Lattice dynamics and reduced thermal conductivity of filled skutterudites

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The great reduction in thermal conductivity of skutterudites upon filling the “void” sites with Rare Earth (RE) ions is key to their favorable thermoelectric properties but remains to be understood. Using lattice dynamic models based on first principles calculations, we address the most popular microscopic mechanism, reduction via rattling ions. The model withstands inelastic neutron scattering and specific heat measurements, and refutes hypotheses of an anharmonic RE potential and of two distinct localized RE vibrations of disparate frequencies. It does indicate a strong hybridization between bare La vibrations and certain Sb-like phonon branches, suggesting anharmonic scattering by harmonic RE motions as an important mechanism for suppression of heat conductivity.

The discovery of new high performance thermoelectrics with complex crystal structures poses an important challenge for theory, which, if met, could lead to the synthesis of materials with substantially higher thermoelectric performance. The key is to learn how the contradictory criteria — high electrical and low thermal conduction — are satisfied. One of the most promising groups of materials are the filled skutterudites. Skutterudites (MPn3: M=Co,Rh,Ir; Pn=P,As,Sb) can be described as a cubic lattice of M atoms with 3/4 of the cubes filled by nearly square Pn4 rings. They have reasonable electronic properties for thermoelectric application, but ordinary values (≈100 mW/cmK at T=300K) of thermal conductivity. It was conjectured by Slack that a great reduction in thermal conductivity could be achieved by filling the empty cubes (voids) with rare gas atoms. The idea was that the fillers would “rattle” inside the voids, strongly scattering low frequency phonons but not charge carriers. It was subsequently found that filling with rare earths (La, Ce) reduces the thermal conductivity by a factor of more than five at room temperature.[2,3] Essentially, regarding the thermal conductivity, these crystalline materials may behave like glasses. The origin of this strange behavior, also seen in some other materials (clathrates, KBr-KCN), is basically not understood. The occasionally discussed possibility that such a large reduction of the lattice thermal conductivity (LTC) is due to scattering by electronic excitations can be rejected by various arguments based on experimental trends[4]. On the other hand, sorting out other mechanisms requires microscopic analysis. The most notable hypothesis relates to anomalous dynamics of RE atoms, namely strongly anharmonic rattling motion. It has also been suggested, from experiment, that there exist two inherent RE vibrations (or perhaps two different two level systems (TLS’s)) of significantly different frequencies implying strong anharmonicity of a different nature than simple rattling. Here, we construct a microscopic model needed to address these issues, demonstrate that it describes the experiments, and use it to discuss possible scenarios for the LTC reduction.

Our lattice dynamical model is based in part on first principles density functional calculations, performed by the linearized augmented planewave (LAPW) method[6], as described in Ref.[5], including directly calculated forces generated by numerous (≈ 40) sets of atomic displacements small enough to represent the harmonic coupling constants along various directions. Previously, we used the LDA to obtain A_9 and A_4 vibrational modes for CoSb3 within a frozen phonon direct method and combined these with results of infrared measurements to develop a valence force field lattice dynamical model. Here we start with the model for CoSb3, and make a minimal number of additions to, and adjustments of parameters needed to reproduce our new LDA results with a reasonable accuracy. However, we shall first address the shape of the RE potential well.

Fig. 1 shows the LDA total energy as a function of RE displacements in (La, Ce)Fe4Sb12. This was calculated for a perfect crystal corresponding to the skutterudite (bcc) lattice with displacements of the RE’s along a trigonal axis. Not only is a double well excluded, but the anharmonicity is of an ordinarily weak nature. In fact, addition of a small quartic anharmonic term is sufficient to fit the results to well within 0.1mRy over the entire (±0.5 Å) range. The harmonic frequencies are 68 and 74 cm⁻¹ for Ce and La in the corresponding materials and the anharmonic shift is less than a few cm⁻¹ at T up to 1000K. (We refer to these frequencies as “bare” frequencies; we emphasize that they are neither crystalline normal mode frequencies nor the “single-ion” frequency of a RE with all other ions fixed including the other RE’s). The crystal symmetry imposes isotropy on the harmonic term but not on higher order terms. We computed the quartic parameter in the La filled material with La displacement
along a cubic axis to be 10.7 mRy/bohr$^4$ as compared with 6.27 mRy/bohr$^4$ for a trigonal axis. These are the extrema of the quartic tensor.

![Figure 1](image1.png)

**FIG. 1.** Calculated LDA energy vs. $RE$ displacement along a trigonal axis of $REFeSb_{12}$. The least square fit parameters are $a=28.82 (24.64)$ mRy/bohr$^2$ and $b=6.27 (5.50)$ mRy/bohr$^4$ for La (Ce).

![Figure 2](image2.png)

**FIG. 2.** La (bottom) and Sb (top) weighted vibrational density of states (WVDOS) for LaFe$_4$Sb$_{12}$. The dashed line shows Sb WVDOS for CoSb$_3$ which is similar to that for FeSb$_3$ within the same dynamical model. The vertical line denotes the “bare” La frequency. The high frequency region where the Fe atoms dominate is not shown.

Now we present the full dynamical model obtained from our LDA results, including the above. We added central force constants between the $RE$ ion and its closest Fe and Sb atoms to the valence force field model [6] for CoSb$_3$. We found this simplest approximation to be quite sensible by comparison with LDA forces for various sets of La, Sb, and Fe displacements. Thus we directly get values of $-0.8$ and $1.64 (10^4$ dyn/cm) for La-Fe and La-Sb force constants, respectively. The $RE$ bare frequency is then reproduced by construction. This intermediate ($I$)-model, based on a CoSb$_3$ model of Ref. [6] and augmented by the above parameters to account for La filling, is useful in analyzing the direct lattice dynamics effect of the $RE$. But, there is also a considerable indirect effect, by changes in other force constants upon $La$ filling and our final ($F$)-model includes these, specifically a 30% reduction of the two central intra-square force constants and a 10% reduction of the M-Sb central force constants. Below $\approx 140 \text{ cm}^{-1}$ both models give similar results. A test of the $F$-model is to compare frequencies of $A_{1g}$ phonons with those calculated by the LDA for a Ce compound $\beta$ (137 and 157 cm$^{-1}$): the $F$-model gives 141 and 162 cm$^{-1}$, and the $I$-model 154 and 179 cm$^{-1}$.

![Figure 3](image3.png)

**FIG. 3.** Dispersions along $\Gamma$-$H$. The widths are the relative La character. Note the break in scale at 80 cm$^{-1}$.

The phonon dispersions of the unfilled material have rather flat Sb derived optic branches quite close to the bare frequency of 74 cm$^{-1}$ of the $RE$ ions as seen in figures 4 through 7 of reference [6]. For example, one observed IR ($F_u$ symmetry) frequency in the unfilled structure is 78 cm$^{-1}$. $F_u$ symmetry allows for $RE$ displacements. We find strong $RE$-Sb coupling that drives predominantly Sb modes up in frequency and predominantly $RE$ modes down. Fig. 2 shows that the Sb weighted VDOS is greatly affected by La-filling in the 80-100 cm$^{-1}$ region. With higher frequencies, or symmetries incompatible with La motion, Sb-like peaks are also shifted up, as the La-Sb force constant is positive, but the shifts are smaller. This is seen in the atom-type ($J$) weighted vibrational density of states (Fig. 3), $G_j(\omega) = \sum_{ij} |e_i(j)|^2 \delta(\omega - \omega_i)$, where the sum on $i$ is over wave vectors and phonon branches and $j$ is over all
type $J$ atoms in the unit cell. Figs. 3a and b show the character of modes in the filled material in the spectral region of interest. The dash lengths are proportional to $|e_{La}|^2$ where $e_{La}$ is the La-projection of the (normalized) polarization vector; e.g. $e_{La}^2 = 1$ would mean the mode involves only the La sublattice - this would then have to be at the “bare” frequency of 74 cm$^{-1}$. Strong coupling of Sb and $RE$ motion is evident for all wavelengths. A resonant interaction between a longitudinal acoustic branch and a low lying ($RE$ dominated) optic branch is found. Fig. 3 shows the region of the acoustic spectrum where resonant scattering by $RE$ ions in disordered material can occur.

Armed with this microscopic model, we can discuss scenarios for LTC reduction and related experiments, particularly inelastic neutron scattering (INS) and specific heat (for $T \leq 45$ K) for $RE$CoFe$_3$Sb$_12$. A rather sharp peak at 50 cm$^{-1}$ and a quite broad peak centered at about 100 cm$^{-1}$ were obtained in a difference spectrum, i.e., subtracting spectra for La and Ce filled samples and noting that the cross section is much larger for La than for Ce, to find $RE$ vibrational contributions. This led to a natural assertion of two distinct $RE$ vibrations.

Using LDA calculations and our model, we can check the main physical assumptions made in the earlier analysis. First, it was assumed that there is no difference in interatomic forces between La- and Ce-filled materials. By LDA calculation we find that the self force constants of the La and Ce do differ by 15%, but, calculating the neutron spectra from our model, we find that the La WVDOS is indeed rather close to the difference in the INS between the La- and Ce-filled materials: two major peaks, centered at 50 cm$^{-1}$ and 100 cm$^{-1}$, in the La weighted VDOS (Fig. 3), are clearly seen in the calculated differential INS spectrum (Fig. 4) as well. These correspond well to the two peaks found by Keppens et al. (As usual, the experimental peaks are broader due to instrumental and intrinsic materials effects like disorder and anharmonicity.) Most importantly, the calculated two peak structure was obtained without an additional localized La mode. Instead, the La spectral weight was transferred by hybridization from the main La peak (downshifted from the bare frequency of 78 cm$^{-1}$ to 50 cm$^{-1}$), to Sb modes at 100 cm$^{-1}$.

Ref. 4 presents more indications of two $RE$ frequencies (and possibly a TLS), namely specific heat differences between $CoSb_3$ and $RE$CoFe$_3$Sb$_12$ and small unusual temperature dependent features of elastic constants. Clearly, a reconciliation of our calculations that do not produce two separate La phonons, and the specific heat experiments is needed. (We cannot address the temperature dependence of the elastic constants in our calculations; this alone, however, cannot be considered as compelling evidence for TLS’s.) Here we present new, improved experimental specific heat data that supersede the earlier data of Ref. 3. The two sets agree below $T=20$K, but considerably disagree at higher $T$. In terms of the previous Einstein modeling of the data for $T \lesssim 50$ K, we find that two frequencies are still needed to give the specific heat difference between the unfilled and filled materials, but the strength of the higher frequency component is much less. The experiments were done on several compounds: $CoSb_3$, $LaCoFe_3Sb_12$ and $LaFe_4Sb_12$. The synthesis procedure was previously described 5. Heat capacity data from 2-300 K were taken with a commercial Quantum Design system. Results from this system are in good agreement with published values for standards like sapphire and copper. Some of the new results are shown in Fig. 4 along with our calculations. The new experimental heat capacity for the filled material is much closer to that of the unfilled material than the earlier experiment.

The agreement with the present theoretical results for $C_V$ is remarkable, especially considering that the model does not have the two additional localized high-frequency modes. Resolution of this seeming paradox lies in an implicit assumption, which lacking force constant information had to be made in Ref. 3, i.e. that interatomic forces are transferable between the filled and unfilled materials and that specific heat differences between the materials are solely from $RE$ vibrations. However, our LDA calculations show an important contribution to the Sb dynamics from La-Sb forces: besides, the intra-square Sb interactions themselves are decreased by approximately 30% upon filling. While new rather localized La modes do appear upon filling in our analysis (at $\approx 50$ cm$^{-1}$), and they are reflected in the increased specific heat at the low temperatures, there are two more changes which greatly affect the specific heat at low temperatures: first, as discussed, certain Sb modes are shifted to higher fre-
quency, which decreases the specific heat; second, the
softening of the Sb-Sb forces increases the specific heat.
At still higher temperature (50–300 K) the lattice specific
heat approaches the harmonic Dulong-Petit value: There
is good agreement with the models, but those measure-
ments are not shown here.

![Graph showing specific heat measurements compared to models](image)

**FIG. 5.** Comparison of specific heat measurements with the harmonic force models for $T < 50K$. The models, 1 and 2, for filled materials are $I$ and $F$. The inset shows the large effect of La modes in the $T \leq 10K$ region. The lower two curves were calculated from the 50 to 70 cm$^{-1}$ spectral region exclusively.

So the origin of the LTC suppression is plainly more subtle than prior speculations about strongly anharmonic $RE$ motions. Aspects of our results suggest scenarios for the role of the $RE$ ions: (1) There is significant harmonic interaction between La and Sb in comparison to the inter-square Sb force constants and most likely this holds for the anharmonic interactions as well. Thus the rare earth vibrations, which are not heat carriers due to their flat dispersion, do interact strongly with heat carrying phonons. Slack and Galginaitis pointed out that the effect of Raman-like scattering of phonons by magnetic impurity levels in CdTe materials could reduce LTC and the reduction would be greater with increasing temperature. Perhaps a similar effect takes place here via the cubic anharmonic interaction between heat carry-
ing phonons and the 50 cm$^{-1}$ predominantly La vibra-
tions even for a perfect crystal. (2) Typically there is a
significant lack of complete rare earth filling in samples.
Harmonic resonant scattering of phonons by “impurity”
La (or La vacancy) vibrations could give short relaxation
times for frequencies near the La modes. These are in a
region of high diffusivity, $G\nu^2$ in the models. Also, the re-
duction in Sb-Sb interactions on filling implies force con-
stant disorder in the Sb sublattice of partly filled samples
(lattice specific heats of LaFe$_4$Sb$_{12}$ and LaCoFe$_2$Sb$_{12}$ are extremely similar in the $T \leq 50K$ region so the reduction in Sb-Sb interactions seems due to $RE$ filling, not substitu-
tion of Co by Fe).

To summarize, we find that the $RE$s are in a harmonic well up to large displacements, implying that the simplest rattling ion models are inapplicable to these filled skutterudites; we explain the two La peak spectrum by harmonic lattice dynamics as follows: Without the dynamical La-Sb interaction the pure La modes would be concentrated around 70 cm$^{-1}$, with a substantial number of Sb modes at slightly higher frequencies. Strong La-Sb hybridization pushes these groups apart, to $\approx 50$ and $\approx 100$ cm$^{-1}$. We suggest, on the basis of our calculations, possible mechanisms for $RE$ induced LTC reduction.

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tivity at a temperature close to the resonant frequency. It can be shown, though, that the dip is due to an inter-
play with strongly temperature dependent scattering by two-level systems, present in that material, but appar-
ently not in skutterudites. Thus an absence of such a dip in the thermal conductivity of the partially filled skut-
terudites does not rule out a strong resonant scattering effect.
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Electronic contributions (substantial only for filled materials) have been extracted from the low-T data and subtracted out at all temperatures assuming linear temperature dependence. The linear coefficients are 10 and 3.4 mJ/g-at. K$^2$ for the Fe and Fe/Co materials, respectively. We neglect the $C_P$-$C_V$ correction as we estimated it to be only of the order 0.15 J/gm-atom K at 300K, less than the uncertainty in the electronic specific heat.

We did some LDA calculations to assess the anharmonic La-Sb coupling; the ratio of the corresponding cubic parameter to the harmonic is 0.7 of that for a Lennard Jones potential at the potential minimum.

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