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Ir 4f photoemission spectrum of $CuIr_2S_4$ analyzed by cluster-model calculation

Katsuyuki KITAMOTO, Yukihiro TAGUCHI*, Kojiro MIMURA, Kouichi ICHIKAWA,
Hiroki ISHIBASHI, Osamu AITA
Osaka Prefecture Univ., Sakai, Osaka 599-8531, Japan

Introduction

Copper thiospinel $CuIr_2S_4$ exhibits simultaneous metal-insulator and paramagnetic-diamagnetic transitions around 230 K with decreasing temperature [1]. The nominal valence of Ir is +3.5 in $CuIr_2S_4$. 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 $CuIr_2S_4$ 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 $CuIr_2S_4$ polycrystal, and the surface was cleaned *in situ* by scraping. The excitation energy was 840 eV. The Ir 4f spectrum of $CuIr_2S_4$ 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 $CuIr_2S_4$ [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 $CuIr_2S_4$ 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_3O_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 $CuIr_2S_4$ than in the transition of 3d transition-metal oxides.

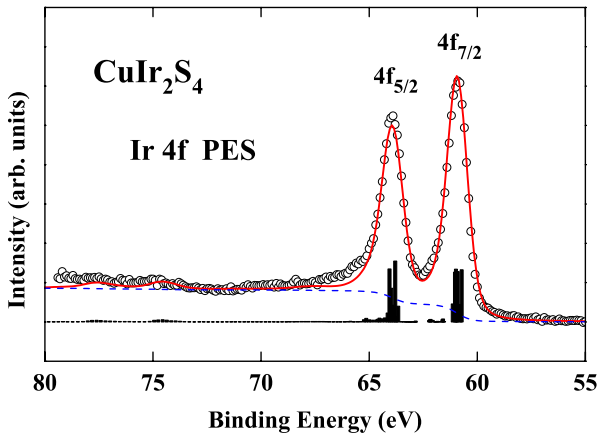

Fig. 1. Experimental (open circles) and calculated (solid curve) Ir 4f photoemission spectra of $CuIr_2S_4$. The experimental spectrum was taken at 273 K with $h\nu$=840 eV. The dashed curve represents the assumed background.

References

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