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Electronic structure of the RBiPt compounds (R≡Y and Yb)

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Abstract

The electronic structure of the semiconducting YBiPt intermetallic compound is compared with the isostructural, but metallic, YbBiPt compound. The difference in the transport properties is found to be governed by the volume, since the smaller volume in YbBiPt results in broader Yb d and Pt d bands and a closing of the semiconducting gap. The closing of the gap in YbBiPt is partly a relativistic effect, since scalar relativistic calculations do not reproduce the metallic ground state, whereas fully relativistic (Dirac) calculations do. In the semiconducting YBiPt intermetallic compound the valence band is found to be dominated by the Pt d states and the conduction band by the Y d states.

1. Introduction

Recent studies [1] have shown a number of interesting properties of the RBiPt (R≡rare earth metal; Nd–Lu) series. The intermetallic compounds form in the AgAsMg structure, which can be viewed as three face-centred sublattices placed at (0, 0, 0), ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) and ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$) [1]. Most unusually, these systems are semiconductors or semimetals, with the exception of YbBiPt and LuBiPt [1]. The gap between the valence and the conduction electrons is further found to decrease monotonically across the series, until it disappears for YbBiPt, which is a metal (as is LuBiPt) [1]. All these compounds are trivalent with a chemically inert 4f shell; studies of YBiPt show the same type of behavior as for instance GdBiPt (a semiconductor with a similar gap and a similar lattice constant) [1]. As expected, there is a slight, but monotonic, contraction of the unit cell volume as the series is traversed, and it has been speculated that most of the physical properties of the RBiPt intermetallic compounds are governed by the volume [1]. The contraction of the unit cell is an effect of the well-known lanthanide contraction and represents therefore a change in volume of the rare earth atom (R) in the RBiPt compounds. More interestingly, YbBiPt has a measured electronic specific heat constant of 8 J mol^{-1} K^{-2}, and it has been suggested that this compound is a heavy-fermion system [1]. If this is true, the electronic specific heat constant is the largest of all heavy fermions [1].

We have been motivated to investigate the unusual trend in the electronic properties of the RBiPt intermetallic compounds as R goes from neodymium to ytterbium and lutetium [1]. For reason we have performed self-

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consistent electronic structure calculations of YbBiPt and YBiPt, in the AgAsMg structure. YBiPt is a representative of the semiconducting compounds, and YbBiPt is one of the two metallic compounds (LuBiPt is the other one) [1]. We shall here concentrate on the question of what determines the semiconductivity of the early RBiPt compounds and the closing of the gap for YbBiPt and LuBiPt. The possibility that YbBiPt is a heavy-fermion system is not investigated here.

2. Details of calculations

As mentioned, the crystal structure is the AgAsMg type, and the calculations were made for this structure and at the experimental volume for each compound. For YBiPt this corresponds to a lattice constant of 6.66 Å, and for YbBiPt to 6.60 Å. There are three atoms per cell, and it has been determined that the bismuth atoms occupy the (0, 0, 0) site [1]. The calculations were done using the fully relativistic linear muffin-tin orbital (LMTO) method [2–4]. The present code (which solves the Dirac equation of a crystal) was developed by Skriver *et al.* [5]. The calculations were done using the atomic sphere approximation (ASA) and the combined correction terms [6]. In order

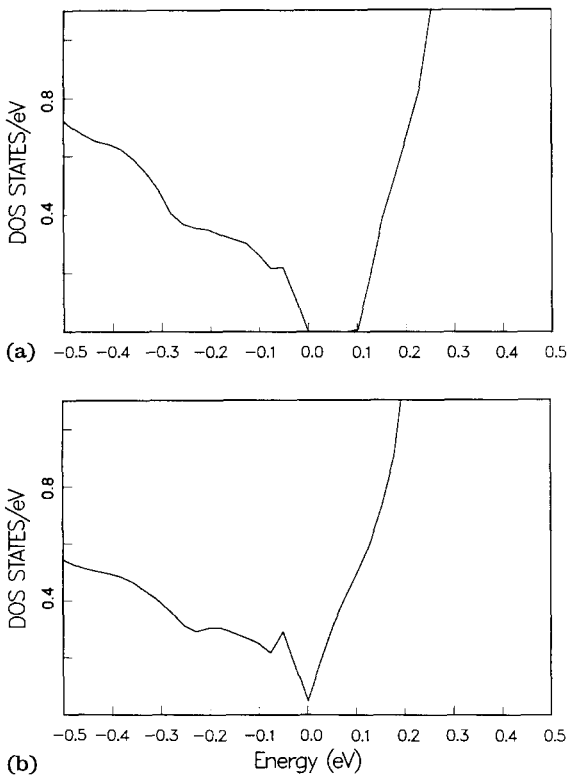

Fig. 1. Calculated total DOS for (a) YBiPt and (b) YbBiPt. E_F is at zero.

to make the overlap between different atoms as small as possible, we introduced one empty sphere at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. The self-consistent calculations were sampled at 240 k points in the irreducible wedge of the Brillouin zone. The von Barth–Hedin [7] parametrization of the local-density approximation (LDA) was used in constructing the exchange and correlation part of the potential. We used s, p and d partial waves for all atoms, and we treated the low-lying Bi 6s orbitals as band states.

3. Results

The calculated density of states (DOS) functions are shown in Figs. 1(a) and 1(b) for YBiPt and YbBiPt respectively. In order to illustrate the states around E_F more clearly, we show in Fig. 1 the total DOSs of YBiPt and YbBiPt over a small energy window around E_F. Figure 1 shows that YBiPt is semiconducting (the gap is found to be indirect) and YbBiPt is metallic. This is in agreement with experimental data [1]. The calculated gap in YBiPt is about 0.08 eV, whereas in YbBiPt the DOS at E_F is low but non-zero. For this latter compound, the Pt d and Yb d bands have become so broad that they overlap. For the discussion of the overall features of the electronic structure of the two compounds, we show their total and partial DOSs over

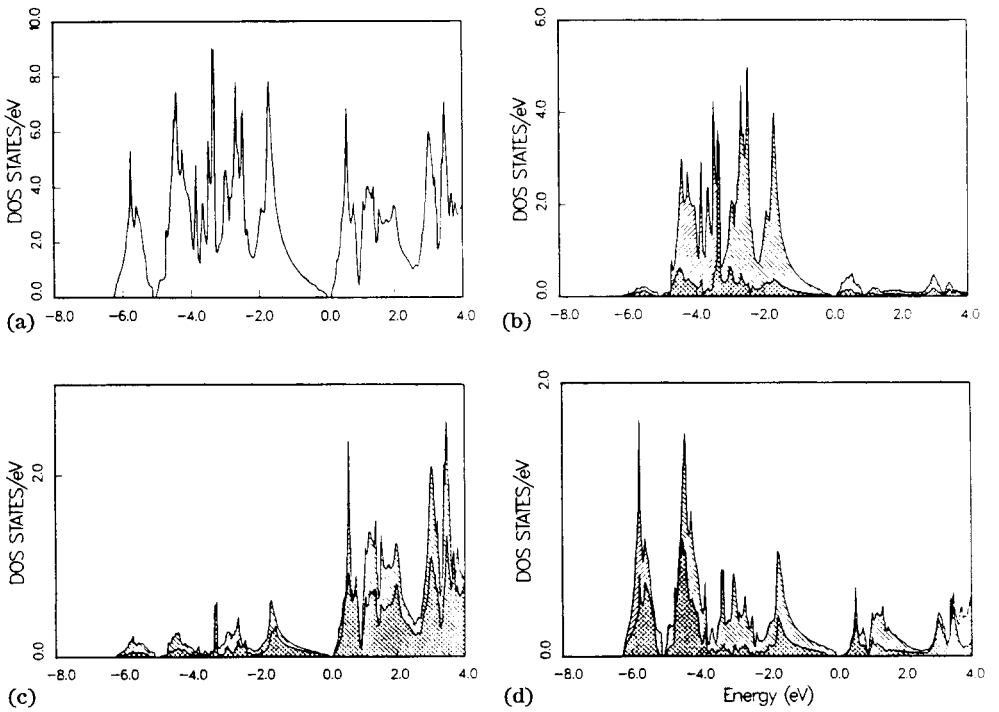

Fig. 2. Calculated DOS for YBiPt. (a) total DOS; (b) Pt d DOS; (c) Y d DOS; (d) Bi p DOS. E_F is at zero. Note the difference in scale for the various l-decomposed DOSs.

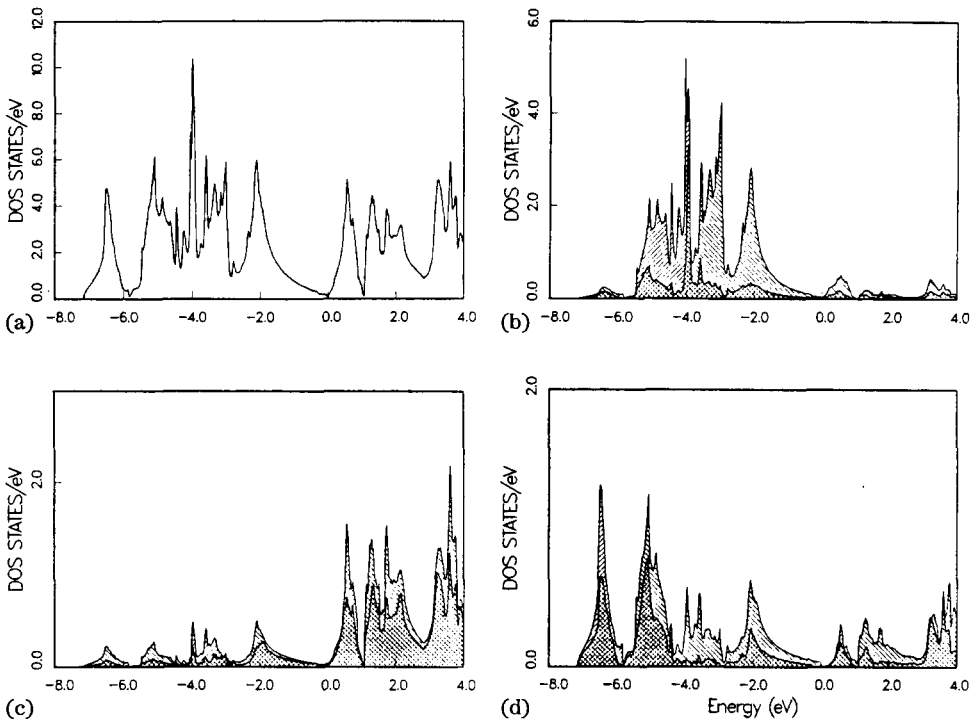

Fig. 3. Calculated DOS for YbBiPt: (a) total DOS; (b) Pt d DOS; (c) Yb d DOS; (d) Bi p DOS. E_F is at zero. Note the difference in scale for the various l-decomposed DOSs.

an energy range that includes all valence states in Figs. 2 and 3. The calculated DOS is shown for YBiPt in Fig. 2 and for YbBiPt in Fig. 3. The total DOS is displayed in Figs. 2(a) and 3(a), the Pt d partial DOS in Figs. 2(b) and 3(b), the R d partial DOS in Figs. 2(c) and 3(c), and the Bi p partial DOS in Figs. 2(d) and 3(d) (the Bi 6s band is about 13 eV below the Fermi level E_F and is not shown). Note that, since we have solved the Dirac equation for the crystal, the DOS can be decomposed to the different relativistic quantum numbers $j=l+\frac{1}{2}$ and $j=l-\frac{1}{2}$. The $j=l-\frac{1}{2}$ partial DOS is shown shaded from left to right, and the $j=l+\frac{1}{2}$ partial DOS is shaded from right to left, in Figs. 2 and 3. As seen in Figs. 2 and 3, the peak in the DOS centered at about 6 eV below E_F is dominated by the Bi p contribution. Furthermore, the Pt d partial DOS is mainly located between about -5 eV and E_F. The R d partial DOS has most weight at energies larger than E_F. Thus the conduction band of YBiPt has mostly Y d character, and the valence band mostly Pt d character. Furthermore, we find that the total occupied bandwidth is about 6.3 eV for YBiPt and about 7.2 eV for YbBiPt. Notice also that the spin–orbit coupling is fairly large for the Pt d states, about 1.4 eV. In fact we found it necessary to include all relativistic effects in the calculations, since scalar relativistic calculations (omitting the spin–orbit interaction) do not reproduce a metallic ground state in YbBiPt. The overall features are very similar for the two systems, but owing to the slightly smaller

volume the valence band (mainly Pt d) and conduction band (mainly R d) broaden so that in YbBiPt the gap has disappeared. The closing of the semiconducting gap in YbBiPt is therefore found to be governed by the slightly smaller volume, as suggested [1]. Furthermore, the DOS of YBiPt is quite similar to the DOS of ThRhSb and ThNiSb [8], which have a related crystal structure and are also semiconducting. However, the calculated gap of these latter compounds is larger than in YBiPt.

4. Conclusion

To conclude we have, using fully relativistic (Dirac) LMTO calculations based on LDA, reproduced the experimental finding that the early RBiPt compounds (YBiPt in the calculations) are semiconducting and YbBiPt is metallic. The closing of the semiconducting gap is found to be caused by the slightly smaller volume of YbBiPt [1], which results in slightly broader Pt d and Yb d bands. It is interesting that intermetallic compounds under specific circumstances become semiconducting or insulating; normally these types of system are good metals. It should be possible to make semiconductors with gaps that can be tuned either by pressure or by alloying amongst the rare earth component of these systems.

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