Orbital-ordering-induced metal–insulator transition in PrRu$_4$P$_{12}$

Shi Kong$^1$, Weiyi Zhang$^2$ and Daning Shi$^1$

$^1$ Department of Physics, Nanjing University of Aeronautics and Astronautics, Nanjing 210016, People’s Republic of China
$^2$ National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People’s Republic of China
E-mail: wyzhang@nju.edu.cn and shi@nuaa.edu.cn

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Abstract. The metal–insulator (M–I) transition in PrRu$_4$P$_{12}$ results neither from magnetic ordering nor from pure local crystal distortion, since small local distortion failed to produce the insulating phase at low temperature. In this paper, we suggest that the M–I transition at $T_{MI} = 62.3$ K might originate from the spontaneous orbital ordering of Pr$^{3+}$ f-electrons. The ‘ferro-orbital’ ordered state and the ‘antiferro-orbital’ ordered state correspond to the $Im\bar{3}$ state above and the $Pm\bar{3}$ state below the M–I transition. These orbital ordered states not only yield the right transport properties and correct crystal field states across the phase transition, but also can be checked by polarized synchrotron x-ray diffraction measurement. This study has been carried out within the framework of the ab initio local density approximation+U method.

The rare-earth-filled skutterudites with general formula ReT$_4$P$_{12}$ (Re = rare earth elements, T = Fe, Ru, Os; Pn = P, As, Sb) have received a great deal of attention recently owing to their rich physical phenomena and their improved thermoelectric properties [1]–[4]. This class of materials covers metals, semiconductors and superconductors depending on material compositions. Among them, the metal–insulator (M–I) transition in PrRu$_4$P$_{12}$ [1] has been intensively studied by both experimentalists [2]–[7] and theorists [8, 9], and the nature of this M–I transition is still seriously debated. It is now well established experimentally that PrRu$_4$P$_{12}$ undergoes an M–I transition at $T_{MI} = 62.3$ K [1]; specific heat measurement [4] clearly demonstrates the nonmagnetic nature of this transition. The M–I transition accompanies a crystallographic transformation [5, 6] from the space group $Im\bar{3}$ at high temperature to $Pm\bar{3}$ at low temperature, but the superlattice peak from the synchrotron x-ray and electron beam
diffraction spectra indicates that lattice distortion is very small [5]. The x-ray absorption near-edge spectra [5, 7] suggested that the valence of Pr ions is in the Pr$^{3+}$ state and the charge-ordering scenario is thus excluded; it was also revealed that relative bond length change \cite{10} is very small and of the order of 10$^{-4}$. The recent inelastic neutron scattering experiment \cite{11} showed that the crystal field state of Pr$^{3+}$ takes an alternating $\Gamma_1$ and one of a combination of $\Gamma_4^{(2)}$ states, but the local tetrahedron symmetry is not significantly distorted since no quadrupole moments are found in this compound. All these experimental data impose serious constraints on the theoretical model to unveil the physical mechanism involved in the M–I transition in PrRu$_4$P$_{12}$.

Prior to the inelastic neutron scattering measurements of bond lengths and crystal field states of Pr$^{3+}$ ions \cite{10, 11}, theoretical studies \cite{8, 9} mainly concentrated on the effect of local crystal distortion; their results showed that undistorted PrRu$_4$P$_{12}$ is characterized by a partial Fermi surface nesting property \cite{9}, which should be unstable under symmetry reduction; a comparative study between LaRu$_4$P$_{12}$ and PrRu$_4$P$_{12}$ compounds \cite{9} suggested that Pr$^{3+}$ f-electrons play an important role in the gap opening mechanism in PrRu$_4$P$_{12}$. Using group theoretical analysis, Curnoe \textit{et al} \cite{8} have considered all the coupling modes between $\Gamma_3$ doublet states of Pr$^{3+}$ ions and corresponding lattice distortion modes. The two types of lattice distortion modes involve Ru and P atoms; the (1,1,1) distortion mode preserves the local tetrahedron symmetry, whereas the \{(-2, 1, 1); (1, -2, 1), (1, 1, -2)\} do not and induce the quadrupole moment. The band structure calculations with both lattice distortion modes do yield the complete band gap across the whole Fermi surface if the lattice distortion is large enough, but the required lattice distortion amplitude is an order of magnitude larger than those measured in x-ray and polarized neutron diffraction experiments \cite{10}. It should also be mentioned that the (1,1,1) distortion mode is accompanied by a certain degree of charge ordering, whereas the second type is associated with a neighboring antiferro-quadrupole ordering; both phenomena are not observed in experiments.

Recently, the inelastic neutron scattering experiment \cite{10, 11} provided further insights into this mysterious M–I transition in PrRu$_4$P$_{12}$. By measuring the induced magnetic moments of Pr$^{3+}$, Iwasa \textit{et al} \cite{11} were able to deduce the crystal field states of Pr$^{3+}$. They showed that the crystal field states correspond to the alternately ordered $\Gamma_1$ singlet and low-lying $\Gamma_4^{(2)}$ triplet first excited states rather than the $\Gamma_3$ doublet states studied by Curnoe \textit{et al} \cite{8}. They also found that the lattice distortion amplitude is of the order of 10$^{-4}$ and an order of magnitude smaller than those used in \cite{8}. In fact, for such a small lattice distortion, a metal rather than an insulator was predicted in the band structures calculated by Curnoe \textit{et al} \cite{8}. Very recently, a phenomenological theory proposed \cite{12} that the nearest-neighbor antiferro-hexadecapole ordering may be responsible for the gap creation, but the hexadecapole moment was not detected in the resonant x-ray scattering \cite{13}; instead, different electronic states of Pr$^{3+}$ are found.

Thus the mechanism concerning the interesting M–I transition in PrRu$_4$P$_{12}$ is still an unsettled problem and further study of this issue is highly desirable. In view of the inelastic neutron scattering experiment that showed that different crystal field states appear for the Pr$^{3+}$ ions at the centers and at the corners, orbital ordering of Pr$^{3+}$ f-electrons must play an important role \cite{13}. Motivated by the orbital-ordering configuration in undoped LaMnO$_3$ \cite{14} where the neighboring $e_g$ electron of Mn$^{3+}$ ions takes alternately $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ orbitals, we have investigated a similar orbital-ordering phenomena in the PrRu$_4$P$_{12}$ compound at low temperature. To see how different orbital ordering affects the electronic band structures, a comparative study is made for the ‘ferro-orbital’ ordered state (local orbital $z$-axes of
Pr\textsuperscript{3+} f-electrons are all taken along the c-axis) and the ‘antiferro-orbital’ ordered state (local orbital z-axes of Pr\textsuperscript{3+} f-electrons are taken alternately along the a- and b-axes). The present study shows that the spontaneous ‘antiferro-orbital’ ordered state yields consistently lower total energy than the ‘ferro-orbital’ ordered state and offers a better candidate for the low-temperature ground state. This state is an insulator and has a band gap with a size similar to that observed in optical spectroscopy\cite{15}. What is more important is that the crystal field states of neighboring Pr\textsuperscript{3+} ions take different orbital states, which resemble the \( \Gamma_1 \) and \( \Gamma_1^{(2)} \) states concluded from the inelastic neutron scattering experiment\cite{11}. The present study suggests that the M–I transition thus takes place between the ‘ferro-orbital’ ordered state above the transition temperature and the ‘antiferro-orbital’ ordered state below the transition temperature.

The band structure calculation is carried out within the framework of the local density approximation+U method; we use the highly accurate WIEN2K package\cite{16, 17}, which implements the linear augmented plane wave (LAPW) method with local orbitals. A similar calculation is also performed with the spin–orbit interaction, but no significant changes are found. We used the experimentally determined crystal structure with space group \( \text{Im}3 \); the lattice parameter is \( a = 8.0424 \) Å. In this method, the wavefunctions are expanded in spherical harmonics inside nonoverlapping atomic spheres of radius \( R_{MT} \) and in plane waves in the interstitial region. In the calculation, we have chosen \( R_{MT} \) of 2.5, 2.34 and 2.07 au for Pr, Ru and P, respectively. The Ewald cutoff radius is \( R_{MT} K_{\text{max}} = 7 \); the maximum \( l \) for the expansion of the wavefunction in spherical harmonics inside the spheres was taken to be \( l_{\text{max}} = 10 \). The total number of k-points is 512 in the whole Brillouin zone (34 k-points in the irreducible wedge of the Brillouin zone in the \( \text{Im}3 \) phase). Although Pr\textsuperscript{3+} has net magnetic moments due to the weak crystal-field-splitting, no long-range magnetic ordering is observed in the experiments. Furthermore, the M–I transition in PrRu\textsubscript{4}P\textsubscript{12} does not change with external magnetic field and is of nonmagnetic origin; thus we concentrate on the paramagnetic states in this paper as was assumed in\cite{8}. To simulate the on-site short-range Coulomb interaction in the transition metal and rare earth elements, a value \( U_{\text{eff}} = 0.4 \) Ryd (\( U = 0.5 \) Ryd and \( J_H = 0.1 \) Ryd)\cite{8} is used for both Pr f-electrons and Ru d-electrons. To test the sensitivity of our results to the on-site effective Coulomb repulsion, somewhat larger and smaller values of \( U_{\text{eff}} \) are also used for Pr f-electrons only and a zero value is used for Ru d-electrons; our conclusion still holds as long as sizeable \( U \) is present at the Pr\textsuperscript{3+} f-electrons. The electronic correlation on Ru ions does not play a significant role though a finite \( U \) does favor the Fermi surface nesting feature. Figure 1 illustrates the total density of states (TDOS) and partial densities of states (PDOS) of the ‘ferro-orbital’ ordered state with space group \( \text{Im}3 \); the result is consistent with the previous calculation done by Curnoe et al\cite{8} and corresponds to a metallic state. The energy of this state is \( -125 749.2989 \) Ryd for the double cell. There is a sharp peak just around the Fermi energy (\( E_F \equiv 0 \)), which signifies the nesting property of the Fermi surface as shown in figure 2.

As is well known, the perfect Fermi surface nesting favors symmetry breaking under the charge, spin or orbital ordering. Since this M–I transition is of a nonmagnetic nature\cite{4, 18}, the valence state of Pr atoms always stays at Pr\textsuperscript{3+} both above and below the transition\cite{1, 3}; the bond-length changes during the transition are small and of the order of 10\textsuperscript{-4}\cite{10}. Therefore, the low-temperature insulating state most probably results from the spontaneous orbital ordering among neighboring Pr\textsuperscript{3+} ions\cite{19}. To simulate the spontaneous orbital ordering, we rotate the nearest-neighbor local orbital z-axes of Pr\textsuperscript{3+} to the a- and b-axes, respectively. Such an orbital ordering only lowers the crystallographic symmetry from space group \( \text{Im}3 \) to \( \text{Pm}3 \), but the average scattering factors of two neighboring Pr\textsuperscript{3+} ions may not be distinguished from the...
unpolarized synchrotron x-ray diffraction. In reality, together with the orbital ordering, bond lengths as well as bond angles may adjust accordingly, but they can be very small; that is why the superlattice peak observed is so weak. To check whether such a spontaneous orbital ordering does take place, the stability of the orbital-ordered structure has to be analyzed. We have computed the electronic structure for such an orbital ordering; the TDOS as well as PDOS are presented in figure 3. These results show that symmetry breaking does create a band gap in the presence of orbital ordering; the peak at the Fermi energy in the TDOS under the $Im3$ symmetry gets split, and a gap with a size of 0.1 eV emerges. Furthermore, this ‘antiferro-orbital’ ordered state not only possesses a band gap, but also its energy is

Figure 1. The densities of states of the ‘ferro-orbital’ ordered state ($Im3$ group). The solid, dotted, dashed and dashed–dotted lines represent TDOS and PDOS for Pr-f, Ru-d and P. The Fermi energy is set as the energy reference point.

Figure 2. The Fermi surface of the ‘ferro-orbital’ ordered state ($Im3$ group).
Figure 3. The densities of states of the ‘antiferro-orbital’ ordered state ($Pm3$ group). The lines are the same as in figure 1.

As was pointed out in the inelastic neutron scattering experiment [11], the metallic state above and insulating state below $T_{MI} = 62.3$ K differ in their crystal field states. While both Pr$^{3+}$ ions are in $\Gamma_1$ singlet state above the transition, Pr$^{3+}$ ions take alternately $\Gamma_1$ state and a linear combination of $\Gamma_4^{(2)}$ triplet states. It would be interesting to see whether the ‘ferro-orbital’ ordered state and the ‘antiferro-orbital’ ordered state yield the experimentally determined crystal field states. In the absence of spin–orbit coupling the f-electron in a tetrahedron surrounding is decomposed into one singlet ($f_{xyz}$) and two triplet states ($f_{x^2}$, $f_{y^2}$, $f_{z^2}$; $f_{x^2-y^2}$, $f_{y^2-x^2}$, $f_{z^2-x^2-y^2}$). From the band structures and eigen-wavefunctions, electronic density distribution in space can be constructed for various energy windows of orbitals; the typical distribution pattern for Pr$^{3+}$ f-electrons in the ‘ferro-orbital’ ordered state is plotted in figure 4. The cube-like shapes in the center and at the corners represent the Pr$^{3+}$ ions, whereas the sphere-like shapes in-between are Ru ions. It is clear that the f-electrons of all Pr$^{3+}$ ions are in the $f_{xyz}$ singlet state, which is in agreement with the observation of the inelastic neutron scattering experiment [11]. For the low-symmetry $Pm3$ state below the transition, a similar distribution pattern is shown in figure 5. One sees that the electronic distribution patterns for Ru atoms are essentially the same as those in the $Im3$ structure; the f-electron shape of Pr$^{3+}$ ions at the corners also remains unchanged. The most striking difference takes place at the central Pr$^{3+}$ ions, which differ from those at the corners. A detailed analysis suggests that the electronic distribution of Pr$^{3+}$ at the center is a linear combination of $f_{x^3}$, $f_{y^3}$ and $f_{z^3}$. Evidently, the rotations of local orbital z-axes to the a- and b-axes not only lift the degeneracy of these triplet states, but also its lowest crystal field state has strong coupling with the $f_{xyz}$ at the corners via the intermediate p-electron of P. As a result, the crystal symmetry reduces from the original space group $Im3$ to $Pm3$; the doubling of the unit cell causes band folding and creates a band gap.

In conclusion, the M–I transition in the PrRu$_4$P$_{12}$ compound may stem from the orbital degrees of Pr$^{3+}$ f-electrons. The properties of the ‘ferro-orbital’ ordered state and the ‘antiferro-orbital’ ordered state are consistent with the $Im3$ state above and $Pm3$ state below.
Figure 4. The valence electron distribution of ‘ferro-orbital’ ordered state (Im3 group). The cube-like shapes in the center and at the corners stand for the Pr$^{3+}$ ions and are enlarged for clarity, whereas sphere-like shapes in-between stand for Ru ions.

Figure 5. The valence electron distribution of ‘antiferro-orbital’ ordered state (Pm3 group). Those in the center and at the corners stand for the Pr$^{3+}$ ions and are enlarged for clarity, whereas sphere-like shapes in-between stand for Ru ions.

the M–I transition. The orbital-ordered states yield the right crystal field states of Pr$^{3+}$ f-electrons and have a band gap with a size similar to that observed in optical spectroscopy measurements. Although the relative orbital orientation of neighboring Pr$^{3+}$ ions cannot be distinguished from the unpolarized synchrotron x-ray diffraction, the polarized synchrotron x-ray diffraction should be able to do the job. In this regard, measuring the orbital orientation of Pr$^{3+}$ f-electrons is a
crucial step to verifying the physical mechanism proposed in this paper for the M–I transition in PrRu$_4$P$_{12}$.

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