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# Soft x-ray emission from valence band to S 2p in $CuIr_2S_4$

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Thiospinel $CuIr_2S_4$ exhibits simultaneous structural, metal-to-insulator (MI) and paramagnetic-to-diamagnetic transitions around 230 K with decreasing temperature. The formal Ir valency is 3.5+. It has been considered that charge ordering (CO) of Ir ions takes place in the insulating phase of $CuIr_2S_4$ [1]. The CO of Ir ions in $CuIr_2S_4$ may partly result from electron correlation among Ir 5d electrons. Such effect has been suggested by the fact that the valence-band (VB) structure of $CuIr_2S_4$ obtained by photoemission spectroscopy (PES) disagrees with band-structure calculations with respect to Ir 5d-derived structure despite qualitative agreement for Cu 3d- and S 3p-derived features [2,3]. It is considered that the electronic states near the Fermi level $E_F$ or the VB maximum plays an important role in the MI and CO transitions of $CuIr_2S_4$. According to the band-structure calculations the states near $E_F$ are mainly ascribed to Ir 5d-S 3p hybridized band [2]. In this work we have investigated the S 3p states hybridized with Ir 5d in $CuIr_2S_4$ by means of soft x-ray emission spectroscopy (XES). When a sulfur 2p core-hole is created, radiative transitions from VB to S 2p reflect the S 3p hybridized with *n*d and/or *n*s orbitals because of the dipole selection rule for XES and of the localized nature of the core hole. Cu ion of $CuIr_2S_4$ has essentially a $3d^{10}$ configuration [3].

Measurements were carried out at beamline BL-19B. The sample used was a sintered poly-crystal. The sample surface was cleaned in situ by scraping.

Fig. 1 shows the S $L_{2,3}$ XES spectrum of $CuIr_2S_4$ at 275 K (open circles). $E_F$ corresponds to the S $2p_{1/2}$ binding energy of $CuIr_2S_4$ determined by PES. A shoulder structure in XES is seen at 0.8 eV below $E_F$ in agreement with the previous PES measurement (dots in Fig. 2). A previous PES study has revealed that the structure has contribution from Ir 5d [4]. Thus the structure in XES results from the S 3p-Ir 5d hybridized band in accord with the band-structure calculations. In order to confirm that the S 2p spin-orbit splitting of ~1.2 eV does not cause the structure, we decomposed the S $L_{2,3}$ spectrum of $CuIr_2S_4$ into $L_2$ ($2p_{1/2}$) and $L_3$ ($2p_{3/2}$) spectra. We assumed that the transition probability from VB to S $2p_{1/2}$ and $2p_{3/2}$ depends only on the statistical weight of each core state, i.e. intensity ratio of 2:1 and that each spectrum can be reproduced by superposition of several Voigt functions. The obtained $L_2$ and $L_3$ spectra are also shown in Fig. 1. The S $L_2$ XES, PES and theoretical spectra are compared in Fig. 2. The S $L_2$ spectrum shows that the S 3p states hybridized with Ir 5d are distributed over almost the entire energy region of VB in good agreement with S 3p partial density of states obtained by the band-structure calculations [2].

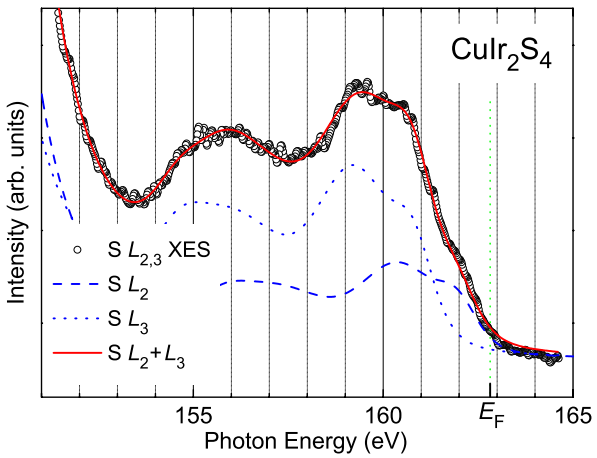


Fig.1. S $L_{2,3}$ soft x-ray emission spectrum of $CuIr_2S_4$ at 275 K (open circles). Broken, dotted and solid lines are decomposed $L_2$ and $L_3$ emission spectra and the sum of them, respectively.

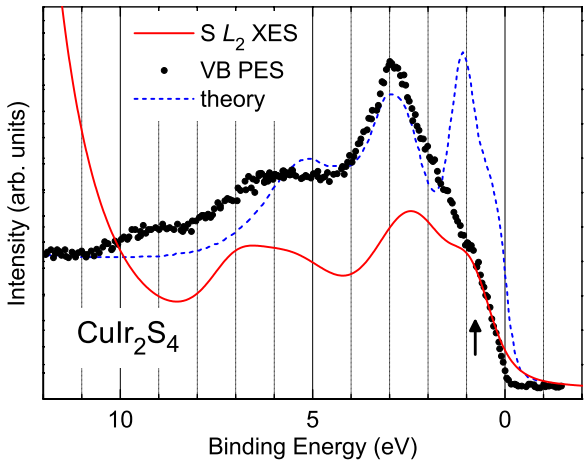


Fig. 2. Comparison of S $L_2$ x-ray emission (solid line) with photoemission (dots) and theoretical spectra (broken line) given in Ref. 3.

## References

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