

## ARTICLES

**Thermoelectric properties of thallium-filled skutterudites**

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Crystallographic data, electrical and thermal transport measurements, and heat-capacity data are reported for several compounds with the filled skutterudite structure:  $\text{Tl}_x\text{Co}_{4-y}\text{Fe}_y\text{Sb}_{12}$  and  $\text{Tl}_x\text{Co}_4\text{Sb}_{12-y}\text{Sn}_y$ , where  $0 < (x,y) < 1$  and  $x \approx y$ . These materials have potential use for thermoelectric power generation. The Tl atomic displacement parameters (ADP's) are large relative to the other elements in the compounds indicating substantial "rattling" of the Tl about its equilibrium position. A simple analysis of the ADP's and low-temperature heat-capacity data indicate an Einstein temperature for the Tl of  $53 \pm 2$  K. The resonant scattering of acoustic phonons by the Tl "rattlers" are believed to be the major cause of the rapid decrease in the lattice thermal conductivity as small amounts of Tl are inserted into the voids of the skutterudite structure. Thermal and electrical transport are investigated as a function of the void filling with monovalent Tl and they are compared to previous data reported for partial filling with trivalent rare-earth ions. For comparable filling fractions, the Tl compounds had higher electron mobilities and a similar depression of the thermal conductivity. Unlike the rare-earth skutterudites, however, within experimental error there was no evidence of mass-fluctuation scattering and the minimum thermal conductivity occurred near complete void filling. At elevated temperatures (800 K), the maximum thermoelectric figure of merit,  $ZT$ , for  $n$ -type samples is estimated from room-temperature data to be about 0.8 for both Tl-filled and rare-earth-filled  $\text{Co}_4\text{Sb}_{12}$ .

**I. INTRODUCTION**

The filled skutterudite antimonides are attracting considerable interest because of their thermoelectric properties at elevated temperatures.<sup>1-3</sup> One of the striking features of the skutterudite compounds is the rapid decrease of the lattice thermal conductivity as undersized filler atoms are added to the cage-like voids in the crystal structure.<sup>3-5</sup> The filler atoms are somewhat weakly bound in the cages and "rattle" about their equilibrium position substantially more than the other atoms in the structure. It is thought that these "rattlers" resonantly scatter the heat carrying phonons, which results in a much lower thermal conductivity for the solid.<sup>1-7</sup>

The most promising skutterudite compounds for thermoelectric applications are based on the semiconductor  $\text{Co}_4\text{Sb}_{12}$  which is a cubic compound (space group  $Im\bar{3}$ ) with two voids in each unit cell. The electronic transport properties of  $\text{Co}_4\text{Sb}_{12}$  are excellent for thermoelectric applications but the lattice thermal conductivity is too large.<sup>8-12</sup> By filling the voids with La or Ce, and compensating for the excess charge using Fe on the Co site or Sn on the Sb site, excellent overall thermoelectric properties are achieved. Between 700 and 1000 K, the dimensionless thermoelectric figure of merit,  $ZT$ , has values between 1 and 1.4 for  $p$ -type samples.<sup>1-3</sup> Although these values are among the best reported for any material, the filling of the voids with electropositive atoms such as La or Ce results in poorer electronic transport than found in the parent compound  $\text{Co}_4\text{Sb}_{12}$ . Previous work has shown that the voids in skutterudites such as  $\text{Co}_4\text{Sb}_{12}$  can be filled or partially filled with a variety of different atoms, including La, Ce, Pr, Nd, Sm, Eu, Yb, Ba, Sr, and Th.<sup>8-16</sup> All of these elements are significantly more electropositive (i.e., have smaller electronegativities) than either Co or Sb which often

results in lower carrier mobility. Recent work<sup>17</sup> has shown that under high pressure (1–5 GPa), Sn and Pb can be inserted into the  $\text{Co}_4\text{Sb}_{12}$  voids, but no transport data has been reported and the thermal stability of the new compounds is not known. Several metastable skutterudites have also been synthesized using superlattice reactants.<sup>18</sup>

Thallium is an unusual element because in some respects it is chemically similar to other heavy metals such as lead, while in other respects it behaves like an alkali-metal element.<sup>19</sup> The electronegativity of Tl is close to that of Sb which suggests that it may have less of an effect on electrical transport than the rare earths. Because of its peculiar chemistry, it was not obvious that Tl would occupy the voids in  $\text{Co}_4\text{Sb}_{12}$  since the radius of the void is close to the radius of  $\text{Tl}^{+1}$  in a 12-coordinated site (1.7–1.8 Å) and from previous work we knew neither Pb or Bi filled skutterudites structures formed.<sup>8,11</sup> We found, however, that Tl-filled skutterudites formed rather easily and up to 22% of the voids in  $\text{Co}_4\text{Sb}_{12}$  could be filled with Tl. Since the formal valence of Tl in these compounds is close to +1, further filling of the voids is possible without straying too far from the  $\text{Co}_4\text{Sb}_{12}$  composition. For example, about 80% of the voids can be filled if the excess charge contributed by the Tl is compensated by either one Fe for one Co (i.e.,  $\text{Tl}_{0.8}\text{Co}_3\text{FeSb}_{12}$ ) or replacing one Sb by Sn (i.e.,  $\text{Tl}_{0.8}\text{Co}_4\text{Sb}_{11}\text{Sn}$ ). The present work describes the thermoelectric properties of these new Tl-filled skutterudites.

**II. EXPERIMENT****A. Synthesis**

The synthesis of the Tl-filled skutterudites ( $\text{Tl}_x\text{Co}_{4-y}\text{Fe}_y\text{Sb}_{12}$  and  $\text{Tl}_x\text{Co}_4\text{Sb}_{12-y}\text{Sn}_y$ , where  $0 < (x,y) < 1$  and  $x \approx y$ ) is

similar to that used to prepare other skutterudite compositions.<sup>3</sup> A thin layer of carbon was deposited on the inside of a round-bottomed silica tube by the pyrolysis of acetone. Stoichiometric amounts of thallium metal pieces (99.999% rod from Alfa Chemical Company), Fe rod (99.9985% from Alfa), Co rod (99.998% from Alfa), Sb shot (99.999% from Alfa), and Sn shot (99.99% from Alfa) were loaded into the precarbonized tube. Thallium metal readily oxidizes in air and was handled and loaded in a helium dry box with a typical oxygen concentration of 5 ppm. Thallium is toxic,<sup>19</sup> and the oxide and other salts can be absorbed through the skin. When working with these compounds, gloves and a hood were used when there was any risk of Tl exposure. The tube was sealed under vacuum at a pressure of  $10^{-3}$  Pa and transferred into a programmable furnace. The silica ampoule was heated to 600 °C at 5 °C/min, left at 600 °C for 3 h, and then slowly (1 °C/min) heated to 1050 °C and left for about 30 h. The long soak for 30 h was found to be necessary to dissolve the 1–3 mm size pieces of Co metal. The silica ampoule containing the homogeneous molten liquid was removed from the furnace at temperature and quenched into a water bath. The same ampoule (containing the prereacted elements) was then placed in a furnace and annealed at 500 °C for several days to form the correct crystallographic phase. The completely reacted solid was removed from the silica tube and cleaned with a wire brush to remove small amounts of carbon from the surface. To form a completely dense polycrystalline solid, the reacted material was transferred to the helium dry box, ground into a fine powder, and loaded into a graphite die. The graphite die plus powder was quickly loaded into a hot press and compressed (35 MPa) in a helium atmosphere at 500 °C for 40 min. For transport measurements, rectangular solids (e.g.,  $6 \times 6 \times 12$  mm<sup>3</sup> or  $7 \times 2 \times 18$  mm<sup>3</sup>) were cut from the hot-pressed material using a low-speed diamond saw. Each sample was characterized using x-ray diffraction, energy dispersive x rays (EDX), electrical resistivity, and Seebeck and thermal conductivity measurements. Metallographic, Hall, heat capacity, and neutron diffraction measurements were performed on selected samples. Most samples had less than 3 vol % of an impurity phase such as FeSb<sub>2</sub> or Sb, were better than 95% of the theoretical density, and had polycrystalline grains in the 5–50 μm range.

### B. Measurements

Powder x-ray diffraction measurements were made using Cu  $K\alpha$  radiation and a commercial SCINTAG diffractometer equipped with a nitrogen-cooled Ge detector. Powder neutron diffraction data were collected at ORNL's High Flux Isotope Reactor (HFIR) using the HB-4 high resolution powder diffractometer. Structure refinements were made by the Rietveld method using general structure analysis system (GSAS) software.<sup>20</sup> The samples were sealed in a vanadium can with He exchange gas for data collection between 10 and 295 K. Additional details of the methods used for the structure refinements are given elsewhere.<sup>21</sup> Chemical composition information was obtained directly using a Princeton Gamma Tech energy dispersive x-ray system and an International Scientific Instruments scanning electron microscope. Metallographic investigations were performed on polished surfaces using standard optical microscopy techniques.

Electrical and thermal transport data from 10–300 K were obtained using a closed cycle helium refrigerator. The sample was suspended from a copper cold finger using EPO-TEK H20E silver epoxy. A small RuO<sub>2</sub> chip resistor (51 Ω) was mounted on a  $5 \times 5 \times 0.1$  mm<sup>3</sup> piece of copper foil using a thermally conducting but insulating epoxy (EPO-TEK 930-4). This heater was attached to the other end of the sample using Dupont 4929N Ag paste. Electrical connections to the heater were made with 0.0075-cm-diam chromel wires. Small temperature differences (1–3 K) across the sample were measured using two 0.0125-cm-diam chromel-constantin thermocouples attached to the sample using silver paste. For Seebeck and resistivity measurements, four 0.0075-cm-diam copper wires were attached to the sample with silver paste. The sample and wires were enclosed in a copper can that was thermally attached to the cold finger. The copper can was at approximately the same temperature as the cold end of the sample. Using this arrangement radiation losses were kept to a minimum. For samples with values for thermal conductivity of 100 mW/cm K and above, the radiation and conduction losses were small enough to be neglected regardless of the geometry of the sample. However, many of the filled skutterudites had thermal conductivities (at room temperature) in the 15–30 mW/cm K range. To obtain reliable thermal conductivity values for these materials, all of the copper leads were removed from the sample and the samples were cut into a specific shape ( $6 \times 6 \times 12$  mm<sup>3</sup>) which had a relatively large ratio of the cross-sectional area to length. This procedure yielded the correct thermal conductivity values for a vitreous SiO<sub>2</sub> standard over the entire 10–300 K temperature interval. The same heater was used for all of the Tl-doped samples to increase the relative precision of the thermal conductivity measurements. If a small bar-shaped sample was used instead, the thermal conductivity of the lattice showed pronounced upward curvature in the 200–300 K temperature range—a feature characteristic of problems with radiation losses. Heat capacity and Hall measurements from 2–300 K were made with a commercial system from Quantum Design.

## III. RESULTS AND DISCUSSION

### A. Crystallography and evidence of “rattling”

The room-temperature lattice constants of all of the Tl-filled skutterudites as determined using powder x-ray diffraction are shown in Fig. 1. The maximum percentage of the voids in Co<sub>4</sub>Sb<sub>12</sub> that could be filled with Tl using the synthesis procedure described above was  $22 \pm 1\%$ , a value close the limit reported by Nolas, Cohn, and Slack for La filled Co<sub>4</sub>Sb<sub>12</sub> alloys.<sup>4</sup> For higher Tl fillings, the charge contributed by the Tl was compensated by either replacing part of the Co by Fe or part of the Sb by Sn. In the present experiments, approximately 80% of the voids are filled with Tl when, per formula unit, 1 Co is replaced by 1 Fe or 1 Sb is replaced by 1 Sn. The lattice constant is roughly linear with the Tl concentration, independent of whether the excess Tl charge is compensated by Fe or Sn.

Structure refinements were performed on three of the Tl-filled skutterudites as a function of temperature using powder neutron diffraction (Tl<sub>0.22</sub>Co<sub>4</sub>Sb<sub>12</sub>, Tl<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Sn<sub>0.5</sub>, and Tl<sub>0.8</sub>Co<sub>3</sub>FeSb<sub>12</sub>). As was the case for the rare-earth-filled

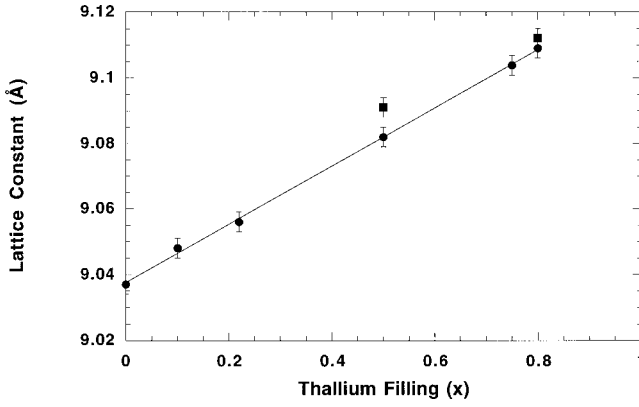


FIG. 1. Room-temperature lattice constant of the cubic skutterudite phase versus fraction of voids filled with thallium. The exact compositions of all of the alloys are given in Table I. The square data points refer to the Fe compensated alloys.

skutterudites,<sup>3,13</sup> unusually large atomic displacement parameters (ADP) (formally called thermal parameters) were found for the Tl atoms in all three compounds. ADP measure the mean-square displacement amplitude of an atom about its equilibrium position. The displacement amplitude can be due to the vibration of the atom or due to static disorder.<sup>22</sup> To ensure that the ADP values were physically meaningful, the occupation of the various crystallographic sites were treated as adjustable parameters during the data refinement. Thus the refined structure also provided another check of the sample composition, including the fraction of voids filled by Tl atoms. Figure 2 shows typical ADP data obtained for the alloy  $\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$ . All of the ADP data have been converted to an isotropic  $U_{\text{iso}}$  value that has the dimensions of  $\text{Å}^2$ .  $U_{\text{iso}}$  measures the mean-square displacement amplitude of the atom averaged over all directions. At all temperatures, the  $U_{\text{iso}}$  values for Tl are significantly larger than the values found for Co and Sb. The partial occupancy of the Tl site (the voids) introduces static disorder which typically results in a constant value for  $U_{\text{iso}}$  as a function of temperature. The low-temperature intercept of the line through the Tl data in Fig. 2 approximately corresponds to the amount of static disorder (the low temperature value due to zero point motion is much smaller, typically  $0.001 \text{ Å}^2$ ). The remaining tem-

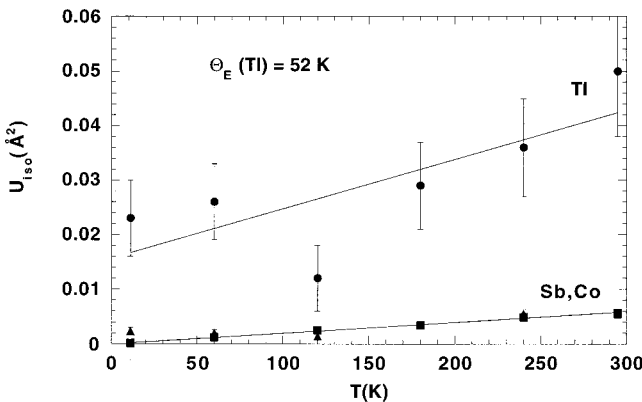


FIG. 2. Isotropic atomic displacement parameters (ADP) versus temperature for the  $\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$  alloy. An Einstein temperature for the Tl atoms of 52 K was estimated from the slope of the Tl ADP data. See text for details.

perature dependence of  $U_{\text{iso}}$  corresponds to the dynamic vibration of the Tl about its equilibrium position. The unusually low value of  $U_{\text{iso}}$  at 120 K is believed to be an artifact since ADP data from two other samples with different Tl fillings showed no anomaly at this temperature.

Interpreting the ADP data requires a model. A model that has been successful in understanding the properties of the filled skutterudites and similar materials treats the ‘‘rattling’’ atoms, such as the Tl, as localized harmonic oscillators (Einstein oscillators) and the remaining atoms as part of a Debye solid.<sup>23</sup> For a quantized harmonic oscillator, the mean-square displacement amplitude  $\langle u^2 \rangle$  is given by<sup>24</sup>

$$U_{\text{iso}} = \langle u^2 \rangle = h / (8 \pi^2 m \nu) \coth(h \nu / 2 k_B T), \quad (1)$$

where  $m$  is the mass of the rattler and  $\nu$  is the frequency of vibration. At high temperatures, where  $h \nu < 2 k_B T$ , Eq. (1) reduces to the classical expression  $U_{\text{iso}} = k_B T / K$ , where  $K$  is the force constant of the oscillator,  $K = m (2 \pi \nu)^2$ . Therefore, from the slope of  $U_{\text{iso}}$  vs  $T$ , the Einstein temperature of vibration ( $\Theta_E = h \nu / k_B$ ) is estimated to be 52 K. Using a similar analysis,<sup>23</sup> the Debye temperature and the Debye velocity of sound for  $\text{Tl}_{0.23}\text{Co}_4\text{Sb}_{12}$  can be estimated from the ADP data resulting in  $\Theta_D = 274 \text{ K}$  and  $v_s = 2640 \text{ m/s}$ . These values, determined using only the ADP data, are about 10% lower than the values ( $\Theta_D = 307 \text{ K}$  and a mean sound velocity of  $v_s = 2930 \text{ m/s}$ ) measured by Caillat, Borschhevsky, and Fleurial<sup>9</sup> on single crystals of  $\text{Co}_4\text{Sb}_{12}$ .

The ADP data from the other two alloys indicated that the Einstein temperature increases with Tl filling from 62 K for the  $\text{Tl}_{0.5}\text{Co}_4\text{Sb}_{11.5}\text{Sn}_{0.5}$  alloy to 69 K for the  $\text{Tl}_{0.8}\text{Co}_3\text{FeSb}_{12}$  alloy. The corresponding Debye temperatures (estimated from the ADP data) were 270 K for the  $\text{Tl}_{0.5}$  sample and 303 K for the  $\text{Tl}_{0.8}$  alloy.

## B. Heat-capacity data

Heat-capacity measurements,  $C_p(T)$ , were made on  $\text{Co}_4\text{Sb}_{12}$  and  $\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$  from 2–300 K. At low temperatures (below 4 K), standard plots of  $C_p/T$  vs  $T^2$  were linear for both samples and yielded Debye temperatures of 302 K. The Tl contribution to the heat capacity was estimated by plotting the heat-capacity difference,  $C(\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}) - C(\text{Co}_4\text{Sb}_{12})$  as a function of temperature. Below 20 K the difference was well within experimental error and is shown in Fig. 3. The excess heat capacity for the Tl-doped alloy is well approximated by an Einstein contribution:

$$C_E(T) = A x^2 e^x / (e^x - 1)^2 \quad (2)$$

with an amplitude  $A$  of  $0.22 \cdot 3R = 5.5 \text{ joule/mole K}$ ,  $x = \Theta_E / T$ , and  $\Theta_E = 55 \text{ K}$ . Note this Einstein temperature is close to the value of 52 K estimated from the ADP data. At high temperatures both the Einstein and Debye models approach the classical Dulong and Petit value of  $3R$  per mole of atoms and the difference  $[C(\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}) - C(\text{Co}_4\text{Sb}_{12})]$  is only 1.3%, which is within the various errors in each measurement (such as the mass of each sample).

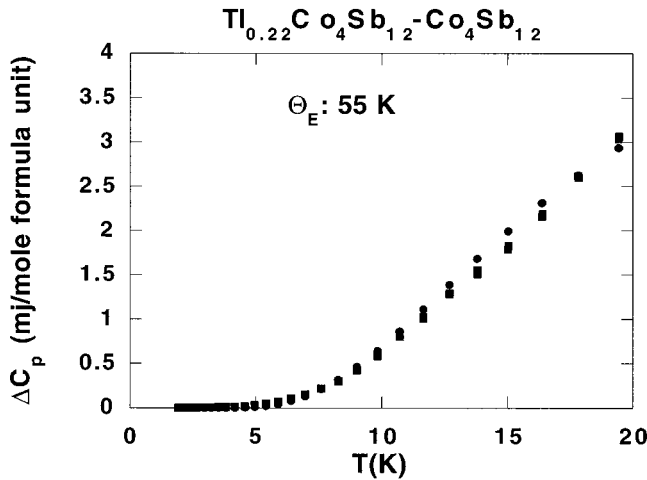


FIG. 3. Difference in heat capacity between a TI-doped alloy ( $\text{Ti}_{0.22}\text{Co}_4\text{Sb}_{12}$ ) and  $\text{Co}_4\text{Sb}_{12}$ . The TI contribution to the heat capacity is accurately described by an Einstein contribution with an Einstein temperature of 55 K. Squares are measured data, circles are calculated.

### C. Rattling and thermal conductivity

The total thermal conductivity as a function of temperature is shown in Fig. 4 for several of the TI-filled skutterudites. As increasing amounts of TI fill the voids in the skutterudite structure the thermal conductivity monotonically decreases for temperatures between 50 and 300 K. Not shown in this figure is the thermal conductivity of polycrystalline  $\text{Co}_4\text{Sb}_{12}$  which has a value of 0.1 W/cm K at room temperature and a maximum of 0.3 W/cm K at 50 K. The mean free path of the heat-carrying phonons in these compounds is determined by the various scattering mechanisms in the crystal such as acoustic phonons, grain boundaries, electron-phonon scattering, static defects, voids, and “rattlers.” Resonant scattering by quasilocalized rattlers appears to be the dominant scattering mechanism responsible for the rapid decrease in the thermal conductivity as small amounts of TI (or rare earths) are placed in the voids. This mechanism is believed to be similar to the resonant scattering described by Pohl for insulating crystals.<sup>25</sup> It has been demonstrated

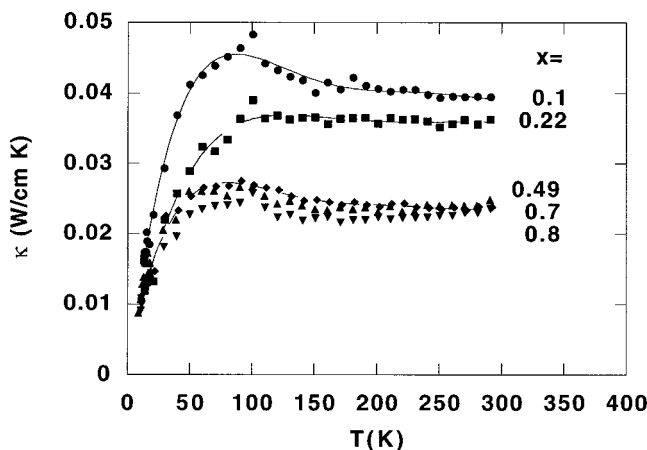


FIG. 4. Total thermal conductivity versus temperature for several TI-doped alloys:  $\text{Ti}_{0.1}\text{Co}_4\text{Sb}_{12}$ ,  $\text{Ti}_{0.22}\text{Co}_4\text{Sb}_{12}$ ,  $\text{Ti}_{0.49}\text{Co}_4\text{Sn}_{0.5}\text{Sb}_{11.5}$ ,  $\text{Ti}_{0.7}\text{Co}_4\text{Sn}_{0.75}\text{Sb}_{11.25}$ ,  $\text{Ti}_{0.8}\text{Co}_4\text{SnSb}_{11}$ .

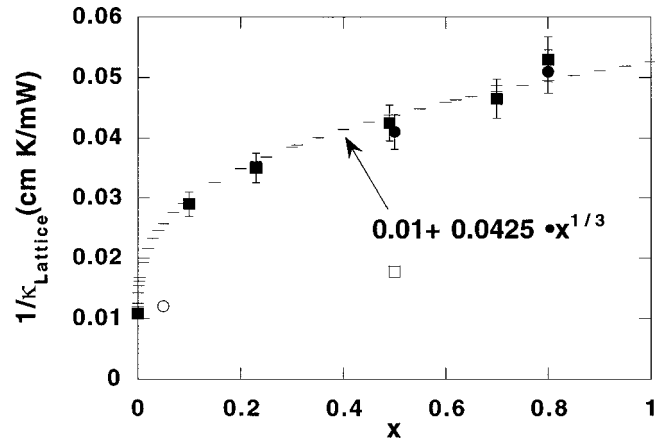


FIG. 5. Thermal resistivity of lattice at room temperature versus TI filling  $x$ . The data are qualitatively described by an  $x^{1/3}$  functional dependence. The filled circles correspond to Fe-compensated alloys. The room-temperature thermal resistivity of the lattice is also shown for a  $\text{Co}_{0.95}\text{Ni}_{0.05}\text{Sb}_3$  and a  $\text{Co}_{0.95}\text{Fe}_{0.05}\text{Sb}_3$  alloy. These alloys were measured to estimate the contribution of electron-phonon scattering to the thermal resistivity of the TI alloys. The thermal resistivities of the  $\text{Ni}_{0.05}$  (open square) and  $\text{Fe}_{0.05}$  (open circle) samples are plotted below TI alloys with similar carrier concentrations (see text for details).

that mass fluctuation scattering is much too weak to explain the rapid decrease in thermal conductivity.<sup>4</sup>

The lattice thermal conductivity for each sample was estimated by subtracting the electronic contribution using the Wiedemann-Franz law. For all of the TI-filled skutterudites, the electronic thermal conductivity at room temperature was less than 25% of the total. The thermal resistivity of the lattice (1/thermal conductivity) at room temperature is shown in Fig. 5. Thermal resistivity is shown rather than thermal conductivity because as a first approximation, the scattering rates for different scattering processes should add (Mathieson’s rule). As small amounts of TI are added to  $\text{Co}_4\text{Sb}_{12}$ , there is a rapid initial increase in the thermal resistance, followed by a gradual saturation of the thermal resistance as higher concentrations of TI are added to the voids. Within experimental error, there is no clear maximum in the thermal resistance data as a function of TI concentration, and the maximum thermal resistance occurs near complete filling for both the Fe and Sn compensated compounds. The maximum attributed to mass fluctuation scattering by Meisner *et al.*<sup>26</sup> as a function of Ce filling is not observed in the present experiments.

As TI (or other filling atoms) are added to the skutterudite structure, the carrier concentration typically changes by several orders of magnitude. Therefore, part of the increase in thermal resistivity may be due to increased electron-phonon scattering. Caillat, Borschhevsky, and Fleurial<sup>9</sup> found that single crystals of  $\text{Co}_4\text{Sb}_{12}$  grown with 1% of the Co replaced by Pd resulted in a lattice thermal resistivity of 0.0175 cm K/mW, and had a carrier concentration of  $1.4 \times 10^{20} \text{ cm}^{-3}$ . If all of the Pd substitutes for Co (as opposed to going into the voids), this would imply that about 30% of the increase in thermal resistivity of the TI alloys with a similar carrier concentration could be due to electron-phonon scattering. For  $n$ -doped samples it is difficult from transport data alone to tell if a dopant like Pd is substituting for Co or is going into



the voids. To further investigate the importance of electron-phonon scattering, two alloys were synthesized and measured:  $\text{Co}_{0.95}\text{Ni}_{0.05}\text{Sb}_3$  and  $\text{Co}_{0.95}\text{Fe}_{0.05}\text{Sb}_3$ . Nickel was selected as the  $n$ -type dopant rather than Pd since Ni is slightly smaller than Pd and is less likely to go into the voids. Fe acts as a  $p$ -type dopant for  $\text{CoSb}_3$ .<sup>8,11</sup>  $\text{Co}_{0.95}\text{Ni}_{0.05}\text{Sb}_3$  has a carrier concentration of about  $5 \times 10^{20} \text{ cm}^{-3}$  and a lattice thermal resistivity of  $0.0175 \text{ cm K/mW}$ , implying that up to 25% of the increase in thermal resistivity could be due to electron-phonon scattering. For the  $p$ -type Fe-doped sample, the carrier concentration is about  $3.8 \times 10^{19}$  and the thermal resistivity is  $0.0125 \text{ cm K/mW}$ . This suggests that for the  $p$ -type samples the importance of electron-phonon scattering is less (about 10%) than for the  $n$ -type samples. This is perhaps not surprising since the electron effective mass is about 30 times larger than the hole effective mass in lightly doped  $\text{Co}_4\text{Sb}_{12}$  alloys.<sup>9,10,11</sup>

A careful study of the lattice dynamics of filled skutterudites indicates that the ‘‘rattler’’ atoms reside in essentially harmonic potential wells.<sup>27,28</sup> These calculations show that normal lattice dynamics for completely filled skutterudites (within the harmonic approximation) can account for the temperature dependence of the heat capacity and the two peaks in the La phonon density of states found using neutron scattering.<sup>29</sup> The reduction in the thermal conductivity as the voids are filled in the skutterudite structure is apparently related to exactly how the partially localized ‘‘rattlers’’ hybridize and/or scatter other low-energy phonons. A detailed theoretical model of this process has not been proposed.

If the Tl atoms are treated as localized Einstein oscillators, as suggested by Keppens *et al.*,<sup>29</sup> then the heat-carrying phonon mean free path  $d$  should be a function of the distance between the Tl atoms in the crystal. The simplest estimate of the phonon mean free path is therefore the average distance between the Tl. This implies that the phonon scattering from the Tl is so strong that  $d$  attains a minimum distance given by the average Tl-Tl separation. The scattering of acoustic phonons by the Tl should be a maximum when the acoustic phonon and rattling frequency are equal.<sup>25</sup> However, even at resonance it seems physically unlikely that  $d$  could be less than the Tl-Tl separation distance. This simple argument suggests that if the role of other scattering mechanisms can be minimized, that the thermal resistivity should vary as  $x^{1/3}$ , where  $x$  is the Tl concentration (the average spacing between Tl atoms varies as  $x^{-1/3}$ ). The additional thermal resistance generated as Tl is added to  $\text{Co}_4\text{Sb}_{12}$  reasonably follows an  $x^{1/3}$  behavior (Fig. 5), even though part of the thermal resistance is due to electron-phonon scattering and other scattering mechanisms.

#### D. Electrical transport

The electrical resistivity and Seebeck data for the Tl-filled skutterudites are shown in Figs. 6 and 7, respectively. The parent compound,  $\text{Co}_4\text{Sb}_{12}$  (see Table I) has a hole carrier concentration of  $1.2 \times 10^{17} \text{ cm}^{-3}$ , a resistivity of  $38 \text{ m}\Omega \text{ cm}$ , and a Seebeck coefficient of  $+310 \mu\text{V/K}$ . As small amounts of Tl are added to the voids of  $\text{Co}_4\text{Sb}_{12}$ , electrons are donated by Tl and the alloys become  $n$  type. The maximum fraction of the voids in  $\text{Co}_4\text{Sb}_{12}$  that could be filled with Tl is 22%. The electron mobility at this filling was  $38 \text{ cm}^2/\text{V s}$  at

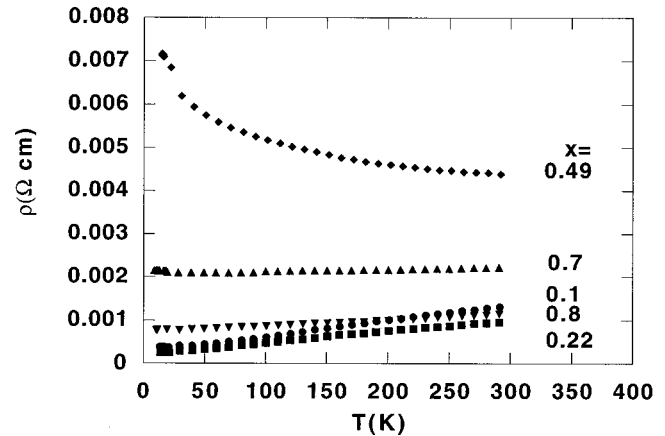


FIG. 6. Electrical resistivity versus temperature for the same Tl-filled skutterudites shown in Fig. 4.

room temperature and increased to  $1500 \text{ cm}^2/\text{V s}$  at 5 K (Fig. 8). Similar Hall data was found for the  $\text{Tl}_{0.1}$  alloy which had a higher electron mobility at room temperature of  $77 \text{ cm}^2/\text{V s}$ . The room-temperature carrier mobility for the polycrystalline  $\text{Tl}_{0.22}$  sample is close to that found by Caillat, Borschhevsky, and Fleurial<sup>9</sup> for a  $\text{Co}_4\text{Sb}_{12}$  single crystal doped with 1% Pd. Both samples had about the same carrier concentration, but the lattice thermal conductivity of the Tl alloy was more than a factor of 2 lower, presumably due to the rattling of the Tl in the voids. Using a single parabolic band and assuming the carriers are scattered primarily by acoustic phonons, gives an effective mass for the electrons in the  $\text{Tl}_{0.22}$  alloy of  $2m_e$ . This value is typical of that found for a variety of  $n$ -type  $\text{CoSb}_3$  crystals<sup>9,5</sup> and is consistent with band-structure calculations for  $\text{CoSb}_3$  (Ref. 30) and La-filled skutterudites.<sup>31</sup>

Filling the voids with higher concentrations of Tl required that the excess charge donated by the Tl atoms be compensated by suitable alloying on either the Co or Sb sites. Either Fe on the Co site or Sn on the Sb site resulted in single-phase samples. Similar behavior has been previously observed with La- and Ce-filled skutterudites.<sup>4,5</sup> For the Tl-filled compounds, relatively high filling levels ( $x=0.8$ ) were achieved without straying too far from the  $\text{Co}_4\text{Sb}_{12}$  composition. The transport data for the Sn compensated alloys are also shown

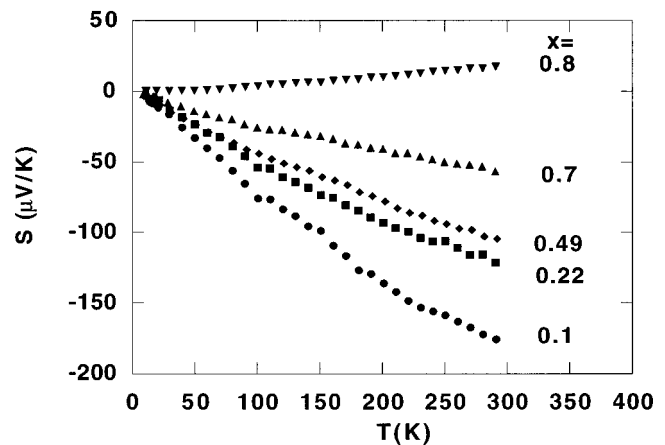


FIG. 7. Seebeck coefficient versus temperature for the same Tl-filled skutterudites shown in Figs. 6 and 4.

TABLE I. Summary of crystallographic, transport, thermodynamic, and physical characteristics of Tl-filled skutterudites at room temperature.

	Co <sub>4</sub> Sb <sub>12</sub>	Tl <sub>0.1</sub> Co <sub>4</sub> Sb <sub>12</sub>	Tl <sub>0.22</sub> Co <sub>4</sub> Sb <sub>12</sub>	Tl <sub>0.5</sub> Co <sub>4</sub> Sb <sub>11.5</sub> Sn <sub>0.5</sub>	Tl <sub>0.5</sub> Fe <sub>0.5</sub> Co <sub>3.5</sub> Sb <sub>12</sub>	Tl <sub>0.75</sub> Co <sub>4</sub> Sb <sub>11.25</sub> Sn <sub>0.75</sub>	TlCo <sub>4</sub> SnSb <sub>11</sub>	TlCo <sub>3</sub> FeSb <sub>12</sub>
Density (g/cm <sup>3</sup> )	6.6	6.54	7.6	7.72	7.0	7.91	7.86	7.83
Lattice constant (Å)	9.0369	9.0483	9.056	9.082	9.091	9.1038	9.109	9.112
X-ray density (g/cm <sup>3</sup> )	7.6	7.66	7.75	7.94	7.91	8.1	8.31	8.3
% theoretical density	87	85	98	97	88	98	95	94
$n$ (carriers/cm <sup>3</sup> )	$1.2 \times 10^{17}$	$6.2 \times 10^{19}$	$1.7 \times 10^{20}$					
$S_{(300\text{ K})}$ ( $\mu\text{V/K}$ )	310	-185	-125	-105	-80	-58	17	70
$\rho_{(300\text{ K})}$ ( $\Omega\text{ cm}$ ) (corrected for density)	0.038	0.001 35	0.000 95	0.0045	0.0045	0.0022	0.0012	0.0023
$\kappa_{\text{lattice}(300\text{ K})}$ (W/cm K)	0.092	0.034	0.0288	0.023	0.024	0.0215	0.019	0.019
Mobility <sub>(300 K)</sub> (cm <sup>2</sup> /V s)	1070	77	38					
Measured thallium content ( $x$ )	0.0	0.1	0.22	0.49	0.5	0.7	0.8	0.8
Thermal expansion (K <sup>-1</sup> ) (180–300 K)			$7.4 \times 10^{-6}$	$9.5 \times 10^{-6}$				$9.5 \times 10^{-6}$

in Figs. 5 and 6. All of the alloys were  $n$ -type with the exception of the Tl<sub>0.8</sub>Co<sub>4</sub>Sb<sub>11</sub>Sn and Tl<sub>0.8</sub>Co<sub>3</sub>FeSb<sub>12</sub> (not shown) samples. The qualitative behavior of the Seebeck and resistivity data with Tl filling is similar to that found by Nolas for the La-filled skutterudites.<sup>4</sup> For the Tl alloys compensated with Sn or Fe, the only selection criterion used in the synthesis of the samples was that the samples be single phase. In the present work, no attempt was made to optimize the carrier concentration for thermoelectric applications.

The dimensionless figure of merit,  $ZT$ , is used to evaluate thermoelectric materials for either refrigeration or power generation applications and is given by

$$ZT = S^2 T / \kappa \rho, \quad (3)$$

where  $S$  is the Seebeck coefficient,  $T$  is the temperature,  $\kappa$  is the total thermal conductivity, and  $\rho$  is the electrical resistivity. Materials with larger values of  $ZT$  result in energy conversion devices with higher efficiencies. State of the art thermoelectric devices use materials with  $ZT$  values slightly less than 1 (0.6–0.9). For the Tl-doped alloys,  $ZT$  versus  $T$  is shown in Fig. 9. At room temperature the maximum value of  $ZT$  was about 0.175 for the Tl<sub>0.1</sub>Co<sub>4</sub>Sb<sub>12</sub> alloy. Although for

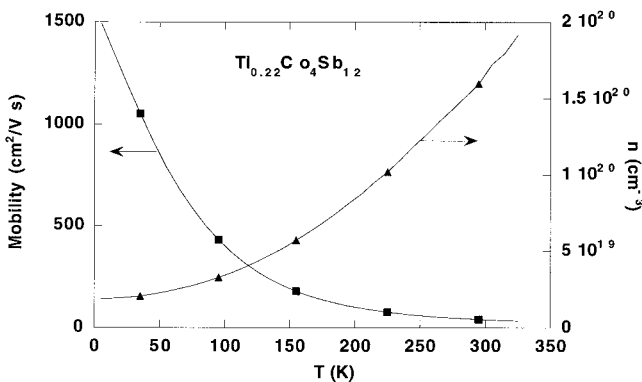


FIG. 8. Mobility and carrier concentration versus temperature for the Tl<sub>0.22</sub>Co<sub>4</sub>Sb<sub>12</sub> alloy.

the same filling level the Tl alloys have higher electron mobilities than the rare-earth-filled alloys, the theoretically estimated<sup>3,32</sup> maximum values for  $ZT$  at elevated temperatures (800 K) for the uncompensated alloys (i.e., no Fe or Sn) are about the same ( $ZT \approx 0.8$ ). Note, this is the maximum for  $n$ -doped samples with no charge compensation. It is possible that a more complete investigation of the Sn or Fe compensated  $n$ -type samples would result in even higher values for  $ZT$ . For  $p$ -type samples the maximum  $ZT$  values are between 1 and 1.4 at elevated temperatures.<sup>1–3</sup> The filled skutterudites are stable in an inert atmosphere up to temperatures near 1000 K. Above this temperature, the compounds decompose.<sup>1–3</sup>

#### IV. CONCLUSIONS

Thallium-filled skutterudites (Tl <sub>$x$</sub> Co<sub>4– $y$</sub> Fe <sub>$y$</sub> Sb<sub>12</sub> and Tl <sub>$x$</sub> Co<sub>4</sub>Sb<sub>12– $y$</sub> Sn <sub>$y$</sub> , where  $0 < (x, y) < 1$  and  $x \approx y$ ) have been synthesized. ADP data measured using powder neutron diffraction on three different alloys (Tl<sub>0.22</sub>Co<sub>4</sub>Sb<sub>12</sub>, Tl<sub>0.5</sub>Co<sub>4</sub>Sb<sub>11.5</sub>Sn<sub>0.5</sub>, and Tl<sub>0.8</sub>Co<sub>3</sub>FeSb<sub>12</sub>), indicate that the Tl atoms

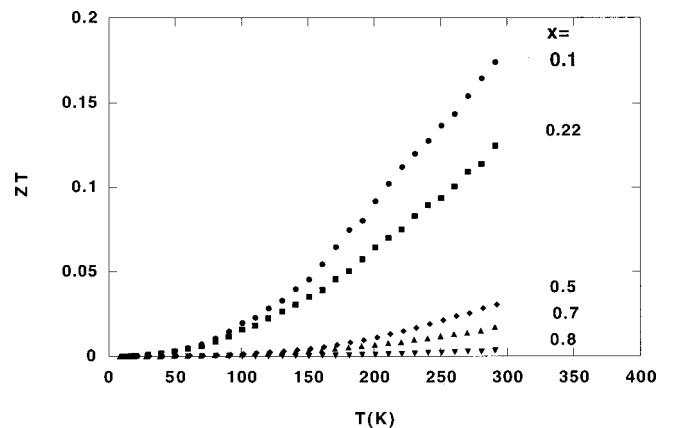


FIG. 9. Dimensionless figure of merit,  $ZT$ , versus temperature for the Tl-filled skutterudites shown in Figs. 4, 6, and 7.

‘rattle’ about their equilibrium positions in the crystal substantially more than the other atoms in the structure. If the Tl atoms are treated as Einstein oscillators, the ADP data can be used to determine the Einstein temperatures. The Einstein temperatures were 52, 62, and 69 K for the  $\text{Tl}_{0.22}$ ,  $\text{Tl}_{0.5}$ , and  $\text{Tl}_{0.8}$  alloys, respectively. Heat-capacity measurements on both  $\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$  and  $\text{Co}_4\text{Sb}_{12}$  showed that the excess heat capacity contributed by the Tl was well described by an Einstein contribution with an Einstein temperature of 55 K, close to the value of 52 K estimated from the ADP data on the same sample. The room-temperature lattice thermal resistivity increased rapidly as small amounts of Tl ( $x < 0.22$ ) were added to the voids and then slowly saturated at higher Tl concentrations. No clear maximum in the thermal resistivity was observed as a function of Tl filling, and the maximum thermal resistivity occurred near complete Tl filling of the voids. The excess thermal resistivity produced by the addition of Tl into the voids in  $\text{Co}_4\text{Sb}_{12}$  is qualitatively described by an  $x^{1/3}$  dependence, where  $x$  is the fraction of voids filled with Tl. For the  $n$ -type samples, the maximum

value of  $ZT$  at room temperature was 0.175 for the  $\text{Tl}_{0.1}\text{Co}_4\text{Sb}_{12}$  alloy. A simple theoretical model<sup>3,32</sup> estimates a maximum  $n$ -type  $ZT$  value of about 0.8 at 800 K for alloys near the  $\text{Tl}_{0.22}\text{Co}_4\text{Sb}_{12}$  composition. Room-temperature crystallographic, thermal expansion, and transport data are summarized in Table I.

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