

## X-Ray Photoemission Study of $\text{CuIr}_2\text{S}_4$ : $\text{Ir}^{3+}$ - $\text{Ir}^{4+}$ Charge Ordering and the Effect of Light Illumination

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We have studied the electronic structure of the spinel-type compound  $\text{CuIr}_2\text{S}_4$  using x-ray photoemission spectroscopy (XPS).  $\text{CuIr}_2\text{S}_4$  undergoes a metal-insulator transition (MIT) at  $\sim 226$  K. In going from the metallic to insulating states, the valence-band photoemission spectrum shows a gap opening at the Fermi level and a rigid-band shift of  $\sim 0.15$  eV. In addition, the Ir  $4f$  core-level spectrum is dramatically changed by the MIT. The Ir  $4f$  line shape of the insulating state can be decomposed into two contributions, consistent with the charge disproportionation of  $\text{Ir}^{3+}:\text{Ir}^{4+} = 1:1$ . XPS measurements under laser irradiation indicate that the charge disproportionation of  $\text{CuIr}_2\text{S}_4$  is very robust against photo-excitation in contrast to  $\text{Cs}_2\text{Au}_2\text{Br}_6$  which shows photo-induced valence transition.

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The spinel-type compound  $\text{CuIr}_2\text{S}_4$  has been attracting much interest because of its first-order metal-insulator transition (MIT) at  $T_{\text{MI}} \sim 226$  K accompanied by the loss of localized magnetic moments [1–6]. Since the valence state of the Cu ion is  $\text{Cu}^+$ , an ionic configuration of  $\text{Cu}^+\text{Ir}^{3+}\text{Ir}^{4+}\text{S}_4^{2-}$  is expected in the insulating phase [7–12]. A recent structural study [13] indicates that the cubic spinel structure of  $\text{CuIr}_2\text{S}_4$  becomes tetragonally elongated along the  $c$  axis and that octamers of  $\text{Ir}^{3+}$  ( $S = 0$ ) and  $\text{Ir}^{4+}$  ( $S = 1/2$ ) are formed below  $T_{\text{MI}}$ . In the  $\text{Ir}^{4+}$  octamer, the  $\text{Ir}^{4+}$  ions are dimerized in two directions (see Fig. 1). Croft *et al.* have found a dramatic electronic structural change above the Fermi level ( $E_F$ ) across the MIT using x-ray absorption spectroscopy [4]. They have proposed that the low-temperature structure can be decomposed into one-dimensional chains and that the dimerization due to charge and orbital ordering, i.e., the charge density wave formation along the chain direction, is responsible for the electronic structural change [4]. Very recently, it has been proposed that the dimerization in  $\text{CuIr}_2\text{S}_4$  and  $\text{MgTi}_2\text{O}_4$  [14] can be understood as an orbitally driven Peierls transition [15]. The experimental and theoretical studies indicate that the electronic structure of  $\text{CuIr}_2\text{S}_4$  itself is very exotic and interesting. Another interesting point is that the resistivity of  $\text{CuIr}_2\text{S}_4$  is dramatically reduced by x-ray or visible light irradiation in the insulating phase [16–18]. It has been proposed that the photo-excitations break the  $\text{Ir}^{3+}/\text{Ir}^{4+}$  charge ordering and induce metallic conductivity.

The nature of charge ordering and the effect of light irradiation are still controversial, partly because of the difficulty in the photoemission measurement. Photoemission spectroscopy is a powerful technique to investigate electronic states below  $E_F$  although it is a surface sensitive

method and clean surface must be prepared to obtain precise information. In previous photoemission studies of polycrystalline  $\text{CuIr}_2\text{S}_4$ , the Ir  $4f$  core-level spectrum was reported to show no spectral change across the MIT [11,12] and no evidence of charge ordering was obtained. The Ir  $4f$  photoemission data can provide information on the magnitude of charge difference between the charge rich and charge poor sites. From the previous x-ray photoemission spectroscopy (XPS) study in which the Ir  $4f$  core level has a single component, it has been conjectured that the charge difference between the two sites is very small in the insulating state of  $\text{CuIr}_2\text{S}_4$ . However, in transition-metal oxides close to structural instability, special care should be taken in surface preparation due to the enhanced sensitivity to local stress. Since the polycrystalline samples were scraped under ultrahigh vacuum condition to remove sur-

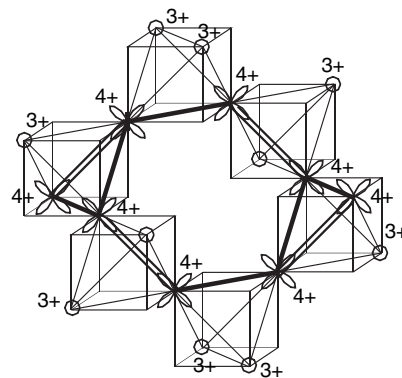


FIG. 1. Charge and orbital ordering pattern in  $\text{CuIr}_2\text{S}_4$  proposed by Khomskii and Mizokawa [15]. The circles are the  $\text{Ir}^{3+}$  ions and the crosses are the  $\text{Ir}^{4+}$  ions with unoccupied  $xy$  orbitals. The double solid lines indicate the  $\text{Ir}^{4+}$ - $\text{Ir}^{4+}$  spin-singlet dimers.

face contaminations in the previous studies, the surface region of the sample would be affected by the stress of scraping. Therefore, whether the Ir  $4f$  core-level spectrum changes across the MIT or not should be reexamined using clean surface obtained by cleaving  $\text{CuIr}_2\text{S}_4$  single crystals. In this Letter, we report results of XPS on cleaved surface of  $\text{CuIr}_2\text{S}_4$  single crystals. It has been found that the Ir  $4f$  core-level spectrum dramatically changes across the MIT and that the Ir  $4f$  spectrum of the insulating phase has two components with large energy difference, consistent with the  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  charge ordering. The XPS measurement under laser irradiation indicates that the  $\text{Ir}^{3+}$ - $\text{Ir}^{4+}$  charge disproportionation by the dimer formation is very robust against the photo-excitation but the long-range charge ordering would be destroyed.

Single crystals of  $\text{CuIr}_2\text{S}_4$  were grown by the bismuth solution method, described previously in detail [19]. The photoemission spectroscopy measurements were performed using a JPS9200 spectrometer equipped with a monochromatized  $\text{AlK}\alpha$  x-ray source ( $h\nu = 1486.6$  eV). The total resolution was  $\sim 0.6$  eV and the pressure of the spectrometer was  $\sim 1 \times 10^{-7}$  Pa during the measurement. Single crystal samples were cleaved *in situ* at room temperature. All the photoemission data were collected within 24 hours after the cleaving. The samples were measured at 300 K and then were cooled to 80 K to be measured again. Finally, the samples were heated and remeasured at 300 K. We have confirmed that the 300 K spectrum taken after heating is essentially the same as that taken just after the cleaving. A Nd:YAG pulsed laser provided optical excitation at energy of 2.3 eV (532 nm) with a pulse frequency of 30 Hz. The beam was focused to a spot of 4 mm diameter.

Figure 2 shows the Cu  $2p$  spectrum of  $\text{CuIr}_2\text{S}_4$  taken at 300 K. The Cu  $2p$  spectrum is similar to that reported previously [11,12,20]. The characteristic satellite structure, found in divalent Cu oxides such as CuO [21], is not observed in this spectrum. Therefore we confirm that the Cu ion of  $\text{CuIr}_2\text{S}_4$  is  $\text{Cu}^+$  also for the cleaved surface. This is consistent with the local-density approximation (LDA) calculations [7,8] and the NMR study [9].

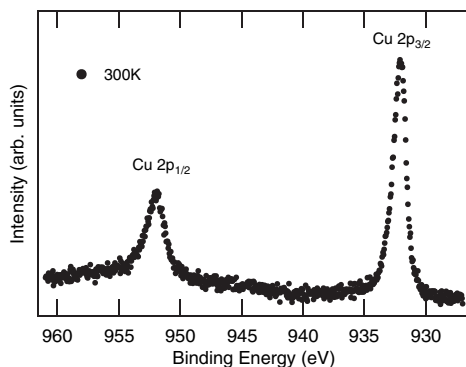


FIG. 2. Cu  $2p$  photoemission spectrum of  $\text{CuIr}_2\text{S}_4$ .

Figure 3 shows the valence-band spectra taken at 300 K and 80 K. The intensity at  $E_F$  is finite at 300 K (metallic phase) but a band gap is seen at 80 K (insulating phase), indicating that the transition from a metal to an insulator has occurred with decreasing temperature. The magnitude of the band gap is  $\sim 0.15$  eV, which is close to that estimated from the resistivity [1,2] and optical [6] measurements. Spectral change occurs not only near  $E_F$ . The entire valence-band spectrum is shifted to higher binding energy by  $\sim 0.15$  eV. The down-shift of the overall valence is consistent with the down-shifted bonding states predicted in the specific electronic structure proposed in [4]. This energy shift was also observed in the core-level spectra of Cu  $2p$  and S  $2p$ . We have confirmed that the photoemission spectra did not shift when the intensity of x ray was changed and that the energy shift across the MIT was not due to a charging effect. Comparing the obtained spectra with the previous x-ray emission spectrum [12] and LDA calculations [7,8], structures A and C can be assigned to the hybridized bands of the Ir  $5d$  and S  $3p$  orbitals, while structure B around  $\sim 3$  eV is derived from the Cu  $3d$  orbital.

Figure 4 shows the Ir  $4f$  XPS spectrum taken at 300 K and 80 K. The Ir  $4f$  peaks are broadened in the insulating phase, while the peaks are rather sharp in the metallic phase. Figure 4 also shows fitted curves for the observed spectra. The Ir  $4f_{7/2}$  spectrum of the metallic phase has been fitted to two components: the main peak is a Lorentzian with FWHM of 0.23 eV convoluted by a

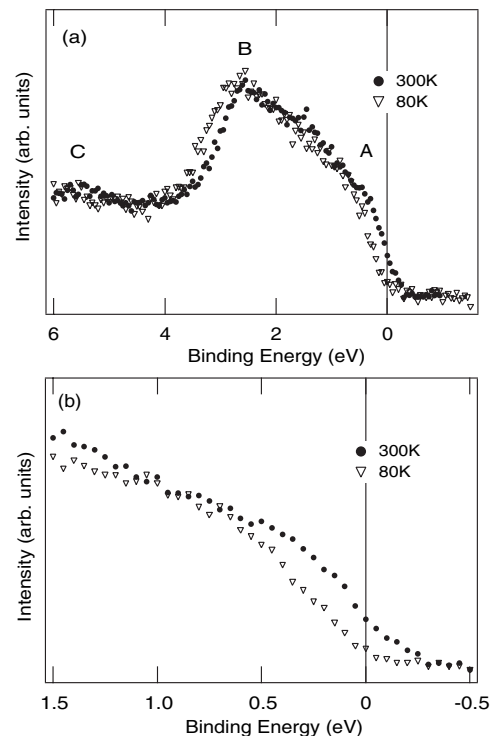


FIG. 3. (a) Valence-band and (b) near  $E_F$  photoemission spectra of  $\text{CuIr}_2\text{S}_4$  taken at 300 K and 80 K.

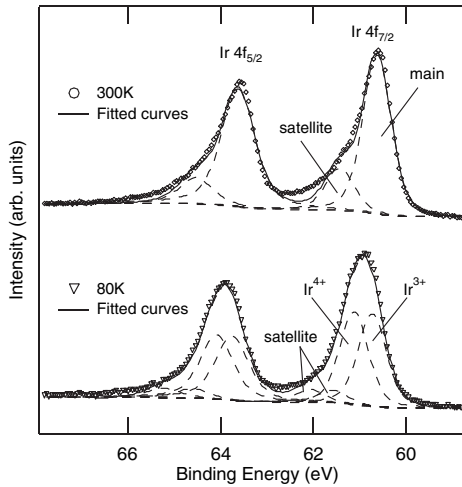


FIG. 4. Ir  $4f$  photoemission spectra of  $\text{CuIr}_2\text{S}_4$  taken at 300 K and 80 K. Solid curves indicate the fitted results.

Gaussian with FWHM of 0.6 eV and the weak and broad satellitelike structure in high binding energy side, respectively. We speculate that the weak structure is due to the correlation satellite and/or the asymmetry of the main peak that comes from the electron-hole pair creation in the photoemission process.

On the other hand, the Ir  $4f_{7/2}$  spectrum of the insulating phase can be fitted to two main components with comparable peak heights and two broad Gaussians corresponding to the satellitelike structures for the two main peaks. The Lorentzian and Gaussian FWHMs are set to 0.23 eV and 0.6 eV for the main components assuming that the instrumental and lifetime broadenings do not change across the MIT. It is also assumed that, for the  $\text{Ir}^{4+}$  site, the orbital angular momentum is quenched and the exchange coupling between the Ir  $5d$  and  $4f$  spins is negligibly small. These assumptions are reasonable since only the  $xy$  orbital is unoccupied among the three  $t_{2g}$  orbital, and the highly extended  $xy$  state accommodates the spin to form a Peierls state in the one-dimensional  $xy$  band [15]. In addition, the assumption on the exchange coupling is also supported by the Ta  $4f$  core-level spectra of another charge density wave system  $\text{TaS}_2$  in which exchange splitting is not observed although the Ta  $5d$  state in  $\text{TaS}_2$  is as itinerant as the Ir  $5d$  state in  $\text{CuIr}_2\text{S}_4$  [22,23]. In this sense,  $\text{CuIr}_2\text{S}_4$  is rather close to conventional charge density wave system and the line shape of the  $\text{Ir}^{4+}$  site is similar to that of  $\text{Ir}^{3+}$  site. The effect of lattice distortion (dimer formation) on the line shape is also expected to be small.

In this fitting procedure, the adjustable parameters are the energy and area of the main and satellite peaks. The two main contributions can be assigned to the  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  components of the charge ordered state. The energy difference between the  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  peaks is  $\sim 0.4$  eV and the intensity ratio is almost 1:1 consistent with the charge ordering of  $\text{Ir}^{3+}:\text{Ir}^{4+} = 1:1$ . The binding energy shift  $\delta E$

has the term  $KQ$  where  $Q$  is the magnitude of the local charge  $Q$  on the ion and  $K$  is the coupling constant [24]. The coupling constant  $K$  is determined by the Coulomb interaction between the core hole and the valence charges. Since, for the Ir  $4f$  core level,  $\delta E$  is approximately 1 eV between  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  compounds [25],  $K$  is expected to be  $\sim 1$ . Therefore, the actual charge difference between the  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  sites in  $\text{CuIr}_2\text{S}_4$  is estimated to be  $\sim 0.4$ . This estimation is also supported by the fact that the Ta  $4f$  spectrum of  $1T\text{-TaS}_2$  shows the energy splitting of  $\sim 0.7$  eV [22] and that, with  $K = 1$ , the charge difference is  $\sim 0.7$  which agrees with the theoretical study [26]. The satellitelike structure is due to the screening effect of the conduction electrons and is almost suppressed in the insulating phase. Therefore, uncertainty in the satellite region does not affect the conclusion on the main peaks. For example, when the spectrum is fitted using two main peaks and one satellite structure, the relative intensity and the energy difference between the two main peaks are also estimated to be 1:1 and 0.4 eV, respectively.

We have also studied the photo-excitation effect on the Ir  $4f$  line shape (Fig. 5). The visible light irradiation from the Nd:YAG laser up to 3 mJ/pulse ( $1.2 \times 10^{22}$  cm $^{-2}$  photons/pulse) did not give any spectral change, indicating that the  $\text{Ir}^{3+}/\text{Ir}^{4+}$  charge disproportionation in the insulating phase is very robust against photo-excitation across the band gap. On the other hand, it has been suggested that the long-range charge ordering is destroyed by the x-ray or electron irradiations [16–18]. The present visible light irradiation also gives the reduction of the resistance similar to those reported in the x-ray or electron irradiation measurements. The present XPS measurement under laser irradiation indicates that the  $\text{Ir}^{3+}-\text{Ir}^{4+}$  charge disproportionation by the dimer formation is very robust against the photo-excitation but the long-range charge arrangement would be destroyed by the excitation. The detailed structural analysis of the insulating phase under x-ray or light irradiation would be required in order to clarify this point.

The robust  $\text{Ir}^{3+}/\text{Ir}^{4+}$  charge disproportionation in  $\text{CuIr}_2\text{S}_4$  is in sharp contrast to the  $\text{Au}^+/\text{Au}^{3+}$  charge disproportionation in  $\text{Cs}_2\text{Au}_2\text{Br}_6$  that can be destroyed by the visible light irradiation of 0.5 mJ/pulse ( $1.9 \times 10^{21}$  cm $^{-2}$  photons/pulse) [27]. While the  $\text{Au}^+/\text{Au}^{3+}$  charge disproportionation in  $\text{Cs}_2\text{Au}_2\text{Br}_6$  is stabilized by the Jahn-Teller-type distortion, the  $\text{Ir}^{3+}/\text{Ir}^{4+}$  charge disproportionation in  $\text{CuIr}_2\text{S}_4$  is stabilized by the dimer formation of the  $\text{Ir}^{4+}$  pair. Probably, this difference in the electron-lattice coupling is the origin of the different response to the photo-excitation. This issue is related to the contrast between the bond-centered ordering (like  $\text{CuIr}_2\text{S}_4$ ) and site-centered ordering (like  $\text{Cs}_2\text{Au}_2\text{Br}_6$ ) generally seen in various transition-metal compounds [28] in which the orbital degeneracy affects the electron-lattice coupling in different manners and provides the different behaviors against the photon irradiation.

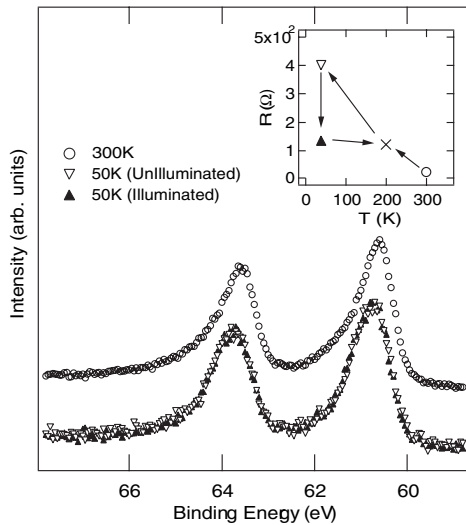


FIG. 5. Ir  $4f$  photoemission spectrum of  $\text{CuIr}_2\text{S}_4$  taken at 300 K and those taken at 50 K before and during the visible light irradiation from the Nd:YAG laser (532 nm). The resistance taken under the same condition as the photoemission measurements is given in the inset.

In conclusion, we have studied the electronic structure of  $\text{CuIr}_2\text{S}_4$  single crystal using x-ray photoemission spectroscopy (XPS). The valence band shows the band gap opening and the rigid-band shift of 0.15 eV across the MIT. In going from the metallic to insulating states, the Ir  $4f$  core-level spectrum changes dramatically due to the splitting of the  $\text{Ir}^{3+}$  and  $\text{Ir}^{4+}$  components. The present XPS results show that  $\text{Ir}^{3+}:\text{Ir}^{4+} = 1:1$  in the insulating phase and support the  $\text{Ir}^{3+}/\text{Ir}^{4+}$  charge ordering model in the insulating phase. The  $\text{Ir}^{3+}/\text{Ir}^{4+}$  charge disproportionation in  $\text{CuIr}_2\text{S}_4$  is robust against photo-excitation in contrast to the  $\text{Au}^+/\text{Au}^{3+}$  charge disproportionation in  $\text{Cs}_2\text{Au}_2\text{Br}_6$ .

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