

S $L_{2,3}$ x-ray emission measurements across the temperature-induced metal-insulator transition in CuIr_2S_4

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Thiospinel CuIr_2S_4 undergoes a first-order transition from a high-temperature, paramagnetic, mixed-valent $\text{Ir}^{3.5+}$, metallic phase to a low-temperature, diamagnetic, charge-ordered $\text{Ir}^{3+}/\text{Ir}^{4+}$, insulating phase around 230 K [1]. It has been considered that Ir 5d and/or Ir 5d-S 3p hybridized states are responsible for the transition [2,3]. Croft and coworkers have shown the redistribution of unoccupied Ir 5d states across the transition by measuring S K and Ir L_3 x-ray absorption spectra [4].

We have investigated change in the occupied S 3p states hybridized with Ir 5d across the transition in CuIr_2S_4 by means of S $L_{2,3}$ soft x-ray emission spectroscopy (XES). When a S 2p core hole is created in CuIr_2S_4 , radiative transitions from the valence band to S 2p reflect S 3p hybridized with Ir 5d. This is because of the dipole selection rule for XES, of the localized nature of the core hole and of the fact that Cu in CuIr_2S_4 has the closed 3d subshell [3].

Polycrystalline CuIr_2S_4 was used and in situ cleaned by scraping. XES spectra were recorded with the excitation photon energy of 188 eV. Energy resolution of the XES analyzer was better than 0.3 eV.

Fig. 1 shows the S $L_{2,3}$ XES spectra of CuIr_2S_4 at 275 (red curves) and 40 (blue) K. The spectra were brought to the scale of binding energies with respect to the Fermi level by referring to the S $2p_{1/2}$ binding energy determined by the photoemission spectrum of CuIr_2S_4 in each phase. The S $L_{2,3}$ XES spectrum appears to shift in energy across the transition. It has been observed that the

photoemission spectrum of CuIr_2S_4 shows almost rigid energy shift due to chemical potential shift across the transition [5]. However, the energy shift in the XES spectra are not constant and the shift around 3-10 eV is much larger than the chemical potential shift of about 0.1 eV. In addition relative intensities of the spectral features of XES spectrum change a little across the transition. In order to see clearly the change in the spectral shape, we have decomposed each S $L_{2,3}$ XES spectrum into L_2 and L_3 spectra as has been done in the previous report [6]. Fig. 2 compares S L_2 XES spectra of CuIr_2S_4 at 275 (red curves) and 40 (blue) K. The bottom of the S 3p-Ir 5d bonding band extends by more than 1 eV toward higher binding energy. Further spectral weight around 1 eV is transferred to that around 3 eV on going from metallic to insulating phase. This behaviour is consistent with the electronic state redistribution across the transition in CuIr_2S_4 which has been proposed in Ref. 4.

References

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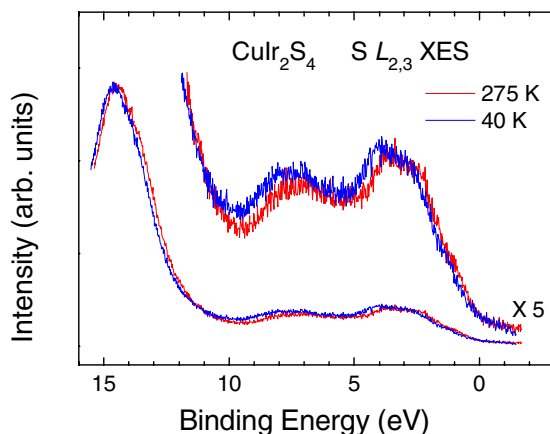


Fig. 1. S $L_{2,3}$ soft x-ray emission spectra of CuIr_2S_4 at 275 (red curves) and 40 (blue) K. Spectra were normalized at the peak due to S 3s-2p transition around 15 eV.

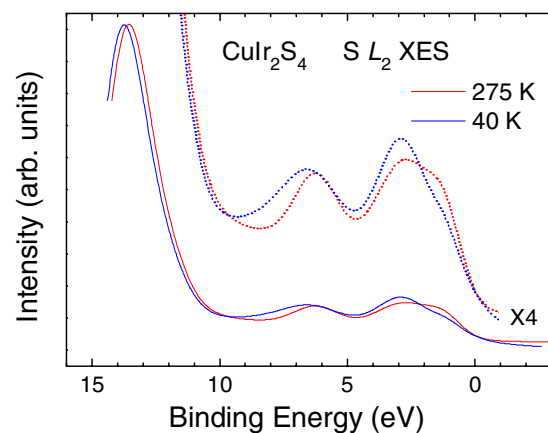


Fig. 2. Comparison of decomposed S L_2 emission spectra of CuIr_2S_4 at 275 (red curves) and 40 (blue) K. Spectra were normalized at the peak around 14 eV.