Electronic structure of CoSb$_3$: A narrow-band-gap semiconductor

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We report calculations which show that the band structure of CoSb$_3$ is typical of a narrow-band-gap semiconductor. The gap is strongly dependent on the relative position of the Sb atoms inside the unit cell. We obtain a band gap of 0.22 eV after minimization of these positions. This value is more than four times larger than the result of a previous calculation, which reported that the energy bands near the Fermi surface are unusual. The electronic states close to the Fermi level are properly described by a two-band Kane model. The calculated effective masses and band gap are in excellent agreement with Shubnikov–de Haas and Hall effect measurements. Recent measurements of the transport coefficients of this compound can be understood assuming it is a narrow-band-gap semiconductor, in agreement with our results. [S0163-1829(98)03647-9]

CoSb$_3$ is one of several compounds with the CoAs$_3$ or skutterudite structure. This family of compounds has been recently identified as candidate for good thermoelectric materials.[1,2] They are good thermoelectrics at high temperatures and offer a possibility for improvement at room temperature.

In addition to their potential applications, skutterudites are a fascinating family of compounds. Their crystal structure, shown in Fig. 1, is characterized by the formation of four-membered pnictide rings that are located in the centers of cubes formed by the metal atoms. For every four metal cubes there is one empty, without the four-membered pnictide ring. This void space can be filled with different atoms such as La or Ce to obtain the related family of compounds called *filled skutterudites* or *stuffed skutterudites*. The filling can be useful for doping or decreasing the thermal conductivity.

Before Caillat and co-workers[1] pointed out the potential of skutterudites as high-performance thermoelectrics, these materials were studied because of their interesting bonding properties.[3–7] This potential was the reason for several experimental[8–12] and theoretical[13–18] studies. Most of this effort have been focused on the transport properties of CoSb$_3$ pure, single crystals. This understanding is necessary to assess the potential and directions for improvement of its thermoelectric properties. Our work builds the basic ingredient for a model of the transport properties of CoSb$_3$. It provides a simple analytical expression for the bands close to the Fermi level, i.e., those bands that are involved in the transport process.

Singh and Pickett[13] described the valence band as parabolic at the Γ point but with a cross over to linear behavior extremely close to the band edge. Based on this characteristic, they called unusual the transport properties predicted for this compound. Most of the recent experimental work on transport properties of CoSb$_3$ (Refs. 8–12) has been motivated by or focused on this prediction.

Here we show that the band structure of CoSb$_3$ is in fact typical of narrow-band-gap semiconductors. We found that the bands close to the Fermi level are well described by the two-band Kane model.[20] We obtain the valence and conduction bands effective masses by fitting this model to the calculated bands. Our results are in excellent agreement with Hall and Shubnikov de Haas measurements. We also show that the band gap is extremely sensitive to the position of Sb atoms, i.e., the size of the pnictides rings. When the pnictide atoms are located at the relaxed (zero force) positions, we obtain a band gap bigger than the result obtained previously by Singh and Pickett.[13] This result is analyzed under the chemical picture given by Jung, Whangbo, and Alvarez,[3] where it is shown that the top of the valence band at Γ is formed by the most antibonding combination of the π_4 orbitals of the ring.

For our calculations we use the full-potential linearized augmented plane-wave method (FP-LAPW).[21] In brief, this is an implementation of density-functional theory with different possible approximations for the exchange and correlation potential, including the local spin-density approximation (LSDA) or generalized gradient approximation (GGA). The Kohn-Sham equations are solved using a basis of linearized
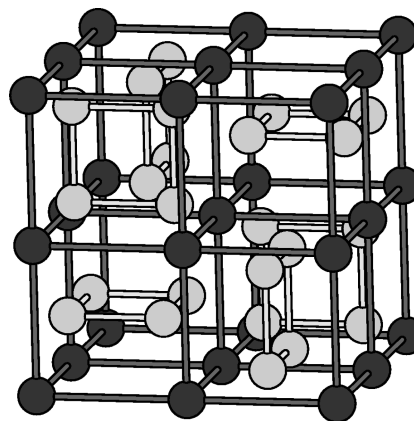

FIG. 1. Skutterudite structure of CoSb$_3$. Black balls represent Co and gray Sb. The size of the atoms is arbitrary.

TABLE I. Comparison between experimental (first four) and theoretical (last two) results for the lattice and internal parameters of the CoSb$_3$ structure.

	a (Å)	u	v
Arushanov *et al.*, Ref. 11	9.036		
Caillat *et al.*, Ref. 10	9.0345		
Mandrus *et al.*, Ref. 9	9.03573(3)	0.3348(1)	0.1570(1)
Schmidt *et al.*, Ref. 4	9.0385(3)	0.33537(4)	0.15788(4)
This work, LDA	8.94	0.3328	0.1599
This work, GGA	9.14	0.3332	0.1594

augmented plane waves.[22] For the exchange and correlation potential we use the Perdew and Wang[23] parametrization of the Ceperley-Alder data in the LSDA case. The LSDA results are also compared with the GGA of Perdew, Burke, and Ernzerhof.[24] Local orbital extensions to the LAPW basis[25] are used to describe the $3s$ and $3p$ orbitals of Co and the $4p$ orbitals of Sb, and to reinforce the description of the $4d$ orbitals of Sb.

We use a well converged basis set of around 2000 plane waves and a sampling of the Brillouin zone (BZ) of 400 points, corresponding to 24 in the irreducible wedge (IBZ). To confirm the convergence of our results, we have checked that the atomic positions and lattice parameters does not change when using 2300 plane waves and 3000 points in the BZ, corresponding to 147 k points in the IBZ. We use a muffin-tin radius of 2.2 Bohr for Co and 2.4 Bohr for Sb.

The skutterudite structure of CoSb$_3$ is formed by a bcc lattice with four formula units per cell. The unit-cell symmetry corresponds to the space group $Im3$ (T_h^5), with 4 Co atoms in the $8e$ positions and 12 Sb in the $24d$.[19] This arrangement has two internal parameters u and v governing the position of the Sb atoms and consequently the size of the Sb$_4$ rings.

The lattice and internal parameters of the crystal structure have been determined experimentally by several authors in the past,[11,10,4] and further refinement of these values were obtained by Mandrus and co-workers.[9] These values are summarized in Table I together with our LSDA and GGA results. Our LSDA result for the lattice constant is 1% smaller than the experimental value. This discrepancy is a typical and well-known consequence of the LSDA. The same result is obtained by Feldman and Singh[16] using similar approximations. The GGA for the exchange and correlation potential yields a lattice constant 1% larger than the experimental value. The internal parameters defining the position of the pnictides are in good agreement with the experimental values for both LDA and GGA.

As a check for our structural results we calculated the bulk modulus obtaining 102 GPa when LDA is used for the exchange and correlation potential, and 89 GPa when using GGA for the calculation. Although we could not find an experimental value reported for the bulk modulus of CoSb$_3$, our LDA result is in close agreement to the 105 GPa calculated by Feldman and Singh.[16] As in the case of Feldman and Singh, the bulk modulus was calculated without relaxing the internal parameters u and v, which determine the position of the Sb atoms. These parameters are kept fixed at the values given in Table I; in this way the forces on the Sb atoms are
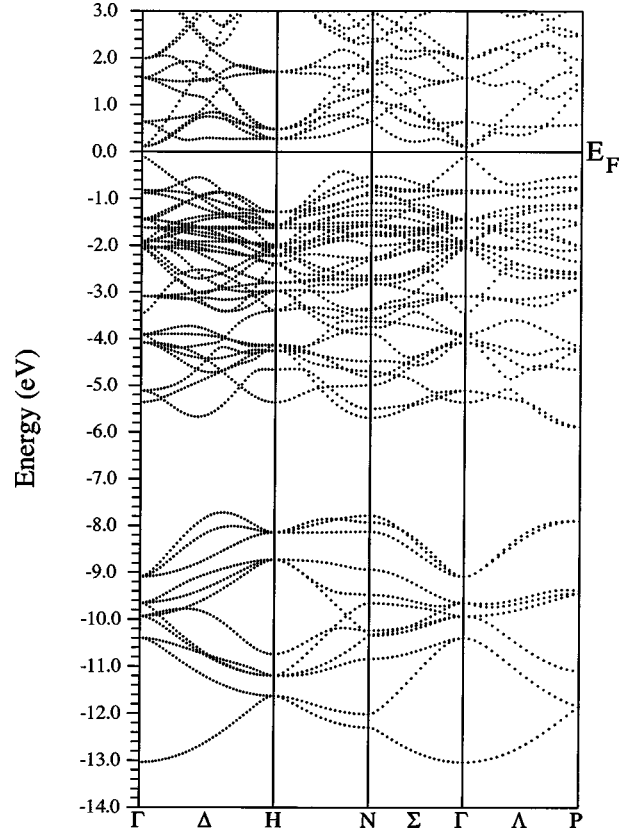

FIG. 2. Electronic band structure of the skutterudite CoSb$_3$ for a path along symmetry points of the bcc Brillouin zone.

zero for the equilibrium volume only. As a test that this is not a bad approximation to the bulk modulus we checked that these forces remained small, i.e., less than 1 mRyd/Bohr, even for a 5% compression in the volume. All these values are in the range of the 112.4 GPa measured by Slack and Tsoukala[2] for IrSb$_3$, which is another member of the same family of compounds.

The band structure of CoSb$_3$ obtained at the LDA equilibrium lattice constant and internal parameters is shown in Fig. 2. The lower set of bands, from approximately -13 eV to -8 eV are the 12 Sb $5s$ bands. The upper set of bands from around -6 eV up to the Fermi level are a mixture of Sb $5p$ and Co $3d$ states. An important feature to notice in the figure is the direct band gap at Γ $E_G = 0.22$ eV when u and v are relaxed to their minimum-energy value. This gap is more than four times bigger than the value found by Singh and Pickett.[13] We found their value of 0.05 eV when, instead of using the internal parameters u and v that minimize the energy, we use the corresponding experimental values. The difference between both sets of parameters is small (Table I) and the energy of the state at the top of the valence band at Γ is very sensitive to these changes.

The question: What is the value predicted by the theory for the energy gap? is not answered. The sensitivity to the atomic positions of the gap, together with the well-known problem of underestimation of the gap by LDA, makes it very difficult to come up with a definite answer. However, to be consistent, the result of the theory should be obtained with the parameters predicted by theory. Following this rule, our result for the band gap of CoSb$_3$ is 0.22 eV, and it should be
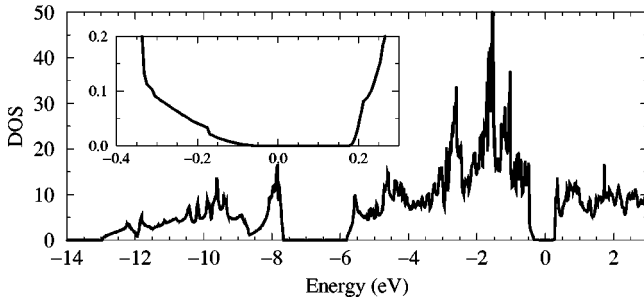
FIG. 3. Electronic density of states of the skutterudite $CoSb_3$ as a function of the energy measured from the Fermi level. The inset shows a close up of the region around the Fermi level.
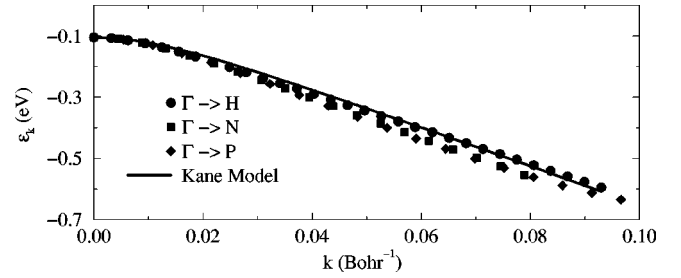

FIG. 4. Close up of the nonparabolic valence band of $CoSb_3$, along three different high-symmetry directions of the Brillouin zone, together with the fitted Kane model band.

considered a lower bound to the actual value. The final answer should be given by the proper spectroscopic experiment.

We also performed the same calculation using GGA. There is no difference in the band structure obtained with GGA when the same lattice constant and internal parameters are used. The results are exactly like those shown in Fig. 2. However, these are not the values minimizing the GGA energy functional. When the band structure is calculated using the atomic positions and lattice parameters that minimize the GGA functional (Table I) the result is a slightly different band structure. The difference is essentially a smaller band gap of the order of 0.17 eV.

The sensitivity of the band gap to the Sb position can be understood using the chemical picture given by Jung and co-workers.[3] The top of the valence band at Γ corresponds to the antibonding combinations of the π_4 orbital of the ring along a crystallographic axis. The energy of these states is mainly determined by the energy of this molecular orbital of the ring. Small changes in the positions of the Sb atoms affect strongly the energy of this molecular orbital opening or closing the gap.

The electronic band gap of the order of 0.2 eV is shown in the density of states plot of Fig. 3. The density of states around the Fermi level is small compared with the contribution of the Co d bands. This feature is clearly seen in the close up of the density of states around the Fermi level shown in the inset of this figure.

As we mentioned before, we do not find the bands of $CoSb_3$ unusual, but typical of a narrow-band-gap semiconductor. To show this, we fitted the two-band Kane model to our calculated bands close to the Fermi level. Other narrow band-gap semiconductors described by the Kane model,[26] such as InSb, HgTe, and CdSe, have a band of heavy holes degenerate at the top of the valence band with the nonparabolic band of light holes. In $CoSb_3$ this band is a heavy electrons band degenerate at the bottom of the conduction band with the nonparabolic band of light electrons.

The nonparabolic valence band of $CoSb_3$ is shown in Fig. 4 along three different high symmetry directions of the Brillouin zone. This band is spherical in k space as can be seen from the small difference in energy between different directions.

In the two-band Kane model, the dispersion relation ε_k of the bands is obtained by $\mathbf{k}\cdot\mathbf{p}$ perturbation theory, and is given by the solution of

$$\frac{\hbar^2 k^2}{2m^*} = \varepsilon_k\left(1 + \frac{\varepsilon_k}{E_G}\right), \quad (1)$$

where m^* is the effective mass at the band edge, E_G is the band gap, and the other symbols have the usual meaning. We fitted our LDA results to the solution of Eq. (1), fixing $E_G = 0.22$ eV and adjusting the effective mass in order to get the best fit. The effective mass obtained in the fitting is $m^*/m_0 = 0.071$ for the $\Gamma \rightarrow H$ dispersion relation, and 0.069 for the $\Gamma \rightarrow N$ and $\Gamma \rightarrow P$ directions. The Kane model band obtained for the $\Gamma \rightarrow H$ direction is shown with full line in Fig. 4. The agreement makes clear that the bands of $CoSb_3$ are properly described by this model.

Our value of effective mass is in remarkable agreement with both, transport and Shubnikov–de Haas effect measurements. Caillat, Borshchevsky, and Fleurial[10] found that their Hall results are explained assuming a hole effective mass of 0.071. Arushanov et al.[12] performed Shubnikov–de Haas oscillation measurements. These authors found a value of $m^*/m_0 = 0.07 \pm 0.01$ from the temperature dependence of the oscillation amplitude.

The conduction band is formed by the nonparabolic band described before, plus a triply degenerate parabolic band degenerate with this at Γ. The effective mass of this band is $m_e^*/m_0 = 0.35$. To the best of our knowledge there is no experimental value of this quantity reported.

The Seebeck coefficient is mainly determined by the band structure of the material. The carrier's scattering processes do not affect its value in a predominant way. In the limiting case where the relaxation time is assumed independent of energy, the Seebeck coefficient becomes independent of the relaxation time. We calculated the Seebeck coefficient assuming a constant relaxation time. The results are shown with solid line in Fig. 5 and compared with experimental results from Arushanov and co-workers,[11] and with the same calculation performed with the bands obtained by Singh and Pickett.[13] We adjusted the carrier's concentration in the calculation in order to reproduce the experimental data at approximately 180 K. Below this temperature the agreement between our results and the experimental data is excellent for both samples. Only the valence band is taken into account for the calculation. The disagreement above 180 K may be due to the appearance of minority carriers, an effect not taken into account in the calculation. For the sample with the highest doping level (empty triangles in Fig. 5) both band structures reproduce the experimental data, as expected, because the difference between both calculations is at the top of
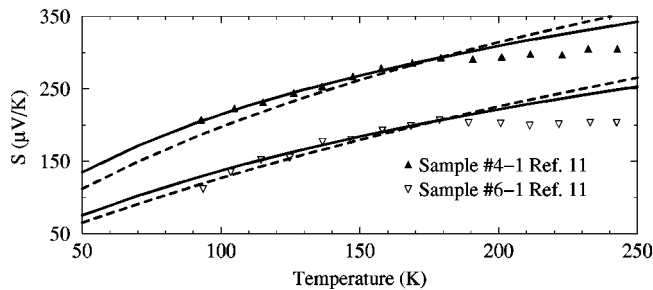
FIG. 5. Seebeck coefficient as function of temperature. The triangles are experimental data taken from Ref. 11. Solid lines are calculated using the bands obtained in this work. Dashed lines are obtained using the bands reported by Singh and Picket (Ref. 13). Both calculations assume a constant relaxation time.

the valence band. However, for the sample with the lowest doping level, where the disagreement between both band structures is shown more evidently, the agreement of our calculation is clearly better.

As a result of the calculations described in the previous paragraph, we noticed that at room temperature and for the doping levels obtained for this samples, this compound is not in the degenerate limit assumed to obtain Eq. (1) of Ref. 13. The chemical potential is, for all the cases considered, within the gap.

In summary, we have performed *ab initio* calculations of the skutterudite CoSb₃. Our results on structural and electronic properties are in excellent agreement with reported measurements on this system. We found that the two-band Kane model is a natural description of the CoSb₃ bands close to the Fermi level. From our calculations we obtain the two parameters necessary for the full determination of the model, the band gap $E_G = 0.22$ eV and the effective mass $m^*/m_0 = 0.071$. A proper description of the bands is the first step towards a model of the transport properties of this compound. This model is a necessary tool for the optimization of CoSb₃ as a good thermoelectric material.

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