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Conduction bands in the filled skutterudites

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Abstract

Some filled skutterudite compounds have recently been found to exhibit very interesting properties: a metal–insulator transition ($\text{PrRu}_4\text{P}_{12}$), an antiferroquadrupole ordering and heavy-fermion behaviour under magnetic fields ($\text{PrFe}_4\text{P}_{12}$) and a new class of heavy-fermion superconductivity ($\text{PrOs}_4\text{Sb}_{12}$). Such varied and interesting physical properties are thought to reflect the Fermi surface properties. Band structure calculations have revealed the characteristics of the conduction bands. The main conduction band consisting of p orbitals of pnictogen surrounding the rare-earth ions has a nesting property, and strongly hybridizes with one of 4f electrons. One of the other conduction bands does not have mixing matrix elements with 4f electrons, resulting in the unique band structure in $\text{CeOs}_4\text{Sb}_{12}$.

1. Introduction

The filled skutterudite compounds with general formula RT_4X_{12} (R = light rare earth, Yb, Th and U; T = Fe, Ru and Os; X = P, As and Sb) have recently attracted much attention as improved thermoelectric materials [1] and because of the variety of their electrical and magnetic properties. Among them, $\text{PrRu}_4\text{P}_{12}$ shows a metal–insulator (MI) transition [2], $\text{PrFe}_4\text{P}_{12}$ undergoes an antiferroquadrupole ordering [3], then shows heavy-fermion behaviour under magnetic fields [4, 5]. Recently, a new class of heavy-fermion superconductivity has been reported in $\text{PrOs}_4\text{Sb}_{12}$ [6, 7]. Such interesting physical properties are thought to reflect Fermi surface properties and the $4f^2$ states under the crystal electric fields.

For the configuration $4f^2$ for the trivalent Pr ion, Hund's rule gives $L = 5$, $S = 1$ and $J = 4$. The ninefold degeneracy of $^3\text{H}_4$ is lifted under crystal electric fields. The rare-earth elements in the filled skutterudite compounds, which belong to space group no 204, T_h^5 , occupy the 2a site, which has the local symmetry $m\bar{3}$, T_h . The crystal electric field for T_h is slightly different from that for O_h and has been discussed [8]. In T_h , the $^3\text{H}_4$ term is split into the singlet Γ_1 , the doublet Γ_{23} and the two triplets Γ_4 . Γ_{23} is a non-Kramers doublet, like Γ_3 in O_h ,

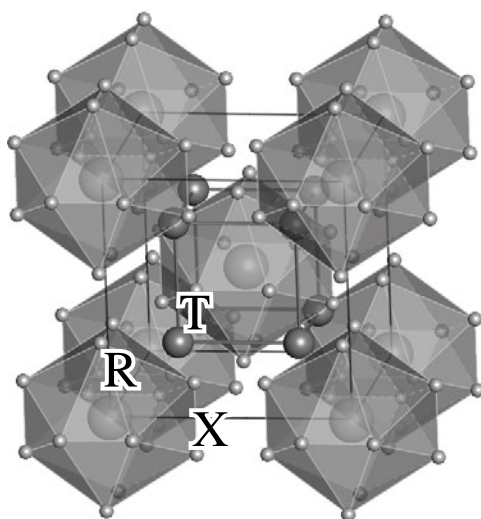


Figure 1. The crystal structure of the filled skutterudite RT_4X_{12} .

carrying quadrupole moments. It is argued that the ground state of $PrFe_4P_{12}$ and $PrOs_4Sb_{12}$ is built upon the non-Kramers doublet [6, 7, 9]. The simple point charge model, however, does not obtain the Γ_{23} ground state for a reasonable parameter region [10]. It does not rule out the Γ_{23} ground state, but a treatment beyond the simple point charge model should be introduced if the unusual physical properties result from the non-Kramers doublet.

Some of the Fermi surfaces have been investigated experimentally and theoretically. The main Fermi surface of $LaFe_4P_{12}$ has a good nesting property [11]. A better nesting property has been found in $LaRu_4P_{12}$ [12]. In fact, it has been suggested that such nesting could be the origin of the MI transition in $PrRu_4P_{12}$ [13, 14]. However, in $LaOs_4Sb_{12}$ and $PrOs_4Sb_{12}$, such nesting is suppressed [15–17]. The filled skutterudite compounds RT_4X_{12} are isoelectronic with the R^{3+} ion, but the different Fermi surfaces are obtained due to the hybridization between T d and X p electrons.

The purpose of this paper is to reveal the characteristics of those conduction bands, which should play a crucial role in the interesting physical properties.

2. Molecular orbitals in the skutterudite structure

The crystal structure of the filled skutterudite RT_4X_{12} is shown in figure 1. The molecular orbitals from the R f, T d and X_{12} p electrons are classified in table 1. 36 bands from X_{12} p hybridize with 20 T d bands, resulting in the 36 bonding and 20 non-bonding/antibonding bands. Therefore, the unfilled skutterudite compound T_4X_{12} (T = Co, Rh and Ir; X = P, As and Sb) becomes an insulator or a semi-metal [18]. The filled skutterudites, due to a lack of one d electron in the T site, should be one-hole systems with R^{3+} , or an insulator or a semi-metal with R^{4+} . The latter case corresponds to Ce or Th filled skutterudites [19].

From the FLAPW band structure calculations for La filled skutterudites, the conduction bands consist of two or three bands. In each case, the a_u band from X_{12} p crosses the Fermi level, so we call it the main conduction band. The a_g band, mainly from T d, forms a closed hole Fermi surface around the Γ point in $LaFe_4P_{12}$ [11], then gets a larger contribution from heavier pnictogens [20]. Only in the case of $LaRu_4P_{12}$ do e_u bands appear at the Fermi level

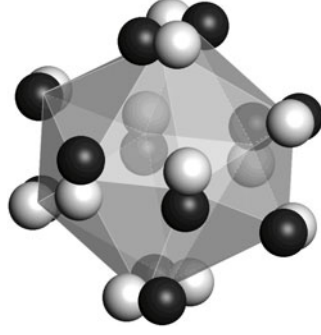


Figure 2. The X_{12} p molecular orbital of the main conduction band. A p orbital is located at each corner of the X_{12} icosahedron, in which a rare-earth ion is centred.

Table 1. The single-valued irreducible representations and the number of the molecular orbitals.

Mulliken	Bethe	Degeneracy	R f	T ₄ d	X_{12} p
a_g	Γ_1^+	1	0	1	2
a_u	Γ_1^-	1	1	0	1
e_g	Γ_{23}^+	2	0	2	2
e_u	Γ_{23}^-	2	0	0	1
t_g	Γ_4^+	3	0	5	4
t_u	Γ_4^-	3	2	0	5
Total			7	20	36

with the a_u band. The a_u band hybridizes well with Γ_5^- (Γ_7^- in the O_h) state of f electrons, while the a_g band never hybridizes with any f-electron orbital at the Γ point, as we will see later.

3. The nesting property of the main conduction band

The main conduction band consists of the unique X_{12} p molecular orbital, whose symmetry is a_u or xyz , as shown in figure 2. When one applies a simple tight-binding model to this molecular orbital, one obtains the energy

$$E = 8t \cos\left(k_x \frac{a}{2}\right) \cos\left(k_y \frac{a}{2}\right) \cos\left(k_z \frac{a}{2}\right), \quad (1)$$

where t (>0) is the two-centre integral (for the X_{12} p molecular orbitals) and a a lattice constant. The above energy function is of the same form as the simple s band for the BCC lattice [21], although $t = (ss\sigma)$ (<0) in the s-band case. The Fermi surface for the band in the half-filled case is a perfect cube (at the Γ point: a hole for $t > 0$ and an electron for $t < 0$), because $k_x = \pm\pi/a$, $k_y = \pm\pi/a$ or $k_z = \pm\pi/a$ gives $E = 0$. Then the Fermi surface exhibits perfect nesting with $q = (1, 0, 0)(2\pi/a)$ with an infinite peak in the density of states.

This nesting property persists even in the real system, as revealed by the band structure calculation for $\text{LaFe}_4\text{P}_{12}$ [11]. Experimentally, the superstructure with $q = (1, 0, 0)(2\pi/a)$ has been observed in $\text{PrFe}_4\text{P}_{12}$ [22] and $\text{PrRu}_4\text{P}_{12}$ [23] suggesting a structural phase transition. For $\text{PrRu}_4\text{P}_{12}$, an LDA + U band structure calculation shows that there exists only an a_u conduction band [13] and that the slight Γ_1 -type distortion of P ions leads to an insulator [14]. The nesting property may also cause the MI transition in $\text{SmRu}_4\text{P}_{12}$ [24]. In $\text{LaFe}_4\text{P}_{12}$ and $\text{PrFe}_4\text{P}_{12}$, the

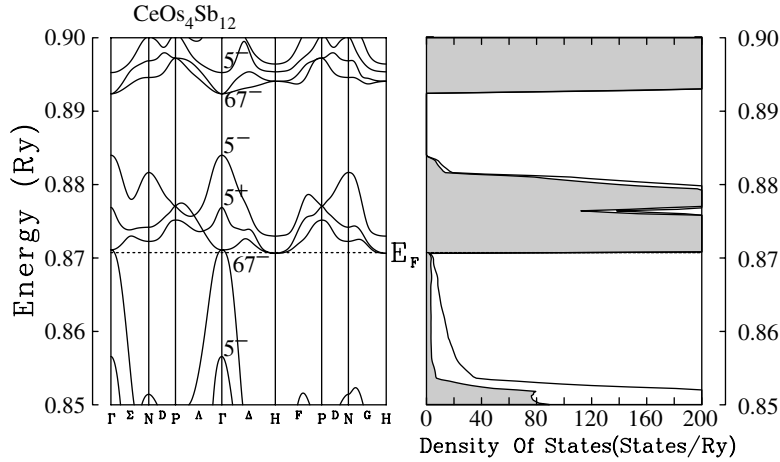


Figure 3. The calculated band structure (left) and the density of states (right) for $\text{CeOs}_4\text{Sb}_{12}$ in the vicinity of the Fermi level denoted by E_F . The shadowed part in the density of states shows the f component from Ce.

a_g band suppresses the nesting; however, the antiferroquadrupolar interaction cooperates with the $q = (1, 0, 0)(2\pi/a)$ ordering in $\text{PrFe}_4\text{P}_{12}$ [25, 26].

It is this nesting property that is the most unique and important characteristic of the filled skutterudites.

4. Hybridization between conduction bands and f electrons

In this section, the band structure of $\text{CeOs}_4\text{Sb}_{12}$ is shown, as a typical example, to assist in investigating the hybridization between the conduction bands and the f electrons.

The distance between R and X ranges from 3.01 Å for $\text{LaFe}_4\text{P}_{12}$ to 3.50 Å for $\text{LaOs}_4\text{Sb}_{12}$, above the range from 2.97 Å for CeP to 3.21 Å for CeSb. Therefore, the hybridization in one pair of R and X, i.e. the two-centre integral, is expected not to be so large. However, each rare-earth ion has 12 nearest-neighbour pnictogens, so the total hybridization could become quite large. Moreover, in the filled skutterudites, each pnictogen belongs to one rare-earth ion—then the mixing matrix elements for R 4f and X_{12} p electrons are independent of k in the BZ; i.e. the RX_{12} molecule behaves like one huge ion. Without spin-orbit coupling, f orbitals are split into one singlet (a_u) and two triplets (t_u), as shown in table 1. It follows that the a_u conduction band hybridizes well with Γ_5^- (Γ_6^- or Γ_7^- in O_h) for f electrons.

Figure 3 shows the band structure for $\text{CeOs}_4\text{Sb}_{12}$ near the Fermi level, calculated by using an LDA and FLAPW method. The $f_{j=5/2}$ bands split by the spin-orbit interaction lie just above the Fermi level and the Γ_5^- bands hybridize well with the $e_u(\Gamma_5^-)$ main conduction band around the Γ point. The hybridization is quite large even for large R–X distances. However, none of the f bands hybridize with the $e_g(\Gamma_5^+)$ conduction band at the Γ point, which is located in the middle of the $f_{j=5/2}$ bands. Therefore the hybridization does not produce an energy gap at the Fermi level, where the sudden upturn appears in the density of states from the unhybridized Γ_{67}^- f bands. The calculated γ -value is estimated to be around $20 \text{ mJ mol}^{-1} \text{ K}^{-2}$, although it is difficult to predict the precise value from such a very steep slope.

Experimentally, $\text{CeOs}_4\text{Sb}_{12}$ exhibits semiconducting behaviour with an energy gap $\Delta E/k_B \sim 10 \text{ K}$ and a large specific heat coefficient $\gamma \sim 92 \text{ mJ mol}^{-1} \text{ K}^{-2}$ [27]. Therefore,

this compound is often categorized as a ‘Kondo Insulator’. Recent pressure-induced change measurements, however, have shown that the low-temperature resistivity follows the hopping conducting mechanism [28]. The resistivity behaviour at low temperatures should be related to the unique band structure in figure 3, but for the present this remains an open question.

The LDA calculation for $\text{PrOs}_4\text{Sb}_{12}$ obtains a band structure similar to that in figure 3, with the Fermi level located in the upper energy region. The calculated Fermi surface does not explain the experimental dHvA measurement. Fermi surface study for $\text{LaOs}_4\text{Sb}_{12}$ and a LDA+ U calculation (the f-localized case) for $\text{PrOs}_4\text{Sb}_{12}$ strongly suggest that the $4f^2$ electrons are localized [15–17].

5. Summary

The conduction bands in the filled skutterudites are a_u (X p), a_g (T d) and e_u (X p) bands. The main a_u band of RT_4P_{12} shows good nesting (a large density of states) and hybridizes well with the $4f$ (Γ_5^-) band.

$\text{PrRu}_4\text{P}_{12}$ is an a_u system, which can exhibit perfect 3D nesting. The origin of the MI transition is the opening of a gap with Γ_1 -type P distortion. $\text{PrFe}_4\text{P}_{12}$ and $\text{LaFe}_4\text{P}_{12}$ have a_u and a_g conduction bands. The a_g band suppresses the nesting, but the antiferroquadrupolar ordering is coupled with the nesting in $\text{PrFe}_4\text{P}_{12}$. Although it is not shown in this paper, the hole Fermi surface around the N points appears in $\text{LaOs}_4\text{Sb}_{12}$ and $\text{PrOs}_4\text{Sb}_{12}$, added to a_u and a_g ; thus the nesting should be strongly suppressed. $\text{CeOs}_4\text{Sb}_{12}$ has a unique band structure. Even for a larger R–Sb distance in $\text{ROs}_4\text{Sb}_{12}$, the hybridization between R f electrons and the a_u band would be quite strong.

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