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Calculations of dynamical properties of skutterudites: Thermal conductivity, thermal expansivity, and atomic mean-square displacement

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While the thermal conductivity of the filled skutterudites has been of great interest it had not been calculated within a microscopic theory. Here a central force, Guggenheim-McGlashen, model with parameters largely extracted from first-principles calculations and from spectroscopic data, specific to $LaFe_4Sb_{12}$ or $CoSb_3$, is employed in a Green-Kubo/molecular dynamics calculation of thermal conductivity as a function of temperature. We find that the thermal conductivity of a filled solid is more than a factor of two lower than that of an unfilled solid, assuming the "framework" interatomic force parameters are the same between filled and unfilled solids, and that this decrease is almost entirely due to the cubic anharmonic interaction between filling and framework atoms. In addition, partially as a test of our models, we calculate thermal expansivity and isotropic atomic mean-square displacements using both molecular dynamics and lattice dynamics methods. These quantities are in reasonable agreement with experiment, increasing our confidence in the anharmonic parameters of our models. We also find an anomalously large filling-atom mode Gruneisen parameter that is apparently observed for a filled skutterudite and is observed in a clathrate.

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I. INTRODUCTION

The skutterudite structured materials are of current interest due to their unusual electronic properties such as heavy fermion behavior, mixed valence states, and unconventional superconductivity[1] and due to their highly promising thermoelectric properties.[2–4] One of the most important requirements for high thermoelectric figure of merit is low lattice thermal conductivity in combination with reasonable electrical conductivity, the so-called phonon-glass electron crystal.[5] The skutterudites seem to be a most interesting material in that regard because the lattice thermal conductivity is found to be strongly reduced by the addition of a rare-earth (filling) atom in the crystal cell[6] and because it had been theorized that the reduction does not depend on changes in electron bonding upon filling. Much discussion of this reduction in thermal conductivity is in terms of the rattling ion model put forth by Slack.[5,7] Most recently there have been numerous syntheses and thermoelectric property measurements of double-filled[8–13] and misch-metal[14,15] materials, where the single-filling element is replaced by two or more different filling elements. In some cases only a small amount of partial filling seems to have a large effect in the thermal conductivity.[16,17] Rattling has taken on different meanings, ranging from a rather harmonic vibrator, but with large mean-square displacements and the ability to resonantly scatter phonons, to a highly anharmonic, flat potential-well situation. That the latter does not exist in several low thermal-conductivity filled skutterudite materials has been shown by numerous theoretical and experimental investigations; e.g., inelastic neutron scattering (INS) (Refs. 18 and 19) and nuclear resonant inelastic scattering (NRIS) (Ref. 20) are well represented by theory within the harmonic approximation, and first-principles calculations show a rather harmonic potential-well corresponding to the filling atom sublattice motion.[21,22]

We also remark that a model where the filling atom can occupy off-center positions and perhaps tunnel between several equivalent low symmetry sites has been employed for explaining extended x-ray-absorption fine structure[23] and ultrasonic[24] data for a few skutterudites, and diffraction measurements[25] on $PrOs_4Sb_{12}$ and $NdOs_4Sb_{12}$ were also found to be consistent with that model upon detailed analysis of data.

In addition to a strongly anharmonic rattling ion mechanism, the proposed mechanisms for reducing the thermal conductivity in filled materials have been *both* the chemical disorder in the occupancy of the transition-metal sites[16] and resonance scattering by the filling atom vibration, for examples Refs. 14, 26, and 27. Very little attention has been given to the Umklapp scattering effect despite the fact that an expression for it is often included in analyses of data. That expression is essentially the Callaway expression[28] derived on the basis of a single-phonon relaxation time approach to the solution of the phonon Boltzmann equation and the Debye approximation.

It was recently suggested based on ultrafast optical measurements that resonance scattering by the filling atom occurs.[14] However, there may be complications in explaining the data since the bare La atom frequency is far removed

from any frequencies observed in this experiment. Furthermore, the A_g frequencies are not the same between filled and unfilled materials[29,30] so the claim that what is seen at intermediate filling are not coherent A_g modes needs verification. Indeed, comparison between theory and experiment that assumes a coherent vibrational structure, i.e., mixed filling atom and cage atom normal modes, tends to argue against resonance scattering. Perhaps recent detailed inelastic neutron-scattering study[19] argues best for the existence of coherent vibrations.

The lack of a more rigorous understanding of the thermal conductivity may be due to the difficulty of obtaining a reliable model to describe both harmonic and anharmonic parameters as well as the general complexity of the problem of calculating thermal conductivity. Here we perform molecular dynamics (MD) Green-Kubo calculations of thermal conductivity, as a function of temperature, of central force models of fully filled and unfilled skutterudites and we rely on some of our previous studies to obtain the necessary potential parameters. We also perform lattice dynamics (LD) calculations of related quantities, including vibrational densities of states, mean-squared displacements, and thermal expansivities. The first Green-Kubo calculation that showed significant lowering of thermal conductivity for a caged structure was performed by Dong *et al.*[31] for clathrates at room temperature.

In earlier work we computed the potential energy as a function of La or Ce displacement in La and Ce filled Fe/Sb skutterudites using linearized augmented plane-wave density-functional calculations[32] within the local density approximation (LDA).[21] We found that a quartic polynomial yields excellent agreement with those calculations which extended to a displacement of 1 bohr. In another paper we employed the direct method for calculating force constants. Atomic displacements were chosen small enough that quartic anharmonic interactions could be ignored[30] and a least-squares method was used to extract the (tensor) second-order force constants and leading-term central-force cubic anharmonic coefficients of a short-ranged model. Additional analysis of those LDA calculations is presented in the Appendix of this paper.

We choose harmonic parameters to be central force parameters of earlier models that we developed[21,33,34] despite the fact that those models also contained three body angular terms. We also consider the Lutz-Kliche central-force model.[35] We isolate different effects by performing calculations for various models and for modifications of potential parameters. Specifically, we numerically examine the following: (a) pristine filling atom effect, (b) La-Sb and La-Fe anharmonic interactions, (c) filling atom frequency effect, and (d) phonon propagation effect, i.e., the effect of mixed modes.

Finally we present MD calculations of mean-square displacements and thermal expansivity for our models, as well as LD calculations of thermal expansivity and mode Grunneisen parameters. We calculate the vibrational density of states of all our models and compare them with experiment in the low-frequency region where the density of states is quadratic in frequency. We also make some comparisons with our harmonic LDA-based, noncentral or tensor, short-range force-constant model[30] (in the remainder of this paper referred to as "LDA model") for assessing the validity of our results for $LaFe_4Sb_{12}$.

II. THEORY

The Green-Kubo formulas relate the thermal conductivity κ to the heat current autocorrelation function[36]

$$\kappa = \frac{V}{3k_B T^2}\int_0^\infty \langle \mathbf{q}(t)\cdot\mathbf{q}(0)\rangle dt, \tag{1}$$

where $\mathbf{q}(t)$ is the instantaneous heat flux, V is the system volume, T is the temperature, and k_B is the Boltzmann constant. For the case of central forces, and ignoring liquidlike diffusive terms, the heat flux can be written as[37]

$$\mathbf{q}V = \frac{1}{2}\sum_{i>j}(\mathbf{v}_i+\mathbf{v}_j)\cdot\mathbf{F}_{ij}\mathbf{r}_{ij}^0, \tag{2}$$

where $\mathbf{v}_i$ and $\mathbf{v}_j$ are velocities of atoms i and j, $\mathbf{F}_{ij}$ is the force on atom i due to the interaction between atoms i and j, and $\mathbf{r}_{ij}^0$ is the fixed equilibrium relative position of atoms i and j. We use the Guggenheim McGlashan potential form[38]

$$U = \sum_{i>j}\left[\frac{1}{2}\phi_{ij}^{(2)}(\Delta r_{ij})^2 + \frac{1}{6}\phi_{ij}^{(3)}(\Delta r_{ij})^3 + \frac{1}{24}\phi_{ij}^{(4)}(\Delta r_{ij})^4\right], \tag{3}$$

where $\Delta r_{ij}=r_{ij}-r_{ij}^0$ and r_{ij}^0 is a fixed equilibrium distance between atoms i and j. Admittedly the forces in the skutterudites are not central in nature as was pointed out in the case of $CoSb_3$.[33] Therefore we present these calculations as an attempt to compute the thermal conductivity for these materials from a microscopic point of view. The same potential form had been employed previously in a MD study of thermal conductivity of a two-dimensional system.[39] Similar to the case of two dimensions, even if ϕ_3 and ϕ_4 were set to zero the potential would still have (Cartesian) anharmonic terms. These so-called nonleading terms involve displacements perpendicular to a bond.[39] If, in the Taylor radial expansion, the ratio of a higher-order term to a lower-order term is sufficiently large only leading order terms are important. If the ratio of an $n+1$ term to an n order term (appropriately scaled by an interatomic distance) is 10, which is typical, non-negligible deviations from the leading term approximation are still present.

The coefficients of the quadratic terms in this work are taken as the central force parameters of three lattice dynamical models in the literature for $CoSb_3$ (Refs. 33 and 35) and $LaFe_4Sb_{12}$.[21] Two models, Feldman and Singh's (FS) (Ref. 33) model B (based on LDA calculations and experimental IR optic mode frequencies measured by Lutz and Kliche[35]), and the model by Lutz and Kliche[35] (LK, fit to their IR frequencies), were developed for the unfilled structure. The third model, published by Feldman *et al.* (FSM),[21,34] was developed for the filled structure by modifying the FS model to fit some LDA force vs. displacement calculations of the filled structure. Since we neglect the noncentral force terms of the FSM and FS models, our models give different vibrational spectra than the original models (See Sec. IV C).

The cubic anharmonic terms are mainly extracted from the LDA calculations;[30] Fe-Fe and Fe-La interactions could not be obtained from those calculations due to symmetry and system-size limitations of the underlying LDA calculations. Here we estimate the Fe-Fe cubic coefficient by assuming $\phi_3 = 10\phi_2 / r_{ij}^0$. For the Fe-La cubic parameter, we use half the Sb-La cubic coefficient, scaled by the interatomic distances. To check the sensitivity of our results to this estimate, we also performed calculations neglecting the Fe-La cubic term altogether. Furthermore, in the FSM and FS models the anharmonic parameters of two "longer-range" Fe-Sb interactions are treated in the same *ad hoc* fashion as above for the Fe-Fe interaction.

For the quartic interactions between La and the framework atoms we use LDA calculations (see Appendix). For the quartic interactions between other atoms we use a generic value of $\phi_4 = 10\phi_3 / r_{ij}^0$. In the Appendix we also test the central force approximation for the anharmonic La framework-atom interactions on the basis of our LDA calculations.

In each case (except where specified) we use the same values of cubic and quartic potential parameters. Most importantly we assume that the anharmonic parameters are the same between filled and unfilled materials, despite the known differences in harmonic properties between the two. For the unfilled skutterudites we present results from three different parameter sets: FSM central force omitting the filling atoms and their interactions (unfilled-FSM-cf), FS central force (unfilled-FS-cf) and the LK parameters (unfilled-LK). For the filled skutterudites we primarily use three different parameter sets: FSM central force (filled-FSM-cf), FS central force with the addition of the same filling atom harmonic terms and the same cubic and quartic anharmonic terms as for filled-FSM-cf (filled-FS-cf), and LK with the likewise addition of filling atom harmonic and all anharmonic terms (although fewer in number because of the shorter range of the LK model) (filled-LK). We also present results for a few modified versions of these models: filled-FSM-cf without the Fe-La cubic interactions (filled-FSM-cf-alt1), filled-FSM-cf-alt1 with four times lower Sb-La cubic interaction (filled-FSM-cf-alt2), and filled-FSM-cf with an artificially low mass for the La atoms (filled-FSM-cf-alt3). For all models we use the volume and equilibrium positions corresponding to the experimental structure of $LaFe_4Sb_{12}$.

III. METHODS

We simulate $6 \times 6 \times 6$ cubic supercells consisting of 6912 and 7344 atoms for unfilled and filled samples, respectively. We carry out MD runs using the velocity Verlet algorithm and a 0.5 fs time step at constant energy and supercell size and shape. Because the results are noisy, we do 40 runs at each temperature with independent sets of initial velocities, and average over the runs. Each run is allowed to equilibrate for 0.25 ns and configurations from an additional 1.25 ns are used to compute the heat current autocorrelations. The thermal conductivity is proportional to the integral from zero to infinity of the heat current autocorrelation, two examples of which are plotted in Fig. 1. For long lags the autocorrelation becomes dominated by numerical noise. We therefore fit the tail to an exponential decay and compute the full integral by adding the explicit numerical integration of the autocorrelation for short times to an analytic integration of the exponential fit.

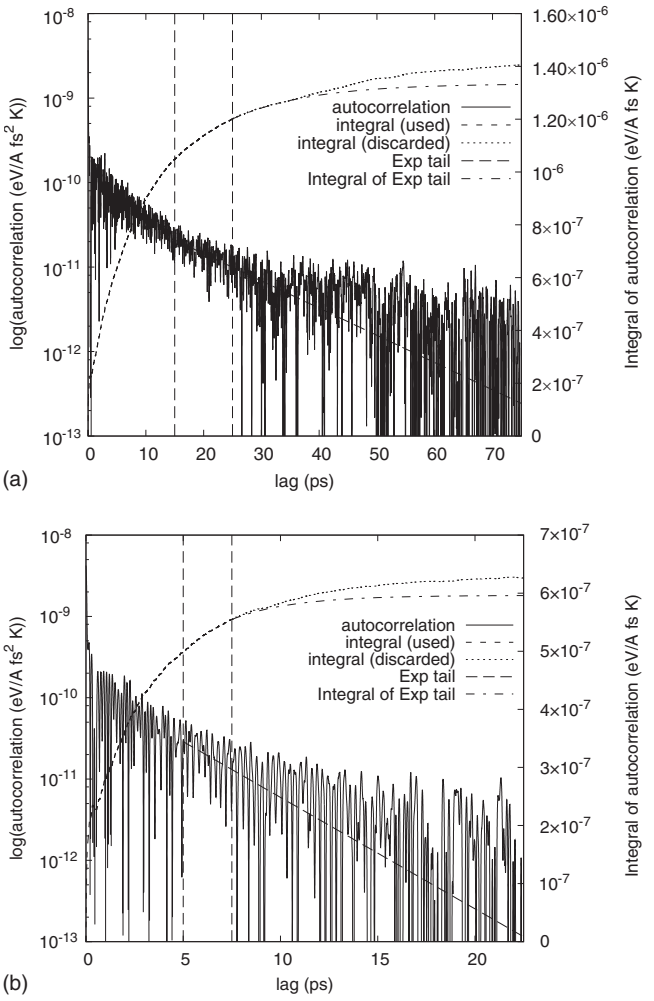

FIG. 1. Example of heat current autocorrelation from MD run for filled-FSM-cf (see text) model at 300 K (top panel) and 900 K (bottom panel). Decaying fluctuating curve is autocorrelation and rising curve is integral of autocorrelation. Vertical lines indicate region over which exponential tail is fit. Decaying long-dashed line is the result of exponential fit and rising dash-dotted curve for t greater than fit range is sum of numerical integral and analytic integral.

We also compute isotropic mean-square displacements (MSDs) from the same MD runs used for the thermal conductivity as a function of temperature by averaging fluctuations of atomic positions over the entire system for 50 ps. Thermal expansivities were computed from MD simulations by averaging the virial pressure for 10 ps at a range of volumes at each temperature and determining the equilibrium volume by interpolating a linear fit of the pressures.

Thermal expansivities were also computed using lattice dynamics from the vibrational modes of a $4 \times 4 \times 4$ supercell at the Γ point. All other lattice-dynamical calculations were based on a dense sampling of the Brillouin zone of a primitive cell. These include MSDs for the LDA model, vibrational density of states $G(\omega)$, sound speeds [from fitting the

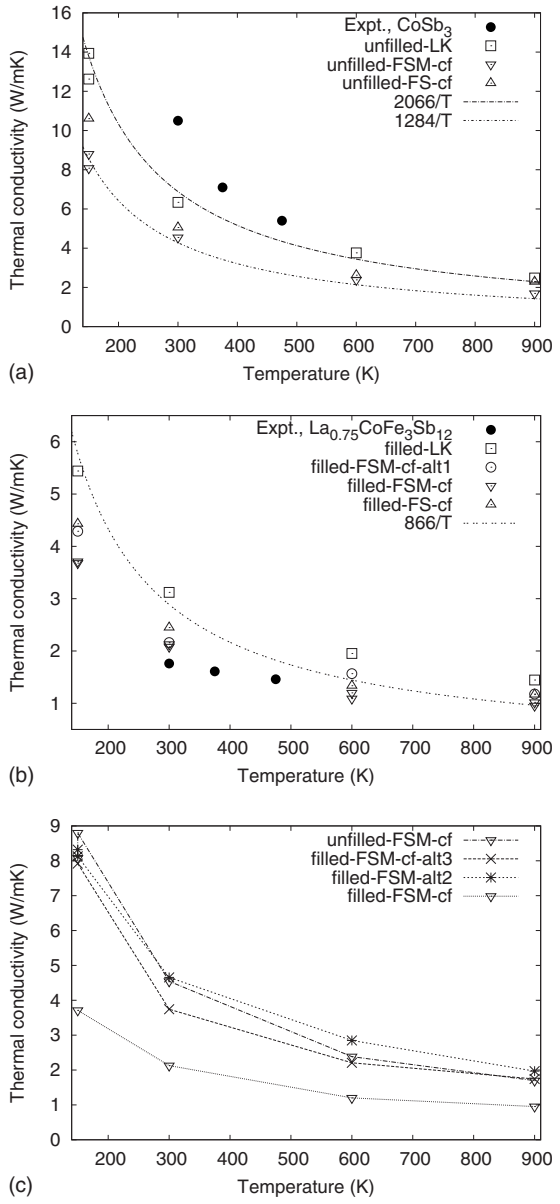

FIG. 2. Results of Green-Kubo calculations of thermal conductivity at fixed volume for filled and unfilled skutterudite structure. Description and notation of models is given in text. The experimental data (shown only sparsely) for the filled $La_{0.75}CoFe_3Sb_{12}$ material correspond to those of the 0.3% porosity sample given in Fig. 4 of Ref. 40 and for the unfilled $CoSb_3$ material correspond to measurements of Katsuyama *et al.* (Ref. 41) (depicted in Fig. 4 of Ref. 40). Curves are guides to the eye proportional to $1/T$, i.e., the expected temperature dependence from lowest-order Boltzmann-Peierls theory.

low-frequency portion of $G(\omega)$], and the Callaway expression[28] for thermal conductivity (see Sec. V).

IV. RESULTS

A. Thermal conductivity

The thermal conductivity for the different models as a function of temperature is plotted in Fig. 2. The thermal conductivity shows a decrease at room temperature by a factor of about 2 when the rare-earth atom is added (see Fig. 2, top and middle panels). The reduction is similar for all our models, whether based on the FSM, FS, or LK harmonic interactions. The consistency of this observation for the different models indicates that this is a robust result. The reduction we obtain is substantial but smaller than the experimentally observed factor of 5 between filled and unfilled materials.[42] We regard this as an estimate of the pristine lattice dynamical effect of the filling atom on the thermal conductivity, since the *harmonic* force constants are the same, aside from the filling atom, between corresponding filled and unfilled models. Other differences that could be caused by filling, in particular, changes in chemical binding of the framework, are included implicitly only via the choice of harmonic parameters (FSM vs FS or LK).

We checked the adequacy of our system size by calculating a few thermal conductivities for $4\times4\times4$ and $8\times8\times8$ supercells. We found that there was a significant difference between the $4\times4\times4$ and $6\times6\times6$ cells but the larger cells did not change the results from the $6\times6\times6$ values. We therefore concluded that $6\times6\times6$ cells are necessary and sufficient for a calculation that is converged with respect to system size.

To test the sensitivity of our model to the Fe-La cubic interactions, which were fixed using a crude estimate, we compare the results of the filled-FSM-cf and the filled-FSM-cf-alt1 (no Fe-La cubic interactions) models. Removing the Fe-La cubic interactions increases the thermal conductivity by a small amount (see Fig. 2, middle panel), much smaller than the difference between filled and unfilled structures (see Fig. 2, middle and top panels, respectively). This indicates that our results are not sensitive to the estimated value of this parameter. It also suggests that Sb vibrations, which dominate the acoustic modes (shown for LDA model calculations in Ref. 18), are more important to thermal conductivity than Fe vibrations. This is consistent with the fact that the Fe-derived modes are generally at higher frequency.

To better understand the source of the thermal-conductivity reduction, we modified the dynamics of the La atom in two different ways: reducing the Sb-La cubic anharmonic interaction (filled-FSM-cf-alt2) and decreasing the filling-atom mass (to increase the associated vibrational frequencies) (filled-FSM-cf-alt3). We find that reducing the Sb-La anharmonic interactions by a factor of 4 increases the thermal conductivity of the filled structure to at least that of the unfilled structure and in fact to a higher value at $T \geq 600$ K (see bottom panel of Fig. 2). Our reduction of the filling-atom mass to a fictitious value of 4.21 amu creates a narrow frequency band at about 430 cm^{-1}, significantly above the maximum frequency of the model of about 270 cm^{-1}, thus essentially eliminating mixing of filling atom harmonic modes and cubic anharmonic coupling of filling atom modes with acoustic modes. This mass reduction also increases the thermal conductivity, almost up to the value of the unfilled structure. The above results are discussed in more detail in Sec. V

We find an interesting temperature dependence for these results: in both filled and unfilled materials the thermal conductivity is monotonically decreasing with increasing tem-

TABLE I. MD MSD linear and quadratic temperature coefficients, A (10^{-5} Å^2/K) and B (10^{-9} Å^2/K^2), room temperature thermal expansivity from MD α and from LD α^* (10^{-6}/K), room temperature Gruneisen parameter γ^*, and averaged sound velocity v_s^* (m/s) (defined in text). Superscript * indicates theoretical values from lattice-dynamics calculations. Values in parenthesis correspond to calculations with $\phi^{(3)}_{\mathrm{La,Fe}}$, or in addition $\phi^{(4)}_{\mathrm{La,Fe}}$ (second MD value), of Eq. (3) set to zero.

Model	A-Fe	A-Sb	A-La	B-La	α	α^*	γ^*	v_s^*
Unfilled-FSM-cf	1.63	2.14			6.71	7.76	1.48	2836
Filled-FSM-cf	1.80	2.06	5.03 ± 0.09	4.1 ± 1.6	9.31(7.95,7.41)	10.9(9.73)	2.00 (1.78)	2813
Unfilled-FS-cf	1.54	2.00			5.26	6.29	1.33	2932
Filled-FS-cf	1.67	1.92	5.10 ± 0.03	-7.3 ± 0.4	7.53	8.80	1.84	2908
Unfilled-LK	2.10	2.28			1.74	3.46	0.68	2462
Filled-LK	2.32	2.13	5.14 ± 0.02	-6.4 ± 0.4	4.28	6.49	1.24	2383
Filled-LDA	1.55*	1.94*	5.12*					2912
Unfilled Exp.[a]						6.36	0.95,1.5	3082
Filled Exp.[b]	1.14	1.79	4.69			9	1.5	2946

[a] α and γ from Ref. 43, v_s from polycrystalline sound velocities in Ref. 44.
[b] A for Fe, Sb, and first La value from values at 200 and 296 K in Table II of Ref. 45, α from Ref. 45, γ from Ref. 46, and v_s calculated from polycrystalline sound velocities in Ref. 44.

perature but only in the unfilled material is it clearly a $1/T$ dependence as expected from a lowest-order Boltzmann-Peierls theory; in the filled material the thermal conductivity decreases more slowly than $1/T$. This unusual result appears to agree with experiment.[40] While the precise reason for the deviation from the linear theory is unclear, the Green-Kubo formalism is nonperturbative with respect to interactions. One obvious way in which the thermal conductivity could increase above the Boltzmann-Peierls treatment is through the explicit anharmonic terms in the heat current derived from Eq. (3); we have checked that removing those terms does not change our observations.

B. Mean-squared displacements

One measure of our models' vibrational properties that can be compared to experiment is the MSD of the atoms. In Table I we list the least-square-fitted linear and quadratic coefficients A and B of the MSD as a function of temperature, extracted from the MD trajectories. The linear coefficients are in reasonable agreement with measured MSDs and with the LDA model MSDs. We find that in the range of temperatures simulated, 150–900 K, the MSDs of Fe and Sb in filled and unfilled models are virtually exactly linear, while the filling La atom MSD deviates from linearity, but only by about 2% despite the high temperatures included. What is somewhat surprising is that we find different signs for the nonlinearity among the different harmonic force models that we used even though the anharmonic terms are the same.

It is also worthwhile to compare the LDA model prediction using LD with the room-temperature experimental MSD results of Braun and Jeitschko,[47] as those measurements were obtained for a nearly stochiometric sample, $La_{0.94}Fe_4Sb_{12}$. The theoretical (experimental) results for the Fe, Sb, and La isotropic MSDs are 0.0049 (0.0031), 0.0059 (0.0040), and 0.0154(0.0165) Å^2, respectively, and the computational and experimental uncertainties in the MSDs are a few percent. Our LDA model and central force models are consistent with experiment for the value of filling atom MSD and in predicting a significantly lower MSD for the framework atoms although the model values of the framework atom MSDs are too high.

In Fig. 3 we show the comparison between theory and experiment for the La MSD as a function of temperature. The temperature dependence of the LDA model results agrees very well with the x-ray measurements by Chakoumakos *et al.*[45] on a 75% La-filled antimonide with a nominal formula of $La_{0.75}CoFe_3Sb_{12}$. The offset may be caused by the La site-occupancy disorder, which would add an approximately temperature-independent contribution to the measured MSD. The figure also shows that our MD results are extremely close to the LDA model ones although the former include anharmonic effects and are based on different harmonic force constants. Finally, we also present results for the MSD within an Einstein approximation, with the Einstein frequency chosen as 74 cm^{-1} from the curvature of the La

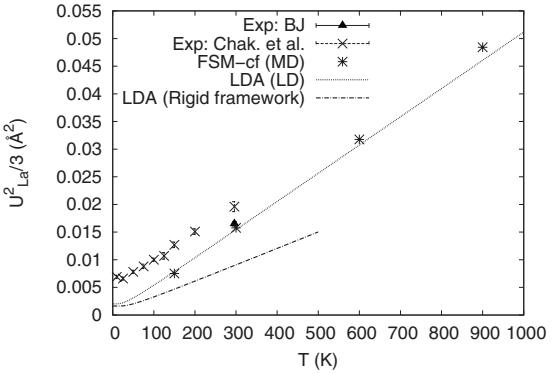

FIG. 3. La MSD as a function of temperature from experiment and models (see text). BJ corresponds to Ref. 47 and Chak. *et al.* corresponds to Ref. 45. LDA model results for the artificial constraint of a rigid Fe-Sb framework are also shown (see text).

potential well calculated in the LDA, although assuming zone-center-like, or uniform, La displacements.[21] (The uniform displacement results probably differ only slightly from the La Einstein oscillator result because of the weak La-La force constants.[48]) The difference between this result and the measured MSD is merely another measure of mixed modes in the La vibrational properties: as we have shown earlier,[21] the La-dominated peak in the vibrational spectrum does not correspond to the same frequency as computed from the La potential well. Nevertheless *effective* Einstein frequencies or temperatures are useful for describing properties of many filled skutterudites (e.g., see Refs. 49 and 50).

C. Vibrational spectrum

The FSM-cf model is expected *a priori* to yield the best results among our filled central force models since the FSM model parameters were partially derived from first-principles calculations for $LaFe_4Sb_{12}$. The FSM-cf model does not accurately reproduce the LDA-model force constant matrices[30] for $LaFe_4Sb_{12}$ but the largest components are given to within a factor of two and in most cases much more accurately than that. On the other hand, it reproduces the LDA results for the (zone-center) frequencies rather accurately. Only the lowest F_u frequency is as much as 14% too small compared to the LDA value of 54 cm^{-1}. All other frequencies are within 8% of corresponding LDA values. Furthermore the FSM-cf model yields agreement with the measured[30] Raman modes of $La_{0.75}Fe_3CoSb_{12}$ to better than 10%. Whereas the FS model gives more accurate vibrational properties than does the LK model in the case of $CoSb_3$, the FS-cf model is not necessarily superior to the LK model due to the uncontrolled approximation made by ignoring the three-body terms of the FS model. Nevertheless we find that the FS-cf model is more accurate than the LK model. Most significantly, the low-frequency A_u mode, for which the LK model yielded a frequency 40% lower than the LDA value, is only 10% too low. Aside from the second lowest-frequency F_g mode, which is 14% too low, all other modes are within 6% of the measured Raman[29] and IR (Ref. 35) frequencies as well as of the LDA-calculated upper A_u frequency.

INS measurements and NRIS measurements have provided experimental data for the full vibrational spectrum as well as the atomic-species projected spectra[18,20,51–53] and these measurements have largely substantiated predictions made on the basis of the LDA and FS models for $LaFe_4Sb_{12}$ and $CoSb_3$, respectively. Recently first-principles calculations of the dispersion curves and vibrational density of states for $CoSb_3$ have also been performed.[22,54] Figure 4 compares the vibrational densities of states for the filled-FSM-cf and LDA models corresponding to $LaFe_4Sb_{12}$, and the FS-cf model corresponding to $CoSb_3$ (however, we use the Fe, rather than Co, mass, affecting by a few percent the spectrum above 200 cm^{-1}). Overall, the main features of these spectra are quite similar including the separated high frequency "Fe" peaks and the maximum frequency of the "Sb" band, where these identifications have been illustrated elsewhere, both experimentally[51] and theoretically.[18,22,54] Figure 4 also shows the La-projected density of states. We

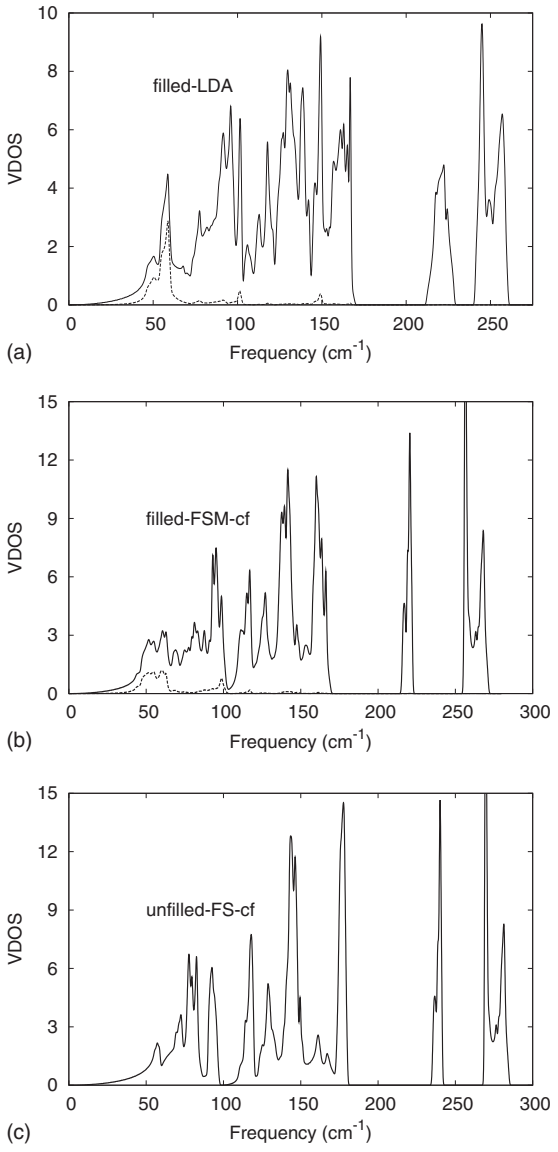

FIG. 4. Calculated vibrational densities of states for selected models. The dashed curves in (a) and (b) are the La-projected densities of states for the filled models.

find that there is much greater dispersion of the La-dominated modes with the central force models than with the LDA model, as illustrated by the broad La-projected vibrational spectrum for the filled FSM-cf model. Indeed this deviation from the LDA model also occurs for the FSM model.[21] Nevertheless all filled models lead to the largest concentration of modes with significant La character in a region centered near 50 cm^{-1} although the peak is sharp only for the LDA model.

Figures 4(a) and 4(b) are essentially a comparison of the FSM-cf model with experiment, as the density of states for the LDA model closely represents the INS spectrum aside from a small shift of the Fe peaks.[18] We believe the comparison is reasonably good considering the sensitivity of the details of the spectrum to the complexity of the dispersion curves. Figures 4(b) and 4(c) give a comparison of central force models for filled and unfilled materials. The differences

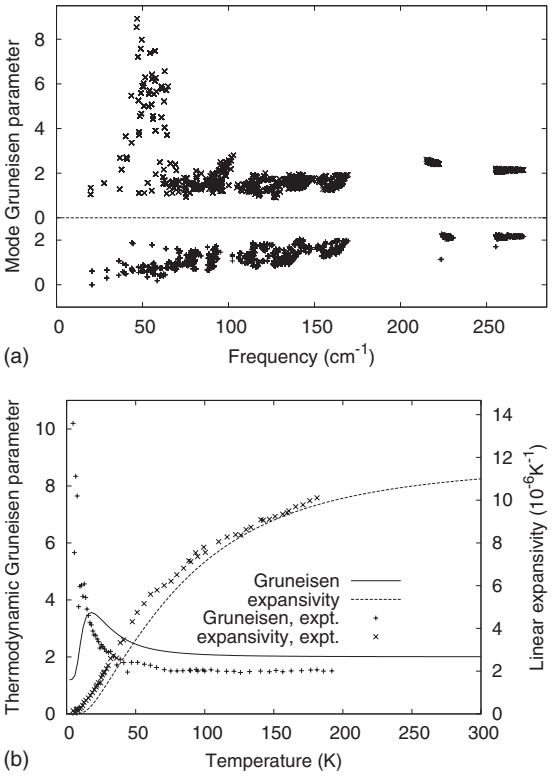

FIG. 5. Upper panel: LD Mode Gruneisen parameters γ_i for filled (top) and unfilled (bottom) systems. Lower panel: thermodynamic Gruneisen parameter $\gamma(T)$ and thermal expansivity for filled systems from LD and experiment (Ref. 46). Theoretical results are for the FSM-cf models.

in the low-frequency (below 200 cm^{-1}) region between filled and unfilled systems are consistent with experimental observations: the near gap around 100 cm^{-1} for $CoSb_3$ but not for $LaFe_4Sb_{12}$ and the higher maximum frequency of the Sb-dominated region of the spectrum (essentially the Raman-frequency region) for $CoSb_3$ than for $LaFe_4Sb_{12}$. On the other hand the noticeable difference in the region of the Fe peaks between filled and unfilled materials is not observed experimentally.[18] Finally, low-frequency effects in the vibrational densities of states of all models are compared with experiment in Table I as an averaged sound velocity, v, defined as $1/v^3 \sim \lim_{\omega \gg 0} G(\omega)/\omega^2$.

D. Thermal expansivity

The thermal expansivity directly depends on cubic anharmonicity and should be a good overall test of our anharmonic parameters. A simplified treatment of lattice thermal conductivity rather directly relates thermal expansivity and thermal conductivity.[55] Among the assumptions of that theory are the leading term central force approximation and a Bravais lattice. The Slack model[7,56] adapts this treatment to complex systems by assuming that only acoustic modes contribute to thermal conductivity. Meisner *et al.*[57] applied the Slack formula without taking into account the differences in Gruneisen parameters between filled and unfilled materials and thereby arrived at a negligible decrease in thermal conductivity upon filling. In fact the Slack model can yield a factor of 2 or so decrease upon taking into account the available experimental values of thermal expansivity but we do not investigate that model here. Mainly we concentrate on treating the thermal expansivity as a necessary, although not sufficient, test of the validity of our cubic anharmonic parameters.

In Table I we list the room-temperature thermal expansivities calculated from our MD simulations on $6\times6\times6$ supercells as well as from our LD calculations on a $4\times4\times4$ supercell. The LD calculations of mode Gruneisen parameters γ_i, the essential anharmonic ingredient for calculating the thermal expansivity,[58] properly account for nonleading-term cubic anharmonic coefficients, as defined earlier, and internal displacement effects.[59,60] Since the difference between our LD calculations on $4\times4\times4$ and $3\times3\times3$ supercells are less than 5%, we estimate that to be the system-size error of our calculations. We consider all differences between MD and LD results as acceptable numerical error except perhaps those for the LK model which are well outside the system-size error of the LD results. However, even for the latter model, the discrepancy is somewhat understandable upon noting that the high-temperature limit of the thermodynamic Gruneisen parameter $\gamma(T)$ is simply the average mode Gruneisen parameter γ_i. Our LD calculations show that the LK model has large negative low frequency γ_i that partially cancel positive higher frequency ones, leading to an anomalously small net positive $\gamma(T)$. We have found that these negative γ_is arise from the aforementioned nonleading-term cubic anharmonic coefficients. We emphasize that this does not occur for our other models.

Generally, the comparisons with experiment for both expansivities and Gruneisen parameters seem satisfactory. We note that the LD-based expansivities correspond to room temperature and that the corresponding Gruneisen parameters involve calculated bulk moduli and heat capacities. The latter two quantities are in reasonable agreement with experiment. It appears that models appropriate to unfilled materials (LK and FS-cf) yield lower thermal expansivity than the FSM-cf model but it is important to emphasize that the anharmonic parameters were assumed to be the same for filled and unfilled materials without justification. The quoted experimental values in the table are also in accord with this relationship between the thermal expansivity of filled and unfilled materials although the experimental data are scant.

Let us next consider recent highly accurate capacitance dilatometer measurements of Viennois *et al.*[46] of the thermal expansivity of $LaFe_4Sb_{12}$ as a function of temperature, plotted in Fig. 5 along with the corresponding experimental thermodynamic Gruneisen parameter, as well as our LD calculated thermal expansivity, mode Gruneisen parameter, and thermodynamic Gruneisen parameter. We find that the FSM-cf model yields excellent agreement with those measurements over a wide temperature region. We also find that the γ_i is strongly peaked for frequencies near the main La peak in the vibrational spectrum (see Fig. 5, upper panel, top). We can explain this behavior as due to a combination of (a) the relatively large value of $r\phi'''/\phi''$ for the La-Sb interaction, (b) the negative value of the Fe-La bond-stretching harmonic force constant, rendering the value $\delta\omega/\omega$ to be

large due to the decrease in ω, and (c) our *ad hoc* choice of the Fe-La cubic anharmonic parameter; we obtain smaller peaks in both mode and thermodynamic quantities by about a factor of 2 if we choose the Fe-La cubic anharmonic parameter to be zero. The primary effect of this peak is to yield a low-temperature peak in $\gamma(T)$ (see Fig. 5, lower panel). At low temperatures Viennois also find unusually high values of $\gamma(T)$ but their analysis does not extract lattice vibrational effects from the data which also includes electronic excitational effects. Interestingly a much closer experimental comparison is between our results and those on a silicon clathrate, Ba_8Si_{48}.[61] Another effect of the low-frequency peak in γ_i is to increase $\gamma(T)$ at room temperature and evidence of this effect is the reduction in the room-temperature expansivity and $\gamma(T)$ when $\phi^{(3)}_{\mathrm{La,Fe}}$ is set to zero (see Table I).

V. APPROXIMATE BOLTZMANN-PEIERLS THERMAL CONDUCTIVITY

It is important to note that our models do not fit into the simplest "rattling" ion picture. Our central-force harmonic and quartic terms roughly agree with LDA-based results (see Appendix). The LDA calculations have already been shown to produce a harmoniclike potential for the filling atom,[21] not a flat-bottomed potential well. The thermal-conductivity reduction in our models occurs through some more conventional type of mode mixing or anharmonicity. We have gained insight into this reduction by turning off the anharmonicity between the La atom and the framework atoms; we find that it is the anharmonicity that gives rise to the lowering and not the mode mixing. In order to gain further insight into the question of the possible role of mode mixing in reducing the thermal conductivity, we apply an approximate Boltzmann-Peierls theory, namely a generalized Callaway formula,[28] to filled and unfilled central force and LDA models.

We use the following high-temperature expression, which is a generalization of the Callaway treatment to a non-Debye approximation

$$\kappa = \frac{k_B}{3V}\int I(\omega)d\omega,$$

where

$$I(\omega) \equiv \langle v_g^2\rangle_\omega G(\omega)\tau(\omega)$$

$\langle v_g^2\rangle_\omega$ is the frequency averaged group velocity, $G(\omega)$ is the density of states, and τ is a relaxation time, which in the Callaway treatment is independent of normal-mode polarization. We also adopt the high T formula $1/\tau = A \times T\omega^2$. Anharmonicity determines τ but the other factors in $I(\omega)$ are harmonic quantities. To appreciate the effects of the changes in the harmonic properties, e.g., the effects of mixing, we plot $\langle v_g^2\rangle_\omega G(\omega)/\omega^2$ for different models in Fig. 6. We see that the effect of filling through the harmonic terms is to *increase* $I(\omega)$ in the region of the filling atom vibration for the central force models. The observed increase is consistent with the small increase in thermal conductivity we see from the unfilled-FSM-cf to the filled-FSM-cf-alt2 (which has filling

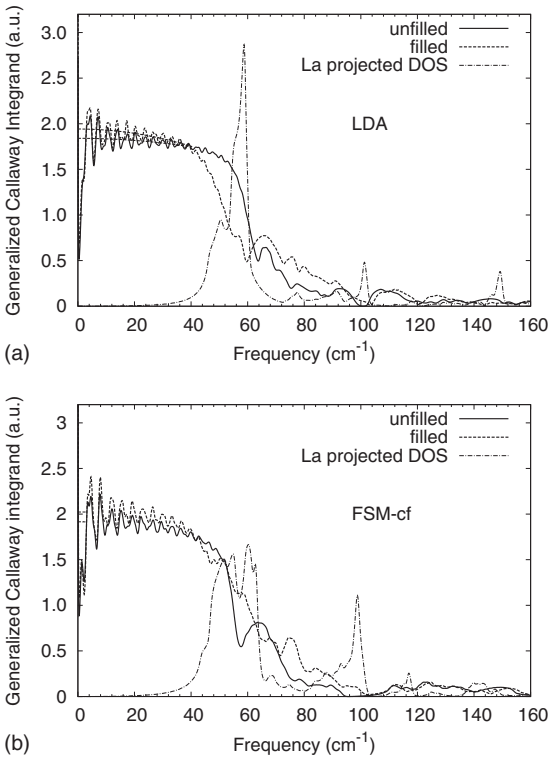

FIG. 6. Thermal-conductivity integrand $I(\omega)$ for the filled (solid line) and unfilled (dotted line) models using LDA model force constants (upper panel) and filled-FSM-cf and unfilled-FSM-cf (lower panel). The small oscillations seen at low phonon energy are due to the finite size k-point grid used and a narrow Gaussian used for representing $\delta(\omega-\omega_i)$. The La-projected density of states (line going to zero at zero frequency) is superimposed in both panels.

atoms but very small anharmonicity). This again shows that anharmonicity is essential for producing our models' thermal conductivity reduction upon filling. In contrast, the LDA model shows a small reduction in $I(\omega)$ in the filling atom frequency region. Perhaps, on the basis of these calculations, our central-force model underestimates the pristine thermal-conductivity reduction due to filling.

We note that several phenomenological treatments have included anharmonic scattering, or Umklapp, terms given by the Callaway expression and with parameters fitted to thermal-conductivity measurements. Wang *et al.*[14] found anharmonic scattering coefficients in reasonable qualitative agreement with our main results, i.e., a much larger amplitude of scattering for the more highly filled materials than for the less filled ones. Nolas *et al.*,[27] on the other hand, obtain much smaller Umklapp scattering terms for the filled materials as compared with the unfilled ones. Care should be taken in interpreting these results, however, because of the severe approximations made in the phenomenological models. For example, they assume a Debye density of states generalized by an exponential factor to allow the application to low temperatures and they include terms that are meant to account for point defects and grain boundary scattering in their polycrystalline samples. The phenomenological models also include resonant scattering terms, which in the case of Wang *et al.* used a resonance frequency arbitrarily taken

from a measured frequency peak that approximately matches the A_g mode frequencies.

VI. CONCLUSIONS

We have calculated the thermal conductivity of filled and unfilled skutterudites from a microscopic description based on central force models and a Green-Kubo molecular dynamics approach. The pristine effect, i.e., the effect of simply introducing filling-atom force constants, is a factor of 2 reduction in thermal conductivity, as compared with a factor of 5 seen in experiment. The effect is robust, occurring for three different sets of harmonic parameters combined with a single set of anharmonic parameters extracted from first-principles simulations of $LaFe_4Sb_{12}$ and some *ad hoc* assumptions. Two of the sets of harmonic parameters are given by the central-force parts of two published fits to experiment and first-principles results and the third set is from a central-force model fit to experiment. An independent test of the accuracy of our force constant models is provided by our calculation of other quantities that can be compared to experiment: vibrational densities of states, thermal expansivities, and atomic mean-square displacements. All of these are in reasonable agreement with experiment, strengthening our confidence in the models. Reducing the La-Sb anharmonicity by a factor of 4 restores the unfilled structure's thermal conductivity, indicating that this anharmonicity is necessary for the thermal-conductivity reduction, and that harmonic mode mixing does not affect the thermal conductivity. Reducing the filling atom mass can also eliminate the thermal-conductivity reduction, indicating that the frequencies of filling-atom vibrational modes are important. An analysis based on the Callaway theory expression for the thermal conductivity confirms that it is the anharmonicity alone that gives rise to the decreased thermal conductivity upon filling as the phonon propagational character is unaffected. However, this is not precisely the case for our LDA model results as a slight decrease in phonon propagational character in the region of the filling atom vibrations is found. We therefore conclude that the difference between the simulation and experimental conductivity reduction might be accounted for by errors in phonon character as well as neglected chemical changes in framework bonding between the filled and unfilled structures.

We get the best agreement between our calculated thermal conductivities and experimental results on the filled material, despite the fact that the simulations are on fully filled ordered structure and the experiment is on 75% filled disordered material. This agreement may not be surprising since at high temperatures anharmonicity is dominant and a 25% La void of the filled sample may not be important (e.g., see Fig. 5 of Ref. 42). The agreement between our calculations on unfilled structures and experiments on unfilled materials are generally not as good, probably because the anharmonic terms (even for the unfilled models) are fit to the filled material. Therefore, it may be that the reason why the thermal conductivity reduction is less than seen experimentally is that while we describe the anharmonicity of the filled compound reasonably, our description of the unfilled compound has too much anharmonic phonon scattering leading to a too low thermal conductivity compared to experiment. In addition, our neglect of disorder, grain size, and quantum effects will lead to incorrect temperature dependence of the thermal conductivity at lower temperatures.

A more complete study should also include noncentral-forces and chemical effects, i.e., differences in anharmonic parameters between filled and unfilled materials. We also conclude that measurements of mode Gruneisen parameters, as can be obtained by measurements of infrared and Raman spectra under pressure, would be of great value in understanding the effect of filling on thermal conductivity. Such measurements could directly test whether the modes we observe with anomalously large mode Gruneisen parameters are indeed present in the real filled skutterudites.

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APPENDIX: FORCE CONSTANT CALCULATIONS

This appendix augments the LDA-based results presented in our earlier paper.[30] We present here our calculations of some two-body cubic and quartic anharmonic force constants involving La atoms that we determined from atomic forces generated by displacements of one La atom along one of the cubic crystalline axes and using group theory to determine other force constants related by symmetry. We used displacements of 0.35 and 0.69 bohr. The larger of these are substantially larger than those used in our previous harmonic force constant determination. From these "data" we estimate third order, $\Phi(\mathrm{Sb,La,La})_{\alpha,\beta,\beta}$, and fourth order, $\Phi_{\alpha,\beta,\beta,\beta}([\mathrm{Sb,Fe}],\mathrm{La,La,La})$ anharmonic force parameters, i.e., third and fourth orders derivatives of the crystal potential energy with respect to displacement (α and β indicate Cartesian components). We present results that correspond to the atoms chosen to represent the second-order force constants of Ref. 30. Thus the table gives the anharmonic force constants for atoms "1"(Fe), "9"(Sb), and "17"(La) defined in Ref. 30. Also obtained from the present analysis were second-order force constants and these were found to be in agreement with the corresponding least-squares fitted values of Ref. 30 to within the reported least-squares uncertainties.

These LDA results were used to obtain our central force La-Sb and La-Fe quartic anharmonic parameters by considering the largest LDA values in the table and assuming the leading term form, whereas we used the least-squares analysis of Ref. 30 to obtain the central force (La-Sb) cubic anharmonic parameter.

As a check of our filled models we compare the LDA Cartesian anharmonic force constants with those generated

TABLE II. Selected nonzero cubic and quartic anharmonic La-Sb and La-Fe force constants. Cubic force constants are in mRy/bohr^3 and quartic ones are in mRy/bohr^4.

Comp.	Filled FSM-cf	Filled FSM-cf-alt1	LDA
La-Sb			
xxx	−1.0		2
zxx	7.9		7
xyy	1.3		1
zyy	−2.8		−2
xzz	−22.9		−21
zzz	40.3		44
xxxx	4.7		0.6
zxxx	−1.5		3.3
yyyy	−1.4		−4.1
xzzz	35.3		32.3
zzzz	−49.1		−55.3
La-Fe			
xyyy	−2.7	−3.6	1.0
yyyy	0.6	−3.6	−3.4
zyyy	2.7	3.6	−0.8

by the models (see Table II), where the La-Fe and La-Sb parameters of the models are, in mRyd/bohr^2, $\phi''=21.1$, $r\phi'''=-375$, and $r^2\phi^{iv}=3.66\times10^3$ for La-Sb ($r=6.444$ bohr) and $\phi''=-10.3$, $r\phi'''=-187$, and $r^2\phi^{iv}=1.81\times10^3$ ($r=7.476$ bohr) for La-Fe and are the same for all three filled (LK, FS-cf, and FSM-cf) models. Note that the Cartesian anharmonic parameters include contributions from the quadratic term in our model potential but we have found those contributions to be small given the values of these central force parameters. For the same reason the choice of cubic central force constants affects the quartic Cartesian force constants, which explains why the filled FSM-cf-alt1 model (where La-Fe ϕ''' is set to zero) has different La-Fe quartic Cartesian force constants than the filled FSM-cf model (see the table). The estimated computational uncertainty in the atomic forces is 0.14 mRy/bohr, which gives rise to estimated uncertainties in the cubic (quartic) LDA anharmonic parameters of ±2 mRy/bohr^3 (±4 mRy/bohr^4). Note that in the filled-FSM-cf model the La-Fe cubic coefficients is guessed to be the same sign and half the magnitude of the La-Sb value (scaled by the bond distances), despite the fact that the corresponding harmonic force constants are opposite in sign.

We find that the La-Sb cubic and quartic force constants are in good agreement with the corresponding LDA values with deviations comparable in magnitude to the uncertainty in the LDA values themselves. The La-Fe quartic terms are very small compared to La-Sb and are in fact indistinguishable from zero within the estimated uncertainty.

Finally, we test our central-force models against the results[21] for the LDA-calculated La potential-well parameter, b, defined as the coefficient of the quartic term in the expansion of the total energy as a function of La displacement, and dependent on direction.[21] The LDA value of a, the coefficient in the corresponding quadratic, or harmonic, term was used as input for our harmonic central-force-model parameters[34] so by construction our models exactly yield the LDA value of a. For FSM-cf, as well as FS-cf and LK, we obtain $b_c=7.48$, $b_t=5.79$ mRy/bohr^4 to be compared with the LDA results $b_c=10.7$, $b_t=6.27$ mRy/bohr^4, where the subscripts refer to displacements along the cubic or trigonal crystallographic axis. These central-force results for b are also sensitive to the *cubic* Taylor expansion term of the central-force models [Eq. (3)]. For example, setting $\phi^{(3)}_{\text{La–Fe}}$ to zero (as in filled-FSM-cf-alt1) leads to $b_c=8.95$, $b_t=6.29$ mRy/bohr^4 in excellent agreement with the LDA. These results further show that our central-force models are reasonably consistent with our LDA first-principles calculation for the energetics of the filling atom.

[1] M. B. Maple, E. D. Bauer, N. A. Frederick, P.-C. Ho, W. A. Yuhasz, and V. S. Zapf, Physica B **328**, 29 (2003).
[2] B. C. Sales, D. Mandrus, and R. K. Williams, Science **272**, 1325 (1996), references therein.
[3] G. S. Nolas, D. T. Morelli, and T. M. Tritt, Annu. Rev. Mater. Sci. **29**, 89 (1999).
[4] G. J. Snyder and E. S. Toberer, Nature Mater. **7**, 105 (2008).
[5] G. A. Slack, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC Press, Boca Raton, FL, 1995), p. 407.
[6] J.-P. Fleurial, T. Caillat, and A. Borshchevsky, Mater. Res. Soc. Symp. Proc. **478**, 175 (1997), and references therein.
[7] G. A. Slack and V. G. Tsoukala, J. Appl. Phys. **76**, 1665 (1994).
[8] D. Li, K. Yang, H. H. Hng, Q. Y. Yan, J. Ma, T. J. Zhu, and X. B. Zhao, J. Phys. D **42**, 105408 (2009).
[9] W. Zhao, P. Wei, Q. Zhang, C. Dong, L. Liu, and X. Tang, J. Am. Chem. Soc. **131**, 3713 (2009).
[10] X. Tang, H. Ll, Q. Zhang, M. Nino, and T. Goto, J. Appl. Phys. **100**, 123702 (2006).
[11] W. Y. Zhao, C. L. Dong, P. Wei, W. Guan, L. S. Liu, P. C. Zhai, X. F. Tang, and Q. J. Zhang, J. Appl. Phys. **102**, 113708 (2007).
[12] J. Y. Peng, P. N. Alboni, J. He, B. Zhang, Z. Su, T. Holgate, N. Gothard, and T. M. Tritt, J. Appl. Phys. **104**, 053710 (2008).
[13] X. Shi, H. Kong, C.-P. Li, C. Uher, J. Yang, J. R. Salvador, H. Wang, L. Chen, and W. Zhang, Appl. Phys. Lett. **92**, 182101 (2008).
[14] Y. Wang, X. Xu, and J. Yang, Phys. Rev. Lett. **102**, 175508 (2009).
[15] J. Yang, G. P. Meisner, C. J. Rawn, H. Wang, B. C. Chakoumakos, J. Martin, G. S. Nolas, B. L. Pedersen, and J. K. Stalick, J. Appl. Phys. **102**, 083702 (2007).
[16] D. T. Morelli, G. P. Meisner, B. Chen, S. Hu, and C. Uher, Phys. Rev. B **56**, 7376 (1997).
[17] M. Puyet, C. Candolfi, L. Chaput, V. Da Ros, A. Dauscher, B. Lenoir, and J. Hejtmanek, J. Phys.: Condens. Matter **18**,

11301 (2006).
[18] J. L. Feldman, P. Dai, T. Enck, B. C. Sales, D. Mandrus, and D. J. Singh, Phys. Rev. B **73**, 014306 (2006).
[19] M. M. Koza, M. R. Johnson, R. Viennois, H. Mutka, L. Girard, and D. Ravot, Nature Mater. **7**, 805 (2008).
[20] G. J. Long, R. P. Hermann, F Grandjean, E. E. Alp, W. Sturhahn, C. E. Johnson, and D. E. Brown, O. Leupold, and R. Rüffer, Phys. Rev. B **71**, 140302(R) (2005).
[21] J. L. Feldman, D. J. Singh, I. I. Mazin, D. Mandrus, and B. C. Sales, Phys. Rev. B **61**, R9209 (2000).
[22] P. Ghosez and M. Veithen, J. Phys.: Condens. Matter **19**, 096002 (2007).
[23] K. Nitta, D. Kikuchi, T. Miyanaga, K. Takegahara, H. Sugawara, and H. Sato, in *X-Ray Absorption Fine Structure-XAFS13*, AIP Conf. Proc. No. 882 (AIP, New York, 2007), p. 265.
[24] T. Yanagisawa, P.-C. Ho, W. M. Yuhasz, M. B. Maple, Y. Yasumoto, H. Watanabe, Y. Nemoto, and T. Goto, J. Phys. Soc. Jpn. **77**, 074607 (2008).
[25] K. Kaneko, N. Metoki, H. Kimura, Y. Noda, T. D. Matsuda and M. Kohgi, J. Phys. Soc. Jpn. Suppl. A **77**, 245 (2008).
[26] J. Yang, D. T. Morelli, G. P. Meisner, W. Chen, J. S. Dyck, and C. Uher, Phys. Rev. B **67**, 165207 (2003).
[27] G. S. Nolas, G. Fowler, and J. Yang, J. Appl. Phys. **100**, 043705 (2006).
[28] J. Callaway, Phys. Rev. **113**, 1046 (1959).
[29] C. A. Kendziora and G. S. Nolas, in *Thermoelectric Materials 2003–Research and Applications*, MRS Symposia Proceedings No. 793 (Materials Research Society, Pittsburgh, 2004), p. 107.
[30] J. L. Feldman, D. J. Singh, C. Kendziora, D. Mandrus, and B. C. Sales, Phys. Rev. B **68**, 094301 (2003).
[31] J. Dong, O. F. Sankey, and C. W. Myles, Phys. Rev. Lett. **86**, 2361 (2001).
[32] D. J. Singh and L. Nordstrom, *Planewaves, Pseudopotentials and the LAPW Method*, 2nd ed. (Kluwer, Boston, 2006).
[33] J. L. Feldman and D. J. Singh, Phys. Rev. B **53**, 6273 (1996); **54**, 712 (1996).
[34] J. L. Feldman, D. J. Singh, and I. I. Mazin, in *Proceedings of the 18th International Conference on Thermoelectrics*, Baltimore, MD (IEEE, Piscataway, NJ, 1999), p. 9.
[35] H. D. Lutz and G. Kliche, Phys. Status Solidi B **112**, 549 (1982); G. Kliche and H. D. Lutz, Infrared Phys. **24**, 171 (1984).
[36] R. Kubo, M. Yokota, and S. Nakajima, J. Phys. Soc. Jpn. **12**, 1203 (1957).
[37] A. J. C. Ladd, B. Moran, and W. G. Hoover, Phys. Rev. B **34**, 5058 (1986).
[38] E. A. Guggenheim and M. L. McGlashan, Proc. R. Soc. London, Ser. A **255**, 456 (1960).
[39] J. Michalski, Phys. Rev. B **45**, 7054 (1992).
[40] L. Yang, J. S. Wu, and L. T. Zhang, J. Alloys Compd. **364**, 83 (2004).
[41] S. Katsuyama, Y. Kanayama, M. Ito, K. Majima, and H. Nagai, in *Proceedings of the 17th International Conference on Thermoelectrics* (IEEE, New Jersey, 1998), p. 342.
[42] G. S. Nolas, J. L. Cohn, and G. A. Slack, Phys. Rev. B **58**, 164 (1998).
[43] T. Caillat, A. Borshchevsky, and J.-P. Fleurial, J. Appl. Phys. **80**, 4442 (1996).
[44] B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens, and J. R. Thompson, Phys. Rev. B **56**, 15081 (1997).
[45] B. C. Chakoumakos, B. C. Sales, D. Mandrus, and V. Keppens, Acta Crystallogr. **55**, 341 (1999).
[46] R. Viennois, S. Charar, D. Ravot, P. Haen, A. Mauger, A. Bentien, S. Paschen, and F. Steglich, Eur. Phys. J. B **46**, 257 (2005).
[47] D. J. Braun and W. Jeitschko, J. Less Common Met. **72**, 147 (1980).
[48] T. Hasegawa, Y. Takasu, N. Ogita, and M. Udagawa, J. Phys. Soc. Jpn. Suppl. A **77**, 248 (2008).
[49] K. Matsuhira, C. Sekine, M. Wakeshima, Y. Hinatsu, T. Namiki, K. Takeda, I. Shirotani, H. Sugawara, D. Kikuchi, and H. Sato, J. Phys. Soc. Jpn. **78**, 124601 (2009).
[50] W. Schnelle, A. Leithe-Jasper, H. Rosner, R. Cardoso-Gil, R. Gumeniuk, D. Trots, J. A. Mydosh, and Yu. Grin, Phys. Rev. B **77**, 094421 (2008).
[51] H.-C. Wille, R. P. Hermann, I. Sergueev, O. Leupold, P. van der Linden, B. C. Sales, F. Grandjean, G. J. Long, R. Rueffer, and Y. V. Shvydko, Phys. Rev. B **76**, 140301 (2007).
[52] S. Tsutsui, Y. Yoda, and H. Kobayashi, J. Phys. Soc. Jpn. **76**, 065003 (2007).
[53] S. Tsutsui, J. Umemura, H. Kobayashi, T. Tazaki, S. Nasu, Y. Kobayashi, Y. Yoda, H. Onodera, H. Sugawara, T. D. Matsuda, D. Kikuchi, H. Sato, C. Sekine, and I. Shirotani, Hyperfine Interact. **168**, 1073 (2006).
[54] M. Rotter, P. Rogl, A. Grytsiv, W. Wolf, M. Krisch, and A. Mirone, Phys. Rev. B **77**, 144301 (2008).
[55] G. Leibfried and E. Schlömann, Nachr. Ges. Wiss. Goettingen. Math.-Phys. K1. **2**, 71 (1954); C. L. Julian, Phys. Rev. **137**, A128 (1965).
[56] G. A. Slack, in *Solid State Physics*, edited by H. Ehrehrech, F. Seitz, and D. Turnbull (Academic Press, New York, 1979), p. 34.
[57] G. P. Meisner, D. T. Morelli, S. Hu, J. Yang, and C. Uher, Phys. Rev. Lett. **80**, 3551 (1998).
[58] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt Saunders, Philadelphia, 1976).
[59] J. Fabian and P. B. Allen, Phys. Rev. Lett. **79**, 1885 (1997).
[60] T. H. K. Barron, J. G. Collins, and G. K. White, Adv. Phys. **29**, 609 (1980).
[61] R. Lortz, R. Viennois, A. Petrovic, Y. X. Wang, P. Toulemonde, C. Meingast, M. M. Koza, H. Mutka, A. Bossak, and A. San Miguel, Phys. Rev. B **77**, 224507 (2008).