

Ir 4f hard X-ray photoemission spectrum of CuIr_2S_4

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Abstract

We have measured Ir 4f core-level photoemission spectra using an excitation photon energy of 6 keV for single crystalline CuIr_2S_4 at 250 and 200 K across the metal–insulator transition temperature of about 226 K. The Ir 4f spin–orbit doublet shifts by about 0.25 eV towards higher binding energy with decreasing temperature. Tails and satellites around 1 and 13 eV, respectively, higher in binding energy than the peaks of Ir 4f doublets are observed in the 250-K spectrum, but they almost disappear at 200 K. The peak analysis here done indicates that the Ir 4f spectrum at 200 K consists of two components 0.2 eV apart corresponding to the charge separation of Ir ions in CuIr_2S_4 .

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1. Introduction

CuIr_2S_4 with spinel structure undergoes simultaneous metal-to-insulator and paramagnetic-to-diamagnetic transitions around 226 K on cooling from room temperature (Furubayashi et al., 1994). The nominal Ir valence-value is presumed to be +3.5 in CuIr_2S_4 since Cu has been proved to be monovalent (Kumagai et al., 1995; Matsuno et al., 1997). It is considered that all the Ir ions in metallic CuIr_2S_4 are electronically equivalent, whereas the charge ordering of Ir takes place in

insulating CuIr_2S_4 according to Mössbauer spectroscopy and various diffraction measurements (Nagata et al., 1998; Radaelli et al., 2002). By comparing valenceband photoemission spectroscopy (PES) measurements with band-structure calculations (Oda et al., 1995), it has been pointed out that the correlation effect on Ir 5d electrons is not negligible in CuIr_2S_4 (Matsuno et al., 1997; Okane et al., 2004) in spite of the common belief that such an effect is very weak in 5d bands. Another interesting fact is that the Ir 4f core-level PES spectrum for CuIr_2S_4 in the insulating phase shows a single spin-orbit Ir 4f doublet, but does not show two distinct doublets as is expected for the charge separation of Ir ions (Matsuno et al., 1997; Okane et al., 2004).

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The notorious surface contribution to PES spectra sometimes confuses the discussion on bulk electronic states in materials of interest. A recent advance in hard X-ray PES (HX-PES) measurements using a photon energy of about 6 keV (Kobayashi et al., 2003; Takata et al., 2004) enables us to acquire more bulk sensitive spectra owing to elongated mean free path (>5 nm) of photoelectrons with higher kinetic energies than ordinary PES measurements. The HX-PES has succeeded in clarifying valence transitions in some materials (Sato et al., 2004; Yamamoto et al., 2004). In this work, we have measured the Ir 4f core-level HX-PES spectra for CuIr_2S_4 across the metal–insulator transition temperature in order to investigate the change in Ir valence.

2. Experimental

HX-PES measurements were performed at an beam line BL29XUL of SPring-8 by using a hemispherical high energy-resolution electron analyzer, SCIENTA SES-2002. Details of the experimental setup have been described elsewhere (Takata et al., 2004). The X-ray energy was 5948 eV and the overall energy resolution was 0.22 eV. Binding energies were calibrated by referring to Au HX-PES spectrum. The sample used was a single crystalline CuIr_2S_4 prepared by solid-state reaction.

3. Results and discussion

Fig. 1 shows Ir 4f HX-PES spectra for CuIr_2S_4 at 250 and 200 K. Two peaks are seen at 60.6 and 63.6 eV in the 250-K spectrum for the metallic phase [Fig. 1(a)]. They correspond to the $4f_{7/2}$ and $4f_{5/2}$ states, respectively, originating from the spin–orbit splitting of the 4f core state. Tails in high binding-energy side of the two peaks are rather intense at 250 K in comparison with ordinary metals. This implies that the observed asymmetric line shape does not come only from metallic response but also from other reasons, for example, redistribution of Ir 5d electrons such as crystal field excitation in the final state of the photoemission process. Satellites are seen around 13-eV higher than the main peaks at 250 K [Fig. 1(b)] as were observed in a previous study at 273 K with $h\nu = 840$ eV (Kitamoto et al., 2003). The satellites are not ascribed to the energy loss features due to plasmon excitation, but are done to so-called charge-transfer satellite. The plasmon losses are observed around 24 eV apart from the main lines for an Ir 3d core-level HX-PES spectrum for CuIr_2S_4 (not shown). In a viewpoint of cluster-model analysis the ground state is expressed by a linear combination of different configurations, d^n , $d^{n+1}\underline{L}$, ... and the PES final state

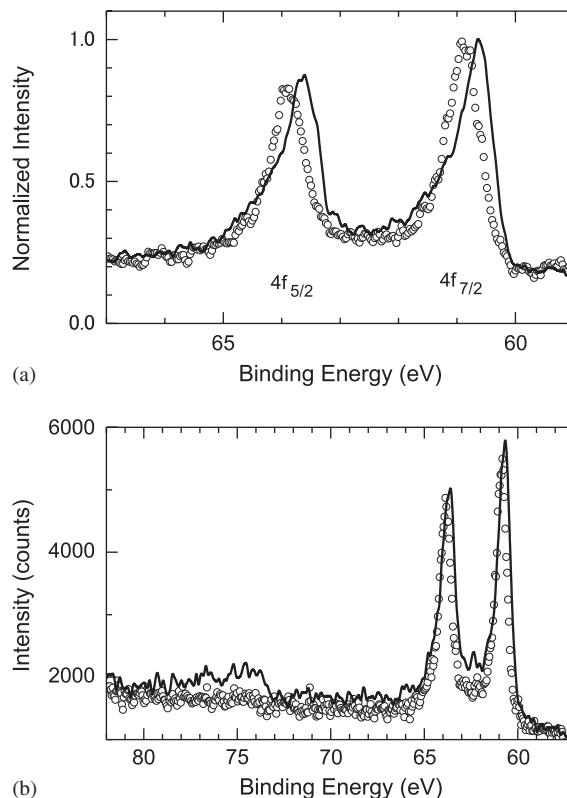


Fig. 1. Hard X-ray photoemission spectra of Ir 4f core-levels for CuIr_2S_4 at 250 K (solid curve) and 200 K (open circles) in the metallic and insulating phases, respectively, (a) in the vicinity of main peaks, where the intensities of the spectra are normalized at the Ir $4f_{7/2}$ peak, and (b) in wider energy region. Excitation photon energy was 5.95 keV.

by that of $\underline{c}d^n, \underline{c}d^{n+1}\underline{L}, \dots$. Here \underline{L} and \underline{c} denote a ligand S 3p hole and an Ir 4f core hole, respectively, and the nominal number n of Ir 5d electron is 5 or 6. The main lines and satellites in the 250-K Ir 4f spectrum are interpreted mainly as the bonding and antibonding states between $\underline{c}d^n$ and $\underline{c}d^{n+1}\underline{L}$, respectively (Kitamoto et al., 2003).

The 200-K spectrum for the insulating phase apparently shows a single spin–orbit doublet as was observed in the previous studies (Matsuno et al., 1997; Okane et al., 2004). Since the present HX-PES measurements are bulk sensitive, this does not result from any surface effect but is inherent in CuIr_2S_4 below the transition temperature. The line shape of main peaks in the 200-K spectrum is more symmetric and these peaks are less sharp than those at 250 K [Fig. 1(a)]. There are shoulders at 0.2 eV just below the peaks. Similar shoulders were also seen in the previous study (Okane et al., 2004) although they were not mentioned explicitly there. The two lines are shifted by about 0.25 eV from

those at 250 K possibly because of poor screening for the core-hole in the insulating phase. Besides the change in the main lines, the satellites around 13 eV almost disappear at 200 K [Fig. 1(b)]. The satellites were not seen also at liquid-nitrogen temperature (Matsumoto et al., 1997) but existed at 273 K (Kitamoto et al., 2003). The disappearance of the satellites in the insulating phase indicates that the electron transfer from adjacent atom(s) to the 5d orbital of the Ir atom which has a 4f hole is suppressed in the insulating phase. When the ground state is described mainly by only a single configuration d^n and contribution from the other configurations is neglected, the subsequent PES final state is composed only of a single configuration cd^n , that is, the PES spectrum shows no charge-transfer satellite. This consideration suggests that the Ir^{3+} and Ir^{4+} states are stabilized at different Ir sites in the initial state of insulating CuIr_2S_4 by taking into account the average Ir valence of +3.5.

Photoemission signals derived from divalent and trivalent rare-earth ions in the same compound are separated by about 10 eV (Sato et al., 2004; Yamamoto et al., 2004). The binding energy difference between Ir^{3+} and Ir^{4+} for insulating CuIr_2S_4 is much smaller even if it exists. We believe that the peaks and the 0.2-eV lower shoulders are responsible for Ir^{4+} and Ir^{3+} states, respectively, although they are not clearly resolved. In order to examine this assumption we have made preliminary curve fitting to the Ir 4f spectrum at 200 K supposing that the spectrum consists of two spin-orbit doublets. The results are shown in Fig. 2. The integrated intensities, the spin-orbit splitting energies and the asymmetric parameters were fixed equal for the two

doublets. An integrating background was used. The other fitting parameters were Lorentzian widths ΔE_L 's fixed equal for $4f_{5/2}$ and $4f_{7/2}$ of each doublet and the binding energies of $4f_{7/2}$ E_B 's. We obtained by a least-squares fitting procedure $\Delta E_L = 0.44(0.43)$ eV and $E_B = 60.80(61.00)$ eV for the low- (high-)binding energy doublet. The two doublets are separated by 0.20 eV. The resultant spectrum reproduces well the experimental spectrum despite simplification.

The very small energy difference of 0.2 eV indicates that the net charges of the two Ir sites are nearly equal. Recently Sasaki et al. (2004) have performed band-structure calculations for CuIr_2S_4 with triclinic crystal structure corresponding to the insulating phase. They have revealed that the numbers of valence electrons differ at most 0.05 among the Ir sites. The existence of the Ir 4f core-hole in the final state in the photoemission process may further reduce the difference between the two Ir sites. An Ir 4f PES spectrum for insulating CuIr_2S_4 with higher energy resolution than the present one is expected to show two distinct spin-orbit doublets (Okane, 2005).

Finally, we consider that the disagreement for metallic CuIr_2S_4 between the valence-band PES spectrum observed previously and calculated Ir 5d partial density of states is hardly caused by the surface effect, because the previous Ir 4f PES spectrum closely resembles the present HX-PES spectrum (Okane et al., 2004). Further both experimental and theoretical studies on the Ir 5d states in CuIr_2S_4 are necessary.

To summarize, we have measured the Ir 4f HX-PES spectrum for CuIr_2S_4 across the metal-to-insulator transition. We have found that the charge-transfer satellites almost disappear at 200 K and that the spectral shape changes across the transition. These are explained in terms of the charge separation of Ir ions. The Ir 4f photoemission signals from the trivalent and tetravalent Ir sites in insulating CuIr_2S_4 are separated by 0.2 eV.

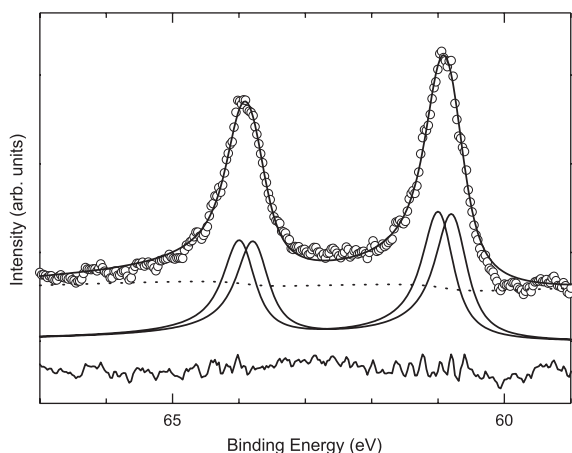


Fig. 2. Ir 4f core-level spectrum for insulating CuIr_2S_4 at 200 K (open circles). Solid lines are the results of a curve fitting analysis. Dotted line represents background. Curve at the bottom shows the difference between the experiment and the fitting.

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