Supplementary information: Pressure-induced anomalous valence crossover in cubic YbCu$_5$-based compounds

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XRD PATTERNS AND PRESSURE DEPENDENCE OF THE VOLUME

We performed x-ray diffraction (XRD) for YbAg$_x$Cu$_{5-x}$ ($x = 0$, 0.5, and 1.0) at 300 K under pressure. The XRD patterns of cubic YbCu$_5$ and hexagonal YbCu$_{6.5}$ are shown in Fig. 1, measured with a Cu $K\alpha$ radiation at 300 K. [1] The x-ray pattern of hexagonal YbCu$_5$ (upper panel, Fig. 1) are distinctly different from those of cubic YbCu$_5$ (lower panel, Fig. 1), confirming the differences of both crystal structures.

Figure 2 shows the diffraction patterns for YbAg$_{0.5}$Cu$_{4.5}$ and YbAgCu$_4$ as a function of pressure. The diffraction peaks of YbAg$_{0.5}$Cu$_{4.5}$ and YbAgCu$_4$ are sharper than those of cubic YbCu$_5$. The line-broadening in cubic YbCu$_5$ may be induced by...
FIG. 3. (Color online). Examples of the XRD spectra of cubic YbCu$_5$ at 0 and 19.05 GPa (open circles) with the fits (solid lines). Difference between the experimental data and the calculated result is shown in lower part of each figure.

FIG. 4. (Color online). Relationship between the volume ($V$) and pressure of cubic YbCu$_5$, where $V_0$ is the volume at ambient pressure. The solid line is a fit of the equation of state to the experimental data.

the process making smaller-sized powder to avoid the hot spots in the two-dimensional diffraction patterns. However, the pattern are still sufficient to study whether or not there is a structural transition. Examples of the fits at 0 and 19.05 GPa for YbCu$_5$ are shown in Fig. 3. There are no structural transitions within the pressure range measured for YbAg$_x$Cu$_{5-x}$ ($x = 0, 0.5, and 1.0$).

Figure 4 shows fits of the pressure-volume relation by using an empirical formula of the equation of state.

$$
\frac{V}{V_0} = \left[1 + \frac{p}{B_0} + \frac{B_0'}{B_0} \right]^{-\frac{1}{\beta_0}}
$$

where $P$, $V$, $V_0$, $B_0$, and $B_0'$ are pressure, volume, volume at ambient pressure, bulk modulus of incompressibility, and fits first derivative with respect to the pressure, respectively. The following parameters are obtained: $B_0 = 127.1$ GPa, $B_0' = 6.91$, $V_0 = 339.9$ Å for cubic YbCu$_5$, $B_0 = 162.5$ GPa, $B_0' = 0.558$, $V_0 = 346.62$ Å for YbAg$_{0.5}$Cu$_{4.5}$, and $B_0 = 145.7$ GPa, $B_0' = 1.33$, $V_0 = 353.03$ Å for cubic YbAgCu$_4$.

FIG. 5. (Color online). Pressure dependence of (a) the PFY-XAS spectra and (b) the RXES spectra of YbCu$_5$ at 300 K.

PFY-XAS AND RXES SPECTRA

In Fig. 5 we show the pressure dependence of the PFY and RXES spectra of YbCu$_5$ at 300 K. The RXES spectra of YbCu$_5$ were measured around the incident energy of the peak of the Yb$_{2+}$ component. The pressure-induced behavior of the each Yb component of the RXES spectra is very similar to that of the PFY-XAS spectra.

Figure 6 shows the pressure dependence of the PFY-XAS spectra of (a) YbAg$_{0.5}$Cu$_{4.5}$ and (b) YbAgCu$_4$ at 300 K. In Figs. 6(a) and 5(b) the dotted lines correspond to the spectra at 2.0 GPa and 0.5 GPa, respectively, which are superimposed by other spectra at given pressures. Vertical offset scales to the pressure measured.

In Fig. 7 we show an example of the fit to the PFY-
ELECTRONIC STRUCTURE CALCULATIONS

The calculated results are shown in Figs. 8-10. The pressure effect is considered by using the experimental lattice constants under pressure, as shown in Fig. 4, in the calculations. We have included the Yb 4f, 5d, 6s and the Cu 3d, 4s orbitals as valence states and the Yb 5s, 5p and Cu 3p orbitals as semicore states. The calculations of self-consistent loops and the density of states (DOS) are performed with a 24 × 24 × 24 mesh of the reciprocal unit-cell vectors.

Figure 8 shows band dispersion weighted by the Yb-f, Cu1-d, and Cu2-d states at 0, 10, and 20 GPa. DOS at ambient pressure is shown in Fig. 9. The bands weighted by the Yb-f states show a clear splitting of the $j = 5/2$ orbitals with lower energy and $j = 7/2$ states around the Fermi level by the spin-orbit coupling, corresponding to the sharp peaks of the DOS as shown in Fig. 9. Pressure increases the width of the conduction bands and leads to the broader energy region where the f states are present through the hybridization, as clearly seen for the energy difference of the f-weighted bands at $\Gamma$ and $X$ points around the Fermi level. This leads to the reduction of the f occupation number by an order of 0.01 within the GGA approximation, but the well-developed $c$-f hybridization under the pressure can act to stabilize the nonmagnetic $f^{14}$ states through the local correlation effect which is not considered in the current band calculations, as discussed below. In Fig. 10 we show the density of states near the Fermi level of Yb f, (b) Cu1 (4c site) d, and Cu2 (16e site) d orbitals at 0, 10, and 20 GPa.

CRYSTAL FIELD EFFECT

Crystalline field effects (CEF) on the valence state based on the single impurity Anderson model are accounted for by [7]

\[
\frac{n_f}{1 - n_f} = \sum_{\Gamma} n_f V_{\Gamma}\rho_{\Gamma} \left( \frac{1}{T_K + \Delta_{\Gamma}} \right) = \sum_{\Gamma} n_f V_{\Gamma}\rho_{\Gamma} \times \left( \frac{1}{T_K + \Delta_{\Gamma}} + \frac{1}{T_K + \Delta_1} + \frac{1}{T_K + \Delta_2} + \ldots \right),
\]

where $n_f$, $n_{\Gamma}$, $V$, $\rho$, and $\Delta_\Gamma$ are occupation number of f states, degree of degeneracy of the $\Gamma$ group, hybridization strength, density of states (DOS) at Fermi level, and crystalline electric field splittings, respectively. The crystal field strength increases with pressure, while $T_K$ decreases. In eq. (2) the first-order expansion term changes largely with pressure, while higher-order terms do not change much, because the decrease of $T_K$ is counterbalanced by the increase of $\Delta$. The right-hand side of eq. (2) diverges for $T_K \rightarrow 0$. This corresponds to the Yb$^{3+}$ state, where

FIG. 6. (Color online). Pressure dependence of the PFY-XAS spectra of (a) YbAg$_{0.5}$Cu$_{1.5}$ and (b) YbAgCu$_4$ at 300 K.

FIG. 7. (Color online). A fit example of the PFY-XAS spectrum of YbCu$_5$ at 12 K and 18.8 GPa.

XAS spectrum of YbCu$_5$ at 12 K and 18.8 GPa. Two Voigt functions are assumed for each Yb component with arctan-like backgrounds.
\( n_f \approx 1 \) (almost no hybridization). Therefore, in general, pressure forces the Yb valence toward the Yb\(^{3+}\) state. Assuming the validity of the Anderson model, the decrease of the Yb valence with pressure should be caused by an increase of the hybridization strength or an increase of the DOS at the Fermi level. The above band calculations suggest a possibility of the pressure-induced change in the DOS at the Fermi level. However, further theoretical and experimental studies will be necessary to understand the anomalous behavior found for cubic YbCu\(_5\).

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FIG. 9. (Color online). The density of states of YbCu$_5$ from Yb $f$, Cu1 $d$, and Cu2 $d$ orbitals.

FIG. 10. (Color online). Density of states near the Fermi level of (a) Yb $f$, (b) Cu1 (4c site) $d$, and (c) Cu2 (16e site) $d$ orbitals at 0, 10, and 20 GPa.

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