

Electronic structure and thermoelectric prospects of phosphide skutterudites

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The prospects for high thermoelectric performance in phosphide skutterudites are investigated based on first-principles calculations. We find that stoichiometric CoP_3 differs from the corresponding arsenide and antimonide in that it is metallic. As such, the band structure must be modified if high thermopowers are to be achieved. In analogy to the antimonides it is expected that this may be done by filling with La. Calculations for $\text{LaFe}_4\text{P}_{12}$ show that a gap can in fact be opened by La filling, but that the valence band is too light to yield reasonable p -type thermopowers at appropriate carrier densities; n -type La-filled material may be more favorable. [S0163-1829(99)08415-5]

There has been considerable recent interest in the electronic and thermal transport properties of skutterudites. This is driven primarily by the discovery of two new high performance thermoelectric (TE) materials in this class.^{1,2} The TE performance is characterized by a dimensionless figure of merit $ZT = \sigma S^2 T / k$, where σ is the electrical conductivity, S is the thermopower, and k is the thermal conductivity; ZT up to 1.4 at $T = 600$ K has been measured in skutterudites. Much of the effort has focused on antimonides³ based on the expectation of lower values of the lattice thermal conductivity related to the heavier mass atoms as well as the likelihood of better carrier mobilities due to the chemistry of Sb as compared to, say, P. In fact, the two high- ZT compositions discovered are both antimonides:^{4,5} $\text{CeFe}_4\text{Sb}_{12}$ and $\text{La}(\text{Fe},\text{Co})_4\text{Sb}_{12}$.

The high ZT values in these compounds derive from two important features: (i) high power factors σS^2 related to their particular electronic structures, which are apparently different both between the two compounds and from the corresponding binary, CoSb_3 ; and (ii) a strong suppression of the thermal conductivity of the binary upon filling. This latter effect, though crucial for the TE performance, is understood only qualitatively in terms of phonon scattering related to rare-earth vibrations. Attempts to obtain even better performance by various alloying and substitutions on each of the three sites have thus far been unsuccessful, although there are still many possibilities remaining to be explored. These efforts are complicated by the large variety of realizable modifications of these skutterudites and the general lack of detailed understanding of their effects on properties relevant to TE. Moreover, TE performance typically is a strong function of the doping level, further complicating the search.

In this paper, we present electronic-structure calculations for the phosphides CoP_3 and $\text{LaFe}_4\text{P}_{12}$, and discuss these in terms of the implications for TE performance and in relation to the corresponding antimonide materials in order to elucidate trends. All previous first-principles calculations point to a particularly important role for bands associated with the chemical bonding of the pnictogen four-membered rings in

the skutterudite structure in determining transport properties—a point that was emphasized early on by Jung, Whangbo, and Alvarez⁶ based on tight-binding calculations. Calculations for $\text{CeFe}_4\text{P}_{12}$, $\text{CeFe}_4\text{As}_{12}$, and $\text{CeFe}_4\text{Sb}_{12}$,⁷ have shown these materials to be hybridization gap semiconductors with decreasing gaps as the lattice parameter increases and Ce- f hybridization decreases down the pnictogen column. Previous calculations for the binaries CoSb_3 and CoAs_3 reveal generally similar electronic structures,⁸ but with differences that are particularly significant in the region near the Fermi energy (E_F) that dominates electronic transport. CoSb_3 is a narrow-gap semiconductor with a highly nonparabolic valence band dispersion, while CoAs_3 was found to be a zero-gap semiconductor with parabolic bands.

Zhukov has reported first-principles band structure calculations for CoP_3 finding the material to be a narrow indirect gap semiconductor.^{9,10} The relatively heavy conduction bands with their multivalley minima would seem initially favorable for the electronic aspect of TE performance with n -type doping. However, the calculations were done with the linear muffin-tin orbital atomic sphere approximation method (LMTO-ASA). Because the skutterudite crystal structure features large voids, low site symmetries, and strong covalent bonding, such calculations are particularly difficult, and in such cases may have band shifts of several tenths of an eV compared to more accurate general potential calculations. Because of the small indirect gap, this is enough to qualitatively change the picture from a transport point of view, implying the need for a general potential investigation as presented here.

Our calculations were done in the framework of density functional theory using the general potential linearized augmented plane wave (LAPW) method,¹¹ which does not make any shape approximations and uses a flexible basis set including LAPW functions and local orbital extensions¹² to relax linearization errors and treat semicore states. Valence states were done in a scalar relativistic scheme while fully relativistic calculations were done for core states in the atomic spheres ($R_{MT} = 2.1, 2.1, 1.9,$ and 2.5 a.u. for Co, Fe,

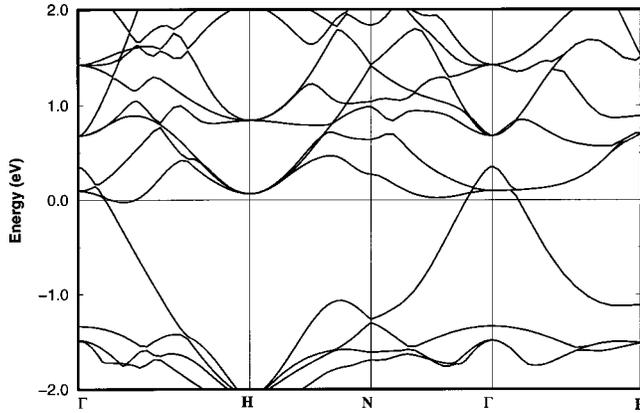


FIG. 1. Band structure for CoP_3 in an energy window centered at E_F . Notice the metallic character due to band crossing at Γ .

P, and La, respectively). The basis set convergence was tested using $R_{min} \cdot k_{MAX}$ from 5.0 to 8.5; a value of 7.0 was found to yield a reasonable computational effort with only a small error with respect the highest $R_{min} \cdot k_{MAX}$ ($\Delta E_T = 0.3$ mRy/atom). We used a (4,4,4) special points grid for the Brillouin zone (BZ) integration, which we found to be converged. The electronic density of states (DOS) was based on a 35 k points tetrahedral sampling in the irreducible BZ. The Hedin-Lundqvist parameterization for the exchange-correlation local-density approximation (LDA) functional is used.

As discussed below, we find, for CoP_3 , a globally similar band structure to Zhukov, but with changes near E_F that are large enough to drastically change the picture in an unfavorable direction from the point of view of TE.

As mentioned, the binary CoSb_3 has a relatively high thermal conductivity and a highly nonparabolic valence band dispersion, which is unfavorable for high p -type TE performance. Meanwhile, $\text{La}(\text{Fe},\text{Co})_4\text{Sb}_{12}$ has both a strongly reduced k and a band structure that is modified in such a way as to improve the electronic properties by shifting the valence band edge downwards due to repulsion from the La f resonance above the Fermi level.¹³ One may conjecture that a similar effect could be present in $\text{La}(\text{Fe},\text{Co})_4\text{P}_{12}$ as the band edge states have the same character, and if so the question arises as to whether the electronic properties relevant to TE may be improved. There is also interest in the electronic structure of filled phosphide skutterudites because of the observation of superconductivity in $\text{LaFe}_4\text{P}_{12}$ with critical temperature, $T_c = 4.1$ K.¹⁴

The skutterudite structure (space group $Im\bar{3}$) consists of a simple cubic transition metal sublattice partially filled by almost square pnictogen groups (P_4). Three quarters of these sites are filled with such rings oriented in [100], [010], and [001] directions according to the cubic symmetry and the remaining one quarter are left empty. In filled skutterudites these remaining sites are occupied by a rare-earth ion, which modifies thermal and electronic properties. Two symmetry-independent parameters u and v determine the position of the P with respect to the metal ion in the center of the cubic cell; they control the size and the squareness of the rings. We start from an experimental crystal structure fixing the position of the pnictogen group, with respect to the transition metal, to $u_e = 0.1453a$ and $v_e = 0.3482a$, where the lattice parameter

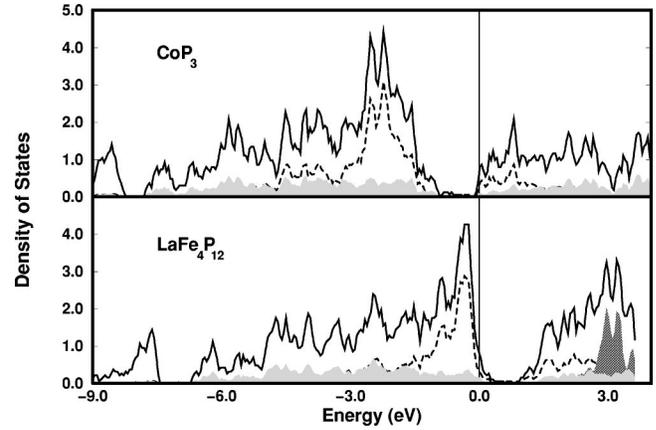


FIG. 2. DOS for CoP_3 (upper panel) and for $\text{LaFe}_4\text{P}_{12}$ (lower panel), the energy is referred to the respective Fermi level. The total DOS (solid line) and the projections on different relevant atomic components that are sketched: P p components (light gray shadow), Co d components (dashed line), and resonant La f components (dark gray shadow).

is $a = 0.77073$ nm for CoP_3 and $u_e = 0.1504a$ and $v_e = 0.3539a$, where $a = 0.78316$ nm for $\text{LaFe}_4\text{P}_{12}$.¹⁵

The band structure of CoP_3 , as given in Fig. 1, is metallic due to the fact that the pseudogap near E_F , which is characteristic of skutterudites, is entirely crossed by a single mostly phosphorus p band. This is the same band that crosses the pseudogap in CoSb_3 and CoAs_3 , but in CoP_3 it crosses the conduction bands above the Fermi level. As such, CoP_3 is not very promising for TE applications unless filling or other modifications alter the band structure enough to open a gap. The corresponding DOS and projections are shown in Fig. 2. In the most relevant region for TE properties (near E_F) our LAPW band structure is quite different from the LMTO-ASA results,¹⁰ which predict an indirect Γ - H energy gap. As already found in Ref. 8 for antimonides, there are (1) a single degenerate band, (2) a twofold degenerate band, and (3) a threefold degenerate band at Γ and above E_F . The first one is mostly P p -derived while the other two are more hybridized with higher contributions from Co d states. The energy alignments of these bands at Γ point are different for different Co-derived skutterudites passing from (1)-(3)-(2) in CoSb_3 , to (3)-(2)-(1) in CoAs_3 , to (2)-(1)-(3) in CoP_3 .

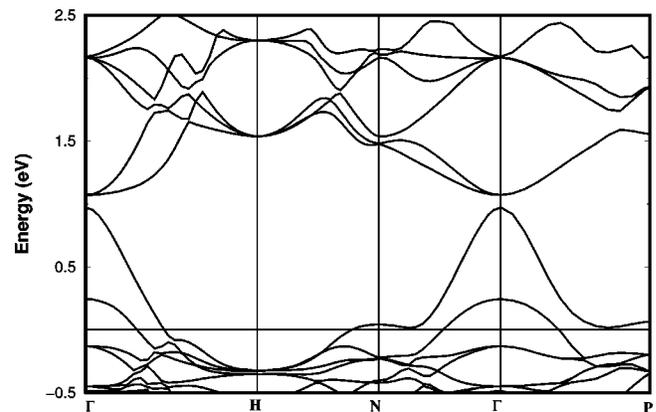


FIG. 3. Band structure for $\text{LaFe}_4\text{P}_{12}$ in an energy window including E_F . Notice the small gap opened at Γ .

TABLE I. Effective masses for $\text{LaFe}_4\text{P}_{12}$ along the high symmetry directions in BZ. $E(\Gamma)$ denotes the band energy (in eV) at Γ relative to E_F (see Fig. 3).

$E(\Gamma)$	$m^*(\Gamma-H)$	$m^*(\Gamma-P)$	$m^*(\Gamma-N)$
-0.1137	-0.99	-2.67	-1.61
	-2.67		-2.85
0.2597	-0.93	-1.14	-1.12
0.9887	-0.32	-0.37	0.34
1.0697	3.02	1.24	1.70
	0.56		0.93

In order to “realize” a favorable band structure for p -type TE properties from CoP_3 , we need to lower the single degenerate band (1) until it crosses band (2) and arrives near to the heavy mass bands forming the bottom of the pseudogap so that we obtain a semiconductor with potentially high Seebeck coefficients analogous to $\text{La}(\text{Fe},\text{Co})_4\text{Sb}_{12}$. The effect of gap opening by means of filling that provides TE performance for antimonides relies on the interaction between rare-earth f states or resonances and the crossing band. This effect is strong because the wave functions of the pseudogap crossing band have f -like symmetry, as discussed in detail in Ref. 13.

Our results on $\text{LaFe}_4\text{P}_{12}$ show that the crossing band is indeed pushed down, as expected, by repulsion of La f -resonance states at about 3.0 eV above E_F (Fig. 2 lower panel) resulting in a small direct gap between bands (1) and (2): $E_g=98$ meV. However, the top of the band crossed by the Fermi level is not close to any lower heavy bands (Fig. 3) so that p -type thermopower cannot be high enough at a reasonable band filling for $\text{La}(\text{Fe},\text{Co})_4\text{P}_{12}$, assuming rigid band behavior upon alloying with Co as found in $\text{La}(\text{Fe},\text{Co})_4\text{Sb}_{12}$

(N.B.: strong nonrigid band behavior, which we do not expect, would also be detrimental to TE as it would indicate strong alloy scattering and low carrier mobility). A study of the effective masses (Table I) for the three bands closest to E_F points out also that because of the double degeneracy and the reasonably high m^* , $\text{La}(\text{Fe},\text{Co})_4\text{P}_{12}$ could be more interesting for n -type TE application, but only if thermal conductivity can be strongly reduced, and well-filled n -type material with low defect concentrations and high mobility can be produced.

The importance of four-membered pnictogen rings for thermoelectricity and also for superconductivity¹⁴ suggests investigation of the A_g Raman active phonon frequencies¹⁶ at Brillouin zone center that are associated with normal modes involving variations of the symmetry-independent parameters (u, v) in the skutterudites structure or, in other words, distortion of the pnictogen rings. We obtain LDA structural parameters ($u_0=0.1462$ and $v_0=0.3478$) near the experimental ones, and $\omega_1=228$ cm^{-1} and $\omega_2=177$ cm^{-1} for CoP_3 . Similar calculations for $\text{LaFe}_4\text{P}_{12}$ give $u_0=0.1537$ and $v_0=0.3522$ for LDA equilibrium parameters, whereas $\omega_1=189$ cm^{-1} and $\omega_2=160$ cm^{-1} . The difference presumably reflects La-P interactions.

In summary, we have presented electronic-structure calculations for CoP_3 and $\text{LaFe}_4\text{P}_{12}$. These show that while CoP_3 is a metal, a gap is opened up upon filling with La. Nonetheless, the band structure does not allow for high p -type thermopowers with reasonable carrier concentrations. The conduction bands are more favorable, having a degenerate heavy mass structure, though we note that n -type filled skutterudites are difficult to prepare.

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¹G. Mahan, B. Sales, and J. Sharp, *Phys. Today* **50** (3), 42 (1997).

²B. C. Sales, D. Mandrus, and R. K. Williams, *Science* **272**, 1325 (1996).

³J.-P. Fleurial, T. Caillat, and A. Borshchevsky, in *Thermoelectric Materials—New Directions and Approaches*, edited by T. M. Tritt, M. G. Kanatzidis, H. B. Lyon, Jr., and G. D. Mahan, MRS Symposia Proceedings No. 478 (Materials Research Society, Pittsburgh, 1997).

⁴J.-P. Fleurial, A. Borshchevsky, T. Caillat, D. Morelli, and G. P. Meisner, in *Proceedings of the 15th International Conference on Thermoelectrics* (IEEE, Piscataway, 1996), p. 91.

⁵T. Caillat, J.-P. Fleurial, and A. Borshchevsky, in *Proceedings of 15th International Conference on Thermoelectrics* (Ref. 4), p. 100.

⁶D. Jung, M.-H. Whangbo, and S. Alvarez, *Inorg. Chem.* **29**, 2252 (1990).

⁷L. Nordström and D. J. Singh, *Phys. Rev. B* **53**, 1103 (1996).

⁸D. J. Singh and W. E. Pickett, *Phys. Rev. B* **50**, 11 235 (1994).

⁹V. P. Zhukov, *Phys. Solid State A* **38**, 90 (1996).

¹⁰M. Lluell, P. Alemany, S. Alvarez, V. P. Zhukov, and A. Verne, *Phys. Rev. B* **53**, 10 605 (1996).

¹¹D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Methods* (Kluwer Academic, Boston, 1994).

¹²D. J. Singh, *Phys. Rev. B* **43**, 6388 (1991).

¹³D. J. Singh and I. I. Mazin, *Phys. Rev. B* **56**, R1650 (1997).

¹⁴G. P. Meisner, *Physica B & C* **108B**, 763 (1981).

¹⁵*Pearson’s Handbook for Crystallographic Data*, edited by P. Villars and L. Calvert (ASM, Material Park, 1991).

¹⁶H. D. Lutz and G. Kliche, *Z. Anorg. Allg. Chem.* **480**, 105 (1981).