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Strong coupling between $4f$ valence instability and $3d$ ferromagnetism in $\mathrm{Yb}_x\mathrm{Fe}_4\mathrm{Sb}_{12}$ studied by resonant x-ray emission spectroscopy

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We have investigated the temperature and pressure dependency of the electronic structure of Yb-filled skutterudites, $\mathrm{YbFe}_4\mathrm{Sb}_{12}$ and $\mathrm{Yb}_{0.88}\mathrm{Fe}_4\mathrm{Sb}_{12}$, using x-ray absorption and emission spectroscopies. An anomalous increase of the Yb valence, which is beyond the conventional Anderson model picture, is found to coincide with the onset of the ferromagnetic order in the $x = 0.88$ sample below 20 K. In contrast, the nearly stoichiometric $\mathrm{YbFe}_4\mathrm{Sb}_{12}$ is paramagnetic down to 2 K and the Yb valence is independent of temperature. This evidences a close interplay between the magnetic instability of the Fe $3d$ electrons and valence instability of the Yb $4f$ electrons. Under pressure, a sudden increase in the valence is found to occur around 13 GPa for $\mathrm{YbFe}_4\mathrm{Sb}_{12}$ and 17 GPa for $\mathrm{Yb}_{0.88}\mathrm{Fe}_4\mathrm{Sb}_{12}$.

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Central issues in magnetism revolve around the critical behavior near a magnetic instability. For example, itinerant d-electron systems close to magnetic order show strong spin-fluctuation, which is often accompanied by metamagnetic behavior, large thermoelectric power, and even superconductivity. Magnetic ordering in a metal occurs via the exchange splitting of the d-electron band, characterized by a large density of state (DOS) at the Fermi level. Another mechanism by which magnetic ordering may occur is through the alignment of localized magnetic moments. Such localized magnetic moments are most often observed in rare-earth systems with a stable f-electron (f) shell, and is mediated by conduction (c) electrons through the Rudermann-Kittle-Kasuya-Yoshida interaction. Strong c-f hybridization can lead to heavy Fermion behavior with an unstable f-shell causing valence instabilities and the vanishing of magnetic ordering.

Generally, coexistence of d- and f-electrons tends to stabilize magnetic ordered states. Permanent ferromagnets, such as Nd-Fe-B and Sm-Co systems, have utilized this property. Furthermore, interaction with a stable f electrons can induce ferromagnetism in a nearly ferromagnetic (FM) itinerant electron system. Hence, in the cage-structure compound $\mathrm{YFe}_2\mathrm{Zn}_{20}$ where Y ions are surrounded by a Zn cage, a small amount of Gd^{3+}-substituted for the Y site was found to cause FM order, which was explained in the frame work of the s-d model [1]. The present study on the skutterudite compound $\mathrm{Yb}_x\mathrm{Fe}_4\mathrm{Sb}_{12}$ [2–8] suggests the opposite case; i.e., magnetic interaction arising from the itinerant Fe $3d$ electrons induces instability in the Yb f-shell, resulting in the fluctuating valence.

Magnetic instability of itinerant d-electron systems and the valence instability of nearly localized f-electrons are two major topics in the physics of strongly correlated electron systems, though these models have yet been reconciled. This letter reports on an interesting manifestation of the strong interplay between these two instabilities. We employ partial fluorescence yield x-ray absorption spectroscopy (PFY-XAS) and resonant x-ray emission spectroscopy (RXES) to study the valence of the Yb ions in $\mathrm{Yb}_x\mathrm{Fe}_4\mathrm{Sb}_{12}$ as a function of x (0.88 and 1), temperature, and pressure. We observe a steady increase of the Yb valence at the ferromagnetic (FM) transition of the FeSb_4 clusters in the $x = 0.88$ compound, which cannot be explained by the conventional Anderson model. Our pressure-dependent results unveil a pressure-induced valence transition in a skutterudite for the first time.

Single crystalline samples of $\mathrm{Yb}_{0.97\pm0.005}\mathrm{Fe}_4\mathrm{Sb}_{12}$ and $\mathrm{Yb}_{0.88\pm0.01}\mathrm{Fe}_4\mathrm{Sb}_{12}$ were synthesized by an Sb-self flux method [6, 7]. The chemical composition ratio was measured by wavelength-dispersive electron probe microanalysis. The $x = 0.97$ sample was synthesized under ∼4 GPa which is known to reduce the concentration of vacancies significantly at the rare-earth site compared with samples synthesized at ambient pressure, and do not show FM order [6]. Thus in this letter we simply denote the $x = 0.97$ sample as $\mathrm{YbFe}_4\mathrm{Sb}_{12}$. The magnetic susceptibility was measured using a superconducting quantum interference device magnetometer. PFY-XAS and RXES measurements were performed at the Taiwan beamline BL12XU at SPring-8. Details of the experimental setup have been published elsewhere [9].

Temperature dependence of the magnetic susceptibility for $YbFe_4Sb_{12}$ and $Yb_{0.88}Fe_4Sb_{12}$ is shown in Fig. 1. While the susceptibilities of the two samples show similar characteristics at high temperatures, they are very different at low temperatures. The susceptibility of $Yb_{0.88}Fe_4Sb_{12}$ is an order of magnitude higher than that of $YbFe_4Sb_{12}$. Whereas the FM transition temperature T_C for $Yb_{0.88}Fe_4Sb_{12}$ is 17 K [7], $YbFe_4Sb_{12}$ does not show FM behavior, and the susceptibility shows a maximum around 50 K. Effective paramagnetic moments are estimated to be about $\mu_{eff} = 3.19\mu_B$/f. u. for $YbFe_4Sb_{12}$ and $3.13\mu_B$/f. u. for $Yb_{0.88}Fe_4Sb_{12}$, where μ_B is the Bohr magnetron. These values of μ_{eff} per formula unit correspond to $\sim 1.6\mu_B$/Fe, similar to that of alkali-metal or alkaline-earth-filled skutterudites of AFe_4Sb_{12}, where A is Na, K, Ca, and Ba [10–12]. It is known that $NaFe_4Sb_{12}$ and KFe_4Sb_{12} are weakly FM with rather high Curie temperatures, and $CaFe_4Sb_{12}$ and $BaFe_4Sb_{12}$ are nearly FM. Therefore the magnetism in $Yb_xFe_4Sb_{12}$ has been considered to arise from itinerant $3d$ electrons [12]. The magnetic moment at low temperature obtained from isothermal magnetization curves as a function of the magnetic field showed a linear relation with T_C for $Yb_xFe_4Sb_{12}$ and $NaFe_4Sb_{12}$ [7]. Moreover, band calculations showed that the $4f$ level is well below the Fermi level so that the $4f$ orbitals do not contribute to the DOS at the Fermi edge [10, 12–14].

Figure 2 shows the RXES spectra measured on $YbFe_4Sb_{12}$ at 300 K as a function of the incident energy across the Yb L_3 edge. The contour intensity plots of the RXES spectra are shown in Fig. 2(c). In ranging from low to high incident photon energy, one can successively observe the Raman regime where the peaks remain at constant energy transfer, progressively evolving into the fluorescence which shifts towards high transferred energies. Each spectrum is well fitted with three peaks corresponding to the Yb^{2+} and Yb^{3+} Raman and the fluorescence components [9]. The fits indicate that the system is weakly valence fluctuating, with a main nonmagnetic Yb^{2+} component. Mostly similar spectra were obtained for $Yb_{0.88}Fe_4Sb_{12}$.

The temperature dependence of the PFY-XAS spectra is shown for both compounds in Fig. 3 along with the valence estimated from the fit of these spectra. The intensity ratio of Yb^{2+} to Yb^{3+} from the RXES spectra measured at the Yb^{2+} resonance is also shown. While no temperature dependence of the Yb valence is observed for $YbFe_4Sb_{12}$ over the entire temperature range of the measurement, a sharp increase of the Yb^{3+} component is found for $Yb_{0.88}Fe_4Sb_{12}$ below about 20 K. This valence increase coincides with the transition to the weak FM order shown in Fig. 1. This suggests a correlation between these two phenomena, especially in view of the absence of both valence change and magnetic ordering in $YbFe_4Sb_{12}$. The mean valence at $T \geq$ 60 K is estimated to be 2.13±0.03 for $Yb_{0.88}Fe_4Sb_{12}$, which is slightly higher than 2.11±0.03 for $YbFe_4Sb_{12}$. The Yb valence remains higher in $Yb_{0.88}Fe_4Sb_{12}$ than in $YbFe_4Sb_{12}$ under pressure too, as shown below. The fact that μ_{eff} is nearly the same for both compounds indicates that although the presence of Yb vacancies results in a slight increase of the magnetic Yb^{3+} component, it does not seem to affect the paramagnetic moment. This again suggests that the magnetism mainly originates from the itinerant $3d$ electrons of the Fe_4Sb_{12}

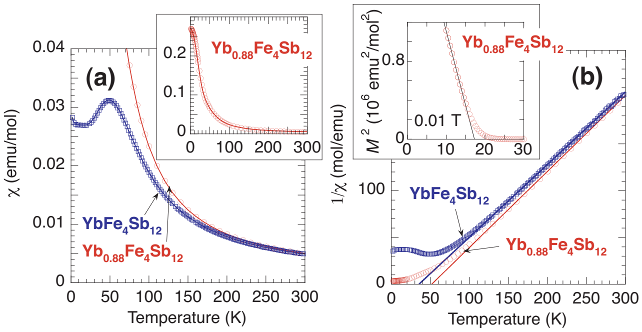

FIG. 1. (Color online). Temperature dependence of (a) magnetic susceptibility (χ) and (b) reciprocal susceptibility of $YbFe_4Sb_{12}$ (open square) and $Yb_{0.88}Fe_4Sb_{12}$ (open circle) at 1 T. Right-upper panel in (a) is the susceptibility of $Yb_{0.88}Fe_4Sb_{12}$ in a reduced vertical scale. Solid lines in (b) correspond to the Curie-Weiss fit at $T > 150$ K. Left-upper panel in (b) is the square of the susceptibility of $Yb_{0.88}Fe_4Sb_{12}$ at 0.01 T. The line is guide for eyes.

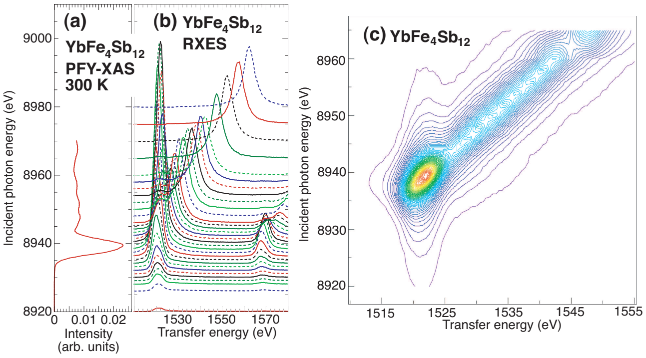

FIG. 2. (Color online). (a) and (b): RXES spectra as a function of the incident photon energies with PFY-XAS spectra at 300 K for $YbFe_4Sb_{12}$. The vertical offset of the RXES spectra in panel (b) corresponds to the incident energy in the PFY-XAS spectrum at which they were measured in panel (a). The energy transfer is difference between the incident and emitted photon energies. (c): Contour image of the RXES spectra.

sublattice, and not from the intermediate-valent Yb.

In the $A^{n+}[\mathrm{Fe_4Sb_{12}}]^{n-}$ skutterudites, the itinerant ferromagnetism of the $3d$ electrons is known to correlate with the number of electrons transferred from the filler ion A to the $\mathrm{Fe_4Sb_{12}}$ cage. Thus, a stronger ferromagnetic character is found for $n = 1$ than $n = 2$, and compounds with $n = 3$ like $\mathrm{LaFe_4Sb_{12}}$ remain in an enhanced paramagnetic state [10–12, 15]. In $\mathrm{Yb}_x\mathrm{Fe_4Sb_{12}}$ there is a direct relationship between the value of the filling ratio x and the ferromagnetism, while the FM quantum critical point is thought to be between $x = 0.88$ and 0.97 [7, 12]. Our results reveal an increase of the Yb^{3+} component in $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$ compared with $\mathrm{YbFe_4Sb_{12}}$. Here we suppose that this higher Yb valence corresponds to the electron transfer to Yb-deficient cages from neighboring Yb sites in $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$. Since the valence difference between the two compounds is on the order of 0.02 above T_C, one can deduce that only a part of the Yb-deficient cages acquire the charge-transferred electrons in the $x = 0.88$ compound. Based on the comparison with $A^{+}[\mathrm{Fe_4Sb_{12}}]^{-}$ skutterudites, the presence of such cages should favor FM ordering at low temperature. Extending this discussion to the temperature dependence of the valence, we understand that as a result of the valence increase of about 0.08 at $T \leq T_\mathrm{C}$ about all Yb-deficient cages should have had an electron transferred from Yb sites, further strengthening the FM character.

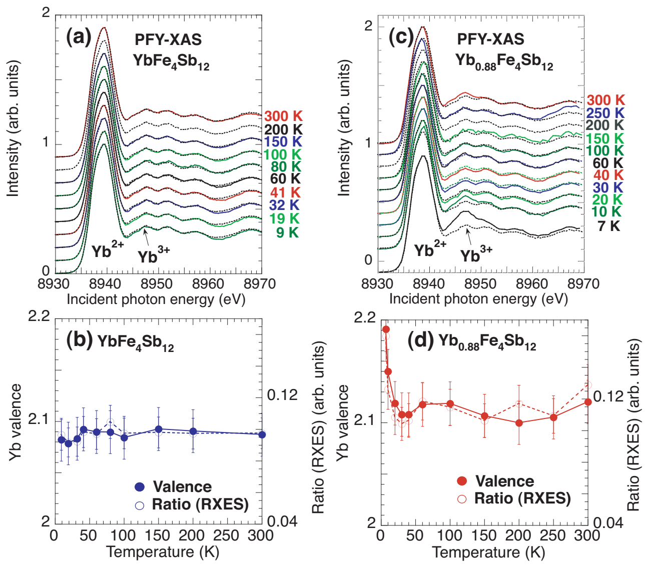

FIG. 3. (Color online). (a) and (c): Temperature dependence of PFY-XAS spectra. Each spectrum (solid line) is compared to the spectrum at 200 K (dished line). (b) and (d): Temperature dependence of the estimated valence (closed circles) from the analyses of the PFY-XAS spectra with the intensity ratio of Yb^{3+} to Yb^{2+} components (open circles) in the RXES spectra at $E_\mathrm{in} = 8939$ eV, where E_in is incident photon energy.

We briefly address the origin of the coincidence between the onset of these valence and magnetic transitions. It is notable that $A\mathrm{Fe_4Sb_{12}}$ compounds have a very steep band structure near the Fermi level [10, 12–14]. Small perturbations to the system, such as inclusion of Yb vacancies, may easily bring the system near the Stoner transition. One could speculate that changes in the Fe d DOS near the Fermi level, caused by the FM transition, affect the charge transfer from Yb-filled to Yb-deficient cages in a way that results in a slight increase of the concentration of the Yb^{3+} sites. It is plausible that the resulting Yb^{3+} moment would in turn enhance the FM interaction, therefore leading to a coupled increase of the valence and magnetic instabilities.

We note that, generally, the temperature dependence of the valence of Yb ions embedded in a metal can be described by the single impurity Anderson model or periodic Anderson lattice model, where the screening of the local moment through c-f hybridization below the Kondo temperature induces a gradual decrease of the valence with decreasing temperature [9]. If the Yb valence is nearly divalent, one may expect no temperature dependence of the valence below room temperature with this model, since the Kondo temperature is much larger than room temperature. On the one hand, our measurement shows that there is no temperature-induced change in the valence down to 9 and 30 K for $\mathrm{YbFe_4Sb_{12}}$ and $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$, respectively. Moreover, the sharp increase of the valence below 20 K in $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$ is a clear indication that this system cannot be described within the framework of the c-f hybridization and the Anderson model. Additionally, we note that no Kondo resonance peak, inherent to c-f hybridization, was observed near the Fermi edge by photoemission spectroscopy [14]. These facts substantiate our interpretation of the Yb^{3+} component in terms of local charge transfer from Yb sites to neighboring Yb-deficient

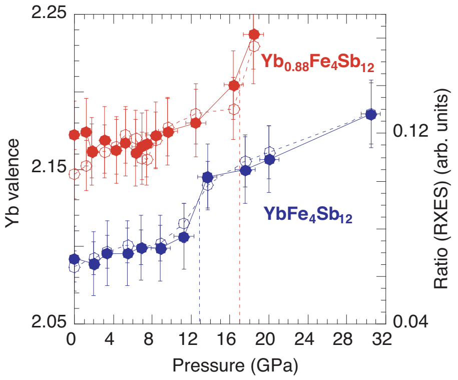

FIG. 4. (Color online) Pressure dependence of the estimated valence (closed circles) from the analyses of the PFY-XAS spectra with the intensity ratio (open circles) of Yb^{3+} to Yb^{2+} components in the RXES spectra at $E_\mathrm{in} = 8939$ eV.

cages.

The pressure dependence of the Yb valence as obtained from the fits the PFY-XAS and RXES spectra is shown in Fig. 4. For both $\mathrm{YbFe_4Sb_{12}}$ and $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$ the valence increases slightly up to ∼10 GPa, which is consistent with a previous study using XANES up to 7 GPa [12]. This is consistent with the idea that the $\mathrm{Yb^{3+}}$ state is favored under compression due its smaller ionic radius compared with $\mathrm{Yb^{2+}}$. Our results unveil a steep valence transition around 13 and 17 GPa for $\mathrm{YbFe_4P_{12}}$ and $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$, respectively. The difference between the lattice constant of the two samples is very small, much less than 0.1% [16], which should not affect the pressure of the valence transition much. It is noted that the average number of electrons transferred from Yb to $\mathrm{Fe_4Sb_{12}}$ per unit cell is, respectively, $0.88 \times 2.13 = 1.87$ for $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$ and $0.97 \times 2.11 = 2.05$ for $\mathrm{YbFe_4Sb_{12}}$. Because the electrons are transferred to the hybridized Fe $3d$ and Sb $4p$ states, which are high densities of states near the Fermi level, more electrons transferred means a larger shift of the Fermi level towards the conduction band. Accordingly, the Fermi level should be higher for $\mathrm{YbFe_4Sb_{12}}$ [8], which may result in a lower transition pressure than $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$.

It is uncommon for materials containing a divalent or nearly divalent rare-earth element to undergo first-order valence transitions under pressure. Valence transition induced by pressure is reminiscent of the $\gamma \rightarrow \alpha$ transition in Ce, which usually occurs through the change in the c-f hybridization and can be understood within the framework of the Kondo volume collapse model [17]. This model is, however, unlikely for the present case, since the change in the valence is very small below 10 GPa, although the volume change of $\mathrm{YbFe_4P_{12}}$ is reported to be about 5% at 9 GPa and the compressibility of $\mathrm{Yb}_x\mathrm{Fe_4Sb_{12}}$ may be twice as large as that of $\mathrm{YbFe_4P_{12}}$ [19]. Moreover strong c-f hybridization is not observed at ambient pressure. On the other hand, in $\mathrm{Yb}_x\mathrm{Fe_4Sb_{12}}$, the Fe $3d$ and Sb $4p$ states which are largely dominant at the Fermi level [18] should undergo drastic changes under pressure, affecting in turn the Yb valence as the Yb $4f$ level approaches the Fermi level. As an additional evidence of the close relationship between ferromagnetism and the Yb valence in this system, we note that an increase of T_C with pressure was reported in $\mathrm{Yb}_x\mathrm{Fe_4Sb_{12}}$ [7]. The valence change at the pressure-induced transition is nearly the same order as that of the temperature-induced transition of $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$. Thus one may speculate that the pressure-induced valence transition induces a transition to a FM ordered state at room temperature.

In this letter we provide evidence for strong correlation between the FM transition caused by the unfilled-Yb sites and an increase of the magnetic $\mathrm{Yb^{3+}}$ component in the skutterudite $\mathrm{Yb_{0.88}Fe_4Sb_{12}}$. We note that the sharp increase of the Yb valence at low temperature is not understandable within the conventional Anderson model picture or in the context of c-f hybridization, which have been commonly applied to understand the behavior of heavy fermion systems. Our results here show the first pressure and temperature induced valence transitions in a skutterudite system. Theoretical study taking into account the unfilled-Yb sites should help further understanding these transitions.

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