SILICON-BASED SEMIMETALS AND SEMICONDUCTORS FOR THERMOELECTRIC APPLICATIONS

By

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ABSTRACT

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The direct conversion between heat and electricity can be achieved by thermoelectric devices. Thus, thermoelectricity is considered as not only an environmentally friendly substitute for compressor-based refrigerators but also a promising energy solution to harvest waste heat. State-of-the-art thermoelectric materials are often comprised of expensive tellurium or germanium elements and hence are hardly suitable for mass production. The silicon-based thermoelectrics, e.g. semimetallic CoSi and semiconducting β -FeSi₂ materials we study here, are composed of abundant elements in nature. They are also chemically stable, non-toxic, and mechanically robust. Despite the above benefits, they exhibit relatively lower efficiencies compared to state-of-the-art materials. In this dissertation, we have intended to understand the thermal and electrical transport in these materials and enhance their thermoelectric performance.

CoSi possesses one of the highest power factors among thermoelectrics due to the sharp features around the Fermi level in its electronic density of states. In order to improve the performance, the effects of p-type dopants, isoelectronic substitutions, n-type dopants, and double doping were systematically studied for arc-melted CoSi samples. The results show that p-type dopants like iron and gallium and n-type dopants like nickel and palladium deteriorate the electrical properties due to the introduction of excess holes and electrons, respectively. Boron and platinum have very limited solubility in CoSi and the segregated impurity phases at grain boundaries are helpful to improve the electrical properties. The isoelectronic substitutions influence the power factor slightly; however, they result in a drastic decrease in the lattice thermal conductivity and hence an enhancement in the figure of merit. In addition, CoSi samples prepared by powder processing were investigated to further reduce the lattice thermal conductivity. Unfortunately, all the consolidated samples show worse performance than the arc-melted CoSi.

 β -FeSi₂ is one of the most cost-efficient thermoelectric materials. Its thermoelectric performance can be tuned by cobalt doping and the highest figure of merit is close to 0.4 at 1000 K. Grain size reduction was also used to reduce the lattice thermal conductivity. However, no improvement has been obtained yet. SiC nanoparticles were dispersed into β -FeSi₂ matrix to form a composite structure. With addition of the nanoparticles, the thermal conductivity is slightly decreased associated with a decrease in the power factor. Although the figure of merit is less than that of some Te-based materials, β -FeSi₂-based thermoelectrics may be suitable in large-scale applications where material abundance and cost are concerns.

DEDICATION

To my loving wife Chengling Gu, wish our love to be eternal. To my cute son You You, wish you full of happiness and vitality. To my dear parents, who support me and believe me every single day.

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Chapter 1 Introduction to Thermoelectricity

1.1 Energy Issues and Thermoelectricity

In the near future, humankind may potentially suffer from a shortage in energy, since the demand for energy is continuously escalating while the traditional energy sources like fossil fuels are being exhausted rapidly. Moreover, the greenhouse effect due to the combustion of fossil fuels can also play a vital role in global warming and climate change [1]. All these concerns impel researchers to address these challenges by two means: either developing renewable energy sources such as solar, wind and geothermal energy, or increasing current energy utilization efficiency.

Among various approaches to promote efficiency, thermoelectric effects are capable of achieving direct conversion between waste heat and electricity and thus have attracted considerable attention for energy recovery. The concept of thermoelectricity can be traced back to 1821, when Thomas Seebeck discovered that a temperature difference between the joints of two dissimilar metals could induce an electromagnetic effect in the loop [2]. Afterward in 1834, Jean-Charles Peltier identified the inverse effect, demonstrating a heating or cooling phenomenon at the junctions of two different conductors when an electric current was applied [2]. Both findings are named after their discoverers as the Seebeck effect and the Peltier effect, respectively. Based on the above two effects, a thermoelectric unicouple composed of p- and n-type semiconductors and metal connectors can be established as shown in Figure 1. If the upper side of the couple is exposed to a heat source and the lower side is fixed to a heat sink (see

Figure 1 left), the hot charge carriers, namely, the holes in the p-leg and electrons in the n-leg, will diffuse down to the cold side and a differential voltage can be developed across the couple via the Seebeck effect. On the contrary, if an electric current is applied through the couple from the n-leg to the p-leg (see Figure 1 right), the charge carriers will absorb the heat at the top junctions and release the heat at the bottom ones by the Peltier effect.



Figure 1 Thermoelectric unicouple for power generation (left) and thermoelectric cooling (right). For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation.

The former effect is capable of creating a thermoelectric device to produce electric power. This kind of thermoelectric power generator can be used to exploit the waste heat produced in power plants or automotive exhaust to enhance vehicle fuel efficiency. Additionally, the Peltier effect can give rise to a thermoelectric refrigerator and air conditioning. Many of other advantages also make these thermoelectric devices highly attractive: they are solid state equipment without vibrating parts and thus are quiet and reliable; they do not require the use of harmful refrigerants and therefore are not detrimental to the environment [3]. It is also promising to combine a thermoelectric power generator with a solar absorber to convert solar thermal energy into electricity [4]. Despite all the benefits demonstrated above, the most successful and

important applications of thermoelectric devices in the past were merely focused on radioisotope thermoelectric generators for deep space exploration and small-scale modules for localized heating and cooling [3]. It is not simple to transfer these devices towards large-scale applications due to the conflict between high manufacturing costs and low conversion efficiencies.

1.2 Thermoelectric Efficiency

Based on the thermoelectric unicouple illustrated in Figure 1 and given that the geometry of the p- and n-legs complies with a certain rule [5], the highest conversion efficiency of a power generator can be obtained as [6]:

$$\eta_{\max} = \frac{T_{h} - T_{c}}{T_{h}} \cdot \frac{\sqrt{1 + Z_{pn}\overline{T}} - 1}{\sqrt{1 + Z_{pn}\overline{T}} + T_{c} / T_{h}}$$
(1)

and the maximum coefficient of performance (COP) for refrigeration can be expressed as [5]:

$$COP_{\max} = \frac{\overline{T}}{T_{\rm h} - T_{\rm c}} \cdot \frac{\sqrt{1 + Z_{\rm pn}\overline{T} - 1}}{\sqrt{1 + Z_{\rm pn}\overline{T} + 1}} - \frac{1}{2}$$
 (2)

where in both cases $T_{\rm h}$ is the absolute temperature of the hot side, $T_{\rm c}$ is the cold side absolute temperature, \overline{T} is the average of $T_{\rm h}$ and $T_{\rm c}$, and $Z_{\rm pn}$ is a parameter dependent on the p- and n-type semiconductors. The expression of $Z_{\rm pn}$ is shown as follows [5]:

$$Z_{\rm pn} = \frac{S_{\rm pn}^2}{\left\{ \left(\frac{\kappa_{\rm p}}{\sigma_{\rm p}}\right)^{1/2} + \left(\frac{\kappa_{\rm n}}{\sigma_{\rm n}}\right)^{1/2} \right\}^2}$$
(3)



Figure 2 (a) Maximum conversion efficiency for power generation, and (b) coefficient of performance for refrigeration as a function of hot side temperature with various dimensionless figure of merit for the unicouple. The cold side temperature is maintained at 300 K and 278 K for (a) and (b), respectively.

where S_{pn} is the differential Seebeck coefficient of p- and n-type semiconductors, κ is the thermal conductivity and σ is the electrical conductivity. It can be seen that both the efficiency and *COP* increase with the increase of Z_{pn} , and thus it is called the thermoelectric figure of merit

for the unicouple. The figure of merit itself has dimensions of the reciprocal absolute temperature. For simplicity, the dimensionless figure of merit $Z_{pn}T$ is generally used. In order to show the relationship between the efficiencies and the dimensionless figure of merit intuitively, the detailed values of η_{max} and COP_{max} at various $Z_{pn}T$ values are presented in Figure 2 (assuming temperature-independent $Z_{pn}T$).



Figure 3 Dimensionless figure of merit vs. temperature for bulk materials investigated over the past decades: (1) $0.9CePd_{2.95}+0.1CePt_3$ [7]; (2) Bi_2Te_3 [8]; (3) $AgPb_{18}SbTe_{20}$ [9]; (4) $Yb_{0.19}Co_4Sb_{12}$ [10]; (5) PbTe+0.055mol%PbI_2 [11]; (6) PbTe+4mol%SrTe+2mol%Na [12]; (7) $Ba_8Ga_{16}Ge_{30}$ [13]; (8) $Hf_{0.6}Zr_{0.4}NiSn_{0.98}Sb_{0.02}$ [14]; (9) $Yb_{14}MnSb_{11}$ [15]; (10) n-type $Si_{0.8}Ge_{0.2}$ [16].

However, the dimensionless figure of merit for the thermoelectric unicouple does not provide instructive information about the selection of p- and n-type materials. Assuming that the two types of materials show the same values of the absolute Seebeck coefficient (considering that the Seebeck coefficients for p- and n-type materials show opposite signs), the thermal conductivity and the electrical conductivity, $Z_{pn}T$ now can be simplified to the material dimensionless figure of merit ZT where Z is expressed as:

$$Z = \frac{S^2 \sigma}{\kappa} \tag{4}$$

In realistic cases, the two types of materials possess comparable transport properties and thus the individual *ZT* value determines the device efficiency. The foremost mission for thermoelectricity is to seek both p- and n-type materials with high *ZT* values.

In spite of decades of research, only a few materials exhibit *ZT* values greater than unity (see Figure 3). This frustrated development of thermoelectric materials has caused the device efficiency to lag far behind that required for practical applications. The reasons for the difficulties to seek high *ZT* materials and the methods to increase the figure of merit for a given material are the foci in the next section.

1.3 Enhancement of the Figure of Merit

Since the figure of merit is determined by the material's physical properties as shown in Equation (4), a straightforward idea to obtain high *ZT* materials is to increase both the Seebeck coefficient and electrical conductivity whereas reduce the thermal conductivity. However, all these properties are interrelated and thus we can hardly tune each property separately. Another key problem is the conflicting change between these thermoelectric properties. For instance, the thermal conductivity of a material is generally the sum of a lattice contribution (κ_1) and an

electronic component (κ_e) as shown in Equation (5):

$$\kappa = \kappa_{\rm l} + \kappa_{\rm e} \tag{5}$$

The contribution of the charge carriers to the thermal conductivity is proportional to the electrical conductivity through the Wiedemann-Franz law [17]:

$$\kappa_{\rm e} = L\sigma T \tag{6}$$

where $L = \frac{\pi^2}{3} \left(\frac{k}{e}\right)^2 \approx 2.45 \times 10^{-8} \text{ J}^2 \text{ K}^{-2} \text{ C}^{-2}$ for free electrons and is called the Lorenz number.

Therefore the increasing thermal conductivity cancels out the benefit of an increase in the electrical conductivity. On the other hand, the Seebeck coefficient usually drops off with the rising electrical conductivity. The extreme examples are the insulators and metals: the former may show very large Seebeck coefficients but they are also poor conductors; the latter are usually good electrical conductors but their Seebeck coefficients approach zero. For the intermediate materials, namely, semiconductors and semimetals, the electrical properties are more suitable for good thermoelectrics.

The partially and completely degenerate semiconductors are employed here to give a quantitative explanation of the interrelationship between the Seebeck coefficient and the electrical conductivity. The carrier concentration (n) for this class of materials can be expressed as [18]:

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} F_{1/2}(\eta)$$
(7)

where m^* is the charge carrier effective mass, k is the Boltzmann constant, h is the Planck

constant and $F_r(\eta)$ is the Fermi-Dirac integral shown as:

$$F_r(\eta) = \int_0^\infty \varepsilon^r f(\varepsilon) \, \mathrm{d}\varepsilon$$

$$f(\varepsilon) = \frac{1}{1 + \exp(\varepsilon - \eta)}$$
(8)

in which $f(\varepsilon)$ is the Fermi-Dirac distribution function, $\varepsilon = E/kT$ is the reduced kinetic energy of carriers and $\eta = E_f/kT$ is the reduced Fermi level and usually greater than -2 for partial degeneracy. The electrical conductivity and the Seebeck coefficient are expressed as [18]:

$$\sigma = \frac{16\sqrt{2\pi}m^{*1/2}e^2}{3h^3} \int_0^\infty \tau_e(E)E^{3/2} \frac{df(E)}{dE} dE$$

$$S = \mp \frac{k}{e} \left[\frac{\left(\frac{5}{2} + \lambda\right)F_{3/2+\lambda}(\eta)}{\left(\frac{3}{2} + \lambda\right)F_{1/2+\lambda}(\eta)} - \eta \right]$$
(10)

where *e* is the elementary electronic charge, τ_e is the charge carrier relaxation time and can be approximated as $\tau_e = \tau_0 E^{\lambda}$ where λ is a constant and τ_0 is a constant pre-factor [19]. The definition of λ in (10) is the same as it is in (9), representing the carrier scattering parameter. The values of λ are usually taken as -1/2 for acoustic phonon-carrier scattering and 3/2 for carriers scattered by ionized impurities. In our discussion, it is more convenient to explain the electrical conductivity with the carrier concentration (*n*) and mobility (μ) as:

$$\sigma = n e \mu \tag{11}$$

The corresponding carrier mobility based on (11) can be deduced from (7) and (9) as:



Figure 4 The Seebeck coefficient, electrical conductivity and power factor as a function of the carrier concentration for a partially or completely degenerate semiconductor.

$$\mu = \frac{2e\tau_0}{3m^*} (kT)^{\lambda} \left(\frac{3}{2} + \lambda\right) \frac{F_{1/2+\lambda}(\eta)}{F_{1/2}(\eta)}$$
$$= \frac{\sqrt{\pi}}{2\Gamma\left(\frac{3}{2} + \lambda\right)} \cdot \frac{F_{1/2+\lambda}(\eta)}{F_{1/2}(\eta)} \cdot \mu_0$$
(12)

and μ_0 is given as [19]:

$$\mu_0 = \frac{4e\tau_0}{3m^*\sqrt{\pi}} \Gamma\left(\frac{5}{2} + \lambda\right) (kT)^\lambda \tag{13}$$

where $\Gamma(x)$ is the Gamma function. The expression of μ_0 is exactly the same as the carrier mobility for a non-degenerate material and it is independent of Fermi level, whereas the mobility for a degenerate material is Fermi-level dependent. Assuming that the material is kept at a certain temperature and its effective mass is proportional to the electron rest mass, meanwhile provided that μ_0 is a constant, then the carrier-concentration-dependent Seebeck coefficient can be calculated according to (7) and (10) and the electrical conductivity can also be determined by (7), (11) and (12) for given values of λ and η . In both cases, the carrier scattering process is assumed to be dominated by acoustic phonons and thus λ is taken as -1/2. As shown in Figure 4, the calculation presents that a saturated $S^2 \sigma$, namely the highest thermoelectric power factor, can be obtained by tuning the carrier concentration for a given material. This modification of electrical properties is typically achieved by replacing some host atoms with dopants and the obtained materials are usually heavily doped semiconductors.



Figure 5 Thermal conductivity of Si-Ge alloys as a function of Ge fraction in Si at room temperature (reproduced from [22]).

Returning to the expressions (4) and (5), one can contemplate two methods to increase ZT: either enhancing the power factor or reducing the thermal conductivity, especially the isolated lattice part. Fortunately, doping not only benefits the electrical properties, but also helps reduce the lattice thermal conductivity. Two ways to reduce the lattice thermal conductivity, i.e. alloying and doping, have long been established. Both the methods introduce impurity atoms into the lattice. The phonons can be strongly scattered due to the mass and size differences between host and impurity atoms [20]. The thermal conductivity reduction by forming solid solutions has been extensively studied for many materials systems such as Si-Ge alloys [21], III-V alloys [22], and Bi₂Te_{3-x}Se_x and Bi_{2-x}Sb_xTe₃ alloys [23]. The effect of solid solution formation on the thermal conductivity for Si-Ge alloys is illustrated in Figure 5.

Another effective way to reduce the thermal conductivity is to extend the complexity of the unit cell for a parent crystal structure. This idea is based on the following expression [24]:

$$\kappa_{\rm l} = \frac{B\bar{M}V^{1/3}\theta^3}{n^{2/3}\gamma^2 T}$$
(14)

where *B* is a constant, \overline{M} is the average atomic mass, *V* is the average volume per atom, θ is the Debye temperature, *T* is the absolute temperature, γ is the Grüneisen parameter and *n* is the number of atoms per primitive unit cell. The lattice thermal conductivity decreases as the number of atoms in the unit cell grows. This idea has been proven quite successful when taking the layered Zintl compounds (e.g. SrZn₂Sb₂) and diamond-like group IV materials (e.g. Si) as the parent crystal structures. A material with much lower thermal conductivity like SrZnSb₂ can be obtained from the former [25]; and the latter can be expanded to I-III-VI₂ (*n*=4), I₂-IV-VI₃ (*n*=6) and I₃-V-VI₄ (*n*=8) compounds, showing reduced thermal conductivity with increasing number of atoms [26]. Moreover, the complex unit cell may also bring about some unconventional thermal properties. For instance, the AgSbTe₂ material (deduced from the PbTe structure)

exhibits extremely low thermal conductivity [27]. The reduction also likely stems from the enhanced anharmonicity in the crystal lattice. A larger Grüneisen parameter represents a stronger anharmonicity in the lattice and thus a lower thermal conductivity as is seen in Equation (14).

Nowadays, a new class of materials with cage-like structures has also attracted much research interest. These materials possess an open crystal framework and thus they show relatively low thermal conductivity themselves. The so-called "rattling" atoms, like rare earth and alkaline earth atoms, can be introduced into the voids of these compounds and thus to scatter the phonons more intensively. On the other hand, the crystalline framework itself can provide for good electrical conduction. The above benefits result in *ZT* values greater than one for these materials, including filled skutterudites and clathrates [28,29].

With the occurrence of nanotechnology, we have witnessed an increasing number of studies on low dimensional thermoelectric materials. In 1993, Hicks and Dresselhaus theoretically predicted that the figure of merit could be enhanced significantly in 2D quantum well structure due to the quantum confinement effect of electrons [30]. This concept has been proven to successfully enhance ZT close to 2.5 for thin film superlattices [31]. Although the thin film materials exhibit alluring ZT values, the chemical and physical stability, fabrication difficulties and manufacturing cost prevent their large-scale application. On the contrary, bulk nanostructured materials are more suitable to be mass produced. The 3D nanocomposites and nanogranular materials have been synthesized to take advantage of numerous interfaces within the materials to reduce the thermal conductivity [32-34]. Generally speaking, the increase of interfaces will also cause a decrease in electrical conductivity [35,36]. The total enhancement stems from the more intensive reduction of thermal conductivity than electrical conductivity.

However, one must keep in mind that it is unrealistic to infinitely minimize the thermal conductivity because the phonon mean free path of a given material cannot be shorter than its interatomic spacing. The "minimal" thermal conductivity [37] eventually constrains the enhancement of the figure of merit by only reducing the denominator in Equation (4). Therefore, this limitation reminds us to consider the other way to increase ZT, namely finding out approaches to enhance the power factor.



Figure 6 Schematic electronic density of states for materials with various dimensions (reproduced from [38]). 3D: bulk crystalline materials; 2D: quantum wells; 1D: nanowires or nanotubes; 0D: quantum dots.

As mentioned above, quantum confinement effects are beneficial to the thermoelectric performance and the improvement can be attributed to an enhanced power factor [30]. The enhancement originates from the unique electronic structure of the low dimensional materials as sketched in Figure 6 [38]. In a simple point of view, the Seebeck coefficient can be understood by the Mott equation [39]:

$$S = \frac{\pi^2 k^2 T}{3e} \left(\frac{\mathrm{d} \ln \sigma(E)}{\mathrm{d} E} \right) \bigg|_{E=E_{\mathrm{f}}}$$
(15)

Provided that the scattering of electrons is independent of energy, then the energy-dependent electrical conductivity is proportional only to the electronic density of states. In the above case, the Seebeck coefficient is the result of the varying rate of the density of states at the Fermi level. As can be seen in Figure 6, abrupt changes can appear in the density of states for low dimensional materials, resulting in rapid variation near the Fermi level and leading to a larger Seebeck coefficient. Usually, the above assumption is too brief and the detailed Mott equation can explain the Seebeck coefficient more clearly as follows [40]:

$$S = \frac{\pi^2 k^2 T}{3e} \left(\frac{\mathrm{d} \ln g(E)}{\mathrm{d} E} + \frac{\mathrm{d} \ln v^2(E)}{\mathrm{d} E} + \frac{\mathrm{d} \ln \tau(E)}{\mathrm{d} E} \right) \bigg|_{E=E_{\mathrm{f}}}$$
(16)

where g is the density of states, v is the average electron drift velocity and τ is the electron relaxation time. The third term in Equation (16) implies that the Seebeck coefficient can be also changed by altering the electron scattering mechanism [41].

In 1996, Mahan and Sofo suggested that a high power factor should take place in any system where sharp discontinuities appear in the material's density of states [42]. The interpretation of their theory is that materials with the similar electronic density of states as low dimensional ones are most likely to exhibit high power factors no matter what length scale they belong to [43]. This boosted theoretical and experimental studies on seeking high power factor bulk materials.

After decades of research, such materials with the unique electronic structure do exist. For instance, the d electrons of transition metals are prone to hybridize with the s or p electrons of



Figure 7 Calculated electronic density of states for RuAl₂ (left) with TiSi₂ structure and Fe₂VAl (right) with BiF₃ structure (reproduced from [44]). The Fermi level is indicated by the dashed line at zero energy.

main group elements, leading to two unique types of density of states in the compounds composed of them. The first type is termed as hybridization gap and the materials are categorized as narrow-band semiconductors (e.g. RuAl₂). The second one is called pseudo gap because the small overlap between the valence and the conduction bands results in a low density of states at the "gap" (e.g. Fe₂VAl). As shown in Figure 7, the densities of states for the two examples both present sharp peaks near the Fermi level [44]. Therefore, one is likely to obtain high power factors for these materials. In general, the position of the Fermi level is not optimized to achieve the highest power factor. The theoretical calculations provide an insightful suggestion that we can improve the electronic properties by tuning the Fermi level to a suitable position where the variation of the density of states is severe.

1.4 Motivation for the Current Work

In the main project, the semimetallic CoSi system is selected as our research object. This material is promising for near-room-temperature thermoelectric applications. The theoretical electronic structure calculations also showed the same feature around the Fermi level for CoSi [45,46] as that for Fe₂VAl, as can be seen in Figure 8. The unique density of states results in a quite large Seebeck coefficient even though its electrical conductivity behaves more like a metal. Since the Fermi level of CoSi is located around the pseudo gap, it should be possible to achieve a higher power factor by tuning its position. We hope to understand the underlying science of the enhancement of the power factor through this investigation and apply the results to other materials systems.



Figure 8 Calculated electronic density of states for CoSi with B20 cubic structure (reproduced from [45]). The Fermi level is indicated by the dashed line at zero energy.

A general approach to adjust the Fermi level is dopant substitution for host atoms. The elements beside both Co and Si in the Periodic Table are candidates for substitutions. In the following text, Chapters 3-5 mainly focus on the substitution effects on the thermoelectric properties of arc-melted CoSi alloys. The materials with chemical formulas like $Co_{1-x}M_xSi$ or $CoSi_{1-x}M_x$ (M = substitution elements) were investigated.

In Chapter 6, the research turns to the preparation of CoSi samples by powder processing. The effects of powder processing under different synthesis conditions were explored. Finally in Chapter 7, another system β -FeSi₂ was studied as a low-cost high-temperature (around 1000 K) thermoelectric material. Its electrical properties could be appropriately tuned by Co doping. In addition, the efforts to prepare nano-grained samples and composite structures are also presented.

Chapter 2 Sample Preparation and Characterization

2.1 Sample Synthesis

The samples in the present work were usually prepared by arc melting the stoichiometric quantities of high purity elements such as Co (99.95%, Alfa Aesar), Si (99.9999%, Alfa Aesar) and the necessary substitution elements on a water-cooled copper hearth under flowing argon. The ingots were flipped and re-melted typically five times to encourage homogeneity. Since a rapid cooling process at an estimated rate of tens of Kelvins per second occurs after melting, the sample tends to crack or crumble once it is completely cooled. To avoid this problem, one should turn over the ingot promptly to re-melt it when it is still hot. The ingots were then sealed in quartz ampoules under vacuum (~ 10^{-5} Torr) and annealed at 900 °C for several days. The arc melting process for FeSi₂ ingots is the same as CoSi. However, the phase obtained from the melt is a mixture of metallic FeSi and α -FeSi₂ phases instead of the semiconducting β -FeSi₂ according to the Fe-Si phase diagram [47]. Therefore, additional processing for these materials is required. The obtained button-like CoSi and FeSi₂ samples are shown in Figure 9.



Figure 9 The arc-melted CoSi and FeSi₂ button-like ingots. The parallelepipeds on the right of each ingot are the typical shapes for transport properties measurements.

In order to form the β -FeSi₂ phase, it is necessary to anneal the ingots under 955 ^oC [47]. However, there are always cracks inside the samples and thus an appropriate section cannot be obtained for transport property measurements. In this case, powder processing was employed to prepare high-quality samples. The standard synthesis procedure is to pulverize the arc-melted FeSi₂ ingots for 30 minutes, press the powders under a pressure of 30 MPa and at a temperature of 1150 ^oC for 8 minutes to form a dense disk, and finally anneal the sealed pellet at 800 ^oC for 100 hours. All the ingot pulverization was completed with an 8004 tungsten carbide vial set in a SPEX SamplePrep 8000M high-energy ball mill. The densification was achieved using a Pulsed Electric Current Sintering (PECS) system from Thermal Technology LLC under argon atmosphere. To minimize oxidation, the vial set was sealed in an argon-filled glove box with Parafilm[®] M barrier film before milling and the powders were also loaded in a glove box and transferred to the PECS system quickly.

The PECS process, also sometimes referred to as spark-plasma sintering, is a pressure-assisted current-activated consolidation technique. This method has been reported to be useful to attain high density samples in a shorter time compared to the traditional hot pressing [48]. Another distinction is that an extremely fast heating rate of about 2000 ^oC/min can be achieved in this system [49]. Recent studies on the sintering mechanisms showed that the pulsing had little effect on the sintering, while the thermal activation only stemmed from the direct current in the form of Joule heating [50]. Some researchers claimed that PECS was beneficial to the thermoelectric properties improvement [51,52]. The grain growth can be suppressed due to the fast heating and consolidation process [53]. Therefore, it is possible to obtain nano-grained
materials, the structures of which are promising for low lattice thermal conductivity. In our work, the influences of ball milling and PECS on the thermoelectric properties of CoSi and β -FeSi₂ samples are investigated. The PECS conditions like temperature, pressure, and ramp rate as well as the ball milling time are the controllable parameters and can be optimized to attain fine microstructures and enhance the thermoelectric performance. The detailed differences between sample preparations will be elucidated in the subsequent chapters where it is necessary.

2.2 Phase Identification and Microstructure Analysis

The phase and crystal structure were generally determined by powder X-ray diffraction (XRD) using a Rigaku Miniflex II desktop X-ray diffractometer with Cu K_{α} (wavelength = 0.154187 nm) radiation at Michigan State University (MSU). The powders were obtained by crushing a portion of each sample with a set of agate mortar and pestle. The XRD patterns were evaluated using a Jade 9.0 software package, which includes a JCPDS XRD database. Some of the samples were also characterized at Oak Ridge National Laboratory (ORNL) using a PANalytical X'pert Pro diffractometer with Cu K_{α} radiation, as independent studies to determine the phase purity.

The microstructures were observed using a JEOL JSM-7500F field-emission scanning electron microscope (SEM) at the MSU Center for Advanced Microscopy. The chemical compositions of certain samples were determined by energy dispersive X-ray spectroscopy (EDS). However, EDS is not sensitive to the light elements, so light element (e.g. B) evaluation was carried out by a physical electronic scanning Auger Nanoprobe (model Phi 680) at ORNL. The backscattered electron (BSE) imaging was selected to distinguish impurity phases from the majority especially when there is a large atomic weight difference between phases. A phase with a larger atomic number (Z-contrast) is usually brighter in color than the lighter one.

2.3 Electrical and Thermal Transport Properties Measurements

The electrical and thermal transport properties measurements are divided to two portions: the low-temperature measurements from 80 K to room temperature (300 K) and the measurements above room temperature, or high-temperature measurements.

For low-temperature measurements, a sample shape of rectangular parallelepiped is required. Generally speaking, the arc-melted samples were sectioned to typical dimensions of $2.5 \times 2.5 \times 7$ mm³ and the PECS samples to $2.5 \times 2.5 \times 10$ mm³ (see Figure 9) with a Buehler IsoMet low speed diamond saw. The measurements were carried out under vacuum (< 10^{-5} Torr) in a Janis model ST-100 cryostat cooled by liquid nitrogen. Figure 10 shows the sample mounting scheme for the cryostat measurement: two thin copper strips were fixed along the length of the sample. One end of the sample was fixed to a copper base and the other to an 800 Ω resistive heater. Copper-constantan thermocouples were soldered directly to the strips. All connections to the sample were implemented using a silver-based epoxy.

Electrical resistivity was obtained using a four-probe DC technique. The two copper leads of the thermocouples acted as the voltage probes, measuring the voltage drop (V_S) when an electric current (I_S) was applied through the sample. The resistivity (ρ) is calculated as:



Figure 10 Schematic sample mounting for low temperature simultaneous measurements of the electrical resistivity, the Seebeck coefficient and the thermal conductivity.

$$\rho = \frac{V_{\rm S}}{I_{\rm S}} \cdot \frac{s}{l} \tag{17}$$

where *s* is the cross-sectional area and *l* is the probe separation between the thermocouples. After measuring the resistivity, the heater was activated by energizing it with another current. A steady temperature difference (ΔT) was established between the probes after a certain time (generally 5 minutes). The Seebeck coefficient (*S*) was then calculated using the induced Seebeck voltage (ΔV) as:

$$S = \frac{\Delta V}{\Delta T} \tag{18}$$

The thermal conductivity (κ) was obtained based on a steady-state condition provided that the

power generated by the heater was totally conducted through the sample to the copper base:

$$\kappa = \frac{V_{\rm H}I_{\rm H}}{\Delta T} \cdot \frac{l}{s} \tag{19}$$

where $I_{\rm H}$ is the electric current through the heater and $V_{\rm H}$ is the heater voltage. All the above data was automatically collected by a LabVIEW program.

The high-temperature electrical resistivity and Seebeck coefficient were simultaneously measured by a commercial ULVAC ZEM-3 system under low-pressure helium atmosphere. This system can carry out measurements from room temperature to 1100 K. The sample geometry and the electrical resistivity measurement are the same as those used in the cryostat. To measure the Seebeck coefficient, three different temperature differences were created and the corresponding voltages were recorded to plot a line of the Seebeck voltage versus the temperature difference. The slope of the line and the contribution of the type-R thermocouples were summed to determine the material's Seebeck coefficient.

The high-temperature thermal conductivity was obtained based on the thermal diffusivity (D), specific heat capacity (C_p) and sample density (d) measurements as:

$$\kappa = D \cdot C_{\rm p} \cdot d \tag{20}$$

The thermal diffusivity and the specific heat capacity were measured using a commercial Netzsch LFA-457 laser flash system (300–1373 K) and a Netzsch DSC-200 F3 system (300–873 K), respectively. Samples used in thermal diffusivity measurements had thin disk geometry with a thickness of 1-2 mm and a diameter of 12.7 mm. The room-temperature sample density was determined by Archimedes method with ethanol as a medium.

2.4 Carrier Concentration and Mobility Measurements

The carrier concentration was determined based on a one-band assumption as follows:

$$R_{\rm H} = \frac{1}{ne} \tag{21}$$

where $R_{\rm H}$ is the Hall coefficient, *n* is the carrier concentration and *e* is the elementary charge (positive for holes and negative for electrons). The low-temperature Hall coefficient measurements (60-300 K) were carried out in a Quantum Design Versalab system with the Electrical Transport Option (ETO) under helium atmosphere. Thin rectangular plate samples of typical dimensions of 2×7×0.5 mm³ were used. Silver leads of diameter 0.127 mm were attached to the sample with a silver-filled adhesive. The sample mounting scheme is shown in Figure 11.



Figure 11 The scheme of low-temperature Hall coefficient measurement.

As shown above, when an electric current (I_x) passes through the sample along the length and a magnetic field (*B*) is applied perpendicular to the sample plane, carriers are driven by the Lorentz force to one side of the sample and a balanced transverse electric field (E_y) as well as a Hall voltage (V_H) is finally established. The Hall coefficient shows a relationship with the Hall voltage as:

$$R_{\rm H} = \frac{E_{\rm y}}{j_{\rm x}B} = \frac{V_{\rm H}t}{I_{\rm x}B}$$
(22)

where *t* is the sample thickness and j_x is the corresponding current density of I_x . The ETO program recorded the virtual Hall resistances (defined by V_H/I_x) induced by different magnetic fields (-3 to 3 Tesla) at each temperature. Then the Hall coefficient at a given temperature was calculated from the slope of the Hall resistance versus the magnetic field curve. The ETO simultaneously measured the electrical resistivity (ρ) through a four-probe DC technique as well. The carrier mobility (μ) was eventually obtained from the Hall coefficient and the electrical resistivity as:

$$\mu = \left| \frac{R_{\rm H}}{\rho} \right| \tag{23}$$

Chapter 3 P-type Dopant Effects on the Thermoelectric Properties of CoSi

3.1 Background and Motivation

Intrinsic CoSi is a diamagnetic semimetal with excess electrons dominating the transport properties [54]. This material crystallizes in the B20 cubic structure (space group $P2_13$) with a lattice constant of 4.443 Å and a theoretical density of 6.59 g/cm³ [55]. The unit cell contains four Co atoms and four Si atoms, as shown in Figure 12. Each Co (or Si) atom is coordinated by seven Si (or Co) atoms with one nearest Si (or Co) atom at 2.286 Å, three second nearest Si (or Co) atoms at 2.329 Å, and three third nearest Si (or Co) atoms at 2.469 Å. The nearest Co-Co and Si-Si distances are 2.727 Å and 2.750 Å, respectively. The former distance is larger than the Co-Co single-bond length (2.46±0.01 Å) proposed by Pauling [56], suggesting weak or no bonds between Co atoms.



Figure 12 B20 cubic structure of CoSi: larger yellow spheres are Co atoms and smaller blue spheres are Si atoms.

In the past decades, substitutions on both Co and Si sites for CoSi have been extensively studied, showing that the neighboring elements in the Periodic Table have considerably good solubility in this material. In general, it is much easier for the materials with the same B20 crystal structure such as MnSi, FeSi and CoGe to form a solid solution with CoSi [57-59]. Among them, FeSi can even form a continuous solid solution with CoSi [58] while the solubility limit for Ge is as high as 67 mol% [59]. On the other hand, the materials with dissimilar crystal structures show lower solubility limit. For instance, the solubility limit for Al in CoSi is between 20 and 30 mol% because CoAl shows another cubic structure (space group $Pm\overline{3}m$) [60] while the solubility limit for Ni is even lower (about 17 mol%) since NiSi is stable with an orthorhombic B31 structure (space group Pmma) [61].

The thermoelectric properties of Fe-doped and Al-doped CoSi alloys have been systematically studied [58,60,62]. Neither of them was beneficial to the thermoelectric performance. However, another p-type dopant, boron (B), was reported to be helpful to enhance the power factor [63]. The study on B substitution was not comprehensive because only one sample with 0.5 mol% B doping was prepared and the reason for the enhancement was not clear [63]. In this chapter, the possible p-type dopants like Ga and B were investigated, and the effects of these p-type dopants on the thermoelectric properties are clarified.

3.2 CoSi_{1-x}Ga_x Alloys

The Ga-doped CoSi samples were all prepared by arc melting. Since Ga has a very low melting point (302.9 K) as well as high vapor pressure, it readily vaporizes compared to Co and

Si during melting. Therefore, the prepared samples always lost some Ga (the weight loss of the ingot was no more than 1%) and the chemical formula only represents the nominal composition. The elements like In and B in the same column as Ga were also attempted. The preparation of $CoSi_{1-x}In_x$ alloys was not successful because In only agglomerated at the bottom of the ingot. The results for $CoSi_{1-x}B_x$ alloys will be discussed in section 3.3.

The XRD patterns for $\text{CoSi}_{1-x}\text{Ga}_x$ alloys with x ranging from 0 to 0.20 only show a CoSi single phase. Figure 13 shows the calculated lattice constant for $\text{CoSi}_{1-x}\text{Ga}_x$ alloys. The linear relation between the lattice constant and the composition suggests the successful formation of solid solutions according to Vegard's law [60]. The solubility limit for Ga in CoSi has not been reached and is more than 20 mol%.



Figure 13 Lattice constant of CoSi_{1-x}Ga_x alloys with various Ga concentration.





Figure 14 Electrical resistivity of (a) $CoSi_{1-x}Ga_x$ alloys with various x and (b) as a function of Ga concentration at 80 K and 300 K, respectively.

Figure 14 displays the electrical resistivity of $\text{CoSi}_{1-x}\text{Ga}_x$ samples. All the resistivity curves show a metallic behavior with a positive temperature coefficient. The resistivity first increases with the increasing Ga concentration up to 10 mol% and then decreases with the further increase of Ga as shown in Figure 14(b). This trend can be ascribed to a two-band conduction model as will be discussed below. All the Ga-doped samples show larger resistivity than the pure CoSi over the entire temperature range except for the x = 0.01 sample. This sample exhibits a little lower resistivity near room temperature compared to CoSi, while it still shows higher resistivity at lower temperature.

Sample	x = 0.00	x = 0.01	x = 0.05
Hall coefficient ($cm^{3}C^{-1}$)	-0.0165	-0.0145	-0.00479
Hall carrier concentration $(10^{20} \text{ cm}^{-3})$	3.78	4.30	13.0
Hall mobility $(cm^2 V^{-1} s^{-1})$	69.5	65.5	11.5

Table 1 Room-temperature Hall results for $CoSi_{1-x}Ga_x$ alloys with x = 0.00, 0.01 and 0.05.

The room-temperature Hall results for the x = 0.00, 0.01 and 0.05 samples are listed in Table 1 and the temperature dependence of the Hall carrier concentration as well as the Hall mobility is shown in Figure 15. The Hall coefficients for samples with $x \ge 0.10$ are too small to be determined, suggesting extremely high carrier concentrations (more than 2×10^{21} cm⁻³) in these samples. Figure 16 shows the temperature-dependent Seebeck coefficient for all Ga-doped samples. The pure CoSi sample shows negative Seebeck coefficients over the entire temperature





Figure 15 Temperature dependence of (a) Hall carrier concentration (calculated with Equation (21)) and (b) Hall mobility for Ga-doped CoSi alloys.



Figure 16 Seebeck coefficients of Ga-doped CoSi alloys with various Ga concentrations as a function of temperature.

range, while the Seebeck coefficients of the x = 0.01 sample are positive below 120 K and become negative at higher temperature. All the other samples doped with more Ga show positive Seebeck coefficients over the investigated temperature range. Generally, the Seebeck coefficient has the same sign as the Hall coefficient, indicating the type of dominant carriers, i.e. negative for electron dominating and positive for hole dominating. However, a contradiction is observed for the 5% Ga-doped sample. This sample shows positive Seebeck coefficients from 80 K to room temperature, whereas its Hall coefficients are always negative at the corresponding temperature. This phenomenon as well as the change of the resistivity is a clear indication of two-band conduction where the conduction and valence bands affect the transport properties simultaneously.

In this conduction model, the conduction band overlaps the valence band to some extent and the negative overlapping energy is defined as ΔE . Since both electrons and holes participate in the transport, the Hall coefficient must be expressed as follows rather than Equation (21) [64]:

$$R_{\rm H} = \frac{p - nb^2}{e(p + nb)^2} \tag{24}$$

where p is the hole concentration, n is the electron concentration and b is the ratio of electron mobility to hole mobility. The concentrations of holes and electrons can be expressed with the reduced Fermi level relative to the top of the valence band and the bottom of the conduction band. The value is positive for the Fermi level within the band and negative for outside the band. The expressions for the carrier concentrations are:

$$p = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi m_{\rm p}^{*} kT}{h^2} \right)^{3/2} F_{1/2}(\eta_{\rm p})$$
(25)

$$n = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi m_{\rm n}^{*} kT}{h^2} \right)^{3/2} F_{1/2}(\eta_{\rm n})$$
(26)

where the subscripts p and n represent holes and electrons and m and η are the effective mass and the reduced Fermi level, respectively. Then ΔE is obtained as:

$$\Delta E = -(\eta_{\rm n} + \eta_{\rm p})kT \tag{27}$$

Provided that acoustic phonons dominate the carrier scattering, the Seebeck coefficient for two types of carriers can be deduced from Equation (10) as follows [58]:

$$S = \frac{S_{\rm p}\sigma_{\rm p} + S_{\rm n}\sigma_{\rm n}}{\sigma_{\rm p} + \sigma_{\rm n}} = \frac{k}{e} \left\{ \frac{p}{p+nb} \left[\frac{2F_{\rm l}(\eta_{\rm p})}{F_{\rm 0}(\eta_{\rm p})} - \eta_{\rm p} \right] - \frac{nb}{p+nb} \left[\frac{2F_{\rm l}(\eta_{\rm n})}{F_{\rm 0}(\eta_{\rm n})} - \eta_{\rm n} \right] \right\}$$
(28)

where σ_p and σ_n are the electrical conductivity for holes and electrons, respectively. Under a rigid band scenario, p-type doping only shifts the Fermi level downward and does not affect the overlap [46]. Using the parameters given in Ref. [65] and assuming that all the parameters are composition independent, the Seebeck coefficient and the Hall coefficient can be calculated as a function of the hole concentration. The parameters used for room-temperature calculations are listed in Table 2 and the results are shown in Figure 17.

Table 2 Parameters used in the two-parabolic-band calculations for the Seebeck coefficient and the Hall coefficient at room temperature. (m_e is the electron rest mass)

Parameter	$-\Delta E$	b	* m _n	$m_{\rm p}^{*}$
Value	0.0156 eV	6.4	2 <i>m</i> _e	6 <i>m</i> e

Ga-doping can move the Fermi level downward to the valence band and thus increase the hole concentration and meanwhile reduce the electron concentration. With the introduction of extra holes, the Seebeck coefficient begins to increase and finally change the sign from negative to positive as can be seen in Figure 17. However, the Hall coefficient is maintained negative even though the Seebeck coefficient has become positive. The reason for the disagreement in sign is the large mobility difference between electrons and holes. As the Hall coefficient is related to the square of b while the Seebeck coefficient is only related to the first power of b, this behavior



Figure 17 Calculated room-temperature Seebeck coefficients (blue squares) and Hall coefficients (pink circles) as a function of the hole concentration for a p-type doped CoSi using the two-parabolic-band model.

can be observed when the value of b is much greater than unity. Besides explaining the interesting contradiction, the two-band model can be used to elucidate the change of the resistivity as well. The electrical conductivity of a material with two types of carriers can be expressed as:

$$\sigma = \sigma_{\rm p} + \sigma_{\rm n} \tag{29}$$

Since the mobility of holes is much smaller than electrons, the rising hole concentration cannot compensate the loss of the mobility initially. However, the further increase of the hole concentration outweighs the mobility loss and finally reduce the electrical resistivity. However,

this cannot explain the fact that the samples with extremely high hole concentrations (i.e. the 20% Ga-doped sample) still show higher resistivity than CoSi. This interesting fact has also been found for Fe and Al doped CoSi alloys. McNeill et al. and Li et al. both proposed a hypothesis that the higher resistivity for Al-doped CoSi samples was ascribed to the additional scattering between electrons and holes [60,66]. The model fitting in the study of Asanabe et al. for Fe-doped CoSi showed enlarged hole effective mass when the dopant level is above 8 mol%, implying that the hole mobility became smaller with the rising hole concentration [58]. Both explanations attributed the enormous increase in the resistivity to the reduction of carrier mobility, which does happen to our Ga-doped samples. As shown in Table 1 and Figure 15(b), the Hall mobility decreases drastically with the rising Ga concentration. Since the electrical resistivity of Ga-doped alloys is escalated while the absolute value of the Seebeck coefficient is smaller than pure CoSi, the thermoelectric power factor is decreased by Ga-doping.

The thermal conductivity continues to decrease with increasing Ga concentration as shown in Figure 18(a). The lattice thermal conductivity can be calculated using Equation (6) with a Lorenz number for free carriers and the results are shown in Figure 18(b). The thermal conductivity reduction totally originates from the reduction of the lattice contribution. The reduction of the lattice thermal conductivity can be understood by the alloying mechanism as we mentioned in section 1.3. Because there are large atomic weight and size differences between Ga and Si, phonons can be scattered quite intensively by the point defects associated with the Ga substitution. The enhanced scattering is more pronounced at low temperature as can be seen in



Figure 18 Temperature dependence of (a) the thermal conductivity and (b) the lattice thermal conductivity for Ga-doped CoSi alloys with various Ga concentrations. The inset in (b) is the lattice thermal conductivity as a function of Ga concentration.

Figure 18(b). The reduction is less near room temperature because the phonon-phonon Umklapp scattering instead of point-defect scattering becomes dominant at higher temperature. The effect of point-defect scattering is roughly proportional to x(1-x), where x is the dopant concentration [62]. Therefore, lower lattice thermal conductivity is expected for higher dopant concentrations up to 50 mol%.



Figure 19 Dimensionless figure of merit as a function of temperature for Ga-doped CoSi alloys with various x.

The dimensionless figure of merit is shown in Figure 19. Even though the thermal conductivity is decreased by Ga doping, the reduction cannot compensate the decreasing power factor. As a result, the 1% Ga-doped sample shows the same room-temperature ZT as the non-doped CoSi while the ZT values for the other samples are much lower.

3.3 CoSi_{1-x}B_x Alloys

In addition to Ga, the other p-type dopants like Fe and Al also led to a severe increase in the resistivity even if only small amounts of dopants were used. The increasing resistivity is definitely detrimental to the power factor. However, in a study on B-doped CoSi, previous researchers found the resistivity was decreased while the Seebeck coefficient was enhanced by 0.5 mol% B doping [63]. They also attributed the enhancement of power factor to the p-type doping effect. Since B is in the same column as Al and Ga in the Periodic Table, it is expected as a p-type dopant when substituting for Si. Based on our previous results and those for Al and Fe doped samples, p-type doping will cause the inverse effect rather than enhance the power factor. Therefore, it is of great interest to investigate the effect of B doping. In this section, we extended the study on $CoSi_{1-x}B_x$ alloys to higher B concentrations (x= 0.00-0.10) and the effect of B substitution is elucidated [67].

All the $CoSi_{1-x}B_x$ alloys in this study were also prepared by arc melting. The B element is from Plasmaterials, Inc. with a purity of 99.9%. In contrast to the pure CoSi, the B-substituted samples were seldom shattered during the preparation. As we shall see, this behavior is due to the unique morphology of these samples.

The XRD patterns show that the CoSi phase is observed in all samples as can be seen in Figure 20(a). However, a secondary phase is detected in the $CoSi_{0.90}B_{0.10}$ sample as shown in Figure 20(b), while this impurity phase is not found in the other B-substituted samples. A successful B substitution effect would be reflected in the change of the lattice parameter due to the large size difference between B and Si atoms (atomic radii of 87 and 111 pm, respectively).



Figure 20 (a) XRD patterns of B-substituted CoSi alloys with various x and (b) magnified region for the x = 0.10 sample with 2θ ranging from 33 to 42 degrees, as indicated by the red dashed box in (a). CoB peaks are indicated based on PDF #03-065-2596.



Figure 21 Lattice constant of $CoSi_{1-x}B_x$ alloys as a function of B concentration.

Consequently, the lattice constant was determined with both the XRD results from MSU and ORNL, as shown in Figure 21. The two independent results agree with each other, showing no pronounced shift in the lattice constant with increasing B concentration. Any difference between the lattice constants is likely due to the experimental effects instead of the compositional differences. The impurity peaks shown in Figure 20(b) were identified as a CoB phase. According to the trend of the lattice constant, we speculate that this impurity phase is likely present in the other samples with lower B concentrations even though the XRD cannot detect it.

Larere et al. found that B segregated at the grain boundaries in their investigation on B-substituted CoSi alloys [68]. Their results imply that the same effect can occur in our samples.



Figure 22 SEM and Auger B map images: (a) and (c) are SEM images of x = 0.02 and 0.10 samples; (b) and (d) are B maps of x = 0.02 and 0.10 samples, respectively. The B distribution is marked by the green color.

In order to verify the above hypothesis, Auger microscopy was used to determine the chemical composition and B distribution for $CoSi_{1-x}B_x$ alloys. As can be seen in Figure 22, B is only present along the grain boundaries as the green phase for both x = 0.02 and 0.10 samples. The chemical compositions within the grains and grain boundaries are listed in Table 3. Both the samples have B only present at the grain boundaries while the B content within the grains cannot be detected. The ratio of Co to B atoms is close to 1, indicating the CoB phase as we observed in XRD patterns. The Auger microscopy provides a strong corroboration of the XRD results and proves our assertion that CoB phase is also present in samples with lower B concentrations. The

	Grains			Grain Boundaries				
Х	В	С	Si	Co	В	С	Si	Co
0.00	0.0	3.0	36.0	61.0	0.0	3.2	37.1	59.7
0.02	0.0	3.1	35.6	61.3	45.5	2.7	1.9	49.9
0.10	0.0	4.9	35.9	59.2	41.9	4.2	2.1	51.8

Table 3 Surface chemical composition (at. %) analyzed by Scanning Auger Nanoprobe.

above two investigations show that the solubility limit for B in CoSi is extremely low, in stark contrast to the reported solubility of 0.5 mol%.

Our collaborators at Northwestern University (NU) carried out atom-probe tomography analysis on the x = 0.02 sample to determine the chemical composition as a function of the distance away from the grain boundaries (the B-rich phase). Their results show that the composition of the B-rich phase at the grain boundaries is also close to CoB (see Table 4). The matrix composition is almost stoichiometric CoSi despite a very low B concentration. The B concentration seems to increase when approaching the grain boundaries. Based on this study, we estimate the solubility limit for B in CoSi is lower than 0.06 mol%. The composition near the center of the tested grain even shows B solubility as low as 0.03 mol%. The existence of Mn is likely due to the impurity of starting Co materials. For CoSi, 1 mol% substitution leads to a replacement of approximately 4.5×10^{20} cm⁻³ host atoms. As a result, this kind of B solubility means no more than 2.7×10^{19} cm⁻³ Si atoms are replaced. Provided that one B atom introduces one hole after doping and based on the semi-quantitative analysis in section 3.2, the increasing

hole concentration can only result in a small downward shift of the Fermi level and thus the p-type doping effect of B is supposed to be negligible.

Element	B-rich phase	$< 1 \ \mu m$ from interface	$\sim 10 \mu m$ from interface
Со	56.21	50.21	50.29
В	43.59	0.03	0.015
С	0.020	0.0022	Not Detected
Mn	0.184	0.0055	0.0024
Si	Not Detected	49.76	49.69

Table 4 Chemical composition (at. %) determined by atom-probe tomography.

The temperature dependence of the electrical resistivity of all the $CoSi_{1-x}B_x$ samples is shown in Figure 23. The resistivity first decreases with increasing B concentration all the way to 2 mol%, then monotonically increases with the further increase of x. The Hall measurements show almost unchanged carrier concentration as shown in Figure 24. The Hall coefficients for all the B-substituted samples are always negative over the entire temperature range, indicating electrons are dominant in transport. These results are consistent with the low B solubility limit in CoSi. The holes introduced by B doping are too few to affect the Hall coefficients as well as the Hall carrier concentration. On the other hand, the mobility is indeed affected by B substitution. Both the x = 0.01 and 0.02 samples show higher carrier mobility than the pure CoSi around room temperature. The mobility for the above two samples is almost proportional to $T^{-3/2}$, indicating



Figure 23 Temperature dependence of the electrical resistivity of $CoSi_{1-x}B_x$ samples.

acoustic phonons dominate the carrier scattering. When the B concentration further increases, the carrier mobility decreases and deviates from the $T^{-3/2}$ relation. Thus, the trend of the resistivity is determined by the compositional dependence of the carrier mobility. The decrease of the mobility with higher B concentrations is understandable because the rising quantities of the B-rich phase at the grain boundaries can intensively enhance the interface scattering. However, it is interesting to elucidate the increasing mobility as found in the x = 0.01 and 0.02 samples. Since the samples used in our study are arc-melted polycrystals, the most influential defect, i.e. cracks, can easily form during the rapid heating and cooling preparation process. The measured resistivity is affected by these defects critically. Figure 25 shows some reported resistivity data



Figure 24 Hall results for $CoSi_{1-x}B_x$ samples as a function of temperature: (a) Hall carrier concentration; and (b) Hall mobility.



Figure 25 Reported electrical resistivity of CoSi (solid lines) and the resistivity of our CoSi_{0.98}B_{0.02} sample (grey dashed line). Data is from [58], [57], [69], [54], [62], [70], and [71] in chronological order. P represents polycrystalline samples and S single crystals.

for pure CoSi samples. We can clearly see huge differences among these studies. The unusually high resistivity of some CoSi specimens can be attributed to the cracks within specimens or the off-stoichiometric compositions. The resistivity of our CoSi_{0.98}B_{0.02} sample is close to those lowest values that have ever been reported, indicating the sample quality is improved by 2 mol% B substitution. The polycrystalline CoSi is a brittle material and tends to crack due to the intergranular failure along the grain boundaries [68]. It has been pointed out that B segregation can enhance the mechanical properties by improving the cohesive strength at grain boundaries

for another intermetallic Ni₃Al system [72]. Our qualitative observation of an increased mechanical integrity of B-substituted samples is consistent with this picture. Thus we hypothesize the same benefit of B to the CoSi intermetallics: modest quantities of B substitution can minimize the possibility of intergranular fracture and hence reduce the microcracks to maintain the low electrical resistivity. The exact effect of B on the fracture performance of CoSi is being investigated by our collaborators at ORNL.

The temperature dependence of the Seebeck coefficients is shown in Figure 26. The Seebeck coefficients for all the samples are negative over the investigated temperature range, consistent with the Hall results. The values are between -90 and -100 μ V/K at room temperature with no clear dependence of B concentrations. Based on the calculated density of states shown in Figure 8, slight p-type doping can probably enhance the Seebeck coefficient because the variation around the Fermi level becomes larger. This is likely the reason for the trivial increase in the Seebeck coefficients for some of the B-substituted samples near room temperature. The power factor is enhanced to 60 μ WK⁻²cm⁻¹ at room temperature for the x = 0.02 sample, a 70% increase relative to our CoSi sample and 50% larger than the typical value of Bi₂Te₃ material [73] (see Figure 27). Some of the other B-substituted samples also show enhanced power factors.

The critical problem for CoSi is the quite high thermal conductivity compared to state-of-the-art thermoelectric materials. B substitution cannot efficiently reduce the lattice thermal conductivity as shown in Figure 28. In the meantime, the electronic contribution to the total thermal conductivity is increased due to the lower resistivity. This disadvantage leads to a



Figure 26 Temperature dependence of the Seebeck coefficient of $CoSi_{1-x}B_x$ samples.



Figure 27 Temperature dependence of the power factor of $CoSi_{1-x}B_x$ samples. The dashed line represents the power factor of the state-of-the-art Bi₂Te₃ material [73].



Figure 28 Temperature dependence of (a) the thermal conductivity and (b) the lattice thermal conductivity of $CoSi_{1-x}B_x$ samples.

room-temperature ZT of only 0.12 for the x = 0.02 sample. A ZT improvement is expected by lowering the lattice thermal conductivity while maintaining the electrical properties. It may be achieved by either isoelectronic substitution or grain size reduction. The results of these two approaches are shown and discussed in the following chapters.

3.4 Summary

According to the calculated density of states, it is promising to obtain a larger Seebeck coefficient by p-type doping because of the sharper features near the top of the valence band. In this chapter, we showed and discussed the thermoelectric properties of Ga- and B-substituted CoSi samples. The solubility limit for Ga in CoSi is more than 20 mol%, while B shows extremely limited solubility below 0.06 mol%. As a result, Ga-doped samples exhibit pronounced p-type doping effects for the semimetallic CoSi. The Seebeck coefficient changes sign from negative to positive with increasing doping level. The Hall coefficient shows opposite signs to the Seebeck coefficients over wide temperature and Ga concentration ranges due to a large electron to hole mobility ratio. With the rising Ga concentration, the hole mobility decreases drastically and thus the increasing hole concentration cannot outweigh the loss of the mobility, resulting in higher resistivity compared to non-doped CoSi. The lattice thermal conductivity is reduced by Ga-doping due to enhanced phonon scattering by point defects. In sum, Ga-doping, like the other p-type dopants such as Fe and Al, is detrimental to the total thermoelectric performance.

On the other hand, B shows trivial p-type doping effect because of the limited solubility. The

extra amounts of B segregate at the grain boundaries in a form of CoB phase. The Seebeck coefficient is almost unchanged and the Hall carrier concentration is maintained the same, showing no dependence of the B concentration. However, B is beneficial to the reduction of the electrical resistivity. This advantage is supposed to originate from the healing effect of B on the internal cracks. The thermoelectric power factor is enhanced due to the improved electrical conductivity for samples with modest B concentrations. It is promising to obtain high-quality polycrystalline intermetallics like CoSi using intentional grain boundary segregations. The important role of B in CoSi alloys will also be seen in the next chapter, where we try to further improve the thermoelectric performance by isoelectronic elemental substitutions.

Chapter 4 Isoelectronic Substitution Effects on the Thermoelectric Properties of CoSi

4.1 Background and Motivation

As we mentioned in section 3.3, some researchers underestimated the thermoelectric power factor of CoSi because the electrical resistivity of their samples was unreasonably high due to extrinsic factors. Modest B substitution is able to improve the quality of the polycrystalline samples and thus maintain the electrical resistivity as low as the handbook value [54]. The decisive drawback for the CoSi_{0.98}B_{0.02} sample is the high thermal conductivity, in spite of the quite high power factor. The large power factor suggests that the electrical properties have been tuned properly. In order to further enhance its thermoelectric performance, we proposed to take advantage of Rh and Ge substitution on Co and Si sites respectively to reduce the lattice thermal conductivity through phonon - point-defect scattering.

Since Rh and Ge are in the same columns as the corresponding host atoms in the Periodic Table, they are supposed to be isoelectronic with Co and Si atoms. So the electronic properties are expected to be unaffected. Ge shows quite large solubility in CoSi as we illustrated in section 3.1 because CoGe and CoSi are isostructural. Even though RhSi is stable with a B31 structure below 1353 K, it has a B20 cubic structure at higher temperature [74]. Since our preparation method is based on arc melting, Rh should possess a large solubility in CoSi because these two monosilicides are also isostructural. In this chapter, the thermoelectric properties of $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ [75] and $CoSi_{0.98-x}Ge_xB_{0.02}$ alloys are presented and discussed. A quantitative analysis of the reduction of the lattice thermal conductivity is highlighted.

4.2 Co_{1-x}Rh_xSi_{0.98}B_{0.02} Alloys

The Rh wire used in this study was from Sigma-Aldrich with a purity of 99.9%. We initially attempted to prepare $Co_{1-x}Rh_xSi$ alloys without B substitution by the same arc melting procedure. However, those samples easily shattered presumably due to intensive internal stress. Thus we could not obtain an appropriate sample to measure the transport properties. We did not meet such issues when preparing $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples, implying that 2 mol% B addition again plays an important role in preserving the sample quality. Although we did not carry out element mapping for these Rh-substituted samples, we assume that B still segregates at the grain boundaries in a form of B-rich phase. The XRD patterns of $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples only show a CoSi B20 structure as can be seen in Figure 29(a). Figure 29(b) displays the lattice constants for these samples. It can be seen that B substitution has trivial influence on the lattice constant of CoSi. The lattice constant varies linearly with the Rh concentration, indicating a solid solution is successfully formed. The solubility limit for Rh in CoSi has not been reached and should be above 20 mol%.

Figure 30 shows the electrical resistivity of the CoSi and $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples as a function of temperature. It can be clearly seen that all B-added samples exhibit similar low resistivity above 200 K due to fewer or no cracks within the samples. The presence of microcracks cannot be excluded for the CoSi sample because its resistivity is much higher than the other samples. At low temperature (around 80 K), the resistivity increases monotonically with the increasing Rh concentration, suggesting enlarged residual resistivity with Rh substitution. The presence of the gap around 300 K is attributed to two independent measurement



Figure 29 (a) XRD patterns of the CoSi and $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples with various Rh concentrations. (b) Lattice constant as a function of the Rh concentration. Closed circles represent $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples and the open square represents CoSi.


Figure 30 Electrical resistivity of CoSi and $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples vs. temperature. systems, and is within the sum of the estimated uncertainties of the two measurement schemes.

The temperature dependence of the Seebeck coefficient of CoSi and $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples is shown in Figure 31. The absolute Seebeck coefficient increases drastically from 15 to 29 μ V/K with increasing Rh concentration at 80 K, which can be understood by Equation (16). The Seebeck coefficient shows a pronounced compositional dependence above room temperature: the value first increases with the Rh concentration and the x = 0.10 sample possesses the largest Seebeck coefficient; whereas the x = 0.20 sample definitely exhibits lower Seebeck coefficients



Figure 31 Seebeck coefficient of CoSi and Co_{1-x}Rh_xSi_{0.98}B_{0.02} as a function of temperature.

than the other two samples from room temperature to 560 K. Compared to CoSi and $CoSi_{0.98}B_{0.02}$, the Seebeck coefficients of the x = 0.10 sample are still lower at temperatures above 400 K. This fact is not consistent with the supposition that Rh does not affect the band structure. Based on our Hall measurements (see Figure 32), we find that the Hall electron concentration increases slightly with the increasing x. In the meantime, the mobility decreases drastically at 80 K with the rising Rh concentration and deviates from the acoustic phonon scattering mechanism. The acoustic phonon scattering is still dominant for all the Rh-substituted samples around room temperature. Thus, the Seebeck coefficient increment at low temperature





Figure 32 Hall results for CoSi and $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples as a function of temperature: (a) Hall carrier concentration; and (b) Hall mobility.

stems from the enhanced carrier scattering, while the decrease at high temperature is attributed to the increasing electron concentration. Based on the above results, Rh substitution still influences the electronic structure even though it is isoelectronic with Co. It likely causes a closing of the pseudo gap or an upward shift of the Fermi level. A better understanding of the change of the electronic structure requires further investigations. As a result, a power factor of $60 \,\mu \text{WK}^{-2} \text{cm}^{-1}$ at room temperature is obtained for the x = 0.10 sample as shown in Figure 33, while the other two Rh-substituted samples show lower power factors at temperatures above 200 K. We did not prepare samples with Rh concentrations over 20 mol% due to the decreasing trend of the power factor.



Figure 33 Power factor of CoSi and Co_{1-x}Rh_xSi_{0.98}B_{0.02} samples vs. temperature.

Figure 34 shows the temperature dependence of the thermal conductivity. Over the entire temperature range, the thermal conductivity drops monotonically with the increasing Rh concentration. The thermal conductivity for the x = 0.20 sample is only 31% of that of the pure CoSi at 80 K and 66% at room temperature. The lattice thermal conductivity can be obtained using the aforementioned method in section 1.3 and the results are shown in Figure 35. It can be clearly seen that the suppression of the thermal conductivity is ascribed to the considerable reduction of the lattice component.



Figure 34 Temperature dependence of thermal conductivity of CoSi and $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples.

In order to illustrate the effect of Rh substitution on the reduction of the lattice thermal conductivity, we use the Debye approximation to evaluate the experimental data. The lattice



Figure 35 Lattice thermal conductivity of CoSi and $Co_{1-x}Rh_xSi_{0.98}B_{0.02}$ samples as a function of temperature. Solid curves are the calculated results using the Debye approximation. The inset is the lattice thermal conductivity as a function of Rh concentration.

thermal conductivity under this approximation can be expressed as [76,77]:

$$\kappa_{\rm l} = \frac{k^4 T^3}{2\pi^2 \hbar^3 v} \int_0^{\theta/T} \frac{x^4 e^x}{\tau^{-1}(x)(e^x - 1)^2} \mathrm{d}x \tag{30}$$

where $x = \hbar \omega / kT$, ω is the phonon frequency, v is the mean sound velocity, θ is the Debye temperature and τ is the phonon relaxation time. The Debye temperature is taken as 625 K as reported in literature [71]. This Debye temperature implies the highest phonon energy of 54 meV in our approximation. According to the inelastic neutron scattering results, the experimental phonon density of states of CoSi almost vanishes when the phonon energy is above 56 meV [78], indicating the Debye temperature used here is quite accurate. The longitudinal sound velocity can be calculated as [79]:

$$v_{\rm l} = \sqrt{\frac{B + \frac{4}{3}G}{\rho}} \tag{31}$$

and the transverse sound velocity can be expresses as [79]:

$$v_{t} = \sqrt{\frac{G}{\rho}}$$
(32)

in both cases, *B* is the bulk modulus, *G* is the shear modulus and ρ is the sample mass density. For a cubic crystal structure, only three elastic constants, i.e. c_{11} , c_{12} and c_{44} , exist and the relations between the elastic constants and the moduli are as follows [80]:

$$B = \frac{c_{11} + 2c_{12}}{3} \tag{33}$$

$$G = \frac{c_{11} - c_{12} + 3c_{44}}{5} \tag{34}$$

With the experimental elastic constants [71], the longitudinal sound velocity is determined as 7313 m/s and the transverse velocity is 4129 m/s at room temperature. The mean sound velocity is calculated as [25]:

$$v = \left(\frac{3}{v_{\rm l}^{-3} + 2v_{\rm t}^{-3}}\right)^{1/3} \tag{35}$$

and it gives rise to a mean velocity of 4600 m/s. The total phonon scattering rate is supposed to be the sum of various scattering processes. In this approximation, we only take into account three types of phonon scattering mechanisms: grain-boundary, point-defect and phonon-phonon Umklapp scatterings. The expression for the scattering rate is [77,81]:

$$\tau^{-1} = \tau_{\rm gb}^{-1} + \tau_{\rm pd}^{-1} + \tau_{\rm Umklapp}^{-1}$$
$$= \frac{v}{L} + A \left(\frac{k_B}{\hbar}\right)^4 x^4 T^4 + B_{\rm U} \left(\frac{k_B}{\hbar}\right)^2 x^2 T^3 e^{-\frac{\theta}{3T}}$$
(36)

where *L* represents the grain size, *A* and B_U are two pre-factors for point-defect and Umklapp scatterings, respectively. Figure 36 shows the grain size distribution evaluated with the SEM images in Figure 22. An average size of 30 μ m is determined by the reported method [82]. Since the preparation procedures for our samples are the same, it is reasonable to fix *L* at this value for all samples. Returning to the point-defect scattering, *A* can be expressed as [81]:





Figure 36 Grain size distribution of polycrystalline $CoSi_{1-x}B_x$ samples in Figure 22.

where V is the average volume per atom and Γ is the point-defect scattering parameter. The expression of B_{U} is as follows [81]:

$$B_{\rm U} = \frac{\hbar \gamma^2}{M v^2 \theta} \tag{38}$$

where γ is the Grüneisen parameter and *M* is the average atomic mass. The scattering parameter Γ for point defects is the sum of two effects, i.e. the mass fluctuation ($\Gamma_{\rm M}$) and the strain field effect ($\Gamma_{\rm S}$) caused by the atomic size differences. For our Rh-substituted samples, we ignore the B substitution effect and only take into account the effect of Rh substitution for Co sites. The two fluctuations contribute to Γ as [83]:

$$\Gamma_{\rm M} = \frac{\sum_{i=1}^{n} c_i \left(\frac{\bar{M}_i}{\bar{\bar{M}}}\right)^2 f_i^1 f_i^2 \left(\frac{M_i^1 - M_i^2}{\bar{M}_i}\right)^2}{\sum_{i=1}^{n} c_i}$$
(39)
$$\Gamma_{\rm S} = \frac{\sum_{i=1}^{n} c_i \left(\frac{\bar{M}_i}{\bar{\bar{M}}}\right)^2 f_i^1 f_i^2 \varepsilon \left(\frac{r_i^1 - r_i^2}{\bar{r}_i}\right)^2}{\sum_{i=1}^{n} c_i}$$
(40)

In both cases, the subscript i represents ith sublattice (i.e. Co and Si sublattices) and the superscripts 1 and 2 represent two different atoms in the sublattice (i.e. Co and Rh). The symbol c is the occupancy for the sublattice ($c_i = 1$ for each Co and Si sublattice), M is atomic mass, f is fractional concentration ($f_i^{1+} + f_i^{2} = 1$), r is atomic radius and ε is an adjustable parameter. The average sublattice mass and radius are defined as [83]:

$$\bar{M}_{i} = f_{i}^{1}M_{i}^{1} + f_{i}^{2}M_{i}^{2}$$
(41)

$$\overline{r_{i}} = f_{i}^{1} r_{i}^{1} + f_{i}^{2} r_{i}^{2}$$
(42)

and the average mass of the alloy is [83]:

$$\overline{\overline{M}} = \frac{\sum_{i=1}^{n} c_i \overline{M}_i}{\sum_{i=1}^{n} c_i}$$
(43)

The adjustable parameter ε is supposed to be related to the Grüneisen parameter [84]. With an experimental Poisson's ratio of 0.27 for CoSi [71], we can estimate the adjustable parameter using the analysis proposed by Abeles as [84]:

$$\varepsilon = 10.76 + 34.45 \gamma + 27.56 \gamma^2 \tag{44}$$

A Grüneisen parameter of 1.73 for CoSi was obtained by Delaire et al. using first-principles calculations [78]. We attempted to use this value to calculate the lattice thermal conductivity for our samples. However, the obtained lattice thermal conductivity values are much higher than the experimental data, implying the calculated Grüneisen parameter is too small for our approximation. Then we tried another calculation results also based on density functional theory [80] to determine the Grüneisen parameter using the following expression [27]:

$$\gamma = \frac{3\beta BV_{\rm m}}{C_{\rm V}} \tag{45}$$

where β is the volumetric thermal expansion coefficient, *B* is the bulk modulus, $V_{\rm m}$ is the volume per mole, and $C_{\rm V}$ is the molar heat capacity at constant volume. Based on the room temperature literature results [80], β is 2.11×10⁻⁵ K⁻¹, *B* is 2.11×10¹¹ Pa, $V_{\rm m}$ is 1.34×10⁻⁵ m³/mol and $C_{\rm V}$ is 40 J/mol K. This gives rise to a Grüneisen parameter of 4.5. Since β and $C_{\rm V}$ have the same temperature dependence while *B* and $V_{\rm m}$ are weakly temperature dependent, we can assume that γ is a constant over our experimental temperature range.

Using the above method and parameter values ($\theta = 625$ K, v = 4600 m/s, $\gamma = 4.5$, $L = 30 \mu$ m), the lattice thermal conductivity is calculated for the x = 0.05 sample as a solid curve shown in Figure 35. It is clearly seen that the calculated curve agrees with the experimental data quite well especially at temperatures ranging from 200 K to 300 K. The pure CoSi is supposed to exhibit no point-defect scattering. However, the calculated values are about 6 times larger at 80 K and 2 times larger at 300 K than the experimental data if we set A as zero. A value of 0.58×10^{-42} s³ for A gives the best match between the calculation and the experimental data, as shown in Figure 35. The non-zero value of A is more reasonable because lattice imperfections always exist in crystalline samples. A little larger A value of 0.94×10^{-42} s³ is used for the x = 0.00 sample because B substitution probably introduces more lattice imperfections. For the x = 0.10 and 0.20 samples, the large Grüneisen parameter makes the calculated values lower than the experimental data. Smaller Grüneisen parameters like 4.15 for the x = 0.10 sample and 3.7 for the x = 0.20sample provide better coincidences. The parameters used in the Debye approximation for various samples are listed in Table 5.

It is surprising that the Grüneisen parameters used in our calculations are two to three times the typical values for intermetallic compounds [78]. This discrepancy was also found in FeSi, which is an isostructural material with CoSi. The first-principles calculations give rise to a Grüneisen parameter of 1.6 for FeSi, while several times larger values ($\gamma > 4$ for various phonon frequencies at temperatures below 300 K) were obtained based on experimental results [78].

Parameter	CoSi	x = 0.00	x = 0.05	x = 0.10	x = 0.20
γ	4.5	4.5	4.5	4.15	3.7
ε	N/A	N/A	724	628	516
<i>L</i> (µm)	30	30	30	30	30
$A(10^{-42} \text{ s}^3)$	0.58	0.94	1.92	3.11	4.82
$B_{\rm U} (10^{-18} {\rm s/K})$	2.23	2.23	2.18	1.81	1.37

Table 5 Values used in the Debye approximation for CoSi and Co_{1-x}Rh_xSi_{0.98}B_{0.02} samples.

Delaire et al. attributed the enlarged values to the electron-phonon coupling and drew a conclusion that the electron-phonon interaction was due to the sharp features around the Fermi level in the electronic density of states [78]. Since the density of states of CoSi also shows such sharp features as illustrated in section 1.4, this material likely exhibits a larger Grüneisen parameter than expected. Even though Delaire et al. pointed out that the coupling in CoSi is weaker than in FeSi, considering the FeSi system shows much larger Grüneisen parameters for the acoustic phonons (9±1 for 26 meV acoustic peak at room temperature) [78], it may be reasonable to use an average Grüneisen parameter of 4.5 for CoSi. The reason for the decreasing γ in the x = 0.10 and 0.20 samples can also be understood by the change of the electronic structure. It was found that the Grüneisen parameter of FeSi became smaller with increasing temperature due to the closing of its narrow band gap. Returning to Figure 32, the rising carrier concentration with the increasing Rh concentration is also likely due to the closing of the pseudo gap as we mentioned before. Moreover, we notice that the Seebeck coefficients of Rh-substituted

samples bend upward at lower temperature compared to the pure CoSi. This fact may also indicate that the pseudo gap is narrowed to some extent by Rh substitution. Thus, Rh substitution probably plays the same role in the electronic structure of CoSi as the thermal disorder effect in FeSi, causing a smaller γ for samples with higher Rh concentrations. A complete understanding of the effect of Rh substitution on the electronic structure of CoSi still requires more investigations like first-principles calculations.

The large Grüneisen parameters directly cause intensive strain field effect on the lattice thermal conductivity reduction based on Equations (40) and (44). The ε values listed in Table 5 are larger than 500 for all Rh-substituted samples. It has been reported that substituted ZrNiSn-based half-Heusler alloys also show a ε value above 500 [83]. It is true for CoSi that the atomic size fluctuation plays a more important role than the mass fluctuation in the lattice thermal conductivity reduction. For instance, Al substitution for Si sites can induce a drastic reduction of the lattice thermal conductivity. Since the mass difference between Al and Si atoms is negligible (< 4%), the reduction is supposed to stem from the atomic radius difference (Al is 125 pm while Si is 111 pm). The peak broadening at high angles in Figure 29(a) also implies a large strain effect within the Rh-substituted samples. In the next section, we will show another example to confirm the large strain field effect in CoSi alloys as well.

The temperature dependence of *ZT* is shown in Figure 37. Compared to CoSi, *ZT* is increased by a factor of 2.5 for the x = 0.10 sample. This sample also shows a 25% increase relative to the x = 0.00 sample, due to the reduction of the lattice thermal conductivity. Unfortunately, the 20% Rh-substituted sample shows a lower *ZT* than the 10% sample at room temperature because of the reduced Seebeck coefficient as well as the power factor. As a result, *ZT* cannot be further improved by more isoelectronic substitutions.



Figure 37 Temperature dependence of ZT of CoSi and Co_{1-x}Rh_xSi_{0.98}B_{0.02} samples.

4.3 CoSi_{0.98-x}Ge_xB_{0.02} Alloys

Ge and Sn are also candidates for isoelectronic substitutions for Si sites in CoSi. As we mentioned in section 3.1, Ge doubtlessly shows a quite large solubility in CoSi. We attempted to prepare $CoSi_{1-x}Sn_x$ alloys with x ranging from 0.05 to 0.20 by arc melting. However, Sn only agglomerated as a separate phase and thus did not form a solid solution with CoSi. The addition of B again facilitated the preparation while the $CoSi_{1-x}Ge_x$ alloys without B addition easily shattered during the processing. As shown in Figure 38(a), the XRD patterns for Ge-substituted



Figure 38 (a) XRD patterns and (b) Lattice constant as a function of the Ge concentration for $CoSi_{0.98-x}Ge_xB_{0.02}$ alloys.

 $CoSi_{0.98}B_{0.02}$ alloys only display a B20 single phase and the peaks continue to shift to lower angles with the increase of Ge concentration. The lattice parameter varies linearly with the substitution concentration, as can be seen in Figure 38 (b).

The thermoelectric properties, i.e. the electrical resistivity, Seebeck coefficient, power factor and thermal conductivity, are shown in Figures 39-42. Unlike the behavior of Rh-substituted samples, Ge substitutions, except for x = 0.05, cause a pronounced increase in the resistivity over a wide temperature range from 80 to 600 K. The Hall results show that the carrier concentration is not affected by Ge substitution (at room temperature, $n = 4.25 \times 10^{20}$ cm⁻³ for x = 0.00, n = 4.11×10^{20} cm⁻³ for x = 0.05 and n = 4.16×10^{20} cm⁻³ for x = 0.10), except for the 20% Ge sample $(n = 6.16 \times 10^{20} \text{ cm}^{-3} \text{ at room temperature})$. Therefore, the rising resistivity is attributed to the decrease of the carrier mobility. The Seebeck coefficients are almost the same for the x =0.00, 0.05 and 0.10 samples from 200 to 300 K, consistent with the constant carrier concentration. The former two samples even show the same values at higher temperature, while the Seebeck coefficients for the x = 0.10 sample are enhanced compared to the other two at temperatures above 300 K. The enhancement is likely due to the enhanced carrier scattering ($\mu = 84 \text{ cm}^2/\text{Vs}$ for x = 0.10 compared to $\mu = 95 \text{ cm}^2/\text{Vs}$ for x = 0.00 at room temperature), provided that the Fermi level of the x = 0.10 sample is the same as that of the parent. The Seebeck coefficients for the x = 0.20 sample are much lower than the other samples over a wide temperature range from 200 to 600 K. According to Equation (10), the Seebeck coefficient is directly related to the Fermi level. Since the rising resistivity indicates additional carrier scattering processes in this sample, the decrease of the Seebeck coefficient is presumably due to its higher Fermi level. This



Figure 39 Electrical resistivity as a function of temperature for CoSi_{0.98-x}Ge_xB_{0.02} samples.



Figure 40 Seebeck coefficient as a function of temperature for $CoSi_{0.98-x}Ge_xB_{0.02}$ samples.



Figure 41 Temperature dependence of the power factor of $CoSi_{0.98-x}Ge_xB_{0.02}$ samples.



Figure 42 Temperature dependence of the thermal conductivity of $CoSi_{0.98-x}Ge_xB_{0.02}$ samples.

is also consistent with the higher carrier concentration observed in this sample. The compositional dependence of the Seebeck coefficient due to Ge substitution is similar to that of Rh substitution as we discussed in section 4.2. Both the isoelectronic substitutions influence the electrical properties to some extent. The power factor is not increased by Ge substitution because the enhancement of the Seebeck coefficient is compensated by the lower carrier mobility for the x = 0.10 sample, as shown in Figure 41. The Ge substitution effect on the thermal conductivity reduction is similar to that of Rh substitution, as can be seen in Figure 42. Based on the electrical properties of the x = 0.05 sample, this substitution level shows a subtle effect on the electronic structure. Thus, we can use the Debye approximation in section 4.2 to calculate the lattice thermal conductivity of this sample with the same Grüneisen parameter.



Figure 43 Lattice thermal conductivity and Debye approximation results with different grain sizes as a function of temperature for the $CoSi_{0.93}Ge_{0.05}B_{0.02}$ sample.

The atomic mass and size of Ge give rise to a smaller pre-factor for point-defect scattering than Rh with a value of 1.55×10^{-42} s³ while the almost same pre-factor for Umklapp scattering. The calculated lattice thermal conductivity curve is shown in Figure 43. The calculation with an *L* value of 30 μ m is quite consistent with the experimental data around room temperature even though it is much higher at low temperature. The discrepancy probably originates from the unknown grain size of this sample. If a smaller *L* value of 7 μ m instead of 30 μ m is used while maintaining the other parameters the same, the calculation coincides with the experimental data, as can be seen in Figure 43.



Figure 44 Experimental lattice thermal conductivity and calculated curves for 5 mol% Ga and 5 mol% Ge substituted CoSi samples.

In section 3.2, the lattice thermal conductivity of Ga-doped CoSi samples has been discussed. We also attributed the reduction to the point-defect scattering. It is noticeable that the lattice thermal conductivity reduction due to Ga doping is more than Ge substitution, as shown in Figure 44. Since the mass difference between Ga and Si is even less than that between Ge and Si, the point-defect scattering parameter $\Gamma_{\rm M}$ for Ga-doping is smaller than that for Ge substitution. Therefore, the further reduction of the lattice thermal conductivity is presumably due to the large strain field effect in Ga-doped samples. The calculated pre-factor *A* value for 5 mol% Ga doping is 2.42×10^{-42} s³, about 1.6 times the value for 5 mol% Ge substitution. With $B_{\rm U}$ of 2.18×10^{-18} s/K and *L* of 30 μ m, we can calculate the lattice thermal conductivity for the 5 mol% Ga-doped sample (see Figure 44). The obtained curves in Figure 44 quantitatively demonstrate the importance of the strain field effect on the lattice thermal conductivity reduction of CoSi. On the other hand, the coincidence between the experimental and calculation results suggests that the large Grüneisen parameter and adjustable parameter ε are reasonable for the CoSi system.



Figure 45 Temperature dependence of ZT of $CoSi_{0.98-x}Ge_xB_{0.02}$ samples.

Enhanced *ZT* values are obtained for the x = 0.05 and 0.10 samples due to the lattice thermal conductivity reduction, as shown in Figure 45. Even for the isoelectronic substitution, it is not trivial to identify an optimized substitution level to achieve the highest *ZT*, because this kind of substitution still affects the electrical properties. The 20% Ge substituted sample exhibits lower *ZT* around room temperature than the parent sample, despite the fact that this sample exhibits the largest lattice thermal conductivity reduction.

4.4 Summary

In this chapter, we studied and discussed the thermoelectric properties of isoelectronic elements, such as Rh and Ge, substituted $CoSi_{0.98}B_{0.02}$ samples. The electrical resistivity is not affected by Rh substitution whereas large Ge substitutions lead to rising resistivity. Both the substitutions show a pronounced effect on the Seebeck coefficients, suggesting the electronic structure are still influenced to some extent. The lattice thermal conductivity is reduced drastically by isoelectronic substitutions due to the point-defect scattering. Both the mass and strain filed fluctuations contribute to the reduction. The Debye approximation can provide a quantitative analysis of the reduction. According to the analysis, the latter plays a more important role in the lattice thermal conductivity reduction because of a large Grüneisen parameter. Two examples, i.e. Al and Ga doping results, are taken to illustrate the presence of the large strain field effect in CoSi samples. All these results prove that the large Grüneisen parameter and adjustable parameter used in our Debye approximation are practical and reasonable. The 10% Rh sample shows an enhanced room temperature *ZT* of 0.15 while a value of 0.14 is obtained for the

5% Ge sample. A further improvement is not possible for each individual substitution because the carrier concentration increases and the power factor starts to decrease rapidly with the increasing substitution level. However, higher *ZT* values are likely obtained when Rh and Ge substitutions are used together.

Chapter 5 N-type and Double Doping Effects on the Thermoelectric Properties of CoSi

5.1 Background and Motivation

As we discussed in section 3.2, p-type dopants like Ga, Al and Fe lead to a drastic increase in the electrical resistivity and hence a decrease in the power factor. Therefore, it is not feasible to use p-type doping to improve the thermoelectric properties of CoSi. On the contrary, n-type doping is likely to reduce the resistivity because of the rising carrier concentration. According to Sakai et al.'s study, the room-temperature Seebeck coefficient is not lowered severely for CoSi samples doped with small amounts of Ni [46]. This probably gives rise to an enhanced power factor in n-type doped CoSi alloys. In the past, the n-type doping effect has been only reported for Ni-doped CoSi samples [57,66]. We intend to explore other possible n-type dopants for CoSi as well as the effects of n-type doping on the thermoelectric properties. The elements such as Pd and Pt in the same column as Ni in the Periodic Table are candidates for n-type doping. Therefore, we investigated the influences of small amounts of these elemental substitutions and the results are discussed in section 5.2 [85].

On the other hand, according to Equation (10) and (16), the Seebeck coefficient can be increased by enhancing the carrier scattering (or increasing the scattering constant λ) for a fixed value of the Fermi level. It is possible to achieve this by appropriate p- and n-type co-doping. Thus, we intend to use the same amounts of Fe and Ni to dope CoSi simultaneously. The co-doping effects on the thermoelectric properties will be discussed in section 5.3.

5.2 Ni-, Pd- and Pt-substituted CoSi Alloys

 $Co_{1-x}M_xSi$ alloys (x = 0.002 and 0.01 for M = Ni; x = 0.01 for M = Pd; and x = 0.01, 0.02, and 0.05 for M = Pt) were also prepared by arc melting. Since NiSi, PdSi, and PtSi all show a MnP-type B31 structure [74], the solubility for these elements is likely not more than that of Ni. The XRD patterns of Ni- and Pd-substituted samples only show a CoSi single phase, as shown in Figure 46(a). However, a tiny impurity peak is observed at $2\theta = 29.95^{\circ}$ for the 1 mol% Pt sample. Samples with higher Pt concentrations, i.e. 2 mol% and 5 mol%, were prepared in order to verify the presence of the secondary phase. It is clearly seen in Figure 46(b) that the impurity peaks also appear in these two samples. The peaks are at the same positions and the intensity becomes stronger with the increasing Pt concentration, suggesting the same composition and the increasing quantities of the secondary phase. We attempted to indentify the phase with the JCPDS database in Jade 9.0; however, no powder diffraction file matches these peaks.

In order to indentify the chemical compositions of the secondary phase, microstructure observations were carried out using SEM with the BSE mode. Figure 47 displays the BSE images of the Pt-substituted samples. A phase separation can be clearly seen in these images. Since the Pt-rich phase has a larger atomic weight, its color is brighter than the matrix CoSi phase. With the increase of Pt concentration, the quantity of the Pt-rich phases increases obviously. It is also noticeable that the impurity phase seems to segregate along the grain boundaries. This can be seen more clearly in Figure 47(c) and (d). These results are similar to those of the B-substituted samples in section 3.3. The average chemical compositions of the dark



Figure 46 XRD patterns of (a) Ni-, Pd-, and Pt-substituted CoSi samples and (b) 1 mol%, 2 mol%, and 5 mol% Pt-substituted CoSi samples.



Figure 47 BSE images of (a) CoSi, (b) 1 mol% Pt, (c) 2 mol% Pt, and (d) 5 mol% Pt samples.

and bright phases for each sample were determined by EDS, and are listed in Table 6. We can see clearly that the dark phase in all samples is stoichiometric CoSi, whereas Pt is only detected in the bright regions. The possible chemical formula for this impurity phase is $PtCoSi_2$ ($Pt_{1.15}Co_{1.13}Si_{2.00}$ for $Pt_{0.01}$, $Pt_{1.10}Co_{1.09}Si_{2.00}$ for $Pt_{0.02}$ and $Pt_{1.15}Co_{1.13}Si_{2.00}$ for $Pt_{0.05}$). The solubility of Pt cannot be detected by EDS, indicating that the solubility limit of Pt in CoSi is extremely low or Pt is completely immiscible with CoSi.

The temperature dependence of the electrical resistivity of Ni- and Pd-doped CoSi samples and that of Pt-substituted samples are shown in Figure 48(a) and (b), respectively. In this chapter, the resistivity of our pure CoSi sample is as low as a single crystal reported in Petrova et al.'s

	Bright				Dark		
Sample	Со	Si	Pt	Co	Si	Pt	
CoSi				50.4	49.6	0.0	
Pt _{0.01}	26.4	46.8	26.8	50.6	49.4	0.0	
Pt _{0.02}	26.0	47.7	26.3	47.9	52.1	0.0	
Pt _{0.05}	26.4	46.8	26.8	49.5	50.5	0.0	

Table 6 Chemical compositions (at. %) of bright and dark regions of CoSi and Pt-substituted samples in Figure 47.

study [71], indicating this is a high-quality sample with a stoichiometric composition. The samples doped with small amounts of Ni show lower resistivity than that of CoSi around room temperature. The reduction is attributed to an increase of the carrier concentration, as shown in Figure 49(a). As we discussed in section 3.2, the Hall results of CoSi samples are influenced by holes and electrons simultaneously. However, the large negative Seebeck coefficient as well as the large electron to hole mobility ratio of CoSi indicates the effect of holes is negligible at room temperature. Since n-type doping further increases the electron concentration, it is reasonable to assume a single conduction band for the transport of n-type doped CoSi samples. Thus, the electron concentrations are calculated based on this one-band model. We will also use this assumption to evaluate the Fermi level and the electron effective mass for Ni-doped CoSi samples in the following text. The Hall mobility decreases with the increasing Ni concentration, as shown in Figure 49(b). In general, one expects that the mobility will be proportional to $T^{-3/2}$





Figure 48 Temperature dependence of the electrical resistivity of (a) Ni- and Pd-doped CoSi samples and (b) Pt-substituted CoSi samples.



Figure 49 Hall results of n-type doped samples: (a) electron concentration and (b) mobility. The solid lines designated "N+A" are fits using a combination of neutral impurity and acoustic phonon scattering.



Figure 50 Reciprocal neutral impurity scattering mobility as a function of Ni concentration.

for acoustic phonon scattering and independent of temperature for neutral impurity scattering. The combination of the two scattering mechanisms leads to an expression of the mobility as:

$$\frac{1}{\mu} = \frac{1}{\mu_{\rm N}} + \frac{1}{\mu_{\rm A}} = C_{\rm N} + C_{\rm A} T^{3/2} \tag{46}$$

where *C* stands for constant and the subscripts N and A represent neutral impurity and acoustic phonon, respectively. By fitting the reciprocal Hall mobility, we can obtain the two best constants for different scattering processes. The results are drawn as solid curves in Figure 49(b). Around room temperature, the mobility is dominated by acoustic phonon scattering and it is not affected severely by Ni doping. The constant $1/C_A$ changes as 614319, 611127 and 582438 for CoSi, Ni_{0.002} and Ni_{0.01} samples, respectively. The differences between the acoustic constants are within 5%. In contrast, the constant C_N varies dramatically as 0.000284, 0.000563 and 0.00214 for CoSi, Ni_{0.002} and Ni_{0.01} samples, respectively. Since the neutral impurity scattering rate is roughly proportional to the neutral impurity concentration [86], C_N increases linearly with the Ni concentration as shown in Figure 50. The enhanced neutral impurity scattering of electrons due to Ni doping leads to the rising resistivity at low temperature as shown in Figure 48(a). The 1 mol% Pd-doped sample shows almost the same electron concentration and mobility as the 1% Ni sample and hence a comparable behavior of the resistivity.

All the Pt-substituted samples show lower resistivity around room temperature than the pure CoSi as shown in Figure 48(b). The carrier concentration also increases with the rising Pt concentration as can be seen in Figure 51(a). This increase can be hardly attributed to the n-type doping effect based on our XRD and BSE studies. One possibility is that the higher carrier concentration stems from the Pt-rich phase. We speculate that this phase is very metallic and it can improve the grain boundary connectivity and hence the electrical conductivity. It can be seen in Figure 51(b) that the mobility remains high for these Pt-substituted samples around room temperature. Furthermore, the decrease of the mobility at low temperature is much less than that of Ni doping. This phenomenon is analogous to skutterudite-silver composites, in which the segregation of conducting silver phase at grain boundaries can also benefit the resistivity reduction [87].

Figure 52 displays the temperature dependence of the Seebeck coefficient. For Ni-doped samples, the room-temperature Seebeck coefficient drops off monotonically with the rising Ni concentration. Using Equations (7) and (10), we can quantitatively evaluate the Fermi level and the electron effective mass of the Ni-doped samples with the Seebeck coefficient and the carrier



Figure 51 Hall results of Pt-substituted samples: (a) carrier concentration and (b) mobility.

Sample	$n(10^{20} \text{ cm}^{-3})$	$\mu \text{ (cm}^2/\text{VS)}$	$S(\mu V/K)$	$\eta (kT, 0.026 \text{ eV})$	$m^*(m_e)$
CoSi	3.94	119	-92.2	2.73	2.49
Ni _{0.002}	4.45	111	-86.7	2.97	2.54
Ni _{0.01}	5.32	92	-83.3	3.13	2.73

Table 7 Room-temperature carrier concentration, mobility, Seebeck coefficient, reduced Fermi level and effective mass of Ni-doped CoSi samples.

concentration data. As we discussed above, the electron scattering is dominated by acoustic phonons at room temperature for all Ni-doped samples. Thus, the scattering constant can be chosen as $\lambda = -1/2$ at room temperature. The calculated results are summarized in Table 7. It can be seen that the Fermi level is increased by Ni-doping and in the meantime the electron effective mass increases with the doping level. The increasing effective mass can also explain the decrease of $1/C_A$, which is supposed to be proportional to $(m^*)^{-5/2}$ [86]. When only taking into account the influence of the effective mass on the carrier mobility, we can obtain the mobility of doped samples using the data of pure CoSi. The calculated room-temperature mobility for Ni_{0 002} and Ni_{0.01} are 113 and 94 cm²/Vs respectively, in good agreement with the experimental data as listed in Table 7. The change of the effective mass implies that the rigid band assumption is not accurate enough for the CoSi system: n-type doping likely broadens the conduction band as the effective mass increases. On the other hand, both the 1 mol% Ni- and Pd-doped samples show quite large Seebeck coefficients at 80 K (-50 μ V/K for Ni_{0.01}). In our aforementioned discussion, the electrons are scattered predominantly by neutral impurities for Ni-doped samples at this

temperature. This scattering mechanism gives rise to a scattering constant of $\lambda = 0$ instead of $\lambda = -1/2$. Assuming that the effective mass is temperature independent, we can determine the Fermi level of the 1% Ni sample using the known effective mass in Table 7 and its carrier concentration in Figure 49(a). With the calculated Fermi level and the given scattering constant, a Seebeck coefficient of -46 μ V/K at 80 K is obtained for this sample, in good agreement with the experimental value of -50 μ V/K.



Figure 52 Temperature dependence of the Seebeck coefficient of Ni-, Pd-, and Pt-substituted CoSi samples. Solid lines are a guide to the eye.

The Seebeck coefficient of the Pt-substituted samples drops off with the rising Pt level around room temperature, due to the increasing carrier concentration as shown in Figure 51(a).

The 1 mol% Pt sample shows the same Seebeck coefficient as CoSi around room temperature. In combination with the lower electrical resistivity, this sample exhibits a higher power factor than CoSi, as shown in Figure 53. It is noticeable that the pure CoSi sample shows a room-temperature power factor of $63 \,\mu W K^{-2} cm^{-1}$, which is already 50 % larger than that of the state-of-the-art Bi₂Te₃ material. The Pt_{0.01} sample exhibits a power factor of 73 $\mu W K^{-2} cm^{-1}$ at room temperature, a 16% increase relative to the CoSi sample. This increase was also confirmed by the ZEM measurements. However, Ni-doped samples show decreased power factors because the reduction of the Seebeck coefficient and the mobility simultaneously outweighs the increase of the carrier concentration.



Figure 53 Power factor as a function of temperature for Ni-, Pd-, and Pt-substituted CoSi samples. Solid lines are a guide to the eye.
The temperature dependence of the thermal conductivity is displayed in Figure 54. The thermal conductivity of Ni-doped samples is almost the same as that of CoSi around room temperature because the mass and size differences between Co and Ni atoms are negligible. It is understandable that the 1% Pd sample shows lower thermal conductivity than the 1% Ni sample due to the larger mass and size differences between Co and Pd atoms. Pt substitutions lead to a significant reduction of the thermal conductivity at low temperature, while the values around room temperature are not decreased too much. As a result, the pure CoSi sample shows a room-temperature ZT of 0.11. All the n-type doped samples exhibit lower ZT values than CoSi. An enhanced ZT of 0.13 is obtained for the 1% Pt sample, while the other two samples with higher Pt concentrations possess lower ZT at room temperature.



Figure 54 Temperature dependence of the thermal conductivity of Ni-, Pd-, and Pt-substituted CoSi samples. Solid lines are a guide to the eye.

5.3 Co_{1-x-y}Fe_xNi_ySi Alloys

CoSi samples doped by equal amounts of Fe and Ni were prepared as $Co_{1-x-y}Fe_xNi_ySi$ alloys, where x = y = 0.025, 0.05 and 0.10 respectively. The XRD patterns only show a single CoSi phase for all the samples. The peaks shift to lower angles for samples with larger x and y, indicating an enlarged lattice constant with the introduction of co-doping atoms.



Figure 55 Temperature dependence of the electrical resistivity of $Co_{1-x-y}Fe_xNi_ySi$ alloys.

The electrical resistivity as a function of temperature is shown in Figure 55. With the rising co-doping concentration, the electrical resistivity increases monotonically and severely. The electrical resistivity shows a metallic behavior for CoSi with a positive temperature coefficient, whereas the temperature coefficients change to small negative values for the three co-doped



Figure 56 Hall results for $Co_{1-x-y}Fe_xNi_ySi$ alloys: (a) carrier concentration and (b) mobility.



Figure 57 Temperature dependence of the Seebeck coefficient of $Co_{1-x-y}Fe_xNi_ySi$ samples.

samples. The Hall measurements show that the carrier concentration increases with the increasing co-doping level, as can be seen in Figure 56(a). Thus, the rising resistivity originates from the severe reduction of the carrier mobility, as shown in Figure 56(b). Since Fe introduces holes while Ni brings about electrons, the carrier concentrations of both types are increased. According to Equation (24), the rising p and n can induce smaller Hall coefficients and hence larger Hall carrier concentrations for a two-band conduction material. It is also noticeable that the mobility for co-doped samples is weakly dependent of temperature. As we discussed in section 5.2, the significant reduction of the mobility is likely caused by the enhanced neutral impurity scattering or even ionized impurity scattering. We do not claim the ionized impurity

scattering in section 5.2 because the use of this mechanism cannot agree with the experimental data for samples doped by small amounts of Ni. In contrast, we consider the ionized impurity scattering for the co-doped samples only because this mechanism fits the experimental data better.

Figure 57 displays the temperature dependence of the Seebeck coefficient. The absolute Seebeck coefficient decreases with the increasing co-doping concentration. There are two possibilities responsible for the reduction: first, provided that the doping efficiency of Fe and Ni is the same, both dopants will introduce the same quantities of holes and electrons. However, the electrons possess smaller effective mass than the holes and thus the Fermi level may be still moved upward, analogous to the n-type doping effect but less than Ni doping alone. This may be proven by the fact that the Seebeck coefficient for the x = y = 0.025 sample is similar to that of the 1% Ni sample in section 5.2. Moreover, the Seebeck coefficient bends upward at higher temperature with the increasing co-doping concentration, implying higher Fermi levels for these samples as well. On the other hand, with the rising hole concentration, the Seebeck coefficient is now influenced by both carriers as indicated by Equation (28). The hole contribution to the Seebeck coefficient is weighted against that of electrons and hence reduce the Seebeck coefficient. This can be confirmed by measuring the Seebeck coefficient of a sample with more Fe than Ni like one of x = 0.06 and y = 0.04 (n_{300K} = 1.0×10²¹ cm⁻³) in comparison with the x = y = 0.05 sample ($n_{300K} = 9.5 \times 10^{20}$ cm⁻³). Based on the former possibility, this sample should have a lower Fermi level and hence a larger Seebeck coefficient because the Ni content is reduced. However, a lower Seebeck coefficient of -45 μ V/K for the x = 0.06, y = 0.04 sample is

obtained at room temperature compared to -69 μ V/K for the x = y = 0.05 sample, indicating a detrimental effect of p-type dopants to the Seebeck coefficient.

As we demonstrated above, the change of the mobility shows the presence of the additional scattering processes in the co-doped samples. Thus, the electrical conductivity deteriorates due to the reduction of mobility. The Seebeck coefficient, however, cannot be improved by co-doping because the introduction of excess holes annihilates the advantage of intensive carrier scattering. As a result, the power factor is decreased by a factor of 3 for the x = y = 0.025 sample and continues to drop off for higher co-doping concentrations compared to CoSi at room temperature, as shown in Figure 58. Even though the maximum power factor shifts to higher temperature with the increasing co-doping level, the values are still much lower than CoSi over the entire temperature range.



Figure 58 Temperature dependence of the power factor of $Co_{1-x-y}Fe_xNi_ySi$ samples.

The electrical properties cannot be improved by the co-doping approach due to the semimetallic nature of CoSi. The electron-dominated Seebeck coefficient is sensitive to the hole concentration. Fedorov and Zaitsev proposed two possible ways to enhance the Seebeck coefficient [54]: either reduce the overlapping between the conduction and valence bands or create a potential barrier to scatter the holes rather than electrons. They proved that the overlapping might be separated to some extent by distorting the lattice. It is likely but not practical to achieve this by applying pressure on samples [54]. They speculated that it is more realistic to deform the lattice using atoms with considerably different size to dope CoSi. However, as we discussed in chapter 4, the isoelectronic substitutions cannot improve the Seebeck coefficient even though the atomic size difference between the impurity and host atoms is already quite large (at least, the improvement is trivial as shown in the 10% Ge sample). On the other hand, it is possible to produce scattering or filtering potential barriers by grain boundary modifications [41,82]. We have shown that both B and Pt substitutions are able to form a secondary phase at grain boundaries. In fact, our collaborators at ORNL suggested the presence of an energy barrier at the grain boundaries for B-substituted samples. Furthermore, considering the higher carrier concentration of the 1% Pt sample, the unchanged large Seebeck coefficient probably implies an energy filtering effect. But we cannot draw a solid conclusion that the filtering effect does exist in these materials because the enhancement is too small. All in all, we indeed obtained enhanced thermoelectric properties by either isoelectronic substitutions or impurity phase formations.

The thermal conductivity is reduced by Fe and Ni co-doping. Since the atomic size and mass

differences between impurity and host atoms are quite small, the lattice thermal conductivity reduction is limited. As a result, *ZT* continues to decrease with the increasing co-doping level due to the drastic reduction of the power factor as shown in Figure 59. Even though the high-temperature thermal conductivity of co-doped samples was not measured, the peak *ZT* values for these samples cannot exceed that of CoSi due to the low power factor.



Figure 59 Temperature dependence of ZT of $Co_{1-x-v}Fe_xNi_vSi$ samples.

5.4 Summary

In this chapter, we studied the thermoelectric properties of CoSi samples doped by small amounts of Group 10 elements such as Ni, Pd and Pt and samples co-doped by Fe and Ni. Ni and Pd are effective n-type dopants, while Pt is hardly miscible with CoSi and it segregates along grain boundaries as a possible phase of PtCoSi₂. In contrast to our expectation, the reduction of the Seebeck coefficient outweighs the decrease of the resistivity and thus the power factor is decreased by n-type doping. By analyzing the Hall and Seebeck coefficient results, we find that the Fermi level is indeed raised by n-type doping while the electron effective mass seems to increase with the increasing doping level. These results indicate that the band structure of the doped samples still change (e.g. conduction band broadening) and thus the rigid band assumption is not perfectly applicable to the CoSi system. An interesting observation is that both 1% Ni and 1% Pd samples show quite large Seebeck coefficients at low temperature. The enhancement can be attributed to the enhanced carrier scattering at that temperature based on the analysis of carrier mobility. It suggests a possibility to enlarge the Seebeck coefficient by enhancing the carrier scattering. The Pt-substituted samples exhibit lower electrical resistivity than CoSi around room temperature due to the increase of the carrier concentration. The Seebeck coefficient is maintained for the 1% Pt sample and thus the power factor is improved by 16% for this sample compared to the high-quality CoSi. The reduction in resistivity due to conducting phases at grain boundaries is a promising method for improving the power factor of these materials and might be effectively applied to other thermoelectric materials.

By co-doping CoSi with the same amounts of Fe and Ni, we attempted to enhance the carrier scattering while maintaining the Fermi level. The drastic mobility reduction indicates additional scattering processes in the co-doped samples. However, the absolute Seebeck coefficient continues to decrease with the increasing co-doping concentration. The reduction can be

attributed to either the rising Fermi level or the detrimental effect of holes. As a result, an improvement can be hardly achieved by the co-doping method.

It is difficult to improve the thermoelectric performance of CoSi due to its nature of band overlapping. We expect that its performance might be enhanced by either band separation or selective carrier filtering. The above two ideas likely correspond to isoelectronic substitutions and grain boundary modifications, respectively. As we discussed in the preceding sections, the enhancement of the Seebeck coefficient is too trivial to be attributed to the two concepts, and thus the performance is mainly improved by the lattice thermal conductivity reduction. Up to now, the improvement of the electrical properties is only observed in the 1% Pt sample, considering that other enhancements, including those reported in literature, are due to the comparison with low-quality (off-stoichiometric or microcracks-filled) parent samples.

The effects of elemental substitutions on the thermoelectric properties of arc-melted CoSi have been systematically and comprehensively investigated so far. The dimensionless figure of merit is still one magnitude lower than state-of-the-art thermoelectrics due to the high lattice thermal conductivity. Grain size reduction or nanostructuring have been proven successful to produce thermoelectric materials with lower lattice thermal conductivity [33]. Thus, the influence of another preparation method, namely powder processing, will be our focus in the subsequent chapter.

Chapter 6 CoSi Samples Prepared by Powder Processing

6.1 Background and Motivation

To the best of our knowledge, CoSi is one of the thermoelectric materials with the highest power factor. However, the advantage of the electrical properties is offset by the high thermal conductivity and thus its ZT is quite less than unity. Since the high power factor induces a large electronic contribution to the thermal conductivity, the lattice thermal conductivity is the only adjustable property. Provided that the lattice contribution can be neglected, the room-temperature ZT is only determined by the Seebeck coefficient and the Lorenz number. It can be enhanced to 0.35 using the values presented in the previous chapters. Even though the value is still below unity, it is worth finding an approach to obtain such a huge improvement.

In past decades, powder processing has boosted the research interest of preparing nanostructured bulk thermoelectric materials [33,88]. The grain size can be reduced down to nano-scale by high-energy ball milling and hence the number of interfaces is escalated after appropriate consolidation. Given that the mean free path of carriers is much shorter than phonons, it is believed that the nanogranular structure is helpful to stimulate intensive phonon scattering at interfaces while maintaining or hardly affecting the electrical properties. The effect of grain size reduction on the lattice thermal conductivity can be evaluated using the aforementioned Debye approximation. Using the same pre-factors A and B_U , we can determine the lattice thermal conductivity of CoSi with various grain sizes, as shown in Figure 60. The lattice thermal conductivity can also be evaluated as [27]:



Figure 60 Lattice thermal conductivity of CoSi samples with various grain sizes. From top to bottom: $30 \,\mu\text{m}$, $1 \,\mu\text{m}$, 500 nm, 100 nm, 20 nm and κ_{min} , respectively.

$$\kappa_{\rm l} = \frac{1}{3} C_{\rm V} v l \tag{47}$$

where l is the phonon mean free path. The minimum value is determined using the aforementioned room-temperature C_V , sound velocity, and interatomic spacing of 0.2286 nm as the mean free path. It is clearly seen that the lattice thermal conductivity continues to approach the minimum value with the decreasing grain size.

On the other hand, the carrier mobility is supposed to decrease with the increasing interfaces and thus the electrical resistivity is raised by nanostructuring [35]. However, it has been reported that the Seebeck coefficient is likely enhanced by energy filtering effect for nanostructured materials (superlattices [89] or nanogranular bulks [41]). Thus, an enhanced Seebeck coefficient is expected to compensate the carrier mobility reduction for powder processed CoSi. It is worth mentioning that the improvement of the Seebeck coefficient is not widely observed. It is more realistic to expect that the reduction of the carrier mobility is less than that of the lattice thermal conductivity and hence an overall improvement can be achieved.

6.2 Ball Milling, Consolidation and Thermoelectric Properties

In this chapter, we intend to prepare CoSi samples with reduced grain sizes by powder processing. The starting CoSi materials were prepared with the same arc melting and annealing procedure as mentioned previously. Subsequently, the ingots were pulverized and milled using the SPEX 8000M high-energy ball mill and the milling time was maintained as 100 minutes. To minimize oxidation, samples were loaded and taken out in an argon-filled glove box and vials were also sealed under argon atmosphere before milling (see section 2.1). We found that the selection of vial set influenced the thermoelectric properties severely. Samples milled in an 8007 stainless steel vial set were contaminated by Fe because their thermoelectric properties are similar to those of p-type doped samples. In contrast, the tungsten carbide vial set shows little impact on the thermoelectric properties.

Powders were compacted under argon atmosphere using either PECS or hot pressing (HP). The sintering temperature, pressure, and ramp rates of the temperature and the pressure were varied for PECS to investigate the influence of densification conditions. Hot pressing is a comparable consolidation method to PECS, except that the high temperature is achieved by heating elements instead of Joule heating for PECS. The samples prepared in various conditions are listed in Table 8, where RR is ramp rate, P is pressure, soak is the holding time at the highest temperature and pressure, and density is relative to the theoretical value of 6.59 g/cm³. It is clearly seen that the density decreases with the decreasing PECS temperature and thus a temperature of 1100 $^{\circ}$ C is required to achieve a relative density above 95%. The decrease of the pressure also leads to a lower density, but not as much as the temperature. The change of the ramp rates shows little effect on the sample quality.

Sample	$T(^{0}C)$	RR of <i>T</i> (^o C/min)	P (MPa)	RR of <i>P</i> (MPa/min)	Soak (min)	Density
PECS-1	1100	50	60	5.5	20	97.9%
PECS-2	1000	50	60	5.5	20	93.3%
PECS-3	900	50	60	5.5	20	91.4%
PECS-4	1100	50	30	5.5	20	94.5%
PECS-5	1100	30	60	3.7	20	96.8%
HP	1100	20	60	4.0	60	98.2%

Table 8 CoSi samples with various preparation conditions.

The XRD pattern of the 100-minute ball-milled powders shows pronounced peak broadening, as shown in Figure 61. The crystallite size estimated by the Scherrer equation is 17 nm. Considering that partial broadening is caused by the strain effect, the actual size should be larger than this value. Peak broadening is not observed for the densest PECS sample (PECS-1) compared to the arc-melted CoSi, implying that their grain sizes are comparable. In fact, the XRD patterns of samples consolidated at lower temperature (PECS-2 and PECS-3) are still the same as the arc-melted one. All these results indicate a substantial grain growth during consolidation.



Figure 61 XRD patterns of the arc-melted CoSi, 100-minute ball-milled CoSi powders, and PECS-1 CoSi sample.

Figure 62 presents the SEM fracture surface images of PECS-1 and HP CoSi samples. These two samples possess the highest densities of 98%. A great number of pores and voids are observed within the grains and grain boundaries of both samples. The theoretical density is hardly achieved due to the presence of the isolated pores. Both samples consist of smaller grains with a size around 2 μ m, compared to the size of tens μ m for the arc-melted CoSi. Submicron

grains can also be found in the PECS-1 sample, while the grains are almost larger than 1 μ m for the HP sample. The average grain composition determined by EDS is close to CoSi for both samples (44.5 at. % Co and 55.5 at. % Si for the PECS-1 sample; 44.7 at. % Co and 55.3 at. % Si for the HP sample).



Figure 62 SEM fracture surface images of the PECS-1 (left) and HP (right) CoSi samples.

The temperature dependence of the electrical resistivity is shown in Figure 63. All the powder processed samples show drastic increase in the resistivity relative to the arc-melted CoSi. It has been reported that the strain and defects produced during ball milling can degrade the electrical conductivity [41,90]. Among them, the PECS samples even show higher resistivity than the HP sample. Considering that the PECS-1 sample possesses the similar density and grain size as the HP one, the huge resistivity discrepancy between them is interesting. The difference probably stems from the sintering method itself. For example, PECS may cause more carriers trapping at grain boundaries [91]. On the other hand, the resistivity is directly related to the porosity, as can be seen in Figure 64. The increasing porosity leads to an increase in the electrical



Figure 63 Temperature dependence of the electrical resistivity of PECS and HP samples.



Figure 64 Room-temperature electrical resistivity as a function of porosity for PECS and HP CoSi samples. The dashed line is a guide to the eye.

resistivity [92]. The drastically rising resistivity is not desired for the improvement of the thermoelectric performance.



Figure 65 Temperature dependence of the Seebeck coefficient of PECS and HP samples.

Figure 65 displays the temperature dependence of the Seebeck coefficient. The Seebeck coefficients of samples prepared by powder processing are all lower than that of arc-melted CoSi around room temperature. The Seebeck coefficient was measured for some of the ingots before powder processing and the reduction was only observed after consolidation. It is also noticeable that all the PECS samples exhibit lower Seebeck coefficients than the HP sample. The origin of the difference has not been elucidated. The PECS samples, except for PECS-1, show similar

Seebeck coefficients around room temperature regardless of the density. The decreasing Seebeck coefficient may be attributed to two reasons. First, the increase of the interfaces and the associated imperfections and defects are possible to produce more carriers in the PECS or HP samples and hence a lower Seebeck coefficient [93]. Second, the potential barrier at grain boundaries is so high that electrons with intermediate energy are also filtered [36]. These electrons, unlike the low energy ones, contribute positively to the Seebeck coefficient. Therefore, the Seebeck coefficient and the electrical conductivity both decrease after powder processing.

	80	K	300 K		
Sample	$n(10^{20} \text{ cm}^{-3})$	μ (cm ² /Vs)	$n(10^{20} \text{ cm}^{-3})$	μ (cm ² /Vs)	
Arc-melted	2.15	916	3.94	119	
PECS-2	2.28	109	4.47	38	
PECS-3	2.25	129	3.83	49	
PECS-4	2.23	158	4.47	52	
HP-0.5 mol% Ni	2.44	168	4.22	68	

Table 9 Hall results of PECS and Arc-melted samples at 80 and 300 K.

The Hall measurements were carried out for some samples to verify the former hypothesis. We did not obtain the Hall results for all samples because cutting of the PECS and HP samples was extremely time-consuming and they tended to chip during sectioning. The 80 K and room-temperature Hall results are listed in Table 9. The carrier concentration of the PECS samples at both 80 and 300 K seems higher than that of the arc-melted one (except for PECS-3, which shows a comparable carrier concentration with the arc-melted one at room temperature). In fact, the PECS samples show a carrier concentration similar to the 0.2 mol% Ni-doped CoSi. Therefore, the slight increase of the carrier concentration cannot result in such a huge decrease in the Seebeck coefficient as we discussed in section 5.2.



Figure 66 Temperature dependence of the Seebeck coefficient of Arc-melted, HP, and HP-0.5 mol% Ni samples.

On the other hand, if the reduction is caused by the latter mechanism, the Seebeck coefficient of a sample with electron distribution moving to higher energy is supposed to be larger. This may be interpreted as that a sample with higher Fermi level contradictorily shows a larger Seebeck coefficient. Thus, another HP sample doped by 0.5 mol% Ni (HP-0.5 mol% Ni, density 97.1%) was prepared the same as the HP one. The Seebeck coefficient of this sample is shown in Figure 66. It can be clearly seen that the Seebeck coefficient of the HP $Co_{0.995}Ni_{0.005}Si$ sample is larger than the HP CoSi sample over the entire temperature range and almost the same as the arc-melted CoSi at room temperature. The Seebeck coefficient is enhanced by n-type doping for powder processed samples, in stark contrast to the conventional concept as we mentioned in section 5.2.

It has been suggested that the prevention of oxidation is of great importance for good electrical properties [93]. Even though we had prepared the samples carefully, the interfaces were inevitably oxidized probably during ball milling, transferring or sintering. The formation of even a thin layer of oxides can substantially produce a high potential barrier at grain boundaries and hence an excessive energy filtering effect. Based on this assumption, it is better to remove the oxides by H₂ reduction after pressing. Besides the above reason, the grain boundary potential barrier also likely stems from the misfit angles of grains or other defects [82], inevitably associated with powder processing. We cannot draw any solid conclusion about the reason for the decreasing Seebeck coefficient unless more investigations are made to identify the oxidation or understand the influence of high-energy ball milling and consolidation.

The thermal conductivity is indeed reduced by powder processing, as shown in Figure 67(a). The reduction of the thermal conductivity is mostly due to the suppression of the lattice part, as shown in Figure 67(b). The behavior of the lattice thermal conductivity is analogous to those with reduced grain sizes (see Figure 60). In fact, the lattice thermal conductivity of the HP sample is similar to the calculation results with a grain size of 1 μ m, which is in agreement with the SEM results. The differences between the PECS and HP samples are still related to the porosity[94], as can be seen in Figure 68. The lattice thermal conductivity systematically decreases with the increasing porosity. The reduction is always less than the decrease of the carrier mobility and the electrical conductivity of the corresponding sample. This fact violates the purpose of the nanostructuring of bulk materials, which involves a larger decrease in the lattice thermal conductivity relative to the carrier mobility reduction.

Since we have exerted ourselves to prepare the samples carefully, the undesired large reduction of mobility likely originates from the material system itself. The mean free path of electrons can be roughly estimated as [95]:

$$l_{\text{electron}} = \frac{1.5\pi h}{e^2 k_{\text{F}}^2 \rho} \tag{48}$$

where ρ is the electrical resistivity and $k_{\rm F}$ is the Fermi wave vector. Using the room-temperature carrier concentration and resistivity of the high-quality CoSi in section 5.2, $l_{\rm electron}$ is estimated as 17.7 nm. In the meantime, the mean free path of phonons can be evaluated with Equation (47) and this gives rise to $l_{\rm phonon}$ of 2.8 nm. It is clearly seen that the phonon mean free path, on the contrary, is shorter than that of electrons. Even though Sales et al. pointed out that the mean free path of phonons was supposed to be longer considering that only acoustic phonons contribute to the specific heat [95], we may still conclude that the two mean free paths lie in the same range. In a calculation study of bulk nano-grained Mg₂Si materials, Satyala and Vashaee found that the decrease of the mobility was always comparable to the lattice thermal conductivity reduction



Figure 67 Temperature dependence of (a) the thermal conductivity and (b) the lattice thermal conductivity of PECS and HP CoSi samples.



Figure 68 Room-temperature lattice thermal conductivity as a function of porosity for PECS and HP CoSi samples. The dashed line is a guide to the eye.

regardless of the chosen grain sizes [96]. Their simulations suggested that the electron and phonon mean free paths of Mg_2Si were in the same range and thus nanostructuring was not expected to enhance *ZT* efficiently. To the best of our knowledge, no experimental *ZT* enhancement has been reported for nanogranular Mg_2Si -based materials thus far [97-99]. Nanostructuring presumably influences the electrical properties so negatively that the advantage of the lattice thermal conductivity reduction is annihilated.

As a result, the total thermoelectric performance of the PECS and HP samples is not improved, as can be seen in Figure 69. The electrical properties are significantly degraded and thus powder processing is not beneficial compared to arc melting. It is worth mentioning that our HP samples show higher *ZT* than those low-quality CoSi alloys reported in literature. An incorrect conclusion thus can be drawn with a choice of a low-quality control sample.



Figure 69 Temperature dependence of ZT of PECS and HP samples.

6.3 Summary

In this chapter, we investigated the possibility to enhance ZT by reducing the grain size of CoSi. The arc-melted ingots can be pulverized down to submicron powders with high-energy ball milling. These powders can be consolidated to dense pellets by either PECS or HP at a temperature of 1100 $^{\circ}$ C and a pressure of 60 MPa. The obtained PECS and HP samples exhibit an average grain size of 2 μ m as indicated by SEM images.

The electrical resistivity is drastically increased while the Seebeck is decreased for the powder processed samples. The increase of the resistivity can be attributed to the strain and

defects produced during ball milling as well as the intensive carrier scattering at interfaces. It is quite surprising to observe the decrease in the Seebeck coefficient. We proposed two possible reasons for this: firstly, the carrier concentration rises due to the introduction of defects; secondly, the excessive energy filtering effect is detrimental to the Seebeck coefficient. According to the Hall measurements, we notice that the increase of the carrier concentration is too slight to cause such a huge decrease in the Seebeck coefficient. On the other hand, a HP sample doped by 0.5 mol% Ni was prepared additionally to demonstrate the presence of excessive filtering. More investigations are required to know the grain boundary constituents to clarify the origin of the potential barrier (oxidation or defects associated with high-energy ball milling or PECS).

The lattice thermal conductivity is reduced as expected. However, the reduction is always less than that of the mobility. By estimating the mean free paths of electrons and phonons, we notice that the electron mean free path is likely in the same range as that of phonons. Since the nanostructuring concept is established on an assumption that phonon mean free path is larger than that of electrons, it may not be feasible for the CoSi system to take advantage of grain size reduction to improve ZT.

Nevertheless, it is still worth studying the thermoelectric properties of various bulk nanostructured materials to understand the fundamental transport principles and find out appropriate processing conditions. It is also more promising to mass-produce thermoelectric elements using the combination of ball milling and pressing. Finally and hopefully, we can improve the thermoelectric properties of any given material under a theoretical direction and bring the products to market.

Chapter 7 High-temperature Thermoelectric Materials based on β-FeSi₂

7.1 Background and Motivation

Nowadays, most high-efficiency thermoelectric materials are based on expensive elemental constituents. The high manufacturing cost may restrict their large-scale applications despite the higher conversion efficiencies. Considering the compromise between the materials abundance and their efficiency, β -FeSi₂ is one of the promising inexpensive materials for high-temperature power generation [100]. This material was first reported by Abrikosov in 1956 [101]. Afterwards in 1964, its thermoelectric properties were studied by Ware and McNeill [102] and its potential for power generation has been explored since then.

Semiconducting β -FeSi₂ shows an orthorhombic crystal structure (space group *Cmca*). Its theoretical density is 4.93 g/cm³ [103] and the relatively low density is another advantage of this material. The nature of the band gap has not been elucidated yet. Experimental results showed a direct band gap of 0.87 - 0.90 eV [104,105], whereas theoretical calculations presented a smaller indirect gap of 0.44 - 0.78 eV [106-109]. The electrical properties can be tuned by p-type (e.g. Al on Si sites [110]) and n-type (e.g. Co, Ni or Pt on Fe sites [111-113]) doping. In the past, the reported highest *ZT* around 900 K ranged from 0.19 to 0.42 for 6 mol% Co-doped samples [114]. The large range in values stems almost completely from the difference in the high-temperature thermal conductivity measurements.

In this chapter, we tried to more fully explore the electrical and thermal transport properties

and verify the thermoelectric performance of Co-doped β -FeSi₂ materials. Since the solubility limit of Co in β -FeSi₂ was reported as high as 12 mol% [115], the dopant concentration up to 11 mol% was intentionally used to replace Fe in our study. Furthermore, the lattice thermal conductivity of Co-doped β -FeSi₂ is about two times that of state-of-the-art materials [116]. Therefore, *ZT* is expected to be further enhanced by reducing the lattice thermal conductivity. In combination with the Co alloying effect, more intensive phonon scattering can be achieved by nanostructuring. Ball milling and PECS thus were employed to prepare nanogranular samples. Alternatively, it is believed that intentionally added nanoparticles can act as phonon scattering centers and thus also reduce the thermal conductivity [33]. A thermal conductivity reduction has been previously demonstrated for Y₂O₃ particles dispersed into the β -FeSi₂ matrix [117]. Therefore, a composite made up of a nano-grained matrix and nano inclusions should exhibit very low thermal conductivity. Based on this idea, composites consisting of β -FeSi₂ and SiC nanoparticles were investigated.

7.2 Co-doped β -FeSi₂ Materials

The preparation procedure of β -FeSi₂ has been illustrated in section 2.1. To prepare the doped samples, Co was melted together with Fe and Si to form Fe_{1-x}Co_xSi₂ (x = 0.05 – 0.11) ingots before milling. All the pellets in this study possessed densities of more than 96% relative to the theoretical value. The XRD patterns only show a β -FeSi₂ single phase for all samples (see Figure 70). The existence of FeSi phase is a well-known issue which affects the purity of β -FeSi₂ [118-121]. This problem was avoided using our preparation method. The chemical composition



Figure 70 XRD patterns of (a) β -FeSi₂ and PDF #01-071-0642; and (b) Co-doped β -FeSi₂ materials.



Figure 71 Electrical resistivity of Co-doped β -FeSi₂ samples vs. reciprocal temperature. The solid curves are only a guide to the eye.

of the x = 0.08 sample determined by EDS also proves a single phase solid solution (determined formula $Fe_{0.920}Co_{0.081}Si_{2.320}$).

Figure 71 displays the temperature dependence of the electrical resistivity. The pure β -FeSi₂ exhibits much higher resistivity than the doped samples. It has been reported that the resistivity of n-type doped β -FeSi₂ at low temperature (below 120 K) was consistent with the variable-range hopping mechanisms [122]. The resistivity of Co-doped β -FeSi₂ between 150 K and 900 K were also analyzed with the small polaron hopping mechanism based on the resistivity and Hall results [111,112,123]. We attempted to measure the carrier concentration and the mobility of our samples. However, no convincible results were obtained because of the

non-linear behavior of the Hall resistance versus the magnetic field. The deviation from the linear relation has been explained by two views: Arushanov et al. believed that the co-existence of light and heavy electrons resulted in the anomalous behavior [124], while Lengsfeld et al. ascribed it to the extrinsic magnetic clusters [125]. Due to the severe deviation, the accurate carrier concentration and mobility cannot be directly obtained through our Hall measurements. In fact, the conclusion of small polaron hopping was drawn based on the direct Hall mobility results [112]. In stark contrast, the room-temperature mobility was an order of magnitude higher when the two-band model was considered [124]. And the results of Arushanov et al. also indicated that the electron scattering was simply dominated by acoustic phonons [124]. In a word, the underlying conduction mechanism is still open to question. Returning to our results, the pure β -FeSi₂ still behaves like a slightly doped sample as its resistivity decreases obviously with the increasing temperature at temperatures below 400 K. This is presumably caused by the impurities in our starting materials (Fe, 99.95% purity) or the Co contamination from the tungsten carbide vial set. The resistivity drops off quickly at temperatures above 700 K, indicating that the intrinsic region has been reached. The resistivity monotonically decreases with the rising Co content, presumably due to the increase of the electron concentration.

The temperature dependence of the Seebeck coefficient is presented in Figure 72. The absolute Seebeck coefficient decreases with the increasing doping level. This agrees with the change of the resistivity and can be also attributed to the increasing carrier concentration. The Seebeck coefficient of β -FeSi₂ shows a negative sign over the entire temperature range. The



Figure 72 Temperature dependence of the Seebeck coefficient of Co-doped β -FeSi₂ samples. Solid lines are a guide to the eye.

un-doped β -FeSi₂ is supposed to have positive and smaller Seebeck coefficients in this temperature range according to previous studies [102]. Therefore, our β -FeSi₂ sample is slightly n-type doped, which agrees with the resistivity behavior. The Seebeck coefficient approaches zero quickly when the temperature is above 700 K, because of the opposite effect of the thermally excited holes on the Seebeck coefficient. Compared to β -FeSi₂, the Co-doped samples exhibit linearly increasing absolute Seebeck coefficient from 300 to 700 K. This behavior was also understood by the small polaron conduction mechanism [114,126]. This trend cannot be understood using the band conduction model for degenerate semiconductors as the Seebeck coefficient is much larger than that determined by band conduction [126].



Figure 73 Temperature dependence of the power factor of Co-doped β -FeSi₂ samples. Solid lines are a guide to the eye.

The power factor of Co-doped β -FeSi₂ samples shows pronounced compositional dependence, as shown in Figure 73. The samples with x ranging from 0.05 to 0.07 all exhibit a peak power factor of 14 μ WK⁻²cm⁻¹ at 850 K, while the highest power factor of the x = 0.08 and 0.09 samples occurs at 950 K and is increased to 15 μ WK⁻²cm⁻¹. A further increase of the Co concentration leads to a decrease in the power factor.

The high-temperature thermal conductivity is determined using Equation (20). The thermal diffusivity and specific heat capacity results are shown in Figure 74(a) and 74(b), respectively. It is clearly seen that the thermal diffusivity of the x = 0.00 and 0.05 samples continues to decrease with the increasing temperature. On the contrary, the thermal diffusivity is much flatter for the samples with higher Co concentrations and it increases a little at temperatures above 900 K. All



Figure 74 High-temperature thermal conductivity measurements for Co-doped β -FeSi₂: (a) thermal diffusivity and (b) specific heat capacity. Dashed line in (b) is the Dulong-Petit value.



Figure 75 Temperature dependence of the thermal conductivity of Co-doped β -FeSi₂ samples.

the samples show less difference in the specific heat capacity. Since the upper temperature limit for our DSC measurement is 600 $^{\circ}$ C, the data was extrapolated assuming that the specific heat capacity is constant above 850 K. This assumption is quite reasonable because the reported Debye temperature for β -FeSi₂ is 630 K [116], which is more than 200 K below the extrapolated onset. The C_p data for all samples is larger than the Dulong-Petit value at temperatures above 600 K and even slightly higher than the literature data [116]. Based on the thermal diffusivity and specific heat capacity data, the thermal conductivity was calculated using the room-temperature density of each sample. The results are shown in Figure 75. The thermal conductivity is slightly increased for the x = 0.08-0.11 samples around the highest temperature, presumably due to the increasing electronic thermal conductivity. It is noticeable that the thermal conductivity is reduced by Co-doping drastically. In fact, the room-temperature thermal conductivity is composed of 98% lattice part and only 2% electronic contribution for the x = 0.05 sample (calculated as a degenerate semiconductor). Thus, the reduction stems completely from the lattice thermal conductivity. As we discussed in section 4.2, the point-defect scattering of Co should be very small due to its similar atomic weight and size to Fe. The drastic decrease in the lattice thermal conductivity is an interesting phenomenon because it may be ascribed to a strong electron-phonon interaction. This hypothesis was proposed based on the low carrier mobility and the possible small polaron conduction for n-type doped β -FeSi₂ samples [113,114,127].



Figure 76 Temperature dependence of ZT of Co-doped β -FeSi₂ samples.
Figure 76 displays the temperature dependence of ZT. The x = 0.05-0.10 samples show comparable ZT values over the entire temperature range. Based on our results, a highest ZT of 0.35 at 950 K is estimated carefully for Co-doped β -FeSi₂. The best ZT occurs within a large range of doping level, implying that an accurate doping concentration and high purity starting materials are not required to achieve the best performance. In addition, the high doping concentration can also resist the deterioration which is induced by impurity diffusion during the high-temperature operation [102]. All the above advantages are very meaningful for practical applications of thermoelectric power generators.

7.3 β-FeSi₂ with Reduced Grain Size and Composites with SiC Inclusions

Since the electronic properties have been tuned properly by Co doping, the further improvement of ZT can be achieved by reducing the lattice thermal conductivity. The decrease is expected to be implemented by reducing the grain size or dispersing nanoparticles into the bulk matrix. We chose the x = 0.08 sample in section 7.2 as the control one (denoted by control). Compared to the control sample, the preparation procedure for samples with reduced grain size was changed as follows: (1) the arc-melted ingots were ball milled for 1.5 hours instead of 30 minutes; (2) the PECS condition was set as 880 $^{\circ}$ C and 40 MPa instead of 1150 $^{\circ}$ C and 30 MPa; (3) the annealing time was shortened from 100 hours to 24 hours. The holding time for PECS was still maintained as 8 minutes. Figure 77 displays the XRD patterns of the ball-milled powders and the annealed pellet (denoted by reduced grain size). The powders obtained from the

ingot are a mixture of ε -FeSi and α -FeSi₂ phases. The peak is broadened obviously after ball milling, showing an estimated crystallite size of 34 nm. The peak broadening disappears after PECS for the reduced grain size sample.



Figure 77 XRD patterns of the control, the powders ball-milled for 1.5 hours and the reduced grain size samples.

Figure 78 shows the SEM images of the control and the reduced grain size samples as well as the ball-milled powders. Most of the powder particles are smaller than 500 nm except for some large agglomerates. The control sample (96% of the theoretical density) shows a very dense texture and its grain size is on the order of 10 μ m. In contrast, the reduced grain size sample possesses numerous internal pores and the grains do not connect as well as those in the control sample. This is consistent with the lower density of this sample (90% of the theoretical value).



Figure 78 SEM images of (a) 1.5-hour ball-milled $Fe_{0.92}Co_{0.08}Si_2$ powders; (b) fracture surface of the control sample; and (c) fracture surface of the reduced grain size sample.

Besides the lower density, this sample also shows a smaller grain size around 1 to 2 μ m. This magnitude of the grain size cannot cause a pronounced peak broadening, in agreement with our XRD results. The XRD and SEM results both indicate a substantial grain growth associated with our preparation method.

The thermoelectric properties of the reduced grain size and the control samples are shown in Figure 79. The electrical resistivity is increased by 52% while the thermal conductivity is decreased by 30% for the reduced grain size sample. This behavior is likely due to a combined effect of the rising porosity and the smaller grain size. Meng et al. reported a drastic decrease in the thermal conductivity of nanostructured β -FeSi₂. However, the samples measured in their



Figure 79 Thermoelectric properties of the control and the reduced grain size samples.

study showed very low density and the reduction could not be merely attributed to the minimization of the grain size [118]. On the other hand, the Seebeck coefficient is unchanged, in stark contrast to the powder processed CoSi samples. Since the thermal conductivity reduction is offset by the rising resistivity, *ZT* is not improved for the reduced grain size sample. A higher density is the key to better electrical conductivity [38]. In order to increase the density while preventing the grain size growth, a higher PECS pressure rather than temperature is required. It

may be also worth trying PECS under vacuum instead of argon atmosphere.

Based on the above results, the nanostructuring of the matrix material was not quite successful. Thus, we decided to prepare the composites using the same preparation procedure as the control sample (β -Fe_{0.92}Co_{0.08}Si₂). The commercial SiC nanoparticles (beta phase, 95% purity, 50-60 nm average particle size) are from NanoAmor. Since SiC is a chemically stable inclusion even at high temperature, it is supposed to only scatter phonons and not affect the carrier concentration. In this study, three composite samples with SiC concentrations of 1, 3 and 5 wt. % (corresponding to 1.5, 4.4 and 7.1 vol. %, respectively) were prepared. All the composite samples possess relative densities above 95%. The XRD patterns of the composites are shown in



Figure 80 XRD patterns of β -Fe_{0.92}Co_{0.08}Si₂ - SiC composites.

Figure 80. It is seen that the β -FeSi₂ phase is formed in each sample. The XRD for the SiC powders was carried out and the pattern shows the most intensive peak at $2\theta = 35.7^{\circ}$. Some small peaks indicate the presence of SiO₂, Si and C impurities in the powders, consistent with the relatively low purity of these nanoparticles. A tiny peak found at $2\theta = 35.7^{\circ}$ for the 5% sample is likely an index to the existence of SiC, but this peak is not observed for the other two composites. It is hard to observe the SiC phase because of its low intensity caused by the small particle size and the low concentration.



Figure 81 BSE images of (a) the control sample; (b) 1 wt. % SiC; (c) 3 wt. % SiC and (d) 5 wt. % SiC composites.

Figure 81 presents the BSE images of the control sample and the composites. A secondary black phase is observed in all the composites and its content increases with the increasing SiC

	Grey Region			Black Region		
Sample	Fe	Co	Si	Fe	Si	С
control	28.83	2.34	68.83			
1 wt. % SiC	28.78	2.55	68.67	7.50	43.61	48.89
3 wt. % SiC	29.70	2.67	67.63	6.28	42.26	51.46
5 wt. % SiC	28.56	2.62	68.82	6.52	38.13	55.35

Table 10 Chemical compositions (at. %) of the grey region and the black region phases for samples in Figure 81.

concentration. The chemical compositions of the grey and dark phases in each sample are determined by EDS and the results are listed in Table 10. The grey region only shows a composition of the matrix material, while the black region is a C-rich phase. The chemical composition suggests it is a SiC phase, although we cannot observe it by the XRD. For the 5% sample, most of the SiC phases show a size around 100-200 nm and only a few large agglomerates are observed. Since the initial SiC nanoparticles possess an average size of 50-60 nm, the comparable SiC size observed in our samples indicates that we can disperse the nanoparticles into the matrix homogeneously without significant agglomeration by the current preparation procedure. On the other hand, all the SiC particles are isolated by the matrix material. This characteristic is helpful to suppress the diffusion among nanoparticles and thus the nanoinclusions will hardly coarsen during high-temperature operation [128].

Figure 82 shows the thermoelectric properties of the composites and the control sample. The



Figure 82 Thermoelectric properties of the control sample and the SiC composites.

resistivity of all the SiC composites is a little higher than that of the control sample due to the high resistivity of the inclusions. It is interesting that the increase of the resistivity shows no clear dependence of the SiC concentration and the increment is relatively small. This phenomenon probably indicates that the matrix material acts as the main electrical conduction paths [129]. The Seebeck coefficient is not affected by 1 and 3 wt. % SiC addition; however, the 5% composite exhibits a lower Seebeck coefficient compared to the control one. As we

mentioned above, SiC itself is an inert inclusion and hence should not affect the carrier concentration. The decrease of the Seebeck coefficient is likely caused by other reasons. In a study of Bi₂Te₃-SiC composites, Zhao et al. also found the similar change of the Seebeck coefficient [130]. They proposed that the contamination from the oxidized surfaces of SiC nanoparticles could decrease the Seebeck coefficient when the SiC concentration reached a certain amount [130]. In fact, the SiC nanoparticles used in our study also contain oxides and Si impurities as illustrated in the XRD results. According to our results of β -FeSi₂-Si composites (not shown in this dissertation), the addition of Si can decrease the Seebeck coefficient drastically. In a word, the decreasing Seebeck coefficient is not purely related to the SiC inclusions but to some extrinsic impurities. The SiC addition only induces a slight decrease in the thermal conductivity. As the resistivity is increased, partial decrease even stems from the reduction of the electronic contribution. This is consistent with Zhao et al.'s observation, where they found that 1 vol. % SiC addition to Bi₂Te₃ matrix even increased the thermal conductivity [130]. They attributed this behavior to the high thermal conductivity of SiC [130,131]. Since the reduction of the thermal conductivity is less than the decrease of the power factor, no improvement is obtained for the composites.

7.4 Summary

Co doping is an effective approach to improve the thermoelectric properties of the semiconducting β -FeSi₂ material. Single phase Co-doped β -FeSi₂ materials can be prepared using the sequent arc melting, ball milling, PECS and annealing procedure. The best *ZT* can be

obtained within a quite large doping range (8-10 mol%) around 950 K. The high lattice thermal conductivity limits the total performance and thus nanogranular samples are expected to show better ZT. However, a substantial grain growth during the preparation is observed even though the sample density is as low as 90% of the theoretical value. The reduced grain size sample shows no gain in the ZT due to its low density. An optimized PECS condition is desired to obtain enhanced performance. In order to improve the density while restraining the grain growth, a much higher pressing pressure should be employed.

In fact, nanogranular samples are not favorable for power generation applications due to their doubtful thermal stability. The nanostructure very likely disappears due to the grain coarsening after long-term utilization at high temperatures [132,133]. Even though nanostructured $Si_{0.8}Ge_{0.2}$ materials have been proven stable after long-time testing [88], the reliable stability may not be the case for other materials. However, a composite structure consisting of large grain matrix and nanoinclusions may not encounter such a problem as long as the inclusions are well-isolated. As a result, it is of great interest to study the nanocomposites rather than the nano-grained materials for high-temperature power generation.

In this chapter, the inert SiC nanoparticles are selected as the inclusions. Using our current method, we can disperse the nanoparticles very well into the matrix material without significant agglomerations. The thermal conductivity is not significantly reduced while the electrical properties are affected to some extent, resulting in no gain in the *ZT*. Since SiC is a high thermal conductivity material, the effect of inclusion scattering may be offset by this nature. It is worth

trying other chemically stable inclusions with lower thermal conductivity. For instance, Y₂O₃ was reported as effective inclusions to reduce the thermal conductivity of β -FeSi₂ composites [117]. Considering that it possesses a lower thermal conductivity than SiC, the improvement is relatively pronounced. Some inert particles including Si₃N₄, TiN, TiO₂ and ZrO₂ and so on are possible candidates. Furthermore, the reduction of the thermal conductivity may also be influenced by the inclusions size. It was pointed out that a critical size around 5 nm was required for inclusions in Si_{0.8}Ge_{0.2} materials to scatter heat-carrying phonons [128,134]. The SiC size approximates to a few hundred nm in our study and they are supposed to scatter the long wavelength phonons. If most of the heat is carried by shorter wavelength phonons, these large inclusions then cannot effectively reduce the thermal conductivity. The aforementioned various nanoparticles with a size down to 20 nm can be readily obtained from the commercial company like NanoAmor. Thus, a more comprehensive understanding of the thermoelectric properties of nanocomposites can be established after investigating a number of inclusions with various average sizes.

Chapter 8 Conclusions and Future Work

Silicon-based materials are composed of relatively abundant elements in nature and much more stable and reliable than tellurium-based state-of-the-art thermoelectric materials. The lower conversion efficiencies however limit their applications despite the above advantages. In this dissertation, we have comprehensively explored the possible approaches to improve the thermoelectric properties of semimetallic CoSi and semiconducting β -FeSi₂ materials.

The electrical properties of CoSi are quite attractive because this compound shows metal-like low resistivity but relatively large Seebeck coefficient around room temperature. Its room-temperature power factor is about 1.5 times that of state-of-the-art Bi₂Te₃ materials, making it promising for near-room-temperature applications. Its thermal conductivity, however, is too high to achieve a good ZT. Using the traditional alloying method, we can use isoelectronic substitutions like Rh on Co sites and Ge on Si sites to enhance the phonon-point defect scattering while maintaining the electrical properties. It is not successful to improve the thermoelectric properties by the ball milling and pressing method because the increase in the resistivity is always much larger than the thermal conductivity reduction. In fact, this nanostructuring approach is only applicable to a few systems like Si-Ge alloys, Bi₂Te₃ and PbTe materials [33]. The electronic and phonon transports are not well understood for these nanostructured materials and some results even contradict the conventional transport theory [36]. Therefore, more investigations are definitely required to clarify the principles of the bulk nanostructuring approach. We expect the answers to some questions like which phonon wavelengths carry most of the heat, what grain size can effectively scatter the dominant phonons, how much the grain size can affect the carrier mobility, etc.. Even though the thermoelectric properties can be improved by reducing the thermal conductivity, very few enhancements of the electrical properties have been obtained so far [36]. It is indeed complicated to improve the electrical properties of CoSi. The introduction of holes can cause a drastic decrease in the carrier mobility while the increasing electrons result in a large decrease in the Seebeck coefficient. An enhanced power factor is only obtained in the Pt-segregated sample. The nature of the band overlapping lowers the Seebeck coefficient and consequently the power factor. Unfortunately, we have not found out a way to engineer the inherent band structure or implement a selective scattering of holes.

The thermoelectric properties of β -FeSi₂ can be tuned properly by Co doping. The best performance does not require an accurate doping level and this feature is quite meaningful for power generation thermoelectrics. The electronic conduction mechanism and the reason for the drastic thermal conductivity reduction associated with Co doping are still open to debate. Compared to nanogranular materials, the nanocomposites with isolated inclusions are more suitable for high-temperature applications. Even though we did not obtain improved results for SiC composites, a plethora of inclusions are still on the waiting list. A number of questions are waiting to be answered, such as what is the critical inclusion size to scatter the dominant phonons, what is the best particle dispersion (e.g. random or homogeneous dispersion) and which type of particles is more helpful (e.g. good or poor electric conductors). Given that the thermal conductivity is dominated by the lattice component and its magnitude is still significantly larger

than the minimum thermal conductivity, the prospects of enhancing ZT further by using this approach are quite good.

The experimental and theoretical studies can cooperate with each other to promote the development of thermoelectrics. The recent discovery of the thermoelectric potential of mineral tetrahedrites is a good example for this: the theoretical calculations indicated that this system had suitable physical properties for thermoelectric applications and the subsequent experimental results proved the prediction [135]. The experimental results can also lead to a supplement to the traditional theory. For instance, the intrinsic low thermal conductivity found in AgSbTe₂ was unusual for bulk crystalline materials [27] and a lone-pair electrons theory was subsequently established to explain the strong anharmonicity [136]. In a word, the development of thermoelectrics does not only give us a new and deep perspective on solid state physics, but can also help to ensure us a clean and green energy future.

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