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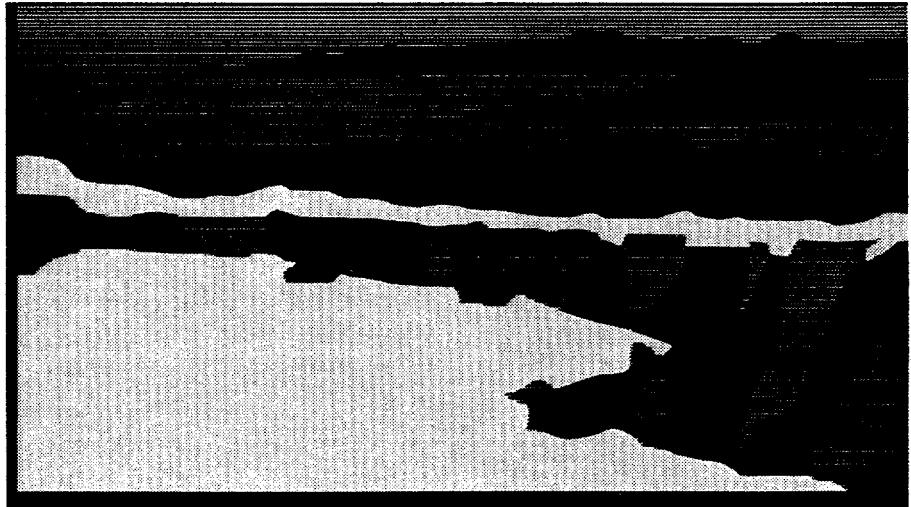
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Filled Skutterudite Antimonides: Validation of the Electron-Crystal Phonon-Glass Approach to New Thermoelectric Materials

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FILLED SKUTTERUDITE ANTIMONIDES: VALIDATION OF THE ELECTRON-CRYSTAL PHONON-GLASS APPROACH TO NEW THERMOELECTRIC MATERIALS

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ABSTRACT

After a brief review of the transport and thermoelectric properties of filled skutterudite antimonides, we present resonant ultrasound, specific heat, and inelastic neutron scattering results that establish the existence of two low-energy vibrational modes in the filled skutterudite $\text{LaFe}_3\text{CoSb}_{12}$. It is likely that at least one of these modes represents the localized, incoherent vibrations of the La ion in an oversized atomic "cage." These results support the usefulness of weakly bound, "rattling" ions for the improvement of thermoelectric performance.

INTRODUCTION

One of the most promising new ideas in the field of thermoelectrics is the "electron-crystal, phonon-glass" (ECPG) concept originally proposed by Slack [1]. In this picture a loosely bound atom with a large thermal parameter scatters phonons much more strongly than electrons, thus permitting a "glasslike" thermal conductivity to coexist with the high electron mobilities found in crystals. Very recently, Sales *et al.* [2] reported a high thermoelectric figure of merit (ZT) in $\text{LaFe}_3\text{CoSb}_{12}$, which was primarily due to a drastic reduction in the lattice component of the thermal conductivity of this material compared to its unfilled analogue. Although it was hypothesized in Ref. 2 that the reason for the large ZT in filled skutterudites was the incoherent "rattling" of the rare earth ions, no evidence for a low frequency local mode existed at that time. Here we present resonant ultrasound, specific heat, and inelastic neutron scattering results that support the existence of a local mode in $\text{LaFe}_3\text{CoSb}_{12}$ and validate the ECPG approach to new thermoelectric materials.

EXPERIMENTAL DETAILS

Polycrystalline samples were synthesized by sealing the starting materials in silica tubes, heating above the liquidus temperature, quenching, annealing, and hot-pressing. All samples were more than 90% dense, and single phase by powder x-ray diffraction. Single crystals were grown using a modified Bridgman method and an Sb-rich melt.

Resonant Ultrasound Spectroscopy (RUS) is a dynamic modulus measurement technique developed by Migliori *et al.* and reviewed at length in Ref. 3. The technique employs tiny LiNbO_3 transducers and a sensitive heterodyne receiver to measure the free-body resonances of a small ($2 \times 2.5 \times 3 \text{ mm}^3$) sample shaped in the form of a rectangular parallelepiped. Once the free-body resonances are known, non-linear optimization methods are employed to extract the elastic constants.

The neutron experiments were conducted at ORNL's High Flux Isotope Reactor. The single-crystal refinements were performed using a 4-circle neutron diffractometer. The inelastic neutron experiments were performed on a triple axis spectrometer using both pyrolytic graphite and Be energy analyzers.

Standard methods were used for the specific heat and resistivity measurements.

RESULTS AND DISCUSSION

A brief review of some important crystal-chemical and transport properties of filled skutterudites will be given first. A diagram of the cubic filled skutterudite crystal structure (space group $Im\bar{3}$, 34 atoms per unit cell) appears in Figure 1. There are two interesting aspects to this structure. First, the rare earth ion sits in an oversized atomic "cage." A typical ionic radius for a rare earth is about 1.4 Å, whereas the radius of the "hole" in the skutterudite structure is about 2.0 Å. This suggests that the rare earth ion is weakly bound and may have a large thermal parameter. That this is in fact the case may be seen in Figure 2, which illustrates the large difference in thermal parameters between the rare earth ion and the other ions in $\text{LaFe}_3\text{CoSb}_{12}$. The second interesting feature in the skutterudite structure is the presence of four-membered Sb rings. These rings suggest that the octet principle may in fact be fulfilled in skutterudites if the Sb-Sb bonds are properly taken into account. In fact, if we apply a slightly modified form of the octet rule known as the generalized 8-N rule [4], we find that the valence electron concentration per anion (VEC) for skutterudites is 6. For example, in CoSb_3 each Co contributes 9 electrons and each Sb contributes 3 electrons; this gives 18 valence electrons per formula unit, and a VEC of 6. This implies that skutterudites can be viewed as simple valence compounds if the two Sb-Sb bonds per Sb are taken into account. Therefore, the generalized 8-N rule predicts that any skutterudite with a VEC = 6 should be a semiconductor, as is CoSb_3 . In

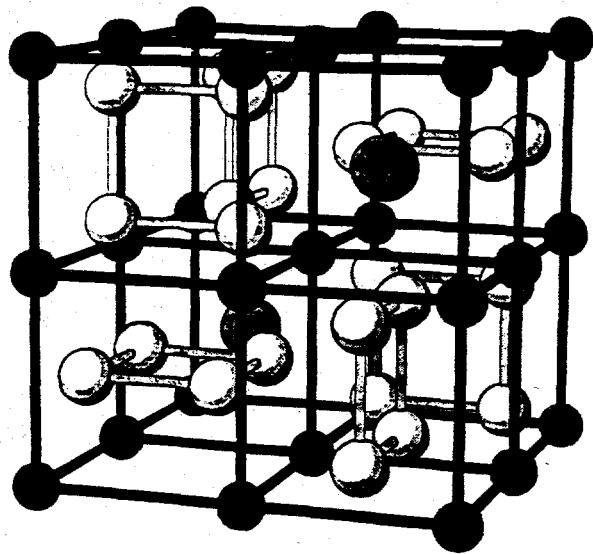


Figure 1. Diagram of the filled skutterudite structure. For $\text{LaFe}_3\text{CoSb}_{12}$ the two large balls represent La ions, the small dark gray balls represent Fe or Co ions, and the light gray balls represent Sb ions. Note the four-membered Sb rings, and the large "cage" in which the La resides.

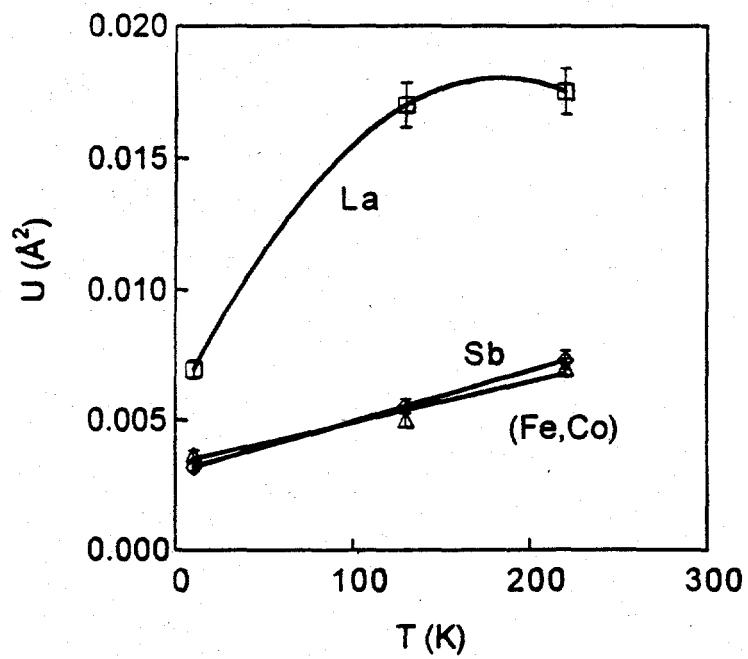


Figure 2. Refined atomic displacement parameters obtained on a single crystal of $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ using a 4-circle neutron diffractometer. The crystal was approximately 2 mm on a side. The large value of the atomic displacement parameter for the La ion is consistent with a large amplitude vibratory motion, although static disorder can also lead to a large value of U .

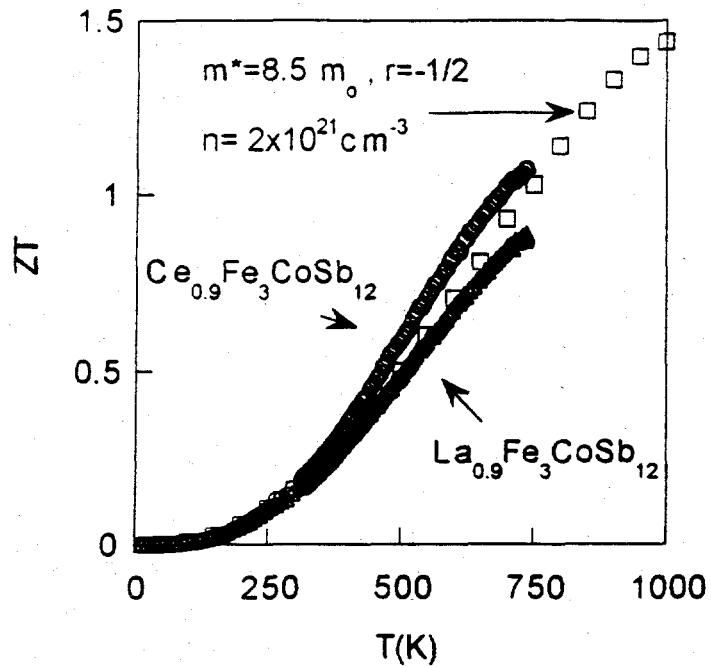


Figure 3. ZT vs. temperature for two filled skutterudite antimonides and a model calculation assuming transport occurs in a single parabolic band. The calculation was performed assuming the relaxation-time approximation, with the energy dependence of the relaxation time given by $\tau = \tau_0 E^r$. For acoustic phonon scattering, $r = -1/2$.

semiconducting $\text{LaFe}_3\text{CoSb}_{12}$, for example, the VEC = 6 and the rule is obeyed. Although these simple electron counting arguments are no substitute for detailed electronic structure calculations [5], they are often useful guides to the synthesis of new materials.

In Figure 3 we plot ZT vs. temperature for two filled skutterudite antimonides. We also plot a model calculation for ZT using generalized Fermi-Dirac statistics and assuming that transport occurs in a single parabolic band. At high temperatures the achievable thermopowers and resistivities of the filled and unfilled materials are not dramatically different, but as we illustrate in Figs. 4 and 5 the lattice component of the thermal conductivity of the filled compounds is an order of magnitude smaller than that of the unfilled at room temperature. Also in Figure 5 we plot the minimum thermal conductivity as calculated by the prescription of Cahill, Watson, and Pohl [6] using sound velocities obtained by RUS. To reach minimum thermal conductivity, heat transport in a material should occur as a random walk of thermal energy between neighboring atoms vibrating with random phases. This implies a mean free path on the order of an interatomic spacing, and is nearly impossible to achieve in real materials. Glasses, for example, have a mean free path of about 10 Å. We can estimate the mean free path in $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ as follows. If we write $\kappa = 1/3 C_v \langle v \rangle \Lambda$, where C_v is the heat capacity per unit

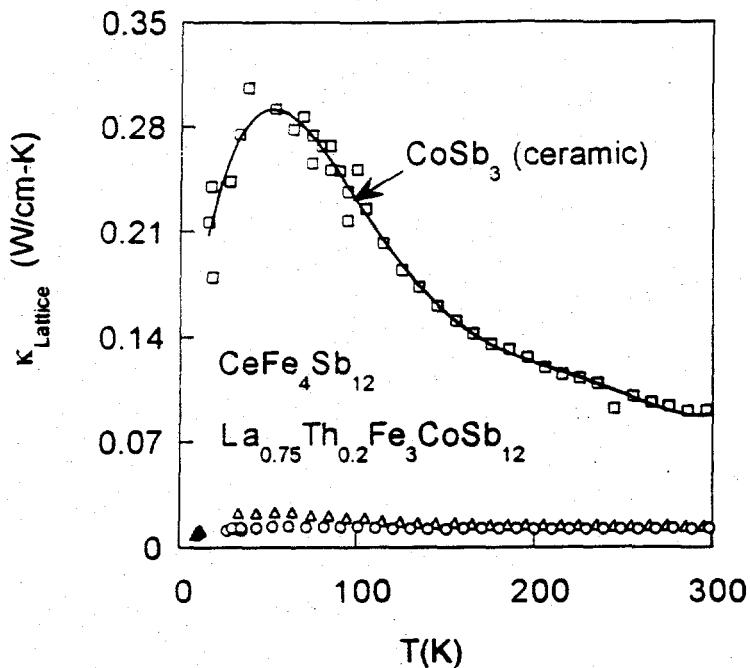


Figure 4. Lattice component of thermal conductivity of CoSb_3 and two filled skutterudites vs. temperature. The reduction in thermal conductivity achieved by filling the rare-earth site is truly remarkable.

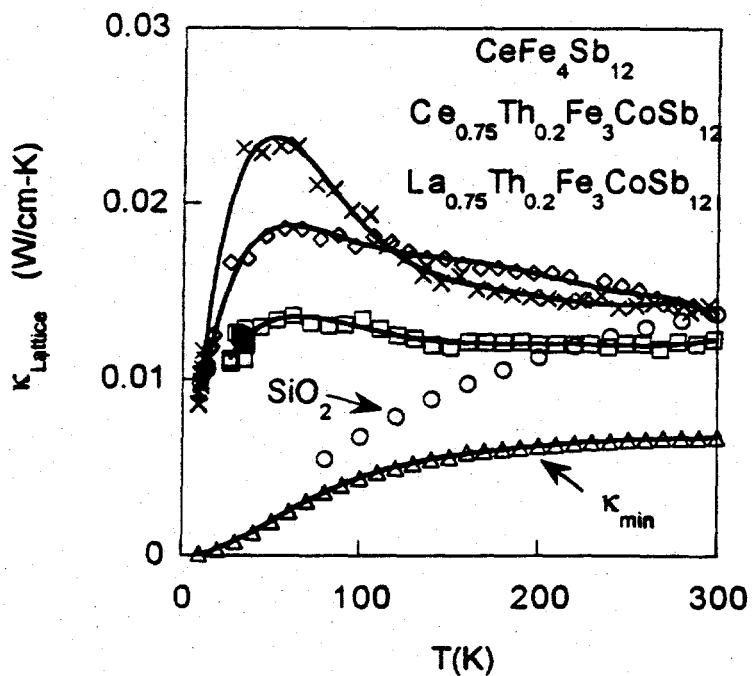


Figure 5. Lattice component of the thermal conductivity of three filled skutterudites and vitreous silica vs. temperature. Also plotted is the minimum thermal conductivity for a filled skutterudite antimonide calculated using Eq. 17 of Ref. 6.

volume, $\langle v \rangle$ = is the average sound velocity, and Λ the phonon mean free path, we find that for $\text{LaFe}_3\text{CoSb}_{12}$ we have $\Lambda = 8.2 \text{ \AA}$. This is comparable to the 7.9 \AA distance between the rare earth ions, and is consistent with the notion that phonons are scattered by incoherently vibrating La ions.

In order to better characterize the lattice dynamics of filled skutterudites, RUS measurements were performed on both CoSb_3 and $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ from 5 to 300 K. The results appear in Figure 6 and in Table 1. The solid line through the CoSb_3 data is a model calculation using the function $c(T) = c_0 - s/(e^{vT} - 1)$; this function, which has some theoretical justification, was shown by Varshni [7] to describe the temperature dependence of the elastic constants of many simple substances and in effect defines "normal" elastic behavior in much the same way that the Debye model defines "normal" specific heat behavior. It is immediately apparent from Figure 6 that although CoSb_3 is well-defined by the Varshni function, the elastic response of $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ is quite unusual. The large change in c_{44} at low temperatures is immediately suggestive of a low energy mode that couples strongly to acoustic phonons, and the two well-defined peaks in the ultrasonic absorption of $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ suggest that two low-energy modes may be present. Although a complete understanding of the elastic response of $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ is not yet available, we can begin to understand the data by considering the elastic response of a two-level system (TLS). First, we recall that the elastic constants are given by the second derivative of the free energy with respect to strain, $c = \partial^2 F / \partial \epsilon^2$. The Helmholtz free energy of a TLS is given by $F = -k_B T \ln(1 + e^{\Delta T})$, where Δ is the level spacing. If we assume that strain couples to the system as $\Delta = \Delta_0 + d\epsilon$, where d is a coupling constant, it is a simple matter to calculate the two-level contribution to the elastic response. As illustrated in Figure 7, we find that we can model the data reasonably well by including 2 TLS's with level spacings of 50 and 200 K.

To further characterize the unusual thermodynamics of filled skutterudites, specific heat measurements were performed on a sample of $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ from 2 K to 45 K. The results appear in Figure 8. In addition to the standard $C_p = \gamma T + \beta T^3$, two Einstein oscillators of the form $C_{\text{Einstein}} = (\theta_E/T)^2 e^{(\theta_E/T)} / (e^{(\theta_E/T)} - 1)^2$ were required in order to successfully model the data. The Einstein temperatures of the two oscillators were $\theta_{E1} = 70 \text{ K}$, and $\theta_{E2} = 157 \text{ K}$. It is tempting to ascribe the lower energy oscillator to the "rattling" of the La ions because the magnitude of the 70 K oscillator contribution is about what we expect. At high temperature we expect each mole of Einstein oscillators to contribute $3R = 24.94 \text{ J/K}$ to the heat capacity. Since only about 1/17 of the atoms are "rattlers," we expect a contribution of about $(1/17)*3R = 1.47 \text{ J/mol-K}$. This is very close to the fitted value of 1.21 J/mol-K .

Localized lattice vibrations such as we have been discussing are expected to produce narrow peaks in the phonon density of states (DOS) [8]. In Figures 9 and 10 we present measurements of the phonon DOS using inelastic neutron scattering. These measurements were

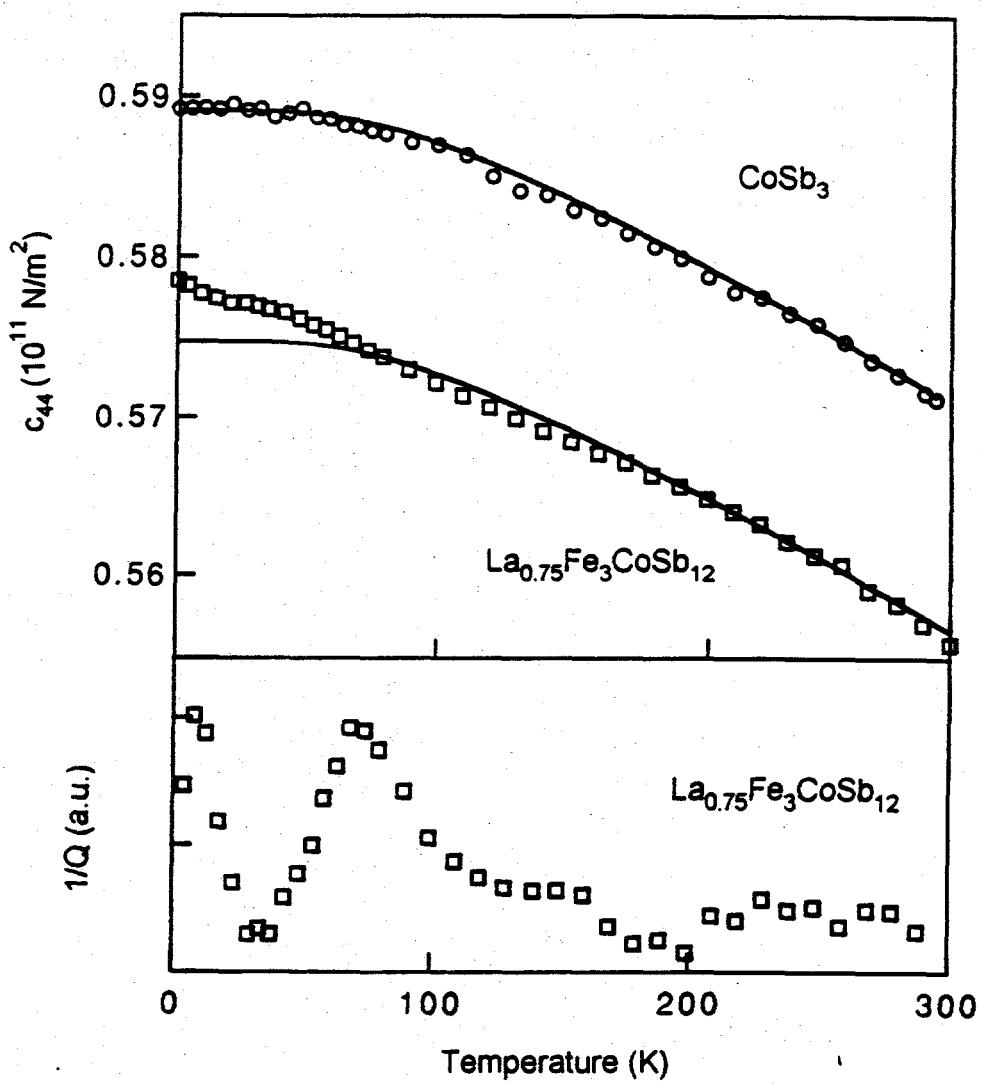


Figure 6. Upper panel. Shear modulus c_{44} vs. temperature for CoSb_3 and $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$. The solid line through the CoSb_3 data is a fit to the function $c(T) = c_0 - s/(e^{t/T} - 1)$. The fitting parameters used were $c_0 = 0.589 \times 10^{11} \text{ N/m}^2$, $s = 0.0275 \times 10^{11} \text{ N/m}^2$, and $t = 265 \text{ K}$. The solid line through the $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$ data is the fit to CoSb_3 displaced downwards by $0.0144 \times 10^{11} \text{ N/m}^2$. Lower panel. $1/Q$ vs. temperature for a sample of $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$. Q is the quality factor for a free-body resonance of the sample, and $1/Q$ is proportional to the ultrasonic absorption.

Table I. Density, elastic constants, bulk modulus, longitudinal and transverse sound velocity, and Debye temperature for CoSb_3 and $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$. These values were derived from RUS measurements.

	CoSb_3	$\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$
$\rho_{\text{theor.}} (\text{g/cm}^3)$	7.64	7.78
$\rho_{\text{exp.}} (\text{g/cm}^3)$	7.29	7.64
$c_{11} (10^{11} \text{ N/m}^2)$	1.58	1.57
$c_{44} (10^{11} \text{ N/m}^2)$	0.57	0.55
$B (10^{11} \text{ N/m}^2)$	0.82	0.84
$v_l (\text{m/s})$	4650	4530
$v_t (\text{m/s})$	2800	2680
$\theta_D (\text{K})$	319	310

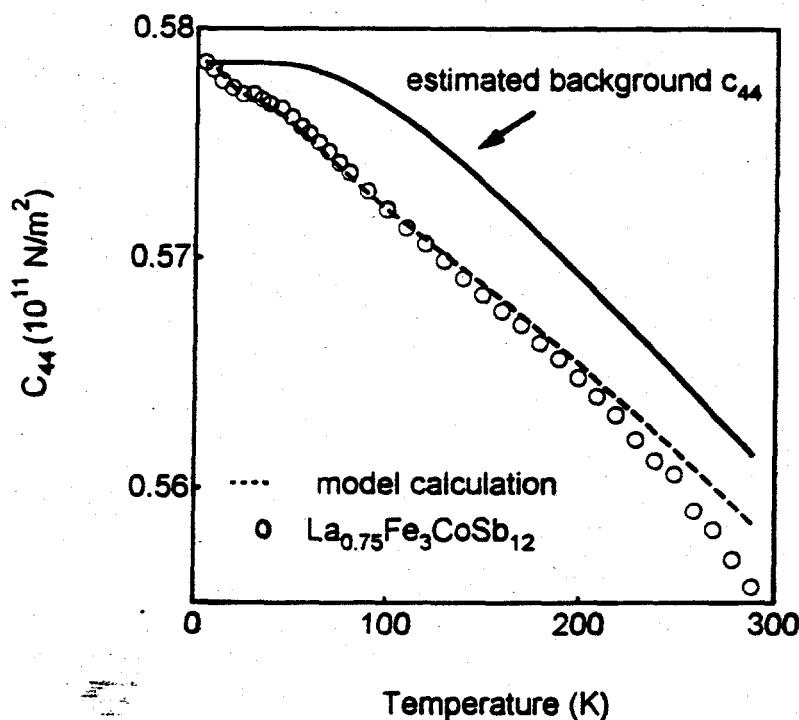


Figure 7. Open circles: shear modulus c_{44} vs. temperature for a sample of $\text{La}_{0.75}\text{Fe}_3\text{CoSb}_{12}$. Solid line: estimated background c_{44} obtained from the function $c(T) = c_0 - s/(e^{tT} - 1)$ taking s and t from the fit to CoSb_3 (see Figure 6) and choosing $c_0 = 0.5785 \times 10^{11} \text{ N/m}^2$ to agree with the data at low temperature. Dotted line: two-level system (TLS) model calculation obtained by taking $c_{44}(\text{model}) = c_{44}(\text{background}) + c_{44}(\text{TLS1}, \Delta = 50 \text{ K}) + c_{44}(\text{TLS2}, \Delta = 200 \text{ K})$.

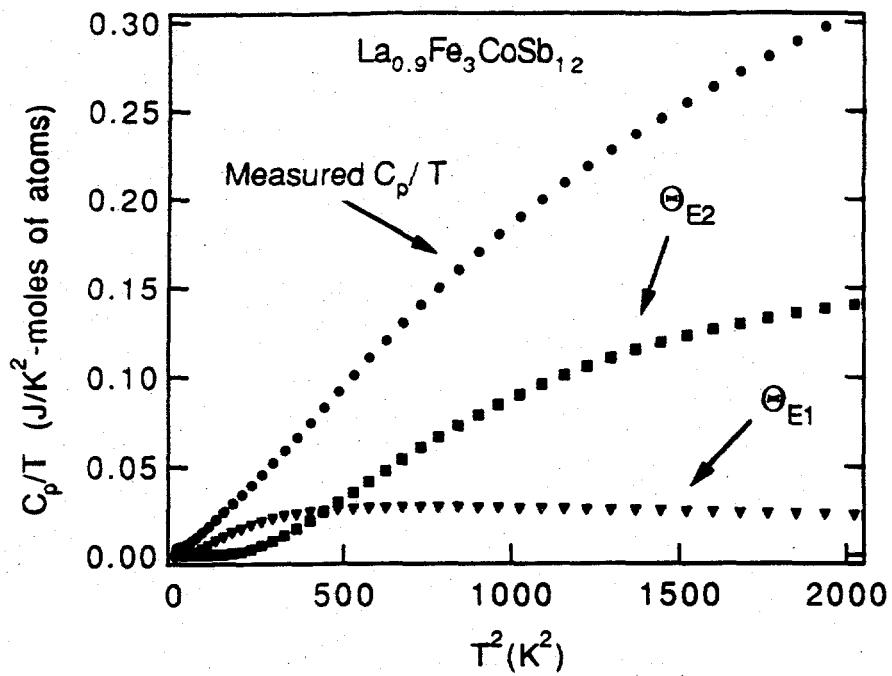


Figure 8. Specific heat C_p divided by temperature vs. temperature squared for $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$. The contributions of the two fitted Einstein oscillators are also shown. A fit to the equation $C_p(\text{J/K-mole-atoms}) = \gamma T + \beta T^3 + A C_{E1}(T) + B C_{E2}(T)$ yielded the following values for the fitting parameters: $\gamma = 0.0037 \text{ J/mol-K}^2$, $\beta = (12/5)\pi^4 k_B N_A / \Theta_D^3 = 6.86 \times 10^{-5} \text{ J/mol-K}^4$, $\Theta_{E1} = 70 \text{ K}$, $A = 1.21 \text{ J/mol-K}$, $\Theta_{E2} = 157 \text{ K}$, $B = 16.00 \text{ J/mol-K}$. The Debye temperature Θ_D obtained from this fit is $\Theta_D = 302 \text{ K}$. This is in excellent agreement with the Debye temperature of 309 K obtained using RUS (see Table 1).

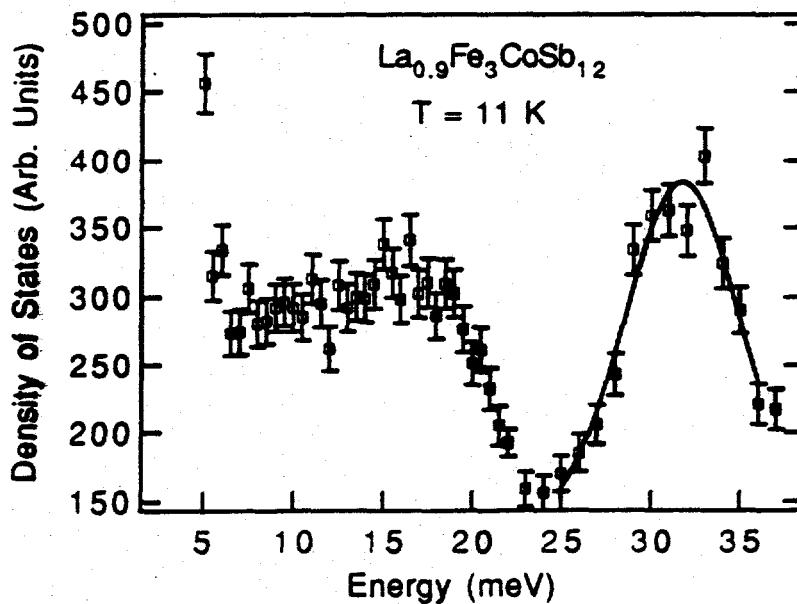


Figure 9. Phonon density of states for $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ obtained by inelastic neutron scattering using a pyrolytic graphite energy analyzer. The solid line represents a Gaussian fit to the peak with a center energy of 31.7 meV.

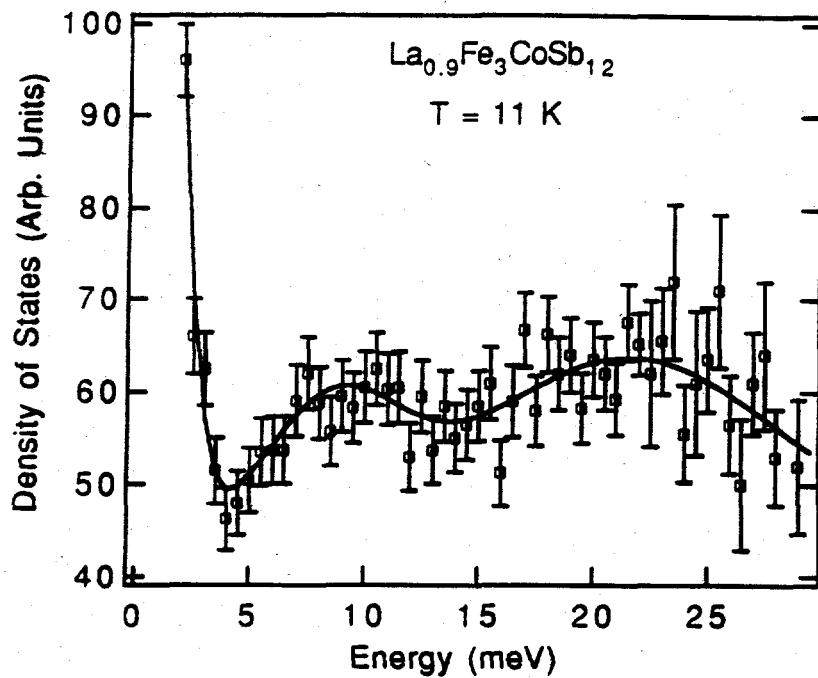


Figure 10. Phonon density of states for $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ obtained using inelastic neutron scattering and a high resolution Be analyzer.

performed at 11 K on a 30 g polycrystalline sample of $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$. Using a high resolution Be analyzer and 4 days of counting time, two low energy peaks were visible, one at 100 K and one at 240 K. Although the energies of these peaks are close to the vibrational energies observed in the ultrasound and specific heat experiments, it is important to note that a calculation of the phonon DOS of CoSb_3 by Feldman and Singh [9] predicts a double peak structure somewhat similar to the one observed in $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$. Given that RUS has shown that the lattice dynamics of CoSb_3 and $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ are very different, it is unclear how much weight to attach to these calculations in the evaluation of data on the filled materials. Measurements of the phonon DOS of CoSb_3 are presently underway, and these should help us determine the source of the peaks in the phonon DOS of $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$.

In conclusion, the filled skutterudite antimonides appear to represent excellent examples of electron-crystal, phonon-glass materials in which the incoherent "rattling" of loosely bound ions greatly reduces the lattice component of the thermal conductivity while only modestly degrading the electronic transport properties. Resonant ultrasound, specific heat, and inelastic neutron measurements have indicated the existence of two low-energy vibrational modes in $\text{La}_{0.9}\text{Fe}_3\text{CoSb}_{12}$ that do not appear to be present in CoSb_3 . It is likely that one, or both, of these modes are associated with the vibrations of the La ion in a shallow potential well.

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