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

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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.

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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$_3$ ($Im3$) structure. This structure has eight formula units, including two voids, per cubic unit cell. 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 $\kappa_g$. 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. Nolas et al. employed the IrSb$_3$ system to show that $\kappa_g$ decreases monotonically with decreasing guest atom radius. An order-of-magnitude decrease in $\kappa_g$ 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, their effects on the lattice modes as investigated by Raman Spectroscopy, and by neutron scattering.

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, $\sigma$ the electrical conductivity, and $\kappa = \kappa_g + \kappa_e$, $\kappa_e$ being the electronic contribution. Although the binary, unfilled skutterudites have relatively good electrical properties their $Z$ values are low due to large values of $\kappa_e$. A substantial reduction in $\kappa_g$ 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, $\kappa_g$ must be reduced towards that of the minimum thermal conductivity $\kappa_{\min}$. Cahill et al. have enumerated a number of crystalline systems that possess low, glasslike $\kappa_g$ values. The relationship between glasslike $\kappa_g$ and $\kappa_{\min}$ was pointed out by Slack. As outlined in a recent review, the crystal 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 $\kappa_{\min}$ values is therefore of interest.

The marked reduction in $\kappa_g$ of fully filled skutterudites has been studied. In the present work we investigate the effect of partial void filling in the skutterudite structure on $\kappa_g$. Zemni et al. have synthesized partially filled skutterudite-phosphide crystals of up to 50% of the maximum $R$ concentration. Recently Morelli et al. 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. 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 $\kappa_g$. 

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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.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Sample</th>
<th>$a_0$ (Å)</th>
<th>grain size (µm)</th>
<th>$D%$</th>
<th>carrier conc. ($10^{19}$ cm$^{-3}$)</th>
<th>mobility (cm$^2$/V sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Co$<em>4$Sb$</em>{12}$</td>
<td>9.032±0.011</td>
<td>7</td>
<td>97</td>
<td>1.88</td>
<td>270</td>
</tr>
<tr>
<td>0.05</td>
<td>La$_{0.05}$Co$<em>4$Sb$</em>{12}$</td>
<td>9.056±0.017</td>
<td>5</td>
<td>94</td>
<td>170</td>
<td>20.5</td>
</tr>
<tr>
<td>0.23</td>
<td>La$_{0.23}$Co$<em>4$Sb$</em>{11.6}$</td>
<td>9.060±0.013</td>
<td>5</td>
<td>93</td>
<td>2010</td>
<td>6.8</td>
</tr>
<tr>
<td>0.31</td>
<td>La$<em>{0.31}$Co$<em>4$Sn$</em>{1.48}$Sb$</em>{12}$</td>
<td>9.064±0.002</td>
<td>4</td>
<td>94</td>
<td>27.0</td>
<td>120</td>
</tr>
<tr>
<td>0.62</td>
<td>La$<em>{0.62}$Co$<em>4$Sn$</em>{2.58}$Sb$</em>{9}$</td>
<td>9.094±0.007</td>
<td>4</td>
<td>93</td>
<td>122</td>
<td>36.6</td>
</tr>
<tr>
<td>0.75</td>
<td>La$<em>{0.75}$Co$<em>4$Sn$</em>{2.58}$Sb$</em>{7.8}$</td>
<td>9.096±0.010</td>
<td>8</td>
<td>85</td>
<td>112</td>
<td>28.9</td>
</tr>
<tr>
<td>0.9</td>
<td>La$_{0.9}$Co$<em>4$Sb$</em>{10.03}$</td>
<td>9.102±0.006</td>
<td>8</td>
<td>94</td>
<td>308</td>
<td>16.7</td>
</tr>
</tbody>
</table>

We note that this is not the case for Fe compensated R-filled-skutterudites which have also resulted in low $\kappa$. The Fe in this system also has an affect on $\kappa$, as shown in Dudkin et al.\textsuperscript{18} where 10% Fe substitution for Co in CoSb$_3$ (10%Fe:CoSb$_3$) resulted in a room temperature value of $\kappa$ 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 $\kappa$ values are consistent with these prior results. At 35 K the reduction in $\kappa$ is even greater with $\kappa$ equal to 100 mW/cmK for 10%Fe:CoSb$_3$ compared to 500 mW/cmK for CoSb$_3$. This reduction in $\kappa$ cannot be explained from the $\kappa_{\text{c}}$ component of $\kappa$, 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 $\kappa_{\text{c}}$. 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.\textsuperscript{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 previously\textsuperscript{3} 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 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 POWD\textsuperscript{7} (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$_2$O$_3$ were identified under XMP examination. This was not observed in similar previous work\textsuperscript{3} 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 epiphoto metallograph in order to measure the average grain sizes.\textsuperscript{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 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 epiphoto metallograph in order to measure the average grain sizes.\textsuperscript{20} Electron back-scattering images, from the XMP, agreed with these grain size measurements.

EXPERIMENTAL RESULTS

Four-probe electrical resistivity, and steady-state thermopower ($S$) and thermal conductivity were used in mea-
measurements in a radiation-shielded vacuum probe. 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, 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 a0; most of the increase in a0 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 samples, 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 \( \rho \) 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 \( \text{CoSb}_3 \) 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 \( \text{CoSb}_3 \). 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 \( S \approx 80 \mu \text{V/K} \) at room temperature 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 \( \text{CoSb}_3 \) 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
what flat temperature dependence of $\kappa_g$ 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 $\kappa_g$ for thermoelectric applications.

From Figs. 4 and 5 we see that only a small amount of La in the voids of CoSb$_3$ reduces $\kappa_g$ substantially. Also $\kappa_g$ 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 $\kappa_g$. The $\kappa_g$ 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
It is possible that the random distribution of the voids still does not result in a maximum exists at approximately $x = 0.5$, 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 Callaway and Abeles. We can calculate the expected effect of this scattering on the room temperature $\kappa$ from this theory. The mass fluctuation scattering parameter $\Gamma$ for a ternary crystal of composition $A_xB_yC_z$ is given by

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

where $M$ is the mass of the 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 $\Gamma$ then becomes

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

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 $\Theta$ is given by Abeles as

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

The various symbols are defined by $V = (\tan^{-1} U)/U$, $U_0 = U(1 + 5\alpha/9)$, $U_0^2 = 3GT/W_p$, and $G = (\pi^4/48)^{1/3}h\delta k^2\Theta$ where $\alpha$ is the ratio of the phonon umklapp scattering relaxation time to the phonon normal scattering relaxation time, $\delta^3$ is the average volume per atom of the crystal, $\Gamma$ is the mass fluctuation scattering parameter, $\Theta$ 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. 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
\[
\frac{dW}{dx} = \frac{27(21 + 42\alpha + 25\alpha^2)}{7(81 + 90\alpha + 25\alpha^2)} \frac{d\Gamma}{dx} G.
\]

For \( \alpha = 2.75 \), then \( dW/dx = 6.63 \text{ cm K/W} \). 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. In this model undersized atoms move about in oversized cages in which they are trapped. This random motion produces a large phonon scattering. The calculated vibration frequencies 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 CoSb\(_3\). A more detailed treatment of the effect of La on \( \kappa_\varepsilon \) of CoSb\(_3\) 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 La\(^{3+}\) ions partially filling the voids was undertaken in order to quantify their effect on \( \kappa_\varepsilon \). It was observed that the reduction in \( \kappa_\varepsilon \) 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 La\(^{3+}\) 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**

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\[\text{TABLE II. Calculated values of the thermal conductivity and resistivity of CoSb}_3 \text{ doped with La at a concentration x at 300 K versus } \alpha.\]

<table>
<thead>
<tr>
<th>( \kappa ) (mW/cm K)</th>
<th>( x )</th>
<th>( \alpha )</th>
<th>( W ) (cm K/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>105</td>
<td>0.0</td>
<td></td>
<td>9.52</td>
</tr>
<tr>
<td>101</td>
<td>0.5</td>
<td>0.0</td>
<td>9.88</td>
</tr>
<tr>
<td>98.8</td>
<td>0.5</td>
<td>1.0</td>
<td>10.12</td>
</tr>
<tr>
<td>92.3</td>
<td>0.5</td>
<td>2.0</td>
<td>10.83</td>
</tr>
<tr>
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<td>2.75</td>
<td>10.98</td>
</tr>
<tr>
<td>90.7</td>
<td>0.5</td>
<td>3.0</td>
<td>11.02</td>
</tr>
<tr>
<td>78.2</td>
<td>0.5</td>
<td>( \infty )</td>
<td>12.79</td>
</tr>
</tbody>
</table>

\( \kappa_\varepsilon \) of a La-doped skutterudite at 300 K for \( x = 0.5 \) for various values of the parameter \( \alpha \). 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 \( \alpha \).

The value of \( \alpha \) appropriate for skutterudites can be obtained from the \( \kappa_\varepsilon \) values observed on IrSb\(_3\)-RhSb\(_3\) mixed crystals. 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 IrSb\(_3\) the value of \( \Gamma = 7.72 \times 10^{-3} \). Using Eq. (4) at 300 K where \( W(\text{Ir}_0\text{Rh}_{0.5}\text{Sb}_3)/W(\text{IrSb}_3) = 1.78 \) we find the best agreement is for \( \alpha = 2.75 \). For Si-Ge mixed crystals Abeles 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 CoSb\(_3\) 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 La\(^{3+}\) ions have a diameter only 77% of the void diameter in CoSb\(_3\). This is reinforced by the x-ray measurements on LaFe\(_3\)Sb\(_{12}\), 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 \( dW/dx = 128 \text{ cm K/W} \). We can also employ the formulas of Abeles to compute the initial slope expected for the mass-fluctuation scattering of La and Ce. The result is, for all values of \( \alpha \).


33 D. J. Singh and J. L. Feldman (private communication).