PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 55, NUMBER 24 **15 JUNE 1997-II**

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Photoemission study of the metal-insulator transition in $CuIr_2S_4$

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(Received 25 February 1997)

We have studied the electronic structure and its changes across the metal-insulator transition in the spinel-type compound $CuIr_2S_4$ using photoemission and inverse-photoemission spectroscopy. Photoemission spectra near the Fermi level show a gap opening of ~20 meV in the insulating phase, consistent with the transport activation energy. Core-level spectra indicate that the Cu ion is monovalent, and hence Ir is in the intermediate valence state of +3.5. Comparison between the spectra and band-structure calculation reveals that the Ir $5d$ density of states is strongly distorted, probably due to electron correlation in spite of the general belief of weak correlation in $5d$-electron systems. [S0163-1829(97)51924-2]

Following the discovery of high-T_c cuprates, metal-insulator transitions (MIT's) in $3d$ transition-metal compounds have attracted renewed interest. The MIT can be seen in various systems, but its origin has remained to be settled in many cases. For example, V_2O_3 shows a MIT at 160 K,[1] and the origin of the MIT was explained in the framework of Mott transition. The MIT in VO_2 has been considered as a Peierls transition[2] while it has also been argued that electron correlation is essential.[3] The MIT in Fe_3O_4, called the Verwey transition, is due to ordering of Fe^{2+} and Fe^{3+} states, but the electronic structure which consistently explains its various physical properties is still controversial.[4] In $4d$ and $5d$ electron systems, on the contrary, only few materials have been reported to show MIT's.

Recently a spinel-type compound $CuIr_2S_4$ was discovered to undergo a MIT at ~226 K from the high-temperature metallic phase to the low-temperature insulating phase.[5,6] At room temperature, $CuIr_2S_4$ has a normal spinel structure, in which the Cu ion is tetrahedrally coordinated and the Ir ion is octahedrally coordinated by sulfur atoms. The MIT is accompanied by a distortion from a cubic to a tetragonal structure, and by a volume decrease of 0.7% in going from the metallic phase to the insulating phase.[7] The electrical conductivity shows an activation energy of 17 meV in the range 30–70 K. Mössbauer spectroscopy[8] has shown that the Ir ion is nonmagnetic, and presumably in a mixed-valence state in the insulating phase. According to band-structure calculations using the local-density-approximation (LDA) (Ref. 9) and NMR measurements,[10] the Cu ion is in the monovalent state. Therefore, the Ir ion has a mean valence of +3.5 and hence an electronic configuration of $d^{5.5}$. Ir $5d$ electrons, which participate in the conduction, are expected to form a relatively wide band compared to d electrons in $3d$ transition-metal compounds, and therefore the electronic structure of $CuIr_2S_4$ is expected to be well described by band theory. However, the band-structure calculation predicts a system with partially filled $5d$ bands to be metallic even with the tetragonal distortion.[9] There are no nesting features in the calculated Fermi surfaces, making a charge-density-wave formation unlikely. If one employs a localized electron picture in the insulating phase in spite of the $5d$ band, a charge ordering is one possibility to explain the insulating behavior.

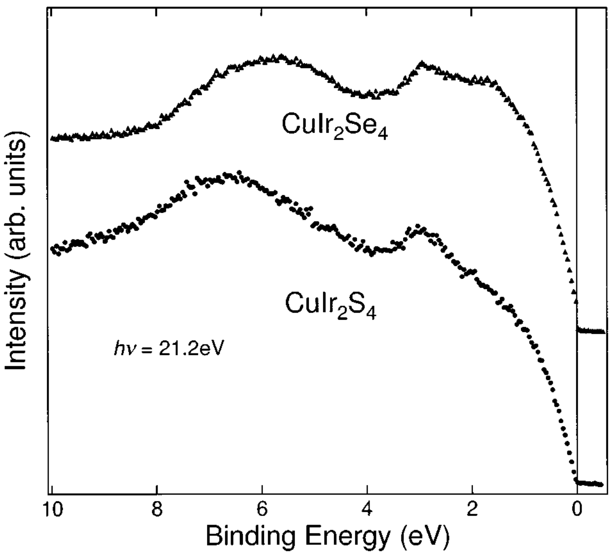

FIG. 1. Photoemission spectra of $CuIr_2S_4$ and $CuIr_2Se_4$ taken at ~30 K.

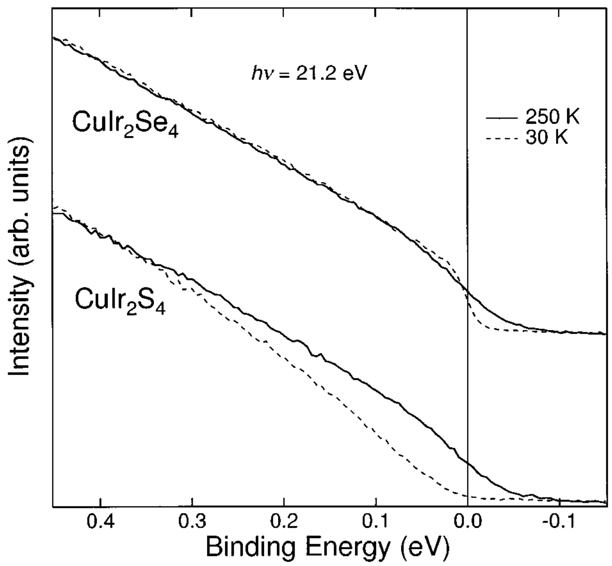

FIG. 2. High-resolution photoemission spectra of $CuIr_2S_4$ and $CuIr_2Se_4$ near E_F.

However, the spin moment has to vanish somehow in the insulating phase, e.g., through the formation of singlet pairs. If this picture is correct, the MIT in $CuIr_2S_4$ would essentially be regarded as a Mott transition. Such a localized electron picture, however, has not been employed to explain the electronic properties of any $5d$ transition-metal compounds to the authors' knowledge. Thus the origin of the metal-insulator transition in $CuIr_2S_4$ remains highly mysterious. In this paper, we present photoemission and inverse-photoemission spectroscopic studies of $CuIr_2S_4$. The experimental spectra are compared with the results of the band-structure calculation. Spectra of $CuIr_2Se_4$, which is metallic down to 0.5 K,[11] are also presented for comparison.

Polycrystalline samples of $CuIr_2S_4$ and $CuIr_2Se_4$ were prepared by a solid-state reaction. A mixture of Cu, Ir, and S powders was sealed in an evacuated quartz tube and was calcined at 850 °C for a period of ten days. Subsequently, the specimens were prepared by sintering into pressed rectangular bars at 850 °C for 48 h after regrinding.

X-ray photoemission spectroscopy (XPS) measurements were carried out using a Mg x-ray source ($h\nu=$ 1253.6 eV). Ultraviolet photoemission (UPS) measurements were made using He I and He II resonance lines ($h\nu=$ 21.2 and 40.8 eV, respectively). He I UPS measurements were performed both at 30 and 250 K in order to study spectral changes above and below the MIT temperature. We also measured inverse-photoemission or bremsstrahlung-isochromat spectroscopy (BIS) spectra by detecting photons of $h\nu=$ 1486.6 eV using a quartz monochromator. He II UPS and all the XPS and BIS measurements were done at liquid-nitrogen temperature. In order to calibrate binding energies and estimate the instrumental resolution, gold was evaporated on the sample surface after each series of measurements. The resolution was 26 meV for He I UPS and ~0.3, 1, and 0.7 eV for He II UPS, XPS, and BIS, respectively. The samples were repeatedly scraped *in situ* with a diamond file; no oxygen signals from contamination were detected by XPS, and all the core levels show single components without a sign of secondary phases. The base pressure of the spectrometers was of $2-7\times10^{-10}$ Torr.

Figure 1 shows valence-band spectra of $CuIr_2S_4$ and $CuIr_2Se_4$ taken with He II radiation. Differences between $CuIr_2S_4$ and $CuIr_2Se_4$ exist mainly within ~3 eV of E_F: $CuIr_2Se_4$ shows higher intensity in this region. We have concluded that contributions from the S $3p$ or Se $4p$ band are significant in this region because the Se $4p$ atomic orbital cross section is larger than that of S $3p$ in this photon energy.[12]

Figure 2 shows high-resolution photoemission spectra of $CuIr_2S_4$ and $CuIr_2Se_4$ near the Fermi level (E_F). The spectra have been normalized at ~3 eV below E_F. In $CuIr_2S_4$, the intensity at E_F is finite at 250 K but vanishes at 30 K. This indicates that the transition from a metal to an insulator occurs with decreasing temperature. We estimate the magni-

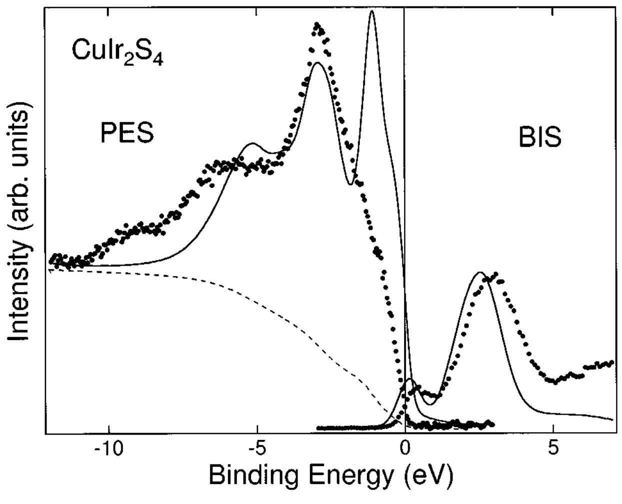

FIG. 3. Comparison between the experimental and theoretical spectra for $CuIr_2S_4$. The solid curves represent the theoretical spectra obtained from the LDA band-structure calculation (Ref. 9), and the dashed curves the assumed background.

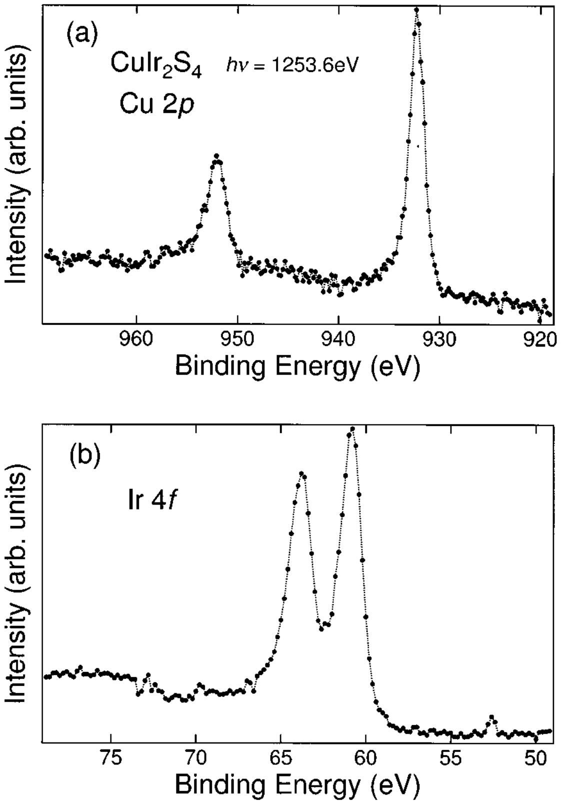

FIG. 4. Cu $2p$ (a) and Ir $4f$ (b) core-level spectrum of $CuIr_2S_4$.

tude of the gap between E_F and the top of the valence band to be $\sim$20 meV, which is consistent with the activation energy (17 meV) deduced from the electrical resistivity (at 30–70 K) if the semiconducting carriers are p type. As for $CuIr_2Se_4$, the spectra both at 30 and 250 K have a finite intensity at E_F, showing that $CuIr_2Se_4$ is metallic at these temperatures. The temperature dependence of the spectra near E_F simply reflects the temperature dependence of the Fermi-Dirac function. However, the 250-K spectrum at E_F is slightly more intense than expected from the 30-K spectrum. This may be interpreted in either of two ways: (i) the density of states (DOS) in the vicinity of E_F increases with increasing temperature, or (ii) there exists a high DOS just above E_F. The band-structure calculation, however, shows a behavior opposite to (ii).[9] In any case, the results imply that the metallic state in $CuIr_2Se_4$ is not entirely a trivial one, and may require further investigation. The spectra of $CuIr_2S_4$ and $CuIr_2Se_4$ near E_F are identical in the metallic phase.

Figure 3 shows a comparison between the measured spectra and theoretical spectra of $CuIr_2S_4$. To obtain the theoretical photoemission spectra, the partial DOS of each atomic orbital component was added after having multiplied by the corresponding photoionization cross section.[12] Then we convoluted the added DOS with a Gaussian of 0.3- eV full width at half maximum (FWHM) for UPS and with a Gaussian of 0.7 eV FWHM for BIS. In order to simulate the lifetime broadening effect, a convolution with a Lorentzian having an energy dependent width the (FWHM is equal to $0.1|E-E_F|$) was applied, as has usually been done.[13] The calculated band structure consists of a Cu $3d$ band centered at ~-3 eV, the Ir $5d$ band (more precisely, the Ir $5d\epsilon$–S $3p$ hybridized band) extending from ~-2 to $\sim$0.5 eV, the Ir $5d\gamma$–S $3p$ bonding band centered at ~-5 eV, and the Ir $5d\gamma$–S $3p$ antibonding band centered at $\sim$3 eV; the Fermi level lies within the Ir $5d$ band. Thus the intense peak at -3 eV is assigned to the Cu $3d$ states. First we notice in the figure that the Ir $5d$ band in the calculated DOS is not clearly seen in the experimental spectrum, and the photoemission intensity at E_F is weaker than the calculation. The spin-orbit splitting of $\sim$0.56 eV (Ref. 14) is not included in the calculation, but it would be large enough to cause pronounced changes. The spin-orbit interaction alone cannot open a gap at E_F, nor account for the insulating ground state because it splits the $d\epsilon$ level into doubly and quadruply degenerate sublevels, while the d-band filling is 5.5. The above observations suggest that electron correlation distorts the Ir $5d$ band, redistributes its spectral weight away from E_F, and even opens the gap at E_F. In the unoccupied states, on the other hand, the experimental line shape is in better agreement with the theoretical spectrum than in the occupied states. Nevertheless, the experimental intensity at E_F is suppressed, and the Ir $5d$-derived DOS is shifted toward higher energies than the theoretical DOS, the same tendency as the photoemission spectrum.

Figure 4(a) shows the Cu $2p$ core-level spectrum of $CuIr_2S_4$. In Cu spinels, the formal valence of copper has been the subject of controversy for a long time.[15,16] Cu-containing compounds, in which Cu is in the divalent state, show a characteristic satellite structure, as has been found for CuO and all high-T_c superconducting cuprates.[17] As seen from Fig. 4, this structure is not observed in the Cu $2p$ spectrum of $CuIr_2S_4$, and therefore we can confirm that the Cu ion of $CuIr_2S_4$ is closer to Cu^+.[18] Furthermore the Cu $2p_{3/2}$ peak position 932.3 eV is closer to that of Cu_2O than to CuO.[17] The monovalence of Cu is consistent with the LDA calculation[9] and the NMR measurements.[10]

A Mössbauer spectroscopy study has shown that Ir ions in the insulating phase are found in two electronically different sites with equal amount. The Ir $4f$ core-level spectrum shown in Fig. 4(b) consists of sharp peaks of a single spin-orbital doublet without any sign of the two distinct Ir sites. This indicates that the net charges of the two Ir sites are not significantly different. Since we have seen that electron correlation is significant for the Ir $5d$ electrons, it might be relevant to start from a model in which the Ir $5d$ electrons are localized in order to consider the insulating phase of $CuIr_2S_4$. If the Ir $5d$ electrons are localized, the ionic configurations in this compound become $Cu^+Ir^{3+}Ir^{4+}S_4^{2-}$, where Ir^{3+} is nonmagnetic (t_{2g}^6: $S=0$) and Ir^{4+} has a local moment of $S=\frac{1}{2}$ if it is in the low-spin state (t_{2g}^5). (It should be noted that the net charges on the Ir atoms should not be much different between the nominally Ir^{3+} and Ir^{4+} sites due to strong hybridization, as indicated by the simple Ir $4f$ core-level spectra.) In order to reconcile these configurations with the fact that the NMR and Mössbauer measurements show no magnetic order down to the lowest temperature studied so far, we have to assume that Ir^{4+} ions form singlet pairs, e.g., as in the low-temperature phase of VO_2. From the x-ray-diffraction measurements, some superstructure spots cannot be assigned to the simple tetragonally distorted spinel structure, which might indicate that dimerization occurs with a small atomic displacement. Structural studies using single crystals would be required to clarify this point.

In conclusion, we have observed a clear indication of the MIT in $\mathrm{CuIr_2S_4}$ by high-resolution photoemission spectroscopy. The spectrum near E_F shows a gap of $\sim$20 meV, which is consistent with the transport activation energy if the semiconducting carriers are p type. The valence-band spectra are compared with the calculated DOS; we found a strong discrepancy between theory and experiment for the Ir $5d$-derived DOS peak in spite of the good agreement for the Cu $3d$ and S $3p$/Se $4p$-derived DOS features. This indicates that electron correlation among Ir $5d$ electrons is significant in $\mathrm{CuIr_2S_4}$ in spite of the widely believed notion that electron correlation is negligibly weak in $5d$ bands. The Cu $2p$ core-level spectrum shows that the Cu ion is in the monovalent state, and therefore that the mean valence of Ir is $+3.5$. In order to reconcile these results with existing experimental results, the transition may be caused by some kind of dimerization between the Ir ions. Further studies on the structural and transport properties are necessary to characterize the nature of the insulating phase, and to elucidate the mechanism of the MIT in $\mathrm{CuIr_2S_4}$.

The authors would like to thank Professor M. Shirai and Dr. Oda for providing us with the results of the band-structure calculation including unpublished results, and A. Sekiyama, K. Kobayashi, and T. Susaki for technical support. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

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