Electronic structure with antiferro-electric-multipole ordering in PrRu$_4$P$_{12}$

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Abstract. Band structure calculations based on an LDA+U method have been performed in order to investigate an origin of the Metal-Insulator transition in PrRu$_4$P$_{12}$. The calculated results show that both antiferro multipole order and structural distortion help to form a pseudo-gap. The magnitude of the gap depends on the multipole arrangement in the crystal structure in non-metallic phase, which means it is necessary to take into account of the multipole ordering and the structural distortion simultaneously to understand an origin of the M-I transition.

1. Introduction

Filled skutterudite compounds with a general formula $RT_4X_{12}$ ($R =$ rare earths; $T =$ Fe, Ru, Os; $X =$ P, As, Sb) show novel physical properties [1]. Among them, PrRu$_4$P$_{12}$ undergoes Metal-Insulator transition (M-I transition) at $T_{MI} =$ 63K and has attracted much attention about an origin of the transition [2] [3]. PrRu$_4$P$_{12}$ does not show a magnetic anomaly [2] and Pr$^{3+}$ ion does not change its valence [4]. Meanwhile, the superstructure has been observed below $T_{MI}$ by electron diffraction measurement, which suggests the crystal structure changes from a body-centered cubic crystal structure (space group Im$ar{3}$) to simple cubic one (space group Pm$ar{3}$) [5]. Moreover, a band structure calculation with an LDA+U method has revealed one of the Fermi surface of PrRu$_4$P$_{12}$ in metallic phase has a good nesting property with $q =$ (1, 0, 0) [6]. Therefore, the formation of the Charge Density Wave (CDW) due to the lattice distortion was considered as a candidate of the origin at first [7]. However, the magnitude of distortion, which is expected from the band calculation including the lattice distortion with paramagnetic state [8], is ten times larger than that of the detected one. Although LaRu$_4$P$_{12}$ has the similar Fermi surface to that of PrRu$_4$P$_{12}$ [9], it does not undergo M-I transition but superconductive transition [10]. Moreover, an inelastic neutron scattering experiment for PrRu$_4$P$_{12}$ has revealed that, in the nonmetallic phase, both Crystal-Electric-Field (CEF) states on the two nonequivalent Pr-sites show peculiar temperature-dependence [11] [12]. From these result, it is considered that an origin of the M-I transition is not a simple CDW but an unconventional system where 4$f$ electrons play an important role. Meanwhile, theoretical studies have suggested that M-I transition and the peculiar temperature-dependence of CEF states can be explained by assuming the higher rank (over hexadeapole) antiferro-electric-multipole ordering [13][14]. The inelastic neutron scattering experiment shows the CEF ground states on the two nonequivalent Pr-sites are different from each other [11], which support the antiferro-electric-multipole ordering scenario. However, the ordered parameter has not been detected directly by any diffraction experiments.
There are two purposes in this study. The first is to investigate effects of the distortion of the crystal structure on the electronic structure by performing band structure calculation with the experimental lattice parameters in non-metallic phase. In the previous band calculation, only the P-distortions were considered [8]. However, the extended X-ray absorption fine structure measurements have revealed that, in the structure phase transition, not only P-positions but also Ru-positions displace [15]. So, in this study, we also consider the Ru-distortion. The second purpose is to reveal the electronic structure with the antiferro-electric-multipole ordering state to investigate the relation between multipole order and M-I transition.

2. research methods

2.1. density matrix in an LDA+U method

We use an LDA+U method to describe the localized 4\(f\) electrons in an open shell. In an LDA+U method, an orbital-dependent one particle potential can be written by using the density matrix \(\rho_{m,m'}^{\nu,\sigma}\), where \(m (m')\) and \(\sigma (\sigma')\) designate the orbital and spin, respectively [16] [17]. Here, the density matrix represents the occupied state of 4\(f\) electrons. Therefore, we can calculate the multiple moments of 4\(f\) electrons from the density matrix.

Although the density matrix should be determined self-consistently, there may be several substable solutions obtained with a local minimum energy, which are obtained depending on initial conditions. Therefore, the choice of the initial condition of the density matrix is important. To define the initial condition, we refer to 4\(f\) electrons occupying these one-electron states like \(\Gamma^1_{\text{12}}, \Gamma^2_{\text{25}}, \Gamma^3_{\text{36}}\) sextet and \(\Gamma^4_{\text{47}}, \Gamma^5_{\text{58}}, \Gamma^6_{\text{69}}\) octet due to the spin-orbital interaction, where \(j = \frac{5}{2}\) sextet is ground state. In \(\text{PrRu}_4\text{P}_{12}\), the site symmetry of Pr-site is \(T_h\). For the cubic system with \(T_h\), \(j = \frac{5}{2}\) sextet splits into one \(\Gamma^5_{\text{5}}\) doublet and one \(\Gamma^6_{\text{67}}\) quartet, while \(j = \frac{7}{2}\) octet splits into two \(\Gamma^5_{\text{5}}\) doublets and one \(\Gamma^6_{\text{67}}\) quartet [18], [19]. Here, it is considered that \(\text{Pr}^{3+}\) ion has two 4\(f\) electrons. In the density matrix picture, the 4\(f^2\) configuration is constituted by two 4\(f\) electrons occupying these one-electron states like \(j\)-\(j\) coupling scheme. In particular, the \(\Gamma^1_{\text{1}}\) singlet ground states can be constituted from \(\Gamma^5_{\text{5}}\) doublet. Then, we introduce the one-electron wave functions corresponding to \(\Gamma^5_{\text{5}}\) doublet. Under the \(T_h\) symmetry, the wave functions for a \(\Gamma^5_{\text{5}}\) doublet in \(j = \frac{5}{2}\) are determined uniquely, \(|\Gamma^5_{\text{5}}(j = \frac{5}{2})\rangle = \frac{1}{\sqrt{6}} \left(|j = \frac{5}{2}, j_z = \frac{5}{2}\rangle - \sqrt{\frac{5}{6}} |j = \frac{5}{2}, j_z = \frac{5}{2}\rangle\right)\). On the other hand, the wave functions for two \(\Gamma^5_{\text{5}}\) doublets in \(j = \frac{7}{2}\) are not determined uniquely. They are represented as liner combinations of \(|\Gamma^5_{\text{5}}^{(\text{1})}(j = \frac{7}{2})\rangle \equiv \sqrt{\frac{7}{12}} |j = \frac{7}{2}, j_z = \frac{1}{2}\rangle + \sqrt{\frac{5}{12}} |j = \frac{7}{2}, j_z = \frac{5}{2}\rangle\) and \(|\Gamma^5_{\text{5}}^{(\text{2})}(j = \frac{7}{2})\rangle \equiv \sqrt{\frac{3}{4}} \left(|j = \frac{7}{2}, j_z = \frac{5}{2}\rangle - \frac{1}{2} |j = \frac{7}{2}, j_z = \frac{1}{2}\rangle\right)\).

2.2. description of the antiferro-electric-multipole ordering

The results obtained by an LDA+U method strongly depend on initial conditions. Therefore, it is important to assume the appropriate initial conditions to describe the antiferro-electric-multipole ordering. In this section, we discuss how to define the initial conditions of the density matrix. Here, the crystal structure in non-metallic phase has two non-equivalent Pr-sites. In this paper, we define Pr-site which is closer to Ru-site as Pr1-site and further as Pr2-site.

First, we consider the initial condition for Pr1-site. According to an inelastic neutron scattering experiment, CEF ground state at Pr1-site is \(\Gamma^1_{\text{1}}(LS)\) singlet [12], where \((LS)\) means the CEF states based on the LS coupling scheme. Meanwhile, the density matrix corresponds to the \(j\)-\(j\) coupling scheme. In the \(j\)-\(j\) coupling scheme, \(\Gamma^1_{\text{1}}\) singlet can be constituted from the \(\Gamma^5_{\text{5}}(j = \frac{5}{2})\) doublet. Then, we assume \(|\Gamma^1_{\text{1}}^{(\text{A})}\rangle = |\Gamma^5_{\text{5}}(j = \frac{5}{2})\rangle \times |\Gamma^5_{\text{5}}(j = \frac{7}{2})\rangle\) singlet state as the initial state of the density matrix on Pr1-site. Here, we should notice that these \(\Gamma^1_{\text{1}}\) singlets based on \(LS\) coupling scheme and \(j\)-\(j\) coupling scheme have the different multipole moments.
In fact, the charge distribution with the $\Gamma_1^+(LS)$ single extend to the $(1,1,0)$ direction (Fig. 1 (a) Pr1) but that with $\Gamma_1^{+(A)}$ singlet state extends to $(1,1,1)$ directions (Fig. 1 (b) Pr1).

Next, we consider the initial condition for Pr2-site. According to an inelastic neutron scattering experiment, CEF ground state on Pr2-site is $\Gamma_4^{+(2)}(LS)$ triplet in the $LS$ coupling scheme [12]. Although $\Gamma_3^+$ triplet can be constituted in $j-j$ coupling scheme, it is difficult to perform the band structure calculation for an unstable system with such the degenerate 4$f^2$ systems. Therefore, to avoid difficulty in investigating an effect of the multipole moments, we assume the $\Gamma_1^+$ single on Pr2-site which has the similar multiple moments with that of $\Gamma_4^{+(2)}(LS)$ triplet. The charge distribution given from the $\Gamma_4^{+(2)}(LS)$ triplet extends to the $(1,0,0)$ direction (Fig. 1 (a) Pr2). Then we take the $|\Gamma_1^{+(B)}(j) = |\Gamma_5^{−(1)}(j = \frac{7}{2})\rangle \times |\Gamma_5^{−(1)}(j = \frac{7}{2})\rangle$ singlet state on Pr2-site which has the charge distribution extending to the $(1,0,0)$ direction (Fig. 1 (b) Pr2). It is noticed that the $\Gamma_5^{−(1)}(j = \frac{7}{2})$ doublet causes energy loss concerning spin-orbit splitting. However, the density matrixes strongly depend on initial conditions and the substable solutions of the density matrixes corresponding to the antiferro-electric-multipole ordering state can be expected.

Figure 1. (Color) Schematic charge distribution of 4$f$ electrons on Pr1 (green color) and Pr2-site (orange color) and Ru atom (red color). To emphasize that Pr1-site is closer to Ru-site than Pr2-site, the Ru-displacements are greatly enlarged. Charge distribution with (a) $\Gamma_1^+(LS)$ single on Pr1-site and $\Gamma_1^{+(2)}(LS)$ triplet on Pr2-site [12] and (b) $\Gamma_1^{+(A)}$ singlet on Pr1-site and $\Gamma_1^{+(B)}$ singlet on Pr2-site.

2.3. lattice parameters

We use experimental lattice parameter of PrRu$_4$P$_{12}$ in the calculations for non-metallic phase [15]. The space group is Pm$\overline{3}$m and the lattice constant $a=8.0360$ Å. The atomic positions of P in Pm$\overline{3}$m are $12j$-sites and $12k$-sites represented as $(0,u+\delta u_j,v+\delta v_j)$ and $(\frac{1}{2},\frac{1}{2}+u+\delta u_k,\frac{1}{2}+v+\delta v_k)$, respectively. Here, $u = 0.35760$ and $v = 0.14440$ are atomic positions of P in metallic phase and $\delta u_j, \delta v_j, \delta u_k, \delta v_k$ represent P-distoritions. Meanwhile, the atomic positions of Ru in Pm$\overline{3}$m are 8-$i$ sites represented as $(\frac{1}{2}+\delta, \frac{1}{2}+\delta, \frac{1}{2}+\delta)$ where $\delta$ is Ru-distortion. The extended X-ray absorption fine structure measurements have revealed that $\delta u_j = 0.00014, \delta v_j = -0.00018, \delta u_k = 0.00070, \delta v_k = -0.00154, \delta = 0.0007$ in non-metallic phase. Pr1-site closer to Ru-site and Pr2-site further from correspond to 1b-site ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and 1a-site (0,0,0), respectively.

2.4. Calculation condition

In an FLAPW method, the scalar relativistic effect is considered for all electrons and the spin-orbit interactions are included self-consistently for all valence electrons in a second variational procedure. The muffin-tin sphere radii are set as 0.2264$a$ for Pr1 and Pr2, 0.1352$a$ for Ru and 0.1388$a$ for P1 and P2. Here, $a$ is the lattice constant. Core electrons (Xe-core minus 5$p^6$ for Pr1 and Pr2, Kr-core minus 4$p^6$ for Ru) are calculated inside the MT sphere in each self-consistent step. 5$p^6$ electrons on Pr1 and Pr2, 4$p^6$ electrons on Ru are calculated as valence
Figure 2. Band structure of PrRu$_4$P$_{12}$ with paramagnetic state. (a) Experimental lattice parameters are used. (b) The Ru-displacements $\delta$ are assumed ten times larger than that of the experimental values. For other lattice parameters, experimental values are used.

electrons by using the second energy window. The LAPW basis functions are truncated at $|\mathbf{k} + \mathbf{G}_j| \leq 7.93(2\pi/a)$, corresponding to 2103 LAPW functions at the $\Gamma$ point. 176 sampling $k$ points in the irreducible BZ (2744 points in the BZ) are used. The LDA+$U$ method has the generalized form for the system in which the spin-orbit interaction is involved. $U$ is set as 0.4Ry.

3. Results

3.1. the electronic structure of PrRu$_4$P$_{12}$ with paramagnetic state

In this section, we investigate the electronic structure of PrRu$_4$P$_{12}$ with paramagnetic state. To describe the paramagnetic state, both of the density matrixes on Pr-sites are assumed $|\Gamma_5^+(\mathbf{J})\rangle = |\Gamma_5^-(j = \frac{5}{2})\rangle \times |\Gamma_5^-(j = \frac{5}{2})\rangle$ singlet state as the initial state, then determined self-consistently. The calculated band structure is shown in Fig. 2 (a). On the boundary of the Brillouin zone (Z, S, T axes), the degeneracy is lifted and pseudo-gap is formed, which indicate the lattice distortions help to form a band gap. However, the lattice distortion is not enough to make Fermi surface completely disappear. To reproduce the M-I transition, other driving forces are necessary. Secondly, we enlarge the Ru-displacements by ten times ($\delta = 0.0007 \rightarrow \delta = 0.0070$) and perform band structure calculation to investigate the effect of the Ru-displacements. The calculated band structure is shown in Fig. 2 (b). The enlargement of the Ru-displacements brings about the perfect insulation of PrRu$_4$P$_{12}$. This means the Ru-displacements strongly contribute to form the band gap.

3.2. the electronic structure of PrRu$_4$P$_{12}$ with antiferro-electric-multipole ordering state

In this section, we discuss the results of the band structure calculation with antiferro-electric-multipole ordering state. Following the discussion §2.2, we assume $|\Gamma_1^{+(A)}\rangle = |\Gamma_5^-(j = \frac{5}{2})\rangle \times \Gamma_5^+(j = \frac{5}{2})\rangle$ singlet state on Pr1-site and $|\Gamma_1^{+(B)}\rangle = |\Gamma_5^-(1)(j = \frac{7}{2})\rangle \times \Gamma_5^-(2)(j = \frac{7}{2})\rangle$ singlet state on Pr2-site as the initial states. First, we tried to determine the density matrixes self-consistently on Pr1 and Pr2-site. The charge distribution given from the calculated density matrixes are shown (Fig. 3 (a)). The charge distribution on Pr1-site is similar to that of $\Gamma_1^+(LS)$ singlet (Fig. 3 (a) Pr1). This is because that $\Gamma_5^-(1)(j = \frac{7}{2})$ doublet and $\Gamma_5^-(2)(j = \frac{7}{2})$ doublet are mixed into $\Gamma_5^+(j = \frac{5}{2})$ doublet to minimize the energy of the system. Meanwhile, the charge distribution on Pr2-site is similar to that of $\Gamma_1^+(LS)$ singlet, too (Fig. 3 (a) Pr2). Probably, this is due to the following reason. Compared to the energy gain of the antiferro-electric-multipole ordering, the spin-orbital splitting is too large and the stable solutions is not obtained. Thus, we could not find the substable solution which describes the antiferro-
Figure 3. The charge distributions of 4f-electrons on Pr1 and Pr2-site given from the density matrices. (a) The density matrices on Pr1 and Pr2-site are calculated self-consistently. (b) The density matrix on Pr1-site is calculated self-consistently with fixed $\Gamma_1^{+(B)}$ singlet on Pr2-site.

Figure 4. Band structure of PrRu$_4$P$_{12}$ with antiferro-electric-multipole ordering state. As the initial states, (a) $\Gamma_1^{+(A)}$ singlet on Pr1-site and $\Gamma_1^{+(B)}$ singlet on Pr2-site are assumed. (b) $\Gamma_1^{+(B)}$ singlet on Pr1-site and $\Gamma_1^{+(A)}$ singlet on Pr2-site are assumed.

electric-multipole ordering from present initial conditions. Then, in this paper, we show the band structure obtained when the density matrix on Pr2-site is fixed with $\Gamma_1^{+(B)}$ singlet and only the density matrix on Pr1-site is calculated self-consistently from $\Gamma_1^{+(A)}$ singlet as the initial state. In this case, the charge distributions on Pr1 and Pr2-site correspond to the $\Gamma_1^{(LS)}$ singlet and $\Gamma_1^{(2)}$ (LS) triplet, respectively (Fig. 3 (b)).

In Fig. 4 (a), the calculated band structure is shown. Compared with the paramagnetic state, the pseudo-gap is enlarged, which means the antiferro-electric-multipole ordering helps to form the band gap.

Moreover, to investigate whether the multiple arrangement in the crystal structure affects on the band gap, we exchanged the multipole moments on Pr1 with that on Pr2. Namely, we assume the density matrix on Pr1-site as $\Gamma_1^{+(B)}$ singlet and that on Pr2-site as $\Gamma_1^{+(A)}$ singlet as the initial state. In this calculation, the density matrix on Pr1-site is fixed with $\Gamma_1^{+(B)}$ singlet and only the density matrix on Pr2-site is calculated self-consistently. In Fig. 3 (b), the calculated band structure is shown. In this case, the pseudo-gap is closed, instead. Therefore, the band gap is strongly depend on the multipole arrangement in the crystal structure.

4. Conclusion
An origin of the M-I transition in PrRu$_4$P$_{12}$ has been studied by using the band structure calculation with an LDA+$U$ method. When only the lattice distortion including the Ru-distortions is considered, it is revealed that it causes the pseudo-gap. However, the Fermi surface does not disappear completely. Secondly, we tried to reveal the band structure of PrRu$_4$P$_{12}$ with the antiferro-electric-multipole ordering state. In order to avoid the difficulty describing
the localized triplet state in calculations, we replace the triplet state with the singlet state. Although we expected the substable solution corresponding to the antiferro-electric-multipole ordering state, such solution has not been found yet.

Here, we comment on the CEF states on Pr2-site. We replace the realistic $\Gamma_4^{+(2)}$ triplet with $\Gamma_1^{+(B)}$ singlet in this paper. Readers may have a question that, if we take into account the $\Gamma_4^{+(2)}$ triplet exactly, it affects the result or not. Indeed, the answer is yes. However, it is difficult to predict how large it affects near the fermi level. This is because $\Gamma_4^{+(2)}$ triplet can be constituted from the $\Gamma_6^+$ quartet in $j$-$j$ coupling and, when the quartet states are occupied by two electrons, the effect of LDA+$U$ corrections can not be described with simple pictures like increasing unoccupied states energy by $(1/2)U$ and decreasing occupied states energy by $(1/2)U$ [16].

Recently, Kong et al have shown that an LDA+$U$ method neglecting the spin-orbit interaction describes the M-I transition induce by orbital-ordering in PrRu$_4$P$_{12}$ [20]. This result can be understood that the energy loss, which is associated with replacing the triplet state with the singlet state, gets to be zero by neglecting the spin-orbit interaction and it helps the orbital-ordering realize. Therefore, we may find the substable solutions with following way. First, we find appropriate initial conditions of the LDA potential and the density matrix by performing the band structure calculation with zero spin-orbital interaction and an LDA+$U$ method. Then, we restore the magnitude of the spin-orbit interaction slowly. This method enable us to investigate the state of the antiferro-electric-multipole ordering. Also, there is another way to study the effect of the antiferro-electric-multipole ordering. We may introduce an artificial potential to reproduce the experimental antiferro-elecric-multipole ordering in self-consistent band structure calculation. These investigations are in progress now.

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