Metal-insulator transition in CuIr₂S₄: XAS results on the electronic structure

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S K and Ir L₃ x-ray absorption measurements across the temperature-induced metal (M) to insulator (I) transition in CuIr₂S₄ are presented. Dramatic S K-edge changes reflect the Ir d-electronic state redistribution across this transition. These changes, along with a detailed consideration of the I-phase structure, motivate a model in which the I-phase stabilization involves an interplay of charge and d-orbital orientation ordering along Ir chains, a quadrupling of the Ir-chain repeat unit, and correlated dimer spin-singlet formation.

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Metal-insulator transitions involving transition metal (T) compounds have been of intense interest in recent years on both fundamental and technological grounds. This field has been dominated by 3d-row T-oxide compounds, by virtue of the renaissance in these materials that followed the discovery of high-T_c superconductivity. The subclass of mixed valent metallic compounds that "charge order" into an insulating state has been the focus of special recent interest. The compound CuIr₂S₄ stands out as unique in this subclass for a number of reasons.

The spinel structure CuIr₂S₄ compound has a paramagnetic, high-temperature, homogeneously mixed Ir⁴⁺/Ir³⁺, metallic (M) phase, which undergoes a first-order transition (near 230 K) to a low-temperature, charge-ordered, diamagnetic, insulating (I) phase. Recent definitive x-ray and neutron scattering measurements showed this I phase to involve a complex ordering of Ir⁴⁺-spin-singlet dimers and undimerized Ir³⁺ sites. This finding is novel, since such dimerization transitions have previously occurred almost exclusively in compounds with clearly defined quasi-one-dimensional (1D) chains, and certainly not in a complex three-dimensional (3D) type structure. Moreover, the complex pairwise ordering of Ir³⁺-Ir³⁺ nondimer and Ir⁴⁺-Ir⁴⁺ singlet-dimer moieties appears not to have been previously observed. In addition, the broadness of the 5d orbitals makes such M-I transitions rare in 5d-row compounds, and still rarer in a nonoxide (i.e., S) 5d compound. These properties, along with the previous dearth of precise structural or electronic information, have hindered the development of the outlines of a theory for the M-I transition in CuIr₂S₄. In this paper, we present S and Ir XAS results spanning the M-I transition in CuIr₂S₄. The S K-edge results, along with a careful review of the dimerized/charge-ordered chain character of the I phase, motivate a proposal for a specific electronic/structural basis from which to approach understanding of this novel I-M transition.

The sample preparation and characterization techniques were as discussed in Ref. 10. The S K and Ir L₃ XAS measurements were, respectively, performed on beamlines X19A and X18B at the Brookhaven National Synchrotron Light Source, using methods discussed in Refs. 12 and 13. The low-temperature XAS measurements on X19A utilizes a nitrogen cryostat (in the fluorescence mode), and those on X18B used a diplex refrigerator (using the transmission mode).

Previous photoemission spectroscopy measurements on CuIr₂S₄ showed a subtle loss of electronic states at 0.2 eV below the Fermi energy (E_F) in the I phase. These photoemission and I-phase inverse photoemission results manifested substantial departures from band-structure predictions on a wider energy scale. Thus the generic gap formation below E_F, and the absence of any information about above-E_F density-of-state (DOS) changes across this M-I transition, have provided little guidance to direct the theoretical attack on this interesting system.

XAS has been important in elucidating atomic/orbital-specific electronic structure in many classes of transition metal compounds. The combination of O K-edge (probing O p states) and Cu L₂,₃-edge (probing Cu d states) measurements emphasized the crucial importance of hybridized O p/Cu d hole states in the physics of high-T_c cuprates. Importantly, O K-edge measurements on VO₂ clarified the specific electronic structure changes behind its metal to dimerized-insulator transition. Systematic O K-edge measurements in T(3d)-O compounds have profiled (via their threshold structure) the important variations in their hybridized O p/T d empty states. 4d/5d-hole states have been studied extensively by T L₂,₃-edge spectroscopy in transition-metal compounds. Finally, T(3d) K-edge XAS has been used to chronicle the valence variations in manganeseates and the charge donation to Cu in electron-doped high-T_c materials. This background motivates our S K- and Ir L₃-edge studies across the M-I phase transition in CuIr₂S₄. Cu K-edge measurements in our laboratory, along with previous NMR and band-structure calculations, indicate a Cu¹⁺ state in CuIr₂S₄, allowing us to neglect Cu d state influences on the S states above E_F.

The elemental S K edge in Fig. 1(a) is dominated by an intense "white line" (WL) feature, due to dipole transitions into empty 3p states. In transition-metal sulfide compounds, one typically observes a diminution of the WL intensity due to T to S charge transfer and the appearance of prominent threshold features, shifted down by 0–5 eV from the elemental-S WL, due to hybridized S p/T d states. The S K threshold features probe the T(d) DOS (weighted by transi-
tion matrix element effects) in sulfides in the same sense as O K threshold features do in oxides. The S K-edge spectra for the spinel compounds CuT₂S₄ (T = Cr, Co, and Ir) in Fig. 1(a) illustrate this for the octahedral ligand field case, where the d orbitals are split into a lower t₂g sextet and an upper e₃g quartet. For the isoelectronic 3d Co and 5d Ir compounds, the empty states are t₂g and e₃g for the Cr compound, and the Cr compound they are t₂g and e₃g. The a and a’ features in the S K spectra are associated with the empty S p states, hybridized with the empty t₂g and e₃g states, respectively. Consistent with band calculations,⁹ the ligand field splitting for T = Ir is large (yielding a resolved a’-a splitting) and smaller for the more localized Co d orbitals (yielding an unresolved a’ shoulder on the a feature). The Cr case, the broader d bands and larger number of t₂g holes broaden the threshold features and enhance the a’-feature intensity. Finally, although not germane to this work, it should be noted that a full treatment of such threshold features should include exchange and multiplet effects, particularly for the Cr compound.

Figure 1(b) compares the S K- and Ir L₃-edge spectra on the same (albeit displaced) energy scale for the I and M phases of CuIr₂S₄. The Ir L₃ edge also manifests an intense WL feature due to the 5d states above E_F. The A feature, at the Ir L₃ edge of CuIr₂S₄, involves the four empty e₃g states per Ir, and the aligned S K a peak is associated with the transitions to S p/Ir d(e₃g) hybridized states. The ½ t₂g hole per Ir makes a weak unresolved contribution to the Ir L₃ WL near the A’ energy range; however, the S K a’ feature, involving

FIG. 1. (a) The S K edges of elemental S and CuT₂S₄, with T = Cr, Co, and Ir. The a’- and a-threshold features are, respectively, associated with T d t₂g and e₃g state hybridization. (b) The S K edges of CuIr₂S₄, at temperatures T = 195 K (in the I phase) and 300 K (in the M phase). (c) The Ir L₃ edges of elemental Ir, IrO₂, CuIr₂Se₄, and CuIr₂S₄. The intensity in the A and A’ positions are associated with Ir d t₂g and e₃g final states, respectively.

S p/Ir d(t₂g) hybridized states, defines these t₂g states much more sharply. The alignment of the Ir L₃ B feature and S K b feature for the CuIr₂S₄ suggests S-Ir hybridization effects at these higher energies.¹²

For comparison, the Ir L₃ edges of IrO₂, CuIr₂Se₄, and Ir metal are also shown in Fig. 1(c). The higher WL intensity and chemical shift of the IrO₂ spectrum reflect its higher valence relative to CuIr₂S₄. The Ir L₃ spectrum of CuIr₂Se₄ shows a greater Ir d DOS near E_F, relative to CuIr₂S₄, consistent with a higher density of overlapping states near E_F in the always-metallic Se isomorph.⁶ The combination of monochromator resolution, core hole broadening, and core-hole/d-electron interactions make the Ir L₃ WL feature essentially identical in the M and I phases of CuIr₂S₄.

S K-edge spectra were taken as the sample slowly warmed through the I-M transition (with temperature measurements being ±5 K) and the details of the discontinuous spectral change can be seen by comparing the T~225 K I-phase and T~239 K M-phase spectra in Fig. 2 (top). The difference between these spectra, shown in Fig. 2 (bottom) provides a direct estimate of the detailed Ir d/S-p state redistribution occurring at the transition. Here we will focus only on the central element of this redistribution, the dramatic shift of the a’ (t₂g) feature to higher energy in the I phase. A proper theoretical treatment of this transition should also replicate the state redistribution on the low energy side of the a feature.

We tacitly assume the S K threshold features are dominated by electronic structure effects in analogy to all past O K-edge threshold measurements.¹⁴–¹⁶ The close quantitative similarity of our I-phase S K threshold spectra to the I-phase inverse photoemission results strongly supports this assumption.

We will pattern our proposals for understanding CuIr₂S₄ after those of the Abbate et al.¹⁵ reformulation of Goodenough’s ideas for the paramagnetic-metal-to-dimerized-insulator transition in VO₂. These authors developed a simple molecular orbital (MO) theory for VO₂, motivated by

FIG. 2. Comparison of the S K edges of CuIr₂S₄ just across the I-phase (225 K) to M-phase (239 K) transition. The difference (bottom) between the I- and M-phase spectra is shown to highlight the full details of the M to I electronic state changes.
The appearance of a prominent $O \, K$ threshold feature in the $I$-phase. The model was based on a strong hybridization-induced splitting of dimer $V \, d$ states ($d_{ij}$ sites) oriented along the chains of edge-sharing VO$_6$ octahedra in the rutile structure.\cite{15,18} Abbate et al.\cite{15} noted, and Sommers et al.\cite{19} emphasized, that Mott-Heitler-London electron correlation effects also contribute to the $d_{ij}$ splitting.

The spinel structure of CuIr$_2$S$_4$ is decidedly three dimensional, however, as Fig. 3(a) illustrates, it also contains criss-crossing Ir chains with an Ir-Ir spacing of $h = 3.48 \, \AA = a\sqrt{2}/4$, where $a$ is the lattice parameter. The chains cross in adjacent planes $a/2$ apart, and cross-linking chains create three-fold chain intersections at the Ir sites (see the cube center). The cell edge-to-edge chain has a length of $4h = 13.92 \, \AA$ and contains four Ir atoms in the cubic cell. In the metallic phase the Ir$^{3+}$ atoms, with a configuration of $t^3_2g^3$, can be thought of as $[t^2_2](t^1_{2g})$, where the former bracket constitutes two filled $d$ orbitals and the latter a $\frac{1}{2}$-filled band for the highest-lying $d_{(2g)}$ orbital.

Space limitations preclude detailed discussion of the complex triclinic $(a = 11.95 \, \AA, \quad b = 6.98 \, \AA, \quad c = 11.93 \, \AA, \quad \alpha = 91.05^\circ, \quad \beta = 108.47^\circ, \quad \gamma = 91.03^\circ)$ $I$-phase structure;\cite{10} however, several crucial points should be noted [see Fig. 3(b)]. All Ir atoms are members of charge-ordered $\cdots$Ir$^{3+}$-Ir$^{4+}$-Ir$^{4+}$-Ir$^{3+}$, with dimerized Ir$^{4+}$-Ir$^{4+}$ pairs. There are two closely related types of chains (I and II) having unit repeat distances of $\sim 4h$, and extending along approximately orthogonal triclinic cell edge-to-edge directions. Planes of chains in these two directions alternate in the third direction. At staggered chain crossing regions, adjacent Ir$^{3+}$-Ir$^{4+}$ atoms are still close (in the 3.43–3.56 $\, \AA$ range); however, the orientation of the crucial near-$E_F$, $d$-orbital charge lobes, within our model, should be along the chains. This should produce minimal overlap between the filled-shell $t^6_2$ Ir$^{3+}$ on one chain, and the transverse $d$ lobe on the Ir$^{4+}$ on the adjacent chain, leading to near-$E_F$ $d$ bands with quasi-1D character (within a 3D geometrical structure).

The four atom repeat unit in the $I$-phase chains is composed of a $t^2_2$-$t^5_2$ dimer, bounded by two filled-orbital $t^5_2$ sites. After Abbate et al.,\cite{15} we denote the last filled $d$ orbital along the chain as $d_i$, and note that the $I$-phase chain sequence would be $d^2_i \!d^1_i \!d^1_i \!d^2_i$. In the extended-zone scheme, the dispersion curve for the $d_{ij}$ band would now have new gaps at $\pi/4h$, $\pi/2h$, and $3 \pi/4h$. The $3 \pi/4h$ gap falls in the range of the Fermi energy of the $\frac{1}{2}$ filled $d_{ij}$ band, and the removal of nested states near $E_F$ should play some role in the $M$ to $I$ transition. Sommers et al.\cite{19} emphasized that electron repulsion/correlation effects were important in VO$_2$, along with direct $d$ overlap effects. We believe the correlated singlet dimerization energy is crucial here also, and while the direct $d$ overlap effects should be enhanced and the correlation effects reduced in this 5$d$ Ir compound, both are anticipated.

In Fig. 4(a) we show a schematic representation of the dimer-containing chain repeat cell indicating the filled $d_{ij}$ sites with circles, and the oriented $d^5_{xy}$-type charge cloud\cite{10} at the $d^1_{ij}$ sites. The intersite direct $d^1_{ij} \cdot d^1_{ij}$ overlap of the dimer, across the shared octahedral edge, is emphasized.

In the $M$ phase of CuIr$_2$S$_4$, the itinerant $d$ holes are hopping on and off Ir sites along three-fold cross-linked chains, with the spatial orientation of the $d_{ij}$ charge lobes also fluctuating. The transition to the $I$ phase involves several components: a Ir$^{4+}$-Ir$^{4+}$-Ir$^{4+}$ charge ordering with a concomitant quadrupling of the chain cell to $\sim 4h$, an orbital ordering of the charge lobes at each site into one chain and across the shared edge of an Ir$^{4+}$-Ir$^{4+}$ dimer, and finally, $d^1_{ij} \cdot d^1_{ij}$ hybridization into a spin singlet dimer with correlation effects.
In Fig. 4(b) the MO proposal for the $M$ phase of CuIr$_2$S$_4$ is shown. The bonding $(\sigma)$–antibonding $(\sigma^*)$ orbitals involve Ir $d(e_g)$ states that point toward the S sites, and induce strongly split hybrid states. The less split bonding $(\pi)$–antibonding $(\pi^*)$ orbitals involve Ir $d$ states that point between the S sites, and hybridize more weakly. The highest-lying Ir $d(t_{2g})$ orbital [labeled in Fig. 4(b)] is partially filled at $E_F$.

In the $I$ phase there will be two differing MO combinations, one for the $d_{xy}^1$–$d_{yz}^1$ dimer and one for the $d_{xy}^2$ sites which are shown in Fig. 4(c). At the dimer site, the splitting of the $d$ states into a bonding $d_{\|}$ and antibonding $d_{\perp}^*$ pair is dramatic. The fact that both the $d_{\|}^*$ and $d_{\perp}$ states carry hybridized S-$p$ states with them, away from $E_F$, has been emphasized in Fig. 4(c) by the additional broader box accompanying these states. At the Ir$^{3+}$ $d_{xy}^2$ site, the closed $d_{xy}^2$ orbital falls below $E_F$. Thus in this MO model the $M$–$I$ transition involves; the redistribution of the near-$E_F$ states in the $M$ phase, into the $I$-phase dimer site bonding/antibonding $(d_{\|}/d_{\perp})$ states, and into the filled $t_{2g}$ states at the Ir$^{3+}$ site.

Referring back to our S $K$-edge results in Fig. 2, in the $M$ phase we associate the high-lying MO $\sigma^*$ states and the near-$E_F$ MO $\pi^*$ $d$ states with the $S$ $K\alpha$ and $\alpha'$ features, respectively. In the $I$ phase, the $\alpha$ feature and $\sigma^*$ states persist relatively unchanged in both the S-K edge results and MO model. The shift of the $\alpha'$ feature to higher energy in the $I$ phase is associated with the splitting of the MO antibonding $d_{\perp}^*$ states to above $E_F$ at the dimer sites. The bonding $d_{\|}$ states at the dimer sites, and the filled $t_{2g}$ states at the Ir$^{3+}$ sites, are both pulled below $E_F$ and do not contribute to the S $K$ edge. Thus, this simple starting-point model involves the $I$ phase arising from orbital ordering of the $d$-orbital charge lobes into in-chain $d_{\|}$ states, and intrachain charge ordering into Ir$^{4+}$–Ir$^{4+}$ ($d_{xy}^1$–$d_{xy}^1$) correlated singlet dimers bounded by Ir$^{3+}$ filled $d_{\perp}^2$ orbital sites.

More generally, the underlying electronic origin of the $M$–$I$ transition in this system appears, at present, unique among 5$d$ row compounds. Besides explaining our XAS results, the proposed MO picture appears to explain the photo-emission gap formation below $E_F$. Interestingly, the fact that the band structure calculation predicts a metallic state, even in a tetragonally distorted phase (Ref. 9), strongly suggests that the electrons in the $I$ phase have localized character, despite the common belief that 5$d$ electrons form broad bands. Hence, the $MI$ transition would appear to involve electron localization due to correlation effects.

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