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Possible Kondo resonance in $PrFe_4P_{12}$ studied by bulk-sensitive photoemission

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Pr $4f$ electronic states in Pr-based filled skutterudites PrT_4X_{12} (T=Fe and Ru; X=P and Sb) have been studied by high-resolution bulk-sensitive Pr $3d \rightarrow 4f$ resonance photoemission. A very strong spectral intensity is observed just below the Fermi level in the heavy-fermion system $PrFe_4P_{12}$. The increase of its intensity at lower temperatures is observed. We speculate that this is the Kondo resonance of Pr, the origin of which is attributed to the strong hybridization between the Pr $4f$ and the conduction electrons.

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The heavy-fermion properties observed in many Ce and U compounds and compounds of some other rare-earth elements emerge when the hybridization between the conduction band in the vicinity of the Fermi level and the f state (c-f hybridization) is moderate. The $4f$ electrons in Pr are more localized and less hybridized with conduction electrons than in Ce. No heavy-fermion Pr compound was known until the discovery of $PrInAg_2$ with a large Sommerfeld coefficient reaching ~ 6.5 J/mol K^2 (Ref. 1). Recently, the heavy-electron mass has been found in $PrFe_4P_{12}$ under high magnetic field.[2] In both $PrInAg_2$ and $PrFe_4P_{12}$, the crystal–electric-field ground state is suggested to be a non-Kramers doublet,[1,3,4] which is nonmagnetic but has an electric quadrupolar degree of freedom. Therefore, the heavy-fermion behaviors in these Pr compounds may result from the quadrupolar Kondo effect,[5,6] which was first applied to U compounds and is in contrast to the usual spin Kondo effect applied to Ce and Yb compounds.

$PrFe_4P_{12}$ is one of the Pr-based filled skutterudites PrT_4X_{12}. Among them are $PrRu_4P_{12}$ known to show the metal-insulator transition at ~ 64 K (Ref. 7) and $PrRu_4Sb_{12}$ and $PrOs_4Sb_{12}$ known as a conventional[8] and heavy-fermion[9] superconductor, respectively. $PrFe_4P_{12}$ is particularly interesting due to the phase transition at around 6.5 K (Ref. 10) and the Kondo-like behaviors. Recent studies suggest that the phase transition is associated with the ordering of quadrupolar moments.[11,12] In the high-temperature phase, Kondo anomalies are found in the transport properties.[13] When the low-temperature-ordered phase is destroyed by high magnetic field, an enormously enhanced cyclotron effective mass ($m_c^* \simeq 81 m_0$) is observed in the de Haas–van Alphen measurement.[2] A large electronic specific heat coefficient of $C_{el}/T \sim 1.2$J/K^2 mol is found under 6 T,[2] which suggests a Kondo temperature T_K of the order of 10 K. These facts suggest the following scenario: quadrupolar degree of freedom of the Pr $4f$ state due to the non-Kramers twofold degeneracy leads to the quadrupolar Kondo effect, and the phase transition at 6.5 K resulting in the antiquadrupolar ordering is driven by the lifting of the quadrupolar degeneracy. In order for the quadrupolar Kondo effect to take place, c-f hybridization must be appreciably strong.

It has recently been demonstrated that high-resolution photoemission (PE) with use of soft x-rays can reveal bulk electronic states.[14] The bulk sensitivity is a result of the long mean free paths of the high-energy photoelectrons. Bulk-sensitive measurement must be crucial in the study of Pr $4f$ states since the c-f hybridization in Ce, Sm, and Yb compounds is known to be much weaker at the surface than in the bulk.[14,15] In addition, as in the case of Ce systems, one needs to enhance the Pr $4f$ contribution in the PE spectrum by means of resonance photoemission (RPE); otherwise, the Pr $4f$ state cannot be accurately distinguished from other states.[16–18]

In this paper, we report the results of the bulk-sensitive Pr $3d \rightarrow 4f$ RPE measurments for $PrFe_4P_{12}$, $PrRu_4P_{12}$, and $PrRu_4Sb_{12}$. It is shown that the Pr $3d \rightarrow 4f$ RPE spectrum of $PrFe_4P_{12}$ has much larger spectral weight just below the Fermi level (E_F) than other systems. We speculate that this spectral weight, which increases at lower temperatures, comes from the Kondo resonance (KR) due to the c-f hybridization. If so, to our knowledge, this is the first observation of the KR in PE of Pr systems.

Single crystals of $PrFe_4P_{12}$ and $PrRu_4Sb_{12}$ and polycrystals of $PrRu_4P_{12}$ were fractured *in situ* for soft-x-ray absorption (XA) and PE measurements at the BL25SU of SPring-8.[19] The total energy resolution of the PE measurement was set to ~ 80 meV in the high-resolution mode and ~ 130 meV otherwise. The samples were cooled and kept at 20 K except for the temperature dependence measurement.

The Pr $3d \rightarrow 4f$ XA spectrum for $PrFe_4P_{12}$ is shown in the inset of Fig. 1(a). This spectrum reflects the predominant Pr^{3+} ($4f^2$) character in the initial state.[20] Spectra of $PrRu_4P_{12}$ and $PrRu_4Sb_{12}$ were also quite similar to this spectrum. Valence-band PE spectra were measured at three photon energies. On-RPE spectra were taken at 929.4 eV, around the XA maximum. Off-RPE spectra were taken at 921 and 825 eV, which were quite similar in shape. The on- and off-(921.0 eV) RPE spectra are compared in the main panel of Fig. 1(a). We consider that mainly the Pr $4f$ contribution is enhanced in the on-RPE spectra[21] and therefore that the difference between the on- and off-RPE spectra mainly reflects the Pr $4f$ spectrum.

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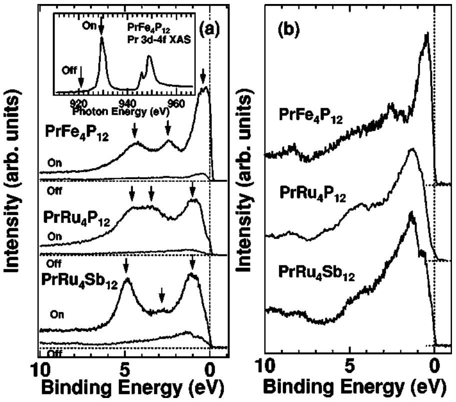

FIG. 1. (a) On- and off-RPE spectra normalized by the photon flux. Inset: Pr $3d \rightarrow 4f$ XA spectrum for $PrFe_4P_{12}$. Arrows show the energies at which spectra in the main panel were taken. (b) Off-RPE spectra taken at 825 eV in an enlarged intensity scale.

The off-RPE spectra taken at 825 eV with better statistics are shown in Fig. 1(b) in a magnified intensity scale. The valence band between E_F and binding energy (E_B) of ~ 7 eV is expected to be composed of Pr $5d$ and $4f$, T d, and X p orbitals. Among these, the main contribution to the off-RPE spectrum (more than 60%) comes from the T d states according to the photoionization cross section.[24] The off-RPE spectral features are reproduced in the theoretical off-RPE spectra based on full potential linearized augmented-plane wave (FLAPW) and local density approximation (LDA)+U band structure calculations [see Fig. 2(b)],[25] where the parameter for the on-site Coulomb interaction U of Pr $4f$ electron is set as 0.4 Ry (5.4 eV).

The on-RPE spectra shown in Fig. 1(a) are characterized by two features. First, the on-RPE spectra have various multiple-peak structures, where peaks (or structures) are indicated by arrows, in contrast to the calculated Pr f partial density of states (PDOS) [see Fig. 2(a)] that has a strong peak and small structures near E_F for all the three compounds. This feature will be interpreted in the next paragraph, taking into account the hybridization between the valence band and the Pr $4f$ states (v-f hybridization) in the *final* states of PE. Second, the intensity near E_F—i.e., between E_F and $E_B \sim 0.3$ eV—is much stronger in $PrFe_4P_{12}$ than in other two systems. Such strong intensity at E_F is neither found in reported Pr $4f$ spectra. Later in this paper, this feature will be attributed the strong c-f hybridization in the *initial* state of $PrFe_4P_{12}$.

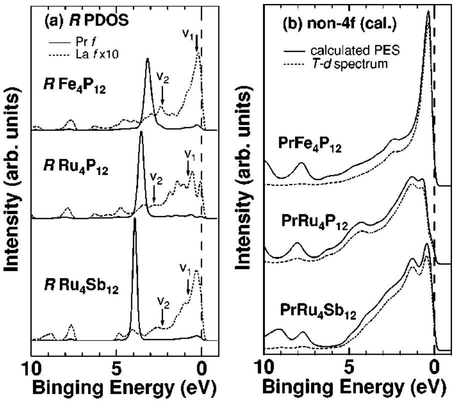

FIG. 2. Calculated PE spectra based on band structure calculation. Density of states is multiplied by the Fermi-Dirac function for 20 K and is broadened by the Gaussian with the full width at half maximum of 80 meV. (a) Calculated Pr (solid line) and La (dashed line: magnified 10 times) f spectra of PrT_4X_{12} and LaT_4X_{12}. (b) Calculated off-RPE spectra (solid lines), where partial density of states except for Pr f are multiplied by the cross sections (Ref. 24) and summed up. Dashed lines show the contribution of the T d state.

Multiple-peak structures observed for various Pr compounds have been interpreted in terms of the v-f hybridization.[16–18] We adopt the cluster model[26]—i.e., the simplified version of the single impurity Anderson model (SIAM).[27] The part of the valence band that hybridizes strongly with the $4f$ state is expected to be similar between PrT_4X_{12} and LaT_4X_{12}. The La f PDOS of LaT_4X_{12} at a certain energy corresponds roughly to the v-f hybridization strength at that energy since La f states below E_F come only from the hybridization with the valence band. As a first approximation, we replace the La f PDOS with two levels v_1 and v_2, the energies of which, $E_B(v_k)$, are shown by the arrows in Fig. 2(a). We now assume that the initial Pr $4f$ state is $|f^2\rangle$. Although it turns out later that deviation from this state is appreciable in $PrFe_4P_{12}$, this is a good approximation when discussing the overall spectral features. Then the final states of Pr $4f$ PE are linear combinations of $|f^1\rangle$, $|(f^2)^*\underline{v_1}\rangle$, and $|(f^2)^*\underline{v_2}\rangle$, where $\underline{v_k}$ denotes a hole at v_k. Since the resulting f^2 state includes all the excited states, it is denoted as $(f^2)^*$ so as to distinguish it from the initial ground state f^2. The average excitation energy $E((f^2)^*)-E(f^2)$ is ~ 1.4 eV according to an atomic multiplet calculation.[20] The main origin of this excitation energy is found to be the exchange interaction. The energies of the bare $|(f^2)^*\underline{v_k}\rangle$ with respect to the initial state $|f^2\rangle$ are hence $E_B(v_k)+[E((f^2)^*)-E(f^2)]$ and are shown by the thin open and solid bars in the upper panels of Figs. 3(a)–3(c). We take the remaining three parameters, E_B of the bare $|f^1\rangle$ (E_0), the hybridization between $|f^1\rangle$, and $|(f^2)^*\underline{v_k}\rangle$ (V_k), to be free parameters and numerically solve the 3×3 Hamiltonian matrix. When the parameters are set as in the upper panels of Figs. 3(a)–3(c), the three final states are obtained as shown in the lower panels. At each of the three eigenenergies of the final states is placed a set of vertical bars, the lengths of which are proportional to the weights of $|f^1\rangle$ (thick solid bar), $|(f^2)^*\underline{v_1}\rangle$ (thin open bar), and $|(f^2)^*\underline{v_2}\rangle$ (thin solid bar). Since we assume that the initial state is $|f^2\rangle$, the Pr $4f$ excitation intensity is proportional to the weight of the $|f^1\rangle$ in each final state. Therefore, the thick solid bars show the obtained line spectrum. The line spectra qualitatively well reproduce the experimentally observed system dependence in the energy positions and intensity ratios of the three-peak structures of the on-RPE spectra [see Fig. 1(a)]. The present analysis revealed the character of each final state. For example, the final state with the smallest E_B is the bonding state between $|f^1\rangle$ and $|(f^2)^*\underline{v_1}\rangle$. The trend in the E_B of bare $|f^1\rangle$ corresponds to some extent with the trend in the peak position of the Pr f PDOS in Fig. 2(a). The origin of these trends could be that E_B of the Pr $4f$ electron becomes

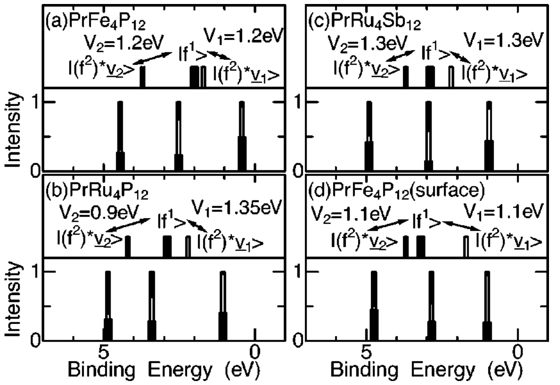

FIG. 3. Pr $4f$ spectrum reproduced by the cluster model for (a) $PrFe_4P_{12}$, (b) $PrRu_4P_{12}$, (c) $PrRu_4Sb_{12}$, and (d) surface of $PrFe_4P_{12}$. Upper panels: binding energies of bare $|f^1\rangle$ and $|(f^2)^*\underline{v_k}\rangle$ final states are shown by the bars and the effective hybridization between $|f^1\rangle$ and $|(f^2)^*\underline{v_k}\rangle$ are written. Lower panels: the resultant final states are shown. The thick solid bars show the weights of the $|f^1\rangle$ state in the final states and correspond to the Pr $4f$ PE line spectrum for the assumed $|f^2\rangle$ initial state. The thin open and solid bars show the weights of $|(f^2)^*\underline{v_1}\rangle$ and $|(f^2)^*\underline{v_2}\rangle$ states, respectively.

smaller because the negative X ion comes closer to the Pr atom in the direction of $PrRu_4Sb_{12}$, $PrRu_4P_{12}$, and $PrFe_4P_{12}$.

The present Pr $4f$ spectrum of $PrFe_4P_{12}$ obtained from the bulk-sensitive $3d \rightarrow 4f$ RPE is qualitatively different from that obtained from the surface-sensitive $4d \rightarrow 4f$ RPE.[28] The surface-sensitive spectrum also has a three-peak structure but the peak at $E_B \sim 4.5$ eV is the strongest and the intensity at E_F is negligible. The origin of the difference is the increase of the localization of $4f$ electrons at the surface—in other words, the increase of the $4f$ binding energy and the decrease of the hybridization. By making such changes in E_0 and V_k, the surface-sensitive spectrum is reproduced [see Fig. 3(d)].

We measured the Pr $3d \rightarrow 4f$ RPE spectra near E_F with high resolution as shown in Fig. 4(a). The most prominent feature is the strong peak of $PrFe_4P_{12}$ at $E_B \simeq 100$ meV. The Pr $4f$ spectra of $PrRu_4P_{12}$ and $PrRu_4Sb_{12}$, on the other hand, decrease continuously with some humps as approaching E_F. Spectral features similar to $PrRu_4P_{12}$ and $PrRu_4Sb_{12}$ have been found for very localized Ce systems such as CePdAs, in which Ce $4f$ takes a nearly pure $4f^1$ state.[15] This indicates that a pure $4f^2$ state is realized in $PrRu_4P_{12}$ and $PrRu_4Sb_{12}$. On the other hand, similarity between the $PrFe_4P_{12}$ and Kondo Ce compound spectra[14] suggests that the Pr $4f^2$-dominant Kondo state, with a finite contribution of the $4f^1$ or $4f^3$ state, is formed in $PrFe_4P_{12}$.

The present energy resolution of ~ 80 meV exceeds the characteristic energy $k_B T_K \sim 1$ meV for $PrFe_4P_{12}$. KR has been observed even in such cases—for example, for $CeRu_2Si_2$ ($T_K \sim 20$ K) (Ref. 14) and $YbInCu_4$ ($T_K \sim 25$ K for $T > 42$ K) (Ref. 29) with an energy resolution of ~ 100 meV.

In the Kondo Ce (Yb) system, the KR is accompanied by the spin-orbit partner, the E_B of which corresponds to the spin-orbit excitation $J = 5/2 \rightarrow 7/2$ ($J = 7/2 \rightarrow 5/2$) of the $4f^1$ ($4f^{13}$)-dominant state.[27] A KR in Pr would then be accompanied by satellites corresponding to excitation from the ground state ($^3H_4$) to excited states ($^3H_5$, $^3H_6$, $^3F_2$, and so on) of the $4f^2$ states. Figure 4(a) shows that the on-RPE spectra of $PrFe_4P_{12}$ have strucures at ~ 0.3 and ~ 0.6 eV which correspond to the lowest few excitation energies.

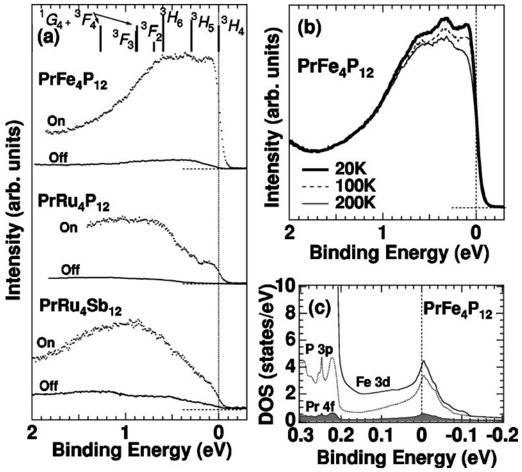

FIG. 4. (a) High-resolution Pr $3d \rightarrow 4f$ on- (dots) and off- (solid lines) RPE spectra near E_F at 20 K. The vertical lines show the energy positions of the atomic $4f^2$ multiplets with the ground-state set at E_F. (b) Temperature dependence of the on-RPE spectrum of $PrFe_4P_{12}$. (c) Calculated partial density of states.

KR is expected to depend upon temperature, reflecting the temperature dependence of the $4f$ occupation number. In fact, a temperature dependence was found as the temperature approaches the suggested $T_K \sim 10$ K as shown in Fig. 4(b). The temperature dependence was reproducible in both heat-up and cool-down processes. The temperature dependence is characterized not only by the narrowing of the ~ 0.1 eV structure but also by the increase of the weight of all the structures at ~ 0.1, ~ 0.3, and ~ 0.6 eV. Although the former can be attributed at least partly to thermal broadening, the latter should be attributed to the intrisic temperature dependence of the excitation spectrum. Therefore it is quite possible that the ~ 0.1 eV structure is the KR and the ~ 0.3 and ~ 0.6 structures are its satellite structures.

The temperature dependence can be a vital clue to check whether the observed structure is the Kondo peak itself or the tail of the Kondo peak centered above E_F. These cases correspond, respectively, to the $c_2|f^2\rangle + c_3|f^3\rangle$ or $d_1|f^1\rangle + d_2|f^2\rangle$ initial states, where the hole or electron in the valence or conduction band is not denoted explicitly. The noncrossing approximation (NCA) calculation based on the SIAM for the Ce system[30] shows that, as temperature is lowered, the Kondo tail is sharpened[31] but the *weights* of both the Kondo tail and its spin-orbit partner *decrease* when the spectra are normalized in a similar way as in Fig. 4(b). This contradicts the present temperature dependence for $PrFe_4P_{12}$. On the other hand, for Yb systems, it is well known that the intensities of both the Kondo peak itself and its spin-orbit partner increase with decreasing temperature.[32] Since this is consistent with the $PrFe_4P_{12}$ temperature dependence, we tend to believe that the observed structure is the Kondo peak itself and, therefore, that the initial state is dominated by $c_2|f^2\rangle + c_3|f^3\rangle$. We consider that the Kondo peak at around $k_B T_K \sim 1$ meV is broadened due to the energy resolution of ~ 80 meV resulting in the observed structure at ~ 100 meV.

The microscopic origin of the *c*-*f* hybridization is considered to be the P 3*p*–Pr 4*f* mixing since the nearest neighbors of the Pr atom are the 12 P atoms. The large coordination number definitely enhances the effective *p*-*f* mixing. It has been pointed out that the calculated P *p* PDOS of $R\mathrm{Fe}_4\mathrm{P}_{12}$ shows a sharp peak in the vicinity of E_{F}.[25,33] This is also the case for $\mathrm{PrFe}_4\mathrm{P}_{12}$ as shown in Fig. 4(c). Therefore, the large P 3*p* PDOS at E_{F} together with the large effective P 3*p*–Pr 4*f* mixing is interpreted to be the origin of the Kondo state in $\mathrm{PrFe}_4\mathrm{P}_{12}$.

In conclusion, our analysis of the data suggests that there may be a Kondo resonance in the 4*f* photoemission spectrum of $\mathrm{PrFe}_4\mathrm{P}_{12}$, whereas no KR was seen in $\mathrm{PrRu}_4\mathrm{P}_{12}$ and $\mathrm{PrRu}_4\mathrm{Sb}_{12}$. The origin of the KR in $\mathrm{PrFe}_4\mathrm{P}_{12}$ is considered to be the Kondo effect caused by the strong hybridization between the Pr 4*f* and P 3*p* states in the vicinity of E_{F}.

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