Calculated thermoelectric properties of La-filled skutterudites

D. J. Singh

Code 6691, Naval Research Laboratory, Washington, DC 20375

I. I. Mazin

Code 6691, Naval Research Laboratory, Washington, DC 20375
and CSI, George Mason University, Fairfax, Virginia 22030

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The thermoelectric properties of La-filled skutterudites are discussed from the point of view of their electronic structures. These are calculated from first principles within the local-density approximation. The electronic structure is in turn used to determine transport related quantities. Virtual-crystal calculations for $La(Fe,Co)_4Sb_{12}$ show that the system obeys near rigid band behavior with varying Co concentration, and has a substantial band gap at a position corresponding to the composition $LaFe_3CoSb_{12}$. The valence-band maximum occurs at the Γ point and is due to a singly degenerate dispersive band, which by itself would not be favorable for high thermopower. However, very flat transition-metal-derived bands occur in close proximity and become active as the doping level is increased, giving a nontrivial dependence of the properties on carrier concentration and explaining the favorable thermoelectric properties. [S0163-1829(97)50432-2]

There has been a recent revival of activity in the search for improved thermoelectric (TE) materials, with an emphasis on novel materials concepts.[1] The utility of a material for TE applications is measured by its dimensionless figure of merit, $ZT = (\sigma/\kappa)S^2T$, where T is temperature, σ is the electrical conductivity, S is the Seebeck coefficient, and κ is the thermal conductivity, which contains both electronic and lattice contributions κ_e and κ_l, respectively. High values of S are characteristic of doped semiconductors; unfortunately, these have low electric conductivity and thus a small ratio (σ/κ). On the other hand, metals usually have this ratio close to the Wiedemann-Franz value, σ/κ_e. If the Wiedemann-Franz law holds, $S = 160$ μV/K is needed for the state-of-the-art value $ZT = 1$. Much TE research over the past 40 years has focused on covalent semiconducting compounds and alloys, composed of 4th and 5th row elements, with a view to finding low thermal conductivity materials that have reasonable carrier mobilities and high band masses. Most current TE materials are of this type, e.g., Bi_2Te_3, Si-Ge, PbTe. Despite research spanning three decades, little progress in increasing ZT has been achieved, and in particular Bi_2Te_3/Sb_2Te_3 has remained the material of choice for room-temperature applications.

Recently, three new materials with $ZT \gtrsim 1$ have been reported,[2–4] and these do not clearly fall in the same class as previous TE materials. β-Zn_4Sb_3, with reported ZT up to 1.3 has a large region of linear temperature dependence of the resistivity, suggestive of a metallic rather than semiconducting material, but unlike normal metals this is accompanied by high thermopowers. $CeFe_4Sb_{12}$ both by itself and doped with Co shows high values of ZT combined with very low thermal conductivities, and depending on the composition can show either metalliclike or semiconducting temperature dependencies of the resistivity. At low temperature, $CeFe_4Sb_{12}$ displays properties reminiscent of heavy fermion materials.[5] Band-structure calculations[6] show that the Ce f states, indeed, contribute significantly to the electronic

structure near the Fermi energy, leading to enhanced band masses, favorable for TE, and producing band gaps via hybridization with the valence states. This would imply a rather different electronic structure for $LaFe_4Sb_{12}$. However, $La(Fe,Co)_4Sb_{12}$ does have $ZT \approx 1$ for appropriate conditions. Here we report first-principles calculations for $La(Fe,Co)_4Sb_{12}$ within the local-density approximation (LDA), similar to our previous calculations for binary and Ce-filled skutterudites.[6–8] We then compute transport properties, based on the calculated band structure, and show them to be in accord with the experiments. An analysis of the underlying band structure reveals the mechanism for high thermopower, and suggests ways to optimize the TE properties.

The calculations were performed using the general potential linearized augmented planewave (LAPW) method.[9] This method makes no shape approximations to either the potential or charge density and uses flexible basis sets in all regions of space. As such it is well suited to materials with open crystal structures and low site symmetries like $La(Fe,Co)_4Sb_{12}$. Well-converged basis sets of ≈ 2100 functions were used. Local orbital extensions to the basis set were used in order to relax linearization errors generally and to include the upper core states of La consistently with the valence states.

The calculations were based on the experimental crystal structure of $LaFe_4Sb_{12}$. The electronic structures of $La(Fe,Co)_4Sb_{12}$ alloys were calculated as for $LaFe_4Sb_{12}$ using the virtual crystal method, i.e., self-consistent LAPW calculations were performed using average ions with fractional charges intermediate between Fe and Co. This approximation includes the average ionic charge and band filling, but is known to distort the electronic structure for alloys when the scattering properties of the ions at the mixed site differ substantially. Calculations were performed for 0, 25, and 50% Co substitution. The calculated bands near the Fermi level differ little, providing *a posteriori* justification of
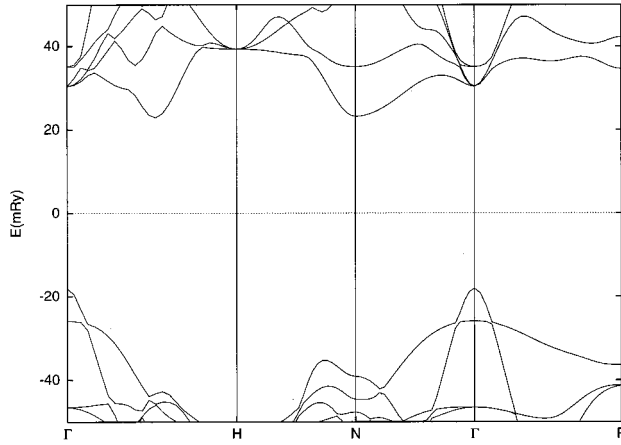
FIG. 1. Virtual-crystal band structure of $La(Fe_{0.75}Co_{0.25})_3Sb_{12}$ near the Fermi level.

the virtual-crystal approximation. Transport properties relevant to TE were determined from the calculated band structures using standard kinetic theory as given by Ziman and others,[10,11]

$$\sigma(T) = \frac{e^2}{3} \int d\epsilon N(\epsilon) v^2(\epsilon) \tau(\epsilon,T) \left(-\frac{\partial f(\epsilon)}{\partial \epsilon} \right),$$

$$S(T) = \frac{e}{3T\sigma(T)} \int d\epsilon N(\epsilon) v^2(\epsilon) \epsilon \tau(\epsilon,T) \left(-\frac{\partial f(\epsilon)}{\partial \epsilon} \right)$$

$$= \frac{1}{3eT\sigma(T)} \int d\epsilon \sigma(\epsilon,T) \epsilon \left(-\frac{\partial f(\epsilon)}{\partial \epsilon} \right). \quad (1)$$

Here $N(\epsilon)$ is the density of electronic states at the energy ϵ per unit volume, τ is the scattering rate for electrons, and the average velocity $v(\epsilon)$ of electrons with the energy ϵ is defined via

$$N(\epsilon) = (2\pi)^{-3} \int \delta(\epsilon_{\mathbf{k}} - \epsilon) d\mathbf{k},$$

$$N(\epsilon) v^2(\epsilon) = (2\pi)^{-3} \int v_{\mathbf{k}}^2 \delta(\epsilon_{\mathbf{k}} - \epsilon) d\mathbf{k}. \quad (2)$$

The above formulas are readily calculated from the band structure, provided that the scattering rate τ is known. Fortunately, in most cases τ does not vary too much with the energy, although there are exceptions to this rule, e.g., Pd metal[12] where E_F occurs near a very sharp feature in $N(\epsilon)$, and Kondo systems where there is resonant scattering.[11] $La(Fe,Co)_4Sb_{12}$, on the other hand, shows no indications of such behavior, and $\tau(\epsilon)$ can be replaced by a constant which then cancels out in many transport properties, like the Seebeck coefficient or Hall number.

The calculated band structure of $La(Fe_{0.75}Co_{0.25})_3Sb_{12}$ near the Fermi level is shown in Fig. 1. Although the initial idea of alloying unfilled skutterudites with La (Ref. 1) was to improve the figure of merit by reducing the lattice thermal conductivity, it turns out that La plays a positive role from the point of view of the electronic structure as well. First-principles calculations for $CoSb_3$ (Ref. 7) show a small band

gap with a highly nonparabolic, quasilinear valence-band dispersion. This result, which now has experimental support,[13–15] combined with the kinetic transport theory above, implies that in p-type $CoSb_3$, the doping level n dependence of S and σ will differ from that of a semiconductor with parabolic bands. In particular, in the constant scattering time, degenerate regime $S \propto n^{-1/3}$ and $\sigma \propto n^{2/3}$ instead of the usual $S \propto n^{2/3}$ and $\sigma \propto n$. This means that the power factor S^2 will be less dependent on doping level than in a conventional case and that it will be more difficult to optimize ZT by adjusting n (but note that κ has an electronic component proportional to σ).

The calculated band structure of $La(Fe_{0.75}Co_{0.25})_3Sb_{12}$ shows an indirect $\mathbf{\Gamma} - \mathbf{N}$ gap of 44 mRy. This is qualitatively different from the band structure of $CoSb_3$. The direct gap at Γ is 56 mRy. Both the conduction and valence-band edges are formed from parabolic bands with mostly Sb p character. In addition, there are some rather flat (heavy mass) primarily Fe/Co d-derived bands near, but not at the band edge, both above and below the gap.

To understand this band structure we first look at the crystal structure. A useful starting point is a hypothetical LaFe compound with the CsCl ($B2$) structure. We then construct a $2 \times 2 \times 2$ supercell, keep two La atoms along (111) directions, and remove the remaining six La's. The resulting pores are filled with the Sb_4 rings, oriented to keep the (111) three-fold axis. The Sb_4 rings form quasimolecules, since the Sb-Sb bonds are the shortest in the crystal ($\approx 2/3$ of the Fe-Fe bond length). 12 p states of Sb atoms in a molecule hybridize with each other forming four strongly bound $pp\sigma$ bonding states (split into two close pairs by weak $pp\pi$ interactions), four $pp\sigma$ antibonding states, and two pairs of weakly bound $pp\pi$ bonding/antibonding states, formed by the orbitals perpendicular to the plane of the ring. Half of these states are occupied by six p electrons of four Sb atoms. Fe/Co d states are close in energy to the Sb p states. They give rise to two sets of bands derived from six t_{2g} states at lower energy and four e_g states at higher energy per metal ion. Three Fe and one Co together have 33 d electrons, of which 24 reside in the t_{2g} bands, and nine, together with three La electrons, fill up 12 more states in Sb rings. Thus, the highest occupied states in the ionic picture occur between antibonding $pp\pi$ Sb bands and t_{2g} Fe/Co states. Let us first discuss the former. With respect to the center of the ring the symmetry of the relevant combination of p orbitals xy is odd with respect to $z \rightarrow -z$ reflection (if z is perpendicular to the ring plane). That is, the symmetry of this composite orbital is close to f_{xyz}. Not surprisingly, these combinations hybridize with the La xyz states, forming a quasi-$ff\delta$ band with the maximum at the Γ point, where the $ff\delta$ interaction is the strongest (by symmetry). The involvement of La states is reflected in the calculation by a large occupancy of the La f states: 0.2 e/La. The symmetry of $LaFe_4Sb_{12}$ is $I3\overline{m}$, and does not have the full set of 48 cubic operations, but the effective mass of this specific band is very isotropic, and rather small, $m^* \approx 0.2 m_e$.

Let us now consider the second highest occupied band at the Γ point, which is a Fe/Co t_{2g} band. With maximal cubic symmetry this band would have been triply degenerate at Γ. Since the actual symmetry of $LaFe_4Sb_{12}$ is lower, the
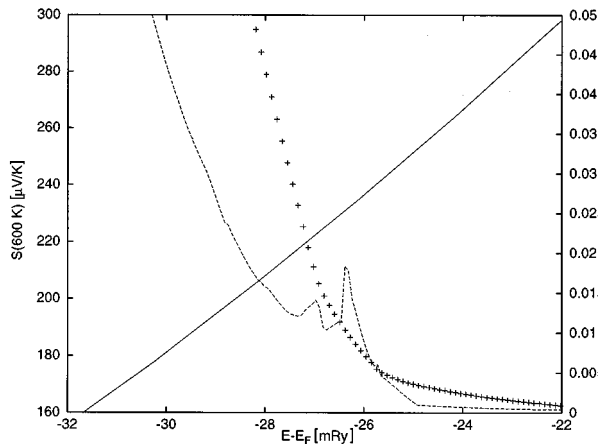
FIG. 2. Hole concentration ($+$), Hall number (dashed), and thermopower at 600 K (solid) as a function of the Fermi-level shift with respect to the center of the gap [Fermi level for stoichiometric La$(Fe_{0.75}Co_{0.25})_3Sb_{12}$]. The band edge is situated at $E-E_F=-18$ mRy.

FIG. 3. Calculated at $E-E_F=30.3$ mRy (dashed) and experimental (solid) thermopower. This energy corresponds to a nominal $Fe_{0.72}Co_{0.28}$ composition.

corresponding state is split into double and single degenerate states, the latter being the most symmetric combination of the three t_{2g} orbitals, $xy+yz+zx$. This state can also be written as $3z'^2-r^2$, where z' is the threefold axis. z' is one of the three principal axis for the mass tensor at the Γ point. Note that this state is directed towards La and thus has little overlap with the d orbitals on the neighboring Fe/Co sites. This results in a low dispersion and a high effective mass,[16] $\langle m^*\rangle\approx 3$. The top of this band is only 7 mRy below the top of the previously described Sb band. The combination of the two bands of such different effective masses in direct vicinity of the Fermi level is what provides high thermopowers in this material.

In order to understand the transport more quantitatively, we have performed calculations of transport properties[17] as a function of hole doping away from the gap based on the 25% Co virtual-crystal band structure of Fig. 1. The Hall number, carrier concentration (doping level), and thermopower at 600 K are shown as a function of E_F in Fig. 2. Over almost all of the range shown the Hall number is lower than the doping level. This deviation, which increases with band filling, reflects deviations from isotropic parabolic band behavior. Although the presence of the heavy band is responsible for the high thermopower of this material, S at 600 K does not show any noticeable structure near -26 mRy, which is the onset of the heavy band. This is because the form of Eq. (1) has strong contributions at energies up to 2–3 kT from the chemical potential[18] and because kT at 600 K is 3.7 mRy. Thus the heavy band contributes to S over the entire range of Fig. 2. However, the carrier concentration increases sharply below the onset of the second band, reflecting its flat dispersion. This provides a mechanism for pinning the Fermi level near the onset, providing high thermopowers even though the carrier concentration is apparently difficult to control in these materials.

Although the Hall number is not reported, the sample shown by Sales, Mandrus, and Williams[4] has $S(600 \text{ K})\approx 180$ μV/K. Comparing with our calculations, this corresponds to a chemical potential of -30 mRy, or 4 mRy below the onset of the heavy band. This implies a dop-
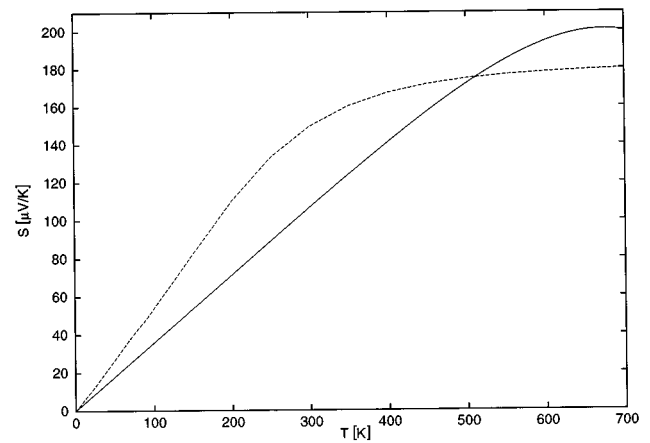
ing level of 0.08 holes per cell and a Hall number of 0.045 holes per cell. The corresponding Hall concentration of 1.2×10^{20} holes/cm^{-3} is consistent with the reported lower end of the range of Hall concentrations reported in Ref. 4 for various samples (1×10^{20} cm^{-3}).

The temperature dependence of S at a chemical potential -30.3 mRy (matching the experimental value of S at 500 K) is shown in Fig. 3. The agreement is fair; the slope at low temperatures is too high and the saturation temperature is too low, although the qualitative fact that S is rather high even at high doping levels is reproduced. One possible reason for the quantitative disagreement is neglect of the energy dependence of τ. Since the two relevant bands have very different characters (one is Sb p and another is Fe/Co d), even if the relaxation rates in each band are energy independent, as is likely, they may be different between the two bands, yielding an effective energy dependence of τ. This can noticeably change the temperature dependence. Roughly, the conductivity is mostly in the light band, so the thermopower is more or less additive for the two bands. Because of very different dispersion laws the temperature dependence of partial thermopower in each band is quite different, thus changing the balance between the two also changes the temperature dependence for the total thermopower. There is, however, another, perhaps more important effect, namely that the calculated band structure is distorted relative to the samples due to the assumption of full La filling. We note the fact that the actual, as measured, material is La deficient, and we observe from our calculations that La f_{xyz} orbitals are directly involved in the formation of the highest occupied (''light'') band. The relative positions of the heavy and light bands, which are key in determining the temperature dependence of S, thus depend strongly on La filling.

Related to this it should be noted that the thermal conductivity for this sample in the temperature range above 500 K is roughly 1/3 electronic and 2/3 lattice in origin. As mentioned κ_l is strongly reduced from κ_l of CoSb$_3$ by La addition, but most of this effect is expected to occur at fairly low La concentrations within the rattling ion framework of Slack, and Cahill, Watson, and Pohl,[19] and supported by measurements for $Ce(Fe,Co)_4Sb_{12}$ on samples with different Ce concentrations.[3] Because of the strong interaction between

the valence bands and La, La vacancies should strongly scatter electrons reducing the electrical conductivity. This is consistent with the wide range in hole mobilities (2–30 cm^2/Vs) measured for the various samples. Based on this, we conjecture that samples with higher La filling, if they can be made, would have higher mobilities and higher values of σ at a fixed band filling. Because of the Wiedemann-Franz relation, this would also lead to higher κ_e. Then the value of S becomes the main factor determining ZT at a given temperature. We speculate it may be quite feasible to increase ZT significantly in this material if the La concentration could be made stoichiometric near 25% Co concentration. Then the doping level for maximum ZT will occur at lower carrier concentrations than any of the reported samples. Depending on how much the mobility can be improved by La filling, it may be possible to obtain high values ZT at lower temperatures by doping so that the chemical potential is roughly kT above the onset of the heavy band (i.e., in the 10^{19} cm^{-3} range). Finally, yet another effect of La vacancies is broadening of the electronic states near the Fermi level, although vacancies at the Fe/Co disorder should also contribute to this broadening. We estimated this effect, assuming a constant lifetime for all states in the relevant energy interval, and found that the finite-lifetime broadening

has a negative effect on S. This provides yet another mechanism for enhancing ZT by increasing La filling, although it is hard to estimate the magnitude of this effect without knowing the actual broadening.

To summarize, we have reported first-principles calculations of band structure and transport properties of La(Fe,Co)$_4$Sb$_{12}$. Despite high ZT and large thermopower this material may be reasonably described as metallic, both from the point of view of experimental measurements and the calculated band structure. The electronic structure of La(Fe,Co)$_4$Sb$_{12}$ is strongly distorted from that of the corresponding binary, CoSb$_3$, implying an important role of La in formation of the valence bands. This fact finds its explanation in the specific character of the Sb states that form the highest valence band. Our results suggest that samples with higher La filling and lower hole concentrations may have even better TE properties.

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[16] For this band the mass tensor is relatively anisotropic. Its principal values are $m_1^* = m_{z'}^* \approx 3.9$, $m_2^* = m_3^* \approx 2.4$.

[17] For the Hall coefficient we used Eq. 2.54 of Ref. 11. 777 first-principle **k** points were used for integration over the Brillouin zone both for the Hall coefficient and for thermopower calculations.

[18] The function $\epsilon\{-[\partial f(\epsilon)/\partial\epsilon]\}$ in Eq. (1) is relatively broad. In metals convergence is usually obtained with an integration range of 5 kT, but because of the strong variation of $\sigma(\epsilon)$ due to the band onsets we had to use 10 kT in the present calculations.

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