

Low-temperature transport properties of the filled skutterudites $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$

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Thermal conductivity, thermoelectric power, electrical resistivity, Hall coefficient, and magnetic susceptibility of the filled skutterudites $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$, with $x=0, 0.5, 1.0, 1.5,$ and 2.0 , have been studied from 2 to 300 K. We find that the substitution of Co at Fe sites has a dramatic effect on all transport properties. While the resistivity of $\text{CeFe}_4\text{Sb}_{12}$ has a metallic character, substitution of Co leads to a progressively stronger activated behavior and a decrease in hole concentration. The thermopower increases with increasing Co, while the thermal conductivity is depressed, notably at low temperatures. Susceptibility data suggest the presence of large effective moments. At high temperatures Ce is nearly trivalent, but valence fluctuations prevail at low temperatures. Strong hybridization of the Ce $4f$ states with the Fe $3d$ and pnictogen p states appears to be important in understanding the physical properties of these compounds. [S0163-1829(97)05904-3]

INTRODUCTION

Much interest is currently focused on the search for novel and efficient thermoelectric materials for cooling and power generation applications. To be a useful thermoelectric, the material must have a large thermoelectric figure of merit, defined as $Z=S^2\sigma/\kappa$, where S is the thermoelectric power, σ the electrical conductivity, and κ the thermal conductivity. To maximize the figure of merit requires a judicious compromise as far as the band structure and the transport properties are concerned, and it turns out that the most prospective candidates are doped semiconductors or small overlap semimetals. For over 30 years thermoelectric cooling technology has been based virtually exclusively on bismuth telluride, antimony telluride, and their alloys. To say that the development of the material base of thermoelectricity has stagnated for over a quarter of a century is an understatement. A much needed renaissance precipitated by the discovery of high figures of merit at high temperatures on a class of materials called skutterudites^{1,2} holds promise for more widespread use of thermoelectricity in a variety of industrial applications.

Skutterudites are binary compounds of the form MA_3 , where M is a metal such as Co, Rh, or Ir and A represents a pnictogen such as Sb, As, or P. Their low-temperature properties have been studied recently,³⁻⁵ and the results seem to support the theoretical predictions⁶ concerning the influence of a highly nonparabolic valence band. While these materials show very high hole mobilities and large thermopower, they also feature a relatively high lattice thermal conductivity, which is a serious drawback from the point of view of an efficient thermoelectric device. Fortunately, the skutterudite structure possesses large voids (cages) that can accommodate foreign atoms. Such structures are then referred to as filled skutterudites. As originally suggested by Slack and

Tsoukala,⁷ loosely bound atoms in the cages of filled skutterudites are expected to vibrate (rattle) out of phase with the normal modes of the parent atoms and thus very effectively impede phonon transport. This prediction was recently verified by Morelli and Meisner⁸ on the filled skutterudite $\text{CeFe}_4\text{Sb}_{12}$ and subsequently by Nolas *et al.*⁹ on several rare-earth filled iridium antimonides.

Recent band-structure calculations on Ce-filled skutterudites¹⁰ indicate that these compounds possess a small band gap that arises from strong hybridization of Ce $4f$ states with both Fe $3d$ and pnictogen p states. Since the replacement of Fe with Co provides an n -type doping mechanism, it is of interest to explore the effect of such a substitution on the transport properties and its influence on the Ce valency. Such an inquiry falls within our general framework of exploring the viability of filled skutterudites as potentially useful thermoelectric materials.

EXPERIMENT

Samples of $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ with Co content spanning the range $0 \leq x \leq 2$ were prepared by the following method. An amount of Ce and of Fe and/or Co was weighed out to give a composition of $\text{Ce}_{1.05}(\text{Fe},\text{Co})_4$ and loaded into a Zr-gettered argon filled arc furnace. The Ce and (Fe,Co) were first melted individually and then combined. The resulting alloy was turned over and remelted from one to three times to ensure homogeneity. These alloys were then loaded into pyrolytic boron nitride crucibles with Sb to give final compositions of $\text{Ce}_{1.05}(\text{Fe},\text{Co})_4\text{Sb}_{12.2}$ and induction melted at ~ 1160 °C. The excesses of Ce and Sb allow for the tendency of the former to oxidize due to its high reactivity and the latter to sublime due to its high vapor pressure and thereby discourage the formation of undesirable phases. The resulting ingots were then annealed in $\frac{1}{3}$ atm of Ar at 700 °C in

sealed quartz ampoules for 20 h. X-ray-diffraction analysis indicated that the samples were the filled skutterudite phase with slight amounts of FeSb_2 and CeSb_2 . Microprobe analysis indicated that these impurity phases were present at a level of less than 5 vol %. A more detailed description of the structural data including lattice constant measurements will be presented elsewhere.¹¹ To prepare samples for transport property measurements, the annealed material was subsequently ground and hot pressed into pellets (>95% theoretical density) from which samples of the desired size and shape could be cut.

Electrical resistivity and Hall coefficient data were taken in the temperature range 2–300 K and in magnetic fields up to 5.5 T using the van der Pauw technique on disks of nominal dimensions of 6 mm in diameter and 1 mm thick. Silver wires were soldered onto each sample using Wood's metal. It was found that the Hall resistance was positive and linear in field for all samples; the hole concentration was thus calculated assuming a single carrier type.

Thermal transport measurements were made from 2 to 300 K using a steady-state longitudinal technique. One end of a bar-shaped sample was thermally anchored to the cold tip of a cryostat, which served as a heat sink. The other end was provided with a small heater to generate the heat current. The resulting thermal gradient along the sample length was measured using a differential chromel-constantan thermocouple that was soldered to two small copper tabs attached to the sample with stycast epoxy. One of the tabs also supported a Cernox thermometer for determining the absolute temperature. Fine copper wires soldered to the sample facing the copper tabs served as Seebeck probes, and the measured thermoelectric voltage was corrected for the probe contribution (which in all cases was less than 2%).

Magnetic susceptibility was measured by inserting a sample into a polyethylene straw and suspending the arrangement in a Quantum Design superconducting quantum interference device magnetometer. The background diamagnetic susceptibility of the straw was negligible relative to the large paramagnetic susceptibility of the samples. Data were taken in a range of fields, but the susceptibility was calculated for a field value of 5000 G, well within the regime for which $M(B)$ was a linear function.

RESULTS AND DISCUSSION

The electrical resistivity values shown in Fig. 1 are plotted on a log-log scale to capture the full range of resistivities measured. Although the parent ternary compound $\text{CeFe}_4\text{Sb}_{12}$ ($x=0$) exhibits a consistently metallic behavior, the Co-containing samples display a distinctly activated behavior. Figure 2 shows the hole concentrations in these samples as determined from the Hall effect measurements. The addition of Co causes a decrease in hole concentration as the electrons from the Co begin to compensate the material. The measured hole concentration at room temperature is shown in Table I. From simple crystal chemistry and valence arguments one can estimate the expected hole concentrations for these compounds using the fact that the parent binary compound CoSb_3 is a semiconductor. Relative to CoSb_3 , in $\text{CeFe}_4\text{Sb}_{12}$ the replacement of Co with Fe produces four holes in the valence band; assuming that the Ce is trivalent, three of these holes

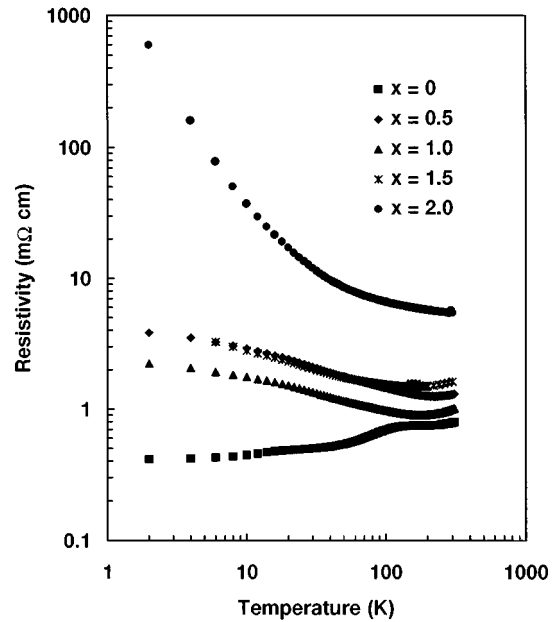


FIG. 1. Temperature dependence of the electrical resistivity of $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ samples for $x=0, 0.5, 1.0, 1.5,$ and 2.0 .

are filled with electrons from the Ce and the material should have a hole concentration of one hole per formula unit. This is consistent with the observed hole concentration. Using this same argument one would expect that the $x=0.5$ sample would have $3.5-3=0.5$ holes per formula unit and that the sample with $x=1$ would be totally compensated. Our measurements show, however, that samples with $x \leq 2$ remain p type. This behavior can be accounted for by our observation that the amount of Ce in the void depends quite strongly on Co content. Figure 3 shows results of a microprobe analysis of these samples that measures the amount of Ce in the $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ phase as a function of Co content. Whereas the sample containing solely Fe is nearly 100% filled, for the

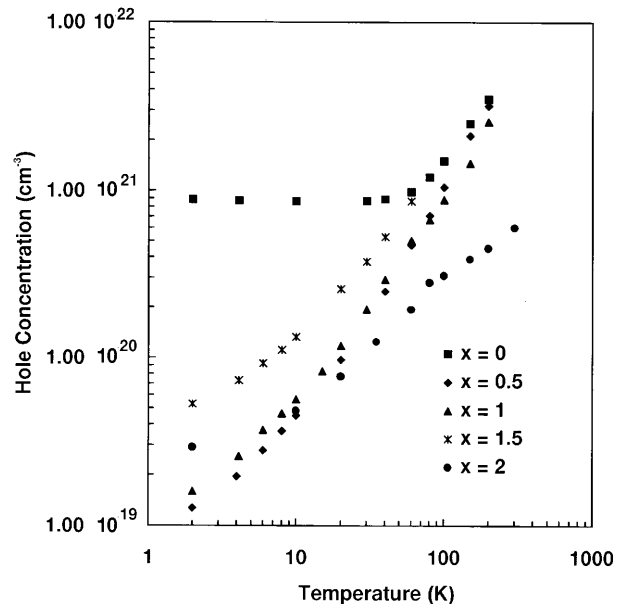


FIG. 2. Hole concentration as determined from Hall coefficient measurements for $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$.

TABLE I. Measured and predicted parameters for $\text{Ce}_\delta\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$ samples.

Compound	Hole concentration (cm^{-3})	No. of holes per formula unit	Predicted no. of holes per formula unit	Ce filling fraction δ	Effective moment	Ce valence at 4 K
$\text{Ce}_\delta\text{Fe}_4\text{Sb}_{12}$	5.5×10^{21}	2.1	1	0.98	4.1	3.74
$\text{Ce}_\delta\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$	5.0×10^{21}	1.9	0.71	0.94	3.55	3.70
$\text{Ce}_\delta\text{Fe}_{3.0}\text{Co}_{1.0}\text{Sb}_{12}$	4.4×10^{21}	1.7	0.6	0.83	2.49	3.61
$\text{Ce}_\delta\text{Fe}_{2.5}\text{Co}_{1.5}\text{Sb}_{12}$	3.4×10^{21}	1.3	0.4	0.71	2.30	3.50
$\text{Ce}_\delta\text{Fe}_{2.0}\text{Co}_{2.0}\text{Sb}_{12}$	6.0×10^{20}	0.23	0.2	0.61	2.52	3.35
$\text{Ce}_\delta\text{Co}_{4.0}\text{Sb}_{12}$	6.0×10^{20}	0.22 electrons	0.2 electrons	0.067		

$x=2$ sample the voids are only 61% occupied. Thus the composition of our samples should be properly written $\text{Ce}_\delta\text{Fe}_{4-x}\text{Co}_x\text{Sb}_{12}$ with $\delta(x)$ given in Table I. Returning to the crystal chemistry argument given above and again assuming that Ce is in the 3+ state, one would expect for the $x=2$ sample, for instance, a hole concentration now of $2-3(0.61) \approx +0.2$ holes per formula unit. Table I shows the measured hole concentrations and those predicted taking into account the partial filling in the Co-containing samples. The agreement is reasonably good, suggesting that Ce is in a nearly 3+ state at room temperature for all compositions x . An extrapolation of the data in Fig. 3 to $x=4$ further suggests that there is a limited nonzero solubility of Ce in CoSb_3 . We have fabricated such a sample and find that its composition is $\text{Ce}_{0.067}\text{Co}_4\text{Sb}_{12}$. Since the parent CoSb_3 binary compound is a semiconductor, the Ce-containing sample should be n type with $3(0.067) \approx 0.2$ electrons per formula unit, just as observed. Our results thus show that *there are effectively two ways of changing the doping level of $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$: by changing the Fe/Co ratio and by altering the amount of Ce filling the voids.*

Results of the thermal conductivity measurements are shown in Fig. 4. The electronic thermal conductivity was

estimated from the electrical resistivity using the Wiedemann-Franz law. The sample with no Co doping ($x=0$) displays a sharp peak near 30 K, and similar but progressively less pronounced peaks were found for samples with Co doping. For the $x=2$ sample the peak is almost smeared out. Some depression in the peak is expected since Co alloying induces mass and strain fluctuations that can be effective in impeding heat flow, although the mass difference between Co and Fe is only about 5%. It is also possible that there is some phonon scattering by a rapid transfer of electrons between Co and Fe atoms of different valence, a mechanism initially suggested by Slack¹² for Fe_3O_4 and more recently by Caillat *et al.*¹³ to explain the low lattice thermal conductivity of $\text{Ru}_{0.5}\text{Pd}_{0.5}\text{Sb}_3$ alloys. At room temperature the thermal conductivity of these compounds lies in the range $2.5\text{--}3.5 \text{ W m}^{-1} \text{ K}^{-1}$ compared to more than $10 \text{ W m}^{-1} \text{ K}^{-1}$ for CoSb_3 . In addition, as much as 25% of the measured thermal conductivity at room temperature may be electronic in origin. The large reduction in the phonon mean free path has been attributed to the rattling motion of the rare-earth element in its Sb cage.^{8,9} While there is no obvious trend in the room-temperature lattice thermal conductivity

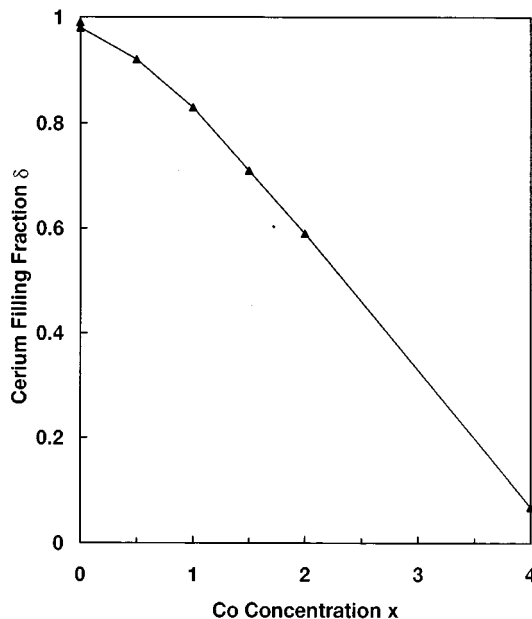


FIG. 3. Fractional filling with Ce of the void in the skutterudite compound $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ as a function of Co concentration x .

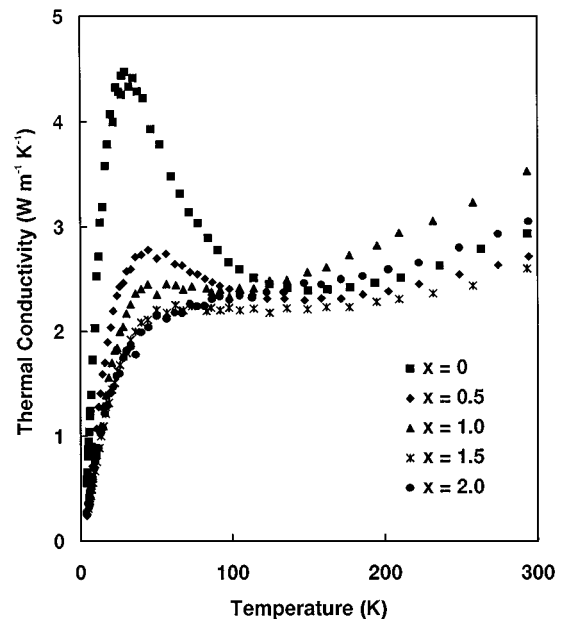


FIG. 4. Total thermal conductivity of $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ compounds.

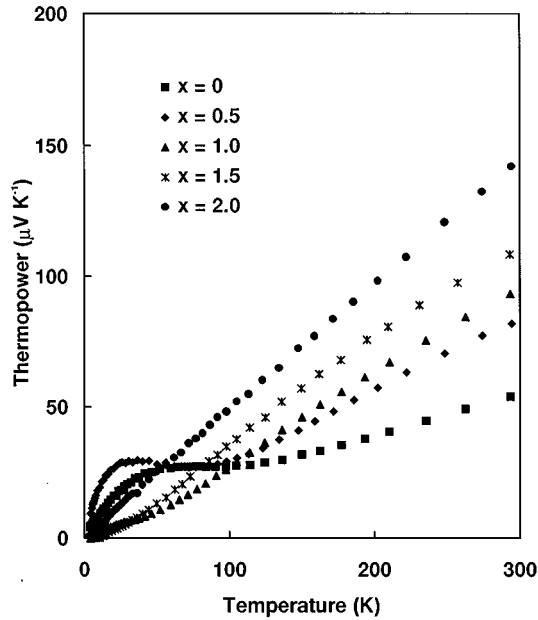


FIG. 5. Thermoelectric power of $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ compounds at low temperature.

with Co content, it must be remembered from the above discussion that the amount of Ce in the voids depends rather strongly on Co content. It has not been established, for instance, that the amount of reduction in the lattice thermal conductivity is greatest for 100% filling. It may be that a partial, random distribution is a more effective phonon scattering arrangement than an arrangement in which all the voids are filled with Ce and the Ce atoms are thus regularly arranged. The influence of partial filling of the voids on the lattice thermal conductivity for a fixed Co concentration is beyond the scope of this work, but would be an interesting and revealing study.

Figure 5 shows the temperature dependence of the thermopower in the five compounds studied. As expected, the thermopower increases as the Co doping increases: at room temperature the $x=2$ sample has a thermopower of $142 \mu\text{V K}^{-1}$, almost three times as large as that of the undoped sample ($54 \mu\text{V K}^{-1}$), reflecting the lower hole concentration in this sample. An interesting feature of Fig. 5 is that the thermopower displays peaks or wiggles at low temperatures before it reaches a linear high-temperature behavior. These anomalies, we believe, have their origin in valence fluctuations in these compounds. Similar behavior has been observed in the thermopower of concentrated Kondo systems and has been explained in terms of the interference between resonant and nonresonant scattering.¹⁴ The introduction of Co seems to reduce the effect of local correlation as almost no wiggle is present in the thermopower of the sample with $x=2.0$. To have a clearer idea of the valence fluctuations in these systems, we have also studied their susceptibility.

Shown in Fig. 6 are the temperature dependences of the inverse susceptibility. For high temperatures the susceptibility nominally follows a Curie-Weiss law, although for samples with $x=0$ and 0.5 the curves have significant curvature over the entire range. From the slope of the linear portion of these curves, and taking into account the fractional filling of the Ce, we derive the high-temperature effective

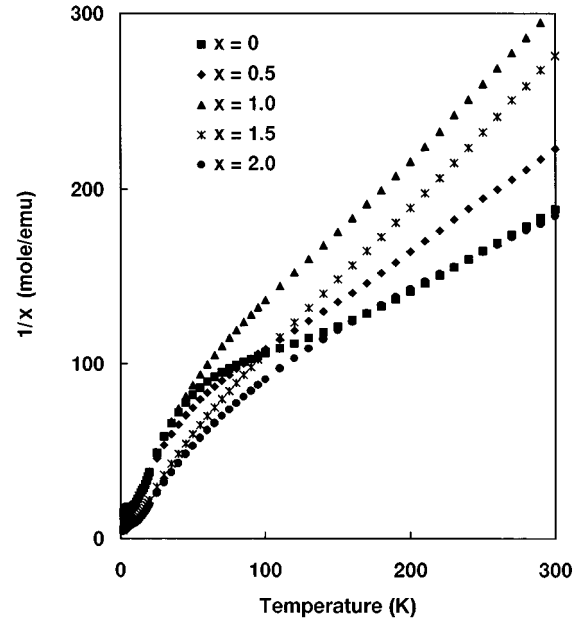


FIG. 6. Inverse susceptibility as a function of temperature for $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$.

moments given in Table I. The effective moment for Ce^{3+} is $2.54 \mu_B$, while for Ce^{4+} one expects an effective moment of zero. Danebrock, Evers, and Jeitschko¹⁵ have recently discussed the magnetic properties of lanthanide-filled iron antimonides. It is expected that for trivalent Ce the $[\text{Fe}_4\text{Sb}_{12}]^{3-}$ polyanion should also carry a magnetic moment since then, in this case, the Fe is in a magnetic d^5 configuration. This may explain the large observed moments for the $x=0$ and 0.5 samples. For higher Co concentrations fewer Fe atoms contribute to the moment and since Co is expected to be in the nonmagnetic d^6 state,¹⁵ the observed magnetization at high temperature is essentially that due to the trivalent Ce.

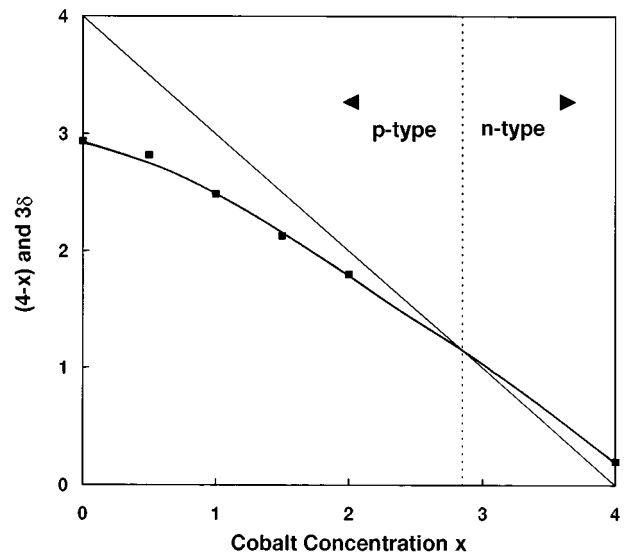


FIG. 7. Number of available holes per formula unit ($4-x$, solid line) in $\text{CeFe}_{4-x}\text{Co}_x\text{Sb}_{12}$ and number of available electrons to fill these holes (3δ , squares). The curves cross near $x=3$, above which these samples will be n type.

Below 100 K the susceptibility shows significant curvature, a feature that is characteristic of strong crystalline field effects and intermediate valency. The curvature seems to weaken with increasing Co concentration and thus this feature correlates with that found in the thermopower at low temperature. From the measured hole concentrations at 4 K one can again estimate the cerium valency based on the simple crystal chemistry arguments given above; the low-temperature valency so derived is displayed in Table I. We thus see that while the Ce seems to be trivalent in all compounds at high temperature, there is a tendency toward a mixed valence state at low temperature. The “shift” in Ce valency toward Ce⁴⁺ at low temperatures is strongest in the $x=0$ sample and becomes systematically weaker with Co alloying, verifying the trend observed in the susceptibility and thermopower results. A direct test of the temperature dependence of the Ce valence could be carried out by x-ray-absorption measurements near the Ce L_{III} absorption edge at both room and low temperatures on samples in this composition range. Such experiments were recently performed on mixed valent Ce₃Bi₄Pt₃,¹⁶ and we strongly suggest that such experiments be performed on these Ce-filled skutterudites. Finally, by extrapolation of $\delta(x)$ to higher values of x we see (Fig. 7) that this compound should become compensated near $x=3$ and for larger values of x the samples will be n type. Following the suggestion of Nordström and Singh,¹⁰ such n -type samples may be very

interesting from a thermoelectric point of view due to their predicted high conduction-band masses.

CONCLUSION

We have systematically studied the effect of Co doping on the low-temperature properties of CeFe_{4-x}Co_xSb₁₂. We have found that the amount of Ce that can be placed in the voids in the unit cell decreases with increasing Co concentration. The addition of Co causes a decrease in hole concentration and a corresponding increase in thermopower as electrons fill the holes in the valence band. With increasing Co concentration the low-temperature thermal conductivity decreases strongly. This effect may be due to mass and strain fluctuations or there may be an as yet unidentified Ce filling fraction that maximizes the phonon scattering. Finally, anomalies in the magnetic susceptibility and thermopower at low temperature suggest that the Ce takes on an intermediate valency character at low temperatures in this system.

ACKNOWLEDGMENTS

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