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Yb L_{III} -edge and Cu K -edge X-ray Absorption Spectroscopy in YbCdCu₄ and YbInCu₄

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Abstract. The electronic structures of YbCdCu₄ and YbInCu₄ have been studied by X-ray absorption spectroscopy at room temperature. We have observed a shoulder structure at 8940 eV on the low-energy side of the Yb³⁺ component in the Yb L_{III} -edge. This structure is assigned to the L_{III} transitions of the Yb²⁺ electronic state, and thus a mixing of the divalent and trivalent states can be expected in both YbCdCu₄ and YbInCu₄. The energy position of the Cu K -edge coincides with that of Cu₂O as reference materials for the $3d^{10}$ electron configuration. Our results suggest that the electron configurations of Yb and Cu ions for YbCdCu₄ are similar to that for YbInCu₄ in the high-temperature phase.

INTRODUCTION

In the Laves-phase cubic system, YbInCu₄ has attracted interest because of the first-order valence transition between $4f^{13}$ (trivalent) and $4f^{14}$ (divalent) electron configurations at $T_V = 42$ K [1, 2]. The Yb valence changes from $z \sim 2.9$ for $T > T_V$ to $z \sim 2.8$ for $T < T_V$ [2, 3]. It has been suggested from photoemission spectroscopy measurements that the conduction electrons on the Cu and In sites mediate the electron transfer in $4f$ orbitals [4, 5]. In contrast, the related cubic compound YbCdCu₄ exhibits no valence transition and keeps a nearly trivalent state [6, 7, 8, 9]. The nominal electronic configurations of the Cd and In atoms are $5s^25p^0$ and $5s^25p^1$, respectively. The valence transition hence is considered to be sensitive to the $5p$ electron number. The material dependence in terms of the conduction electrons provides key insights for understanding the emergence of the valence transition phenomenon in YbInCu₄.

X-ray absorption spectroscopy (XAS) is a bulk probe that measures both unoccupied and occupied states with elemental and orbital selectivity. XAS research on YbCdCu₄ has not been reported so far, whereas a number of XAS experiments have been performed on YbInCu₄ and have investigated the Yb $4f$ electronic state [2, 4, 10, 11, 12]. Here, we report on the electronic structures of YbCdCu₄ and YbInCu₄ obtained by XAS measurements at room temperature. The electron configurations of Yb and Cu ions are determined by comparing with the spectra of reference materials and fitting the Yb L_{III} XAS spectra to a phenomenological function. We propose that the $5p$ electron plays the important role for valence transition of YbInCu₄.

EXPERIMENTAL DETAILS

High-quality single crystals of YbCdCu₄ and YbInCu₄ were synthesized by using the flux method [6, 8, 13]. The reference samples were prepared using commercially available powders of Yb₂O₃, Cu₂O, and CuO. The XAS experiments were performed at beamline 7C of the Photon Factory in Japan. The spectra were collected in the transmission mode using ionization chambers at room temperature ($T = 300$ K). The energy resolution was ~ 1 eV around the Yb L_{III} -edge. The energy was calibrated with the XAS spectrum of Cu.

RESULTS AND DISCUSSION

Figure 1(a) shows XAS spectra of YbCdCu_4 and YbInCu_4 over a wide photon energy of $8920 < h\nu < 9020$ eV. Well-defined peaks of the Yb L_{III} -edge and the Cu K -edge are observed at ~ 8950 and ~ 8995 eV, respectively. The line shape of YbCdCu_4 is similar to that of YbInCu_4 including the features of oscillation peaks at $h\nu > 9000$ eV. This similarity indicates that the electronic structure and the coordination environment around Cu between the two materials are not so different at 300 K.

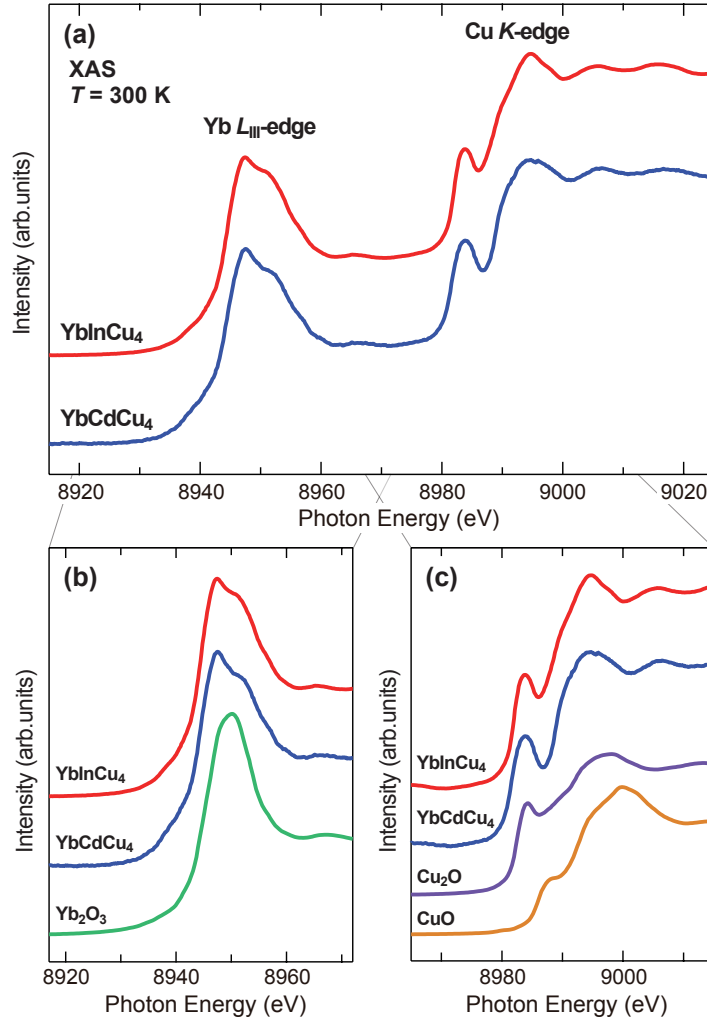


FIGURE 1. (a) XAS spectra of YbCdCu_4 and YbInCu_4 at 300 K. (b) Magnified view around the Yb L_{III} -edge in (a). Also shown is the spectra of Yb_2O_3 as a reference material for the $4f^{13}$ electron configurations of Yb ions. (c) Magnified view around the Cu K -edge in (a), together with the spectra of Cu_2O and CuO as reference materials for the $3d^{10}$ and $3d^9$ electron configurations, respectively.

In Fig. 1(b), we plotted the magnified view around the Yb L_{III} -edge, together with the spectrum of Yb_2O_3 as a standard for the $4f^{13}$ electron configuration of Yb ions. Their spectra exhibit a large peak at ~ 8950 eV in common. For YbCdCu_4 and YbInCu_4 , a shoulder structure is observed at 8940 eV on the low-energy side of the Yb^{3+} peak. This structure can be attributed to the L_{III} transitions of the Yb^{2+} electronic state [2, 10, 11, 12]. Therefore, the $4f$ -electron occupancy of YbCdCu_4 consists essentially of mixing between the divalent and trivalent states at 300 K, as in the case of YbInCu_4 [7, 9]. We note that the Yb L_{III} -edge has doublet peaks at 8947 and 8952 eV, which are derived from the energy separation of the Yb $5d$ unoccupied density of states [12].

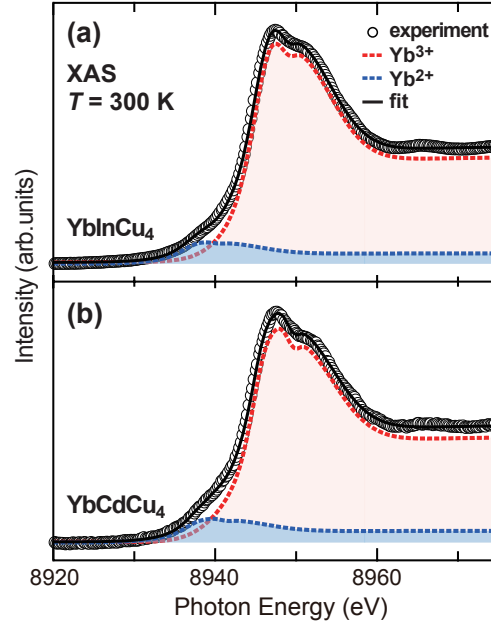


FIGURE 2. Fitting results for the Yb L_{III} XAS spectra of (a) YbInCu₄ and (b) YbCdCu₄ at 300 K. Open circles are the Yb L_{III} XAS spectra from the same data set in Fig. 1. The black curves represent the results of fitting analysis. The contributions of the Yb²⁺ and Yb³⁺ components are shown by the dashed blue and red lines, respectively.

To extract the Yb²⁺ and Yb³⁺ components quantitatively, we have performed a fitting analysis of the Yb L_{III} XAS spectra. Two Lorentzians are applied for each edge in accordance with the observation of doublet peaks at 8947 and 8952 eV. Moreover, the fitting function includes an arctangent background in energy for an incoherent spectral weight at higher energies. The parameters of the doublet peaks, such as the energy splitting, the peak intensity ratio, and the peak width ratio, are fixed for two valence components. Therefore, once the shape of spectrum is determined, the fitting parameters of the Yb²⁺ and Yb³⁺ components are the unique parameter set. This procedure is widely used and accepted for the analysis of XAS spectra in Yb compounds [2, 10, 12]. The fitting results are shown by black curves in Figs. 2(a) and 2(b). We note that the fitting function well captures the line shape of the shoulder structure at ~ 8940 eV and the doublet peaks in the Yb³⁺ component.

The Yb valence can be evaluated by the form $z = 2 + [I_3/(I_2 + I_3)]$, where I_2 and I_3 are integrated intensities of the Yb²⁺ and Yb³⁺ components [2, 10]. The Yb valence for YbCdCu₄ at 300 K is estimated as $z = 2.90$ from the fitting analysis shown in Fig. 2. This value is consistent with the result obtained by hard X-ray photoemission spectroscopy measurements [5]. The Yb valence, $z = 2.93$, for YbInCu₄ is also in agreement with that from previous studies [2, 10, 11].

Figure 1(c) shows a magnified view around the Cu K -edge, together with the spectra of Cu₂O and CuO as reference materials for the $3d^{10}$ and $3d^9$ electron configurations, respectively. For YbInCu₄ and YbCdCu₄, a pre-edge peak and a large absorption peak are visible at 8985 and 8995 eV, respectively. Their energy positions coincide with the peak energies for Cu₂O. Thus, the electron configuration of the Cu atom is in the $3d^{10}$ electronic state as a closed shell not only for YbInCu₄ but also for YbCdCu₄ [4]. These findings indicate that the electron configurations of Yb and Cu ions for YbCdCu₄ are similar to that for YbInCu₄ in the high-temperature phase.

We now discuss the role of the conduction electron for the valence transition. An extra $5p$ electron in YbInCu₄ entails an energy shift of the valence bands and changes the energy and momentum region where the valence bands and $4f$ states are interacting. The increase of the hybridization strength induces a robust charge transfer from the conduction bands into the Yb $4f$ states and consequently promotes the valence transition at low temperature [4]. For YbInCu₄, the hybridization strength between the conduction and the $4f$ -derived bands has been quantified from angle-resolved photoemission spectroscopy measurements [14]. More detailed experiments for YbCdCu₄ over wide temperature and momentum regions are required to establish the mechanism for the valence transition phenomenon.

CONCLUSION

We have investigated the electronic structure of YbCdCu₄ and YbInCu₄ by means of XAS at 300 K. From the fitting analysis of the Yb *L*_{III} spectra, the Yb valences are estimated to be 2.90 for YbCdCu₄ and 2.93 for YbInCu₄. We found that the electron configurations of Yb and Cu ions for YbCdCu₄ are similar to that for YbInCu₄ in the high-temperature phase. The electron transfer from the conduction bands to the Yb 4*f* states and the hybridization effect play an important role in the mechanism of the valence transition in YbInCu₄.

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