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# Photoemission spectroscopy of the filled skutterudite compound $\text{YbFe}_4\text{Sb}_{12}$

T Okane<sup>1</sup>, S-i Fujimori<sup>1</sup>, K Mamiya<sup>1</sup>, J Okamoto<sup>1</sup>, Y Muramatsu<sup>1</sup>,  
A Fujimori<sup>1,2</sup>, Y Nagamoto<sup>3</sup> and T Koyanagi<sup>3</sup>

<sup>1</sup> Synchrotron Radiation Research Centre, Japan Atomic Energy Research Institute, Mikazuki, Hyogo 679-5148, Japan

<sup>2</sup> Department of Complexity Science and Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan

<sup>3</sup> Department of Electrical and Electronic Engineering, Yamaguchi University, 2557 Tokiwadai, Ube 755-8611, Japan

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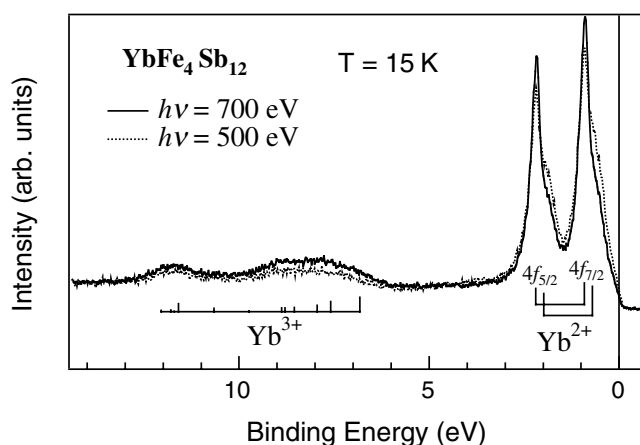
## Abstract

The electronic structure of  $\text{YbFe}_4\text{Sb}_{12}$ , which shows heavy-fermion or mixed-valence behaviour, are studied by high-resolution photoemission spectroscopy. The observed  $\text{Yb}^{2+}$  signal is composed of two spin-orbit doublets which might be interpreted as bulk and surface contributions. The relationship between the energy positions of the two doublets is anomalous compared to those of the conventional mixed-valence Yb compounds.

## 1. Introduction

The filled skutterudite compounds  $\text{RT}_4\text{X}_{12}$  ( $\text{R}$  = alkaline earth, rare earth, actinide;  $\text{T}$  = Fe, Ru, Os;  $\text{X}$  = pnictogen: P, As, Sb) exhibit a variety of physical properties such as superconductivity, magnetic ordering, heavy-fermion behaviour, and metal-insulator transition. Among them,  $\text{YbFe}_4\text{Sb}_{12}$  shows heavy-fermion or intermediate-valence behaviour in the magnetic, electrical transport, and thermal properties, which might be associated with a valence instability of the Yb atom [1]. The characteristic temperature for the valence fluctuation was estimated to be  $T^* \approx 70$  K [1].

We have performed high-resolution ultra-violet photoemission spectroscopy (UPS) and soft-x-ray synchrotron radiation photoemission spectroscopy (SRPES) experiments to elucidate the valence-band electronic structure of  $\text{YbFe}_4\text{Sb}_{12}$ . The SRPES measurement was aimed at obtaining more bulk-sensitive information, while the UPS measurement was performed with a better energy resolution. The spectra of  $\text{LaFe}_4\text{Sb}_{12}$ , used as a reference compound which contains no 4f electrons, were also measured.



**Figure 1.** The dependence on  $h\nu$  of the valence-band SRPES spectra of  $\text{YbFe}_4\text{Sb}_{12}$ .

## 2. Experiment

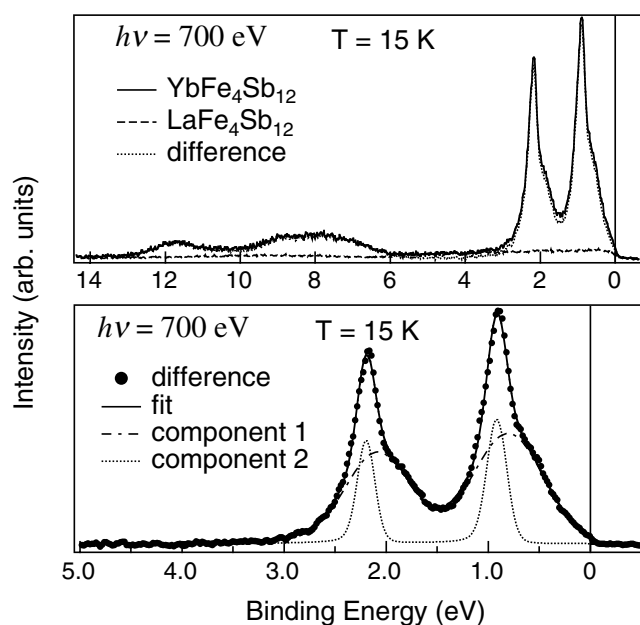
Polycrystalline samples of  $\text{MFe}_4\text{Sb}_{12}$  ( $\text{M} = \text{La}, \text{Yb}$ ) were prepared from high-purity metals:  $\text{M}$  (99.9%),  $\text{Fe}$  (99.9985%), and  $\text{Sb}$  (99.9999%), using the spark plasma sintering method performed under a pressure of 30 MPa.

The photoemission experiment was performed using a GAMMADATA SES2002 electron energy analyser. The light sources were the He II resonance line (40.8 eV) produced by a He discharge lamp and synchrotron radiation (500 and 700 eV) at the beamline BL23SU of SPring-8. The overall instrumental resolution was 11 meV for the UPS and  $\sim 200$  meV for the SRPES. The samples were cooled down to 15 K. Clean surfaces of the samples were obtained *in situ* by scraping with a diamond file for the SRPES and fracturing for the UPS.

## 3. Results and discussion

Figure 1 shows the valence-band SRPES spectra of  $\text{YbFe}_4\text{Sb}_{12}$  measured at  $h\nu = 500$  and 700 eV. The dominant features from the Fermi level  $E_F$  to 3 eV are attributed to the  $\text{Yb}^{2+}$  signal, and those from 6 to 13 eV to the  $\text{Yb}^{3+}$  signal. The  $\text{Yb}^{2+}$  signal is interpreted as a spin-orbit doublet of the  $4f_{7/2}$  and  $4f_{5/2}$  components. The features in the figure are composed of sharp main doublet peaks and shoulder-like doublet structures on the lower-binding-energy side of the main peaks. Usually the  $\text{Yb}^{2+}$  photoemission signal of mixed-valence Yb compounds is composed of two doublets of surface and bulk contributions [2], and the same interpretation might be applied to the results here. The spectrum measured at 500 eV is more surface sensitive than the spectrum measured at 700 eV due to the shorter electron mean free path. Since the shoulder-like structures have a higher intensity for  $h\nu = 500$  eV, the main peaks and the shoulder-like structures can be attributed to the bulk and surface contributions, respectively.

The overall line shape of the  $\text{Yb}^{3+}$  signal can be described in terms of the calculated atomic multiplet lines [3] shown by a bar diagram in the figure, although the line shape is quite obscure. This may possibly indicate an overlapping of different components which have energy positions shifted from each other. The intensity of the  $\text{Yb}^{3+}$  signal is higher in the spectrum for  $h\nu = 700$  eV than for 500 eV. Therefore, the  $\text{Yb}^{3+}$  signal observed here is attributed dominantly to the bulk contribution.

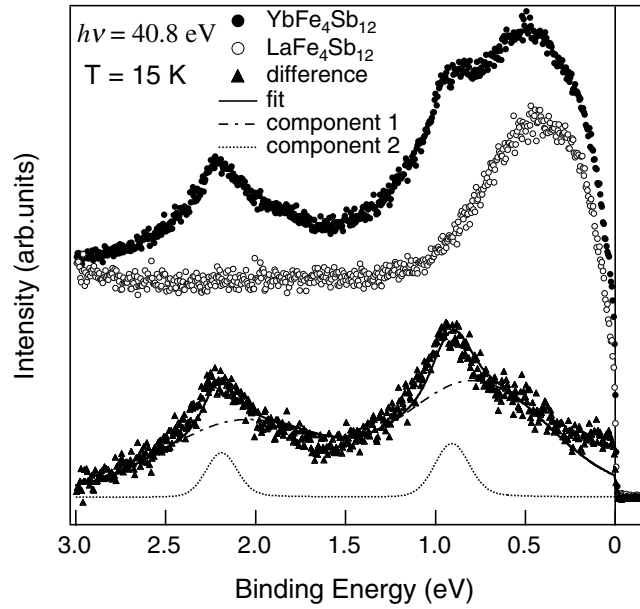


**Figure 2.** Upper panel: valence-band SRPES spectra of  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{LaFe}_4\text{Sb}_{12}$  and the difference. Lower panel: the fit for the  $\text{Yb}^{2+}$  signal of the difference spectrum.

To extract the Yb 4f component from the valence-band spectra, we have subtracted the spectrum of  $\text{LaFe}_4\text{Sb}_{12}$  from that of  $\text{YbFe}_4\text{Sb}_{12}$ . The result is shown in the upper panel of figure 2. The line shape analysis has been performed on the difference spectrum as shown in the lower panel of figure 2. In the analysis, the  $\text{Yb}^{2+}$  signal is decomposed into two spin-orbit doublets. The line shape of each component is a convolution of Gaussian and Lorentzian functions with the Doniach–Sunjic asymmetric broadening. The relative intensity of the  $4f_{5/2}$  and  $4f_{7/2}$  components has been fixed at 3:4. From the intensity ratio between the areas of the  $\text{Yb}^{3+}$  signal and the bulk component of the  $\text{Yb}^{2+}$  signal obtained from the fitting, we have estimated the valence of the Yb atom as 2.62, which is close to the value 2.68 estimated from the  $L_{\text{III}}$  x-ray absorption study [4].

The peak positions of the bulk and surface  $4f_{7/2}$  peaks are determined as 0.91 and 0.79 eV, respectively. The relationship between the energy positions of the bulk and surface components here is quite anomalous: usually in the mixed-valence Yb compounds, the energy position of the surface component is deeper than that of the bulk since the lower valence is favoured at the surface compared to the bulk [2]. This anomaly may be relevant to the crystal structure of the filled skutterudite compounds, in which the  $\text{Yb}^{2+}$  configuration is highly favourable because the smaller radii of the  $\text{Yb}^{3+}$  ion prevent adequate bonding in an oversized atomic cage.

The energy position 0.91 eV of the bulk  $4f_{7/2}$  peak is close to those for pure divalent Yb metal ( $\sim 1.2$  eV) rather than those for the conventional mixed-valence Yb compounds ( $< 0.1$  eV) [2]. Therefore, the position observed here seems to be too deep to explain the heavy-fermion behaviour of  $\text{YbFe}_4\text{Sb}_{12}$  with a characteristic temperature of  $T^* \approx 70$  K [1]. The one possible scenario for solving this discrepancy is the existence of irregular trivalent-like Yb sites besides the regular divalent-like Yb sites. However, we could not observe a distinct 4f signal such as a Kondo peak just below  $E_F$  in the SRPES spectra, possibly due to insufficient energy resolution.



**Figure 3.** Valence-band UPS spectra of  $\text{YbFe}_4\text{Sb}_{12}$  and  $\text{LaFe}_4\text{Sb}_{12}$ , the difference, and the fit for the difference.

To clarify the Yb 4f signal just below  $E_F$ , a UPS measurement with a better energy resolution was performed as shown in figure 3. To extract the Yb 4f signal, we have subtracted the spectrum of  $\text{LaFe}_4\text{Sb}_{12}$  from that of  $\text{YbFe}_4\text{Sb}_{12}$ . In the difference spectrum, we find the two spin-orbit doublets at the same energy positions as in the SRPES spectra. The difference spectrum is fitted with the same energy positions for all the components and the same widths for the bulk component as for the SRPES spectrum, while the relative intensity and the width of the surface component are varied to obtain better fitting, as shown in the figure. One can see the extra 4f intensity just below  $E_F$  which cannot be fitted, while the fitted curve slightly deviates from the measured spectrum at around 1.3 eV, separated from  $E_F$  by the energy of the spin-orbit splitting. Therefore, the result indicates the possibility of the existence of a trivalent-like electronic state for Yb besides the major divalent-like state.

#### 4. Summary

In summary, the electronic structure of  $\text{YbFe}_4\text{Sb}_{12}$  has been investigated by means of UPS and SRPES. The anomalous relationship between the energy positions of the bulk and surface components of  $\text{Yb}^{2+}$  signal has been observed. The major Yb 4f signal seems to be divalent-like, while the possibility of the existence of irregular trivalent-like (Kondo-like) Yb sites is indicated.

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