

Divalent state of ytterbium in $\text{YbFe}_4\text{Sb}_{12}$ filled skutterudite

Yu.S. Dedkov^{a,*}, S.L. Molodtsov^{a,b}, H. Rosner^c, A. Leithe-Jasper^c,
W. Schnelle^c, M. Schmidt^c, Y. Grin^c

^a Institut für Festkörperphysik, Technische Universität Dresden, 01062 Dresden, Germany

^b Institute of Physics, St. Petersburg State University, 198504 St. Petersburg, Russia

^c Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Street 40, 01187 Dresden, Germany

Available online 27 March 2007

Abstract

High-resolution photoemission and X-ray absorption measurements of $\text{YbFe}_4\text{Sb}_{12}$ 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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Keywords: Filled skutterudites; Photoemission; X-ray absorption; Valence

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 TX_3 ($T = \text{Co, Rh, Ir}$; $X = \text{P, As, Sb}$) can be considered as prototypes for these compounds. For $T = \text{Fe, Ru, Os}$, however, the crystal lattice needs to be stabilized by a third electropositive element, i.e. rare-earth (RE) filler. This leads to filled skutterudites $\text{RE}_{1-x}\text{T}_4\text{X}_{12}$ [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. $\text{LaFe}_4\text{Sb}_{12}$ is paramagnetic down to 0.4 K revealing Curie–Weiss properties with negative $\Theta \approx -42$ K and reduced magnetic moment $\mu_{\text{eff}} = 2.26 \mu_{\text{B}}$ [2]. Ytterbium is well known for its static or fluctuating mixed valence in different compounds.

In previous studies [3–5] $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$ 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 spe-

cific 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 $\text{Yb}_{1-x}\text{Fe}_4\text{Sb}_{12}$ 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 Yb^{2+} 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 $\text{YbFe}_4\text{Sb}_{12}$ single crystals (grown and characterized as described in Ref. [6]) performed with different photon energies. We found only a weak Yb^{3+} signal in the PE spectra taken with higher surface sensitivity. X-ray absorption spectra (XAS) support divalent state of bulk ytterbium. Our band-structure calculations demonstrate similarity (except for the 4f electrons) of density of states (DOS) for Yb- and Ca-filled skutterudites. As concluded from the electronic structure calculations, both compounds with divalent fillers are nearly ferromagnetic, in accordance with our experimental observations [6,7].

Fig. 1 shows valence-band PE spectra of $\text{YbFe}_4\text{Sb}_{12}$ measured with $h\nu = 150$ 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

* Corresponding author. Tel.: +49 351 46335648; fax: +49 351 46333457.

E-mail address: dedkov@physik.phy.tu-dresden.de (Yu.S. Dedkov).

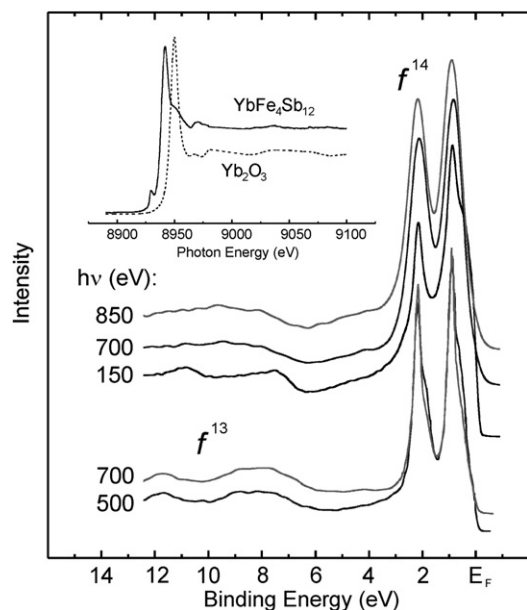


Fig. 1. PE spectra of $\text{YbFe}_4\text{Sb}_{12}$ measured at 100 K. Two bottom spectra are taken from Ref. [5] for comparison. The inset shows XAS spectra of $\text{YbFe}_4\text{Sb}_{12}$ and Yb_2O_3 at the ytterbium L_{III} edge at room temperature.

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 $\text{YbFe}_4\text{Sb}_{12}$ 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 $\text{YbFe}_4\text{Sb}_{12}$ and Yb_2O_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_2O_3 spectrum. This peak

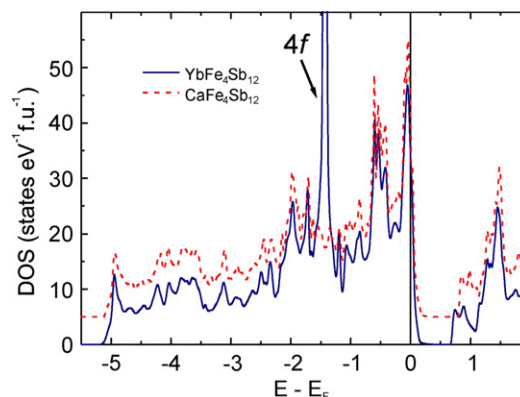


Fig. 2. Total DOS for Ca- and Yb-filled skutterudites calculated for $U = 6$ eV. Upper curve is shifted by five units for clarity.

for $\text{YbFe}_4\text{Sb}_{12}$ 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 $\text{Yb}_{0.93}\text{Fe}_4\text{Sb}_{12}$ [9].

The electronic structure of $\text{YbFe}_4\text{Sb}_{12}$ 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_2O_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 $\text{CaFe}_4\text{Sb}_{12}$ (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 $\text{eV}^{-1} \text{f.u.}^{-1}$ for $\text{CaFe}_4\text{Sb}_{12}$ and $\text{YbFe}_4\text{Sb}_{12}$, respectively. Both compounds with divalent fillers are found to be nearly ferromagnetic.

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