\text{Nd}_2\text{Zn}_3\text{Ge}_6$. This compound also undergoes a transition as evidenced by the abrupt slope change, though it is at a considerably higher field of about 8 kOe, as compared to the Ce and Pr analogs, which

have critical fields of 1 and 3.6 kOe respectively. Above 8 kOe the moment increases rapidly with field up to 12 kOe. At which point the slope decreases, and the moment slowly rises up to the highest field attainable increasing to a final value of $2.8 \mu_B$. This is again about only 60% of the value of the calculated saturation moment which is $4.6 \mu_B$.



(A)



(B)

Figure 7-6 (A) Magnetic susceptibility data for $\text{Ce}_2\text{Zn}_3\text{Ge}_6$ collected from 2 to 300K in both field cooled and zero field cooled modes. (B) Magnetization curve for $\text{Ce}_2\text{Zn}_3\text{Ge}_6$ collected at 2 K.

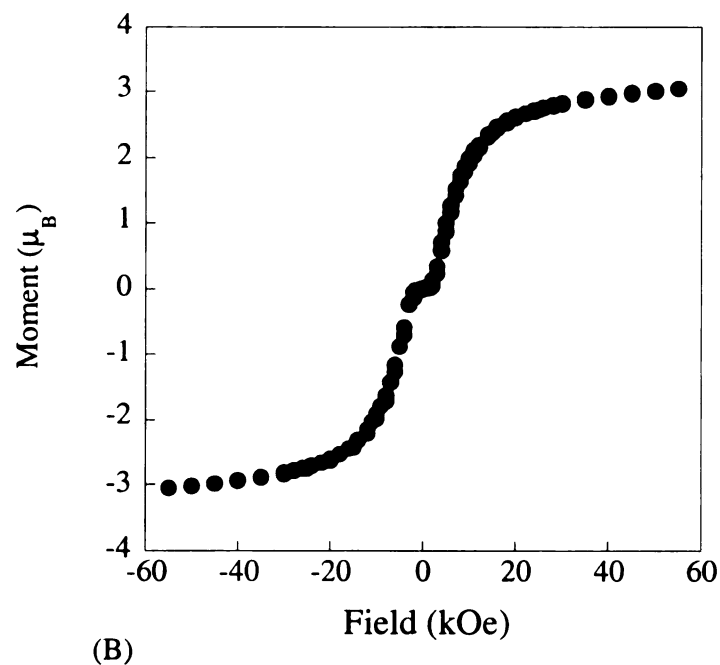
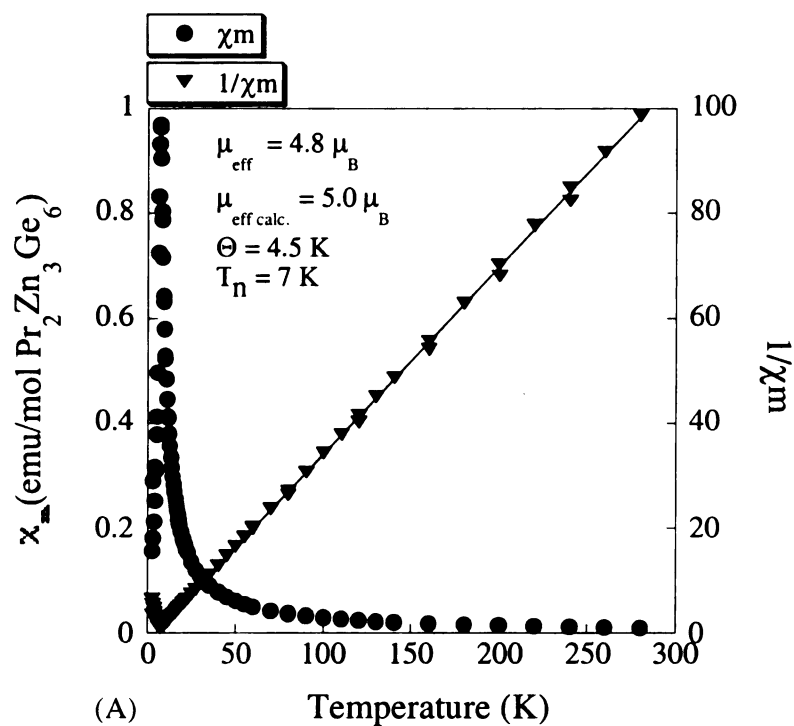
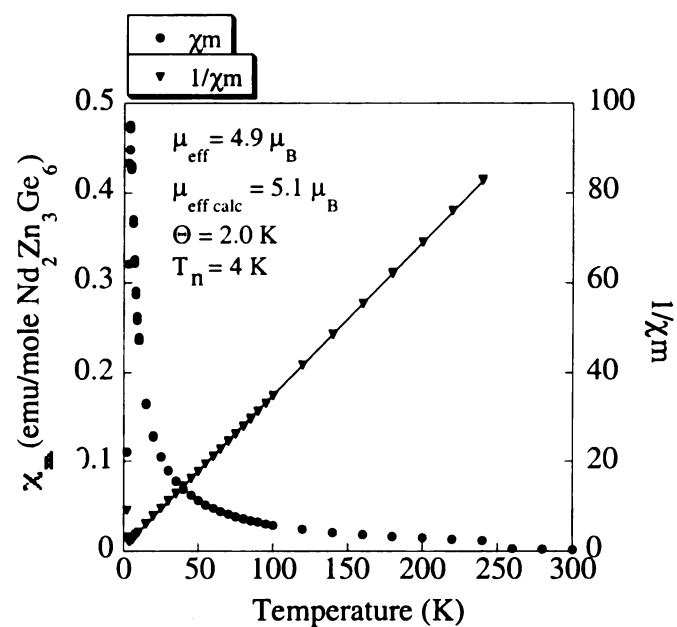
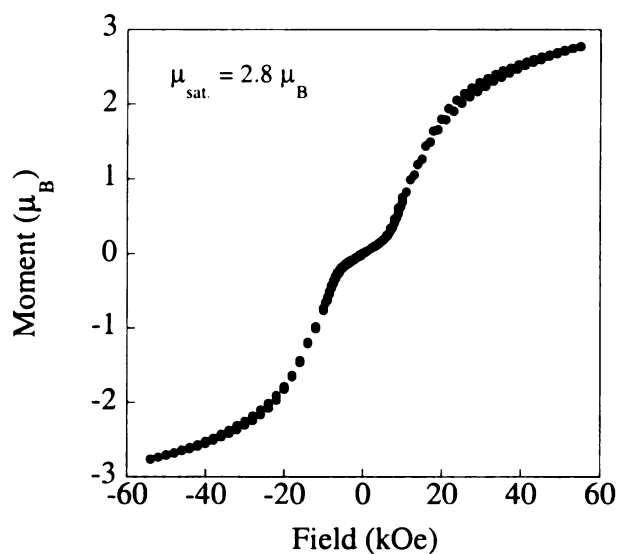


Figure 7-7 (A) Magnetic susceptibility data for $\text{Pr}_2\text{Zn}_3\text{Ge}_6$. The data show an antiferromagnetic transition at 7 K. (B) The magnetization curve for $\text{Pr}_2\text{Zn}_3\text{Ge}_6$. The data show a transition at 3.6 kOe, the μ_{sat} ($3.1\mu_B$) is approximately 65% of the calculated value of $4.8 \mu_B$.



(A)



(B)

Figure 7-8 (A) Magnetic susceptibility data for $\text{Nd}_2\text{Zn}_3\text{Ge}_6$ exhibiting antiferromagnetic ordering at 4 K and Curie/Weiss behavior above this temperature. (B) Magnetization curve for $\text{Nd}_2\text{Zn}_3\text{Ge}_6$ showing a transition at 8 kOe.

The magnetic behavior of this series of compounds, $\text{RE}_2\text{Zn}_3\text{Ge}_6$ ($\text{RE} = \text{La}, \text{Ce}, \text{Pr},$ and Nd), has several things in common. All of the compounds follow the Curie/Weiss law above their respective Néel temperatures with effective magnetic moments that are consistent with 3+ ions with the exception of $\text{La}_2\text{Zn}_3\text{Ge}_6$, which possesses temperature independent diamagnetic behavior. Also in all of these compounds the rare earth ions make the only contribution to the paramagnetic susceptibility.

The magnetization data for each of the $\text{Ce}_2\text{Zn}_3\text{Ge}_6$, $\text{Pr}_2\text{Zn}_3\text{Ge}_6$, and $\text{Nd}_2\text{Zn}_3\text{Ge}_6$ compounds show that they all undergo field induced transitions at increasingly higher fields. In each case the moment nearly saturates in the high field region but to only 65 % of the theoretical value. This is likely due to the fact that the samples are polycrystalline, and only a fraction of the sample is aligned appropriately with the magnetic field for saturation. The remainder makes a much smaller contribution to the induced moment as the spins are not aligned with the field. A similar result is often observed when making susceptibility measurements on polycrystalline samples that order antiferromagnetically. The extrapolated value for $\chi(0)$ (the susceptibility at 0 K) when the moments are aligned with the field is formally 0. Conversely if the field is applied perpendicular to the magnetic ordering χ remains constant below the Néel temperature. Polycrystalline samples have a $\chi(0)$ that extrapolates to 2/3 the value of $\chi(0)$ perpendicular.²⁸

7-4 Conclusions.

The family of intermetallic compounds, $\text{RE}_2\text{Zn}_3\text{Ge}_6$, has structure and bonding that can be rationalized with the Zintl concept. These compounds are important new members of a narrow class of compounds that lie near the border between classical Zintl phases and intermetallics. The compounds are semi-metallic, which can be rationalized by incomplete electron transfer in the Zn/Ge sub-lattice leading to small, but significant density of states at the fermi level. The calculated band structure in fact shows that there is a negative gap in these compounds brought about by the hybridization of the Zn and Ge orbitals. The rare earth ions are in a 3+ oxidation state, and make the only paramagnetic contribution to the susceptibility.

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Chapter 8

RE₄Ni₂InGe₄ A New Quaternary Intermetallic Grown from Molten

Indium: The First Bulk Representative of the Mg₅Si₆ Structure Type.

8-1 Introduction

The systematic study of intermetallics that form in molten metal fluxes has two important purposes. The first, and most significant from a chemical standpoint, is to learn new solid state chemistry, and expand the toolbox of synthetic methodologies available to the solid state inorganic chemist. Conditions used for these molten metal reactions allow the elements to react at much lower temperatures than typically used for the synthesis of intermetallic compounds, thereby potentially stabilizing phases that are kinetically stable, or only thermodynamically stable at lower temperatures. We have demonstrated previously that when reactions are carried out by using molten In the phase β -RENiGe₂ can be stabilized even though it was shown to be a kinetic phase.¹ The second purpose of this research is to obtain insight into intermetallic phases that form during the production of metal matrix composites as well as solder interfaces and other electronic junctions.² This information can be vital in the design of materials with

applications ranging from structural to electronic components.

The compound presented here $\text{RE}_4\text{Ni}_2\text{InGe}_4$ ($\text{RE} = \text{Dy}, \text{Ho}, \text{Er}, \text{and Tm}$) is interesting from two different standpoints. First, it is the first system in which we have been able to incorporate In along with Ge into a compound to produce an ordered quaternary phase. Indeed $\text{RE}_4\text{Ni}_2\text{InGe}_4$ is the first reported quaternary intermetallic phase of the type RE/TM/In/Ge (where RE is a rare or alkaline earth metal and TM is a transition metal). Other metals used as fluxes for carry out reactions, most notably Al have been found to produce complex intermetallics of the type RE/TM/Al/Si or Ge. These systems form quaternary phases exclusively when this combination of reactants is used.³ Similarly quaternary phase form readily in systems such as RE/TM/Ga/Ge ⁴ though it is considerably more difficult to form correspond Si compounds when Ga is used as a flux.⁵ We have found it to be increasingly more difficult to form quaternary phase in the RE/TM/In/Ge as compared to the corresponding Ga/Si systems. In fact other groups working with these particular combination of elements do so using In to re-crystallize known thermodynamic ternary phases of the type RE/TM/Ge .⁶

Secondly, $\text{RE}_4\text{Ni}_2\text{InGe}_4$ is the first example of the production of a compound with the Mg_5Si_6 structure type in bulk crystal form. The previous report of this structure was as an intermetallic that formed in an Al matrix as a result of aging an Al ingot with the addition of a few atomic percent of Mg and Si to enhance tensile strength.⁷ The structure of Mg_5Si_6 was elucidated by area selected electron diffraction of isolated islands of the

compound embedded in the Al metal matrix.⁷ Here we show a way to produce a compound that is an ordered isostructural quaternary variant of the Mg_5Si_6 structure type is bulk from molten In reactions.

8-2. Experimental Section:

Reagents:

The following reagents were used as received without further purification: Er metal(powder ground from chunk, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), Dy metal(powder ground from chunk, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), Ho metal(250 mesh powder 99.9 % Cerac Milwaukee, WI), Tm metal(ground chunk, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), Ni metal(-325 mesh, 99.9%, Cerac, Milwaukee, WI), Ge (ground from 2-5 mm pieces, 99.99%, Plasma Materials, Livermore, CA), and In (tear drops, 99.99%, Cerac, Milwaukee, WI).

Synthesis:

An amount of 3 mmol of the corresponding rare earth metal, 1.0 mmol Ni, 2 mmol, Ge and 10 mmol In were combined in an alumina tube under an inert N_2 atmosphere in a dry box. The reaction vessel and reactants were then flame-sealed in a fused silica tube under a reduced atmosphere to prevent oxidation during heating. The

samples were heated to 1000 °C over 10 h, and held at that temperature for an additional 4 h. The temperature was then ramped down to 850 °C, and held for 48 h, then subsequently cooled to room temperature over the course of another 48 h. Product isolation from the excess indium was accomplished by centrifugation, where a coarse frit was placed in the open end of the reaction vessel, which was then re-sealed under a reduced atmosphere in a Pyrex tube. The vessel and products were heated to 300 °C, and held there for 10 to 15 min to ensure the excess indium was molten, then the sample was centrifuged for 5 min. This process was repeated two more times. The centrifugation removed almost all excess indium though the flux did tend to wet the product. Further purification was carried out by a 72h submersion and sonication in glacial acetic acid. This proved to be an excellent method for removing In without etching or otherwise deteriorating the target phase. The product grows as large silver bars, which tend to aggregate along the long axis.

Several attempts to form this phase by direct combination of the elements were also made. One method used was induction heating the reactants in their stoichiometric ratios in a water cooled reaction chamber purged with Ar. The radio signal was generated by an Ameritherm radio frequency (rf) induction furnace, and reactions were carried out in graphite reaction crucibles with a spot welded molybdenum foil jacket which acted as a coupler. Reactions were run at the maximum power available of 1.8 kW for 2, 5, 15, min periods. The products formed as melted balls that did not wet the interior

of the crucible and were malleable on the exterior. X-ray powder diffraction revealed that the phase was a mixture of RENiGe and other unidentified phases.

Attempts were also made to form the title compound by arc melting the elements in their stoichiometric ratios. Powdered forms of the elements (with the exception of In) were cold pressed into pellets and placed in a vacuum chamber for reaction. The chamber was evacuated and back filled with Ar 3 times before the atmosphere was further purified from oxygen by gettering with a Zr pellet. Reactions were carried out on a water cooled copper plate, and were flipped several times and re-melted to ensure a homogenous distribution of the elements. The product distribution was quite similar to that received in the induction furnace reaction as determined by powder x-ray diffraction.

Elemental Analysis:

Semiquantitative microprobe elemental analysis was performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with the Noran energy dispersive spectrometer (EDS). Data were acquired using an accelerating voltage of 20 kV and 60 s acquisition times. A high magnification was used during data collection in order to minimize the possibility of surface contamination by In, which was not fully removed during the isolation process. Clean surfaces were selected for elemental analysis. Several crystals from the Dy reaction were analyzed, and they were found to be truly quaternary phases with the resulting composition of 40% Dy, 10% In, 35% Ge and 15% Ni. This is

in good agreement with the composition predicted by single crystal x-ray diffraction, which is 36% Dy, In 9% Ge 36 % and Ni 18 %. A possible reason for the small discrepancy in the Dy and Ni ratios may be due to the Ni $K\alpha$ line and the Dy L line overlapping significantly in the x-ray fluorescence spectrum.

X-ray Crystallography:

Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART CCD diffractometer with graphite monochromatized Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Unit cell refinement and data merging were done with the program SAINT, and an empirical absorption correction was applied using the program SADABS.⁸ A monoclinic C centered cell was found immediately from the data collected in the orientational matrix of the Ho analog, with lattice parameters that were quite similar to those of the orthorhombic I β -ErNiGe₂,¹ but with a non-orthogonal angle ($\beta=108^\circ$). As the lattice parameters seemed to be related to β -ErNiGe₂, but otherwise not reported for any known ternary compounds of RE Ni and Ge a full sphere of data was collected. Systematic absences inspections of the full data set confirmed the initial finding that the hkl , $h+k = 2n$ condition was present, and was the only unique condition. This lead to several possible space groups, which include C 2, Cm and $C 2/m$. The mean $|E^2-1|$ value of 0.819 is suggestive of a centrosymmetric space group, and as $C2/m$ was

the only centrosymmetric choice it was selected first. The structure of $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ was solved by direct methods using the program SHELXS, and the final structure refinement was performed with SHELXL. Subsequent solutions of other rare earth analogs were obtained by using the $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ positions as a starting point. The data collection and refinement details for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Dy and Ho) can be found in Table 8-1, and for RE = Er and Tm in Table 8-2. The atomic positions and isotropic displacement parameters for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Dy and Ho) are listed in Table 8-3, and for RE = Er and Tm in Table 8-4. The anisotropic temperature parameters for the Dy and Ho analogs can be found in Table 8-5, and the Er and Tm analogs in Table 8-6.

Phase identity and purity of polycrystalline samples was determined by powder X-ray diffraction; carried out with an Inel Cu anode diffractometer. Phase identity was assessed by comparing the experimental powder patterns to patterns calculated from the structural refinements. The calculated powder patterns were generated using the CERius² suite of programs.⁹

Magnetic Measurements:

Magnetic susceptibility measurements were made on hand selected crystals from samples that had been screened by powder x-ray diffraction. Measurements were performed with a Quantum Design, MPMS SQUID magnetometer in both field cooled and zero field cooled settings at temperatures between 2K and 300K with an applied field

of 2000 Oe for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$, 500 Oe for the Ho analog, and 1000 Oe for $\text{Er}_4\text{Ni}_2\text{InGe}_4$ and $\text{Tm}_4\text{Ni}_2\text{InGe}_4$. Additionally isothermal magnetization measurements were made at 2 K with fields sweeping from -55 kOe to 55 kOe at 2K for all analogs.

Differential Thermal Analysis:

Differential thermal analysis (DTA) was performed on 20 mg of hand selected single crystals of $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ using a Shimadzu DTA 50. The sample was flame sealed in a carbon coated fused silica ampoule under a reduced atmosphere of 10^{-4} mbar. A similar mass of $\alpha\text{-Al}_2\text{O}_3$, also flame sealed in a fused silica ampoule, was used as a reference as it is known to be stable over the temperature range of the experiment. The sample was heated to 1000°C from room temperature at a rate of $10^\circ\text{C}/\text{min}$. It was then cooled to 150°C at the same rate, and then reheated to 1000°C at $10^\circ\text{C}/\text{min}$. The sample was finally cooled to room temperature at the same rate. If the sample melted on the first heating cycle, the second heating cycle was required to determine if $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ melted congruently, or if it decomposed upon melting.

Table 8-1. Crystal data and structure refinement for RE₄Ni₂InGe₄ (RE=Dy, Ho).

Formula	Dy ₄ Ni ₂ InGe ₄	Ho ₄ Ni ₂ InGe ₄
Formula weight	1172.6	1182.32
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal System/Space group	Monoclinic C 2/m	Monoclinic C 2/m
Unit cell dimensions	a = 15.420(2) Å b = 4.2224(7) Å c = 7.0191(11) Å β = 108.589(2)°	a = 15.373(4) Å b = 4.2101(9) Å c = 6.9935(15) Å β = 108.600(3)°
Volume	433.18(12) Å ³	428.99(16) Å ³
Z, Density(calculated)	2, 8.990 g/cm ³	2, 9.153 g/cm ³
Absorption coefficient	54.430 mm ⁻¹	57.013 mm ⁻¹
F(000)	994	1002
Crystal size	0.02x0.02x0.1	0.01x0.015x0.08
Theta range for data collection	2.79 to 27.97°.	2.80 to 28.13°.
Index ranges	-19<=h<=20 -5<=k<=5 -9<=l<=8	-19<=h<=19 -5<=k<=5 -9<=l<=9
Reflections collected / unique	2310 / 551	1779 / 549
R(int)	0.0323	0.0256
Completeness to θ_{max}	92.6 %	91.6
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	551 / 0 / 36	549 / 0 / 36
Goodness-of-fit on F²	1.177	1.230
Final R indices [I>2σ(I)]	R1 = 0.0222, wR2 = 0.0540	R1 = 0.0281 wR2 = 0.0685
R indices (all data)	R1 = 0.0233, wR2 = 0.0544	R1 = 0.0302 wR2 = 0.0694
Extinction coefficient	0.00201(14)	0.00126(15)
Largest diff. peak and hole	2.095 / -1.600 e/Å ³	2.809 / 2.497 e/Å ³

$$R1 = \Sigma \|F_o\| - |F_c\| / \Sigma |F_o| \text{ and } wR2 = [\Sigma (|F_o^2 - F_c^2|)^2 / \Sigma (w F_o^2)^2]^{1/2}$$

Table 8-2. Crystal data and structure refinement for RE₄Ni₂InGe₄ (RE=Tm, Er).

Formula	Tm ₄ Ni ₂ InGe ₄	Er ₄ Ni ₂ InGe ₄
Formula weight	1198.32	1191.64
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal System /Space group	Monoclinic C 2/m	Monoclinic C 2/m
Unit cell dimensions	a = 15.253(2) Å b = 4.1747(6) Å c = 6.9460(9) Å β = 108.535(2)°	a = 15.334(7) Å b = 4.1937(19) Å c = 6.975(3) Å β = 108.472(7)°
Volume	419.35(10) Å ³	425.4(3) Å ³
Z, Density(calculated)	2, 9.490 g/cm ³	2, 9.303 g/cm ³
Absorption coefficient	62.902 mm ⁻¹	59.749 mm ⁻¹
F(000)	1018	1010
Crystal size	0.02x0.02x0.06	0.01x0.01x0.05
Theta range for data collection	2.82 to 27.69°.	2.80 to 27.95°.
Index ranges	-19<=h<=19 -5<=k<=5 -8<=l<=8	-19<=h<=19 -5<=k<=5 -9<=l<=9
Reflections collected / unique	2212 / 536	2379 / 555
R(int)	0.0285	0.0287
Completeness to θ _{max}	95.4%	95.8
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	536 / 0 / 36	555 / 0 / 36
Goodness-of-fit on F ²	1.214	1.228
Final R indices [I>2σ(I)]	R1 = 0.0237, wR2 = 0.0582	R1 = 0.0218 wR2 = 0.0508
R indices (all data)	R1 = 0.0249, wR2 = 0.0587	R1 = 0.0237 wR2 = 0.0512
Extinction coefficient	0.0058(3)	0.0071 (2)
Largest diff. peak and hole	2.002 / -1.816 e/Å ³	1.754 / -1.983 e/Å ³

$$R1 = \frac{\sum \|F_o\| - \|F_c\|}{\sum \|F_o\|} \text{ and } wR2 = [\sum (F_o^2 - F_c^2)^2 / \sum (w F_o^2)^2]^{1/2}$$

Table 8-3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Dy, Ho).

Atom	Wyckoff Position	x	y	z	U(eq)*
Dy(1)	4i	4088(1)	0	6107(1)	4(1)
Dy(2)	4i	3448(1)	0	10624(1)	4(1)
In	2d	5000	5000	0	8(1)
Ge(1)	4i	2033(1)	0	2701(2)	5(1)
Ge(2)	4i	5644(1)	5000	6617(2)	4(1)
Ni	4i	2168(1)	0	6432(2)	7(1)
Ho(1)	4i	4086(1)	0	6100(1)	6(1)
Ho(2)	4i	3446(1)	0	10629(1)	7(1)
In	2d	5000	-5000	10000	10(1)
Ge(1)	4i	2026(1)	0	2683(2)	7(1)
Ge(2)	4i	5645(1)	-5000	6620(2)	7(1)
Ni	4i	2170(1)	0	6427(3)	10(1)

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

Table 8-4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Er, Tm).

Atom	Wyckoff Position	x	y	z	U(eq)*
Er(1)	4i	4091(1)	0	6107(1)	5(1)
Er(2)	4i	3447(1)	0	10633(1)	5(1)
In	2d	5000	5000	0	9(1)
Ge(1)	4i	2018(1)	0	2659(2)	6(1)
Ge(2)	4i	5649(1)	5000	6618(2)	6(1)
Ni	4i	2176(1)	0	6407(2)	8(1)
Tm(1)	4i	4094(1)	0	6112(1)	5(1)
Tm(2)	4i	3447(1)	0	10633(1)	6(1)
In	2d	5000	5000	0	10(1)
Ge(4)	4i	2009(1)	0	2629(2)	6(1)
Ge(5)	4i	5652(1)	5000	6623(2)	6(1)
Ni	4i	2181(1)	0	6384(2)	8(1)

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

Table 8-5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_4\text{Ni}_3\text{InGe}_4$ (RE = Dy, Ho).

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Dy(1)	4(1)	6(1)	2(1)	0	1(1)	0
Dy(2)	4(1)	7(1)	1(1)	0	0(1)	0
In	8(1)	13(1)	4(1)	0	3(1)	0
Ge(1)	5(1)	6(1)	3(1)	0	2(1)	0
Ge(2)	5(1)	7(1)	1(1)	0	0(1)	0
Ni	4(1)	8(1)	7(1)	0	-1(1)	0
Ho(1)	8(1)	6(1)	6(1)	0	3(1)	0
Ho(2)	8(1)	6(1)	5(1)	0	2(1)	0
In	11(1)	10(1)	9(1)	0	5(1)	0
Ge(1)	9(1)	5(1)	8(1)	0	4(1)	0
Ge(2)	9(1)	7(1)	6(1)	0	3(1)	0
Ni	8(1)	8(1)	12(1)	0	1(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 8-6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Er and Tm).

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Er(1)	4(1)	8(1)	4(1)	0	1(1)	0
Er(2)	3(1)	8(1)	3(1)	0	-1(1)	0
In	7(1)	13(1)	6(1)	0	2(1)	0
Ge(1)	5(1)	8(1)	6(1)	0	1(1)	0
Ge(2)	4(1)	9(1)	4(1)	0	-1(1)	0
Ni	4(1)	10(1)	9(1)	0	-2(1)	0
Tm(1)	4(1)	8(1)	4(1)	0	1(1)	0
Tm(2)	4(1)	9(1)	3(1)	0	-1(1)	0
In	8(1)	16(1)	7(1)	0	2(1)	0
Ge(4)	4(1)	8(1)	5(1)	0	1(1)	0
Ge(5)	4(1)	9(1)	3(1)	0	-1(1)	0
Ni	3(1)	10(1)	9(1)	0	-2(1)	0

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

8-3 Results and Discussion:

Structure:

$\text{RE}_4\text{Ni}_2\text{InGe}_4$ crystallizes as an ordered variant of the Mg_5Si_6 structure type in the monoclinic space group $C 2/m$. The overall structure of the title compound as viewed down the b -axis can be seen in Figure 8-1. The rare earth and In atoms of the title compounds occupy the Mg sites of the Mg_5Si_6 structure, while the Ge and Ni atoms occupy the Si sites.

The InNi_2Ge_4 sub-lattice is composed of the same structural units found in the structure of $\beta\text{-RENiGe}_2$, specifically the Ge dimers, and the Ni_2Ge_2 parallelograms.¹ Figures 8-2 (A) and (B) show the structures of the title compound and $\beta\text{-RENiGe}_2$, respectively to illustrate the building unit similarities. The darker shaded regions of these figures highlight the Ge dimers, while the more lightly shaded regions emphasize the Ni_2Ge_2 units. These perspective views of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ and $\beta\text{-RENiGe}_2$ shown in Figures 8-2 (A) and (B) illustrate the structural variety that is possible for intermetallics to display, despite being composed of similar building blocks as these two phases are. Figure 8-2(C) is a view of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ viewed along the ac plane diagonal. We see from this view that $\text{RE}_4\text{Ni}_2\text{InGe}_4$ is similar in appearance to the structure of $\beta\text{-RENiGe}_2$ when viewed down the b -axis Figure 8-2 (D). There are channels in both of these

compounds formed by the Ni_2Ge_2 units and the Ge dimers that run along their respective directions containing the rare earth atoms.

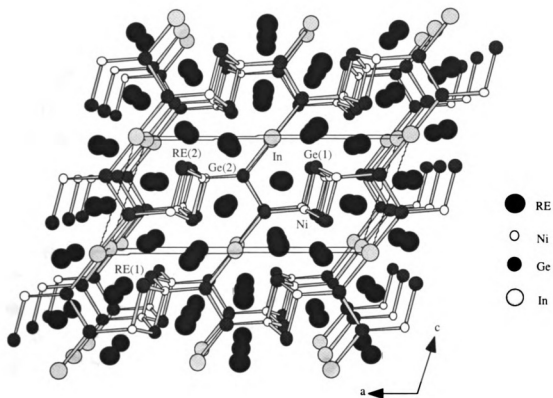


Figure 8-1 Overall structure of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ as viewed along the b -axis.

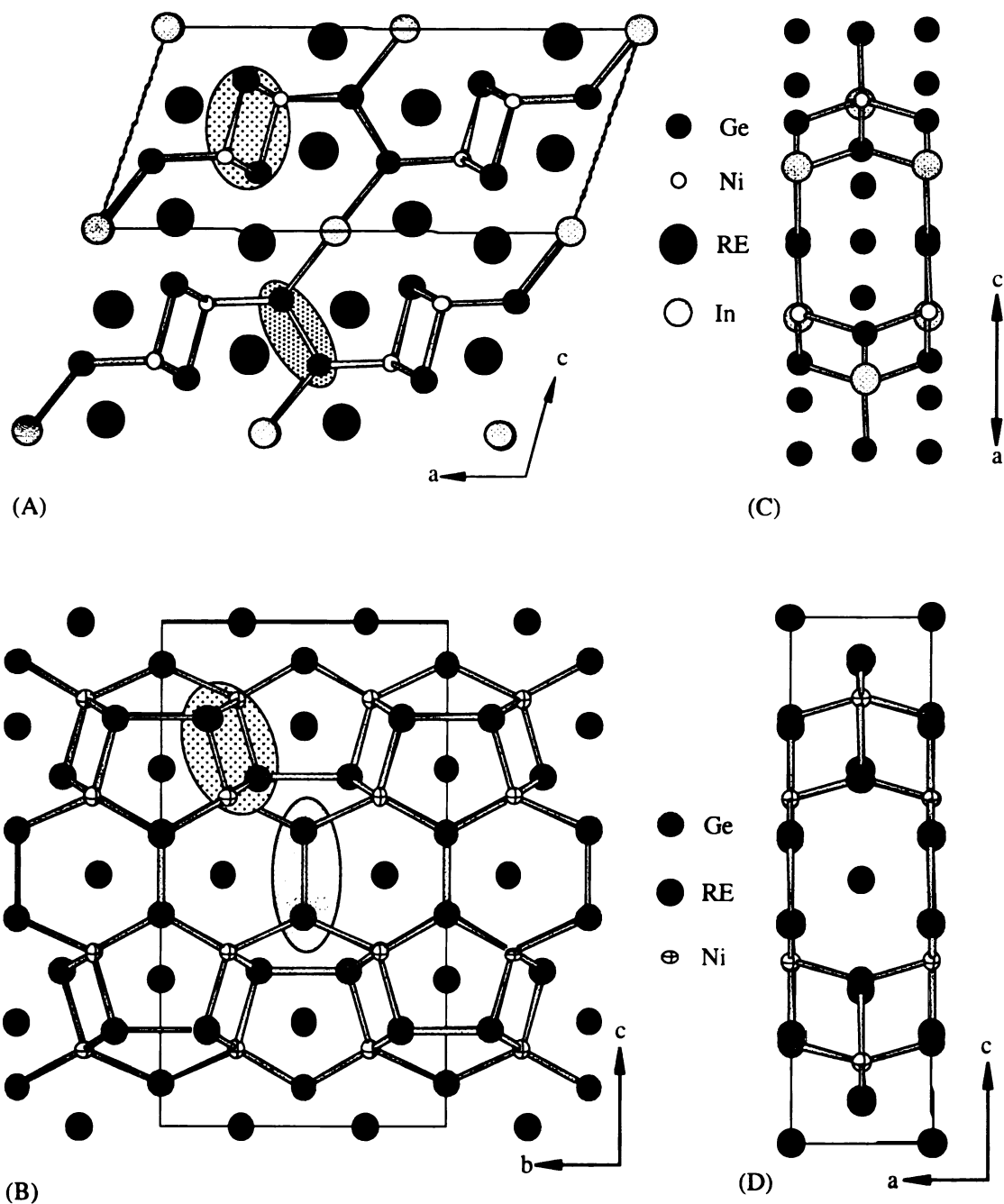


Figure 8-2 (A) The view of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ along the b -axis. (B) The view of $\beta\text{-RENiGe}_2$ as viewed along the a -axis and also along the b -axis. The light shaded circles in (A) and (B) view of $\beta\text{-RENiGe}_2$ show the Ni_2Ge_2 structure common to both phases. The darker circles show the Ge dimers common to both phases. (C) The view of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ along the ac plane diagonal. (D) The view of $\beta\text{-RENiGe}_2$ along the b -axis. The projections of the 2 structures in (C) and (D) show the similarity in the channels containing the rare earth ions.

The structure of $\text{RE}_4\text{Ni}_2\text{InGe}_4$ is built up from Ni atoms which are tetrahedrally coordinated by 3 Ge(1) atoms and 1 Ge(2) atom. This is a common coordination geometry for Ni atoms to adopt in intermetallic compounds as is seen in a wide range of compounds like RENi_2Ge_2 and BaNiSn_3 .¹⁰ The Ge(1) atoms are in a trigonal pyramidal 3 coordinate bonding geometry, forming zigzag chains by making two bonds with the Ni atoms along the *b*-axis. The third Ge(1) bond fuses the chains together forming a NiGe ribbon, Figure 8-3. The Ge(1)-Ni bond distances in the chain range from 2.4221(9) Å for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ to 2.412(1) Å for the Tm analog. The third Ge(1)-Ni bond, which fuses the chains together is slightly longer, with distances ranging from 2.560(2) Å for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ to 2.536(2) Å for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$.

The view of the fused NiGe chains seen in Figure 8-3 looks much like the PbO layer structure so often found in intermetallic phases. However, in $\text{RE}_4\text{Ni}_2\text{InGe}_4$ this NiGe structure is not a two-dimensional slab as found in the BaAl_4 or ThCr_2Si_2 structure, but is instead a one-dimensional ribbon. Ge(2) as mentioned above is in a trigonal planar environment making bonds to three different atoms, one to Ni with bond lengths ranging from 2.395(2) Å for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ to 2.390(2) Å for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$, one bond to In, and the third to its symmetry generated equivalent to form the Ge-Ge dimer with a distances of 2.494(2) Å for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ and 2.487(2) Å for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$. The Ni-Ge and Ge-Ge bond distances are comparable to those of other RE/Ni/Ge intermetallics and indicate strong bonding interactions.^{6, 10, 11}

The one crystallographically distinct In atom is in an unusual 2-coordinate linear environment by forming bonds with 2 Ge(2) atoms. The distances range from 2.8511 Å for Dy₄Ni₂InGe₄ to 2.8231 Å for Tm₄Ni₂InGe₄. These In-Ge bond distances compare well to other such distances that have been reported in Zintl phases such as SrInGe¹² and Ca₂LiInGe₂,¹³ which range from 2.751 to 2.8867 Å even though the In atoms are tetrahedrally coordinated in these examples. The distance between Ge(1) and In range from 3.1038 Å in Dy₄Ni₂InGe₄ to 3.0275 Å for Tm₄Ni₂InGe₄, and are considered too long to be strong bonding interactions.¹⁴

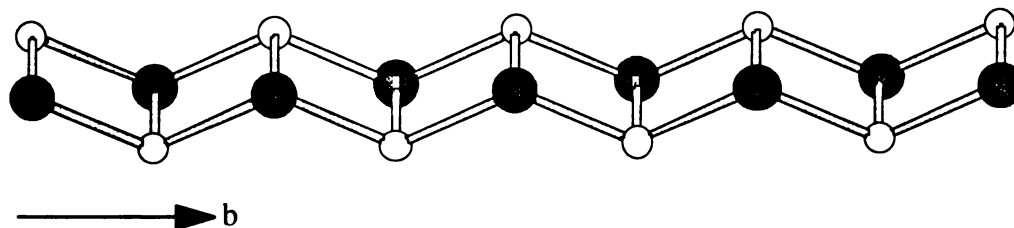


Figure 8-3 The Ni-Ge(1) ribbon which runs along the *b*-axis.

The coordination environments of the 2 crystallographically distinct rare earth atoms are quite different from one another. The RE(1) ion is 11 coordinate, making 3 bonds to Ni, 6 bonds to Ge (4 to Ge(2) and 2 to Ge(1)), and 2 to In, Figure 8-4 (A). The RE(2) atom is only 8 coordinate forming 5 bonds to Ge (3 to Ge(1) and 2 to Ge(2)), 2 to In, and 1 to Ni, Figure 8-4 (B). What is interesting about the rare earth sub-lattice in these compounds is the inter-rare earth distances, which range from 3.484 Å for Dy(2)-

Dy(2) to 3.622 Å for Dy(1)-Dy(1), are similar to those found in elemental Dy, which is 3.385 Å. The same applies for the other rare earth analogs. A complete list of bond distances for $\text{RE}_4\text{Ni}_2\text{InGe}_4$ (RE = Dy, Ho, Er, and Tm) can be found in Table 8-7.

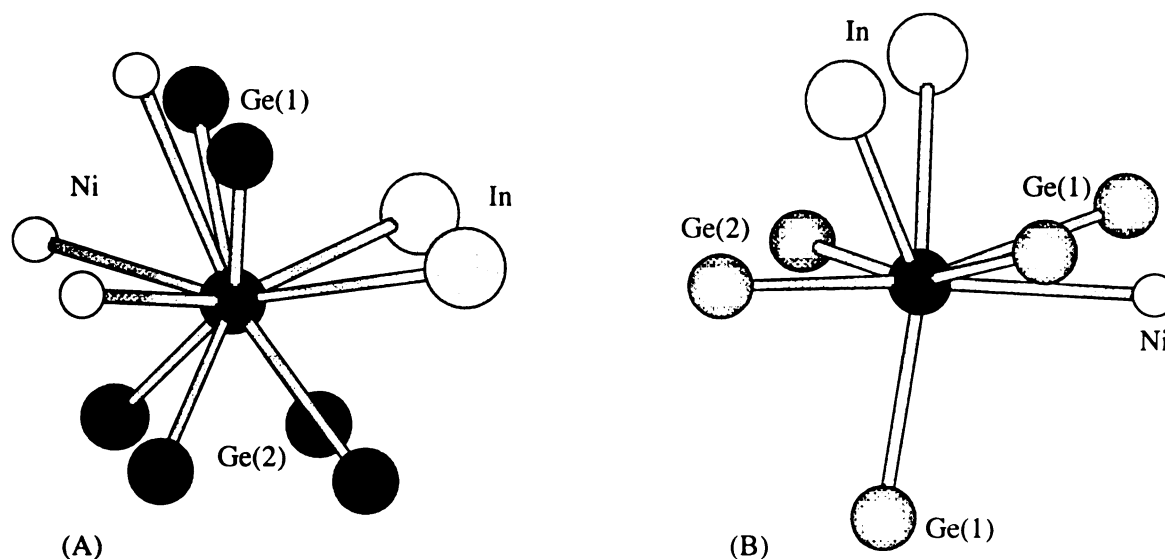


Figure 8-4 (A) The coordination environment of $\text{RE}^{3+}(1)$ ion. (B) The coordination environment of $\text{RE}^{3+}(2)$ ion.

•

1

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I

A

1

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F

5.

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R

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4

1

23

3

3

2

Table 8-7 Bond lengths [Å] for RE₄Ni₂InGe₄ (RE = Dy, Ho, Er, Tm)

	RE = Dy	RE = Ho	RE=Er	RE=Tm
RE(1)-Ge(2)	2.9645(9)	2.9537(12)	2.9412(12)	2.9296(10)
RE(1)-Ge(1)	3.0108(9)	3.0008(12)	2.9923(12)	2.9811(10)
RE(1)-Ni	3.0306(11)	3.027(2)	3.0086(19)	2.9836(16)
RE(1)-Ni	3.0404(16)	3.0182(14)	3.0143(13)	2.9998(12)
RE(1)-Ge(2)	3.1298(10)	3.1218(12)	3.1135(13)	3.0972(10)
RE(1)-Ge(1)	3.3054(13)	3.3042(17)	3.3232(17)	3.3279(14)
RE(1)-In	3.3840(5)	3.3761(7)	3.3636(11)	3.3450(5)
RE(2)-Ge(2)	2.9052(9)	2.8931(12)	2.8826(12)	2.8658(9)
RE(2)-Ni	2.9747(15)	2.967(2)	2.9744(18)	2.9697(16)
RE(2)-Ge(1)	2.9860(13)	2.9728(17)	2.9607(16)	2.9441(14)
RE(2)-Ge(1)	3.0580(10)	3.0416(13)	3.0230(13)	2.9959(10)
RE(2)-Ni	3.2988(12)	3.2882(16)	3.2903(14)	3.2907(13)
RE(2)-In	3.3233(5)	3.3164(7)	3.3054(11)	3.2900(5)
RE(2)-RE(2)	3.4843(9)	3.4698(11)	3.4629(13)	3.4440(9)
In-Ge(2)	2.8511(12)	2.8395(16)	2.8356(15)	2.8238(13)
In-Ge(1)	3.1038(12)	3.0806(16)	3.0622(16)	3.0275(13)
Ge(1)-Ni	2.4221(9)	2.4199(12)	2.4164(12)	2.4116(10)
Ge(1)-Ni	2.560(2)	2.556(3)	2.547(2)	2.536(2)
Ge(2)-Ni	2.3951(19)	2.392(2)	2.393(2)	2.3902(19)
Ge(2)-Ge(2)	2.494(2)	2.490(3)	2.492(2)	2.487(2)

Synthesis:

The compound $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ was first discovered in a reaction that was designed to produce $\beta\text{-HoNiGe}_2$, a phase that can only be synthesized from an In flux.¹ The Ho metal used for this particular preparation was in the form of large foil pieces with dimensions of 2-3 mm on an side and approximately 0.2mm thick. The yield for this initial reaction was rather poor, but gave several single crystals with rod like morphology. These rod shaped crystals were mistakenly identified as $\beta\text{-HoNiGe}_2$, but were later determined to be $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ after single crystal diffraction experiments and subsequent elemental analysis were performed.

Once the elemental composition was determined from these methods, reactions were carried out where Dy, Ni, Ge and In were combined in a 2:1:2:10 ratio, the difference from the initial reaction conditions being that the Dy metal was first ground into a fine powder. The reaction was carried out using the same temperature profile used to form $\beta\text{-RENiGe}_2$. Curiously enough, this reaction yielded mainly $\beta\text{-DyNiGe}_2$ as determined by powder x-ray diffraction. Several other attempts with other rare earth metals, also in the form of powders, had similar outcomes. It was only after the Dy metal powder ratio was increase from 2 to 3, while keeping all other parameters the same, did $\text{Dy}_4\text{Ni}_2\text{InGe}_2$ form as the dominant phase.

This result and the fact that the phase was found originally in the Ho reaction where the Ho was in the form of large foil pieces can be understood in terms of kinetic arguments. We have found that often reactions carried out in molten indium work poorly if the reactants, particularly the rare-earth metals, are left in large chunks (3-5 mm pieces).¹ Specifically, the reactions tend to have poor yields or do not work at all. This is likely due to the kinetics of metal solvation in the molten indium, which are apparently, based on our experience, rather sluggish. Large pieces of poorly dissolved metals chunks will lead to high local concentrations of the metals in the immediate vicinity of the undissolved piece.

These were the reaction conditions present in the sample where $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ was first discovered, and it may be this elevated concentration of metal that is required for the title compounds to form. Therefore, in order to obtain $\text{RE}_4\text{Ni}_2\text{InGe}_4$ in high yields the metal concentration must be elevated, which likely would not happen under conditions where the reactants were combined in their ideal stoichiometric ratios as powders. The excess rare earth metal used in the reaction forms the cubic REIn binary with the excess indium in the reaction. This phase is presumably destroyed during the isolation process, as it is not stable in acetic acid.

Several attempts to produce $\text{RE}_4\text{Ni}_2\text{InGe}_4$ by direct combination of the elements were unsuccessful. When the reaction was run in a radio frequency furnace the In was always excluded from the product. It was apparent by visual inspection of the melt that

the surface was coated by In, which was malleable, and the product underneath was brittle. X-ray powder patterns indicate that the target phase was not produced, but instead DyNiGe was produced with the CeCu₂ structure type. Other phases were present as well but could not be identified. A similar result was obtained when the reactions were carried out by arc-melting.

Differential thermal analysis performed on hand selected single crystals of Dy₄Ni₂InGe₄ found that no phase transition took place up to 1000 °C. Visual inspection of the crystals after the DTA found that they were completely intact, and retained their morphology. Additionally there was no change in the x-ray powder pattern after the DTA experiment when compared to the pattern taken before. These compounds are not however, resistant to chemical attack by strong mineral acids such as concentrated HCl, HNO₃ and HF, as all of these badly etched them. This is not a terribly surprising finding since the β -RENiGe₂ compounds were badly etched if left in concentrated HCl, or dilute solutions of HCl for extended periods (2-3 hours).

Magnetic Properties:

The rare earth ions in the title are in much closer proximity than in many other rare earth containing intermetallics that have been described previously, as they have inter-rare earth distances comparable to those found in the rare earth metals.¹⁰ We may thus predict that the magnetic interactions will be quite strong in these compounds as

compared to other phases we have investigated whose inter rare earth distances are closer to 4 or 5 Å

Dy₄Ni₂InGe₄: A sample of Dy₄Ni₂InGe₄ single crystals was hand selected for the magnetic susceptibility measurements, and were not oriented in any particular way. The susceptibility data can be seen in Figure 8-5 (A). The data obey the Curie/Weiss law from 35 to 300 K. The resulting effective magnetic moment obtained from the slope of the inverse susceptibility versus temperature was 21.7 μ_B per formula unit. This is in good agreement with the value calculated for 4 independent Dy³⁺ ions which is 21.4 μ_B .¹⁵ The Weiss constant was determined to be -35.9 K, indicating a rather substantial antiferromagnetic interaction between the Dy³⁺ ions. At approximately 30 K there is a maximum in the susceptibility, below this temperature there is a small decrease in the susceptibility, before it begins to increase again. There is a second maximum in the susceptibility data at 11 K, and below this temperature the susceptibility decreases down to 2 K. The value of the Weiss constant (-35 K) is in good agreement with possible antiferromagnetic ordering which occurs around 30 K.

Several samples have been measured and it was found that this double maximum behavior in the susceptibility data is fully reproducible. It is possible that this behavior may be due to an impurity, though a search of the literature did not reveal any ternary Dy/Ni/Ge or Dy/Ni/In phases that have Néel temperatures corresponding to those found

here.¹¹ It cannot be ruled out that an, as yet unidentified, impurity in our samples is resulting in the behavior we observe though given the nature of sample preparation this is unlikely.

Figure 8-5 (B) shows the magnetization curve for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$. In the low field region the moment is weakly dependant on the applied field. At 16.3 kOe the sample seems to undergoes a sharp transition above which the slope of the magnetization curve is much higher. This could be due to a meta-magnetic transition where the field disrupts the antiferromagnetic order of the rare earth moments. After the order had been broken the system behaves as a typical paramagnet with a linear increase of the moment with applied field. The compound gives no indication of saturating at the highest attainable field, as it continues to increase linearly up to 55 kOe. Indeed only 50 % of the moment is recovered at this field. It is possible that the system would saturate if much larger applied fields were used.

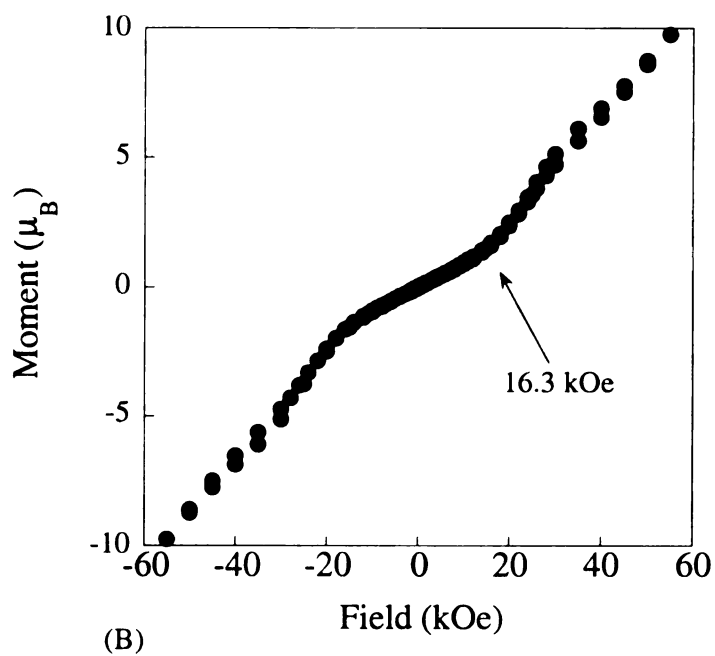
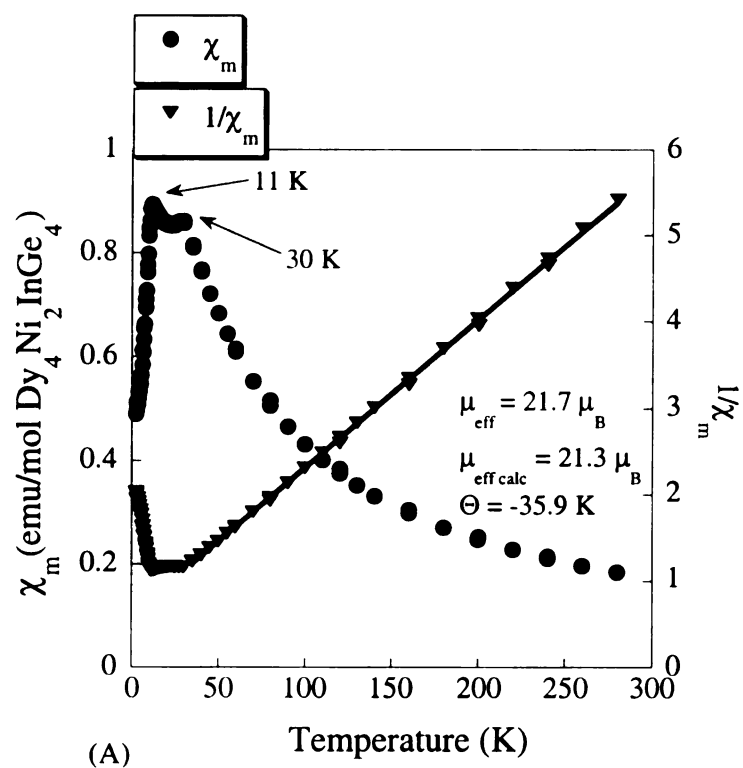


Figure 8-5 (A) Susceptibility and inverse susceptibility data for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ collected with an applied field of 2000 Oe (B) Magnetization curve for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ collected at 2 K.

Ho₄Ni₂InGe₄: Hand selected single crystals were used to measure the magnetic properties of Ho₄Ni₂InGe₄. The susceptibility and inverse susceptibility data can be found in Figure 8-6 (A). The Ho analog also has multiple peaks in the susceptibility data, again suggestive of multiple antiferromagnetic ordering transitions. The inset of Figure 8-5(A) shows this more clearly. There is a maximum in the susceptibility data at 10 K below which, the susceptibility decreases slowly until 4 K, at which point it decreases much more quickly down to 2 K. Above 10 K the susceptibility data follow the Curie/Weiss law with a resulting effective magnetic moment of 21.08 μ_B per formula unit, and a Weiss constant (θ), equal to -13 K. The effective magnetic moment obtained from the data is in excellent agreement with the theoretical value of 21.2 μ_B . The negative Weiss constant (θ) again indicates antiferromagnetic interactions. The double maximum behavior observed for Ho₄Ni₂InGe₄ was reproducible with several samples, but again the possibility of an impurity cannot be ruled out at this time.

The magnetization curve for Ho₄Ni₂InGe₄ can be found in Figure 8-6 (B). It is qualitatively similar to the magnetization curve measured for the Dy analog. In the low field region there is a weaker dependence of the moment on the applied field until, again, a critical field is reached at 5000 Oe, and then there is an increase in the slope. As was the case with Dy₄Ni₂InGe₄, Ho₄Ni₂InGe₄ also increases linearly above the critical field up to

the highest fields attainable. The moments give no indication of saturating and again reach only 50% of the theoretical μ_{sat} value.

Er₄Ni₂InGe₄: The magnetic sample for the Er analog again consisted of hand selected crystals. The susceptibility and inverse susceptibility for Er₄Ni₂InGe₄ can be found in Figure 8-7 (A). The behavior of this compound is different from the previous two cases, in that it has only one maximum in the susceptibility data. This would suggest only one antiferromagnetic ordering step. Above this temperature the inverse susceptibility data is, again, linear following the Curie/Weiss law with a resulting effective magnetic moment of 18 μ_{B} per formula unit, and a Weiss constant equal to -7 K. The moment obtained from the data is in good agreement with the calculated value for 4 Er³⁺ ions, which is 19 μ_{B} . The negative Weiss constant indicates antiferromagnetic interactions though its magnitude is smaller than the previous 2 examples. This is consistent with the fact that the maximum in the susceptibility data is at a lower temperature indicating the possible onset of antiferromagnetic order.

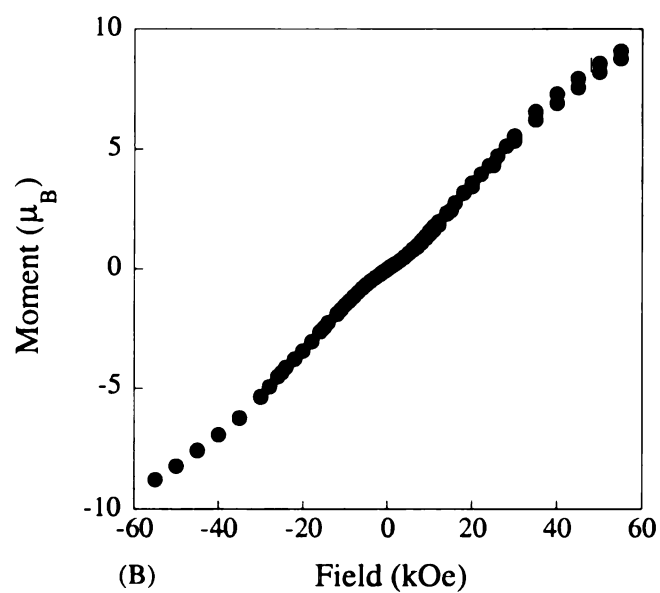
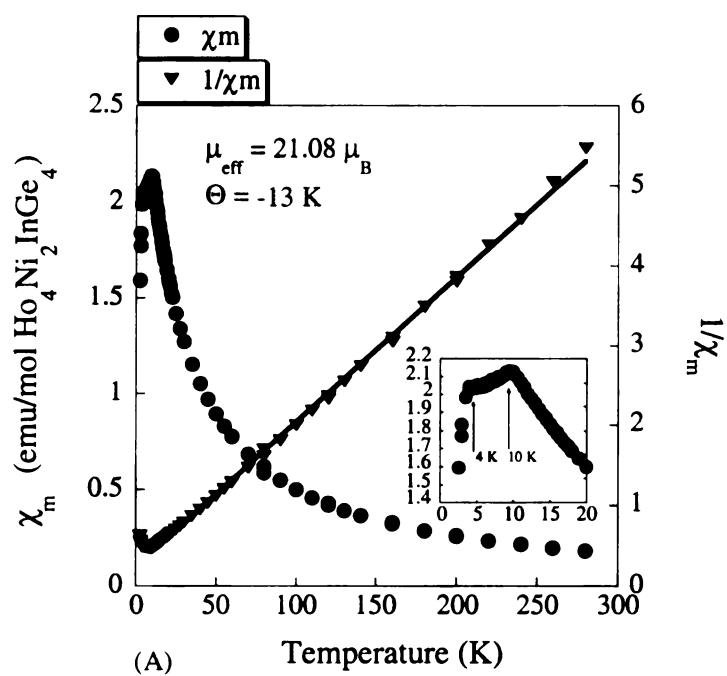


Figure 8-6 (A) Susceptibility and inverse susceptibility data for $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ collected with an applied field of 500 Oe. (B) Magnetization curve for $\text{Ho}_4\text{Ni}_2\text{InGe}_4$ collected at 2K.

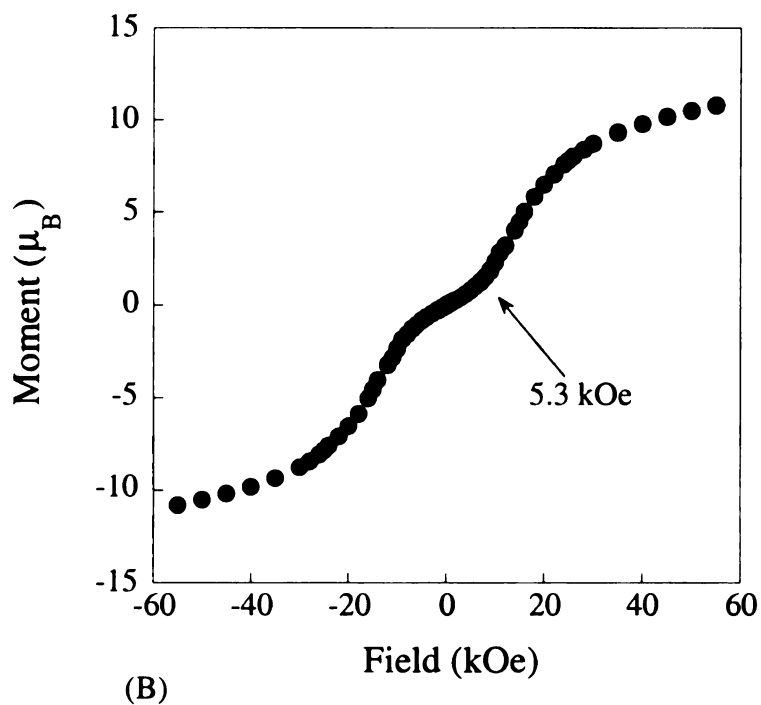
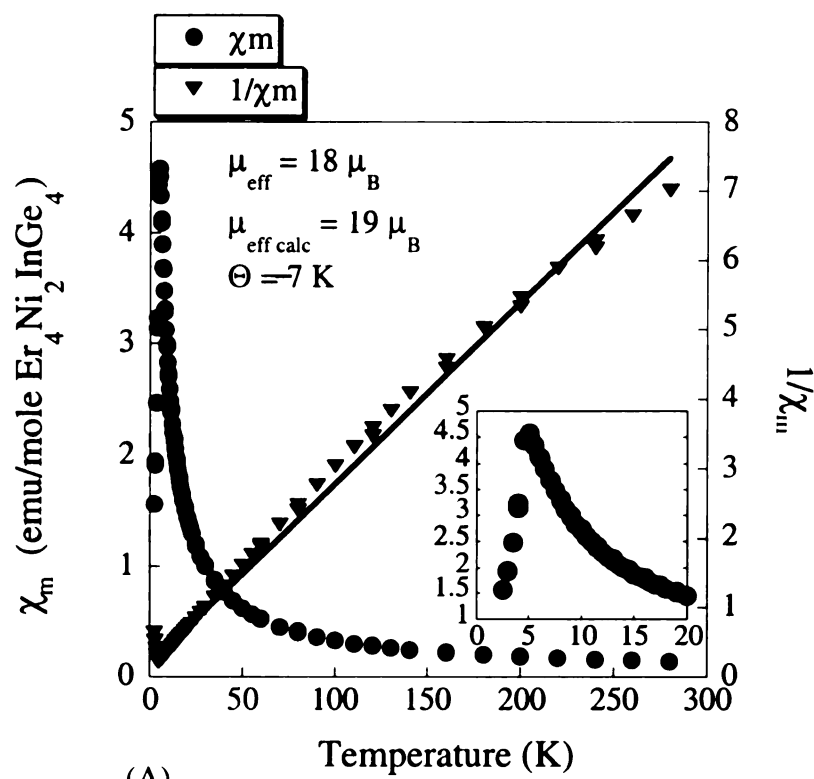


Figure 8-7 (A) Susceptibility and inverse susceptibility data for $\text{Er}_4\text{Ni}_2\text{InGe}_4$ collected with an applied field of 1000 Oe. (B) Magnetization data for $\text{Er}_4\text{Ni}_2\text{InGe}_4$ collected at 2 K.

The magnetization curve for $\text{Er}_4\text{Ni}_2\text{InGe}_4$ can be found in Figure 8-7 (B). Once again, in the low field region of the magnetization data the moment has a weak dependence on the applied field. At a critical field of about 5.3 kOe there is a transition, and above this field the moment has a much stronger dependence. Unlike the two previous examples whose moment increased linearly up to 55 kOe, the Er analog begins to saturate at 30 kOe. At the highest attainable field the moment only reached about 55 % of the saturation value, this despite the negative divergence of the moment as a function of applied field above 30 kOe.

$\text{Tm}_4\text{Ni}_2\text{InGe}_4$: The magnetic measurements performed on $\text{Tm}_4\text{Ni}_2\text{InGe}_4$ were also done on a sample of hand selected single crystals. The magnetic behavior of the Tm analog is quite different than that of the previous 3 examples. First there is no maximum in the susceptibility data, but instead it continues to increase down to the lowest temperature attainable (2 K). This is the first $\text{RE}_4\text{Ni}_2\text{InGe}_4$ analog that showed no susceptibility maximum, Figure 8-8 (A). The inverse susceptibility is linear with temperature from 300 K down to about 50 K, where it begins to negatively diverge. The resulting effective magnetic moment for the region fit to the Curie/Weiss law was $14.14 \mu_B$, and a Weiss constant equal to - 10 K. The calculated value for the effective magnetic moment for 4 Tm^{3+} ions is $15.0 \mu_B$ which is slightly higher than the value we obtained from measurements, but is still in reasonably good agreement. The negative Weiss constant indicates antiferromagnetically interacting moments, though as mentioned above no

ordering was found. The negative divergence in the inverse susceptibility data can be caused by several factors. The most likely of which, is crystal field splitting of the ground state multiplets of the Tm^{3+} ion.¹⁶

The magnetization curve for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$ can be seen in Figure 8-7 (B). Unlike the other 3 examples all of which, apparently underwent transitions at a specific applied field; we do not observe any change in the slope of the magnetization curve in the lower field regions for the Tm analog. The reason being is, there is apparently no magnetic order for the applied field to disrupt. The only change in slope that occurs is in the high field region between 15 and 25 kOe, and this is caused by the onset of magnetic saturation. Above 30 kOe the moment again has a linear dependence on the field though the slope is much shallower due to this saturation. The moment at the highest attainable field is about $8 \mu_B$, and is about 60 % of the value expected for 4 Tm^{3+} ions.

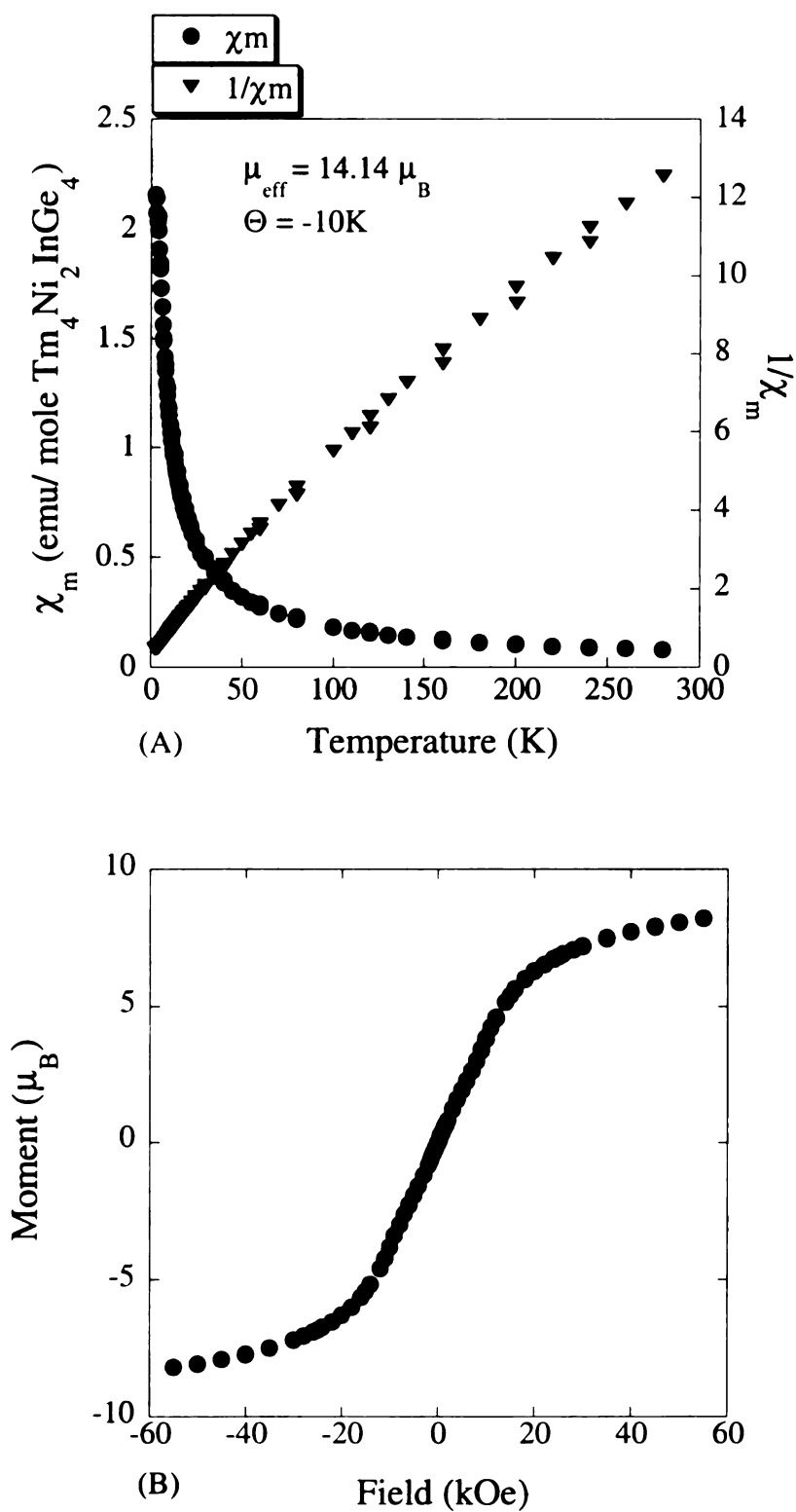


Figure 8-8 (A) Susceptibility and inverse susceptibility for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$ collected with an applied field of 1000 Oe. (B) Magnetization curve for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$ collected at 2 K.

Summary: In each of the cases presented the only species in the system that makes a contribution to the magnetic susceptibility is the rare earth ion. The Ni atom has a diamagnetic d^{10} configuration, a common feature of intermetallic compounds containing electropositive elements.¹⁷ The compound can best be described as a polar intermetallic with the following charge balancing scheme $(RE^{3+})_4^{12+}(Ni_2InGe_4)^{12-}$. The Ni_2InGe_4 sublattice is presumably metallic possessing delocalized electrons that are free to move about this frame work.

In rare earth containing metallic systems the predominant mechanisms for magnetic exchange will likely be indirect ones such as Ruderman-Kittel-Kasuya-Yosida (RKKY) coupling.¹⁸ In this mechanism conduction electrons are polarized by the magnetic moments of the rare earth ions as they pass by. This polarization is imparted on adjacent rare earth ion acting to couple the two moments, either ferromagnetically or antiferromagnetically, the nature of the interaction is dependent on the inter-ionic distance. This is the dominant magnetic exchange mechanism found in the rare earth metals, despite the fact that they are in direct contact with one another. The fact that the f electrons are so contracted makes it impossible for direct exchange to take place even in the elemental form. Indeed we noted above that the rare earth ions in the title compounds are quite close to one another with distances comparable to those found in the corresponding element. When the RKKY mechanism is the main mechanism of exchange it has been found that the magnetic ordering temperatures scale with the magnitude of the

moment in the system with a value known as the de Gennes factor which is defined in

(1).¹⁹ In Equation 1 λ is the Lande's factor, which takes into account noncollinear

$$(1) \quad DG = (\lambda - 1)^2 J(J + 1)$$

effects of the angular momentum, and is defined in (2). J is simply the total angular momentum of the rare earth ion. This assumes that all other factors remain constant such as the conduction electron concentration and fermi surface geometry. This is almost

$$(2) \quad \lambda = 1 + \left(\frac{J(J + 1) - L(L + 1) + S(S + 1)}{2J(J + 1)} \right)$$

always the case when investigating rare earth analogs of intermetallic phases, as the rare earth f electrons do not play a significant role in the states near the fermi level. Figures 8-9 (A) and (B) show the temperatures where the maxima were observed as a function of the de Gennes factor. Figure 8-9 (A) shows the higher temperature transition and Figure 8-9(B) shows the lower temperature transition. We indeed see that the temperatures where the maxima are observed vary almost linearly with the de Gennes factor suggesting indirect magnetic exchange is the dominant mechanism in this system.

The proposed multi-step antiferromagnetic ordering suggested by the multiple maxima observed in the susceptibility data can be rationalized by inspection of the inter-rare earth ion distances in $\text{RE}_4\text{Ni}_2\text{InGe}_4$. RE(2)-RE(2) distances are the closest RE-RE contacts found in this structure ranging from 3.4843(9) Å for $\text{Dy}_4\text{Ni}_2\text{InGe}_4$ to 3.4440(9) Å for $\text{Tm}_4\text{Ni}_2\text{InGe}_4$. The other RE-RE distances are somewhat longer with RE(1)-RE(2) at

approximately 3.61 and 3.76 and, RE(1)-RE(1) distances of 3.62 Å for the Dy analog. The rare earth ions with the closest contact (RE(2)-RE(2)) will likely be more strongly magnetically coupled than the ions which are separated by 3.6 or 3.7 Å such as RE(1)-RE(2) and RE(1)-RE(1). The RE(2) ions could order magnetically at a higher temperature due to this higher degree of coupling, while the balance of the system is still disordered, causing the decrease in the susceptibility that was found in the Dy and Ho compounds. The remaining moments separated by a larger distance, and hence coupled magnetically to a lesser extent, will order only at a lower temperature giving the large decrease in susceptibility that we observe in the low temperature data of Dy₄Ni₂InGe₄ and Ho₄Ni₂InGe₄. In the case of the Er analog we only observe one ordering step. It is possible that the Er(2)-Er(2) ions do not order first as the coupling of the ions is too weak as compared to the Dy and Ho analogs. Instead in the case of Er₄Ni₂InGe₄ the system orders in one step.

Systems displaying multi-step magnetic ordering behavior are rare, but are not unprecedented. For example there is accumulating evidence for multi-step antiferromagnetic ordering in DyNi₂B₂C.²⁰ Additionally it has been shown by the neutron diffraction measurements of Dy₃Ge₄ that the two different rare earth sub-lattices order antiferromagnetically at two different temperatures.²¹

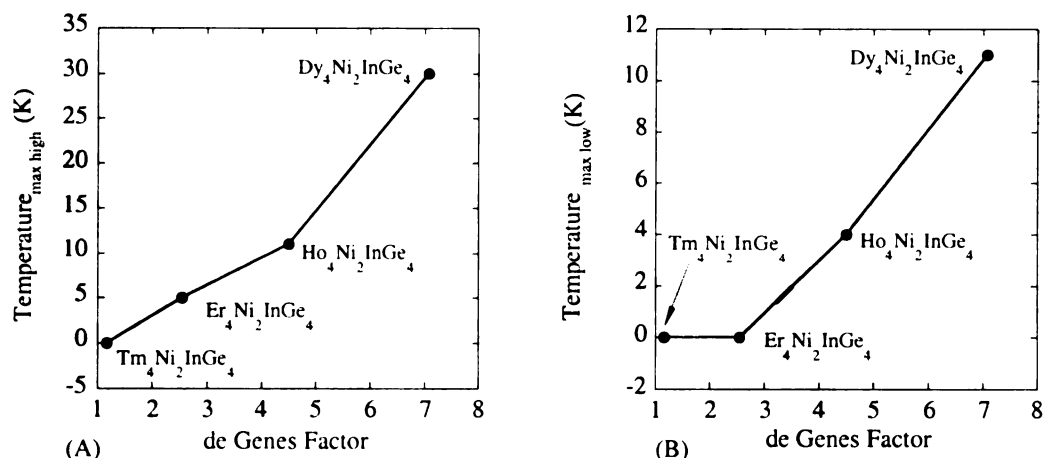


Figure 8-9 (A) The higher temperature susceptibility maximum as a function of the de Genes factor. (B) The lower temperature susceptibility maximum as a function of the de Genes factor.

8-4 Conclusions:

The compounds $\text{RE}_4\text{Ni}_2\text{InGe}_4$ were synthesized from a melt composed of excess In. Indium was incorporated into the structure at a specific atomic site resulting in an ordered quaternary variant of the Mg_5Si_6 structure. It was found by synthetic investigations that these compounds could only be produced from a molten indium reaction, and that the reaction conditions needed to be carefully controlled to produce $\text{RE}_4\text{Ni}_2\text{InGe}_4$ in large yields. Specifically the melt needed to be rich in rare earth metal in order to form. This is an excellent demonstration of the stabilization of a new intermetallic compound by altering reaction conditions. Indeed this system is particularly sensitive to the concentrations of reactants dissolved in the melt.

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Chapter 9

Indium Flux Synthesis of REAu_2In_4 (RE = La, Ce, Pr, Nd) a New Indium Rich Ternary Intermetallic Phase.

8-1 Introduction:

Investigations into the ternary phase diagram of rare earth/ gold / indium have yielded numerous new phases and structures including: EuAuIn which crystallizes in the Fe_2P structure type,¹ REAu_2In (RE = Tb-Lu) which has the BiF_3 structure,² $\text{RE}_2\text{Au}_2\text{In}$ (RE = La-Gd) which adopts the U_3Si_2 structure,³ $\text{RE}_2\text{Au}_2\text{In}$ (RE = Tm-Lu) which crystallize in the Zr_3Al_2 structure type, which is an ordered super structure of U_3Si_2 .³ More indium rich examples have also been found such as $\text{La}_3\text{Au}_4\text{In}_7$,⁴ $\text{RE}_2\text{Au}_3\text{In}_5$ (RE = Ce, Pr, Nd, Sm),⁵ and $\text{Eu}_2\text{Au}_3\text{In}_4$, which crystallizes as the anti $\text{Hf}_2\text{Co}_4\text{P}_3$ structure,⁶ and YbAuIn_2 an ordered variant of the ReB_3 structure.⁷ There have been several examples of indium rich compounds that display heavy fermion behavior for example Ce_2MIn_8 (M = Rh and Ir).⁸ The compounds $\text{Ce}_n\text{MIn}_{3n+2}$ (n = 1, 2 M = Co, Ir) were found to be both superconducting, and also to display heavy fermion behavior.⁹ The discovery of these compounds, and their properties helps drive the exploratory synthesis of RE/TM/In systems. Attempts to produce other compounds which display these exotic electronic properties will facilitate a better understanding of the structural/property relationships that govern them.

We have recently begun to investigate the use of In as a flux for the exploratory synthesis of intermetallic compounds. Prior work has been done using In as a flux for the crystal growth of known phases,¹⁰ however considerably less work has been reported regarding the use of molten indium as a medium for exploratory synthesis of intermetallic compounds. While exploring systems of the type RE/Ni/Ge/In we were able to demonstrate that kinetically stable phases can be produced from reactions carried out in excess indium.¹¹ Our success up to this point has been rather limited, and many of the reactions carried out in excess In resulted in the generation of large high quality crystals of several known phases including: RENi_2Ge_2 , crystallizing in the ThCr_2Si_2 structure type, RENiGe , which crystallizes in the CeCu_2 and Co_2Si structure types, and RENi_3Ge_3 which has the YNi_3Si_3 structure type. Additionally, generating quaternary phases containing a rare earth, transition metal, germanium and indium proved extremely difficult.¹¹ These results led us to eliminate Ge from the reaction mixture, and explore the ternary phase systems of a rare earth metal, a late transition metal and indium.

Presented here is a new member of the rare earth / gold / indium system. REAu_2In_4 (RE = La, Ce, Pr, Nd). This phase is the most indium rich phase yet reported for this system and crystallizes as a new structure type. The crystal structure, synthesis, thermal stability, and magnetic properties of these compounds are presented.

8-2 Experimental Section

Reagents:

The following reagents were used without further purification: La metal(~40 mesh powder, 99.9%, Cerac, Milwaukee, WI), Ce metal(~250 mesh powder, 99.9%, Research Chemicals, Phoenix, AZ), Pr metal (~ 250 mesh, 99.9%, Research Chemicals, Phoenix, AZ), Nd metal(~250 mesh powder, 99.9%, Research Chemicals, Phoenix, AZ), Au metal(ingot. 99.9%. Research Chemicals. Phoenix, AZ), and In (3-5 mm teardrops, 99.99% Cerac Milwaukee, WI).

Synthesis:

Method A: REAu₂In₄ (RE = La, Ce, Pr, Nd) was produced by combining 0.5 mmol of the rare earth metal, 1 mmol Au and 8 mmol In in an Al₂O₃ crucible then flame sealing them under a reduced atmosphere of 10⁻⁴ mbar in a fused silica tube. The reactants were then heated to 1000 °C over the course of 10 h held at 1000 °C for 72 h, then cooled to 150 °C over 24 h. To isolate the resulting product a coarse frit was placed in the open end of the reaction crucible, and then flame sealed in a Pyrex tube under a reduced atmosphere of 10⁻⁴ mbar. The crucible was heated to 300 °C held for 10- 15 min, and then spun in a centrifuge for 5 min. This process was repeated twice to remove as much excess indium as possible. Indium did tend to wet the surface of the product, and so further isolation was carried out by etching with glacial acetic acid. Acetic acid did not

effect the crystal quality of the target phase even after submersion for several days. The yields were generally 70% based on the initial rare earth mass, with a purity of 70 to 80%. The main impurity was cubic AuIn_4 , which can be etched away by acetic acid over the course of a week. Crystals of REAu_2In_4 grow as large silver needles with typical lengths in excess of 2 mm. The crystal sizes obtained are impressive given the scale of the reaction, and the relatively quick cooling rate employed.

Method B: REAu_2In_4 was also made by combining the reactants in their stoichiometric ratios in an Al_2O_3 crucible, then flame sealing the reactants under a reduced atmosphere of 10^{-4} mbar in a fused silica tube. The reactants were then heated to 1000 °C over 10 h and held there for an additional 120 h before cooling back to room temperature over the course of 48 h. The target phase was obtained in a pure form in nearly quantitative yields by this method, though crystal size and quality was poor.

X-ray Crystallography:

Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART CCD diffractometer with graphite monochromatized Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Unit cell refinement and data merging were done with the SAINT program, and an empirical absorption correction was applied using the program SADABS.¹² The original determination of the unit cell of LaAu_2In_4 lead to the

assignment $a = 4.6865(6) \text{ \AA}$, $b = 7.3414(9)$, $c = 18.506(2)$. Inspection of the systematic absences found the cell to be primitive with the unambiguous determination of the space group *Pcmn*. A structural solution in *Pcmn* was obtained for LaAu_2In_4 by direct methods using the program SHELXS, and the final structural refinement was completed with the SHELXL suite of programs.¹³ The space group *Pcmn* is a non-standard representation of the space group *Pnma*; the appropriate transformation matrix was applied to convert the original *a*-axis to *b*, the *b*-axis to *c*, and the *c*-axis to *a*. The structure was then refined using the standard setting. Solutions of the Ce, Pr, and Nd analogs were obtained by using the solution of LaAu_2In_4 as a starting point, then refining from this point with SHELXL. Data collection and refinement details for LaAu_2In_4 and CeAu_2In_4 can be found in Table 9-1, and information for PrAu_2In_4 and NdAu_2In_4 are presented in Table 9-2. Atomic coordinates and isotropic displacement parameters for LaAu_2In_4 , CeAu_2In_4 , and PrAu_2In_4 , and NdAu_2In_4 can be found in Table 9-3 and 9-4 respectively. The anisotropic displacement parameters LaAu_2In_4 , CeAu_2In_4 , and PrAu_2In_4 , NdAu_2In_4 can be found in Tables 9-5 and 9-6 respectively.

Phase identity and purity was confirmed by powder X-ray diffraction carried out on an Inel diffractometer with Cu K α radiation. The experimental powder patterns were compared with the calculated powder patterns generated from the single crystal structural refinements. Powder patterns were calculated using the CERIUSt² software package.¹⁴

Elemental analysis:

Semi-quantitative microprobe elemental analysis was performed on several single crystals of each of the analogs, including the crystals used for single crystal X-ray diffraction experiments. Spectra were collected on a JEOL JSM 35C scanning electron microscope equipped with a Tracor Noran energy dispersive spectrometer (EDS) with a Norvar window capable of standardless quantitation of elements with $Z \geq 4$. Spectra were collected with an accelerating voltage of 25 kV and 60 s acquisition times. Standardless quantitation of these compounds led to the following atomic ratios: 1: 2.3: 3.6 for La Au and In respectively. This is in reasonably good agreement with the stoichiometric ratios obtained from the crystallographic refinement. Similar stoichiometric ratios were determined for the other analogs as well.

Differential Thermal Analysis:

Differential thermal analysis (DTA) was carried out with Shimadzu DTA 50. Hand selected crystals were placed in a fused silica ampoule, which was carbon coated in order to prevent glass attack upon melting of the product, and then flame sealed under a reduced atmosphere of 10^{-4} mbar. α - Al_2O_3 powder was used as a standard reference as it is known to be stable up to 1000°C. The thermal analysis was done by heating the sample at a rate of 10 °C per minute up to 1000 °C, then cooling to 150 °C at the same rate. The cycle was repeated up to 1000 °C with the same heating and cooling rates. In the event

that REAu_2In_4 did melt on the initial heating cycle, recycling the program would allow us determine if it melted congruently or if it decomposed upon melting.

Magnetic Measurements:

Magnetic measurements were carried out on a Quantum Design MPMS SQUID magnetometer. Measurements were performed on handpicked single crystals, which were placed in an envelope made of Kapton tape. Temperature dependant susceptibility data was collected in both field cooled and zero field cooled modes with an applied field of 1000 Oe for LaAu_2In_4 500 Oe for the Ce analog and 2000 Oe for PrAu_2In_4 and NdAu_2In_4 . Magnetization data was also collected at 2 K for all the compounds with a fields sweeping from - 55 kOe to 55 kOe.

Table 9-1. Crystal data and structure refinement for REAu₂In₄ (RE=La, Ce).

Formula	LaAu ₂ In ₄	CeAu ₂ In ₄
Formula weight	992.13	993.33
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i> (#62)	<i>Pnma</i> (#62)
Unit cell dimensions	a = 18.506(2) Å b = 4.6865(6) Å c = 7.3414(9) Å	a = 18.514(3) Å b = 4.6624(8) Å c = 7.3888(12) Å
Volume	636.69(14) Å ³	637.79(18) Å ³
Z, Density(calculated)	4, 10.350 g/cm ³	4, 10.345 g/cm ³
Absorption coefficient	66.544 mm ⁻¹	66.869 mm ⁻¹
F(000)	1644	1648
Theta range for data collection	2.20 to 27.98°.	4.40 to 30.07°.
Index ranges	-24<= <i>h</i> <=22 -6<= <i>k</i> <=6 -9<= <i>l</i> <=9	-25<= <i>h</i> <=25 -6<= <i>k</i> <6 -10<= <i>l</i> <=10
Crystal size	0.1x0.05x0.05	0.2x0.05x0.05
Reflections collected / unique	5596 / 813	6701 / 1037
R(int)	0.0427	0.0681
Completeness to $\theta_{\max}$	94.4 %	99.0
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	813 / 0 / 44	1037 / 0 / 44
Goodness-of-fit on F ²	1.195	1.084
Final R indices [<i>I</i> >2σ(<i>I</i>)]	R1 = 0.0316, wR2 = 0.0845	R1 = 0.0382 wR2 = 0.0950
R indices (all data)	R1 = 0.0349, wR2 = 0.0859	R1 = 0.0430 wR2 = 0.0968
Extinction coefficient	0.00069(9)	0.0043(3)
Largest diff. peak and hole	2.734 / -2.484 e/Å ³	4.520 / -2.912e/Å ³
$R1 = \frac{\sum \ F_o\ - F_c }{\sum \ F_o\ } \text{ and } wR2 = [\sum (F_o^2 - F_c^2)^2 / \sum (w F_o^2)^2]^{1/2}$		

Table 9-2. Crystal data and structure refinement for REAu₂In₄ (RE=Pr, Nd).

Formula	PrAu ₂ In ₄	NdAu ₂ In ₄
Formula weight	994.13	997.46
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pnma</i> (#62)	<i>Pnma</i> (#62)
Unit cell dimensions	a = 18.420(4) Å b = 4.6202(9) Å c = 7.3760(15) Å	a = 18.4059(18) Å b = 4.6114(5) Å c = 7.4073(7) Å
Volume	627.7(2) Å ³	628.71(11) Å ³
Z, Density(calculated)	4, 10.519 g/cm ³	4, 10.538 g/cm ³
Absorption coefficient	68.452 mm ⁻¹	68.852 mm ⁻¹
F(000)	1652	1656
Theta range for data collection	2.21 to 27.93°	4.94 to 31.38°
Index ranges	-23 ≤ h ≤ 23 -6 ≤ k ≤ 5 -9 ≤ l ≤ 9	-26 ≤ h ≤ 26 -6 ≤ k ≤ 6 -10 ≤ l ≤ 10
Crystal size	0.1x0.05x0.05	0.15x0.05x0.05
Reflections collected / unique	5183 / 819	8100 / 1118
R(int)	0.0522	0.0454
Completeness to θ _{max}	97.2 %	97.1%
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	819 / 0 / 44	1118 / 0 / 44
Goodness-of-fit on F ²	1.128	1.140
Final R indices [I>2σ(I)]	R1 = 0.0330, wR2 = 0.0755	R1 = 0.0363 wR2 = 0.0891
R indices (all data)	R1 = 0.0382, wR2 = 0.0778	R1 = 0.0375 wR2 = 0.0898
Extinction coefficient	0.00295(16)	0.00269(17)
Largest diff. peak and hole	4.566 / -2.579 e/Å ³	7.337 / -3.438 e/Å ³
$R1 = \frac{\sum F_o - F_c }{\sum F_o } \text{ and } wR2 = [\sum (F_o^2 - F_c^2)^2 / \sum (w F_o^2)^2]^{1/2}$		

Table 9-3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for REAu_2In_4 (RE = La, Ce).

Atom	Wyckoff Position	x	y	z	U(eq)*
Au(1)	4c	2820(1)	2500	5291(1)	12(1)
Au(2)	4c	376(1)	2500	7417(1)	13(1)
La	4c	1406(1)	7500	5174(1)	12(1)
In(1)	4c	4316(1)	2500	4894(2)	15(1)
In(2)	4c	349(1)	2500	3481(2)	13(1)
In(3)	4c	1841(1)	2500	8215(2)	11(1)
In(4)	4c	1892(1)	2500	2283(2)	10(1)
Au(1)	4c	2825(1)	2500	5314(1)	12(1)
Au(2)	4c	379(1)	2500	7433(1)	12(1)
Ce	4c	1411(1)	7500	5208(1)	11(1)
In(1)	4c	4324(1)	2500	4875(2)	14(1)
In(2)	4c	348(1)	2500	3536(2)	12(1)
In(3)	4c	1844(1)	2500	8234(2)	11(1)
In(4)	4c	1888(1)	2500	2318(2)	10(1)

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

Table 9-4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for REAu_2In_4 (RE = Pr, Nd).

Atom	Wyckoff Position	x	y	z	U(eq)*
Au(1)	4c	2820(1)	2500	5340(1)	12(1)
Au(2)	4c	383(1)	2500	2417(1)	13(1)
Pr	4c	1406(1)	7500	5174(1)	12(1)
In(1)	4c	4316(1)	2500	-106(2)	15(1)
In(2)	4c	349(1)	2500	3481(2)	13(1)
In(3)	4c	1841(1)	2500	8215(2)	11(1)
In(4)	4c	1892(1)	2500	2283(2)	10(1)
Au(1)	4c	2819(1)	2500	351(1)	9(1)
Au(2)	4c	383(1)	2500	2443(1)	9(1)
Nd	4c	1420(1)	7500	251(1)	9(1)
In(1)	4c	4329(1)	2500	-136(1)	10(1)
In(2)	4c	350(1)	2500	-1413(1)	9(1)
In(3)	4c	1848(1)	2500	3268(1)	8(1)
In(4)	4c	1884(1)	2500	-2636(1)	7(1)

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

Table 9-5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for REAu_2In_4 (RE = La, Ce).

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Au(1)	12(1)	14(1)	11(1)	0	0(1)	0
Au(2)	11(1)	16(1)	13(1)	0	1(1)	0
La	11(1)	12(1)	11(1)	0	2(1)	0
In(1)	10(1)	23(1)	12(1)	0	-2(1)	0
In(2)	8(1)	15(1)	16(1)	0	-2(1)	0
In(3)	11(1)	15(1)	9(1)	0	-2(1)	0
In(4)	10(1)	14(1)	6(1)	0	2(1)	0
Au(1)	9(1)	15(1)	12(1)	0	0(1)	0
Au(2)	8(1)	17(1)	12(1)	0	-1(1)	0
Ce	9(1)	14(1)	12(1)	0	-1(1)	0
In(1)	8(1)	22(1)	11(1)	0	2(1)	0
In(2)	6(1)	17(1)	14(1)	0	2(1)	0
In(3)	8(1)	16(1)	8(1)	0	1(1)	0
In(4)	8(1)	15(1)	6(1)	0	-2(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 9-6. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for REAu_2In_4 (RE = Pr, Nd).

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Au(1)	6(1)	9(1)	13(1)	0	0(1)	0
Au(2)	5(1)	12(1)	13(1)	0	1(1)	0
Pr	6(1)	9(1)	13(1)	0	2(1)	0
In(1)	4(1)	16(1)	13(1)	0	-2(1)	0
In(2)	2(1)	12(1)	14(1)	0	-2(1)	0
In(3)	6(1)	11(1)	10(1)	0	-1(1)	0
In(4)	6(1)	11(1)	10(1)	0	-1(1)	0
Au(1)	7(1)	13(1)	7(1)	0	0(1)	0
Au(2)	6(1)	15(1)	7(1)	0	1(1)	0
Nd	6(1)	11(1)	9(1)	0	2(1)	0
In(1)	6(1)	18(1)	7(1)	0	-2(1)	0
In(2)	4(1)	14(1)	8(1)	0	-2(1)	0
In(3)	6(1)	14(1)	4(1)	0	-2(1)	0
In(4)	6(1)	13(1)	2(1)	0	2(1)	0

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

8-3 Results and Discussion:

Structure:

REAu₂In₄ crystallizes as a new structure type, and is composed of a complex Au/In polyanion network in which the rare earth ions are embedded. Figure 9-1 shows the overall structure of the title compound as viewed along the *b*-axis. The Au/In network is a three-dimensional entity composed of In tetramer units shown in Figure 9-2 (A). The bond distances in these tetramers range between 3.1294(17) and 3.1721(13) for In(1)-In(2) in LaAu₂In₄ and NdAu₂In₄ respectively. The bonds between In(2) and In(4) range between 2.9874(17) and 2.9656(13) for LaAu₂In₄ and NdAu₂In₄ respectively, and the In(3)-In(4) bonds range between 2.9878(16) and 3.0346(13) for LaAu₂In₄ and NdAu₂In₄ respectively. These tetrameric units stack along the *b*-axis. Each of the Au atoms forms 7 bonds to the surrounding In atoms with distances ranging from 2.7843(14) Å to 2.8651(8) Å for Au(1) in LaAu₂In₄, from 2.7996 (6) to 2.8054(10) Å for Au(1) in NdAu₂In₄, and from 2.7728(14) to 3.0202(9) Å for Au(2) in LaAu₂In₄ and from 2.7782(14) to 2.9687(9) for Au(2) in NdAu₂In₄. The bonding geometries for the 2 crystallographically unique Au sites are identical; they differ only which In atoms they bind and slightly different distances. The coordination environment for Au(1) and Au(2) can be seen in Figures 9-2 (B) and (C) respectively. Figure 9-2 (D) shows the basic building unit of the InAu polyanion, this unit extends along the *b*-axis and inter-connects to other units in the *ac* plane to generate the three-dimensional architecture. The Au/In

distances listed below agree quite well with other reported Au-In distances of related compounds, and indicates strong metallic bonding between Au/In and In/n atoms.¹⁻⁷

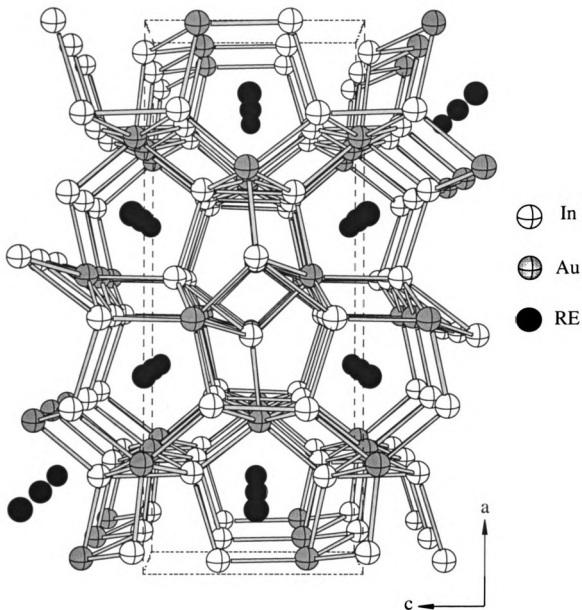


Figure 9-1 Overall structure of REAu_2In_4 as viewed along the b -axis.

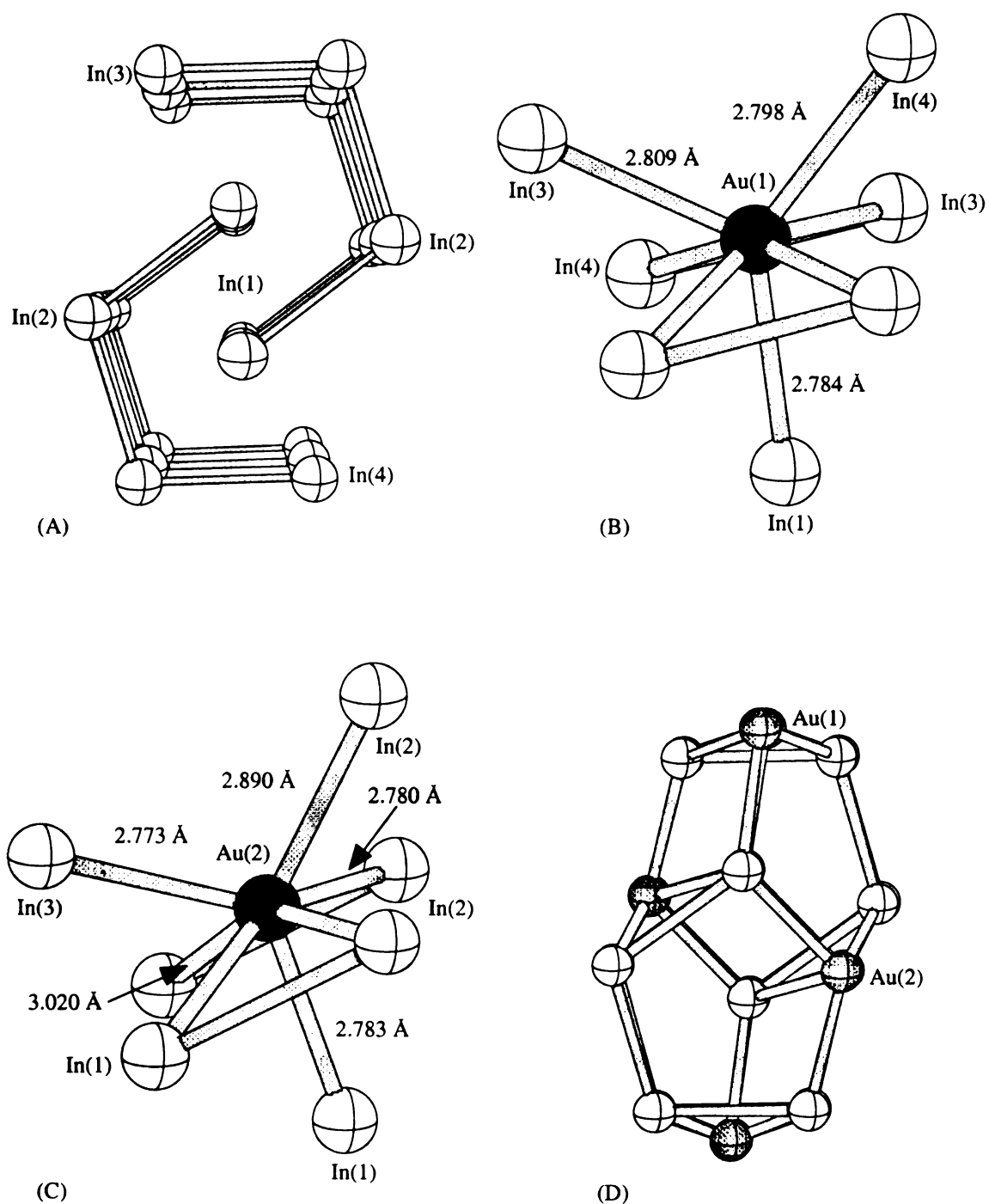


Figure 9-2 (A) REAu₂In₄ as viewed along the *b* axis. The Au atoms have been removed to show the In tetramers. (B) The coordination sphere of Au(1) out to 3.3 Å, bond distances listed are for LaAu₂In₄. (C) The coordination sphere of Au(2) out to 3.3 Å, bond distances listed are for LaAu₂In₄. (D) Segment of the Au₂In₄ polyanionic network as viewed along the *b*-axis.

The one crystallographically distinct rare earth ion resides in the center of a pentagonal channel that runs parallel to the *b*-axis. The coordination environment can be seen in Figure 9-3. The rare earth ion is coordinated by 9 In atoms and 5 Au atoms. A complete list of bond distances for REAu₂In₄ (RE = La, Ce, Pr, and Nd) can be found in Table 9-7.

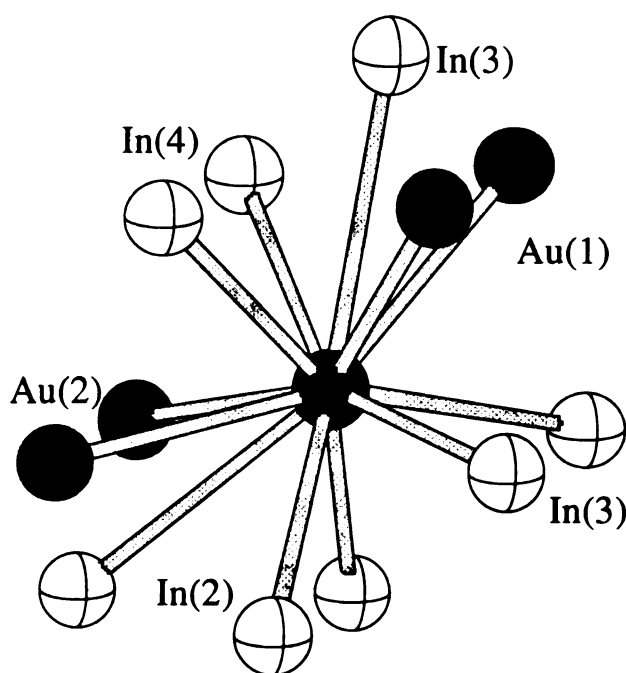


Figure 9-3 The coordination environment of the one crystallographically unique rare earth site in REAu₂In₄.

Table 9-7 Bond distances (Å) for REAu₂In₄ (RE = La, Ce, Pr, Nd)

	RE = La	RE = Ce	RE = Pr	RE = Nd
Au(1)-In(1)	2.7843(15)	2.8002(14)	2.7963(14)	2.8026(11)
Au(1)-In(4)	2.7979(13)	2.8093(13)	2.7973(12)	2.7996(6)
Au(1)-In(3)	2.8089(13)	2.8167(13)	2.8021(12)	2.8052(10)
Au(1)-In(4)	2.8129(8)	2.8135(8)	2.7980(8)	2.8037(10)
Au(1)-In(3)	2.8651(8)	2.8602(8)	2.8389(8)	2.8052(10)
Au(1)-RE	3.5138(9)	3.5013(9)	3.4670(9)	3.4583(7)
Au(2)-In(3)	2.7728(14)	2.7751(13)	2.7660(13)	2.7636(10)
Au(2)-In(2)	2.7798(8)	2.7856(8)	2.7756(8)	2.7780(6)
Au(2)-In(1)	2.7831(14)	2.7875(13)	2.7793(13)	2.7823(10)
Au(2)-In(2)	2.8899(14)	2.8800(14)	2.8566(13)	2.8567(10)
Au(2)-In(1)	3.0202(9)	2.9985(9)	2.9740(9)	2.9689(7)
Au(2)-RE	3.4397(9)	3.4338(9)	3.4059(8)	3.4044(6)
RE-In(4)	3.2872(11)	3.2820(11)	3.2585(10)	3.2590(8)
RE-In(2)	3.2953(11)	3.2921(11)	3.2748(10)	3.2731(8)
RE-In(3)	3.3351(11)	3.3275(11)	3.3081(10)	3.3061(8)
RE-In(2)	3.3943(16)	3.3869(15)	3.3711(15)	3.3682(11)
RE-In(4)	3.5101(15)	3.5135(14)	3.4930(15)	3.4930(11)
In(1)-In(2)	3.1294(17)	3.1534(17)	3.1590(16)	3.1721(13)
In(2)-In(4)	2.9874(17)	2.9896(16)	2.9688(16)	2.9656(13)
In(3)-In(4)	2.9878(16)	3.0190(17)	3.0159(16)	3.0346(13)

There are no gold / gold interactions present in REAu_2In_4 , this is a common feature of compounds composed of Au, In, and a highly electropositive species such as an alkaline earth (AE) or rare earth metal. This is generally thought to be caused by the mutual repulsion of the Au atoms to one another as they are the most electronegative species in the system, and as such, are likely to be reduced to a d^{10} , close shelled configuration. The gold atoms instead of self-bonding; bond with In to form Au_2In_2 parallelograms, a common structural feature of the RE and AE/Au/In structures such as $\text{RE}_2\text{Au}_3\text{In}_5$,⁵ and $\text{La}_2\text{Au}_3\text{In}_4$.⁴ The tremendous structural diversity observed in systems containing these Au_2In_2 units is due to the variety of ways in which this unit can pack and condense to form extended structures. Figures 9-4 (A) (B) and (C) show the wire frame structure of the previously reported $\text{RE}_2\text{Au}_3\text{In}_4$, $\text{RE}_2\text{Au}_3\text{In}_5$ and the title compound respectively. The shaded regions of Figure 9-4 (A) highlight the Au_2In_2 parallelograms of $\text{RE}_2\text{Au}_3\text{In}_4$. In this case they condense to form a ring with a 3-fold rotational axis at the center. These rings are then interconnected through In-In and In-Au bonds. The shaded regions of Figure 9-4 (B) also highlights the Au_2In_2 units of $\text{RE}_2\text{Au}_3\text{In}_5$. In this example these units form edge-sharing trimers, which propagate along the *b*-axis. These trimers are interconnected via corner sharing Au_2In_2 units along the *c*-axis, and are thus not isolated units as they are in $\text{RE}_2\text{Au}_3\text{In}_4$, Figure 9-4 (A). The title compounds also possess edge-sharing parallelograms that propagate along the long axis of the structure forming a ribbon 5 units long. These pentamers are interconnected along the *b*-axis via corner

sharing of the Au_2In_2 units similar to the $\text{RE}_2\text{Au}_3\text{In}_5$ example in Figure 9-4 (B). These figures illustrate that even though these structures are all built from Au_2In_2 parallelograms, the overall structure are quite different because of their mode of connectivity.

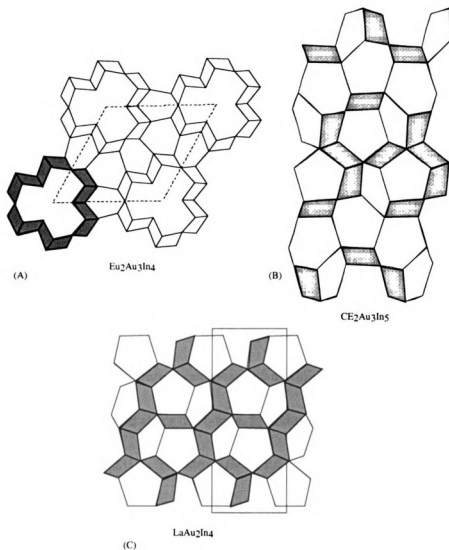


Figure 9-4 (A) Wire frame structure of $\text{RE}_2\text{Au}_3\text{In}_4$ as viewed along the c -axis. Shaded regions highlight Au_2In_2 units. Look closely. See the frog? (B) Wire frame structure of $\text{RE}_2\text{Au}_3\text{In}_5$ as viewed along the a -axis showing the connectivity of the Au_2In_2 units. (C) Wire frame structure of REAu_2In_4 as viewed along the b -axis shading regions are the Au_2In_2 parallelograms which are interconnected by common Au atoms.

A thorough search of the literature found no examples of a phase isostructural to REAu_2In_4 , however it is closely related to the UNi_5Ge_3 structure.¹⁵ Figures 9-5 (A) and (B) show views of UNi_5Ge_3 and REAu_2In_4 respectively, both are projected along the *b*-axis. Both compounds are primitive orthorhombic crystallizing in the *Pnma* space group, also both compounds are composed of parallelograms consisting of Ni_2Ge_2 in the case of UNi_5Ge_3 and Au_2In_2 for REAu_2In_4 . In the case of UNi_5Ge_3 the Ni atoms also occupy opposite corners of the parallelogram, probably for the same reason the Au atoms in RE/Au/In compounds do, that is electrostatic repulsion. Ni atoms as well as Au are often in reduced *d*¹⁰ configurations in intermetallic compounds containing electropositive elements.¹⁶ The major difference between these 2 structures is the extra Ni and Ge atoms that are introduced into the UNi_5Ge_3 lattice because of their smaller atomic radius. These “extra” atoms pack more closely, and lead to a more highly condensed structure. For example the UNi_5Ge_3 structure is composed of an infinite chain of edge sharing Ni_2Ge_2 units, which propagate along the *c*-axis. In addition edge sharing trimers form along the *a*-axis, Figure 9-5 (C). The structure of REAu_2In_4 contains 2 fewer atoms per formula unit, and as a result the atoms are not as tightly packed, and thus adopt a more open, corner sharing connectivity in the *c*-direction, Figure 9-5 (D). The extra Ni atom in UNi_5Ge_3 alters the coordination environment of the uranium atom to a distorted hexagonal channel as compared to the pentagonal channels found in the title compound.

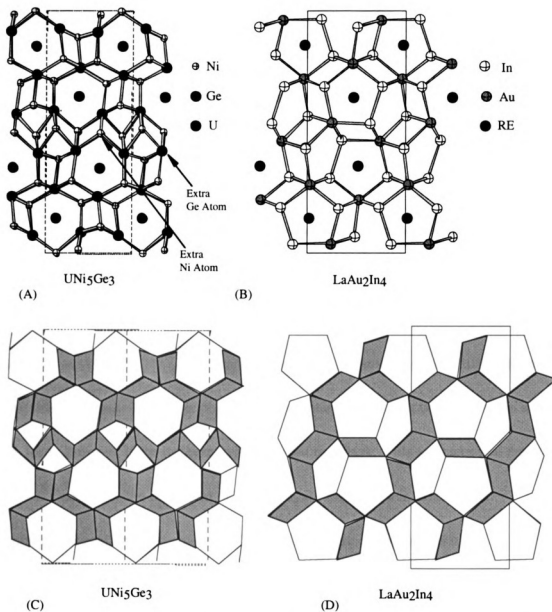


Figure 9-5 (A) The overall crystal structure of UNi_5Ge_3 , as viewed along the b -axis. (B) A view of the overall structure of LaAu_2In_4 along the b -axis. (C) The wire frame structure of UNi_5Ge_3 , as viewed along the b -axis. The shaded regions are Ni_2Ge_2 parallelogram. (D) Wire frame structure of LaAu_2In_4 as viewed along the b -axis to compare the connectivity of the Au_2In_2 units of this structure to the Ni_2Ge_2 units.

Synthesis:

All rare earth analogs of REAu_2In_4 can be produced either by using excess molten In as a flux or by direct combination of the elements. Crystals of REAu_2In_4 grown from the In flux are quite large and are of excellent quality. Figure 9-6 shows a scanning electron micrograph of a LaAu_2In_4 crystal grown from excess In. The products from the direct combination reactions formed as pellet that did not wet the walls of the Al_2O_3 crucible. It was slightly malleable with poor crystal quality. The reactions run in excess In were run at an isotherm of 1000 °C for 72 h. It was found that if the direct combination reaction was stopped after 72 h the target phase was contaminated with AuIn_2 and other unidentified phases. The target phase could be obtained by direct combination in a nearly pure form, however if the isotherm was extended to 5 days. This indicates that the reaction kinetics for the formation of REAu_2In_4 are much slower in the direct combination reaction as compared to the reaction where excess In was used.

Differential thermal analysis performed on LaAu_2In_4 showed no sign of a phase transition up to 1000 °C, and therefore its melting point is above the temperature used for synthesis. Since the formation of REAu_2In_4 results in the formation of a solid, the kinetics of the direct combination reaction would be diffusion limited. The reactions run with excess In, have conditions more like those found in traditional solution chemistry. REAu_2In_4 could either remain dissolved in the excess In and then crystallize during the cooling step, or crystals could form during the isotherm step. Either scenario would lead

to faster reaction kinetics as the reactants would have a much lower energetic barrier to overcome by diffusing through a liquid. The direct combination reaction will proceed quickly at first as the reactants will form a melt at 1000 °C, until the bulk of the reactants have been converted to the target phase which is a solid at this temperature. After this point the reaction will in all likelihood be limited by the rate of diffusion of the reactants through a solid which are, in general, quite slow compared to diffusion through a liquid.

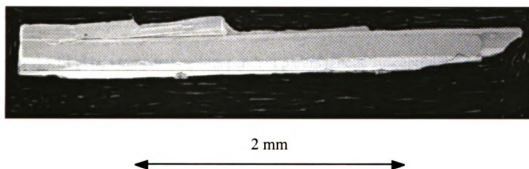


Figure 9-6 Scanning electron micrograph of a LaAu₂In₄ crystal showing that the length of the needle is in excess of 2.5 mm.

Magnetic Measurements:

LaAu₂In₄: Temperature dependent susceptibility measurements performed on LaAu₂In₄ found that it displayed temperature independent diamagnetism, Figure 9-7. The data shown are for the field cooled step only. There was a great deal of data scatter in the 0 field cooled data, a phenomenon still not fully understood. The field cooled data however, are diamagnetic and temperature independent in the range from 300 K to 20 K. Below this temperature the data are again rather scattered and the majority of the data has

a positive susceptibility. This could be due to a small amount of a paramagnetic impurity.

The temperature independent diamagnetic response in the higher temperature regions

indicates that the La has a f^0 electronic configuration and is in the 3+ oxidation state.

Also the Au atoms are reduced to a d^{10} closed shell configuration as is often the case in polar intermetallics.¹⁶ The fact that the susceptibility is negative suggests that the charge carrier concentration is quite small, and that this compound maybe semi-metallic.

Generally metallic compounds that are formally diamagnetic (no unpaired electronic spins) will give a temperature independent paramagnetic susceptibility due to the polarization of the conduction electrons by the applied magnetic field, a phenomenon known as Pauli paramagnetism. If the susceptibility is negative it indicates that there are no, or very few conduction electrons to polarize, and the diamagnetic contribution from the core electrons of the compound dominates.

CeAu₂In₄: The magnetic susceptibility data for CeAu₂In₄ can be seen in Figure 9-8 (A).

The data follow the Curie/Weiss law from 300 K to 2K, and there is no indication that the compound magnetically orders. The effective magnetic moment obtained from the inverse susceptibility versus temperature was $2.41 \mu_B$, which is in reasonably good agreement with the calculated value for a Ce^{3+} ion, which is $2.54 \mu_B$. The Weiss constant is small and negative, indicating weak antiferromagnetic interactions among the rare earth ions. We see from the resulting effective magnetic moment that the Ce^{3+} ion is the only species contributing to the magnetic susceptibility, all other species are diamagnetic.

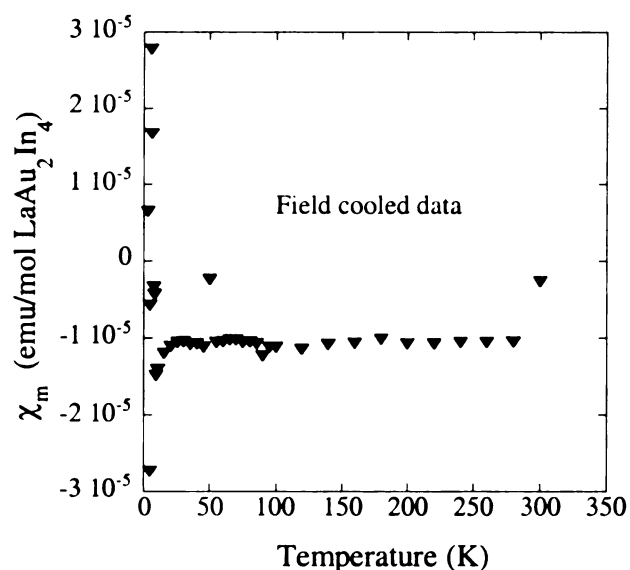


Figure 9-7 Magnetic susceptibility data for LaAu_2In_4 . The diamagnetic response at high temperatures is indicative of semi-metallic behavior. The upturn in the data in the low temperature regions is likely due to a paramagnetic impurity.

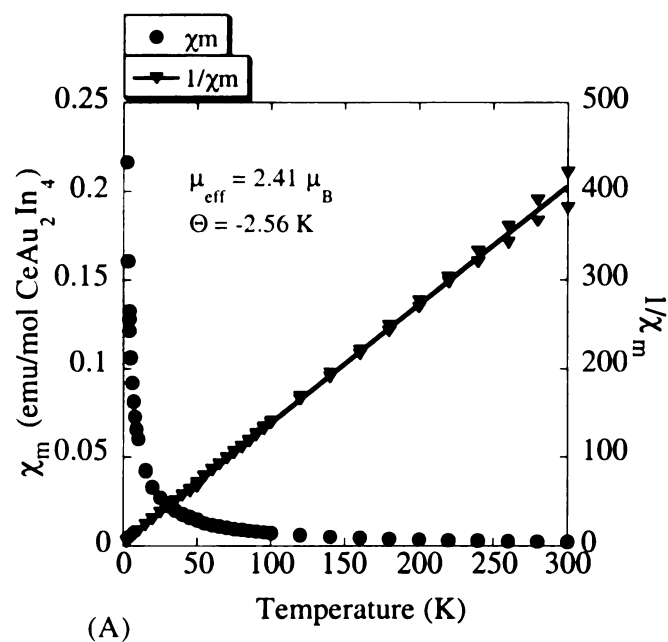
The magnetization data for CeAu_2In_4 can be found in Figure 9-8 (B). There is a linear response in the magnetization curve up to a field of 22 kOe, at which point the slope continuously changes until approximately 30 kOe when it again becomes linear, but with a much shallower slope. The response remains linear up to the 55 kOe. The material does not appear to saturate as the moment still has a strong dependence on the applied field up to the highest attainable field. Also the moment reaches a value of only $1.0 \mu_B$ at 55 kOe, a value that is about half that predicted for a Ce^{3+} ion which is about $2.2 \mu_B$.

PrAu_2In_4 : Figure 9-9 (A) shows the magnetic susceptibility data for PrAu_2In_4 . This compound also obeys the Curie/Weiss law over the entire temperature range investigated with a resulting effective magnetic moment of $3.8 \mu_B$ and a Weiss constant of 2.6 K. The

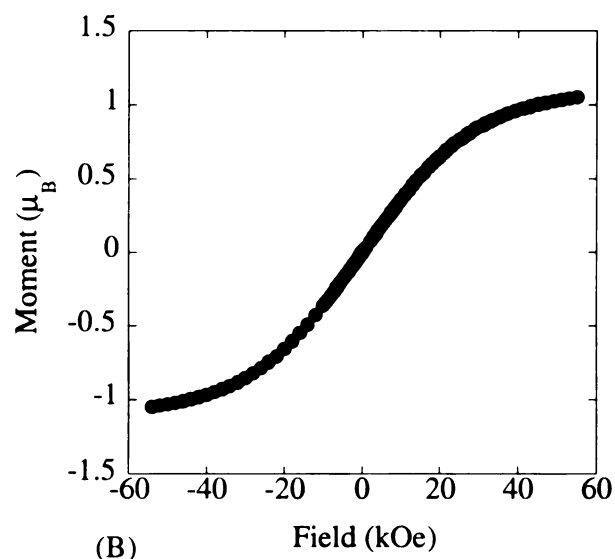
effective magnetic moment obtained from the susceptibility measurements is in good agreement with the theoretical value for a Pr^{3+} ion, which is $3.7 \mu_B$. The small positive Weiss constant indicates very weak ferromagnetic interactions. As was the case with CeAu_2In_4 , the Pr^{3+} ion is the only paramagnetic species in the compound.

The magnetization curve for PrAu_2In_4 can be found in Figure 9-9(B). The moment increases linearly with applied field up to about 15 kOe. At which point the field dependence becomes weaker, and the moment begins to saturate. The field dependence again becomes linear though with a shallower slope similar to the behavior observed for CeAu_2In_4 . This trend continues out to 55 kOe, the highest attainable field. The moment reaches a value of about $1.4 \mu_B$ at 55 kOe which is about half of the value anticipated for the fully saturated moment of a Pr^{3+} ion.

NdAu_2In_4 : The temperature dependent susceptibility data for NdAu_2In_4 is shown in Figure 9-10(A). As was the case with the other analogs there is no magnetic ordering down to 2 K, and the inverse susceptibility data obeys the Curie/ Weiss law from 300 to 2 K. The effective magnetic moment obtained from fitting the data to the Curie/Weiss law was $3.7 \mu_B$. This value agrees quite well with the calculated moment for a Nd^{3+} ion, which is $3.6 \mu_B$. The Weiss constant is small and positive ($\theta = 1.0$ K), indicating weak ferromagnetic interactions between the ions.



(A)



(B)

Figure 9-8 (A) Magnetic susceptibility for CeAu_2In_4 collected with an applied field of 500 Oe. (B) Magnetization data for CeAu_2In_4 collected at 2 K.

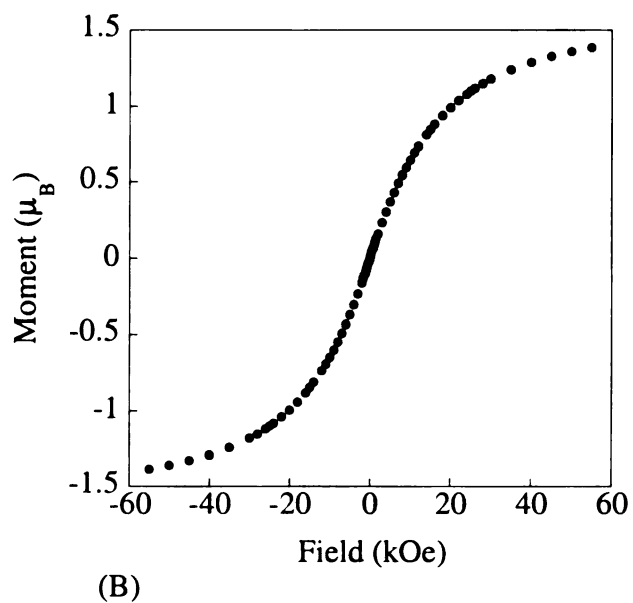
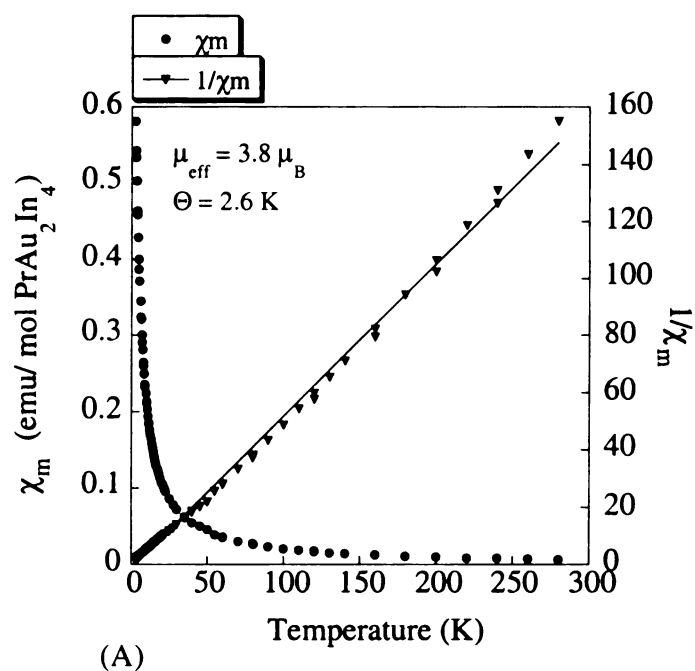
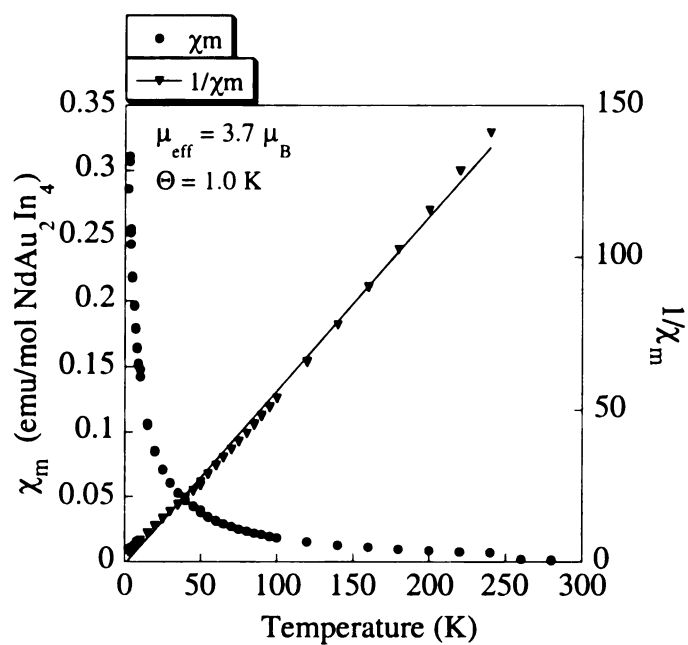
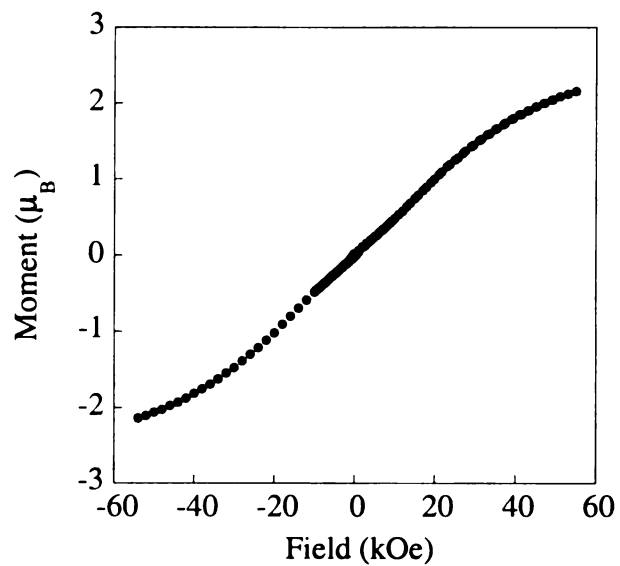


Figure 9-9 (A) Magnetic susceptibility data for PrAu_2In_4 collected with an applied field of 2000 Oe. (B) Magnetization data for PrAu_2In_4 collected at 2 K.



(A)



(B)

Figure 9-10 (A) Magnetic susceptibility data for NdAu_2In_4 collected with an applied field of 2000 Oe. Magnetization curve for NdAu_2In_4 , data collected at 2 K.

The magnetization curve for NdAu_2In_4 , seen in Figure 9-10 (B), is linear up to approximately 40 kOe. Above this field the slope of the curve changes slightly and becomes shallower, but continues to be linear up to the highest applied field of 55 kOe. NdAu_2In_4 shows no sign of saturation and only reaches $2.1 \mu_B$ at the highest field. This is less than $2/3$ the value expected for a saturated system.

Summary: In each of the analogs the magnetic measurements indicate that the rare earth ion is in the 3+ oxidation state as indicated by the measured effective magnetic moments, and that they are only weakly magnetically coupled to the other ions in the compound as evidenced by the small Weiss constants. The poor coupling is likely due to the semi-metallic nature of these compounds. The rare earth ions in REAu_2In_4 are separated by too great a distance for direct magnetic exchange to be effective. Systems of this type often have indirect mechanisms for magnetic exchange. The most common is the Ruderman Kittel Kasuya Yosida (RKKY) mechanism.¹⁷ In RKKY the exchange is mediated by the conduction electrons that are polarized by passing an isolated magnetic moment, like those of a rare earth ion, they then pass the polarization on to adjacent ions. This mechanism is capable of magnetically coupling spins over larger distances. However these systems seem to be semi-metallic as indicated by the diamagnetic behavior of LaAu_2In_4 . RKKY exchange would be poor in semi-metallic systems as the conduction electron concentration would be small. Consequently the magnitude of the magnetic exchange would be small as we observed in the title compounds as the absence of

magnetic order.

The magnetic measurement results also indicate that the rare earth ion is the only species that contributes to the paramagnetic susceptibility, and that the remaining atoms are closed shell and diamagnetic. We can therefore think of the compound as a polar intermetallic with the charges $\text{RE}^{3+} (\text{Au}_2\text{In}_4)^{3-}$.

9-4 Conclusions:

The new compounds REAu_2In_4 ($\text{RE} = \text{La, Ce, Pr and Nd}$) have been presented. They represent a new indium-rich member of the ternary system, and the most indium rich compound in this phase system to date. $\text{RE Au}_2\text{In}_4$ can be made by direct combination of the elements or grown from excess indium. The crystals grown from molten indium were large and of good quality.

The reactions carried out in molten indium proceeded at a much faster rate than the direct combination reactions run at the same temperature. This is most likely due to the fact that the product melts above this temperature as determined by DTA, and the kinetics of its formation are diffusion limited. In the molten indium the diffusion rate for reactants is likely much quicker, and therefore the target phase forms more quickly.

The magnetic susceptibility of LaAu_2In_4 is negative and temperature independent indicating diamagnetic behavior. This points to the compound being semi-metallic. The susceptibility for the other analogs obey Curie/ Weiss law from 300 to 2 K and the

resulting effective magnetic moments are in good agreement with those calculated for the corresponding rare earth ions in a 3+ oxidation state. In all cases the Weiss constant was quite small indicating weak magnetic interactions between the ions. This is consistent with the fact that none of the compounds orders magnetically down to 2 K.

This work shows the ability of molten indium reactions to form new and complex intermetallic compounds. The formation of REAu_2In_4 is particularly interesting because of the number of ternary phases already described in this system, and gives credence to the notion of using liquid In as a medium for exploratory intermetallic synthesis.

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Chapter 10

YbAu₂In₄ a New Indium Rich Intermetallic Exhibiting a Novel First Order Valence Transition

10-1 Introduction:

Over the last decade considerable attention has been given to systems of the type Yb/M/In where M is a coinage metal such as Cu, Ag or Au due to their anomalous valence fluctuation and heavy fermion behavior. Of particular interest are the series of compounds YbCu_{5-x}In_x.^{1, 2} These compounds together with their Ag and Au analogs³ display a variety of mixed and intermediate valent behavior including: temperature induced first order valence fluctuations from Yb³⁺ to Yb²⁺, and pressure induced valence transition.⁴ These systems have been indispensable in helping more fully understand the physical phenomenon underlying these behaviors.

Much effort has been focused on synthesis and characterization of new RE/TM/In (TM = Ni, Pt, Pd, Cu, and Au) especially with RE = Ce, Eu and Yb, due to their ability to have multiple oxidation states. This effort hopes to produce new compounds that display valence fluctuation and heavy fermion behavior. The predominance of the work involved the RE / 3d transition metal systems such as LaNi₃In₆,⁵ Ce₄Ni₇In₈,⁶ and CeNiIn₄.⁷

Also a large class of compounds of the type RE/Au/In has been reported and includes $\text{RE}_2\text{Au}_3\text{In}_5$,⁸ REAuIn ,⁹ REAu_2In ,¹⁰ and $\text{RE}_2\text{Au}_2\text{In}^{11}$.

We describe here a new indium rich member of the Yb/Au/In system, YbAu_2In_4 . This compound is an interesting discovery for several reasons. First, it is the most In rich compound thus far reported for the Yb/Au/In phase diagram. Its discovery is likely a reflection of the fact that it was produced from reactions carried out in excess liquid indium. The second point of interest is the fact that this compound is unique to flux synthesis. Several attempts to produce it by direct combination reactions failed. Finally, YbAu_2In_4 exhibits a first order temperature induced valence fluctuation where evidently the high temperature form is diamagnetic containing Yb^{2+} ions, and the low temperature form has Yb^{3+} . At elevated temperatures YbAu_2In_4 displays diamagnetic behavior, and as the temperature is decreased to 15 K the magnetic susceptibility of the compound increases dramatically and become paramagnetic and follow a Curie Weiss law. Presented here are the crystal structure and magnetic measurements of this unusual compound.

10-2 Experimental Section:

Reagents:

All materials were used as received without further purification. Yb metal(ingot, 99.9%, Chinese Rare Earth Information Center, Inner Mongolia, China), Au(ingot,

99.9%, Research Chemicals , Phoenix, AZ), and In (3-5 mm teardrops, 99.5%, Cerac, Milwaukee, WI).

Synthesis:

1 mmol Yb metal, which was finely ground with a file, 3 mmol Au metal slivers and 15 mmol In were combined in an Al_2O_3 crucible then flame sealed under a reduced atmosphere of 10^{-4} mbar in a fused silica tube. The reactants were then heated to 1000 °C over the course of 12 h, then held at 1000 °C for 72 h, before ramping down to room temperature over the course of 48 h. The compound was isolated from the excess indium by span centrifugation. This was carried out by flame sealing the reaction tube fitted with a coarse frit into a Pyrex tube under a similar atmosphere as was used during the synthesis. The product was heated to 300 °C for 15 min, then spun in a centrifuge for 10 min. This process was repeated 3 times to ensure effective removal of In. The remaining In, which tended to wet the surface of the product, was etched away by soaking in glacial acetic acid for 24 to 48 h. The acetic acid did not etch the product noticeably, though the surface of some crystals, which are normally metallic silver in color, were gold coated by the etch.

Several attempts to make YbAu_2In_4 by direct combination of the element failed. The elements were combined in an Al_2O_3 tube in their stoichiometric ratios and heated for 5 days at 1000 °C. This did not yield the target phase nor did reactions run by arc melting or using a radio frequency induction furnace.

X-ray crystallography:

Single crystal X-ray diffraction data were collected at room temperature using a Bruker AXS SMART CCD diffractometer with graphite monochromatized Mo K α ($\lambda = 0.71073$ Å) radiation. Unit cell refinement and data merging were done with the SAINT program, and an empirical absorption correction was applied using the program SADABS.¹² The original determination of the unit cell of YbAu₂In₄ lead to a monoclinic cell with lattice parameters: $a = 7.6536$ (19) Å, $b = 4.5424$ (11) Å, $c = 9.591$ (2) Å and $\beta = 107.838(4)^\circ$. No hkl extinction condition was found, indicating the cell was primitive. The program XPREP was used to determine the space group. The mean $|E^2 - 1|$ value was 0.81 suggesting a centrosymmetric space group. The only systematic absence was the $0k0$ $k = 2n$, which yielded two possible space groups $P 2_1$ and $P 2_1 / m$. Based on the mean $|E^2 - 1|$ value the centrosymmetric option, $P 2_1 / m$, was chosen. The details of the data collection and crystallographic refinement of YbAu₂In₄ can be found in Table 10-1. A list of the atomic positions and isotropic displacement parameters are listed in Table 10-2, and the anisotropic displacement parameters can be found in Table 10-3.

Phase identity and purity of the product was determined by powder x-ray diffraction experiments that were carried out on an Inel diffractometer using Cu K α radiation. Experimental powder patterns were compared to patterns calculated from the

structural refinement. Powder patterns were calculated using Cerius² modeling software.¹³

Elemental Analysis:

Semi-quantitative microprobe elemental analysis was performed on several single crystals including the crystals used for the single crystal x-ray diffraction experiments.

Spectra were collected on a JEOL JSM 35C scanning electron microscope equipped with a Tracor Noran energy dispersive spectrometer with the NorvarTM window capable of standardless quantitation of elements with $Z \geq 4$. Spectra were collected with an accelerating voltage of 25 kV and 60 s acquisition times. The quantitative elemental content varied greatly from sample to sample ranging from 1:4.2 : 2.6 for Yb, Au and In respectively to 1: 2.0 : 4.2 for Yb, Au, and In respectively. The reason some of the samples are Au rich is likely due to the coating they received during the isolation process. The samples that more closely match the atomic ratios predicted from the crystal structure refinement were not coated.

Table 10-1. Crystal data and structure refinement for YbAu₂In₄.

Empirical formula	YbAu ₂ In ₄
Formula weight	1026.26
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system / Space group	Monoclinic / P 2 ₁ / m
Unit cell dimensions	a = 7.6536(19) Å α = 90°. b = 4.5424(11) Å β = 107.838(4)°. c = 9.591(2) Å γ = 90°.
Volume	317.41(13) Å ³
Z	4
Density (calculated)	10.738 g/cm ³
Absorption coefficient	74.741 mm ⁻¹
F(000)	848
Theta range for data collection	5.01 to 30.98°.
Index ranges	-10 ≤ h ≤ 10, -6 ≤ k ≤ 6, -13 ≤ l ≤ 13
Reflections collected / Unique	3939 / 1079 [R(int) = 0.0501]
Completeness to theta = 27.11°	95.7%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	1079 / 0 / 43
Goodness-of-fit on F ²	1.101
Final R indices [I > 2σ(I)]	R1 = 0.0466, wR2 = 0.1205
R indices (all data)	R1 = 0.0487, wR2 = 0.1218
Largest diff. peak and hole	5.322 and -6.694 e.Å ⁻³

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \text{ and } wR2 = \left[\frac{\sum (|F_o|^2 - |F_c|^2)^2}{\sum (w |F_o|^2)^2} \right]^{1/2}$$

Table 10-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for YbAu_2In_4 .

Atom	Wyckoff Position	x	y	z	U(eq)*
Au(1)	2e	2743(1)	2500	596(1)	7(1)
Au(2)	2e	2767(1)	-7500	-4204(1)	7(1)
Yb	2e	1664(1)	-2500	-2117(1)	8(1)
In(1)	2e	-967(2)	2500	-1228(1)	5(1)
In(2)	2e	-1047(2)	-7500	-4288(1)	7(1)
In(3)	2e	4621(2)	2500	3683(1)	8(1)
In(4)	2e	4959(2)	2500	-1287(1)	5(1)

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

Table 10-3. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for YbAu_2In_4 .

Atom	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Au(1)	9(1)	6(1)	5(1)	0	0(1)	0
Au(2)	9(1)	8(1)	3(1)	0	2(1)	0
Yb	14(1)	7(1)	3(1)	0	2(1)	0
In(1)	5(1)	9(1)	2(1)	0	2(1)	0
In(2)	9(1)	10(1)	4(1)	0	-2(1)	0
In(3)	13(1)	10(1)	3(1)	0	4(1)	0
In(4)	5(1)	7(1)	2(1)	0	-1(1)	0

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

Differential Thermal Analysis:

Differential thermal analysis (DTA) was carried out with a Shimadzu DTA 50. Samples were placed in a carbon coated fused silica ampoule in order to prevent glass attack upon melting of the product, and then flame sealed under a reduced atmosphere. An α -Al₂O₃ tube was used as a standard reference. Melting point determination was done by heating the sample at a rate of 10°C per minute up to 1000 °C, then cooled to 150 °C then the cycle was repeated at the same heating rate.

Magnetic Measurements:

Magnetic measurements were carried out on a Quantum Design MPMS SQUID magnetometer. Measurements were performed on hand selected single crystals, which were ground and screened by powder x-ray diffraction to verify phase identity and purity. The powder was placed in an envelope made of Kapton tape. Magnetic susceptibility data was collected in both field cooled and zero field cooled modes, with an applied field of 1000 Oe. Magnetization data was also collected at 2K with field sweeping from - 55 kOe to 55 kOe.

9-3 Results and Discussion

Structure:

YbAu_2In_4 is a new structure type, but has similar building units to other RE/Au/In compounds. The distribution of gold atoms in YbAu_2In_4 is similar to that of REAu_2In_4 , presented previously,¹⁴ as there are no gold / gold contacts, but instead they occupy the opposite sides of Au_2In_2 parallelograms. This is a common feature of RE/Au/In systems and is most likely a result of the Au atoms being the most electronegative elements in the structure and thus electrostatically repulsed. These parallelograms condense to form a complex three-dimensional Au/In polyanion. The overall structure of YbAu_2In_4 as viewed along the *b*-axis can be seen in Figure 10-1. The main difference between the structures of YbAu_2In_4 and REAu_2In_4 is the connectivity of the In sub-lattice. In REAu_2In_4 the In atoms formed isolated tetramers, which interpenetrated and propagated along the *b*-axis, while YbAu_2In_4 contains only In dimers formed by In(1) and In(2) with a distance of 2.917(2) Å. The remaining In distances are well over 3.2 Å, and are too long to be considered strong bonding interactions.¹⁵

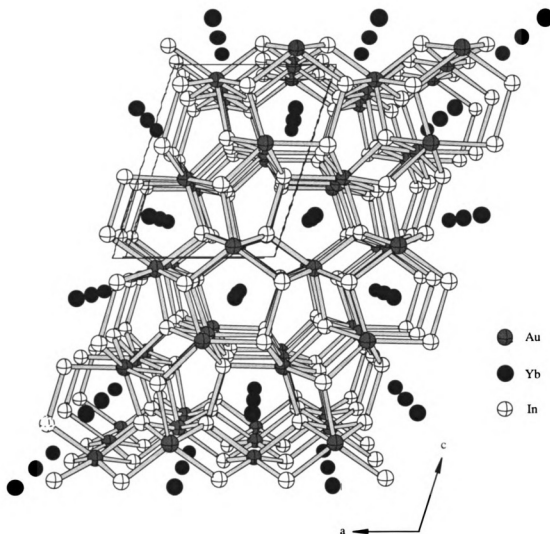


Figure 10-1 The overall structure of YbAu_2In_4 as viewed along the b -axis.

Figures 10-2 (A) and (B) show the bonding environment of the Au(1) and Au(2) atoms of YbAu_2In_4 respectively. As was the case in REAu_2In_4 the 2 crystallographically distinct Au atoms of YbAu_2In_4 have nearly identical bonding environments; both are bound to 7 surrounding In atoms. Au(1) forms 3 bonds to In(1) with 2 at a distance of

2.807(1) Å, and one at 2.8425(15) Å, 3 bonds to In(4) with 2 at 2.824(1) Å, one at 2.8310(15) Å, and one bond to In(3) at 2.8678(15) Å. Au(2) is bound to 3 In(2) atoms, 2 with distances of 2.796(1) Å, and the third at 2.8958(17) Å; 3 bonds are formed with In(3) with 2 of the atoms at 2.9651(11) Å, and one at 2.8070(15). The seventh bond is formed with In(4) at a distance of 2.7869(15) Å.

The coordination environment of the one crystallographically distinct Yb site is shown in Figure 10-2 (C). It is coordinated by 11 atoms, 4 Au and 7 In. The two Yb-Au(1) bond distances are 3.3608(9) Å, the two Yb-Au(2) distances are 3.3038(9) Å, In(1) forms 2 bonds at 3.315(1) Å, In(2) forms three bonds two at 3.339(1) Å, and the third at 3.333(2) Å, In(4) forms the final two bonds with a distance of 3.3053(12) Å.

As was mentioned previously systems of the type M/Au/In (M = alkaline earth or rare earth metal) often contain Au₂In₂ parallelograms, and the great deal of structural diversity found in these compounds comes from the variety of ways in which these building units can condense. We saw in the prior example REAu₂In₄ (RE = La, Ce, Pr and Nd) that these building units condensed as edge sharing units along the *a*-axis and connected along common Au atoms along the *c*-axis. We see that a similar configuration exists for YbAu₂In₄, in that the Au₂In₂ units are condensed to form edge-sharing ribbons along the *c*-axis and these ribbons are connected via corner sharing units along the *a*-axis. This arrangement is depicted in the wire frame structure of YbAu₂In₄ seen in Figure 10-3.

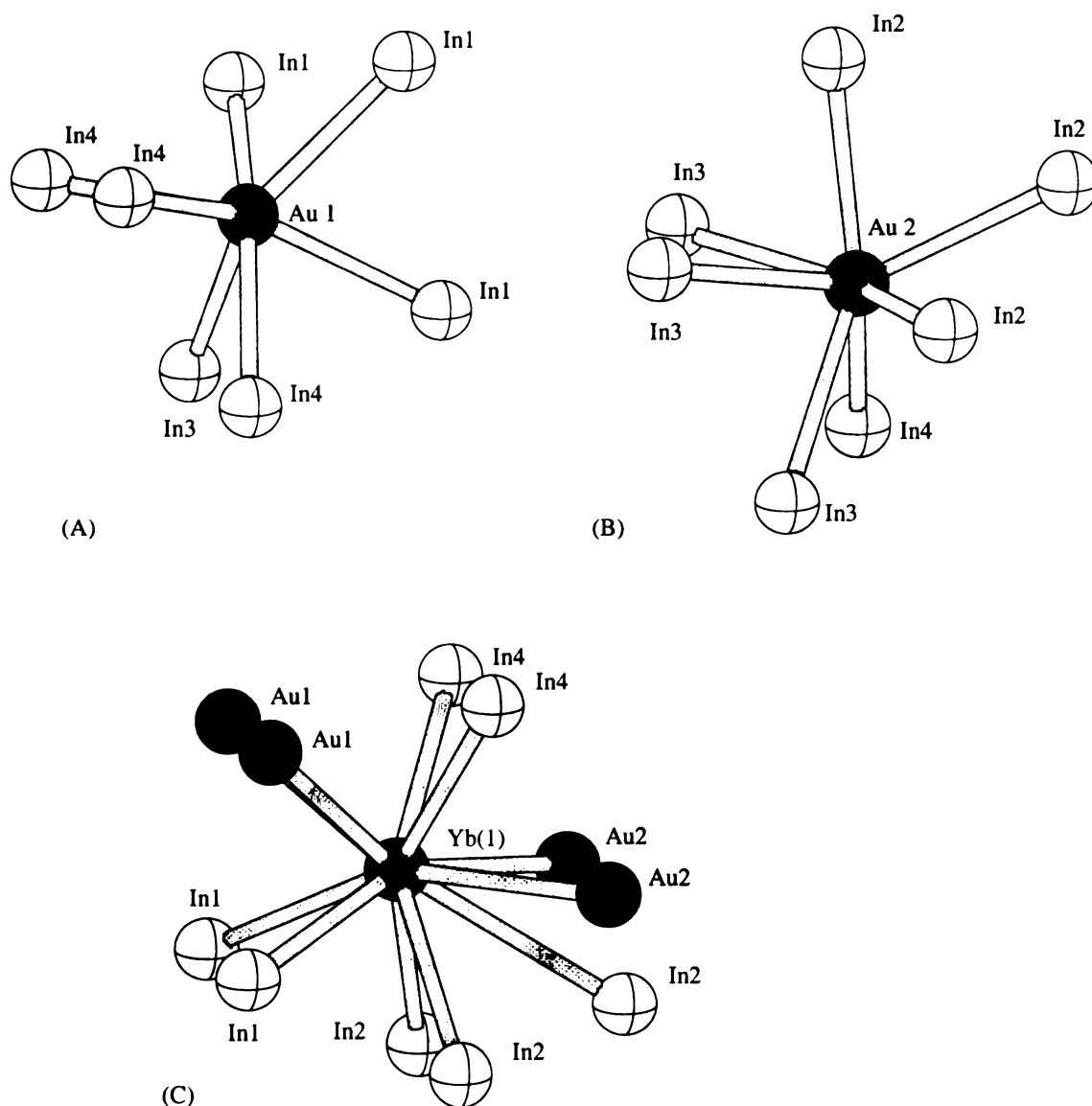


Figure 10-2 (A) Coordination environment for Au(1) out to 3.5 Å. (B) Coordination environment for Au(2) out to 3.5 Å. (C) Coordination environment for Yb out to 4.0 Å. No atoms are shown that have bond distances longer the 3.5 Å as they are too long to be considered bonding.

Synthesis:

YbAu_2In_4 is a product that is exclusive to the In flux. The flux reaction was run at 1000 °C for 72 hours, and yielded large high quality single crystals of the target compound. Several attempts to make this compound by direct combination of the elements failed to yield the monoclinic phase even when the flux heating profile was followed, or when the reaction time was increased to one week. Instead an as yet identified phase or phases were produced. The product was a pellet indicating a good melt. Reactions run in a radio frequency induction furnace, and an arc welder also did not yield the target phase, but instead formed YbAuIn and an In rich AuIn binary. This system presents another example where molten indium was able to stabilize a phase that could not be synthesized by other methods.

YbAu_2In_4 proved to be a rather stable compound. Differential thermal analysis found that it did not undergo any phase transition up to 1000 °C. DTA was performed on single crystals, and they maintained their morphology during the heating process. The powder pattern taken after the DTA experiment was also unchanged from the one taken prior to the experiment.

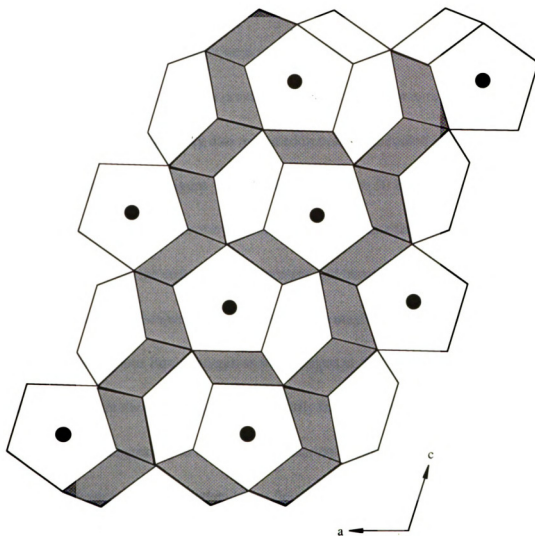


Figure 10-3 Wire frame view of YbAu_2In_4 with shading of the Au_2In_2 parallelograms. YbAu_2In_4 is composed of edge sharing parallelograms propagating along the c -axis and interconnected by corner sharing parallelograms along the a -axis with common Au atoms.

Magnetic Measurements:

Susceptibility measurements were made on single crystals of YbAu_2In_4 hand picked from a product that had been previously screened by powder x-ray diffraction for identity and purity. Susceptibility data collected in both field cooled and zero field cooled modes are shown in Figure 10-4 (A). From 300 K to 50 K, YbAu_2In_4 displays diamagnetic behavior as is evident by the negative temperature independent susceptibility. At 50 K the susceptibility increases and becomes positive, but still has only a weak temperature dependence. This transition may be due to the paramagnetic transition of adventitious liquid oxygen as it condenses at 50 K. A second transition is found at 16 K where the susceptibility dramatically increases over a very small temperature range suggesting a first order transition. Also there is a small amount of hysteresis between the field cooled and zero field cooled data, which is also indicative of a first order transition. Below 16 K the data follow a Curie/Weiss law, Figure 10-4 (B), with a resulting effective magnetic moment of $0.9 \mu_B$. This value is less than a quarter of the value expected for an Yb^{3+} ion, the only ion expected to make a paramagnetic contribution to the susceptibility. It cannot be ruled out that the transition at 50 K is not an intrinsic property of the system as this transition was seen each time the measurements were made.

A possible explanation for this behavior is the Yb ion is undergoing a first order valence transition from the diamagnetic Yb^{2+} state with a filled f shell to an intermediate

valence state with an oxidation state between 2+ and 3+, therefore becoming paramagnetic. First order valence fluctuations of this type are not unprecedented, and have been observed in the system YbCu₄In where the Yb undergoes an Yb³⁺ to Yb²⁺ transition at 20 K¹, although there have been no cases reported where an Yb²⁺ to Yb³⁺ transitions take place.

The magnetization curve for YbAu₂In₄ which was measured at 3K can be seen in Figure 10-4 (C). The moment has a nearly linear dependence on the applied field up to 20 kOe, at which point the dependence begins to weaken up to about 40 kOe. Above 40 kOe the moment regains its linear dependence though the slope is shallower than at lower fields. This behavior is consistent with a paramagnetic system, which is what we would expect based on the proposed valence transition explained above.

The valence transition can be explained in terms of the Yb ion responding to physical pressure on the system. The Yb ion in YbAu₂In₄ is in a state that is prone to valence fluctuation. This situation is not unlike those found the Sm and Tm chalcogenide compounds, which undergo RE²⁺ to RE³⁺ transitions with the application of pressure.¹⁶¹⁷ In this case the pressure is applied by the lattice contraction resulting from the normal thermal contraction of the metal upon cooling. This internal strain of the system likely causes the transition of the “valence fragile” material. As can be seen from the susceptibility data, the transition is fully reversible as a function of temperature. This fact

makes it unlikely that there is not a substantial structural rearrangement as a result of the valence transition, and that it is likely electronic in nature.

Further experiments were conducted to investigate the pressure dependence of the magnetic susceptibility. The compound was pressed with an IR pellet press under a pressure of 10^5 psi then placed in the magnetometer for susceptibility measurements. It was found that the nature of the sample did not change, it was still diamagnetic at high temperatures and underwent the transition at 16 K. The result indicates a few possibilities, first that the pressure induced valence change is reversible as the temperature change is, and after the pressure was released it relaxed to the original state before the susceptibility measurements could be performed. Second the pressure obtained by the pellet press may not be sufficient to bring about a change in the compound, and third the process may be strictly electronic in nature, and cannot be brought about by simply applying mechanical pressure to the system.

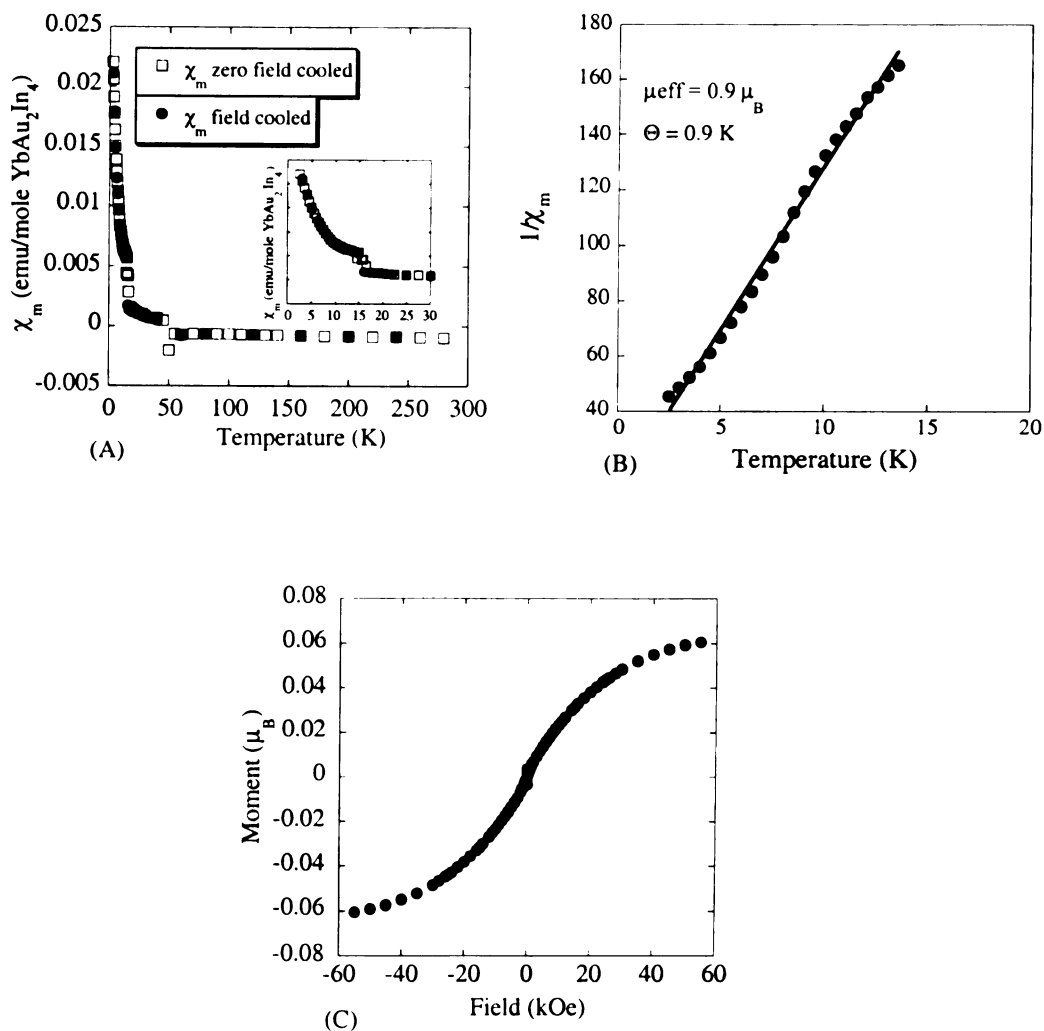


Figure 10-4 (A) Magnetic susceptibility for YbAu_2In_4 showing the first order valence transition at 16 K. (B) The inverse susceptibility plot of YbAu_2In_4 for data below 16 K. (C) Magnetization curve for YbAu_2In_4 at 3 K displaying normal paramagnetic behavior.

10-4 Conclusions and Future Work:

Presented here is the new compound YbAu_2In_4 which forms as a new structure type crystallizing in the monoclinic space group $P 2_1/m$. The structure is composed of a

complex polyanion $[\text{Au}_2\text{In}_4]^{2-}$ the charge is balanced by Yb^{2+} ions, which are placed in the anionic network interstitially. YbAu_2In_4 is diamagnetic over the temperature range 300 to 50 K, at which point it undergoes a transition and begins to display temperature independent paramagnetism. A second transition take place at 16 K such that the Yb ion becomes partially oxidized to $\text{Yb}^{(2+\gamma)}$. The effective magnetic moment measured from 2 to 15 K is only $0.9 \mu_B$, and it is clear from this that the Yb ion is not fully oxidized to a 3+ state rather it is partially oxidized possibly to an intermediate valent state.

These results are preliminary and point to a wealth of future experiments to more fully characterize the nature of this anomalous behavior. These experiments should include pressure dependent magnetic studies, and electrical transport measurements down to liquid helium temperatures. X-ray absorption measurements should be performed at temperatures above and below the transition temperature to better characterize the mixed or intermediate valent nature of the Yb ion. Finally and probably most importantly a low temperature x-ray diffraction study of YbAu_2In_4 should be performed in order to determine if a structural change accompanies the valence transition, or if there is simply an isostuctural volume collapse.

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Chapter 11

Conclusion and Future Work

In the previous chapters I have shown the ability of liquid Ga and In to stabilize new intermetallic phases. In most of the cases presented the flux plays a spectator role acting as a solvent, and is not incorporated into the final structure. This was the case with Ga in each of the systems presented. There were 2 examples of Ga stabilizing phases which could not be made by other methods, these being the $\text{RE}_{3-x}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ ($\text{RE} = \text{Tb}$ and Er), and the new binary phase $\beta\text{-SiB}_3$. In both of these cases it was shown that the compounds could not be synthesized by direct combination of the elements with a radio frequency induction furnace or arc welding reaction routes. In both of these cases the compounds formed only under flux conditions with the rigorous exclusion of Ga despite the fact that it was in large mass excess. Both of these compounds are semiconductors with moderate band gaps. $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ was found to have a band gap of 0.9 eV, and $\beta\text{-SiB}_3$ was found to have a band gap of 2.0 eV.

The band gap in $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$ was determined to be caused by the rare earth vacancy. Band structure calculations carried out on the fully occupied hypothetical compound $\text{La}_3\text{C}_2\text{Si}_8(\text{B}_{12})_3$, found the system to be metallic with a small density of states at the Fermi level. If this electron density was removed by the creation of a vacancy at the

rare earth ions then a band gap of almost 1.0 eV is established according to the calculation. This was in fact found to be the case when absorption measurements were made on $\text{Tb}_{1.8}\text{C}_2\text{Si}_8(\text{B}_{12})_3$.

In the case of $\beta\text{-SiB}_3$, the structure was fully crystallographically ordered with no vacancies or mixed occupancies. This is an important fact because prior to this work there were no reports of B/Si binary phases that were crystallographically ordered. It is likely that this order is responsible for its comparably large band gap ($\alpha\text{-SiB}_3$ has a band gap of only 0.2 eV), and its high resistance to thermal oxidation as compared to other Si/B binary phases.

In the cases of RENiSi_3 and $\text{RE}_5\text{Co}_4\text{Si}_{14}$ Ga again played a purely spectator role in their formation. What is more, both of these compounds can be made by a direct combination of the elements by arc melting. RENiSi_3 (RE = Dy-Er, Yb and Lu) could be made as pure phases by a combination of arc melting and annealing the melt.

The other compounds $\text{RE}_5\text{Co}_4\text{Si}_{14}$ (RE = Ho, Er, Tm and Yb), could not be made as pure phases by direct combination of the elements, and their purity was not improved by any annealing process that was tried. It was concluded that the only way to obtain a pure sample of $\text{RE}_5\text{Co}_4\text{Si}_{14}$ for physical characterization was to hand select single crystals obtained from the molten Ga reactions. Using this method it was possible to evaluate the magnetic properties of the compounds, and to determine their resistance to chemical attack and thermal oxidation. It was found that these compounds are extremely refractory,

showing resistance to oxidation at 1000 °C for prolonged periods of time (24 h). In addition, because crystals of this phase could be produced we were able to observe the different oxide formations on different crystallographic faces. It is apparent from sample preparation for powder experiments, that these materials are quite brittle. It would be interesting to perform stress strain measurements to see if their mechanical properties improve with increasing temperature, as many refractory intermetallics do. This may help determine its suitability as a compound for refractory applications.

Large high quality single crystals of RENiSi_3 could be grown from a Ga melt. These crystals allowed for the evaluation of their anisotropic magnetic behavior. Each of these compounds ordered antiferromagnetically with Néel temperatures that scaled with the de Gennes factor. In each of these compounds the antiferromagnetic order could be broken by the application of a magnetic field applied along the appropriate crystallographic axis in the basal plane. The nature of the magnetic ordering of these compounds is not entirely clear from the experiments that were performed. Single crystals of adequate size and quality for single crystal neutron diffraction can easily be grown from molten Ga. It would be of interest to investigate the zero field magnetic structures of each of these compounds as it is not at all certain that each of the compounds would have the same type of magnetic order.

When indium was used as a molten metal solvent for conducting reactions, we were able to show that the kinetically stable phase $\beta\text{-RENiGe}_2$, which crystallizes in the

YIrGe₂ structure type, could be formed only by the use of molten In. This was a particularly interesting discovery, because β -RENiGe₂ could be formed preferentially to α -RENiGe₂, a thermodynamically stable phase crystallizing in the well known CeNiSi₂ structure, by carefully controlling the reaction times and temperatures. This example showcases the ability of the molten metal to stabilize compounds that cannot be obtained by other methods.

Compounds of the type RETMGe₂ (RE is a late rare earth metal TM = Pd Pt Ir) have been investigated intensely from a magnetic structure perspective, and have been found to display a wide variety of exotic magnetic ordering, as mentioned previously. It would be of great interest to investigate the magnetic structure of β -RENiGe₂, as several of the analogs do appear to order magnetically at low temperatures. This may aid in the understanding of the role the *d* electrons of the transition metal may play in determining what magnetic ordering is favored.

It was also shown that molten indium could produce the compounds RE₂Zn₃Ge₆ (RE = La, Ce, Pr, and Nd). The indium flux was successful in producing these compounds because they require low temperatures, 790 to 820 °C, in order to form. It was found that these compounds decompose upon melting at temperatures lower than 850 °C. We determined that they could also be produced by a direct combination of the elements by heating them at lower temperatures (790 to 820 °C). RE₂Zn₃Ge₆ is

interesting because it falls on the line between polar intermetallic compounds and Zintl phases. The charges of the ions in the system can be balanced by invoking the Zintl/Klemm concept, and as such semiconducting behavior is predicted. Band structure calculations performed on $\text{La}_2\text{Zn}_3\text{Ge}_6$ found that these materials had a very small, but significant, density of states at the fermi level, and therefore semi-metallic behavior was predicted. Indeed the band structure shows a negative band gap that is likely caused by the incomplete electron transfer between the Zn and Ge atoms in the Zn_3Ge_6 sub lattice. Magnetic susceptibility measurements performed on $\text{La}_2\text{Zn}_3\text{Ge}_6$ found temperature independent diamagnetic behavior. Metals generally exhibit temperature independent paramagnetism also called Pauli paramagnetism. Therefore these compounds are not simply metals like those we have listed above like RENiSi_3 or $\beta\text{-RENiGe}_2$, and at the same time while the charges of the system can be balanced, the phases lack a band gap that is predicted for closed shell compounds. It is therefore an intermediate case.

As this compound is a representative of a small but growing group of intermediate case compounds, charge transport measurements should be made on these materials. These include conductivity and thermopower. It maybe that semimetallic compounds such as these offer a unique combination of high conductivity due to the small but finite density of states at the fermi level while still maintaining a large thermopower often found in narrow band gap semiconductors.

The intermetallic compounds $\text{RE}_4\text{Ni}_2\text{InGe}_4$ ($\text{RE} = \text{Dy-Yb}$) were found to be ordered quaternary variants of the Mg_5Si_6 structure. It is the first such compound of this structure type to be grown in bulk form, and is one of the first ordered quaternary compounds containing a rare earth metal, a transition metal, In and Ge. The compound was grown from an indium melt that was required to be rich in rare earth metal. Several attempts to produce it by direct combination reactions failed. It is therefore inferred that these compounds are somehow stabilized by the molten indium or the elevated rare earth concentration. It is not at all clear if this phase is thermodynamically stable at the lower temperatures used to produce it, or if it is a kinetically stable phase. Future work will need to be done on this system by using longer heating times to see if another phase is preferentially formed over time as was the case with $\beta\text{-RENiGe}_2$, or if higher temperatures will cause a different phase to form.

What is also unclear about this compound, is if the multiple peaks in the magnetic susceptibility measurements were caused by an impurity in the sample, or if there is in fact multiple magnetic ordering steps. This is a problem that could be solved by performing a neutron diffraction experiment just below the temperatures that correspond to the maxima in the susceptibility. This will also give insight into the nature of the ordering to see if it is one of the rare earth sub-lattices that is ordering, and not the other and which set of rare earth ions order first.

With regards to the last two structure types which both have the composition REAu_2In_4 the first structure was found with early lanthanide metals (La, Ce, Pr and Nd), and crystallizes in the orthorhombic $Pnma$ space group. The second was found only with Yb and is monoclinic $P2_1/m$. Despite the stoichiometric coincidence of these two phases they are quite different structurally. The orthorhombic phase could be produced by a molten indium reaction or by a direct combination of the elements. The target phase grown from the melt formed as long needle shaped crystals typically in excess of 2 mm in length. Magnetic measurements found that in each case the rare earth ion was the only species contributing to the paramagnetic susceptibility, and in each case the effective magnetic moment was consistent with that expected for RE^{3+} ions. The La analog was found to have a temperature independent diamagnetic susceptibility suggesting that these compounds are likely semi-metallic in nature.

YbAu_2In_4 can only be produced from melts containing excess indium. It grows as large crystals with a needle habit, with dimensions typically in excess of 1.5 mm. This compound was found to have rather anomalous magnetic behavior. At elevated temperatures (greater than 20 K) samples were found to be diamagnetic and temperature independent. This indicates that at these temperatures the Yb ion is in the closed shell f^{14} $2+$ oxidation state. At approximately 16 K the susceptibility abruptly becomes paramagnetic, and no longer temperature independent, but instead roughly obeys Curie /

Weiss law down to 2 K. This is suggestive of a first order valence transition involving Yb in which the diamagnetic Yb^{2+} ion becomes Yb^{3+} which is f^{13} and paramagnetic.

These findings are quite preliminary, and substantial work needs to be done to confirm this finding. The first, would be to do low temperature X-ray diffraction experiments above and below the transition temperature to see if the transition is an isostructural one, or if there is a change in the structure accompanying the transition. Secondly, if the transition happens to be isostructural a large volume collapse accompanying the transition is expected due to the transformation of the larger Yb^{2+} ion to smaller Yb^{3+} ions a feature easily seen by X-ray diffraction experiments. Another experiment that is crucial in characterizing the transition is to do x-ray absorption edge spectroscopy of the Yb ion. The spectrum taken above and below the transition temperature would be diagnostic for the valence transition, and would also be able to tell if there is a mix of Yb^{3+} and Yb^{2+} below the transition temperature as the susceptibility measurements indicate or if the ion is completely converted to Yb^{3+} .

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