Divalent state of ytterbium in YbFe₄Sb₁₂ filled skutterudite

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Abstract

High-resolution photoemission and X-ray absorption measurements of YbFe₄Sb₁₂ single crystals are performed. The experimental data are compared to the results of LDA + U calculations. Ytterbium was found to be mainly divalent in the bulk of the filled skutterudite.

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Compounds with the filled skutterudite structure are currently under intense investigation due to a wide variety of their interesting low-temperature ground-state properties. Binary systems like TX₃ (T = Co, Rh, Ir; X = P, As, Sb) can be considered as prototypes for these compounds. For T = Fe, Ru, Os, however, the crystal lattice needs to be stabilized by a third electropositive element, i.e. rare-earh (RE) filler. This leads to filled skutterudites RE₁−ₓT₄X₁₂ [1].

RE atoms, which can fit in the Fe–Sb host’s icosahedral void, are La–Eu, and Yb. Magnetic behavior of the filled skutterudites depends on RE element considered. Some RE fillers carry a localized magnetic moment. LaFe₄Sb₁₂ is paramagnetic down to 0.4 K revealing Curie–Weiss properties with negative Θ ≈ −42 K and reduced magnetic moment μ_eff = 2.26 μ_B [2]. Ytterbium is well known for its static or fluctuating mixed valence in different compounds.

In previous studies [3–5] Yb₁₋ₓFe₄Sb₁₂ has been characterized as a compound with an intermediate valence of Yb. The temperature dependences of the electrical resistivity and the moderately enhanced linear coefficient of the specific heat have been interpreted as due to Kondo effect and the formation of a heavy-fermion state below 50 K. Particularly, in Ref. [5] the electronic structure of polycrystalline Yb₁₋ₓFe₄Sb₁₂ has been investigated by means of ultra-violet and soft X-ray photoemission (PE). The anomalous relationship between the energy position of the bulk and surface components of the Yb³⁺ signal has been observed. Both divalent and trivalent configurations were found to contribute to the Yb 4f signal.

In this contribution we present results of high-resolution photoemission study of YbFe₄Sb₁₂ single crystals (grown and characterized as described in Ref. [6]) performed with different photon energies. We found only a weak Yb³⁺ signal in the PE spectra taken with higher surface sensitivity.

Fig. 1 shows valence-band PE spectra of YbFe₄Sb₁₂ measured with hν = 150 eV, 700 eV, and 850 eV at the Russian–German beamline at BESSY (Berlin). The dominant features in the energy region from the Fermi level (E_F) to
3 eV binding energy (BE) are attributed to the Yb $^{2+}$ signal (spin–orbit $4f^{7/2}$–$4f^{5/2}$ doublet), while the structures between 6 eV and 13 eV BE are assigned to the Yb $^{3+}$ contribution. The overall line shape of the Yb $^{3+}$ signal could be described in terms of the calculated atomic multiplet lines [5,8]. The intensity of the Yb $^{3+}$ signal is higher and its structure is clearer pronounced in the more surface sensitive spectrum taken at $h\nu = 150$ eV than at 700 eV or 850 eV photon energies. Therefore, the Yb $^{3+}$ signal observed here is attributed predominantly to the surface contribution. In the previous study [5] the Yb $^{3+}$ signal was found to be essential also in bulk sensitive PE spectra taken at $h\nu = 500$ eV and 700 eV (two bottom spectra in Fig. 1). The observed discrepancy can possibly be ascribed to the more irregular polycrystalline samples measured in Ref. [5], while the high-quality single crystals were investigated in our experiments. The almost divalent state of ytterbium in YbFe$_4$Sb$_{12}$ is also supported by our XAS data measured at the EXAFS II beamline E4 of HASYLAB at DESY (Hamburg). The inset in Fig. 1 presents absorption spectra of YbFe$_4$Sb$_{12}$ and Yb$_2$O$_3$ taken as a reference of the Yb $^{3+}$ state. The spectrum of the skutterudite is dominated by a peak shifted by 8 eV toward lower $h\nu$ relative to the main maximum of the Yb$_2$O$_3$ spectrum. This peak for YbFe$_4$Sb$_{12}$ is assigned to the $4f^{14}$ configuration. A weak high-energy shoulder in the spectrum indicates that the skutterudite sample contains a slight contribution of the $4f^{13}$ configuration. Evaluation of the spectrum results in an effective Yb valence $\nu = 2.10 \pm 0.05$. A similar value $\nu = 2.16$ was recently reported for Yb$_{0.99}$Fe$_4$Sb$_{12}$ [9].

The electronic structure of YbFe$_4$Sb$_{12}$ was calculated within the non-relativistic LDA + $U$ approach for different representative values of $U$. First, the value of 8 eV was adopted from the energy shift of the main XAS peak of skutterudite with respect to the peak of Yb$_2$O$_3$, and then, alternatively, $U = 4$ eV, 6 eV, and 10 eV were considered. Except for the 4f states, the resulting band structures differ only in small details from that of CaFe$_4$Sb$_{12}$ (Fig. 2). The influence of $U$ on DOS is reflected solely by a shift in energy of the 4f peak, which for all $U$ negligibly contributes to the DOS at $E_F$. The DOS at $E_F$ are 32 and 31 states eV$^{-1}$ f.u.$^{-1}$ for CaFe$_4$Sb$_{12}$ and YbFe$_4$Sb$_{12}$, respectively. Both compounds with divalent fillers are found to be nearly ferromagnetic.

References