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Electronic structure of Ce-filled skutterudites

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The electronic structure of $CeFe_4P_{12}$ and $CeFe_4Sb_{12}$ have been studied with density-functional calculations. Both are small band-gap semiconductors within the local-density approximation. The Ce is near trivalent in both compounds, and the Ce $4f$ states hybridize strongly with both Fe $3d$ and pnictogen p states in the vicinity of the Fermi energy. The band gaps are the result of this hybridization.

I. INTRODUCTION

There has been renewed interest of late in complex semiconducting compounds with potential for thermoelectric applications. The efficiency of thermoelectric devices is limited by the figures of merit, Z, of the semiconductors from which they are fabricated. This is given by a combination of electrical and thermal transport coefficients, in particular,

$$Z = \frac{S^2 \sigma}{\kappa}, \qquad (1)$$

where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. Good thermoelectric systems are characterized by a combination of high mobilities (for high σ with reasonable carrier concentrations), high band masses (to obtain high values of S), and low lattice thermal conductivities. This latter requirement leads to the consideration of complex (i.e., many atoms per unit cell) solids since this is necessary for very low thermal conductivities in crystalline materials.[1]

One class of materials apparently fitting these criteria are the binary skutterudites, MA_3, where M is Co, Rh, or Ir and A is a pnictogen, and as such they have been proposed and studied as potential thermoelectrics.[2–5] These materials, although cubic in symmetry, have rather complex structures containing large voids and four formula units per cell. They form as very well ordered line compounds, with high hole mobilities. Moreover, they appear to have rather unusual electronic structures, including zero gap semiconductors and compounds with highly nonparabolic valence bands;[4,5] these make the skutterudites of interest in their own right. Nonetheless, measurements have made apparent the fact that these materials will not outperform existing thermoelectrics, without modification. In particular, the lattice thermal conductivities are too high. As such, interest is shifting to various modifications of the skutterudite structure.

Several such modifications are feasible, including substitutions on the anion and/or cation sites and filling of the voids in the skutterudite structure with another atom. This latter possibility seems particularly promising because it avoids formation of a disordered alloy which may be expected to adversely affect the carrier mobilities, and because of the expectation, based on the size of the voids, that low frequency and highly anharmonic optical phonons will be associated with heavy atoms in those sites; these may lead to enhanced phonon scattering and lower thermal conductivity.

In this paper we study the electronic structure of $CeFe_4P_{12}$ and $CeFe_4Sb_{12}$ using density-functional calculations within the local-density approximation (LDA). It has been suggested that the cerium atoms are tetravalent and fully ionic in these compounds, which would lead to a close relationship with the then isovalent CoP_3 and $CoSb_3$ skutterudite compounds.[6] This would then explain the reported semiconductivity and semimetallicity[7] of the cerium compounds, as in the cobalt pnictides. Recently Singh and Pickett[4] have reported a band-structure calculation where $CoSb_3$ was found to be semiconducting, but with a very small gap, 50 meV, since there is a single band with a peculiar linear dispersion crossing most part of a larger "pseudogap," 0.57 eV. This finding seems to be in some accordance with a reported nonobserved optical gap in this compound.[8] The same study reports a 0.45 eV gap for the CoP_3 compound for which the band structure, however, is not known. Another fact that is in favor of cerium tetravalency is that there is a clear departure from the lanthanide contraction of the lattice constant for cerium compared to the other rare-earth-filled skutterudites, at least for the phosphides and arsenides.[7] This indicates a nontrivalency of cerium. For the antimonides this dip in the lattice constant is much smaller, which might be either due to the much larger unit cell for which the cerium valency has a smaller influence or a closeness to trivalency of cerium in the antimonide.

Another view of the cerium valency in this type of compounds was suggested by Meisner *et al.*[9] after comparing

properties of $CeFe_4P_{12}$ with the isostructural compounds UFe_4P_{12} and $ThFe_4P_{12}$. While the cerium and uranium compounds are found to be semiconducting, the thorium compound is metallic. This is in contradiction to what one might expect, assuming that both cerium and thorium are tetravalent and should consequently have a similar ground state. The authors argued instead that it is the hybridization of the Ce and U f electrons with the Fe and P valence electrons that is responsible for the formation of the observed gap. This picture was supported by recent electron spin resonance experiments on rare-earth impurities in $CeFe_4P_{12}$ (Ref. 10) and can actually also explain the above-mentioned lattice constant anomaly through the extra bonding arising from these f states, as seen, e.g., in cerium-nickel compounds where similar effects are observed but where they can be attributed to itinerant $4f$ states and their hybridization with the Ni $3d$ states.[11]

Very recently low temperature experiments on $CeFe_4Sb_{12}$ have also been reported.[12] It is found that this compound is metallic and has anomalies in the susceptibility, resistivity, and the thermoelectric power, which lead the authors to characterize this compound as heavy-fermion-like.

After brief descriptions of the numerical details and of the crystal structure, we will present the calculated electronic structure for $CeFe_4P_{12}$ and $CeFe_4Sb_{12}$. It is found that they are both semiconducting within the LDA and that the Ce $4f$ states are important in the formation of the gaps. Results are analyzed in terms of the degree of ionicity of cerium and its formal valency.

II. COMPUTATIONAL DETAILS

The electronic structure was calculated with the full-potential linearized-augmented-plane-wave (LAPW) method,[13] using the Hedin-Lundquist version of the local approximation[14] to the density-functional theory. Local orbitals[15] were used to treat the ''semicore'' states, Ce $5p$ and Sb $4d$, on the same basis as the valence states. The core states were calculated fully relativistically while the valence states were calculated within the semirelativistic approximation but with the spin-orbit coupling reintroduced in a second variational step. For the basis functions a plane-wave cutoff G_{max} given by $R_{min}G_{max} = 7.75$ (9.0) was used for $CeFe_4P_{12}$ ($CeFe_4Sb_{12}$), where R_{min} is the radius of the smallest muffin-tin sphere. The angular momentum expansion within the muffin-tin spheres, whose radii were 1.00 Å for P and 1.19 Å for the rest, was cut off after $\ell = 8$.

For the Brillouin-zone integration eighth special points were used in the irreducible $\frac{1}{24}$th part during the self-consistent calculations.

III. CRYSTAL STRUCTURE

The filled skutterudite structure is derived from the skutterudite ($CoAs_3$-type) structure by filling a large empty void which exists in this structure. This filling does not lower the symmetry, which is still given by the cubic space group $Im3$. While the unit cell of the filled skutterudite contains one formula unit, it is convenient to look at the conventional bcc cell with two formula units. The iron atoms then span this cubic cell with a simple-cubic substructure, which be-

sides the corners and the body center also include all face and edge centers. Now the small cubes formed by this iron substructure are filled alternatively by four pnictogen atoms forming almost square rectangles and by a cerium atom. Totally, in the conventional cell, six cubes are filled by the four-membered pnictogen rings and the remaining two by lanthanide atoms. The rings are centered around the body center of the subcube and have three different orientations, with the normals in the x, y, and z directions respectively, in such a way that an edge is always directed towards the cerium atom in the neighboring subcube. The pnictogen atoms form rotated and distorted octahedra around the iron atoms. In this structure the cerium atoms have 12 pnictogen nearest neighbors and 8 iron next-nearest neighbors, and the Ce-Ce distance is large ($a\sqrt{3}/2$, where a is the lattice constant).

The electronic structure was calculated at the experimental lattice constants:[7,16] $a = 7.792$ Å and $a = 9.135$ Å, respectively, for the P and Sb compounds. In addition to the lattice constant there are two free structural parameters u and v not determined by the symmetry. These give the positions of the pnictogen atoms. They are related to the lengths of the two sides of the A_4 rectangles, which are given by $1 - 2u$ and $2v$. In the case of $CeFe_4P_{12}$, we used in our calculation the parameters obtained from x-ray diffraction, $u = 0.3522$ and $v = 0.1501$.[7] However, in the case of $CeFe_4Sb_{12}$ they have not been determined experimentally so in this case we calculated them by minimizing the total energy while keeping the volume fixed at the experimentally observed value. In this way we determined the values $u = 0.333$ and $v = 0.163$, which subsequently were used when studying the electronic structure. That the pnictogen atoms almost form squares can be seen from the small deviations from Oftedal's criterion, $u + v = 1/2$.

In the procedure of determining the internal parameter for $CeFe_4Sb_{12}$ the Raman active A_{1g} phonon modes were also calculated. They correspond to the symmetry conserving vibrations of the antimonide rectangles and were obtained as 137 and 157 cm^{-1}.

IV. RESULTS

A. Band structure

From the band structures of $CeFe_4P_{12}$ and $CeFe_4Sb_{12}$ shown in Figs. 1 and 2 one can directly see that the calculations yield band gaps at the Fermi energy for both materials. They are situated below the flat bands arising from the Ce $4f$ levels, and have the magnitudes 0.34 and 0.10 eV, for the phosphide and antimonide, respectively.

The top valence bands have characters of hybridized Fe $3d$ and A p states (where A is P or Sb), as can be seen in the density of states (DOS) of Figs. 3 and 4, while the lower lying ones are mainly of A p character. Not shown in the figures are the ''semicore'' states and the low lying pnictogen s states. The lowest lying conduction bands are dominated by the narrow spin-orbit split Ce $4f$ bands, which appear to be situated in a gap formed by the other conduction states. However, from the DOS projected on to the cerium LAPW sphere it is obvious that there is also a significant contribution from the Ce $4f$ states to the highest lying valence bands.

In order to study more closely the bands around the Fermi energy, these bands have been replotted on an expanded en-
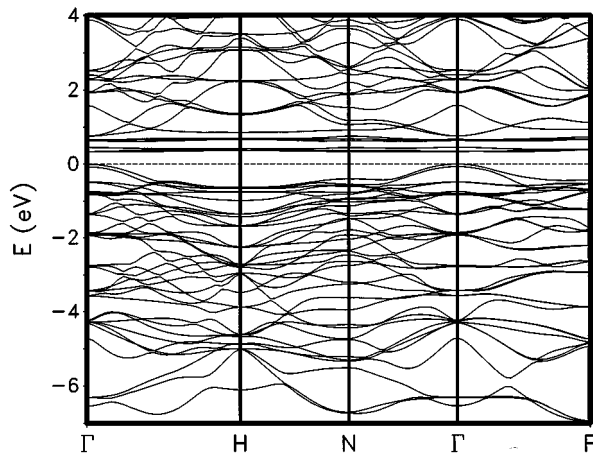
FIG. 1. The band structure of $CeFe_4P_{12}$ along some symmetry directions in the bcc zone. The energy zero is at the valence band maximum and is denoted with a dashed line.

ergy scale in Figs. 5 and 6. Here one can see more clearly that there are some differences between the two compounds besides the already mentioned size of the gap. In the phosphide there are two parabolic bands at the valence maximum at Γ, while there is only one in the antimonide. When one compares the character of these bands one sees that there is a close relation between the second highest valence band ($v2$) in the phosphide and the highest ($v1$) in the antimonide. These bands are of mainly Fe $3d$ character ($\sim 80\%$), slightly hybridized with A p but with zero Ce $4f$ character at Γ. The phosphide $v1$ band, on the other hand, has a close resemblence with the $v4$ band situated 0.4 eV below the valence band maximum (VBM) in the antimonide. These bands have predominantly Ce $4f$ character at Γ ($\sim 60\%$ respectively $\sim 40\%$ for the P and Sb compounds). That these latter bands are formed from a strong hybridization of Ce $4f$, Fe $3d$, and A p states can be seen most clearly for the $v1$ band of the phosphide. While the Ce $4f$ character dominates at Γ, there is mainly Fe $3d$ character when going to the zone boundary at N but with significant contributions from the other two types of states, and almost equal contri-
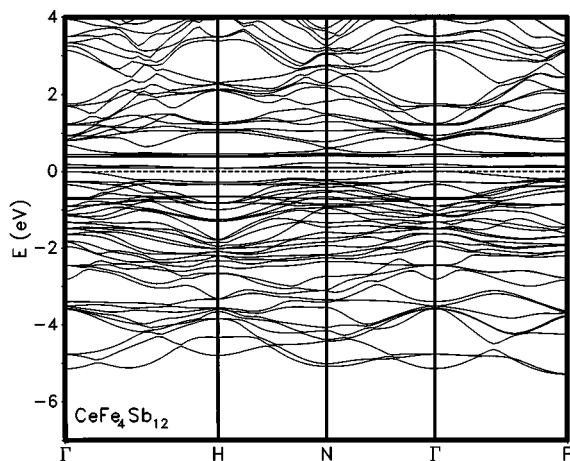

FIG. 2. The band structure of $CeFe_4Sb_{12}$ plotted in the same way as in Fig. 1.
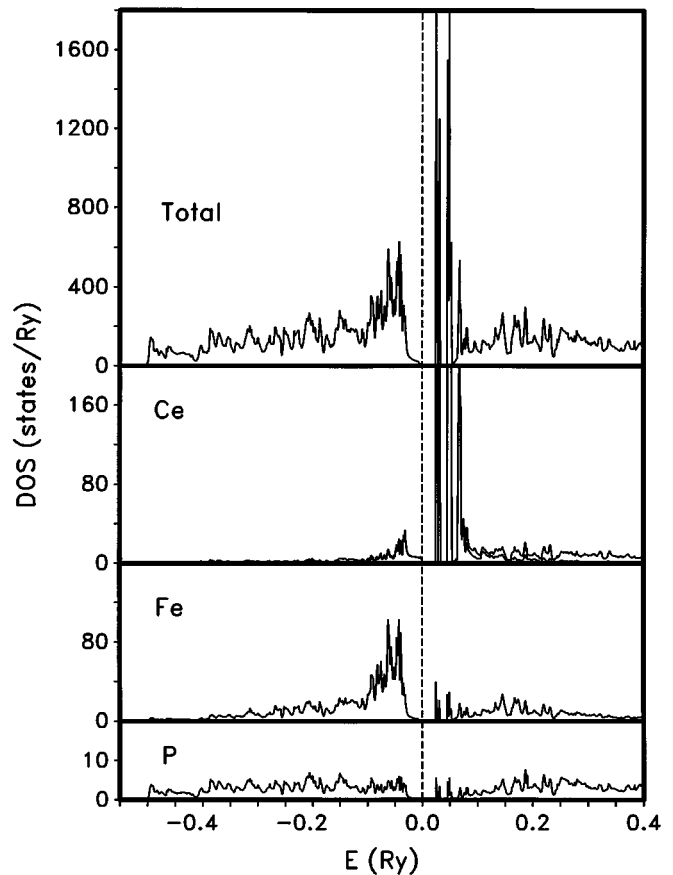

FIG. 3. The total and site projected density of states for $CeFe_4P_{12}$. The site projected DOS are per atom, and for the case of Ce the f part is shown also. The energy zero is at the VBM, which is indicated with a horizontal dashed line.

butions from all three at the P point with the largest coming from P $2p$. For the antimonide it is slightly more complicated since the $v4$ band crosses, or hybridizes with, other close lying bands, with a resulting distribution of the Ce $4f$ character among several bands when going away from the Γ point. It is interesting to note that this occupied "f band" is situated at the same energy distance from the lowest lying unoccupied f bands in the two compounds, 0.4 eV at Γ.

The hybridization of Ce $4f$ states with the surrounding valence states are also observable in the very flat lowest unoccupied bands. Although they are almost entirely of f character there are small contributions from Fe $3d$ and A p states, especially at the Γ and N points, which is reflected in the increased dispersion for some of the bands in those regions. This is maybe seen clearly for the seventh lowest conduction band ($c7$) of $CeFe_4Sb_{12}$ in Fig. 6, which is slightly split off from the other f bands and with strong parabolic maxima at these two symmetry points. This effect is even larger for $CeFe_4P_{12}$, where the corresponding band is above the energy range of Fig. 5. In Fig. 1, however, one can see this band as $c9$ 1.6 eV above VBM at Γ, and in the DOS of Fig. 3 it turns up as a third smaller f peak.

The $v1$ valence bands in Figs. 5 and 6 have effective masses 0.8 and 2.2 at their maxima at the Γ point for the phosphide and antimonide, respectively. However, the flat
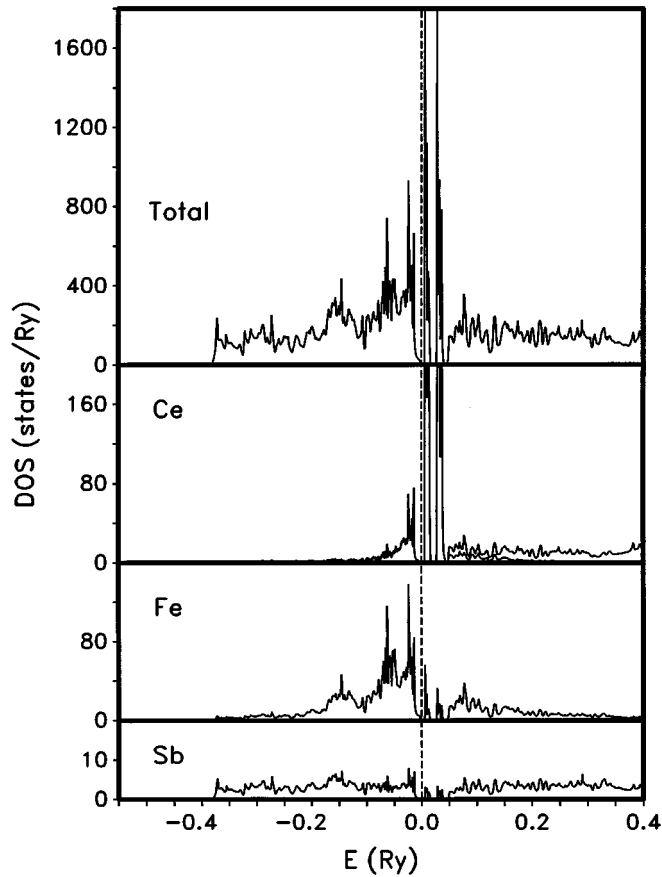
FIG. 4. As in Fig. 3 but for $CeFe_4Sb_{12}$.

conduction bands have larger masses, which have some un-certainty in the present calculation but are 10–20 at the band minima, which are slightly off Γ for $CeFe_4Sb_{12}$, and 6–8 slightly off N for $CeFe_4P_{12}$.
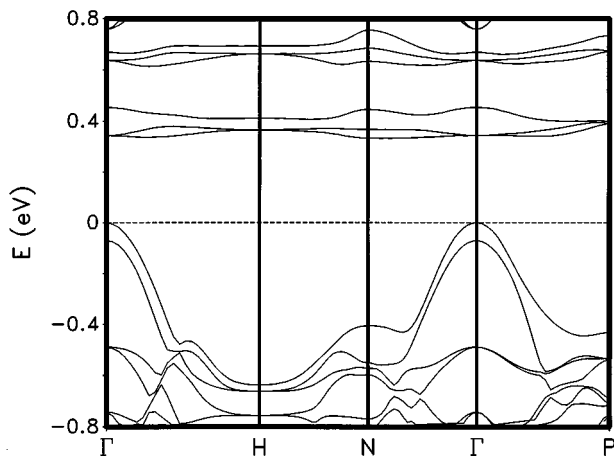

FIG. 5. The band structure of Fig. 1 for energies close to the Fermi level.
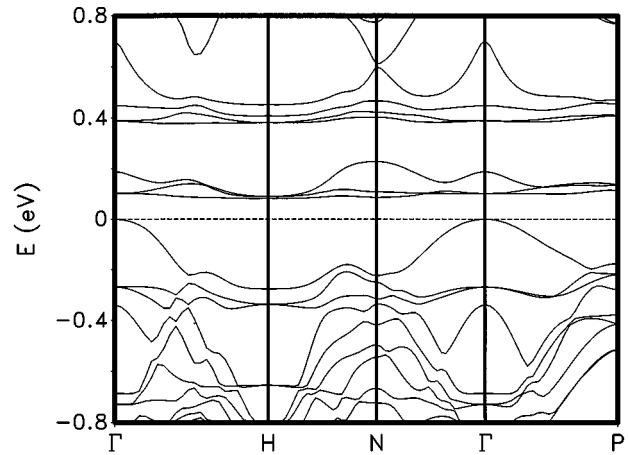

FIG. 6. The band structure of Fig. 2 for energies close to the Fermi level.

B. Ionicity of cerium

Although the concepts of valency or ionicity are very popular and useful concepts in discussions of electronic structure and bonding in solid state physics, they are some-what ill-defined due to the problem of attributing charge to a specific atom within a solid. A direct and naive way is to divide space into cells around each atom and attribute the integrated charge within the cell to that atom. However, this inevitably leads to ambiguities, because there is no obvious way of dividing space and since there always will be orbitals centered at one atom but extending into the neighboring cell and hence contributing to the charge of that atom.

As mentioned in the Introduction there are two views for the "valency" of cerium in the skutterudites. The difference between these two models actually regards the occupancy of the Ce $4f$ level; either it is unoccupied, f^0, or it has occu-pancy one, f^1. These two cases are usually referred to in the literature as tetravalent and trivalent, respectively (the actual average occupancy may, of course, be intermediate as well). Here we follow this convention, but would like to remind the reader that this concept of valency, although related to it, should not be confused with the ionicity of the cerium atom, which we will study independently in the following analysis. When discussing the orbital character of different band states in the preceding section, we used the common but ambigu-ous method of integrating charge within the muffin-tin sphere. This analysis has more meaning the more localized the atomic orbital is, and is expected to be quite reasonable for the Ce $4f$ states.

A more consistent way to determine ionicities is, however, to compare which kind of overlapping ionic charge densities are closest to the self-consistently calculated one. By calcu-lating the electronic structure from these non-self-consistent charge densities and comparing with the result of the self-consistent calculation one can see which ionic charges attrib-uted to the different atoms give the best result, and hence are the most realistic. The ionic charge densities were obtained from atomic calculations where the negative ions were sta-bilized with a circumscribing Watson sphere. In the calcula-tions presented here the extra electrons taken from cerium

TABLE I. One-electron energies, calculated from overlapping ionic charge densities with different choices of ionic charges and valence configurations for the cerium atoms in $CeFe_4P_{12}$, are compared to the full self-consistent calculation (Self-cons.). The excessive charge has been evenly distributed among the iron atoms. The energies are given for the lowest "f" valence band (see text) and the $4d_{5/2}$ core state and are given in Ry. The energy zero is at the average interstitial potential, the so-called muffin-tin zero.

Ionicity	Config.	ε_f	ε_{4d}
+4	f^0	-0.38	-8.08
+3.5	$f^{0.5}$	0.10	-7.56
+3	f^1	0.50	-7.07
+3	d^1	0.02	-7.66
+2.5	$d^{0.5}f^1$	0.64	-6.90
+2	d^1f^1	0.81	-6.76
+2	s^1f^1	0.62	-6.94
Self-cons.		0.72	-6.80

are evenly distributed among the iron atoms. Putting them on the phosphorous atoms instead only alters the results in minor details. The influence on the iron and phosphorous states is rather small since the cerium charge is redistributed among 4 or 12 atoms, respectively.

In Table I some results from different trial densities are compiled and compared to the result of the self-consistent calculation for the case of $CeFe_4P_{12}$. We have chosen to compare two quantities: the energy of a valence state at the Γ point and the energy of a cerium core state. As the valence state we take the lowest state at Γ with more than 30% Ce $4f$ character. This corresponds to the $v1$ state in Fig. 5. It is found that this one-electron energy level is very sensitive to the ionicities used and a bad trial density gives far from physical results. For instance, in the calculation from the trial density based on Ce^{4+} (i.e., f^0) all 14 $4f$ states become occupied, which indeed indicates a nonphysical density far from self-consistency. As representative for the Ce core we give the energies for the highest lying core state, $4d_{5/2}$.

From these results one can directly, and most importantly, deduce that in order to get decent energies cerium has to be trivalent, i.e., f^1. The worst results among those cases considered is actually found for the tetravalent case. This is, of course, in accordance with the discussion in the preceding section about the strong Ce $4f$ hybridization, where significant $4f$ character is found below the Fermi energy. In fact, if one integrates the f character inside the Ce muffin tin, one ends up with 1.0 electron for $CeFe_4P_{12}$ (a slightly larger value of 1.2 is obtained for $CeFe_4Sb_{12}$).

However, an even slightly better correspondence is achieved if the trivalent cerium is not "fully ionized," but there are between 0.5–1.0 additional valence electrons, primarily of $5d$ character. This is what one usually finds in this type of material — the bonding is usually not purely ionic but rather there is also a non-negligible contribution from covalent bonding. In this case both $4f$ and $5d$ states on cerium seems to be contributing to this.

Since both the $4f$ and the $5d$ wave functions are rather well localized, they contribute significantly to the 1.9 electrons found within the cerium muffin tin. This *a posteriori*

gives some significance to the latter as a measure of the ionicity in the present case, in spite of the criticism given above.

V. DISCUSSION

From the above analysis we conclude that cerium is trivalent in these compounds, and that the Ce $4f$ states are active in the bonding via the hybridization with the Fe $3d$ and A p orbitals. In fact, this hybridization is crucial for the formation of the band gaps around the Fermi levels, which are found in both compounds, $CeFe_4P_{12}$ and $CeFe_4Sb_{12}$, but which is not fully developed in the isovalent $CoSb_3$.[4] This is in accord with a parallel calculation for $LaFe_4P_{12}$ where the corresponding band gap is found 1 eV above the Fermi energy. In that compound the $4f$ states lie too high to contribute to gap formation and the magnitude of the gap is found to be a minute 0.06 eV, in comparison with the gap of the related $CeFe_4P_{12}$, i.e., 0.34 eV. Since the LDA tends to underestimate the intra-atomic correlation of Ce $4f$ electrons and hence overestimates the hybridization, one can expect that the calculated band gaps are overestimated rather than underestimated, which is otherwise the usual tendency in the LDA. This may explain the apparently metallic character of $CeFe_4Sb_{12}$ as determined by experiments.

The calculated band gaps are small, 0.34 and 0.10 eV, respectively, but the corresponding bands have large band masses. This is an unusual situation (most small gap semiconductors are also found to have low effective band masses) and arises because of the f electron hybridization.

As regards the thermoelectric properties, it was mentioned in the Introduction that there are three quantities which enter the figure of merit [Eq. (1)]. First, it has recently been found[12] that $CeFe_4Sb_{12}$ indeed has a low thermal conductivity, in accordance with our anticipation in the Introduction. Second, in the present study we have found that the two compounds are both semiconducting, with small band gaps but with large band masses of the lowest lying conduction bands. Although the calculated conduction bands are very flat they should not be so atomiclike as to prevent conduction. Hence it is predicted that n-type doping, for instance, alloying with cobalt at the iron sites, might lead to high Seebeck coefficients. This deserves to be further studied.

While $CeFe_4Sb_{12}$ is observed experimentally to be metallic, although with a small κ, both $CeFe_4P_{12}$ and $CeFe_4As_{12}$ are found to be semiconducting. The calculated band masses of the antimonide are larger than the phosphide and the masses of the arsenide are expected to be in between, as for instance seen in the trend of the magnitude of the band gap. This suggests that maybe the best candidate as a high performance thermoelectric material would be $CeFe_4As_{12}$.

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