FLAPW electronic band structure of the filled skutterudite ThFe$_4$P$_{12}$

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Abstract

The electronic band structure is calculated for ThFe$_4$P$_{12}$ by using an FLAPW method. The result reveals that, between the filled valence bands and empty conduction bands, there is a direct band gap at the Γ point with gap width of 33.1 mRy (0.45 eV), contrary to experimental results.

Key words: ThFe$_4$P$_{12}$; electronic band structure; FLAPW method

1. Introduction

The family of compounds known as the filled skutterudites with a general formula RT$_4$X$_{12}$ (R = rare earth, Th and U; T = Fe, Ru and Os; X = P, As and Sb) has recently attracted much attention as improved thermoelectric materials[1] and for various interesting physical properties [2–4].

LaFe$_4$P$_{12}$ has been known to be the metal with one hole per formula unit (F.U.) [5]. Thus ThFe$_4$P$_{12}$ is expected to be semiconducting, since Th ion is believed to be tetravalent. However, the electric resistivity and infrared reflectance spectroscopy measurements have suggested that ThFe$_4$P$_{12}$ behaves like metal [6,7].

In this work, to clarify the electronic structure of ThFe$_4$P$_{12}$, we have carried out the band structure calculation.

2. Band Structure and Discussion

The space group of the crystal structure is Im$\bar{3}$ (T_h^5, #204). This is the body centered cubic but there is no Umklappung and fourfold symmetry axis [8].

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Band structure calculation is carried out by using an FLAPW method with the local density approximation for the exchange correlation potential. The details of the calculation are the same as those of previous calculation for LaFe$_4$P$_{12}$[5] except for followings. The lattice constant and internal parameters used in the calculation are the measured ones [9]. The LAPW basis functions are truncated at $|\mathbf{k} + \mathbf{G}_i| \leq 9.90 \times 2\pi/a$, corresponding to 2093 LAPW functions at the Γ point because the band gap width is sensitive to the number of LAPW functions in the binary skutterudite compounds [10].

The resultant band structure and the calculated density of states are shown in Fig. 1. The bands up to the 15th mainly originate from the P-s and Th-p states. The lowest band derived from the Th-p state is not shown but locates at -1.05 Ry. Note that all the bands have an even-fold degeneracy. In the bands above the 16th band, P-p components are uniformly distributed, but Fe-d components are strongly hybridized with P-p components. The bands up to the 51st-band are occupied by electrons while the bands above the 52nd-band are empty. Thus we denote that the top of the 51st-band is the Fermi level E_F. Between the 51st-band and 52nd-band, there is a direct gap of 33.1 mRy at the Γ point.

The symmetry label for the top of the 51st-band is
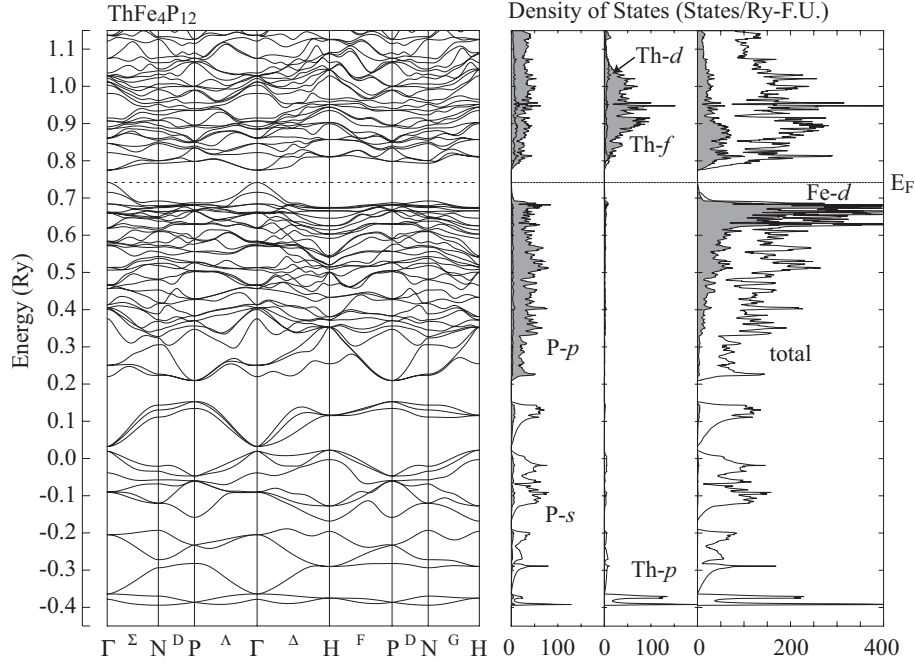
Fig. 1. The FLAPW energy band structure and calculated total and partial densities of states for $ThFe_4P_{12}$. Th-p, Th-d and Th-f mean the p, d and f components inside one Th MT sphere, respectively. Fe-d means the d component inside four Fe MT spheres. P-s and P-p mean the s and p components inside twelve P MT spheres, respectively.

Γ_5^- and for the bottom of the 52nd-band Γ_{67}^+ [8]. The charge distribution of these states is as follows; Th-f 16%, Fe-p 7% and P-p 29% for the Γ_5^- state and Th-d 4%, Fe-d 51% and P-s, p, d 2∼7 % for the Γ_{67}^+ state. Thus, around the Γ point, the top of the 51st-band is depressed by the Th-f bands via the hybridization between Th-f and P-p orbitals.

This overall feature is similar to that of previous calculation for $LaFe_4P_{12}$ [5]. However, in $LaFe_4P_{12}$, the gap width of direct gap at the Γ point is 5.7 mRy, about 1/6 of that in $ThFe_4P_{12}$. This is due to the more spatially localized La-$4f$ orbital relative to the Th-$5f$ orbital and the reduction of hybridization between La-f and P-p orbitals. Actually, the charge distribution of the Γ_5^- state is that La-f 11%, Fe-p 8% and P-p 34%.

In $CeFe_4P_{12}$, our calculated band gap width is 19.6 mRy (3,300 K), while the electric resistivity has shown an activation type with band gap of 1,500 K [11]. Thus we consider that the actual band gap of $ThFe_4P_{12}$ may be narrower than the calculated one but the band gap does not disappear. It is impossible for us to find any reason for discrepancy between the experimental and calculated results. Finally, it is noted that new interesting physical properties may be expected in Sb-based Th skutterudite compounds, because $CeRu_4Sb_{12}$ shows the non-Fermi liquid behavior [4].

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