Ir 4f photoemission spectrum of CuIr$_2$S$_4$ analyzed by cluster-model calculation

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**Introduction**
Copper thiospinel CuIr$_2$S$_4$ exhibits simultaneous metal-insulator and paramagnetic-diamagnetic transitions around 230 K with decreasing temperature [1]. The nominal valence of Ir is +3.5 in CuIr$_2$S$_4$. It is considered that all the Ir ions in the metallic phase are electronically equivalent, whereas simultaneous octamer-type charge ordering and spin-lattice dimerization in the insulating phase have been proposed [2]. The importance of the correlation effect among the Ir 5d electrons, unlike other 5d transition-metal compounds, has been suggested in a previous electronic-structure study [3]. We have measured the Ir 4f photoemission spectrum of CuIr$_2$S$_4$ in order to estimate the on-site Ir 5d Coulomb energy $U_{dd}$ with the aid of IrS$_6$-cluster-model calculations for the present 4f spectrum and previous valence- and conduction-band spectra [3]. The core-level photoemission spectrum is necessary for adjustment of parameters, especially hybridization strength $V$ between Ir 5d and S 3p, in the calculations [4].

**Results and Discussion**
The sample used was a sintered CuIr$_2$S$_4$ polycrystal, and the surface was cleaned *in situ* by scraping. The excitation energy was 840 eV. The Ir 4f spectrum of CuIr$_2$S$_4$ at 273 K is shown by open circles in Fig. 1. The 4f spectrum well resembles the one reported previously [3], but shows better energy-resolution and statistics than that. The branching ratio of the spin-orbit doublet, the relative intensity of 4f$_{5/2}$ (63.9-eV) to 4f$_{7/2}$ (60.9-eV) peak, is approximately 6/8 expected from the degeneracy for the 4f$_{5/2}$ and 4f$_{7/2}$ states. This indicates that the exchange interaction between Ir 4f and 5d electrons is not so large in CuIr$_2$S$_4$ [4]. Two weak satellite structures are seen around 74.5 and 77.5 eV. These are attributed to the charge-transfer satellite because they are reminiscent of the spin-orbit doublet.

Also shown in Fig. 1 are the calculated 4f spectrum (solid curve), a constituent line spectrum (vertical bars) and assumed background (dashed curve). The calculated spectrum reproduces the experimental one, except for the asymmetric line shape of the spin-orbit doublet as is observed in the experimental spectrum. Similarly calculated Ir 5d photoemission and bremsstrahlung-isochromat spectra qualitatively reproduce the experimental ones with a single set of the parameters of the model employed. We have estimated for CuIr$_2$S$_4$ the d-d Coulomb repulsion energy $U_{dd}$ and the p-d hybridization strength $V(e_g)$ at 3.5 and 3.8 eV, respectively. The Coulomb energy of Ir 5d electrons is much smaller than those for 3d-transition-metal oxides and the hybridization strength larger. For example, Fe ions sitting on the octahedral sites in Fe$_3$O$_4$ has $U_{dd}$ of about 7 eV and $V(e_g)$ of 2.3 eV [5]. This indicates that the lattice distortion plays a more important role in the charge-order transition of CuIr$_2$S$_4$ than in the transition of 3d transition-metal oxides.

![Ir 4f PES](image)

**References**

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