

Ir 5d state in CuIr_2S_4 studied by photoemission and x-ray emission spectroscopies

Katsuyuki KITAMOTO, Yukihiro TAGUCHI*, Tatsunori NODA, Yukihiro FUJITA,
Kojiro MIMURA, Kouichi ICHIKAWA, Hiroki ISHIBASHI, Osamu AITA
Osaka Prefecture University, Gakuencho, Sakai, Osaka 599-8531, Japan

Introduction

CuIr_2S_4 exhibits metal-insulator and paramagnetic-diamagnetic transitions around 226 K [1]. It is considered that the transitions are associated with simultaneous charge-ordering and spin-dimerization of Ir ions [2]. While band-structure calculations show a sharp peak of Ir 5d partial density of states at 1 eV below the Fermi level for CuIr_2S_4 with the crystal structure corresponding to the high-temperature metallic phase [3], there has not existed a corresponding sharp structure in the photoemission spectrum [4]. In this work we have measured the photoemission spectrum of CuIr_2S_4 at various excitation photon energies in order to identify Ir 5d in the valence band by the use of energy dependence of photoionization cross-section. A sulfur $L_{2,3}$ x-ray emission spectrum has also been measured to confirm the hybridization of S 3p with Ir 5d states.

Results and Discussion

Fig. 1 shows the valence-band photoemission spectra of CuIr_2S_4 taken with $h\nu=180, 480,$ and 630 eV at room temperature. The sample used was a sintered polycrystal. The sample surface was cleaned *in situ* by scraping. The spectra are normalized at 14 eV, a peak due to S 3s. The intensity of peak at 2.8 eV and that of shoulder around 6 eV show photon-energy dependence similar to ionization cross-sections of Cu 3d and S 3p, respectively. The inset of Fig. 1 shows photon-energy dependence of intensity at

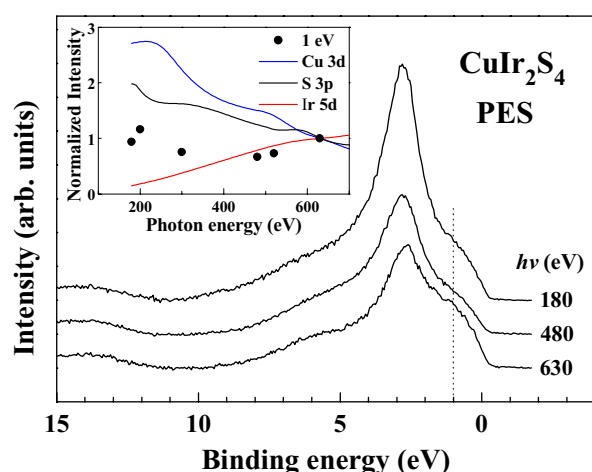


Fig. 1. Valence-band photoemission spectra of CuIr_2S_4 taken with $h\nu=180, 480$ and 630 eV at room temperature. The spectra are normalized at 14 eV. Solid circles in the inset denote the intensity at 1 eV relative to that at 14 eV.

1 eV (solid circles) relative to that at 14 eV along with the atomic photoionization cross-sections of Cu 3d (blue line), Ir 5d (red) and S 3p (solid) relative to that of S 3s. All the ratios in the inset of Fig. 1 are normalized at 630 eV. With increasing excitation-photon energy the relative intensity at 1 eV decreases up to ~ 480 eV and then increases. Only the ratio of (Ir 5d)/(S 3s) increases monotonically in the energy region from 180 to 630 eV. This indicates that the shoulder structure at 1 eV has contribution from Ir 5d, although not so large as is predicted by the calculations. The degeneracy of Ir 5d t_{2g} is the cause of the sharp peak at 1 eV in the calculations. The IrS_6 octahedron suffers trigonal field even in the high-temperature cubic phase [2]. This lifts the degeneracy of t_{2g} and may be partly responsible for the discrepancy between experiments and calculations. Alternatively the correlation effect on Ir 5d electrons may result in the discrepancy. We note that the contribution from Ir 5d to the 1-eV shoulder in the photoemission spectrum was neglected in our previous analysis with cluster-model calculations [5] and that we overestimated the on-site Ir 5d Coulomb energy for CuIr_2S_4 .

It is considered that the decrease of relative intensity at 1 eV in the photon-energy region below 480 eV is caused mainly by S 3p hybridized with Ir 5d. A shoulder structure at the energy corresponding to 1 eV below the Fermi level is also seen in the S $L_{2,3}$ x-ray emission spectrum of CuIr_2S_4 taken with excitation-photon energy of 188 eV at room temperature (not shown). According to the $E1$ selection rule the x-ray emission spectrum corresponds to the radiative transition from the sulfur-derived states with d- and/or s-symmetry in the valence band to the S 2p levels.

References

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* taguchi@ms.osakafu-u.ac.jp