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Ir 5d state of CuIr$_2$S$_4$: A cluster-model approach

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The Ir 5d state in CuIr$_2$S$_4$ is investigated by using IrS$_6$-cluster-model calculations for the Ir 4f core-level and valence-band photoemission and bremsstrahlung isochromat spectra. The three experimental spectra are consistently reproduced in such a localized picture with a single parameter set of the model. The average d-d Coulomb energy between Ir 5d electrons in CuIr$_2$S$_4$ is 3.5 eV smaller than those for 3d transition-metal oxides, while the hybridization between Ir 5d and S 3p orbitals is larger. This indicates that the lattice distortion is important in the charge-order transition of CuIr$_2$S$_4$.

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I. INTRODUCTION

Copper thiospinel CuIr$_2$S$_4$ undergoes simultaneous metal-insulator and paramagnetic-diamagnetic transitions around 226 K.[1] In the compound Cu has been proved monovalent by nuclear magnetic resonance, Cu 2p core-level photoemission spectroscopy (PES) measurements,[2,3] and local-density-approximation band-structure calculations.[4] The nominal valence of Ir is, therefore, +3.5 in CuIr$_2$S$_4$. It is considered that all the Ir ions in metallic CuIr$_2$S$_4$ are electronically equivalent, whereas the charge ordering of Ir takes place in the insulating phase according to Mössbauer spectroscopy measurements.[5,6] Recently Radaelli *et al.* determined the precise crystal structure of CuIr$_2$S$_4$ below the transition temperature by using electron, neutron, and x-ray diffractions, and they proposed the simultaneous octamer-type charge ordering and spin-lattice dimerization in the insulating phase.[7] The electrical conductivity of CuIr$_2$S$_4$ below 50 K has been described by the Efros-Shklovskii hopping with long-range Coulomb correlation.[8,9] It is considered that the correlation effect among the Ir 5d electrons in CuIr$_2$S$_4$ plays an important role in the charge-order transition, although the electronic states of 5d transition-metal compounds have not been usually described by the localized picture. Matsuno *et al.* have investigated both occupied and unoccupied electronic structures of CuIr$_2$S$_4$ using PES and bremsstrahlung isochromat spectroscopy (BIS).[3] They have emphasized the importance of Ir 5d correlation in CuIr$_2$S$_4$ by comparing the valence-band (VB) PES spectrum and the results of the band-structure calculation.[4]

In this study we have performed cluster-model calculations for the Ir 4f core-level and VB PES and BIS spectra of CuIr$_2$S$_4$ in order to evaluate the correlation energy of Ir 5d electrons in CuIr$_2$S$_4$. The configuration-interaction cluster-model approach[10] explicitly takes into account the intra-atomic d-d Coulomb interaction of transition-metal ion in contrary to the band-structure calculation. The key parameters to describe the d electronic state in the cluster model, such as d-d Coulomb energy U_{dd}, charge-transfer energy Δ, and so on, have been deduced for numbers of 3d transition-metal compounds.[11,10,12] Thus one can discuss the correlation effect on the Ir 5d electrons in CuIr$_2$S$_4$ within the same framework by comparing with the results for 3d transition-metal compounds.

II. CLUSTER MODEL

We have used a single IrS$_6$ cluster with O_h symmetry, where an Ir ion is octahedrally coordinated by S ions, to simulate Ir 5d electronic state of CuIr$_2$S$_4$ and to calculate core-level and VB spectra. We have focused our attention on the intra-atomic correlation among the Ir 5d electrons in CuIr$_2$S$_4$. We have neglected here, for simplicity, the lattice distortion and the charge order of Ir in the insulating phase of CuIr$_2$S$_4$.[7] In order to investigate the Ir 5d state of CuIr$_2$S$_4$ in the insulating phase, it would be necessary to use a larger cluster with lower symmetry if one applied similar cluster-model approach.

Our system is composed of Ir 4f-core, Ir 5d, and S 3p states and is described by a Hamiltonian

$$\begin{aligned} H = & \sum_{\gamma} \epsilon_d(\gamma) d^\dagger_\gamma d_\gamma + \epsilon_P \sum_{\gamma} P^\dagger_\gamma P_\gamma + \sum_{\gamma} V(\gamma)(d^\dagger_\gamma P_\gamma + P^\dagger_\gamma d_\gamma) \\ & + U_{dd} \sum_{\gamma > \gamma'} d^\dagger_\gamma d_\gamma d^\dagger_{\gamma'} d_{\gamma'} - U_{dc} \sum_{\gamma,\xi} d^\dagger_\gamma d_\gamma (1 - c^\dagger_\xi c_\xi) \\ & + H_{mult}. \end{aligned} \tag{1}$$

Here $d^\dagger$, $c^\dagger$, and $P^\dagger$ are electron creation operators for Ir 5d, 4f orbitals, and S 3p molecular orbitals, respectively, and indices γ and ξ represent both orbital and spin states. The first and second terms of the Hamiltonian describe one-particle energies of Ir 5d and S 3p states, respectively, and the third term their orbital mixing through p-d hybridization $V(\gamma)$. The fourth and fifth terms are Coulomb interaction U_{dd} between 5d electrons and attractive 4f core-hole potential U_{dc} acting on the 5d electrons, respectively. The last term contains the multipole part of Coulomb interaction and the spin-orbit interaction. Multiplet coupling parameters of Slater integrals F^k and G^k and spin-orbit coupling constant ζ

were obtained through the ionic Hartree-Fock-Slater calculation, and the Slater integrals were reduced to 85%.

Wave functions of the system are described by appropriate linear combinations of three different configurations. Since the mean valence of the Ir ion in $CuIr_2S_4$ is $+3.5$, we describe the ground state $|g\rangle$ by

$$|g\rangle=\alpha_0|d^5\rangle+\alpha_1|d^6\underline{L}\rangle+\alpha_2|d^7\underline{L}^2\rangle. \qquad (2)$$

Here $\underline{L}$ denotes a ligand S $3p$ hole. The three configurations are mixed with each other through the p-d hybridization. Then the final states for Ir $4f$, Ir $5d$ (VB) PES and BIS spectra are described by

$$|f_{4f\mathrm{PES}}\rangle=\beta_0|\underline{c}d^5\rangle+\beta_1|\underline{c}d^6\underline{L}\rangle+\beta_2|\underline{c}d^7\underline{L}^2\rangle, \qquad (3)$$

$$|f_{5d\mathrm{PES}}\rangle=\beta_0'|d^4\rangle+\beta_1'|d^5\underline{L}\rangle+\beta_2'|d^6\underline{L}^2\rangle, \qquad (4)$$

and

$$|f_{5d\mathrm{BIS}}\rangle=\beta_0''|d^6\rangle+\beta_1''|d^7\underline{L}\rangle+\beta_2''|d^8\underline{L}^2\rangle, \qquad (5)$$

respectively. Here $\underline{c}$ denotes a hole in the $4f$ level. Hamiltonian (1) is diagonalized by these bases. The spectra have been calculated under the sudden approximation. The PES spectra are calculated by

$$F(E_B)=\sum|\langle f_{\mathrm{PES}}|T|g\rangle|^2\delta(E_B+E_g-E_f), \qquad (6)$$

where T denotes the electric dipole transition, and E_g, E_f, and E_B are the ground-, final-state, and binding energies, respectively. Similarly the BIS spectrum is

$$F(E)=\sum|\langle f_{\mathrm{BIS}}|T|g\rangle|^2\delta(E+E_g-E_f), \qquad (7)$$

where E is the kinetic energy of an incident electron.

We define the charge-transfer energy as $\Delta=E(d^6\underline{L})-E(d^5)$, where $E(d^5)$ and $E(d^6\underline{L})$ represent the configuration-averaged energies of d^5 and $d^6\underline{L}$ configurations, respectively. In this study, we treat Δ, U_{dd}, U_{dc}, $V(e_g)$, and the crystal-field splitting energy $10Dq=\epsilon_d(e_g)-\epsilon_d(t_{2g})$ as adjustable parameters and assume, for simplicity, the relationship $V(e_g)=-2V(t_{2g})$. The correction factors R_c and R_v for hybridization strength depending on the configuration[13] are also included in our calculation and have been fixed to 0.95 and 0.9, respectively. The parameters have been estimated through the Ir $4f$ and VB PES and BIS analyses. U_{dc} and $V(e_g)$ have been determined mainly by the position and intensity of the charge-transfer (CT) satellite in the $4f$ PES spectrum, $10Dq$ by BIS, Δ by VB PES, and U_{dd} by the relative position of the VB PES spectrum to the BIS spectrum. The obtained parameter values are listed in Table I, together with the average $5d$ electron number n_d in the ground state.

We have referred to the experimental results for VB PES and BIS spectra of $CuIr_2S_4$ measured by Matsuno *et al.*[3] Although these experimental spectra were taken at liquid-nitrogen temperature below the transition temperature, we have assumed that those spectra do not change significantly above the transition temperature.[14] We have measured an Ir $4f$ PES spectrum of $CuIr_2S_4$ at 273 K above the transition temperature, which will be shown shortly. By taking account of difference in energy resolution and statistics, our $4f$ spectrum is almost identical to that taken at liquid-nitrogen temperature.[3] Because of the better energy resolution and statistics, we have referred to our $4f$ PES spectrum here. As described before it is important to distinguish the CT satellite to determine the parameter values. Further the polycrystalline $CuIr_2S_4$ sample used in Ref. 3 was possibly subject to an x-ray irradiation effect on the crystal structure. It has been reported that x rays induce an apparent triclinic-to-tetragonal transition accompanied by a 1000-fold reduction in the electrical resistivity of $CuIr_2S_4$ at low temperatures.[15] It is necessary that one should measure the PES and BIS spectra of a $CuIr_2S_4$ single crystal in order to analyze the electronic structures in the insulating phase.

TABLE I. Adjustable parameter values in electron volt and parameters R_c and R_v are for the configuration dependence of hybridization strength in the present analysis. n_d is the average electron number in the ground state.

Δ	U_{dd}	U_{dc}	$V(e_g)$	$10Dq$	R_c	R_v	n_d
0.5	3.5	4.5	3.8	2.3	0.95	0.9	5.91

III. RESULTS AND DISCUSSION

A. Ir 4*f* PES spectrum

The Ir $4f$ core-level PES spectrum of $CuIr_2S_4$ taken at 274 K is shown by open circles in Fig. 1. The PES measurements were performed at the beamline BL-19B at Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK-PF). The sample used was a sintered $CuIr_2S_4$ polycrystal. The sample surface was cleaned *in situ* by scraping with a diamond file. The excitation energy was 840 eV. The overall energy resolution was 0.2 eV. Incident photon and electron binding en-

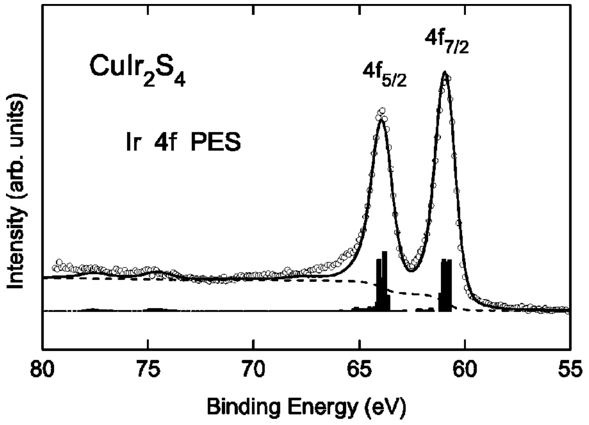

FIG. 1. Experimental (open circles) and calculated (solid curve) Ir $4f$ photoemission spectra of $CuIr_2S_4$. The experimental spectrum was taken at 273 K with $h\nu=840$ eV. The dashed curve represents the assumed background.

ergies were calibrated by referring to the Au PES spectra taken before and after the Ir $4f$ PES measurements. The $4f$ PES spectrum well resembles the one reported previously in Ref. 3. Two peaks at 60.9 and 63.9 eV originate from the spin-orbit splitting of the $4f$-core state. The branching ratios of the spin-orbit doublet, the relative intensity of $4f_{5/2}$ to $4f_{7/2}$ peak, and also that for the previous spectrum[3] are $\approx 6/8$ expected from the degeneracy for the $4f_{5/2}$ and $4f_{7/2}$ states by taking account of background due to secondary electrons. In addition to the doublet, two weak satellite structures are seen around 74.5 and 77.5 eV. These satellites are reminiscent of the spin-orbit doublet, and attributed to the CT satellite, not to an energy-loss caused by the plasmon excitation.

The calculated Ir $4f$ PES spectrum for CuIr$_2$S$_4$ is also shown as a solid curve in Fig. 1. The calculated line spectrum is convoluted with the Lorentzian and Gaussian functions with the half width at half maximum $\Gamma_L = 0.15$ eV and $\Gamma_G = 0.45$ eV, respectively. The calculated spectrum well reproduces the experimental one, except for the asymmetric line shape of the spin-orbit doublet observed in the experimental spectrum. The asymmetry comes from the electron-hole pair creation in the photoemission process, but the effect was not included in the calculation. It is noted that we neglected the exchange interaction between Ir $4f$ and $5d$ electrons, that is, we omitted Slater integrals $G^k(4f,5d)$ in the term H_{mult} of Eq. (1). The integrals for an Ir ion are at most 1.8 eV. The total spin S of $5d$ electrons is 0.82 for the ground state of the IrS$_6$ cluster. However, CuIr$_2$S$_4$ shows the Pauli paramagnetism in its metallic phase.[1] Therefore, the present model overestimates the $4f$-$5d$ exchange interaction. The calculated branching ratio becomes about 0.6 smaller than the experimental value of 0.75, when this exchange interaction is included. The interaction broadens, especially, the $4f_{5/2}$ peak and lowers the peak height in the calculated spectrum.

B. Ir $5d$ BIS and PES spectra

Figure 2 shows the calculated results of Ir $5d$ BIS and Ir $5d$ PES spectra (solid curves) for CuIr$_2$S$_4$ along with the experimental BIS and VB PES spectra (dots) measured by Matsuno *et al.*[3] Theoretical spectra (broken curves) obtained from the band-structure calculation[3,4] are also shown in Fig. 2. Spectral features in the experimental BIS spectrum of CuIr$_2$S$_4$ reflect mainly the Ir $5d$ unoccupied state because localized states exhibit large intensities in the BIS spectrum and because Cu has been considered to be monovalent in CuIr$_2$S$_4$. The VB PES spectrum taken with the Al $K\alpha$ irradiation has contribution from Ir $5d$ electrons larger than those from Cu $3d$ and S $3p$, but the Cu $3d$ photoemission is appreciable at this photon energy.[16] The calculated Ir $5d$ BIS line spectrum is convoluted with the Lorentzian of $\Gamma_L = 0.4$ eV and the Gaussian of $\Gamma_G = 0.7$ eV functions. The energy distance between two peaks in the calculated BIS spectrum is nearly the same as $10Dq$, and depends weakly on the hybridization strength V. The latter alters the effective crystal-field splitting width through the p-d hybridization. Two peaks at -0.4 and -3.0 eV in the experimental spectrum are thus attributed to Ir $5d$ t_{2g} and $5d$ e_g orbitals, respectively. This is consistent with the results of band-structure calculation.[4] Higher-energy tail around -5 eV in the calculated spectrum is almost insensitive to all the parameters and ascribed to the atomic multiplet structure.

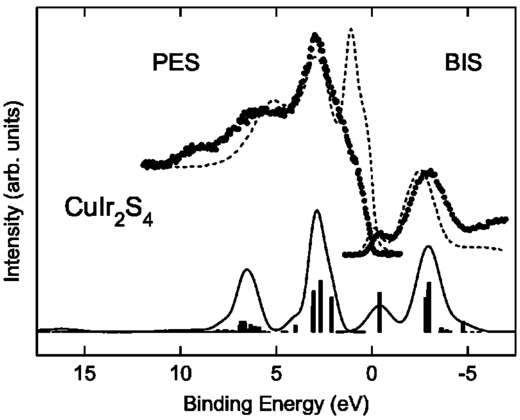

FIG. 2. Comparison between the experimental and theoretical spectra of CuIr$_2$S$_4$. Dots represent the experimental valence-band photoemission and bremsstrahlung isochromat spectra, and broken curves calculated spectra obtained from band-structure calculation (Ref. 3). Solid curves represent Ir $5d$ spectra obtained from cluster-model calculation.

The calculated Ir $5d$ PES spectrum for CuIr$_2$S$_4$ is obtained by convoluting the line spectrum with the Lorentzian of $\Gamma_L = 0.1$ eV and the Gaussian of $\Gamma_G = 0.4$ eV. The spectrum consists of three parts different in the binding energy: around 3, 6.5, and 16 eV, which are the bonding, nonbonding, and antibonding states, respectively, between d^4, $d^5\underline{L}$, and $d^6\underline{L}^2$ configurations in the Ir $5d$ PES final state. If the crystal-field and the multiplet splittings, and the configuration dependence of hybridization strength are neglected, the energies of the three states are approximately given by a Hamiltonian matrix

$$H = \begin{pmatrix} 0 & V_{\mathrm{eff}} & 0 \\ V_{\mathrm{eff}} & \Delta - U_{dd} & V_{\mathrm{eff}} \\ 0 & V_{\mathrm{eff}} & 2\Delta - 2U_{dd} \end{pmatrix} \tag{8}$$

by taking account of the hybridization between configurations. Here V_{eff} denotes the effective p-d hybridization and is defined by

$$V_{\mathrm{eff}} = [N(e_g)V(e_g)^2 + N(t_{2g})V(t_{2g})^2]^{1/2} \tag{9}$$

being $N(e_g)$ and $N(t_{2g})$ the numbers of $5d$ hole in the d^4 configuration.[10] With the parameters in Table I, the $d^5\underline{L}$ configuration has the lowest energy and the d^4 and $d^6\underline{L}^2$ configurations are higher by $U_{dd} - \Delta = 3.0$ eV and $\Delta = 0.5$ eV, respectively, without the p-d hybridization. The highest binding-energy part around 16 eV in the calculated Ir $5d$ PES spectrum is very weak and not observed in the experimental spectra in Fig. 3 of Ref. 17. The intensity around 9 eV in the calculated spectrum is much weaker than an experimental peak observed there. The observed peak at 9 eV may be attributed to the S $3p$ band state. The broad structure around 6.5 eV in the experimental PES spectra is most intense when measured with the He I irradiation.[3,14] This indicates that the structure has large contribution from S $3p$ orbital.[14,16] We note that our calculated spectrum has only Ir $5d$ contribution.

The calculated Ir $5d$ PES and BIS spectra are placed according to the calculated energy gap E_{gap}

$$E_{\text{gap}}=E(N+1)+E(N-1)-2E(N), \tag{10}$$

where $E(N-1)$, $E(N+1)$, and $E(N)$ are the energies of the lowest ionized, the lowest electron-affinity, and the ground states, respectively.[17] We have adjusted the d-d Coulomb interaction U_{dd} so that peaks in both PES and BIS calculated spectra may reproduce corresponding prominent peaks at -3, -0.4, 3, and around 6.5 eV seen in the experimental spectra. The lowest binding-energy peak in the Ir $5d$ PES spectrum shifts by 1.7 eV in comparison with the spectrum obtained from the band-structure calculation. This results from the d-d Coulomb interaction U_{dd} taken into account in the present calculation. The peak at 3 eV in the VB PES spectrum, however, has been attributed to Cu $3d$ according to the band-structure calculation.[3,4] In order to distinguish experimentally Ir $5d$ from Cu $3d$ in the VB PES spectrum, it is necessary, for example, to carry out Ir np-$5d$ resonant PES measurements. The d-character density of states at the Fermi level has been invoked in the analysis of the electrical conductivity of $\mathrm{CuIr_2S_4}$.[8] The corresponding d character may come from Cu $3d$, if the peak at 3 eV in the VB PES spectrum is assigned to Ir $5d$. By comparing the ultraviolet and x-ray VB PES spectra[3,14] and taking into account the energy-dependent photoionization cross section of atomic orbitals,[16] the contribution from Cu $3d$ appears to exist below about 3 eV.

Some $3d$ transition-metal (V, Mn, Fe, or Ni) oxides also exhibit the charge-order transition. The d-d Coulomb repulsion energy of 3.5 eV estimated for $\mathrm{CuIr_2S_4}$ is much smaller than those for typical Mn, Fe, and Ni oxides, for example, $U_{dd}=7$–7.5 eV for $\mathrm{Fe_3O_4}$.[18] Vanadium oxides, however, have the relatively small U_{dd} values ranging from 3.5 to 6 eV.[12] On the other hand, the hybridization strength V for $\mathrm{CuIr_2S_4}$ is larger than those for $3d$ transition-metal oxides,[10–12] for example, $V(t_{2g})$ of 2.3 eV for $\mathrm{Fe_3O_4}$.[18] These reflect the difference between $5d$ and $3d$ atomic orbitals, especially in their spatial extent. The large V and small Δ for $\mathrm{CuIr_2S_4}$ result in the strongly mixed ground state between the d^5 and d^6L configurations. In other words the intersite hopping of Ir $5d$ electrons is expected to be relatively large. We consider that the change in the lattice energy by the lattice distortion accompanied by the charge-order transition of $\mathrm{CuIr_2S_4}$ (Ref. 7) plays an important role in the transition in addition to the competition between the d-d Coulomb repulsion and the intersite hopping.

IV. SUMMARY

We have presented the study of the Ir $5d$ state of $\mathrm{CuIr_2S_4}$ by analyzing the Ir $4f$-core and valence-band photoemission and bremsstrahlung isochromat spectra with the $\mathrm{IrS_6}$-cluster-model calculations which take into account the on-site d-d Coulomb interaction among the $5d$ electrons. Most of the features observed in the experimental spectra have been reproduced consistently with a single set of the parameters. The localized picture approach has been proved to be valid, at least, for the Ir $5d$ state of $\mathrm{CuIr_2S_4}$. The d-d Coulomb energy of Ir $5d$ electrons in $\mathrm{CuIr_2S_4}$ is estimated at 3.5 eV, which is smaller than the $3d$ transition-metal oxides showing the charge-order transition. On the other hand, the hybridization of Ir $5d$ state with ligand S $3p$ state is large. It is considered that not only the intersite Coulomb interaction but also the lattice distortion accompanied by the charge-order transition of $\mathrm{CuIr_2S_4}$ is important to stabilize the charge-ordered state.

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