

Temperature dependence of Yb valence in the sub-surface of YbB₁₂(001)

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Abstract. The typical Kondo insulator, YbB₁₂, is a candidate of topological Kondo insulators. To clarify the surface electronic structure of not only bulk but also surface by photoelectron measurements, we developed a method to obtain a clean surface of YbB₁₂(001) by annealing at 1650 K in an ultra-high vacuum. By surface-sensitive photoelectron measurements, it was known that the surface consists of only B atoms without Yb. In the sub-surface region, Yb atoms exist and the temperature dependence of the valence agrees with those of previous HAXPES results. Here we report the cleaning method to obtain well-defined YbB₁₂(001) surfaces and the temperature-dependent Yb valence obtained from Yb 3*d* core-level and valence photoelectron spectra.

1. Introduction

YbB₁₂ is a typical Kondo insulator with the Kondo temperature (T_K) of about 230 K [1, 2]. The bulk of YbB₁₂ possesses a clear energy gap with the gap size of about 40 meV detected by an optical conductivity measurement [3]. However, it was reported that a finite density of states (DOS) has been observed at lower temperatures than that of the full gap opening [4]. The observed finite DOS at E_F is considered to originate from a metallic surface state. In fact, recently, the metallic surface state has been confirmed by an electrical transport measurement [5]. A theoretical study in which the metallic surface conductivity originates from a topological surface state is one of hot topics in condensed-matter physics recently [6]. So far, the bulk electric structure of YbB₁₂ has been studied by hard-X-ray angle-“integrated” photoelectron spectroscopy (HAXPES) and soft-X-ray angle-“integrated” photoelectron spectroscopy (SXPES) measurements [7, 8]. However, angle-“resolved” photoelectron spectroscopy (ARPES) on a well-defined YbB₁₂ surface has not been performed because the well-defined clean surface can not be obtained by conventional methods such as cleaving.

Then, to clarify the surface metallic state as well as to obtain the band structure of surface and bulk, we performed ARPES of a well-defined YbB_{12} (001) surface prepared by using a newly developed high-temperature annealing method in an another paper [9]. In this paper, we report the method to obtain the well-defined surface and the character of the obtained surface and sub-surface state by photoelectron spectroscopies (PESs) of Yb $3d$ core level and valence band. We show that the obtained YbB_{12} (001) surface consists of only B_{12} molecules without Yb atoms. Yb atoms exist at the sub-surface and the temperature dependence of the valence is consistent with those of previous HAXPES data [7]. This result suggests that the electronic structure and physical properties of the obtained sub-surface state is the same as those of the bulk.

2. Experimental

The single crystalline YbB_{12} was grown by the floating-zone method by using an image furnace with four xenon lamps [1]. The crystal was cut by a diamond saw along (001) plane based on an *in-situ* Laue pattern and then polished in the air by diamond lapping films until a mirror-like shining plane was obtained. The polished YbB_{12} (001) crystal was heated up to 1650 K in ultra-high vacuum chambers ($P < 2 \cdot 10^{-8}$ Pa) for ~ 10 sec. For the heating, we adopted a SiC wafer laid under YbB_{12} (001) as depicted in Fig. 1. The sample temperature was monitored by a radiation thermometer.

PES measurements were performed with synchrotron radiation at the BL-2A Musashi of Photon Factory, KEK, Japan, and CASSIOPÉE beamline of synchrotron SOLEIL, France. The photon energies of 80 eV and 1600 eV were used for a wide valence and Yb $3d_{5/2}$ core level (the binding energy is ~ 1540 eV) measurements, respectively, because of the high surface and sub-surface sensitivity of the photoelectron with the kinetic energy of 50–100 eV [10]. The incident-photons were linearly polarized and the electric field of photons lies in the incident plane (so-called p polarization). The photoelectron kinetic energy at the Fermi level (E_F) and the overall energy resolution of the PES setup (~ 100 meV) were calibrated by the Fermi edge of the photoelectron spectra from Ta foils attached to the sample. The base pressure of the PES main chamber was about $5 \cdot 10^{-9}$ Pa.

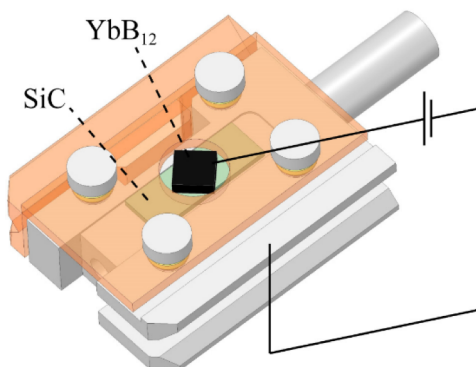


Fig. 1. A schematic drawing of the sample mounting on a sample folder for the PES measurement at KEK-PF. An SiC wafer laid below the YbB_{12} sample is the heater for annealing. Direct current for heating up flows through the sample and the SiC wafer.

3. Results and discussion

Figure 2 shows the annealing-temperature dependence of wide valence PES spectra of YbB_{12} with the photon energy of 80 eV at 20 K. At each spectrum, $4f$ peaks of Yb^{2+} and Yb^{3+} are observed at the similar energy positions to those in previous papers [7, 8] measured with scraped or cleaved YbB_{12} single crystals. The most evident difference between these spectra are the absence of Yb^{2+} $4f$ peaks at around 0.9 and 2.2 eV, which are assigned to be from the surface Yb atoms [11]. In addition, the intensity ratio of the Yb^{3+} $4f$ multiplet peaks to the Yb^{2+} spin-orbit peaks increases with increasing annealing

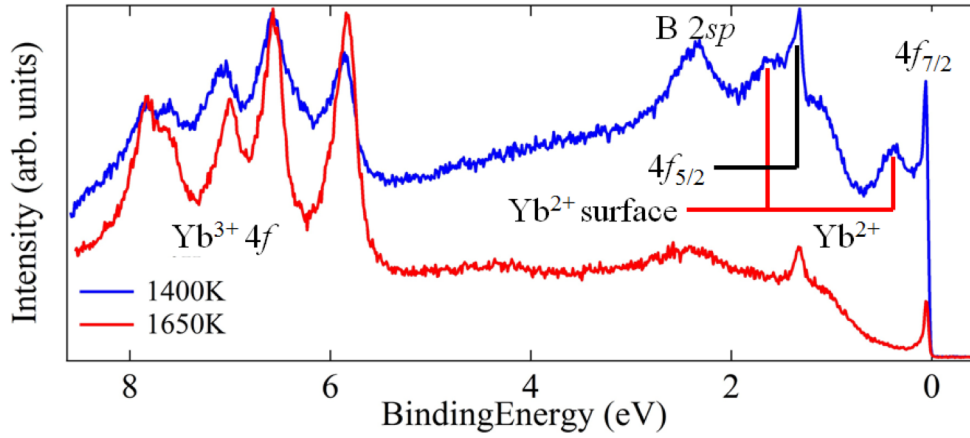


Fig. 2. Annealing-temperature-dependent PES spectra in a wide valence region taken by 80 eV photons at 20 K. Each spectrum is normalized to its maximum value.

temperature. The Yb^{3+} features should be from the bulk states, because most of valence-fluctuating materials, such as Yb and Eu compounds, tend to have smaller valence values at surface, where the coordination number is usually smaller than that in the bulk and the lattice constant increases [11]. Both of these results suggest that the Yb atoms are absent at the topmost surface, possibly because they were desorbed from the surface during the heating process up to 1650 K.

We measured the temperature dependence of the Yb $3d_{5/2}$ core level spectra of YbB_{12} with the photon energy of 1600 eV to obtain the temperature-dependent mean valence of the sub-surface. Figure 3 (a) shows the spectra after the subtraction of parabolic backgrounds. Since the binding energy of the Yb $3d_{5/2}$ core level is about 1540 eV, the kinetic energy of the Yb $3d_{5/2}$ electrons becomes about 60 eV, which is sensitive to surface and sub-surface state because of the short electron mean free path at the kinetic energy. In Fig. 3 (a), a single peak at the kinetic energy of 65 eV and peaks at 50 – 60 eV originate from the Yb^{2+} $3d$ state ($3d^9 4f^{14}$ final state) and the Yb^{3+} $3d$ state ($3d^9 4f^{13}$ final state), respectively. The latter has a multiplet structure.

From the integrated intensities of the Yb^{2+} state [$I^{(2+)}$] and the Yb^{3+} state [$I^{(3+)}$], the mean valence can be calculated according to the function $3 - I^{(2+)}/(I^{(2+)} + I^{(3+)})$ as shown in Fig. 3 (b). The mean valences at 20 and 300 K were evaluated as 2.92 ± 0.01 and 2.90 ± 0.01 , respectively. In the figure, the Yb valence evaluated from the Yb $3d$ HAXPES spectra at $h\nu = 8000$ eV (the most bulk sensitive because the kinetic energy is about 6500 eV) and Yb $4f$ SXPES spectra at $h\nu = 700$ eV (it contains both of bulk and surface characters) in previous papers [7, 8] are also plotted. These Yb $4f$ data were taken by using a cleaved surface. In all cases, Yb valence clearly shows a decrease on cooling from room temperature to 20 K. The origin of such decrease can be explained to be owing to the appearance of the Kondo effect because the hybridization between conduction bands and Yb $4f$ states, namely c - f hybridization, appears below the Kondo temperature of ~ 220 K, which band dispersion has been observed at lower temperatures by our ARPES measurement directly [9]. The Yb valence evaluated from the Yb $3d$ core level is almost the same as those from previous HAXPES results [7] but is much different from the lower mean valence of SXPES results [8]. The HAXPES spectra contain only the bulk property but the SXPES spectra contain properties not only from the bulk but also from the surface because the surface Yb ions are divalent. Therefore, it is confirmed that the Yb^{2+} ions at the topmost surface prepared in this study are desorbed from the surface with annealing up to 1650 K.

4. Conclusions

To summarize, we established the method to obtain a well-defined $\text{YbB}_{12}(001)$ surface by using a high-temperature annealing method to elucidate the origin of the metallic surface electronic structure of

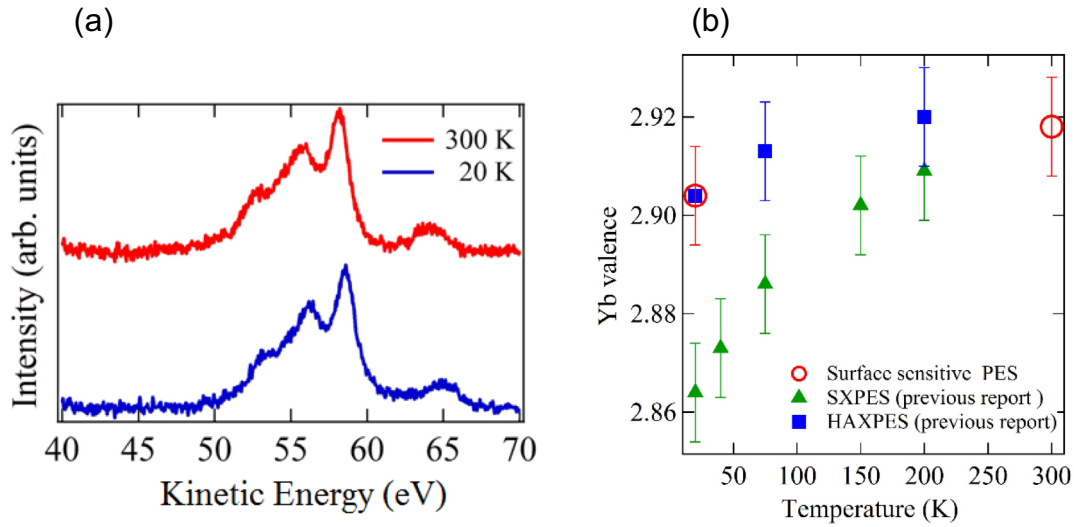


Fig. 3 (a) Yb 3d PES spectra taken with 1600 eV photons. Parabolic backgrounds were subtracted. (b) Yb valence evaluated in this work (PES) compared with the previous data taken by HAXPES and SXPES measurements [7, 8].

the Kondo insulator YbB₁₂. We observed that the topmost surface state contains only B atoms except for Yb atoms and Yb atoms exists at the sub-surface state by the cleaning method. The Yb valence at the sub-surface is 2.92 ± 0.01 and 2.90 ± 0.01 at 300 and 20 K, respectively, which are consistent with those of bulk observed by a HAXPES measurement.

Acknowledgments

We also acknowledge D. Ragonnet and F. Deschamps for their support during the experiments on the CASSIOPEE beamline at the SOLEIL synchrotron. This work was performed by Photon Factory Proposal No. 2015G540. The JSPS Grant-in-Aid also supported this work for Scientific Research (B) (Grant No. 15H03676).

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