

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 (MPn_3 ; $M = \text{Co, Rh, Ir}$; $Pn = \text{P, As, Sb}$) can be described as a cubic lattice of M atoms with $3/4$ of the cubes filled by nearly square Pn_4 rings. They have reasonable electronic properties for thermoelectric application, but ordinary values (≈ 100 mW/cm K at $T = 300$ K) 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.^{1,2} 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.³ On the other hand, sorting out other mechanisms requires microscopic analysis. The most notable hypothesis relates to anomalous dynamics of rare-earth (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 plane wave (LAPW) method,⁴ 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, we⁶ used the LDA to obtain A_g and A_u vibrational modes for CoSb_3 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 CoSb_3 , and make a minimal number of additions to, and adjustments of parameters needed to reproduce our new local-density approximation (LDA) results with a reasonable accuracy. However, we shall first address the shape of the RE potential well.

Figure 1 shows the LDA total energy as a function of RE displacements in $(\text{La,Ce})\text{Fe}_4\text{Sb}_{12}$: 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 0.1 mRy 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 1000 K. (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/bohr⁴ as compared with 6.27 mRy/bohr⁴ for a trigonal axis. These are the extrema of the quartic tensor.

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

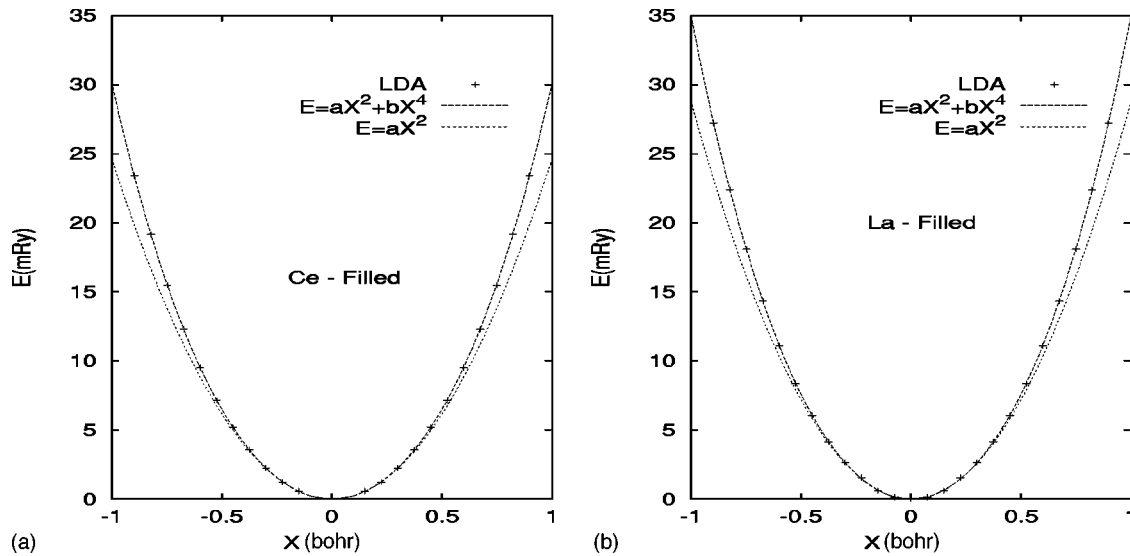


FIG. 1. Calculated LDA energy vs RE displacement along a trigonal axis of $\text{REFe}_4\text{Sb}_{12}$. The least square fit parameters are $a = 28.82$ (24.64) mRy/bohr² and $b = 6.27$ (5.50) mRy/bohr⁴ for La (Ce).

atoms to the valence force field model⁶ 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 (\mathcal{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 (\mathcal{F}) model includes these, specifically a 30% reduction of the two central intrasquare force constants and a 10% reduction of the M-Sb central force constants. Below ≈ 140 cm^{-1} both models give similar results. A test of the \mathcal{F} model is to compare frequencies of A_{1g} phonons with those calculated by the LDA for a Ce compound⁷ (137 and 157 cm^{-1}): the \mathcal{F} model gives 141 and 162 cm^{-1} , and the \mathcal{I} model 154 and 179 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 Figs. 4–7 of Ref. 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. Figure 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. 2), $G_J(\omega) = \sum_{ij} |\mathbf{e}_i(j)|^2 \delta(\omega - \omega_i)$, where the sum on i is over wave vectors and phonon branches and j is over all type J atoms in the unit cell. Figures 3(a) and (b) show the character of modes in the filled material in the spectral region of interest. The dash lengths are proportional to $|\mathbf{e}_{La}|^2$, where \mathbf{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. Figure 3 shows the region of the acoustic spectrum where resonant scattering by RE ions in disordered material can occur.⁸

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 $\text{RECoFe}_3\text{Sb}_{12}$.⁹ 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.⁹ This led to a natural assertion of two distinct RE vibrations.

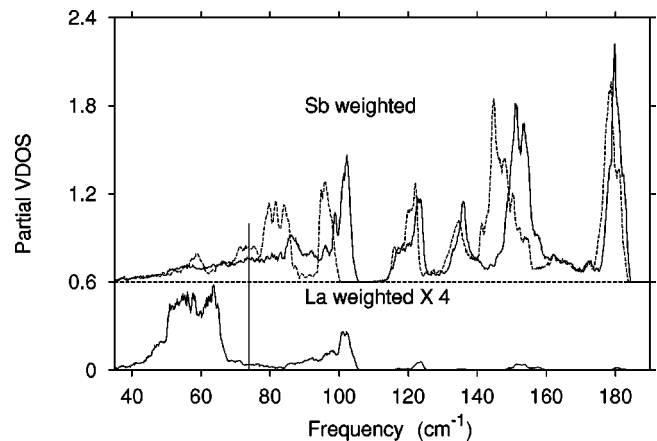


FIG. 2. La (bottom) and Sb (top) weighted vibrational density of states (WVDOS) for $\text{LaFe}_4\text{Sb}_{12}$. The dashed line shows Sb WVDOS for CoSb_3 which is similar to that for FeSb_3 within the same dynamical model. The vertical line denotes the “bare” La frequency. The high-frequency region where the Fe atoms dominate is not shown.

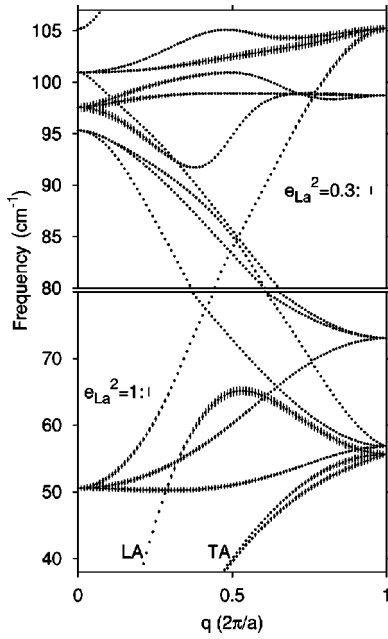


FIG. 3. Dispersions along Γ -H. The widths are the relative La character. Note the break in scale at 80 cm^{-1} .

Using LDA calculations and our model, we can check the main physical assumptions made in the earlier analysis.⁹ First, it was assumed that there is no difference in interatomic forces between La- and Ce-filled materials. Through LDA calculations we find that the self-force-constants of the La and Ce do differ by 15%, but upon 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: major peaks centered at 50 cm^{-1} and 100 cm^{-1} in the La weighted VDOS (Fig. 2), are clearly seen in the calculated differential INS spectrum (Fig. 4) as well. These correspond well to the two peaks found by Kepens *et al.*⁹ (As usual, the experimental peaks are broader due to instrumental and intrinsic materials effects such as

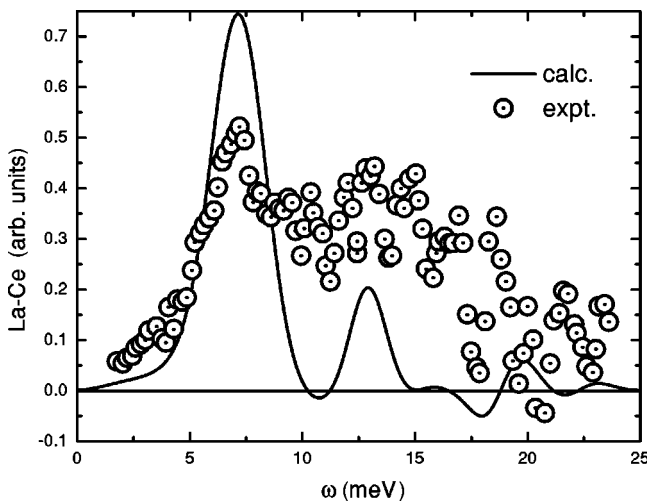


FIG. 4. INS spectral difference between La- and Ce-filled compounds. Differences in the high frequency spectral region where the Fe and Co atoms contribute heavily are not shown. Theoretical results are based on model \mathcal{F} (see text) and experimental results are from Ref. 9.

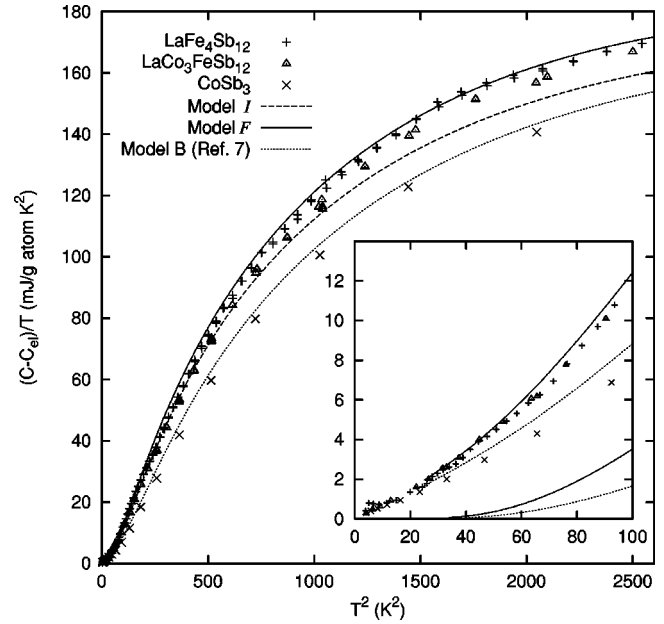


FIG. 5. Comparison of specific-heat measurements with the harmonic force models for $T < 50 \text{ K}$. The models, 1 and 2, for filled materials are \mathcal{I} and \mathcal{F} . The inset shows the large effect of La modes in the $T \leq 10 \text{ K}$ region: The lower two curves were calculated from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

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} .

Reference 9 presents more indications of two RE frequencies (and possibly a TLS), namely specific-heat differences between CoSb_3 and $\text{RECoFe}_3\text{Sb}_{12}$ 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 experimental specific-heat data that supersede the earlier data of Ref. 9. The two sets agree below $T = 20 \text{ K}$, but considerably disagree at higher T . In terms of the previous Einstein modeling of the data for $T \leq 50 \text{ K}$, 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 , $\text{LaCoFe}_3\text{Sb}_{12}$, and $\text{LaFe}_4\text{Sb}_{12}$. The synthesis procedure was previously described in Ref. 1. 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 such as sapphire and copper. Some of the current results are shown in Fig. 5 (Ref. 10) along with our calculations. The current 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 additional localized high-frequency mode. Resolution of this seeming paradox lies in an implicit assumption, which lacking force constant information, had to be made in Ref. 9, 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 intrasquare Sb interactions themselves are decreased by approximately 30% upon filling. While new rather localized La modes do appear upon filling in our analysis (at $\approx 50 \text{ cm}^{-1}$), 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 frequency, 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 measurements are not shown here.

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 intersquare Sb force constants and most likely this holds for the anharmonic interactions as well.¹¹ Thus the rare-earth vibrations, which are not heat carriers due to their flat dispersion, do interact strongly with heat carrying phonons. Slack and Galginitis¹² 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 carrying phonons and the 50 cm^{-1} predominantly La vibrations 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, Gv^2 in the models. Also, the reduction in Sb-Sb interactions on filling implies force constant disorder in the Sb sublattice of partly filled samples (lattice specific heats of $\text{LaFe}_4\text{Sb}_{12}$ and $\text{LaCoFe}_3\text{Sb}_{12}$ are extremely similar in the $T \leq 50 \text{ K}$ region so the reduction in Sb-Sb interactions seems due to RE filling, not substitution 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 ≈ 50 and $\approx 100 \text{ cm}^{-1}$. We have suggested possible mechanisms for RE induced LTC reduction on the basis of our calculations.

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³LTC reduction by electron-phonon scattering is at odds with the lack of correlation between the LTC and Hall coefficient, e.g., J.L. Cohn *et al.*, Phys. Rev. Lett. **82**, 779 (1999); scattering by RE magnetic excitations would be very different for Ce and La.

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the resonant frequency. It can be shown, though, that the dip is due to an interplay with strongly temperature dependent scattering by two-level systems, present in that material, but apparently not in skutterudites. Thus an absence of such a dip in the thermal conductivity of the partially filled skutterudites does not rule out a strong resonant scattering effect.

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¹⁰Electronic contributions (substantial only for filled materials) have been extracted from the low- T data and subtracted out at all temperatures assuming a linear temperature dependence. The linear coefficients are 10 and 3.4 mJ/g at. K² 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/g at. K at 300 K, less than the uncertainty in the electronic specific heat.

¹¹We did some LDA calculations to assess the anharmonic La-Sb coupling; the ratio of the corresponding cubic parameter to the harmonic one is 0.7 of that for a Lennard Jones potential at the potential minimum.

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