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Physica B 378–380 (2006) 561–562
PHYSICA B
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Valence-band structure of $CuIr_2S_4$ studied by photoemission and S *L* X-ray emission spectroscopies

K. Kitamoto[a,b,*], Y. Taguchi[b], T. Noda[b], Y. Fujita[b], K. Mimura[b], K. Ichikawa[b], H. Ishibashi[c], S. Shin[a], O. Aita[b]

[a] *RIKEN/SPring-8, Mikazuki-cho, Hyogo 679-5148, Japan*
[b] *Graduate School of Engineering, Osaka Prefecture University, Gakuencho 1, Sakai 599-8531, Japan*
[c] *Graduate School of Science, Osaka Prefecture University, Gakuencho 1, Sakai 599-8531, Japan*

Abstract

Valence-band photoemission and S *L* X-ray emission spectroscopies have been performed for $CuIr_2S_4$ in order to investigate the electronic structure of the valence band. A structure around 1 eV below the Fermi level in the photoemission spectrum consists of Ir 5d as well as S 3p by taking into account its photon-energy dependent intensity. The S $L_{2,3}$ emission spectrum also shows a structure around 1 eV below the Fermi level, indicating that the state around 1 eV has the d-like or s-like character. These results indicate that S 3p has contribution to the electronic states near the Fermi level to some extent, and that the hybridization of Ir 5d with S 3p is important in understanding the electronic property of $CuIr_2S_4$.
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PACS: 71.20.Be; 71.28.+d; 78.70.En; 79.60.−i

Keywords: $CuIr_2S_4$; Ir 5d; Photoemission spectroscopy; X-ray emission spectroscopy

$CuIr_2S_4$ exhibits metal-insulator and paramagnetic–diamagnetic transitions around 226 K [1]. The nominal Ir valence is +3.5 in $CuIr_2S_4$ since Cu has been proved to be monovalent [2]. Radaelli et al. have proposed that these transitions are associated with simultaneous charge-ordering and spin-dimerization of Ir ions [3]. It is considered that not only the lattice distortion but also the Coulomb interaction of Ir 5d electrons are important to the charge-order transition of $CuIr_2S_4$. It is, therefore, necessary to investigate the Ir 5d state in order to understand the nature of transitions of $CuIr_2S_4$.

In this work we have measured the valence-band photoemission (PES) spectrum of $CuIr_2S_4$ with various photon energies in order to identify Ir 5d. The valence band of $CuIr_2S_4$ consists of Cu 3d, Ir 5d and S 3p orbitals which have different photoionization cross-sections from one another. The S $L_{2,3}$ X-ray emission (XES) spectrum has been also measured in order to investigate the hybridization of S 3p with Ir 5d by making use of the *E*1 selection rule. PES and XES measurements were performed at the beam line BL-19B at the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF). Total energy resolution was about 0.4 eV for PES. The resolution of the XES analyzer was better than 0.3 eV. The sample used was a sintered $CuIr_2S_4$ polycrystal. The clean sample surface was obtained in situ by scraping. All measurements were made at room temperature and for $CuIr_2S_4$ in metallic phase.

Fig. 1 shows valence-band PES spectra of $CuIr_2S_4$ taken at photon energies of 180, 480 and 630 eV. The spectra are normalized at 14 eV, a peak due to S 3s, after subtracting background. The spectrum at 630 eV resembles well with that previously obtained at 700 eV [4]. Features are seen around 1, 2.8 and 6 eV in the valence band of $CuIr_2S_4$. By considering the photoionization cross-sections of atomic orbitals and the energy dependence of observed spectra, the features around 2.8 and 6 eV are ascribed mainly to Cu 3d and S 3p, respectively, which is consistent with band

*Corresponding author. RIKEN/SPring-8, Mikazuki-cho, Hyogo 679-5148, Japan. Tel.: +81 791 58 2919; fax: +81 791 58 2934.
E-mail address: kitamoto@spring8.or.jp (K. Kitamoto).

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doi:10.1016/j.physb.2006.01.252

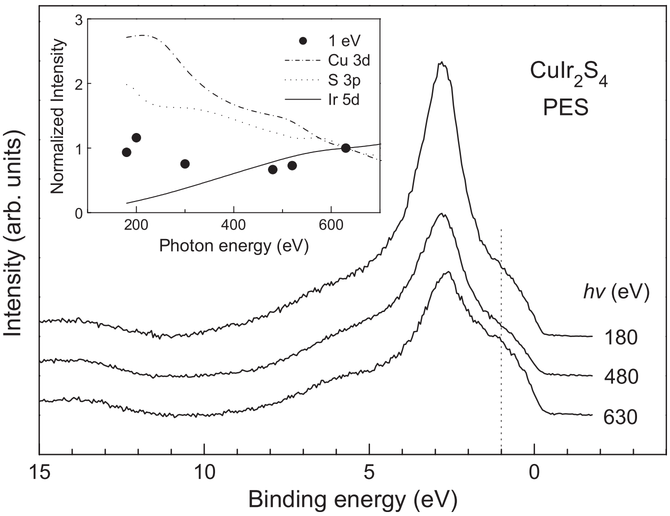

Fig. 1. Photon-energy dependence of valence-band photoemission spectrum for $CuIr_2S_4$ at room temperature. All the spectra are normalized at 14 eV. The inset shows photon-energy dependence of intensity at 1 eV (•) relative to that at 14 eV along with the ionization cross-sections of Cu 3d, Ir 5d and S 3p divided by that of 3s. All the data in the inset are normalized at 630 eV.

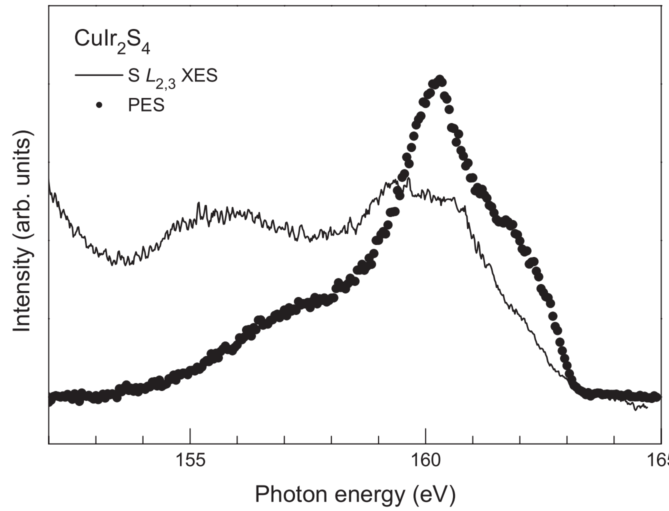

Fig. 2. Comparison between S $L_{2,3}$ XES and PES spectra measured at photon energies of 188 and 630 eV, respectively, for $CuIr_2S_4$ at room temperature.

structure calculations [5,6]. The calculated Ir 5d partial density of states (PDOS), however, shows a sharp peak around 1 eV below the Fermi level due to degenerate Ir 5d t_{2g} and is in disagreement with the valence-band PES spectrum [2,4]. The photon-energy dependence of intensity observed at 1 eV relative to that at 14 eV is shown in the inset of Fig. 1 along with the atomic ionization cross-sections of Cu 3d, Ir 5d and S 3p relative to S 3s [8]. All the ratios are normalized at 630 eV. With increasing photon energy the relative intensity at 1 eV slowly decreases up to 480 eV and then increases up to 630 eV. It is noted that only the ratio of Ir 5d/S 3s increases monotonically in this energy region. This establishes the contribution from Ir 5d at 1 eV, although not so large as predicted by the band-structure calculations. The band-structure calculations have shown that the sharp 5d PDOS around 1 eV is depressed for $CuIr_2S_4$ in the low-temperature crystal structure [6]. This suggests some local lattice distortion in the high-temperature phase or the correlation effect on Ir 5d electrons which is not dealt with band-structure calculations. We note here that the contribution from Ir 5d to the 1-eV structure was neglected in our previous study and that the Ir 5d–5d Coulomb energy was overestimated [7].

It is considered that the decrease of intensity at 1 eV observed in low photon-energy region is caused mainly by S 3p hybridized with Ir 5d since the PES spectra obtained previously have shown the photon-energy dependence at 1 eV similar to the cross-section of S 3p [2,9]. This interpretation is further supported by an S $L_{2,3}$ XES spectrum shown in Fig. 2. The 630-eV PES spectrum is also shown in Fig. 2 where the two spectra are aligned by referring to an S 2p PES spectrum of $CuIr_2S_4$. A shoulder structure is also seen in the S $L_{2,3}$ XES spectrum at the energy corresponding to 1 eV below the Fermi level. The structure has possibly d-like character through the hybridization with Ir 5d. An infrared spectroscopy study for $CuIr_2S_4$ has revealed that the Ir t_{2g} band hybridized with S 3p brings about the metallic response in the paramagnetic phase [10]. Thus the electronic states of $CuIr_2S_4$ near the Fermi level consist of Ir 5d and S 3p.

This work was carried out under the approval of the KEK-PF Program Advisory Committee (Proposal No. 2003G008).

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