Theory of Metal-Insulator Transition in Praseodymium Skutterudite Compounds

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The metal-insulator transition of $PrRu_4P_{12}$ and the non-magnetic phase transition of $PrFe_4P_{12}$ are theoretically investigated. The nesting property of the Fermi surface with $\boldsymbol{q} = (1,0,0)$ is coupled, through Fe/Ru displacements, with anti-quadrupolar ordering at the phase transitions. Coupling between phonon modes of the displacements of the Fe/Ru ions and the Pr $4f^2$ ground state doublet leads to a symmetry lowering $(1,1,-2)$ type distortion of the Fe/Ru positions and a simultaneous splitting of the $4f^2$ doublet into eigenstates with quadrupole moments ± 8. The sign of both the distortion and the quadrupole moment alternate from site to site, resulting in anti-quadrupolar ordering. The difference between these two compounds stems from another small Fermi surface in $PrFe_4P_{12}$; the presence of this band would suppress the metal-insulator transition in $PrFe_4P_{12}$, even after the nesting effect is taken into account. Therefore, the low temperature state of $PrFe_4P_{12}$ is expected to remain metallic.

KEYWORDS: Skutterudite, metal-insulator transition, quadrupolar ordering, Fermi surface, LDA+U method

§1. Introduction

The filled skutterudite with a 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[1,2] and for the variety of the electrical and magnetic properties,[3–6] such as superconductivity, semiconductivity, ferromagnetism and antiferromagnetism.

Among them, $PrRu_4P_{12}$ shows a metal-insulator transition at $T_{\rm MI} = 60$K.[7,8] XANES study for $PrRu_4P_{12}$ indicates that the valency of Pr is $+3$.[9] The filled skutterudite compound PrT_4X_{12} is an uncompensated metal with Pr^{3+}, then it could not be an insulator within the same primitive unit cell.

$PrFe_4P_{12}$ undergoes a non-magnetic ordering at $T_{\rm A} = 6.5$K after showing the $-\log T$-dependence between 30 and 100 K in the resistivity,[6] then very heavy cyclotron masses larger than 80 m_0 have been found after meta-magnetic transition under applied magnetic field.[10,11] The specific heat coefficient γ reaches over 1 J/K$^2\cdot$mol.[12] Above the meta-magnetic transition, larger dHvA frequencies are observed, but the angular dependence is quite different with that of $LaFe_4P_{12}$. Below the meta-magnetic transition, there are only small frequencies observed indicating low carriers in the ordered state.

The filled skutterudites crystallizes in a unique body-centered cubic (BCC) structure of a space group $Im\bar{3}$ (T_h^5, # 204),[13] as shown in Fig. 1. The local symmetry at Pr site is T_h, and the crystal electric fields is slightly different from that of O_h: the singlet Γ_1 remains unchanged, the doublet Γ_{23} (within $4f^2, J=4$) in T_h is basically the same as Γ_3 in O_h and the two triplets Γ_4 in T_h correspond to Γ_4 and Γ_5 in O_h.[14] The doublet Γ_{23} has an electric quadrupole moment.

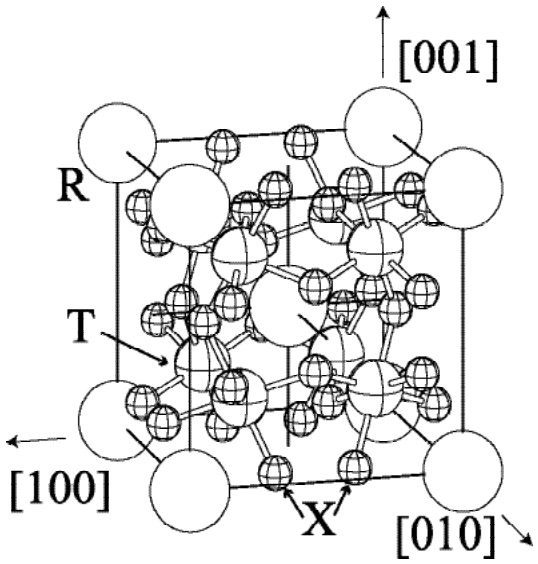

Fig.1. Crystal structure of the filled skutterudite RT_4X_{12}.

The specific heat measurement suggests the doublet ground state in $PrFe_4P_{12}$.[15] The ultrasonic study of softening of elastic constants of C_{11} and $(C_{11}-C_{12})/2$, also indicates the doublet Γ_{23} ground state.[16] In the case of $PrRu_4P_{12}$, the specific heat measurement could not specify the ground state.[17]

In the study of Fermi surface of $LaFe_4P_{12}$, it is emphasized that the nesting with $\boldsymbol{q} = (1,0,0)$ is likely in the skutterudite compounds, because the main Fermi surface is a distorted cube and the volume is almost a half of the BCC BZ with a sharp peak in the density of states at the Fermi level.[18]

Recently, structural phase transitions with $\boldsymbol{q}$ =

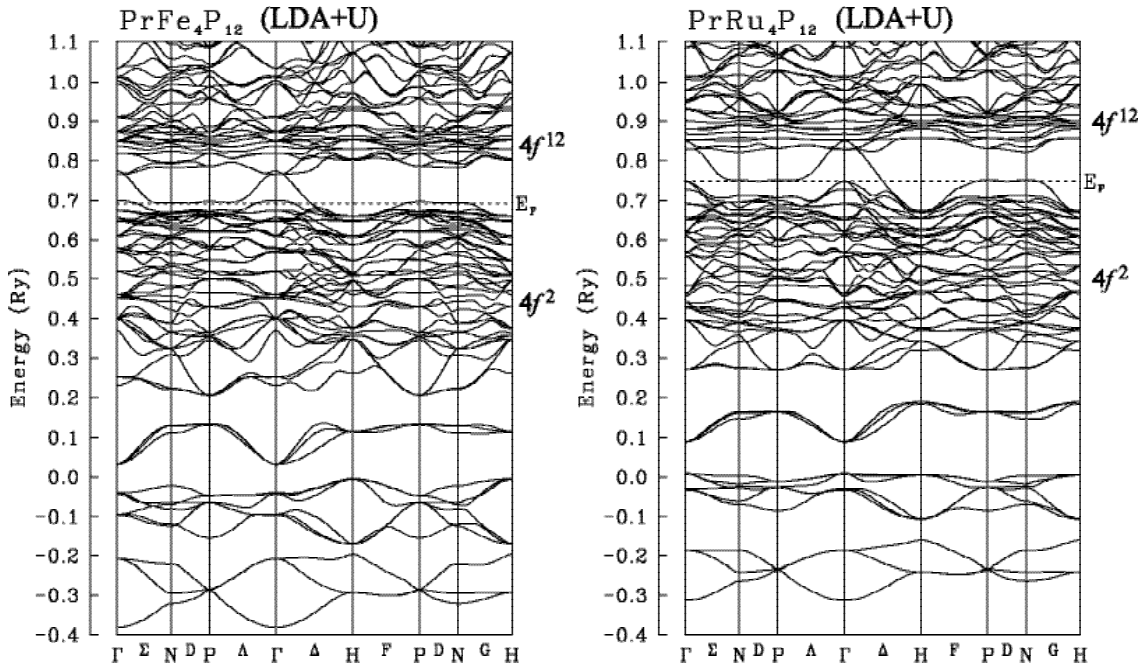

Fig. 2. Calculated bandstructures for $PrFe_4P_{12}$ (left) and $PrRu_4P_{12}$ (right). For both, the singlet $4f^2$ is assumed and U is set as 0.4 Ry. Thus the occupied $4f^2$ electrons are located around 0.5 Ry.

$(1,0,0)$ have been observed below $T_{\rm MI}$ and $T_{\rm A}$ in $PrRu_4P_{12}$[19] and $PrFe_4P_{12}$,[20] respectively. These experiments show that the unit cell becomes doubled from the body centered lattice (BCL) to the simple lattice (SL), then they could be a semi-metal or an insulator.

From the above experimental facts, it is natural to imagine that the structural phase transitions coincide with the anti-quadrupolar ordering in the both Pr filled skutterudites. In this paper, the phase transitions are investigated from the points of the bandstructure and the lifting degeneracy of $4f^2$ doublet coupled with the displacement of Fe/Ru ions.

§2. Fermi Surface Nesting

Although the Fermi surface for $LaFe_4P_{12}$ has the nesting property, Fermi surfaces may have different topology depending on the lattice constant etc., even in the iso-electronic R^{3+} filled skutterudite. Actually, Fermi surfaces of $LaRu_4Sb_{12}$ are very different from those of $LaFe_4P_{12}$ and have no nesting property with $\boldsymbol{q} = (1,0,0)$.[21] $PrRu_4Sb_{12}$ is a normal metal and the dHvA measurements show that the Fermi surfaces of $PrRu_4Sb_{12}$ are very similar to those of $LaRu_4Sb_{12}$,[21] probably due to the singlet ground states in Pr of $PrRu_4Sb_{12}$.[5]

The recently developed LDA+U method including the spin-orbit interaction can describe the localized $4f$ state within the band theory.[22] Then, the Fermi surfaces have been calculated for $PrFe_4P_{12}$, $PrRu_4P_{12}$ and $PrRu_4Sb_{12}$ under the space group $Im\bar{3}$ by using an FLAPW and the LDA+U method.[23] In the calculation, the occupied $4f$ states are determined self-consistently, but the initial configuration is assumed as the singlet ground states $(\Gamma_1 = \{\Gamma_7(j=5/2) \times \Gamma_7(j=5/2)\})$. Although the mixing with the other $4f$ electrons results in more than two occupied $4f$ electrons in the Pr-site, the occupied and unoccupied $4f$ states are located below and above the Fermi level, respectively, and then they can be considered to be well localized, as shown in Fig. 2. It means that neither the $4f$ electrons nor the slight difference of the atomic parameters significantly affects the Fermi surfaces within the singlet ground state.

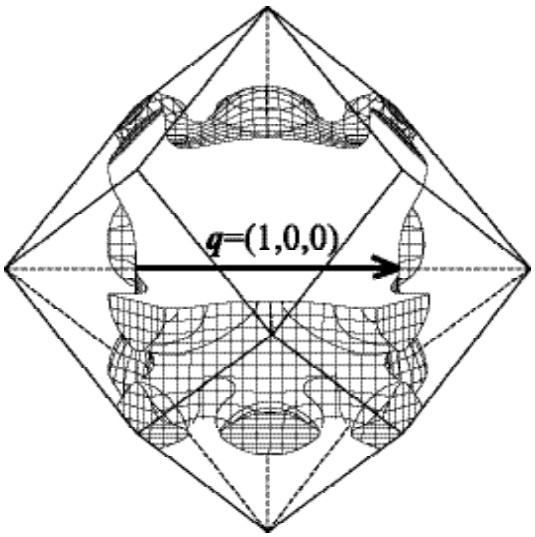

Fig. 3. Fermi surface of the bandstructure for $PrRu_4P_{12}$ (Fig. 1 right) and the nest vector $\boldsymbol{q} = (1,0,0)$. The volume of the Fermi surface is the half of the BCC BZ.

Figure 3 shows the calculated Fermi surface of $PrRu_4P_{12}$. The main Fermi surfaces of $PrRu_4P_{12}$ and $PrFe_4P_{12}$ (not shown) are thought to be a distorted cube, therefore the nesting with $\boldsymbol{q} = (1,0,0)$ is likely and follows the doubled unit cell from BCL to SL in the com-

pounds. Moreover, there is only one Fermi surface in $PrRu_4P_{12}$, so the nesting could wipe out the whole of the carriers leading to the metal-insulator transition. In $PrFe_4P_{12}$, there exists an extra hole-like band crossing the Fermi level; the presence of this band would suppress the metal-insulator transition in $PrFe_4P_{12}$, even after the nesting effect is taken into account.

Although the Fermi surface has such the nesting property, the slight modification in the conduction band is necessary to become an insulator. Otherwise, carriers will survive even in $PrRu_4P_{12}$. Both $LaRu_4P_{12}$ and $LaFe_4P_{12}$ have also such the nesting property, but undergo no structural phase transition. Therefore, the $4f^2$ state should play a crucial role for the structural phase transitions, where the conduction band is modified from Fig. 2. It should be noted that the main conduction band hybridises well with $4f$ electrons in $LaFe_4P_{12}$.[18)]

§3. Lattice Distortion Coupled to $4f^2$ doublet

From the X-ray diffraction measurement for $PrFe_4P_{12}$, mostly Fe ions are moved, though the atomic displacements remain undetermined.[20)] To elucidate the structural transition, we consider the phonon mode for the displacement of the nearest eight Fe/Ru ions ($8c$ site) coupled to the Pr Γ_3 $4f^2$ doublet ground state under O symmetry.[24)] Then it is found that the only possible displacements are $\pm(\delta,\delta,-2\delta)$, $\pm(\delta,-2\delta,\delta)$ and $\pm(-2\delta,\delta,\delta)$. The displacement of Fe/Ru ions lowers the crystal symmetry to cause two different crystallographic Pr sites, as shown in Fig. 4. The eigenstates at A-site and B-site are:

$$|\Gamma_3^-\rangle = \sqrt{1/2}|-2\rangle + \sqrt{1/2}|+2\rangle,$$
$$|\Gamma_3^+\rangle = \sqrt{7/24}|-4\rangle - \sqrt{5/12}|0\rangle + \sqrt{7/24}|+4\rangle,$$

respectively, and carry quadrupole moments of ∓ 8, where $|J_z\rangle$ stands for $|J{=}4, J_z\rangle$ state. It follows that the ground state will have anti-quadrupolar ordering. The volume of the ordered unit cell becomes doubled .

As seen in Fig. 4, P atoms lower the symmetry to Pmmm (#47, D_{2h}^1), then it should be noticed that the displacement of Fe/Ru ions will be a mixture of $(\delta,\delta,-2\delta)$ and $(\delta,-\delta,0)$ so that the anti-quadrupole moment will be reduced.

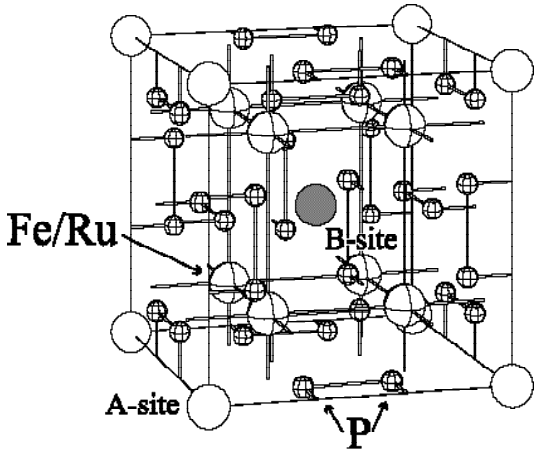

Fig. 4. The suggested displacement of Fe/Ru ions. Pr-site is split into two sites, then Pr ion on A- and B-sites has an opposite quadrupole moment.

Anyway, the anti-quadrupolar ordering accompany the structural phase transition with $\boldsymbol{q} = (1,0,0)$. It explains that the structural phase transition is suppressed in $LaFe_4P_{12}$ and $LaRu_4P_{12}$.

§4. Anti-Quadrupolar Ordered States in LDA+U Method

The nesting with $\boldsymbol{q} = (1,0,0)$ could stabilize the anti-quadruploar ordering through Fe/Ru displacements. The LDA+U calculation with the corresponding superlattice (Fig. 4), with anti-quadrupolar ordering would be expected to reveal the above situation clearly,

In a band calculation, $4f^2$ state should be described as the product of the one-particle wave functions. Here we take the states as follows:

$$|\Gamma_{23}^+\rangle = \{|\Gamma_8\kappa\rangle \times |\Gamma_8\nu\rangle\},$$
$$|\Gamma_{23}^-\rangle = \{|\Gamma_8\lambda\rangle \times |\Gamma_8\mu\rangle\},$$

where $|\Gamma_8 i\rangle$ are written with one-particle j=5/2 j_z eigenstates ($|j_z\rangle$) as

$$|\Gamma_8\kappa\rangle = \sqrt{5/6}|-5/2\rangle + \sqrt{1/6}|+3/2\rangle,$$
$$|\Gamma_8\lambda\rangle = |+1/2\rangle,$$
$$|\Gamma_8\mu\rangle = |-1/2\rangle,$$
$$|\Gamma_8\nu\rangle = \sqrt{5/6}|+5/2> + \sqrt{1/6}|-3/2\rangle.$$

We take Fe/Ru displacement of 1%, though it is reported about 0.02 % in $PrFe_4P_{12}$,[20)] to see clearly the effect of the displacement. The unit cell contains 34 atoms with the lower space group Pmmm (#47, D_{2h}^1), then the calculations are very time-consuming and still in progress. The result of the band calculations will be reported in another paper.

§5. Summary

Very recently, in $PrFe_4P_{12}$, a neutron diffraction experiment has revealed that superlattice reflection induced by external magnetic field in the low-temperature phase.[25)] This indicates an appearance of a field induced antiferromagnetic component in the anti-quadrupolar ordering. This might be the direct evidence of the anti-quadrupolar ordering in this compound. Therefore, the quadrupole moment should be responsible for the physical properties around the phase transition of $PrFe_4P_{12}$. For example, the $-\log T$ dependence in the resistivity should be ascribed to quadrupole Kondo effect.

We would mention that the metal-insulator transition reported in $SmRu_4P_{12}$.[26)] The successive transitions and the B-T phase diagram in $SmRu_4P_{12}$ look similar to those of anti-quadrupolar ordered CeB_6.[27)] Sm^{3+} ($4f^5$, $J = 5/2$) corresponds to Ce^{3+} ($4f^1$, $J = 5/2$), so it might be anti-quadrupolar ordering of $4f^5(J = 5/2)$. The ordering associated with $\boldsymbol{q} = (1,0,0)$ brings the metal-insulator transition also in this compounds, though the lattice distortion and the quadrupolar states might be

different from Pr skutterudites.

In conclusion, anti-quadrupolar ordering takes place below the transition temperature in $PrFe_4P_{12}$ and $PrRu_4P_{12}$. Driving force of the anti-quadrupolar ordering is the coupling with local distortion of Fe/Ru ions. The origin of the metal-insulator transition is the opening of a gap in the main conduction band which has a good nesting property. The detailed bandstructure calculations under the anti-quadrupolar ordering are now in progress and will be reported.

Acknowledgments

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