First-principle calculations for electronic properties of PuX₃ (X=Rh, Pd, Pt)

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Abstract. Energy band structures of PuX₃ (X=Rh, Pd, and Pt) are investigated by a relativistic linear augmented-plane-wave method with the exchange-correlation potential in a local density approximation. It is found in common that the energy bands in the vicinity of the Fermi level are mainly due to the hybridization between Pu 5f and X d electrons.

1. Introduction

The transuranium compounds PuX₃ with the AuCu₃-type cubic crystal structure, where X means Rh, Pd, and Pt in the periodic table, show an interesting trend of 5f-electron characters. In the cerium and uranium compounds with this cubic type structure have studied a lot in experimental and theoretical ways. On the other hand, there are only few theoretical studies for these compounds.

These three compounds order antiferromagnetically with Néel temperature $T_N$ of 6.6, 2.4, and 40 K, respectively[1]. From the other magnetic susceptibility and heat capacity measurements on PuPd₃ indicate an antiferromagnetic transition at $T_N = 24.6 \pm 0.4$ K reported by M. D. Le et al.[2]. Photoelectron spectroscopy measurements indicate that the Pu f-states in PuPd₃ are well localized[3]. The lattice constant (PuRh₃: 4.008 Å, PuPd₃: 4.102 Å, PuPt₃: 4.013 Å) increases with increasing the atomic number of X (Rh=45, Pd=46, and Pt=78)[1].

In this paper, we research what the key issues are to construct the energy band structures around the Fermi energy for PuX₃ we attempt to unveil 5f electron properties purely originating from actinide atoms.

2. Method of Band Calculation

The calculations for the energy band structures are carried out by using the relativistic linear augmented-plane-wave (RLAPW) method[4]. All 5f electrons are assumed to be itinerant and the calculations are performed in the paramagnetic phase. To explain the electronic structure of PuPd₃, a LDA+U calculation might be needed because photoelectron spectroscopy measurements indicate that the Pu f-states are localized. We will discuss a LDA+U method applying to PuX₃ in a future paper. Note here that relativity should be taken into account, because of large atomic numbers of the constituent atoms. The spatial shape of the one-electron
potential is determined in the muffin-tin approximation, and we use the exchange and correlation potential in the local density approximation (LDA). The self-consistent calculation is carried out for the experimental lattice constant.

PuX$_3$ (X=Rh, Pd, and Pt) materials are categorized into the AuCu$_3$-type structure, which is characterized by the space group Pm3m. The 5$f$ electrons in PuX$_3$ are assumed to be itinerant. The iteration process for solving the Dirac one-electron equation starts with the crystal charge density that is constructed by superposing the relativistic atomic charge densities for neutral atoms Pu([Rn]5$f^5$6$d^1$7$s^2$), Rh([Kr]4$d^8$5$s^1$), Pd([Kr]4$d^{10}$), and Pt([Xe]5$d^9$6$s^1$), where [Rn], [Xe], and [Kr] symbolically indicate the closed electronic configuration for radon, xenon, and krypton, respectively. In the relativistic atomic calculation, the spin-orbit splitting in Pu 5$f$, and Rh 4$d$, Pd 4$d$, and Pt 5$d$ states are found to be 80 mRyd., 29 mRyd., 35 mRyd., and 98 mRyd., respectively. Note here that mRyd. denotes milli-Rydberg and 1 Ryd.=13.6 eV.

3. Results of Band Calculation
First let us discuss the calculated results for PuRh$_3$ and PuPd$_3$ as shown in Figure 1(a) and (b), in which we depict the energy band structure along the symmetry axes in the Brillouin zone in the energy region from 0 to 1.0 Ryd. The Fermi levels are found to be 0.760 Ryd., 0.711 Ryd., and 0.854 Ryd. for PuRh$_3$, PuPd$_3$, and PuPt$_3$, respectively. Concerning the energy band structure in the vicinity of $E_F$, we emphasize that there always occurs a hybridization between actinide 5$f$ and X $d$ states among three materials. Above $E_F$ near the $\Gamma$ point in PuPd$_3$, the flat 5$f$ bands split into two groups, corresponding to the total angular momentum $j=5/2$ (lower bands) and 7/2 (upper bands).

The calculated total density of states (DOS) for (a) PuPd$_3$ and (b) PuPt$_3$ are shown in Figure 2. The bold line, dashed line, and thin line indicate the total and partial DOS for $d$ and $f$ components, respectively. The 5$f$ bands are split into two subbands by the spin-orbit interaction.
interaction and due to the hybridization between Pu 5f and X d electrons, finite DOS always appear at the Fermi level. Since the Fermi level $E_F$ lies between the 5f subbands, the density of states has sharp peaks in the vicinity of $E_F$. The total density of states at $E_F$ are evaluated as $D(E_F) = 131.7$ states/Ryd.cell, 4.5 states/Ryd.cell, and 151.9 states/Ryd.cell in PuRh$_3$, PuPd$_3$, and PuPt$_3$, respectively. By using these values, the theoretical specific heat coefficient $\gamma_{\text{band}}$ are 22.8, 0.79, and 26.3 mJ/K$^2$.mol for PuRh$_3$, PuPd$_3$, and PuPt$_3$, respectively. The experimental $\gamma$ value for PuPd$_3$ is $71.1 \pm 0.1$ mJ/K$^2$.mol [2]. The d components in Rh, Pd, and Pt are distributed around the $E_F$.

In figure 1(a), four bands cross the $E_F$ so that PuRh$_3$ has four Fermi surfaces, three hole sheets in the 16th-18th bands and one electron sheet in the 19th band. Figure 3 shows (a) the hole sheets in the 17th, (b) 18th band, and (c) electron sheet in the 19th band for PuRh$_3$. The Fermi surface in the 16th band not shown here is a small cube-like hole sheet which is centered at the $\Gamma$ point. The 17th band has a rugged hole sheet centered at the $\Gamma$ point and a spherical small centered at the R point. Also, there are eight hole pockets lying on the $\Lambda$ axis and small pockets on general points in the Brillouin zone. The 18th band is composed of a small spherical hole sheet centered at the R point and a large hole sheet centered at the $\Gamma$ point, which

**Figure 2.** Density of states for (a) PuPd$_3$ and (b) PuPt$_3$. The total density of states, $d$ components in X atoms, and $f$ components in Pu atom are shown by the bold line, dashed line, and thin line, respectively. $E_F$ indicates the Fermi energy.

**Figure 3.** (a) The hole-Fermi surfaces in the 17th, (b) 18th bands, and (c) electron sheet in the 19th band for PuRh$_3$. The center point in each Brillouin zone is the $\Gamma$ in (a) and (b), and R point in (c).
Figure 4. (a) The electron Fermi surface in the 20th band for PuPd$_3$ centered at the R point. (b) The hole- and (c) electron Fermi surfaces in the 19th and 20th bands for PuPt$_3$ centered at the Γ and R points, respectively.

is multiply connected from zone to zone on each cubic plane. The 19th band has three dog’s bone-like electron sheets centered at the each M point and eight small electron pockets lying on the T axis.

The Fermi surfaces of PuPd$_3$ are composed of two kinds of electron sheets. The 19th band has a small spherical electron sheet centered at the R point and six tablet-like electron sheets lying on the T axis. The 20th band has twelve small pockets, as shown in Figure 4 (a). The total number of holes equal to that of electrons in these Fermi surface sheets, which represents that PuPd$_3$ is a compensated metal.

PuPt$_3$ has three Fermi surfaces. The Fermi surfaces in the 18th and 19th bands of PuPt$_3$ look like same shapes but the 18th bands has a smaller Fermi surface than that of 19th band shown in Figure 4 (b), which is constructed by a octahedron-like hole sheet centered at the Γ point and three small spherical hole sheets centered at the each X point. Figure 4 (c) shows the electron sheet in the 20th band of PuPt$_3$ centered at the R point. This Fermi surface is composed of twelve complicated electron sheets. The number of carries contained in these Fermi surface sheets are 0.016 holes, 0.114 holes, and 0.130 electrons in the 18th, 19th, and 20th bands, respectively. The total number of holes is equal to that of electrons, which represents that PuPt$_3$ is a compensated metal.

4. Discussion and Conclusion

We have applied the RLAPW method to the self-consistent calculation of the electronic structure for PuRh$_3$, PuPd$_3$, and PuPt$_3$ on the basis of the itinerant 5f electron picture by assuming the non-magnetic phase. We found that a strong hybridization between Pu 5f and X d states occurs in the vicinity of $E_F$, and this makes these Fermi surfaces complicated. To clarify the magnetism in PuX$_3$, the study in a hybridization between the 5f and d characters (f-d model) is now in progress.

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