Structure and Lattice Thermal Conductivity of Fractionally Filled Skutterudites: Solid Solutions of Fully Filled and Unfilled End Members

G. P. Meisner,[1] D. T. Morelli,[1] S. Hu,[2] J. Yang,[1,2] and C. Uher[2]

[1]*Physics & Physical Chemistry Department, General Motors Global Research and Development Operations, Warren, Michigan 48090-9055*
[2]*Department of Physics, University of Michigan, Ann Arbor, Michigan 48109*
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The structure of the skutterudite $CoSb_3$ contains two large empty cages, or voids, per unit cell. Compounds obtained by filling these cages with rare earth atoms possess an enhanced thermoelectric figure of merit. Control of the electronic and thermal transport properties of these materials can be achieved over an extremely wide phase space by partial cage filling in conjunction with Fe alloying on the Co site. We show that such partially filled skutterudites can be rationalized as solid solutions of fully filled $CeFe_4Sb_{12}$ and $\square Co_4Sb_{12}$, where $\square$ is a vacancy. [S0031-9007(98)05818-9]

The recent discovery [1] of high thermoelectric figure of merit Z in a class of materials called filled skutterudite compounds has generated the need for further fundamental information on the physical properties of these interesting materials. The figure of merit of a material is given by $Z = S^2\sigma/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. Traditionally, high Z has been found in moderately to heavily doped semiconductors with low lattice thermal conductivity. Binary, unfilled skutterudite compounds AB_3, where $A = $ Co, Rh, or Ir, and $B = $ P, As, or Sb, crystallize in a body-centered cubic (bcc) structure consisting of a simple cubic array of A atoms at the $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$ crystallographic site of the unit cell, each surrounded by distorted octahedra of B atoms, Fig. 1. These octahedra are corner sharing and tilted to form planar rectangular groups of B atoms which are centered at the edge centers of the unit cell. Structural vacancies at the corner (000) and body center $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ of the unit cell are sixfold coordinated by the B atom planar groups and are thereby enclosed by an irregular dodecahedral cage of B atoms. Several of the compounds in this family exhibit high hole mobilities which, combined with the fact that the unit cell is quite complex (16 atoms/primitive unit cell) and contains atoms of heavy atomic mass (average atomic mass $M = 106$), suggests that these materials might be candidate advanced thermoelectric materials. Although the thermal conductivity of these binary skutterudites is moderately low [2,3], it is, unfortunately, about a factor of 10 higher than that typical of state-of-the-art thermoelectric materials such as Bi_2Te_3. It was suggested by Slack [2], however, that compounds with rare earth atoms filling the vacancies in the skutterudite structure might exhibit a much lower lattice thermal conductivity. These so-called filled skutterudites were discovered about 20 years earlier [4] and the basis of Slack's suggestion was the observation that the rare earth atoms exhibit large x-ray thermal parameters and that this "rattling" motion should give rise to strong phonon scattering. The predicted reduction in

lattice thermal conductivity upon filling of the skutterudite structure was experimentally confirmed recently [5,6].

Filling adds electrons to the skutterudite structure, however, and structural stability requires A atoms to be replaced correspondingly by atoms with fewer electrons, namely, an element to the left in the periodic table. For example, the binary unfilled skutterudite $CoSb_3$ corresponds to the ternary filled skutterudite RFe_4Sb_{12}, where R is a rare earth element. Because $CoSb_3$ is a diamagnetic semiconductor, replacing Co with Fe leads to the creation of four holes in the valence band. A trivalent rare earth atom R does not provide enough electrons to fill these holes and RFe_4Sb_{12} is metallic. The filled skutterudite $CeFe_4Sb_{12}$, however, is a p-type semimetal with
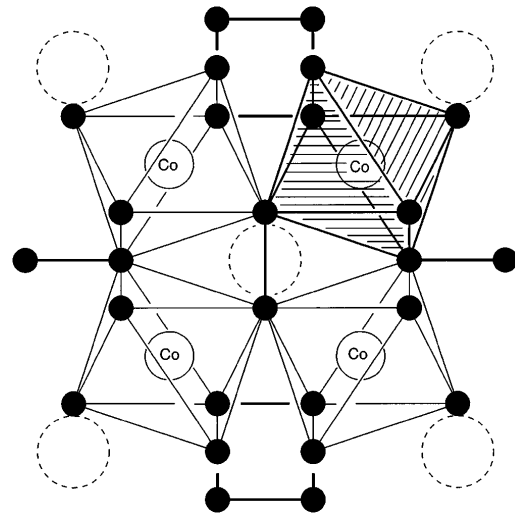

FIG. 1. The skutterudite structure of $CoSb_3$ viewed in a direction parallel to a cube edge. Solid circles are Sb, open circles are Co, and dashed circles are large vacancies at the corner and body center site of the structure which may be filled with a rare earth element. Thin lines delineate tilted corner-sharing Sb octahedra centered by Co, and one is shaded for emphasis. Heavy lines delineate the nearly square planar Sb groups, the centers of which are located at the edge centers of the conventional bcc unit cell.

heavy fermion correlations at low temperatures [5] suggesting that the Ce valence may be greater than 3 and that hybridization exists between the f electron and the conduction band. These results are analogous to those for the filled phosphide skutterudites which have narrower bands and stronger covalent bonds relative to the antimonides; namely, $LaFe_4P_{12}$ is a superconductor at 4.0 K [7], and $CeFe_4P_{12}$ is a semiconductor with an energy gap of about 0.13 eV [8].

To enjoy the advantage of low lattice thermal conductivity in the filled skutterudite antimonides for thermoelectric applications, it is necessary to reduce the hole concentration in order to increase the Seebeck coefficient. In both of the studies reporting high Z in these compounds [1], this was performed by partially alloying the Fe with Co. Recently, we observed [9] that, when Co is substituted for Fe in $CeFe_4Sb_{12}$, the amount of Ce that can be incorporated into the structure decreases significantly; however, for 100% Co a small amount (~10%) of the structure can still be filled with Ce. This subtle interplay of the Fe/Co ratio and the corresponding optimum Ce filling fraction affects not only the location of the Fermi level and the carrier type and concentration, but also the nature of the phonon scattering and lattice thermal conductivity. Thus, understanding this interdependence is crucial for optimization of the thermoelectric properties of these compounds. Perhaps the most puzzling feature of this interplay was the observation [10] that the lattice thermal conductivity was diminished not only by Ce filling but apparently also by alloying on the Fe/Co site. This is surprising since Fe and Co are nearly the same atomic mass and size and their intersubstitution should provide little additional phonon scattering.

In this Letter, we show that the main features of the structure and lattice heat conduction in these optimally filled skutterudites (which in the notation of Refs. [9,10] are designated $Ce_yFe_{4-x}Co_xSb_{12}$) can be understood if these compounds are considered as solid solutions of the fully filled skutterudite $CeFe_4Sb_{12}$ and the unfilled skutterudite $\square Co_4Sb_{12}$, where $\square$ represents a vacancy.

Following the results of Ref. [9] regarding the optimum amount of Ce for a given Fe/Co ratio, a series of fractionally filled skutterudite samples was fabricated as indicated in the first column of Table I. Figure 2 shows the lattice, or phonon, thermal conductivity κ_p of this series of optimally filled skutterudites. In agreement with earlier studies [5,6,9–11], it is seen that all samples containing Ce (and Fe) exhibit a remarkably depressed lattice thermal conductivity relative to $CoSb_3$ ($\square Co_4Sb_{12}$). Before discussing the composition dependence of κ_p, we wish to touch on a few interesting aspects of the temperature dependence. For the unfilled skutterudite $CoSb_3$, one can calculate the expected lattice thermal conductivity (in units of $W\,m^{-1}\,K^{-1}$) for phonon-phonon scattering at the Debye temperature θ according to the relation [12] $\kappa_p(\theta) = 3.04 \times 10^{-6} M\delta\theta^2/(\gamma^2 n^{2/3})$, where $n = 16$ is the number of atoms per primitive unit cell, $\gamma = 0.95$ is the Grüneisen constant [13], and $\delta^3 = 23.1$ Å^3 is the volume/atom. Using $\theta = 308$ K [13], this yields $\kappa_p(\theta) = 15.2$ W m^{-1} K^{-1}, quite close to the experimental value of (11 ± 1) W m^{-1} K^{-1}. For the completely filled skutterudite $CeFe_4Sb_{12}$, $n = 17$, $M = 108$, and $\delta^3 = 22.4$ Å^3. The Debye temperature of $CeFe_4Sb_{12}$ has not been determined. Sales et al. [11] found $\theta = 310$ K for $La_{0.75}Fe_3Co_1Sb_{12}$, suggesting that, upon filling, the Debye temperature remains essentially unchanged. Using this value for $CeFe_4Sb_{12}$ yields $\kappa_p(\theta) = 14.9$ W m^{-1} K^{-1}, nearly an order of magnitude higher than the experimental value. Thus, in $CeFe_4Sb_{12}$ there are additional phonon scattering mechanisms which depress the thermal conductivity below that expected due only to phonon-phonon scattering. The most obvious candidate is the rattling atom mechanism mentioned above and which has been discussed in detail in the literature [5,6,9–11]. This mechanism is expected to scatter phonons over a very wide frequency range, which would lead to a corresponding reduction in κ_p over a wide temperature range, as observed.

We turn now to a discussion of the composition dependence of the thermal conductivity. The trend in κ_p in Fig. 2 is that the lattice thermal conductivity first decreases with Ce filling, reaches a minimum near a filling fraction of 0.6 (corresponding to a Fe:Co ratio of 2.5:1.5), and increases again for higher Ce concentrations. As mentioned earlier, this result is surprising for two reasons: (1) One does not expect strong scattering on the Fe/Co

TABLE I. Properties of $(CeFe_4Sb_{12})_\alpha(\square Co_4Sb_{12})_{1-\alpha}$ solid solutions; $\square$ represents a vacancy.

| Nominal composition	Composition from chemical analysis	Lattice constant (Å)	Solid solution composition
Co_4Sb_{12}	$Co_4Sb_{11.8}$	9.0385	$\square Co_4Sb_{12}$
$Ce_{0.22}Fe_{0.5}Co_{3.5}Sb_{12}$	$Ce_{0.18}Fe_{0.48}Co_{3.52}Sb_{11.51}$	9.0503	$(CeFe_4Sb_{12})_{0.13}(\square Co_4Sb_{12})_{0.87}$
$Ce_{0.35}Fe_{1.0}Co_{3.0}Sb_{12}$	$Ce_{0.32}Fe_{0.99}Co_{3.01}Sb_{11.92}$	9.0633	$(CeFe_4Sb_{12})_{0.25}(\square Co_4Sb_{12})_{0.75}$
$Ce_{0.47}Fe_{1.5}Co_{2.5}Sb_{12}$	$Ce_{0.42}Fe_{1.51}Co_{2.49}Sb_{11.77}$	9.0765	$(CeFe_4Sb_{12})_{0.38}(\square Co_4Sb_{12})_{0.62}$
$Ce_{0.6}Fe_{2.0}Co_{2.0}Sb_{12}$	$Ce_{0.58}Fe_{2.03}Co_{1.97}Sb_{11.88}$	9.0907	$(CeFe_4Sb_{12})_{0.50}(\square Co_4Sb_{12})_{0.50}$
$Ce_{0.71}Fe_{2.5}Co_{1.5}Sb_{12}$	$Ce_{0.69}Fe_{2.52}Co_{1.48}Sb_{11.97}$	9.1033	$(CeFe_4Sb_{12})_{0.62}(\square Co_4Sb_{12})_{0.38}$
$Ce_{0.82}Fe_{3.0}Co_{1.0}Sb_{12}$	$Ce_{0.78}Fe_{3.01}Co_{0.99}Sb_{11.80}$	9.1152	$(CeFe_4Sb_{12})_{0.75}(\square Co_4Sb_{12})_{0.25}$
$Ce_{0.93}Fe_{3.5}Co_{0.5}Sb_{12}$	$Ce_{0.84}Fe_{3.49}Co_{0.51}Sb_{11.61}$	9.1266	$(CeFe_4Sb_{12})_{0.87}(\square Co_4Sb_{12})_{0.13}$
$Ce_{0.98}Fe_4Sb_{12}$	$Ce_{0.99}Fe_4Sb_{11.85}$	9.1385	$CeFe_4Sb_{12}$
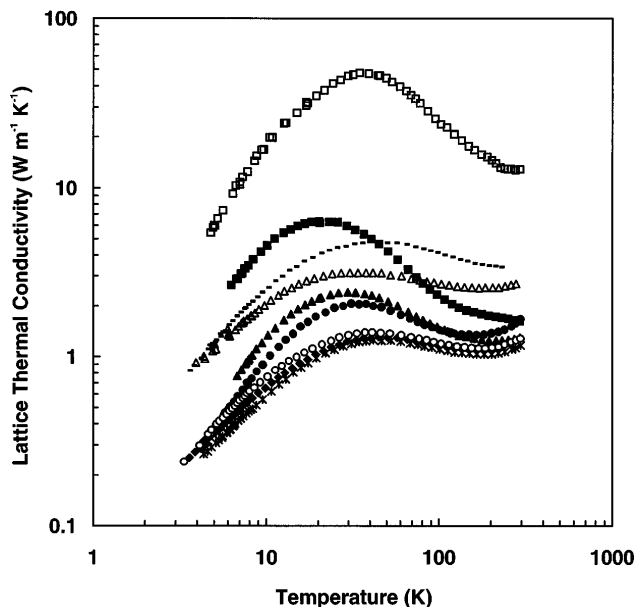
FIG. 2. Lattice thermal conductivity of $Ce_yFe_{4-x}Co_xSb_{12}$ samples. Sample designation: □: Co_4Sb_{12}; –: $Ce_{0.22}Fe_{0.5}$-$Co_{3.5}Sb_{12}$; △: $Ce_{0.35}Fe_1Co_3Sb_{12}$; ○: $Ce_{0.47}Fe_{1.5}Co_{2.5}Sb_{12}$; ◆: $Ce_{0.6}Fe_2Co_2Sb_{12}$; ∗: $Ce_{0.71}Fe_{2.5}Co_{1.5}Sb_{12}$; ●: $Ce_{0.82}Fe_3$-Co_1Sb_{12}; ▲: $Ce_{0.93}Fe_{3.5}Co_{0.5}Sb_{12}$; ■: $CeFe_4Sb_{12}$.

site since Fe and Co have nearly the same size and mass, thus minimizing the mass and strain fluctuations which determine the scattering rate; and (2) for both rattle and magnetic scattering due to the Ce, one would expect the thermal conductivity to decrease monotonically with increasing Ce concentration.

The results can be understood quite nicely, however, if the compounds studied here are thought of not as "fractionally" or "optimally" filled skutterudites but rather as solid solutions of completely filled and unfilled end members. In other words, the compositions can be written as solid solutions of $CeFe_4Sb_{12}$ and $□Co_4Sb_{12}$; see the fourth column of Table I. Thus, the predominant mass fluctuation scattering is not between Fe and Co but between Ce and □, which is a very strong effect since the mass difference is 100%.

To quantify this approach, we can compare the observed thermal resistivity with that predicted based on point defect scattering. The theory for this effect was originally introduced by Klemens [14] and Callaway and von Baeyer [15], and later applied to the solid-solution problem by Abeles [16]. For high defect concentrations, such as is the case in a solid solution, the thermal conductivity is given by $\kappa_p = k_B/[4\pi v_s(ACT)^{1/2}]$. Here, CT is the relaxation time for phonon-phonon scattering (where C is a constant and T is the temperature), and $v_s = 2934$ m s^{-1} is the mean sound velocity [13]. The phonon-phonon relaxation time can be determined from the measured thermal conductivity of the pure material at high temperature using $\kappa_{pure} = k_B^2\theta/(2\pi^2 v_s\hbar CT) = 11$ W m^{-1} K^{-1} at 300 K. This yields $CT = 8.8 \times 10^{-16}$ s. The parameter A is the coefficient for the Rayleigh-type point defect

scattering rate: $t_{pd}^{-1} = A\omega^4$, where ω is the phonon frequency. This coefficient is given by $A = \Omega_o\Gamma/(4\pi v_s^3)$, where Ω_o is the unit cell volume and Γ is the scattering parameter. For impurity atoms on a single atomic site $\Gamma = \sum f_i(1 - M_i/M_{av})^2$, where $M_{av} = \sum f_iM_i$. Here, f_i is the fractional concentration of impurity atom i and M_i is its mass. In principle, one should also include the influence of strain, but, since the lattice constants of $CeFe_4Sb_{12}$ and $□Co_4Sb_{12}$ differ by only 1% (see Table I), this effect will be small in comparison to the mass fluctuation. For a single type of impurity atom with relative concentration α, the scattering parameter reduces to $\Gamma = \alpha(1 - \alpha)(\Delta M/M_{av})^2$, where ΔM is the difference between the mass of the impurity and that of the host. For a compound $U_uV_vW_w$, the composite Γ, denoted by $\Gamma(U_uV_vW_w)$, is given by [17]

$$\Gamma(U_uV_vW_w) = \frac{u}{u + v + w}\left(\frac{M_U}{M_m}\right)^2\Gamma(U)$$
$$+ \frac{v}{u + v + w}\left(\frac{M_V}{M_m}\right)^2\Gamma(V)$$
$$+ \frac{w}{u + v + w}\left(\frac{M_W}{M_m}\right)^2\Gamma(W),$$

where $M_m = (uM_U + vM_V + wM_W)/(u + v + w)$. For $(CeFe_4Sb_{12})_\alpha(□Co_4Sb_{12})_{1-\alpha}$ solid solutions, $U = (Ce, □)$, $V = (Fe, Co)$, and $W = Sb$. Now, Fe and Co have only 3% mass difference so the majority of the mass fluctuation scattering occurs for $(Ce, □)$. Thus, $\Gamma(CeFe_4Sb_{12}) \approx (1/17)(140.12/108.01)^2\Gamma(Ce) = 0.099\Gamma(Ce) = 0.099\alpha(1 - \alpha)$, since $\Delta M/M = -1$ for the vacancy. This yields $A = 2.3 \times 10^{-40}\alpha(1 - \alpha)$ s^3. The thermal resistivity due to solid solution formation is, thus, $W = 4\pi v_s(ACT)^{1/2}/k_B = 1.2[\alpha(1 - \alpha)]^{1/2}$ m K W^{-1}. Figure 3 is a plot of the lattice thermal resistivity at 300 K across the solid solution series from $□Co_4Sb_{12}$ to $CeFe_4Sb_{12}$. The solid line is the behavior predicted by the above equation. We see that this expression, *which contains no adjustable parameters,* accounts quite well for the increase in thermal resistivity due to the formation of the solid solution.

Further support for this picture is provided by the lattice constant measurements. Figure 4 shows a plot of lattice constant versus concentration across the solid solution series from $□Co_4Sb_{12}$ to $CeFe_4Sb_{12}$. We have observed that, for a given Fe:Co ratio, there is a range of Ce concentrations over which a single phase sample can be made. For the Fe:Co ratio of zero, this Ce concentration range extends from 0 to 0.1, while for a ratio of 2:2, it extends from approximately 0.5 to 0.6. For higher Fe concentrations, the solubility range of Ce becomes very narrow and we have not probed this regime in detail. The solid lines represent the variation in lattice constant according to Vegard's law for cases of composition $(CeFe_4Sb_{12})_\alpha(□Co_4Sb_{12})_{1-\alpha}$ and $(CeFe_4Sb_{12})_\alpha(Ce_{0.1}Co_4Sb_{12})_{1-\alpha}$. Virtually all of the lattice constant data fall between these two extremes,
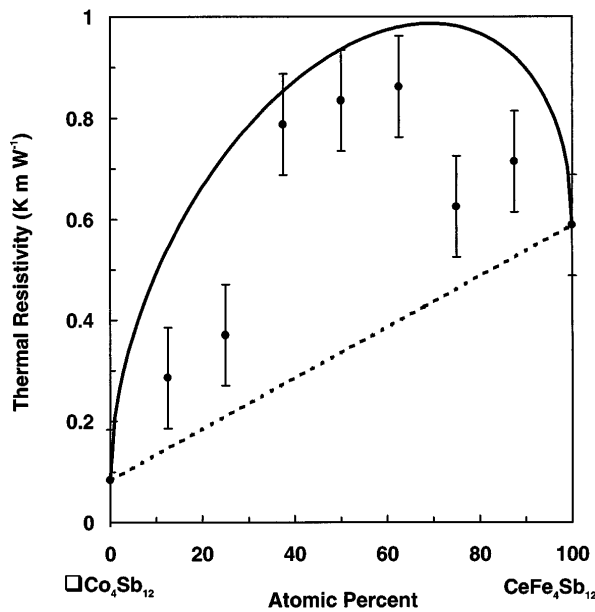
FIG. 3. Variation of the thermal resistivity of $(CeFe_4Sb_{12})_\alpha(\square Co_4Sb_{12})_{1-\alpha}$ solid solutions at 300 K. Dashed line represents variation from the rule of mixtures. Solid line includes additional thermal resistivity due to solid solution formation calculated from the theory of Callaway and von Baeyer [15].

lending strong support to the solid solution picture for these fractionally filled skutterudites. Thus, these solid solutions actually can be considered as combinations of two sublattices, the first a fully filled Fe_4Sb_{12} sublattice and the second a Co_4Sb_{12} sublattice which can be vari-

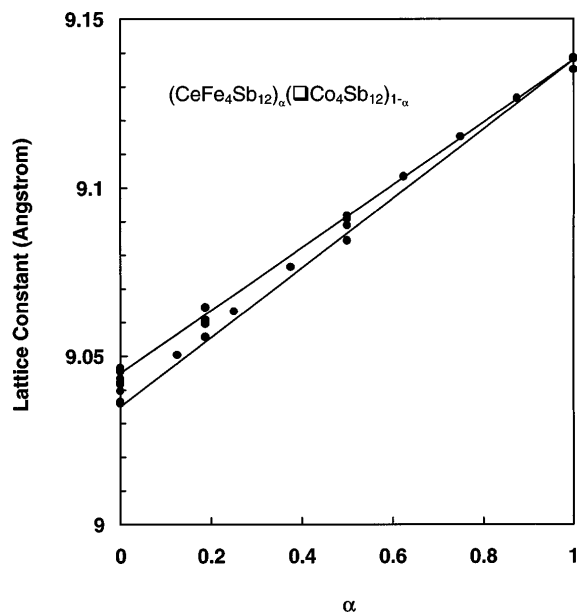ably filled between 0% and 10%. Then the maximum Ce filling fractions across the series in Table I would be given by $\alpha + 0.1(1 - \alpha)$, or 0.21, 0.33, 0.44, 0.55, 0.66, 0.78, 0.89, and 1.00, which are very close to the actual compositions determined from chemical analysis. Further, the solid solution picture can explain our observation that the solubility range of Ce in the solid solutions decreases with increasing Fe content. This is because the variability in Ce solubility arises only from the Co_4Sb_{12} sublattice which is becoming a smaller fraction of the total. Thus, for $\alpha = 0$, the solubility range is from 0 to 0.1; for $\alpha = 0.25$, it is from 0.25 to 0.33; and for $\alpha = 0.75$, it is 0.75 to 0.78.

In conclusion, we have shown that various aspects of the thermal transport and structural properties of fractionally filled skutterudite compounds can be understood if these materials are thought of as solid solutions of $CeFe_4Sb_{12}$ and $\square Co_4Sb_{12}$. This significant result will allow the determination of the optimum compositions for obtaining a high figure of merit in this important class of new thermoelectric materials.

FIG. 4. Lattice constant for $(CeFe_4Sb_{12})_\alpha(\square Co_4Sb_{12})_{1-\alpha}$ solid solutions. Solid lines represent Vegard's law for no Ce on the vacant site (bottom line) and 10% Ce on the vacant site (top line).

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