

Effect of partial void filling on the lattice thermal conductivity of skutterudites

G. S. Nolas

Research and Development Division, Marlow Industries, Dallas, Texas 75238

J. L. Cohn

Department of Physics, University of Miami, Coral Gables, Florida 33124

G. A. Slack

Department of Physics, Rensselaer Polytechnic Institute, Troy, New York 12180

(Received 11 December 1997; revised manuscript received 30 March 1998)

Polycrystalline samples of antimonides with the skutterudite crystal structure with La partially filling the voids have been prepared in an effort to quantify the impact of partial void filling on the lattice thermal conductivity of these compounds. It is observed that a relatively small concentration of La in the voids results in a relatively large decrease in the lattice thermal conductivity. In addition, the largest decrease in the lattice thermal conductivity, compared to “unfilled” CoSb_3 is not observed near 100% filling of the voids with La, as was previously believed. This suggests a point-defect-type phonon scattering effect due to the partial, random distribution of La in the voids as well as the “rattling” effect of the La ions, resulting in the scattering of a larger spectrum of phonons than in the case of 100% filling. An additional benefit of partial filling in thermoelectric materials is that it may be one way of adjusting the electronic properties of these compounds. Seebeck, resistivity, Hall effect and structural data for these skutterudite compounds are also presented.

[S0163-1829(98)02926-9]

INTRODUCTION

There is now a renewed interest in research on improved materials for thermoelectric applications. One family of compounds that has received recent attention is the skutterudite family with the CoAs_3 ($Im\bar{3}$) structure. This structure has eight formula units, including two voids, per cubic unit cell.¹ This system has generated considerable interest because the filling of the voids in the structure with undersized rare-earth (R) atoms yields a marked reduction in the lattice thermal conductivity κ_g . The void-filling atoms “rattle” in their voids and substantially affect the phonon propagation through the lattice. This effect was first postulated by Slack and Tsoukala.² Nolas *et al.*³ employed the IrSb_3 system to show that κ_g decreases monotonically with decreasing guest atom radius. An order-of-magnitude decrease in κ_g was observed compared to unfilled IrSb_3 at room temperature, while a much larger decrease was found at lower temperatures. The rattling of the void-filling R atoms is evidenced by their large x-ray thermal parameters,⁴ their effects on the lattice modes as investigated by Raman Spectroscopy,⁵ and by neutron scattering.⁶

The importance of a very low thermal conductivity in a potential thermoelectric material can be seen from the figure of merit Z (Ref. 7)

$$Z = \frac{S^2 \sigma}{\kappa}, \quad (1)$$

where S is the Seebeck coefficient, σ the electrical conductivity, and $\kappa = \kappa_g + \kappa_e$, κ_e being the electronic contribution. Although the binary, unfilled skutterudites have relatively good electrical properties their Z values are low due to large

values of κ_g .^{2,8} A substantial reduction in κ_g is therefore a key goal for potential applications.

As seen from Eq. (1), improving the electronic properties also improves Z . However, if the skutterudite system is to find use as a thermoelectric material in cooling applications, κ_g must be reduced towards that of the minimum thermal conductivity κ_{\min} .⁹ Cahill *et al.*¹⁰ have enumerated a number of crystalline systems that possess low, glasslike κ_g values. The relationship between glasslike κ_g and κ_{\min} was pointed out by Slack.⁹ As outlined in a recent review,¹¹ the crystalline systems that possess glasslike thermal properties have features in common with the skutterudite system. Investigating the possibility that this system may be synthesized to possess κ_{\min} values is therefore of interest.

The marked reduction in κ_g of fully filled skutterudites has been studied.³ In the present work we investigate the effect of partial void filling in the skutterudite structure on κ_g . Zemni *et al.*¹² have synthesized partially filled skutterudite-phosphide crystals of up to 50% of the maximum R concentration. Recently Morelli *et al.*¹³ synthesized polycrystalline samples with up to 10% Ce in the voids of CoSb_3 . Higher concentrations of Ce were achieved when Fe was partially substituted for Co in an effort to compensate for Ce^{3+} charge.

In the present investigation we use trivalent lanthanum La^{3+} as the R void-filling ions because they do not possess $4f$ electrons which may produce an additional phonon scattering.^{3,14} We therefore distinguish the effects of La^{3+} rattling from other possible scattering mechanisms that may influence the transport properties. For this same reason Sn is used in an attempt to charge compensate for La^{3+} . Sn is very similar to Sb in size and mass and is therefore not expected, when substituted for Sb, to have a significant effect on κ_g .

TABLE I. The concentration of La^{3+} in the voids x using XMP analysis, cubic x-ray lattice parameter a_0 , grain size, bulk density as a fraction of theoretical density $D\%$, and the carrier concentration and mobility for the partially filled skutterudites in this study. The electrical data are for 300 K. All samples are P type with the exception of the $x=0.05$ and $x=0.23$ samples which were N type. The cubic unit cell in each case contains twice the number of formula units shown.

x	Sample	a_0 (Å)	grain size (μm)	$D\%$	carrier conc. (10^{18} cm^{-3})	mobility ($\text{cm}^2/\text{V sec}$)
0	$\text{Co}_4\text{Sb}_{12}$	9.032 ± 0.011	7	97	1.88	270
0.05	$\text{La}_{0.05}\text{Co}_4\text{Sb}_{12}$	9.056 ± 0.017	5	94	170	20.5
0.23	$\text{La}_{0.23}\text{Co}_4\text{Sb}_{11.6}$	9.060 ± 0.013	5	93	2010	6.8
0.31	$\text{La}_{0.31}\text{Co}_4\text{Sn}_{1.48}\text{Sb}_{11.2}$	9.064 ± 0.002	4	94	27.0	120
0.62	$\text{La}_{0.62}\text{Co}_4\text{Sn}_{2.4}\text{Sb}_{9.9}$	9.094 ± 0.007	4	93	122	36.6
0.75	$\text{La}_{0.75}\text{Co}_4\text{Sn}_{2.58}\text{Sb}_{9.78}$	9.096 ± 0.010	8	85	112	28.9
0.9	$\text{La}_{0.9}\text{Co}_4\text{Sri}_{2.44}\text{Sb}_{10.03}$	9.102 ± 0.006	8	94	308	16.7

We note that this is not the case for Fe compensated R -filled-skutterudites which have also resulted in low κ .^{15,16,17} The Fe in this system also has an affect on κ , as shown in Dudkin *et al.*¹⁸ where 10% Fe substitution for Co in CoSb_3 (10% Fe: CoSb_3) resulted in a room temperature value of κ that was reduced two-fold compared to that of pure CoSb_3 . We have synthesized a polycrystalline pressed powder sample of 10% Fe: CoSb_3 and our measured κ values are consistent with these prior results. At 35 K the reduction in κ is even greater with κ equal to 100 mW/cmK for 10% Fe: CoSb_3 compared to 500 mW/cmK for CoSb_3 . This reduction in κ cannot be explained from the κ_e component of κ , nor by Rayleigh type scattering produced by the mass and size difference of Fe in the metal sites of CoSb_3 . This work will be reported elsewhere, however the main point here is that in the present study we isolate the mechanism(s) introduced by the void-filler ions in order to study their effect on κ_g . The Fe-compensated skutterudites introduce some as yet not understood additional phonon scattering due to the substitution of Fe on the Co sites, as has been speculated recently by Morelli *et al.*¹³

SAMPLE PREPARATION

Table I lists the samples synthesized in this study along with the La^{3+} concentration, x , their measured cubic x-ray lattice parameters, a_0 , grain sizes, their fraction of theoretical densities and their room temperature carrier concentrations and mobilities. The stoichiometries shown were determined by electron-beam microprobe (XMP) analysis of each sample and were normalized to yield four Co atoms per formula unit. This gives a maximum void filling at $x=1.0$. The partially filled polycrystalline samples were prepared by the mixing and reacting of stoichiometric amounts of high purity elements as described previously³ with the exception that the elements were reacted at 800 °C and densification of the powdered samples was accomplished using a graphite die in a hot press under argon (Thermal Technology Inc. model MP20 hot press). Typically densification was accomplished at 26 KSI and 600 °C for 2 h. The density of each sample was measured by both the Archimedes technique and by weighing precisely cut cubes. The resulting skutterudite samples had slightly smaller La concentrations than expected from the amount of elemental La in the starting mixtures.

Pieces of the polycrystalline samples were ground and analyzed by a Philips model PW 1729 x-ray diffractometer using $\text{Cu } K_\alpha$ radiation and a scintillation detector along with powdered LaB_6 (NIST Standard Reference Material 660) as an internal standard. The x-ray spectra revealed sharp skutterudite lines. In the case of the samples with $x > 0.23$ small amounts (< 5 wt. %) of LaSb_2 were also identified. The intensities of the x-ray reflections agreed with those calculated for different concentrations of La atoms in the voids using POWD7 (Ref. 3) and LAZY (Ref. 19) software. In addition, metallographic and XMP (JOEL 733 superprobe with an energy dispersive analysis attachment) examination of a polished surface of each sample confirmed the x-ray diffraction results and verified the stoichiometry of each sample. Individual grains all possessed the same average chemical composition. We note that trace amounts of La_2O_3 were identified under XMP examination. This was not observed in similar previous work³ on 100% filled skutterudites densified using sealed capsules in a hot isostatic press and is attributed to our densification procedure using the simpler hot pressing technique. In addition, XMP analysis indicated that the La concentration in the partially filled skutterudites varied by a maximum of 5 at. % from one grain to the next across the ~ 2.5 cm length of the polished samples. In the case of the $x=0.05$ sample, the variation in La concentration was less than the experimental accuracy of the XMP. Optical microscope images of polished samples etched in aqua regia were taken with a Nikon epiphot metallograph in order to measure the average grain sizes.²⁰ Electron back-scattering images, from the XMP, agreed with these grain size measurements.

We note that for noncompensated La filling in CoSb_3 saturation was reached at 23% La filling. Upon attempting to synthesize samples with $x > 0.23$ without Sn substitution for Sb the samples possessed both a skutterudite phase and other phases (i.e., LaSb and CoSb_2). The volume fraction of these other phases increased as the amount of elemental La used for synthesis was increased. Also some single crystals were grown using a modified version of the Bridgman crystal growth technique from an Sb rich melt. These crystals, however, were much too small for transport property measurements, and are not considered further.

EXPERIMENTAL RESULTS

Four-probe electrical resistivity, and steady-state thermopower (S) and thermal conductivity were used in mea-

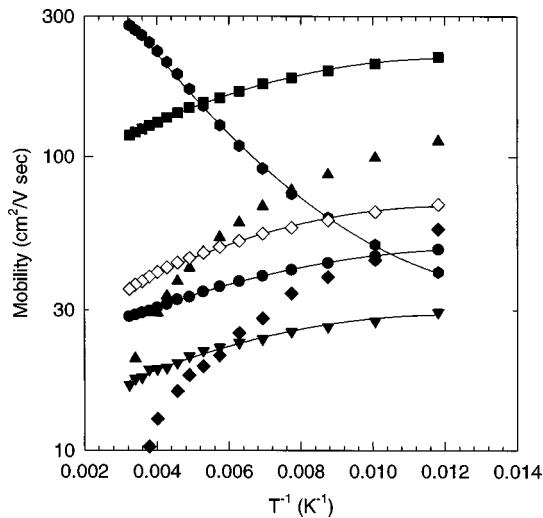


FIG. 1. Hall mobility vs inverse temperature for the skutterudite samples [$x=0$ (closed hexagon), $x=0.05$ (▲), $x=0.23$ (◆), $x=0.31$ (■), $x=0.62$ (◇), $x=0.75$ (●), $x=0.9$ (▼)] synthesized for this study. In the case of the $x=0.05$ and $x=0.23$ N -type samples the electron mobility is shown; the hole mobility is shown for the other P -type samples.

measurements in a radiation-shielded vacuum probe.²¹ Heat losses via conduction through lead wires and radiation were determined in separate experiments and the data corrected accordingly. These corrections were 10–15% near 300 K and <3% at temperatures below 150 K. The measured zero values of the partially filled skutterudites (see Table I) vary monotonically but not quite linearly with the void filler concentration x . It is not expected that the Sn substitution for Sb will have a significant effect on a_0 ; most of the increase in a_0 is caused by the La addition. The hot pressed samples were cut with a wire saw (Unipress wire saw model WS-22) in the shape of parallelepipeds for transport properties measurements. The Hall coefficient (R_H) measured in the range from 310 to 85 K using the four-probe technique was weakly temperature dependent for all samples except the $x=0.05$ and $x=0.23$ N -type specimens, for which R_H decreased with increasing temperature. Figure 1 shows the mobility as a function of inverse temperature for all the samples shown in Table I. The two N -type samples display a sharper decrease in mobility at increasing temperatures than do the P -type samples. The lines in the figure connect the data points in an effort to aid the eye in distinguishing between the different samples shown in this figure. Figure 2 shows the electrical resistivity ρ in the temperature range from 300 down to 6 K for six of the partially filled skutterudites prepared for this study. Although the carrier concentration in the CoSb_3 sample is relatively high, see Table I, this sample exhibits semiconductor behavior. Figure 3 shows the absolute S as a function of temperature from 300 down to 6 K for the $x=0.75$, 0.23, and 0.05 La-filled-skutterudite samples as well as for CoSb_3 . The data for $x=0.75$ is typical in magnitude and temperature dependence of the P -type, partially filled skutterudites measured. The absolute S decreases with decreasing temperature in this temperature range. This is similar to measurements on other R -filled skutterudites.^{3,16,17} In the present study the relatively low absolute S at room temperature (as compared to $S=80 \mu\text{V/K}$ at room temperature

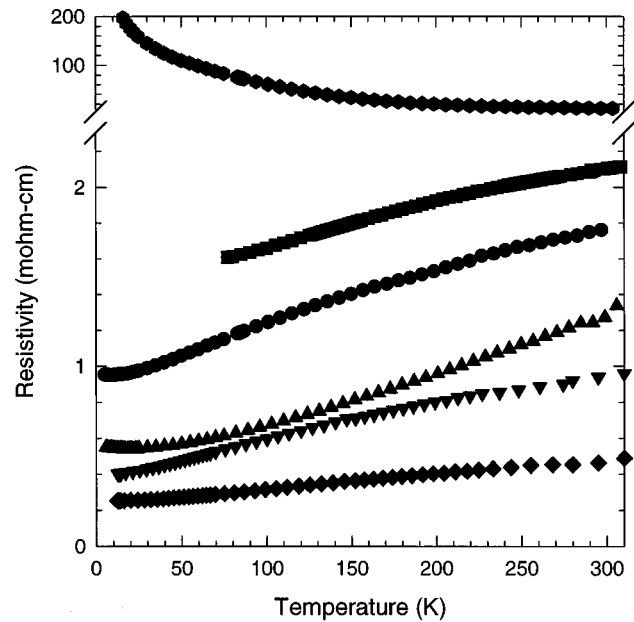


FIG. 2. Resistivity as a function of temperature from 6 to 300 K for six partially filled skutterudite samples [$x=0$ (closed hexagon), $x=0.05$ (▲), $x=0.23$ (◆), $x=0.31$ (■), $x=0.75$ (●), $x=0.9$ (▼)] synthesized for this study.

for previous results^{16,17} in the case of Fe-compensated samples) may be due to the fact that a stoichiometry with a La to Sn ratio of exactly 1:3 was not achieved in these samples resulting in high carrier concentrations. The two N -type samples clearly show a higher magnitude of absolute S . From Fig. 3 we see that for the $x=0.05$ sample the magnitude and temperature dependence is similar to that of undoped CoSb_3 even though the $x=0.05$ sample has a carrier concentration 80 times larger. The sign of S , of course, reversed. From Table I we see that the P -type samples are Sb

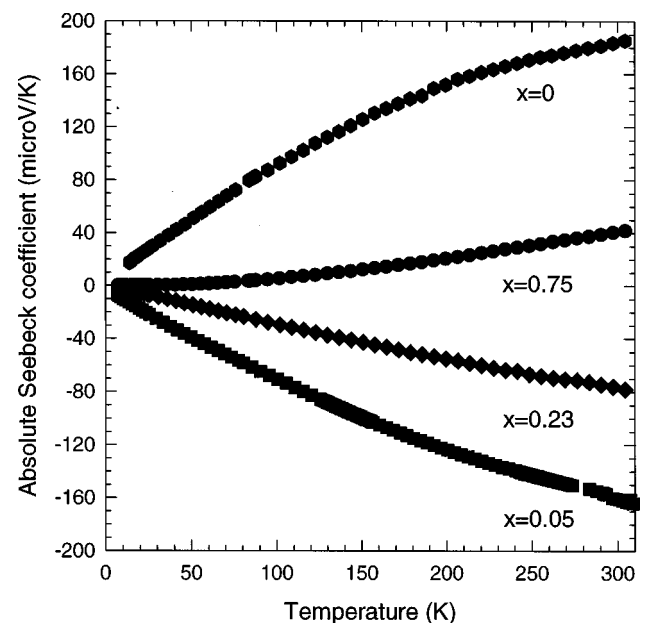


FIG. 3. Absolute Seebeck coefficient vs temperature from 6 to 300 K for the partially filled skutterudites $x=0.05$, 0.75, and 0.9 as well as unfilled CoSb_3 ($x=0$).

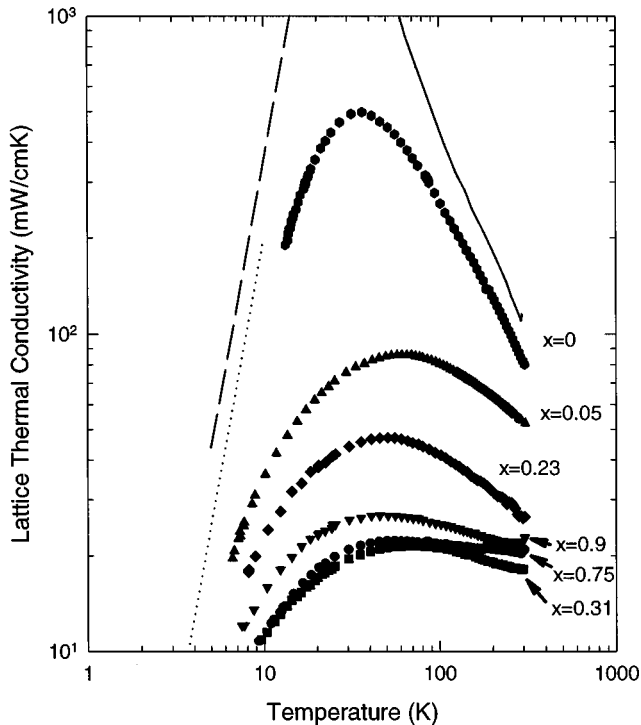


FIG. 4. Lattice thermal conductivity vs temperature from 6 to 300 K for six partially filled skutterudite samples. Single crystal κ values for CoSb_3 are also shown as a solid line. The dotted and dashed lines are calculations of κ_g for 4 and 7 μm grain sizes, respectively.

rich (i.e., Co deficient) in agreement with previous results.^{3,8,13} The $x=0.23$ N -type sample is Sb deficient. These results are within the accuracy of the XMP measurements.

Figure 4 shows κ_g in the temperature range from 300 down to 6 K for the partially filled skutterudites with $x = 0.5, 0.23, 0.31, 0.75, 0.9$ and for $x=0$, i.e., unfilled CoSb_3 . In addition the κ_g values due to boundary scattering calculated for 4 and 7 μm grain sizes are also included. The κ_g is isotropic since the skutterudite structure is cubic. From the measured values of ρ , shown in Fig. 1, and the Wiedemann-Franz law, with the Lorenz number taken to be $2.44 \times 10^{-8} \text{ V}^2/\text{deg}^2$,²² we have estimated and subtracted the κ_e values to yield the κ_g values shown in Fig. 4. This amounted to a maximum 30% correction at room temperature and a smaller correction at lower temperatures. Single crystal κ measurements⁸ for unfilled CoSb_3 are also shown in Fig. 4.

The temperature dependence of κ_g for pure CoSb_3 is typical of crystalline compounds. The peak value for our pure unfilled CoSb_3 is suppressed with respect to the single crystal results due to grain-boundary scattering in our polycrystalline sample. In the case of the slightly porous $x=0.75$ sample the κ_g values were corrected for porosity^{23,24} in order to more accurately compare it to the other samples. In the case of the partially filled skutterudites the grain sizes were all $\geq 4 \mu\text{m}$, therefore the magnitude and temperature dependence of κ_g for all samples for temperatures greater than 45 K are not due to grain boundary scattering. In the case of the samples with grain sizes of 8 μm (see Table I) scattering due to boundary scattering begins well below this temperature. From Fig. 4 we see that the $x \geq 0.31$ samples show a some-

what flat temperature dependence of κ_g between 30 and 300 K similar to that of 100% filled skutterudites.³

DISCUSSION

As seen in Table I the Sn-compensated compounds are P type and the uncompensated, La-doped compounds are N type. P -type behavior for Sb-rich CoSb_3 has been previously reported.¹⁸ The N -type behavior is most likely due to the fact that the La^{3+} ions donate their electrons without charge compensation. The ideal skutterudite has an electron count of 144 per cubic unit cell as described in Tritt *et al.*²⁵ Electrons in excess of this number produce N -type behavior. It should also be noted that these uncompensated, La-filled skutterudites as well as the Sn-compensated samples have a larger carrier mobility than Fe-compensated^{16,17} samples with similar carrier concentration. It is apparent that there is substantially more carrier scattering caused by Fe substitution in Co skutterudite compounds than by Sn substitution. From Fig. 1 a general trend is also apparent; the lower La^{3+} concentration, partially filled skutterudites have a higher mobility than the completely filled ones, adjusted to the same carrier concentration. This adjustment is needed since the mobility is dependent on the carrier concentration and therefore the exact stoichiometry of a particular compound. The R^{3+} ions in the voids appear to scatter charge carriers as well as phonons. Partial filling of the voids may therefore be an approach for increasing the mobility in these compounds for thermoelectric applications.

The absolute S values are somewhat dependent on the carrier concentration, as observed in Table I and Fig. 3. The relatively large absolute S for the N -type samples are presumably due to their large effective mass. These observations corroborate those of previous work on doped N -type CoSb_3 .²⁶ Employing Fig. 3 an estimate of the electron effective mass m^* for the two N -type samples can be made in a straightforward fashion using Fermi statistics and assuming acoustic phonon scattering in a single-band model.²⁷ The m^* values thus calculated are $3.0m_0$ and $2.7m_0$ for the $x=0.05$ and $x=0.23$ N -type partially filled skutterudite samples, respectively, where m_0 is the free electron mass. These relatively large m^* values are in agreement with band structure calculations which predict a heavy conduction band mass in N -type skutterudites.²⁸ It may be that the La^{3+} ions in these samples do not affect the band structure of CoSb_3 a great deal even though they dope the samples N type. Partial filling may be a route toward optimizing both the electronic properties and κ_g for thermoelectric applications.

From Figs. 4 and 5 we see that only a small amount of La in the voids of CoSb_3 reduces κ_g substantially. Also κ_g is similar in temperature dependence for the $x=0.9$ and $x=0.31$ skutterudite samples with the exception that $x=0.31$ has a lower κ_g . The κ_g of the $x=0.75$ sample is also lower than that of the $x=0.9$ sample. The random distribution of La^{3+} ions seems to be more effective in scattering phonons than an arrangement in which all, or most, of the voids are filled. This seems to indicate that more than one phonon scattering mechanism exists. The partial, random distribution of La^{3+} in the voids may introduce additional phonon scattering, other than the dynamic, or rattling, effect of La^{3+} in the voids. This would therefore result in a larger decrease in

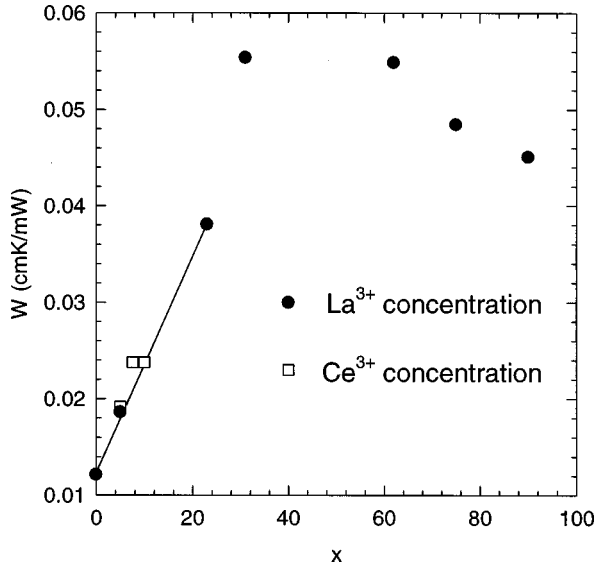


FIG. 5. Room temperature thermal resistivity W as a function of La^{3+} concentration x in the voids of the skutterudite structure. The solid line is a simple quadratic equation fit to the data.

κ_g . Given that the masses and sizes of Sn and Sb do not differ substantially we would not expect a significant effect on κ_g , as observed (see Table I).

Figure 5 shows the thermal resistivity W at room temperature as a function of the La^{3+} concentration of the voids x . Data for Ce^{3+} versus x from Ref. 13 are also included. The solid line is a simple linear fit to the data points up to $x=0.2$. From Fig. 5 we see an initial steep increase in W from only a small amount of La^{3+} in the voids, in agreement with a recent report.¹³ The W levels off somewhat due to the disorder produced by the rattling La^{3+} in the voids of this structure. This rattling is the major phonon scattering mechanism that produces the low κ_g values. We see, however, that a maximum exists at approximately $x=0.5$, or 50% void filling. This is similar to mass-fluctuation-type scattering as outlined by Abeles.²⁹ It is possible that the random distribution of La^{3+} and voids in the skutterudite lattice introduces this additional phonon scattering, as opposed to an “ordered” system where all the voids are filled with La^{3+} or all are empty.

As seen in Fig. 4, the further reduction in κ_g due to the partial filling of the voids still does not result in $\kappa_g \approx \kappa_{\min}$, calculated to be 3.1 mW/cm K at room temperature for CoSb_3 . As outlined previously,³ this value of κ_{\min} was calculated following Slack⁹ taking the minimum mean free path of the acoustic phonons as $\lambda/2$ instead of λ , as suggested by Cahill *et al.*,¹⁹ where λ is the phonon wavelength. This modest additional reduction of κ_g due to partial La^{3+} filling may, however, be enhanced by other choices of R^{3+} ions, for example the larger mass R^{3+} ions or actinide ions. In addition, recent x-ray diffraction data reveal that the smaller size, larger mass R^{3+} ions may, at room temperature, reside in a corner of the void as opposed to the larger size, smaller mass R^{3+} ions which statistically occupy the center of the void.³⁰ This may introduce a static disorder in the lattice, in addition to the dynamic disorder due to the rattling of these ions in their voids. Such a disordered system would be quite interesting in light of the effect of partial void filling on κ_g dis-

cussed here. A study of the influence of this static disorder on κ_g is currently underway. The lowest κ_g values will probably be produced in crystals with several different void occupants chosen so that they individually interact with the phonons in many different parts of the whole phonon spectrum. Since the La scattering is most effective at $x=0.25$ to $x=0.30$, this means that three or four different filling atoms would be more effective than any single kind of atom for 100% void filling.

MASS FLUCTUATION SCATTERING

The increase in the room temperature W of CoSb_3 caused by the lanthanum additive appears to reach a maximum (or at least a saturation value) at $x=0.5$, i.e., when just half of the voids are filled. The random occupation of the void sites produces a mass fluctuation scattering of phonons. The theory of this scattering has been worked out by Callaway³¹ and Abeles.²⁹ We can calculate the expected effect of this scattering on the room temperature κ from this theory. First the mass fluctuation scattering parameter Γ for a ternary crystal of composition $A_aB_bC_c$ is given by

$$\Gamma = \sum \chi_i \left(1 - \frac{m_i}{M}\right)^2, \quad (2)$$

where M is the mass of an average ternary cluster with a total number of atom sites equal to $a+b+c$. Then m_i is the mass of the particular cluster i . If $A=\text{Co}$, $B=\text{Sb}$, and $C=\text{La}$ or a vacancy, then $c=1$ when $a=4$ and $b=12$ and $M=4M(\text{Co})+12M(\text{Sb})+xM(\text{La})$ with $0 < x < 1$. Here x is the fractional occupation of the voids by La. The expression for Γ then becomes

$$\Gamma = \sum \chi(1-\chi) \left[\frac{M(\text{La})}{M}\right]^2 \quad (3)$$

and at $x=0.5$, $\Gamma = 1.5464 \times 10^{-3}$. For very small x values we obtain $\Gamma = 6.7026 \times 10^{-3}$. W in the high-temperature region where the temperature is comparable to the Debye temperature Θ is given by Abeles²⁹ as

$$\frac{W}{W_p} = \left[1 + \frac{5\alpha}{9}\right] \times \left[V + \frac{(1-V)^2}{[(1+\alpha)/5\alpha]U^4 - (1/3)U^2 + (1-V)}\right]^{-1}. \quad (4)$$

The various symbols are defined by $V=(\tan^{-1}U)/U$, $U_0=U\sqrt{(1+5\alpha/9)}$, $U_0^2=3GT/W_p$, and $G=(\pi^4/48)^{1/3}h\delta/k^2\Theta$ where α is the ratio of the phonon umklapp scattering relaxation time to the phonon normal scattering relaxation time, δ^3 is the average volume per atom of the crystal, Γ is the mass fluctuation scattering parameter, Θ is the Debye temperature of CoSb_3 , W_p is the thermal resistivity of pure, undoped CoSb_3 at the temperature in question, h is Planck's constant, and k is Boltzmann's constant.

The parameter values for CoSb_3 at 300 K taken from Caillat *et al.*²⁶ are $\Theta=307$ K, $W_p=9.52$ cm K/W, and $\delta=2.846 \times 10^{-8}$ cm. These yield $G=408.0$ cm K/W, $\Gamma(x=0.5)=1.5464 \times 10^{-3}$, and $U_0(300 \text{ K}, x=0.5)=0.4458$. From these numbers we can compute the expected

TABLE II. Calculated values of the thermal conductivity and resistivity of CoSb₃ doped with La at a concentration x and at 300 K versus α .

κ (mW/cm K)	x	α	W (cm K/W)
105	0.0		9.52
101	0.5	0.0	9.88
98.8	0.5	1.0	10.12
92.3	0.5	2.0	10.83
91.1	0.5	2.75	10.98
90.7	0.5	3.0	11.02
78.2	0.5	∞	12.79

κ_g of a La-doped skutterudite at 300 K for $x=0.5$ for various values of the parameter α . The results are tabulated in Table II. From these results we see that the simple mass fluctuation scattering produced by the La in the voids is nowhere nearly sufficient to explain the observed W at $x=0.5$, 300 K, of about 55 cm K/W for any value of α .

The value of α appropriate for skutterudites can be obtained from the κ_g values observed on IrSb₃-RhSb₃ mixed crystals.² The Ir and Rh atoms have almost identical radii in the skutterudite structure. Thus the strain-field scattering is zero, and Rh behaves almost as a light isotope of Ir. In this case for 50 at. % Rh in IrSb₃ the value of $\Gamma=7.72\times 10^{-3}$. Using Eq. (4) at 300 K where $W(\text{Ir}_{0.5}\text{Rh}_{0.5}\text{Sb}_3)/W(\text{IrSb}_3)=1.78$ we find the best agreement is for $\alpha=2.75$. For Si-Ge mixed crystals Abeles²⁹ found $\alpha=2.5$, so our present value is reasonable. If we use $\alpha=2.75$ in Table II, we see that at 50% La filling in CoSb₃ the calculated W from the mass fluctuation is much lower than the observed effect. There is almost zero strain-field scattering to be expected for La atoms in the voids. The La³⁺ ions have a diameter only 77% of the void diameter in CoSb₃. This is reinforced by the x-ray measurements on LaFe₄Sb₁₂,³² which show that the Fe-Sb framework is too large for the La ions.

SMALL LANTHANUM CONCENTRATIONS

We now consider the linear $W(x)$ behavior shown in Fig. 5 for $x\leq 2$. Both La and Ce give $dW/dx=128$ cm K/W. We can also employ the formulas of Abeles²⁹ to compute the initial slope expected for the mass-fluctuation scattering of La and Ce. The result is, for all values of α ,

$$\frac{dW}{dx} = \frac{27(21+42\alpha+25\alpha^2)}{7(81+90\alpha+25\alpha^2)} \frac{d\Gamma}{dx} G. \quad (5)$$

For $\alpha=2.75$, then $dW/dx=6.63$ cm K/W. Thus the observed dW/dx is 19 times larger than would be expected from the mass fluctuation scattering of the La and Ce alone. Some other phonon scattering mechanism(s) is involved.

RATTLE SCATTERING

The concept of ‘‘rattle scattering’’ of phonons has been suggested by Slack.¹¹ In this model undersized atoms move about in oversized cages in which they are trapped. This random motion produces a large phonon scattering.³ The calculated vibration frequencies³³ of La and Ce atoms trapped in Fe-Co skutterudites are 74 and 68 cm⁻¹, respectively. This is in great contrast to the mass-fluctuation scattering calculated above, which peaks at a phonon energy $k\Theta$ of 213 cm⁻¹ in CoSb₃. A more detailed treatment of the effect of La on κ_g of CoSb₃ presumably involves resonant phonon scattering at these rattling frequencies and is an interesting topic for further theoretical investigation.

CONCLUSIONS

The synthesis and investigation of compounds with the skutterudite crystal structure with La³⁺ ions partially filling the voids was undertaken in order to quantify their effect on κ_g . It was observed that the reduction in κ_g is greatest for samples with partial filling as opposed to more fully filled skutterudites. This suggests phonon scattering effects due to the partial, random distribution of La³⁺ in the voids of this structure. In addition, partial filling was observed to enhance the carrier mobilities, suggesting that partially filled skutterudite compounds may be the most promising for cooling applications.

ACKNOWLEDGMENTS

The authors are grateful to A. Thompson for experimental assistance and Dr. B. C. Sales of Oak Ridge National Laboratory for simulations using LAZY software. One of the authors (G.S.N.) wishes to thank Dr. D. C. Johnson of the University of Oregon for stimulating discussions. This work was supported, in part, by NASA Grant No. NAS9-19358.

¹N. N. Zhuravlev and G. S. Zhdanov, *Krystallogr.* **1**, 509 (1956) [*Sov. Phys. Crystallogr.* **1**, 404 (1956)].

²G. A. Slack and V. G. Tsoukala, *J. Appl. Phys.* **76**, 1665 (1994).

³G. S. Nolas, G. A. Slack, D. T. Morelli, T. M. Tritt, and A. C. Ehrlich, *J. Appl. Phys.* **79**, 4002 (1996).

⁴C. B. H. Evers, W. Jeitschko, L. Boonk, D. J. Braun, T. Ebel, and U. D. Scholz, *J. Alloys Compd.* **224**, 184 (1995), and references therein.

⁵G. S. Nolas, G. A. Slack, T. Caillat, and G. P. Meisner, *J. Appl. Phys.* **79**, 2622 (1996).

⁶D. Mandrus, B. C. Sales, V. Keppens, B. C. Chakoumakos, P.

Dai, L. A. Boatner, R. K. Williams, T. W. Darling, A. Migliori, M. B. Maple, D. A. Gajewski, and E. J. Freeman, in *Thermoelectric Materials—New Directions and Approaches*, edited by T. M. Tritt, G. Mahan, H. B. Lyon, and M. G. Kanatzidis, MRS Symposia Proceedings No. 478 (Materials Research Society, Pittsburgh, 1997).

⁷See, for example, H. J. Goldsmid, *Electronic Refrigeration* (Pion, London, 1986).

⁸D. T. Morelli, T. Caillat, J.-P. Fleurial, A. Borschchevsky, J. Vandersande, B. Chen, and C. Uher, *Phys. Rev. B* **51**, 9622 (1995).

- ⁹G. A. Slack, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1979), Vol. 34, p. 1.
- ¹⁰D. G. Cahill, S. K. Watson, and R. O. Pohl, *Phys. Rev. B* **46**, 6131 (1992).
- ¹¹G. A. Slack, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC, Boca Raton, FL, 1995), p. 407.
- ¹²S. Zemni, D. Tranqui, P. Chaudouet, R. Madar, and J. P. Senateur, *J. Solid State Chem.* **65**, 1 (1986).
- ¹³D. T. Morelli, G. P. Meisner, B. Chen, S. Hu, and C. Uher, *Phys. Rev. B* **56**, 7376 (1997).
- ¹⁴G. A. Slack and D. W. Oliver, *Phys. Rev. B* **4**, 592 (1971).
- ¹⁵D. T. Morelli and G. P. Meisner, *J. Appl. Phys.* **77**, 3777 (1995).
- ¹⁶B. C. Sales, D. G. Mandrus, and R. K. Williams, *Science* **272**, 1325 (1996).
- ¹⁷B. Chen, J. Xu, C. Uher, D. T. Morelli, G. P. Meisner, J.-P. Fleurial, T. Caillat, and A. Borshchevsky, *Phys. Rev. B* **55**, 1476 (1997).
- ¹⁸L. D. Dudkin and N. Kh. Abrikosov, *Sov. Phys. Solid State* **1**, 126 (1959).
- ¹⁹K. Yvon, W. Jeitschko, and E. Parthe, *J. Appl. Crystallogr.* **10**, 73 (1977).
- ²⁰*Metals Handbook*, 9th ed. (American Society of Metals, Metals Park, OH, 1985), Vol. 9, pp. 122–134, and references therein.
- ²¹C. P. Popoviciu and J. L. Cohn, *Phys. Rev. B* **55**, 3155 (1997).
- ²²G. A. Slack, D. W. Oliver, and F. H. Horn, *Phys. Rev. B* **4**, 1714 (1971).
- ²³S. L. Loeb, *J. Am. Ceram. Soc.* **37**, 96 (1954).
- ²⁴J. Franci and W. D. Kingery, *J. Am. Ceram. Soc.* **37**, 99 (1954).
- ²⁵T. M. Tritt, G. S. Nolas, G. A. Slack, A. C. Ehrlich, D. J. Gillespie, and J. L. Cohn, *J. Appl. Phys.* **79**, 8412 (1996), and references therein.
- ²⁶T. Caillat, A. Borshchevsky, and J.-P. Fleurial, *J. Appl. Phys.* **80**, 4442 (1996).
- ²⁷G. A. Slack and M. A. Hussain, *J. Appl. Phys.* **70**, 2694 (1991).
- ²⁸D. J. Singh and W. E. Pickett, *Phys. Rev. B* **50**, 11 235 (1994).
- ²⁹B. Abeles, *Phys. Rev.* **131**, 1906 (1963).
- ³⁰M. D. Hornbostel, E. J. Hyer, J. H. Edvalson, and D. C. Johnson, *Inorg. Chem.* **36**, 4270 (1997).
- ³¹J. Callaway, *Phys. Rev.* **113**, 1046 (1959).
- ³²D. J. Braun and W. Jeitschko, *J. Less-Common Met.* **72**, 147 (1980).
- ³³D. J. Singh and J. L. Feldman (private communication).