Kondo resonance in PrTi$_2$Al$_{20}$: Photoemission spectroscopy and single-impurity Anderson model calculations

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The Kondo resonance at the Fermi level is well established for the electronic structure of Ce (4f$^1$ electron) and Yb (4f$^3$ hole)-based systems. In this work, we report complementary experimental and theoretical studies on the Kondo resonance in the Pr-based 4f$^2$ system, PrTi$_2$Al$_{20}$. Using Pr 3d-4f resonant photoemission spectroscopy and single impurity Anderson model (SIAM) calculations including the full multiplets of Pr ions, we show that a 4f$^2$ system can also give rise to a Kondo resonance at the Fermi level. The Kondo resonance peak is experimentally observed through a final-state-multiplet dependent resonance and is reproduced with properly tuned hybridization strength in SIAM calculations.

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The Kondo effect represents a typical manifestation of many-body phenomena and its experimental signature is a logarithmic temperature dependence in the electrical resistivity, $\rho(T) \sim -\log T$. It arises from the spin-flip scattering of conduction (c) electrons by a local magnetic impurity, and leads to an energetically narrow feature in the density of states (DOS) at the Fermi level ($E_F$), often referred to as Abrikosov-Suhl or Kondo resonance. This feature can be observed even in the case of a periodic array of magnetic ions such as Ce-based intermetallics exhibiting heavy-fermion behavior at low T. The electronic structure and the Kondo resonance peak of Ce- and Yb-based systems (characterized by a formal 4f$^1$ configuration, Ce$^{3+}$: 4f$^3$ electron, Yb$^{3+}$: 4f$^1$ hole), have been successfully described within the framework of the single-impurity Anderson model (SIAM) based on c states hybridizing with localized f states. Subsequent studies have also shown the importance of lattice effects based on the periodic Anderson model. On the other hand, although the importance of hybridization effects has been nicely clarified in the electronic structure of the single-impurity Anderson model (SIAM) based on c states hybridizing with localized f states, they have been experimentally observed even for an f$^2$ configuration (Pr$^{3+}$, 4f$^2$ electron). While spectroscopic experiments for U-based 5f$^2$ electron systems have shown the Kondo resonance in analogy to Ce-based systems, a combined validation of Kondo resonance in experiments and SIAM calculations including the full multiplets of the f$^2$ configuration has not been established. In this Brief Report, we carry out experimental and theoretical verification of the f$^2$ Kondo resonance at $E_F$ in PrTi$_2$Al$_{20}$, a recently discovered 4f$^2$ Kondo system.

Among Pr-based compounds, the $-\log T$ dependence in $\rho(T)$ has been observed so far in systems PrSn$_3$, PrFe$_2$P$_{12}$, Pr$_2$Ir$_2$O$_7$, and very recently in PrM$_2$Al$_{20}$ ($M$ = Ti and V). PrM$_2$Al$_{20}$ crystallizes in the cubic CeCr$_2$Al$_{20}$ structure, characterized by a cagelike coordination of Al ions surrounding Pr ions. The $\rho(T)$ in PrTi$_2$Al$_{20}$ decreases monotonically with cooling, and shows two shoulders at ~50 and ~2 K. The magnetic contribution in $\rho(T)$, which is obtained by subtracting $\rho(T)$ of LaTi$_2$Al$_{20}$, shows a maximum at ~50 K and $-\log T$ dependence at higher T. The anomaly at ~2 K is also observed in the specific heat but not so clearly in the magnetic susceptibility, suggesting a nonmagnetic phase transition such as a quadrupolar ordering.

In this study, we address the Kondo resonance in the 4f$^2$ configuration using photoemission spectroscopy (PES) of PrTi$_2$Al$_{20}$. In order to directly probe the Kondo resonance feature with PES, we need to specifically enhance the Pr 4f component with enough bulk sensitivity for the following reasons. In the case of low concentration of the rare-earth element such as PrTi$_2$Al$_{20}$, it is difficult with use of normal (nonresonant) PES to extract the 4f electron signal from the total DOS in the presence of many other orbital contributions. In addition, it is well known that 4f electrons in the surface have a greater tendency to localize acting to prevent the Kondo behavior. Accordingly, we have selected Pr 3d-4f resonant PES as a bulk sensitive probe. The obtained resonance (Pr 4f) spectra for PrTi$_2$Al$_{20}$ reflect the strong c-f hybridization and reveal the existence of the Kondo resonance peak just at $E_F$. No such feature is observed in elemental Pr metal, used as a prototypical system of localized 4f electrons. Furthermore, we analyze the 4f spectra within the framework of SIAM including the full multiplets of Pr ions and discuss the relationship between a Kondo resonance and a valence instability in 4f$^2$ configuration.

Single crystals of PrTi$_2$Al$_{20}$ were grown by the Al self-flux method. Clean sample surfaces were obtained by fracturing in situ. Pr metal was prepared as thin films by in situ evaporation. Pr 3d-4f x-ray absorption spectroscopy (XAS) and resonant PES were performed at the undulator beamline BL17SU in SPring-8. XAS spectra were recorded using the total electron yield method. PES spectra were measured using a hemispherical electron analyzer, Scienta SES-2002. The total energy resolution of PES was set to 250 and 100 meV for the measurements of the overall valence-band region and near-$E_F$ region, re-
spectively. $E_F$ of the samples was referenced to that of evaporated Au film. PES spectra were normalized to the incident photon flux, measured as the drain current at the focusing mirror. The $T$ was 25 K and the vacuum was below $4 \times 10^{-3}$ Pa during all the measurements.

Figure 1 shows the Pr 3d-4f XAS spectra of PrTi$_2$Al$_{20}$ and Pr metal in comparison with those calculated by the SIAM with the hybridization strength $V = 0.55$ eV and the atomic multiplet model for the Pr$^{3+}$ ion. The labels $A - J$ indicate the selected photon energies at which the resonant PES spectra in Figs. 2 and 3 are measured.

FIG. 1: (Color online) Pr 3d-4f XAS spectra of PrTi$_2$Al$_{20}$ and Pr metal in comparison with those calculated by the SIAM with the hybridization strength $V = 0.55$ eV and the atomic multiplet model for the Pr$^{3+}$ ion. The labels $A - J$ indicate the selected photon energies at which the resonant PES spectra in Figs. 2 and 3 are measured.

Figure 2 shows the Pr 3d-4f resonant PES spectra of PrTi$_2$Al$_{20}$ (a) and Pr metal (b). For Pr metal, both on-resonance ($G$) and off-resonance ($A$) spectra are qualitatively similar to the previous data. Taking into account the photoionization cross sections and the elemental composition, the off-resonance spectrum is expected to be dominated by Ti 3d, Al 3s, and 3p states in PrTi$_2$Al$_{20}$ and Pr 5d and 4f states in Pr metal. Due to the resonance enhancement of the Pr 4f state, the evolution of two prominent features at 3-5 eV of the binding energy ($E_B$) and near $E_F$ ($E_B = 0 - 2$ eV) is confirmed for both materials, which can be attributed to the $f^1$ and $f^2$ final states, respectively. In contrast to the unshifted $f^1$ final state for both materials as indicated by the solid lines in Fig. 2, the peak maximum of $f^2$ final state shifts in $E_B$, depending on the incident photon energy. This is caused by the multiplet effect as discussed later, and is not due to the Auger effect. The weight of the $f^2$ final state relative to that of the $f^1$ final state, which gives a measure of the degree of $f$-electron localization, is much stronger in PrTi$_2$Al$_{20}$, suggesting the existence of itinerant $f$ electrons due to the stronger hybridization effect. Also, the positions and the separation of two features are quite different for the two materials. As another remarkable difference, an additional peak or shoulder can be seen at $\sim 2.7$ eV for on-resonance spectra only in PrTi$_2$Al$_{20}$. A similar feature has been reported in the filled skutterudite compounds.

Next, we focus on the $f^2$ final state. Figures 3(a) and (b) show the high-resolution spectra measured at the incident energies $C$, $F$, and $G$ for PrTi$_2$Al$_{20}$ and Pr metal, respectively, along with the corresponding spectral DOS obtained by dividing the resolution-convoluted Fermi-Dirac distribution (FDD) function. The observed fine structures are attributed to the multiplets of the $f^2$ final state as also confirmed by our SIAM calculations. Crucially for the spectra $C$ and $F$ in PrTi$_2$Al$_{20}$, the midpoint of the leading edge in the PES spectra locates slightly above $E_F$ as is typically seen in many Ce systems and in contrast to the case of Pr metal for which it locates at $E_F$. This observation leads to the characteristic feature in the spectral DOS, in which the sharp rise at $E_F$ toward the unoccupied side is obtained for PrTi$_2$Al$_{20}$.
increasing incident energy toward the absorption peak gradually gets buried in the higher-
state). The enhancement of individual final-state multiplet effect in the resonant process (equivalent to the XAS final state is most strongly enhanced. It suggests a multiplet dependent resonance in the $f^2$ final state, which moves to higher $E_B$ with increasing incident energy as seen in the inset of Fig. 3(a). Such behavior, which is similar in Pr metal as shown in the inset of Fig. 3(b), can be described by considering the intermediate-state multiplet effect in the resonant process (equivalent to the XAS final state). The enhancement of individual final-state multiplet depends on the corresponding intermediate-state multiplet. For Pr$_2$Al$_2$, the Kondo resonance peak derived from the lowest-$E_B$ final-state multiplet resonates at the incident energy of absorption prepeak. Then, it gradually gets buried in the higher-$E_B$ multiplets with increasing incident energy toward the absorption peak maximum ($G$). Indeed, the slope of Kondo resonance peak at $E_F$ is sharper in spectrum $C$ than in $F$. The main part of resonance in spectrum $F$ moves to slightly higher $E_B$. Thus, the on-resonance spectra obtained at the absorption prepeak energies such as $C-E$ correspond to the genuine Pr 4$f$ spectra reflecting the Kondo resonance at $E_F$.

To reproduce the Pr 4$f$ spectra of Pr$_2$Al$_2$, we have performed SIAM calculations as a function of $V$. The basis set consisting of 4$f^1$, 4$f^2$, and 4$f^3$ configurations is used to describe the ground state. The $V$ between the 4$f$ and c band depends on the c band energy. For the c band states, we use a Lorentzian profile. The Slater integrals and spin-orbit coupling constants are calculated by the Hartree-Fock method with relativistic corrections and are reduced to 85% and 96%, respectively. To take into account the configuration dependent hybridization, $V$ is reduced by a factor $R_C$ (=0.8) in the presence of a core hole and enhanced by a factor $1/R_V$ ($R_V = 0.95$) in the presence of an extra 4$f$ electron. Details of the model calculations are standard and are described in earlier work. In order to obtain the best fit of calculations to the experimental data of Pr$_2$Al$_2$, we needed to use the following parameter values: bare 4$f$ energy $\varepsilon_f=-3.2$ eV, on-site Coulomb repulsion $U_{ff}=7$ eV (standard in Pr-based compounds), core-hole potential $U_{fc}=10$ eV, and c bandwidth $W=1.6$ eV. In addition to the PES spectra, the bremsstrahlung isochromat (BIS) spectra shown in Fig. 4(b) and the XAS spectra shown in Fig. 1 have also

FIG. 3: (Color online) High-resolution Pr 3d-4$f$ resonant PES spectra measured at the incident energies $C$, $F$ and $G$ labeled on XAS spectra in Fig. 1 for Pr$_2$Al$_2$ (a) and Pr metal (b), alongside the corresponding spectral DOS obtained by dividing the resolution-convoluted FDD function. The shaded area shows the region of $E_B < -5k_B T$.

FIG. 4: (Color online) The SIAM simulations for Pr ($f^2$) systems. (a) Calculated Pr 4$f$ PES spectra as a function of $V$. (b) PES and BIS spectra. (c) The $V$ dependence of the distribution of 4$f$ weights (left axis) and the 4$f$ electron count $n_f$ (right axis).
been calculated using the same parameters. It should be emphasized that the full multiplet structures of Pr ions are included in our calculations. It was found to play an essential role in analyzing the Pr 4f spectra, since they show pronounced multiplet features.

Figure 4(a) shows the calculated Pr 4f PES spectra as a function of V. With increasing V, the peak at 3-4 eV corresponding to the f^1 final state shifts toward higher E_F together with splitting off to the lower-E_F shoulder. Then, the f^2 final state at 0-2 eV gradually develops to compensate the suppressed weight of the f^1 final state. Moreover, the intense part in the f^2 final state moves closer to E_F, leading to the Kondo resonance peak. Such behavior is consistent with the spectral variation from Pr metal to PrTi_2Al_20. The calculation corresponding to ~0.55 eV shows the best match to the experimental data of PrTi_2Al_20 in terms of the multiplet lineshape of the f^2 final state and the splitting between the f^1 final state and its lower-E_F shoulder. This demonstrates that a fractional valence (n_f~2.06 at V = 0.55 eV) is indeed realized in PrTi_2Al_20, which should be closely related to the Kondo effect in \rho(T)\, as a valence instability of the Pr ion was also reported in the dilute alloy Pr (1.4%) in Pd metal, which exhibits a Kondo effect in \rho(T) and a fractional valence (~+3.1).

The evolution of the Kondo resonance peak is more clearly seen in BIS spectra as shown in Fig. 4(b). Here, the PES and BIS spectral weights are normalized to be n_f and N_f - n_f, respectively, where n_f is the calculated f electron count and N_f (=14 in this case) is the degeneracy of the f electron. For BIS, the multiple peaks around -2 to -9 eV for V=0.2 eV and the near-E_F peaks around 0 ~ -3 eV for V=0.7 eV are attributed to the f^3 (f^2 ~ f^3) and the f^2 (f^1 ~ f^2) final states, respectively. With increasing V, the spectral weight transfers from f^3 to f^2 final state, while in the case of PES, it transfers from the f^1 (f^2 ~ f^1) to the f^2 (f^3 ~ f^2) final state, giving rise to an effective incoherent-to-coherent crossover. A major part of the f^2 final state including the Kondo resonance peak exists in the BIS side, providing the peak top of Kondo resonance in the unoccupied DOS, as in the case of Ce systems. This is also consistent with our experimental findings.

Of particular interest is that n_f indicates a plateau above V=0.5 eV as shown by the dashed line in Fig. 4(c). This indicates that the initial growth in f^3 weight gets compensated by the f^1 weight on increasing V above 0.5 eV. Since this compensation is due to the fluctuation between an electron-in (f^3) and an electron-out (f^1) of the f shell with respect to the f^2 ground state through the c-f hybridization, it is related with the evolution of the Kondo resonance. This fact suggests that the n_f can be stabilized by the Kondo resonance. The V~0.5 eV provides a boundary for distinguishing the Pr 4f electronic states near E_F between the Kondo resonance regime and the nearly localized regime, which PrTi_2Al_20 and Pr metal belong to, respectively. It is important that the n_f (~2.06) in PrTi_2Al_20 shows only a little deviation from Pr^{3+} and a little difference between PrTi_2Al_20 and Pr metal in spite of the large spectral variation in PES. A similar n_f stabilization with varying V has been reported in the study of Pu metal with 5f^3 ground state. Further experimental and theoretical investigations on other 4f or 5f electron systems are necessary to establish the relationship between the n_f stabilization and the Kondo resonance for f^n systems in general.

To summarize, we have performed Pr 3d-4f resonant PES on PrTi_2Al_20 and Pr metal. The intense f^2 final state is observed for Pr 4f spectra in PrTi_2Al_20, reflecting the stronger V and the Kondo resonance behavior. The f^2 final state shows a multiplet-dependent resonance. The Kondo resonance peak at E_F in PrTi_2Al_20 is identified in the spectra measured at absorption prepeak energies, while it is suppressed in Pr metal. The spectral variation between PrTi_2Al_20 and Pr metal can be reproduced by the V-dependent SIAM calculations including full multiplets of Pr ions. The SIAM calculations suggest that n_f is stabilized by the Kondo resonance.

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