

**Transport properties of  $\text{CoGe}_{1.5}\text{Se}_{1.5}$** G. S. Nolas,<sup>1</sup> J. Yang,<sup>2</sup> and R. W. Ertenberg<sup>1</sup><sup>1</sup>*Department of Physics, University of South Florida, Tampa, Florida 33620, USA*<sup>2</sup>*Materials Processes Laboratory, GM R&D and Planning, Warren, Michigan 48090, USA*

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We have synthesized and characterized polycrystalline *n*- and *p*-type  $\text{CoGe}_{1.5}\text{Se}_{1.5}$ , a member of the class of compounds with the skutterudite crystal structure. Both specimens have large room temperature Seebeck coefficients and resistivities. The carrier type depends very sensitively on the atomic ratio between Ge and Se. For both specimens, the carrier mobilities are very low and the thermal conductivity is lower than that of the binary skutterudite  $\text{CoSb}_3$ . Some of these properties can be attributed to the vacancies in the crystal lattice due to the nonstoichiometric nature of the specimens studied. The transport properties are compared with those of  $\text{CoSb}_3$ , and the potential for thermoelectric applications is discussed. This work is part of a continuing effort to explore the large phase space of many possible compositions of skutterudites, a promising class of high-efficiency thermoelectric materials.

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**INTRODUCTION**

Compounds with the skutterudite crystal structure are of scientific interest due to their unique physical properties.<sup>1,2</sup> They continue to be of technological interest as well, in particular as potential thermoelectric materials.<sup>1-3</sup> One important feature of these materials is the large number of different isostructural compositions that can be synthesized. The physical properties of these materials depend sensitively on their compositions. This provides the means for optimizing their transport properties for advanced thermoelectric applications. The diversity of potential compositional variants remains one of the key reasons why this material system continues to be investigated by many research groups.<sup>1,2</sup>

Ternary skutterudite compounds with simultaneous substitution of group IV and VI atoms on the pnictogen sites have been previously reported.<sup>4,5</sup> These compounds should be semiconductors, as they are isoelectronic with  $\text{CoSb}_3$ . In fact, resistivity measurements on  $\text{IrGe}_{1.5}\text{S}_{1.5}$  and  $\text{IrGe}_{1.5}\text{Se}_{1.5}$  showed semiconducting temperature dependences.<sup>5</sup> In this paper we present electrical resistivity, Seebeck coefficient, thermal conductivity, magnetic susceptibility, and Hall measurements on two polycrystalline  $\text{CoGe}_{1.5}\text{Se}_{1.5}$  samples, and compare the results to those for  $\text{CoSb}_3$ .

**EXPERIMENTAL TECHNIQUES**

The  $\text{CoGe}_{1.5}\text{Se}_{1.5}$  specimens prepared for this paper were synthesized by mixing and reacting high purity constituent elements at 700 °C inside boron nitride crucibles that were themselves sealed inside fused quartz ampoules under a nitrogen atmosphere for several days. Different starting Ge and Se compositions were used in order to prepare both *n*- and *p*-type skutterudites. The products were ground to fine powders inside a glove box, cold pressed into pellets, and sintered at 700 °C for several more days. For transport measurements and electron probe microanalysis (EPMA), the powdered specimens were hot pressed in a nitrogen atmosphere at 600 °C and  $25 \times 10^3$  psi for 2 h, yielding pellets that are 90% of their theoretical (x-ray) densities. A careful

EPMA analysis indicated that the specimens were uniform and single phase with compositions  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$ , with the Ge and Se concentrations assigned relative to that of a full occupation of Co on the *c* crystallographic site. It is apparent that the relatively high Se vapor pressure resulted in a reduced amount of Se as compared to Ge in our specimens. The vacancies on the *g* crystallographic site may also affect the transport properties. An x-ray diffraction analysis of the powdered specimens revealed only the diffraction lines associated with the skutterudite structure (space group *Im*3) with lattice parameters of  $8.306 \pm 0.008$  and  $8.301 \pm 0.008$  Å for the aforementioned two samples, respectively.

Four-probe electrical resistivity ( $\rho$ ), steady-state Seebeck coefficient ( $S$ ) and steady-state thermal conductivity ( $\kappa$ ) measurements were performed in a radiation-shielded vacuum probe. Heat losses via conduction through lead wires and radiation were determined in separate experiments, and the data were corrected accordingly. The Hall coefficient was measured using a 16-Hz linear research ac resistance bridge in conjunction with a cryostat equipped with a 5 T superconducting magnet. The Hall resistance was measured in both positive and negative magnetic fields to correct for any misalignment of the Hall probes. The advantage of the ac technique is that it compensates for the thermal electromotive force generated within the specimen. Thin slabs with less than 0.5 mm thicknesses were cut for Hall measurements in order to increase the Hall signal. We were not able to resolve the Hall resistance for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  below 125 K or for  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  below 160 K because the specimens were very resistive. Magnetic susceptibility measurements were performed using a Quantum Design magnetometer with a magnetic field strength up to 5 T. For the transport measurements care was taken to prepare the specimen surface well before making electrical contact to prevent unwanted conduction from surface defects.

**RESULTS AND DISCUSSION**

The magnetic moment  $M$  varies linearly with the magnetic field  $H$  for  $H < 0.5$  T between 2 and 300 K. The mag-

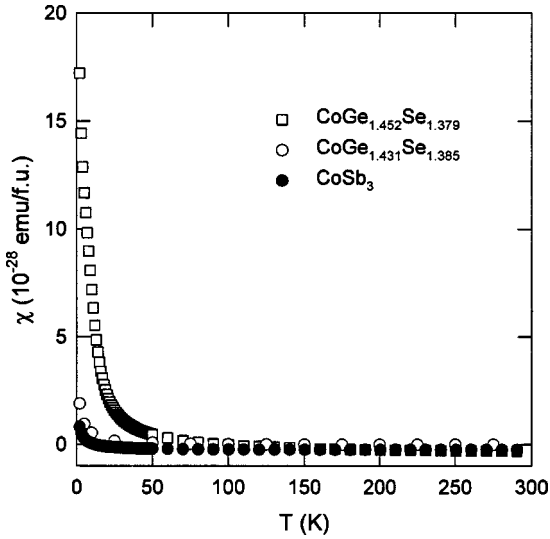


FIG. 1. Magnetic susceptibilities of polycrystalline  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  between 2 and 300 K. Data for polycrystalline  $\text{CoSb}_3$  from Ref. 6 are also shown for comparison.

netic susceptibilities ( $\chi = M/H$ , measured at  $H = 0.5$  T) as a function of temperature for both samples are shown in Fig. 1. Data for polycrystalline  $\text{CoSb}_3$  from Ref. 6 are also shown for comparison. For  $T > 100$  K, both samples exhibit diamagnetic behavior almost identical to that of  $\text{CoSb}_3$ . This indicates that Co atoms in  $\text{CoGe}_{1.5}\text{Se}_{1.5}$  assume the low-spin  $d^6$  electronic configuration, similar to  $\text{CoSb}_3$ . The much larger Curie-Weiss type component for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  at  $T < 100$  K is believed to be due to the magnetic impurities (Fe and Ni) in the starting material Co.<sup>2,7</sup> We note that the starting Co powders for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and for  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  are from different batches, thus resulting in a dissimilar amount of magnetic impurities in these two specimens. We did not detect any magnetic ordering in the temperature range investigated.

As shown in Fig. 2, the lattice thermal conductivity,  $\kappa_L$ , of  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  shows a typical temperature dependence for crystalline materials with a room temperature value of  $6 \text{ W m}^{-1} \text{ K}^{-1}$ . The total thermal conductivity can be written as  $\kappa = \kappa_L + \kappa_e$ . The electronic thermal conductivity  $\kappa_e$  can be estimated using the Wiedemann-Franz relation ( $\kappa_e = L_0 T / \rho$  with  $L_0 = 2.45 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ ) from the measured  $\rho$ . In this approximation almost all the contribution to the thermal conduction is from lattice phonons because at all temperatures  $\kappa_e$  is less than 1% of  $\kappa$ . The  $\kappa_L$  values are lower than those of  $\text{CoSb}_3$  (with  $\kappa_L \sim 8 \text{ W m}^{-1} \text{ K}^{-1}$  at room temperature).<sup>8-10</sup> The solid line in Fig. 2 is a theoretical fit of the data using the Debye approximation<sup>8,10,11</sup>

$$\kappa_L = \frac{k_B}{2\pi^2 v} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\tau_C^{-1} (e^x - 1)^2} dx, \quad (1)$$

where  $x = \hbar \omega / k_B T$  is dimensionless,  $\omega$  is the phonon frequency,  $k_B$  is the Boltzmann constant,  $\hbar$  is the reduced Planck constant,  $\theta_D$  is the Debye temperature,  $v$  is the veloc-

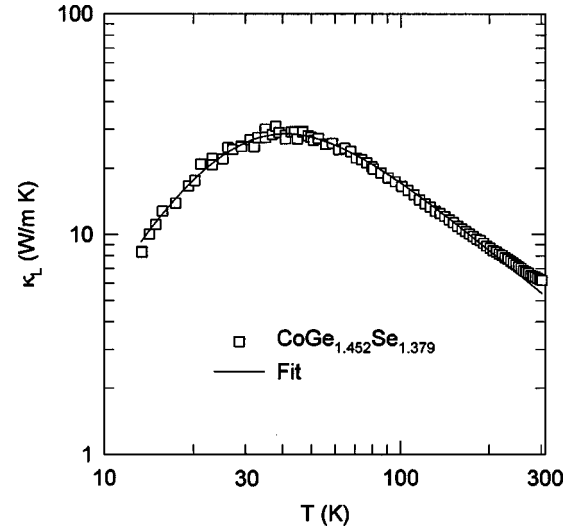


FIG. 2. Lattice thermal conductivity for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  vs temperature. The open squares are the experimental data and the line is a fit based on Eqs. (1) and (2).

ity of sound, and  $\tau_C$  is the phonon scattering relaxation time. The phonon scattering relaxation rate  $\tau_C^{-1}$  can be written as

$$\tau_C^{-1} = \frac{v}{L} + A \omega^4 + B \omega^2 T \exp\left(-\frac{\theta_D}{3T}\right), \quad (2)$$

where  $L$  is the grain size and the coefficients  $A$  and  $B$  are the fitting parameters. The terms in Eq. (2) represent grain boundary scattering, point defect scattering, and phonon-phonon umklapp scattering, respectively. From our theoretical fit (solid line in Fig. 2) we obtain  $L = 1.3 \mu\text{m}$ ,  $A = 4.70 \times 10^{-43} \text{ s}^3$ , and  $B = 6.66 \times 10^{-18} \text{ s K}^{-1}$ . The fitting parameters are very close to those of  $\text{CoSb}_3$ ,<sup>8,10</sup> except that  $A$  (the prefactor for point defect scattering) is approximately two times larger. This is reasonable in light of the large number of vacancies on the  $g$  crystallographic site indicated by EPMA. We expect that alloy scattering between Ge and Se plays a smaller role in the enhanced point defect phonon scattering in this specimen because of the small mass difference ( $\sim 8\%$ ) between Ge and Se. The solid line in Fig. 2 models the overall temperature dependence of  $\kappa_L$  quite well over the entire two orders of magnitude temperature span.

Figure 3 shows  $\rho$  data for the  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  samples. Data for polycrystalline  $\text{CoSb}_3$  from Ref. 6 are also shown for comparison.  $\rho$  decreases with increasing temperature for both samples, showing a typical semiconducting behavior. Over the entire temperature range  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  have higher  $\rho$  values than  $\text{CoSb}_3$ . The straight line is a fit to the higher temperature data ( $T > 300$  K) using  $\rho = \rho_0 \exp[E_a/k_B T]$  for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$ , where  $E_a$  is the activation energy. The fit results in  $E_a = 0.168 \text{ eV}$  and could imply an intrinsic semiconducting band gap of  $\sim 0.336 \text{ eV}$ . A fit for  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  yields the same activation energy. This estimated intrinsic band gap is higher than that for  $\text{CoSb}_3$ , with a value of  $0.102 \text{ eV}$ .<sup>6</sup> We note that similar estimates<sup>5</sup> on  $\text{IrGe}_{1.5}\text{S}_{1.5}$  and  $\text{IrGe}_{1.5}\text{Se}_{1.5}$  indicated an activation energy of

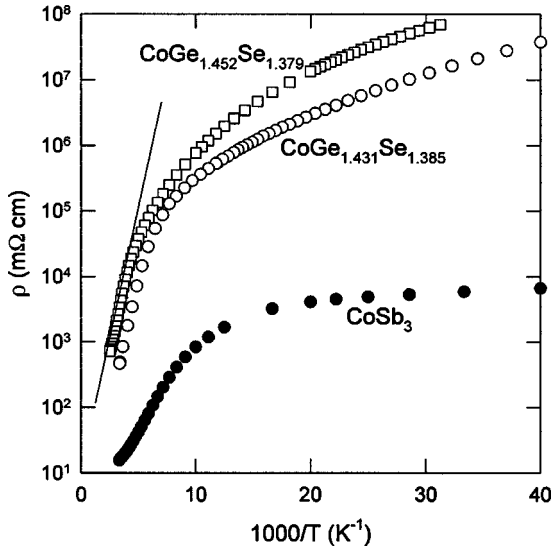


FIG. 3. The electrical resistivity of  $\text{CoGe}_{1.452}\text{Se}_{1.379}$ ,  $\text{CoGe}_{1.431}\text{Se}_{1.385}$ , and  $\text{CoSb}_3$  (from Ref. 6) vs temperature. The solid line is a fit of the form  $\rho = \rho_0 \exp[E_a/k_B T]$  to the higher temperature data, indicating  $E_a = 0.168$  eV.

$\sim 0.1$  eV; however, the authors of Ref. 5 suggest that the intrinsic gap may be even higher. We know of no band structure calculations for this material. At room temperature,  $\rho = 3.37 \times 10^3$  and  $4.703 \times 10^2$  mΩ cm for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$ , respectively. The difference increases with decreasing temperature. According to our Hall data, discussed later in this paper, the lower resistivity observed for  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  is primarily due to its much higher hole mobility, even though the room temperature carrier concentration of  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  ( $p$ -type) is about an order of magnitude lower than that of  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  ( $n$ -type).

The small compositional difference between the two specimens has a dramatic effect on the carrier type, carrier

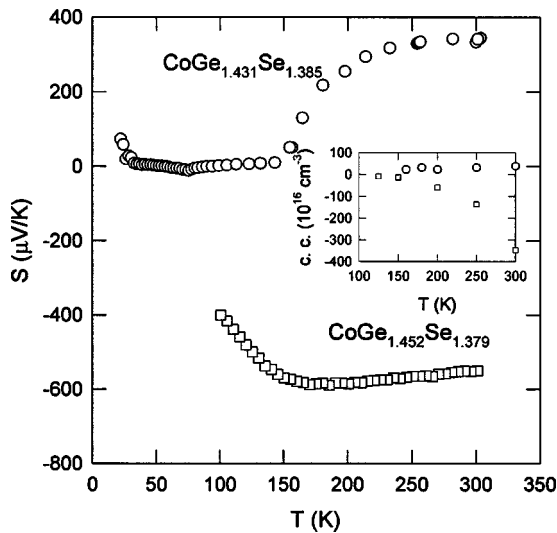


FIG. 4. Seebeck coefficient vs temperature of  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$ . The inset shows carrier concentrations (c.c.) of the two samples from Hall measurements.

concentration, and  $S$  values, as shown in Fig. 4. The negative  $S$  values for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  indicate that electrons are the majority carriers. A small change in the Ge to Se ratio alters the sign of  $S$ , making  $\text{CoGe}_{1.431}\text{Se}_{1.385}$   $p$ -type. At room temperature high  $S$  values of  $-550$  and  $341 \mu\text{V K}^{-1}$  are observed for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$ , respectively. Consistent with the  $S$  data, our Hall measurements also show that the carriers are electrons and holes for the respective specimens. The inset in Fig. 4 shows the carrier concentrations (c.c.) of  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  obtained from Hall measurements. At room temperature  $n = 3.5 \times 10^{18} \text{ cm}^{-3}$  and  $p = 3.8 \times 10^{17} \text{ cm}^{-3}$ . Our Seebeck coefficient and Hall data show that  $n$ - or  $p$ -type electrical conduction depends very sensitively on the atomic ratio between Ge and Se for  $\text{CoGe}_{1.5}\text{Se}_{1.5}$ .<sup>12,13</sup>

The temperature dependence of  $S$  for  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  is similar to that observed for the  $p$ -type  $\text{CoSb}_3$  with a comparable carrier concentration, except that the temperature at which  $S$  starts to increase rapidly is  $\sim 70$  K for the  $p$ -type  $\text{CoSb}_3$ .<sup>6</sup> It has been suggested that at these low carrier concentration levels, impurity band conduction may play an important role in electrical transport at low temperatures.<sup>6,14</sup> We speculate the low  $S$  values at low temperatures are due to impurity band conduction, in which  $S$  can be written as

$$S = \frac{\sigma_a S_a + \sigma_d S_d}{\sigma_a + \sigma_d}, \quad (3)$$

where  $\sigma_a$  and  $\sigma_d$  are the partial electrical conductivities, and  $S_a$  and  $S_d$  are the partial Seebeck coefficients of the acceptors and compensating donors, respectively. Because of the different signs of  $S_a$  and  $S_d$ ,  $S$  can be very small. At high temperatures the impurities are depleted, leading to acceptor-dominated  $S$  values. The lack of low temperature Hall data due to the resistive nature of the specimens, however, prevents us from clearly ascertaining this mechanism.

Hall data for  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  produces an electron mobility that varies roughly as  $T^{0.66}$  at room temperature with values of  $0.53$ – $0.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  from room temperature to 125 K. This indicates mixed ionized impurity and acoustic lattice scattering for electrons. For a single parabolic band  $S$  and  $n$  are given by<sup>15</sup>

$$S = \pm \frac{k_B}{e} \left( \frac{(2+r)F_{1+r}(\eta)}{(1+r)F_r(\eta)} - \eta \right), \quad (4)$$

$$n = \frac{\sqrt{2}}{\pi^2} \left[ \frac{m_n^* k_B T}{\hbar^2} \right]^{3/2} F_{1/2}(\eta), \quad (5)$$

where  $r$  is the exponent of the energy dependence of the electron mean free path,  $m_n^*$  is the electron effective mass,  $e$  is the electron charge,  $\eta = E_F/k_B T$  is the reduced Fermi energy,  $E_F$  is the Fermi energy, and  $F_x$  is the Fermi integral of order  $x$ . The  $+$  and  $-$  signs in Eq. (4) are appropriate for holes and electrons, respectively. For electrons scattered by ionized impurities and acoustic phonons,  $r=2$  and  $0$ , respectively. We use the intermediate value  $r=1$  for mixed scattering.<sup>16</sup> The room temperature  $S$  and  $n$  data yield  $m_n^* = 2.55 m_e$ , where  $m_e$  is the electron mass. This value of  $m_n^*$

is slightly smaller than that of  $\text{CoSb}_3$ .<sup>6</sup> The hole mobility for  $\text{CoGe}_{1.431}\text{Se}_{1.385}$  has a room temperature value of  $\sim 35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , and it varies approximately as  $T^6$  between 160 and 300 K. With the limited data points, it is difficult to ascertain the hole scattering mechanism. Based on the much higher hole mobility, we speculate that the effective mass for holes is much smaller than that of electrons. Similar results were found in  $\text{CoSb}_3$ .<sup>6</sup> A more complete theoretical analysis of the energy band gap and carrier effective masses for this compound would enhance our understanding, as well as provide direction for future experimental work.

### SUMMARY

We report on the synthesis and transport properties of the skutterudites  $\text{CoGe}_{1.452}\text{Se}_{1.379}$  and  $\text{CoGe}_{1.431}\text{Se}_{1.385}$ . These compounds are diamagnetic semiconductors with a relatively large band gap, as compared to  $\text{CoSb}_3$ . The electrical and thermal conduction are influenced by the vacancies in the crystal lattice because of the non-stoichiometry of the specimens. The low mobility of  $\text{CoGe}_{1.5}\text{Se}_{1.5}$  precludes it from

being a useful thermoelectric material; however, the large Seebeck coefficient makes it interesting for further investigation. The carrier types in these compounds depend very sensitively on the atomic ratio between Ge and Se. This offers a method for tuning the electrical transport properties of these compounds. At room temperature the dimensionless thermoelectric figure of merit ( $ZT = S^2 T / \rho \kappa$ ) of these compounds is 0.0005. Further research, including void filling and doping, is therefore of interest and may result in improved thermoelectric properties.

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