Strong Coupling between 4f Valence Instability and 3d Ferromagnetism in Yb₂Fe₄Sb₁₂ 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, YbFe₄Sb₁₂ and Yb₀.₈₈Fe₄Sb₁₂, 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 YbFe₄Sb₁₂ 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 YbFe₄Sb₁₂ and 17 GPa for Yb₀.₈₈Fe₄Sb₁₂.

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The 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 are mediated by conduction (c) electrons through the Rudermann-Kittel-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, the 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 electron can induce ferromagnetism in a nearly ferromagnetic (FM) itinerant electron system. Hence, in the cage-structure compound YFeₓZn₁₋ₓ where Y ions are surrounded by a Zn cage, a small amount of Gd³⁺ 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 Yb₁₋ₓFeₓSbₓ₁₂ [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 not 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 Yb₀.₈₈Fe₄Sb₁₂ as a function of x (0.88 and 1), temperature, and pressure. We observe a steady increase of the Yb valence at the FM transition of the FeSb₄ 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 Yb₀.₉₇±₀.₀₀₅FeₓSb₁₂ and Yb₀.₈₈±₀.₀₁FeₓSb₁₂ 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 YbFe₄Sb₁₂. The magnetic susceptibility was measured using a superconducting quantum interference
Temperature dependence of the magnetic susceptibility for YbFe₄Sb₁₂ and Yb₀.₈₈Fe₄Sb₁₂ 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 Yb₀.₈₈Fe₄Sb₁₂ is an order of magnitude higher than that of YbFe₄Sb₁₂. Whereas the FM transition temperature Tₐ for Yb₀.₈₈Fe₄Sb₁₂ is 17 K [7], YbFe₄Sb₁₂ does not show FM behavior, and the susceptibility shows a maximum around 50 K. Effective paramagnetic moments are estimated to be about μₑffective = 3.19 μᵤₐ / f.u. for YbFe₄Sb₁₂ and 3.13 μᵤₐ / f.u. for Yb₀.₈₈Fe₄Sb₁₂, where μᵤₐ is the Bohr magneton. These values of μₑffective per formula unit correspond to ~1.6 μᵤₐ/Fe, similar to that of alkali-metal or alkaline-earth-filled skutterudites of AFe₄Sb₁₂, where A is Na, K, Ca, and Ba [10–12]. It is known that NaFe₄Sb₁₂ and KFe₄Sb₁₂ are weakly FM with rather high Curie temperatures, and CaFe₄Sb₁₂ and BaFe₄Sb₁₂ are nearly FM. Therefore the magnetism in Yb₁Fe₄Sb₁₂ 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 Tₑ for Yb₁Fe₄Sb₁₂ and NaFe₄Sb₁₂ [7]. Moreover, band calculations showed that the 4f level is well below the Fermi level so that the magnetic moment mainly originates from the itinerant 3d electrons and not from the sublattice, and not from the sublattice, and not from the 4f orbitals do not contribute to the DOS at the Fermi edge [10,12–14].

Figure 2 shows the RXES spectra measured on YbFe₄Sb₁₂ at 300 K as a function of the incident photon energy across the Yb L₃ 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 Yb²⁺ and Yb³⁺ Raman and the fluorescence components [9]. The fits indicate that the system is weakly valence fluctuating, with a main nonmagnetic Yb²⁺ component. Mostly similar spectra were obtained for Yb₀.₈₈Fe₄Sb₁₂.

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 Yb²⁺ to Yb³⁺ from the RXES spectra measured at the Yb²⁺ resonance is also shown. While no temperature dependence of the Yb valence is observed for YbFe₄Sb₁₂ over the entire temperature range of the measurement, a sharp increase of the Yb³⁺ component is found for Yb₀.₈₈Fe₄Sb₁₂ 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 YbFe₄Sb₁₂. The mean valence at T = 60 K is estimated to be 2.13 ± 0.03 for Yb₀.₈₈Fe₄Sb₁₂, which is slightly higher than 2.11 ± 0.03 for YbFe₄Sb₁₂. The Yb valence remains higher in Yb₀.₈₈Fe₄Sb₁₂ than in YbFe₄Sb₁₂ under pressure too, as shown below. The fact that μₑffective is nearly the same for both compounds indicates that although the presence of Yb vacancies results in a slight increase of the magnetic Yb³⁺ 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 Fe₁₂Sb₁₂ sublattice, and not from the intermediate-valent Yb.

In the A⁺[Fe₄Sb₁₂]³ⁿ⁻ skutterudites, the itinerant ferromagnetism of the 3d electrons is known to correlate with the number of electrons transferred from the filler ion A to

![FIG. 1 (color online). Temperature dependence of (a) magnetic susceptibility (χ) and (b) reciprocal susceptibility (1/χ) for YbFe₄Sb₁₂ (open square) and Yb₀.₈₈Fe₄Sb₁₂ (open circle) at 1 T. Right-upper panel in (a) is the susceptibility of Yb₀.₈₈Fe₄Sb₁₂ at 0.01 T. The line is a guide for the eyes.](image-url)

![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 YbFe₄Sb₁₂. 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 the difference between the incident and emitted photon energies. (c) Contour image of the RXES spectra.](image-url)
the Fe$_4$Sb$_{12}$ cage. Thus, a stronger ferromagnetic character is found for $n = 1$ than $n = 2$, and compounds with $n = 3$ like LaFe$_4$Sb$_{12}$ remain in an enhanced paramagnetic state [10–12,15]. In Yb$_2$Fe$_4$Sb$_{12}$ 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 Yb$_{0.88}$Fe$_4$Sb$_{12}$ compared with YbFe$_4$Sb$_{12}$. Here we suppose that this higher Yb valence corresponds to the electron transfer to Yb-deficient cages from neighboring Yb sites in Yb$_{0.88}$Fe$_4$Sb$_{12}$. Since the valence difference between the two compounds is on the order of 0.02 above $T_C$, one can deduce that only some of the Yb-deficient cages acquire the charge-transferred electrons in the $x = 0.88$ compound. Based on the comparison with $A^3$[Fe$^8$Sb$_{12}$]$^-$ 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 $T = T_C$ about all Yb-deficient cages should have had an electron transferred from Yb sites, further strengthening the FM character.

We briefly address the origin of the coincidence between the onset of these valence and magnetic transitions. It is notable that $A$Fe$_4$Sb$_{12}$ 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 YbFe$_4$Sb$_{12}$ and Yb$_{0.88}$Fe$_4$Sb$_{12}$, respectively. Moreover, the sharp increase of the valence below 20 K in Yb$_{0.88}$Fe$_4$Sb$_{12}$ 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 cages.

The pressure dependence of the Yb valence as obtained from the fits of the PFY-XAS and RXES spectra is shown in Fig. 4. For both YbFe$_4$Sb$_{12}$ and Yb$_{0.88}$Fe$_4$Sb$_{12}$ the valence increases slightly up to $\sim 10$ GPa, which is consistent with a previous study using XANES up to 7 GPa [12]. This is consistent with the idea that the Yb$^{3+}$ state is favored under compression due its smaller ionic radius compared with Yb$^{2+}$. Our results unveil a steep valence transition around 13 and 17 GPa for YbFe$_4$Sb$_{12}$ and Yb$_{0.88}$Fe$_4$Sb$_{12}$,

![FIG. 3 (color online).](image)

(a) and (c) Temperature dependence of PFY-XAS spectra. Each spectrum (solid line) is compared to the spectrum at 200 K (dashed 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 $E_{in} = 8939$ eV, where $E_{in}$ is incident photon energy.

![FIG. 4 (color online).](image)

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 $E_{in} = 8939$ eV.
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 Fe$_4$Sb$_{12}$ per unit cell is, respectively, 0.88 $\times$ 2.13 = 1.87 for Yb$_{0.88}$Fe$_4$Sb$_{12}$ and 0.97 $\times$ 2.11 = 2.05 for YbFe$_4$Sb$_{12}$. 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 YbFe$_4$Sb$_{12}$ [8], which may result in a lower transition pressure than Yb$_{0.88}$Fe$_4$Sb$_{12}$.

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 YbFe$_4$P$_{12}$ is reported to be about 5% at 9 GPa and the compressibility of Yb$_4$Fe$_5$Sb$_{12}$ may be twice as large as that of YbFe$_4$P$_{12}$ [18]. Moreover strong c-f hybridization is not observed at ambient pressure. On the other hand, in Yb$_x$Fe$_4$Sb$_{12}$, the Fe 3d and Sb 4p states which are largely dominant at the Fermi level [19] 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 Yb$_x$Fe$_4$Sb$_{12}$ [7]. The valence change at the pressure-induced transition is nearly the same order as that of the temperature-induced transition of Yb$_{0.88}$Fe$_4$Sb$_{12}$. 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 Yb$^{3+}$ component in the skutterudite Yb$_{0.88}$Fe$_4$Sb$_{12}$. 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 in understanding these transitions.

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