

Electronic structure of the honeycomb iridate Cu_2IrO_3 at high pressure

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Cu_2IrO_3 has attracted recent interest due to its proximity to the Kitaev quantum spin liquid state and the complex structural response observed at high pressures. We use x-ray spectroscopy and scattering as well as electrical transport techniques to unveil the electronic structure of Cu_2IrO_3 at ambient and high pressures. Despite featuring a $\text{Ir}^{4+} J_{\text{eff}} = 1/2$ state at ambient pressure, Ir L_3 -edge resonant inelastic x-ray scattering reveals broadened electronic excitations that point to the importance of Ir $5d$ -Cu $3d$ interaction. High pressure first drives an Ir-Ir dimer state with collapsed $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ and $\langle L_z \rangle / \langle S_z \rangle$, signaling the formation of $5d$ molecular orbitals. A novel $\text{Cu} \rightarrow \text{Ir}$ charge transfer is observed above 30 GPa at low temperatures, leading to an approximate Ir^{3+} and $\text{Cu}^{1.5+}$ valence, with persistent insulating electrical transport seemingly driven by charge segregation of $\text{Cu}^{1+}/\text{Cu}^{2+}$ ions into distinct sites. Concomitant x-ray spectroscopy and diffraction measurements through different thermodynamic paths demonstrate a strong electron-lattice coupling, with $J_{\text{eff}} = 1/2$ and $\text{Ir}^{3+}/\text{Cu}^{1.5+}$ electronic states occurring only in phases 1 and 5, respectively. Remarkably, the charge-transfer state can only be reached if Cu_2IrO_3 is pressurized at low temperature, suggesting that phonons play an important role in the inhibiting this phase. These results point to the choice of thermodynamic path across interplanar collapse transition as a key parameter to access novel states in intercalated iridates.

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I. INTRODUCTION

The realization that strong spin-orbit coupling can drive electronic correlation and emergent phenomena has revolutionized research on heavy transition metals materials [1–3]. Particular attention has been devoted to the emergence of $J_{\text{eff}} = 1/2$ orbitals in Ir^{4+} and its consequences [4,5], with recent focus centered on the theoretically predicted Kitaev quantum spin liquid (QSL) state due to its potential use in topologically protected quantum computing [6]. Fundamentally, the Kitaev QSL is an analytically solvable Hamiltonian that relies on a combination of a 2D honeycomb structural lattice and bond-directional exchange interaction, with the spin-orbit-driven $J_{\text{eff}} = 1/2$ state of honeycomb iridates being a strong candidate to realize these conditions [5]. However, stabilizing the Kitaev QSL state has proven to be difficult since, in real materials, other magnetic interactions are not fully quenched and compete with the Kitaev exchange [7], usually leading to magnetic order as in Li_2IrO_3 and Na_2IrO_3 [8–12]. The recent development of intercalated honeycomb iridates, namely Cu_2IrO_3 [13], $\text{Ag}_3\text{LiIr}_2\text{O}_6$ [14], and

$\text{H}_3\text{LiIr}_2\text{O}_6$ [15], has re-ignited the field since magnetic order is suppressed in these materials. However, the intercalation process drives structural disorder and can disrupt the Ir $J_{\text{eff}} = 1/2$ orbital [16–18], raising questions on whether the Kitaev QSL has indeed been stabilized.

Cu_2IrO_3 is distinct to other intercalated iridates by the presence of Cu ions both between and within the Ir honeycomb layers [Figs. 1(a) and 1(b)] [13,19]. This leads to the unusual octahedrally coordinated Cu^{1+} ions in plane. There is evidence for the presence of magnetic Cu^{2+} ($\sim 10\%$), which is argued to be nucleated in $\text{Cu}^{2+}/\text{Ir}^{3+}$ domains [16]. The apparent proximity between these charge states raises the potential for structural control of the electronic and/or magnetic properties. Indeed, Cu_2IrO_3 displays a very rich high-pressure structural phase diagram [20–22], featuring five different crystal structures (phases 1 through 5) and distinct sets of phase transitions at room and low temperatures [Figs. 1(c) and 1(d)] [20]. Low pressures (~ 6 – 7.5 GPa) drive Ir-Ir dimerization (phase 2) [20–22], similar to reports on Li_2IrO_3 polymorphs [23–26] and $\text{Ag}_3\text{LiIr}_2\text{O}_6$ [27]. Higher pressures lead to the collapse of the interplanar distance and a distinct structural temperature dependence, with phase 3 appearing around 15 GPa at room temperature (RT), and phases 4 and 5 around 18 GPa and 30 GPa at low temperature, respectively [20].

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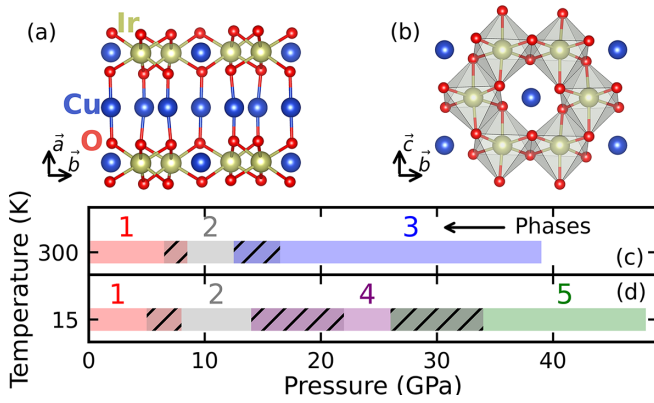


FIG. 1. [(a) and (b)] Crystal structure at ambient pressure featuring Ir honeycomb layers and interplanar O-Cu-O dumbbells. [(c) and (d)] High-pressure structural phase diagram of Cu_2IrO_3 at room and low temperature [20], respectively, as determined through isotherm measurements. The dashed areas are regions of coexistence of two phases.

While a substantial drop in resistance was observed at onset of phase 3 [21,22], there is little information on if and/or how the electronic structure is coupled to these phase transitions.

In this work, we investigate the relationship between the crystal and electronic structure in Cu_2IrO_3 using x-ray absorption near edge structure (XANES), x-ray magnetic circular dichroism (XMCD), resonant inelastic x-ray scattering (RIXS), x-ray powder diffraction, and electrical transport measurements as a function of pressure and temperature. The data reveal that the Ir-Ir dimerization in phase 2 suppresses the localized $J_{\text{eff}} = 1/2$ state, which is phenomenologically similar to Li_2IrO_3 polymorphs [23,24,26,28]. Further compression at low temperature drives a $\text{Cu} \rightarrow \text{Ir}$ electron transfer at the onset of phase 5. Despite the Cu mixed valency, Cu_2IrO_3 remains an insulator in phase 5, which appears to be due to charge segregation into $\text{Cu}^{1+}/\text{Cu}^{2+}$ sites. No charge transfer occurs at similar pressure at RT (phase 3). Remarkably, no electronic or structural phase transition is observed upon cooling from phase 3 (RT to 15 K) or warming from phase 5 (15 K to RT). This demonstrates a strong electron-lattice coupling as the charge transfer is intrinsically connected to the phase 5 structure. It also points to an intricate phase stability landscape in Cu_2IrO_3 , with distinct phenomenology driven by the specific thermodynamic path.

II. ELECTRONIC STRUCTURE OF PHASE 1 AT AMBIENT PRESSURE

We start by addressing the electronic structure of Cu_2IrO_3 in phase 1 at ambient pressure. Intercalated honeycomb iridates were conceived to reduce the exchange interaction between the honeycomb layers, while preserving the well defined $J_{\text{eff}} = 1/2$ character seen in Na_2IrO_3 and Li_2IrO_3 , leading to a more 2D structural motif that better mimics the Kitaev model [6]. To explore the detailed electronic structure of Cu_2IrO_3 , XANES and XMCD were measured at the 4-ID-D and RIXS at the 27-ID beamlines of the Advanced Photon Source (APS), Argonne National Laboratory (ANL). All measurements were performed on powdered samples that

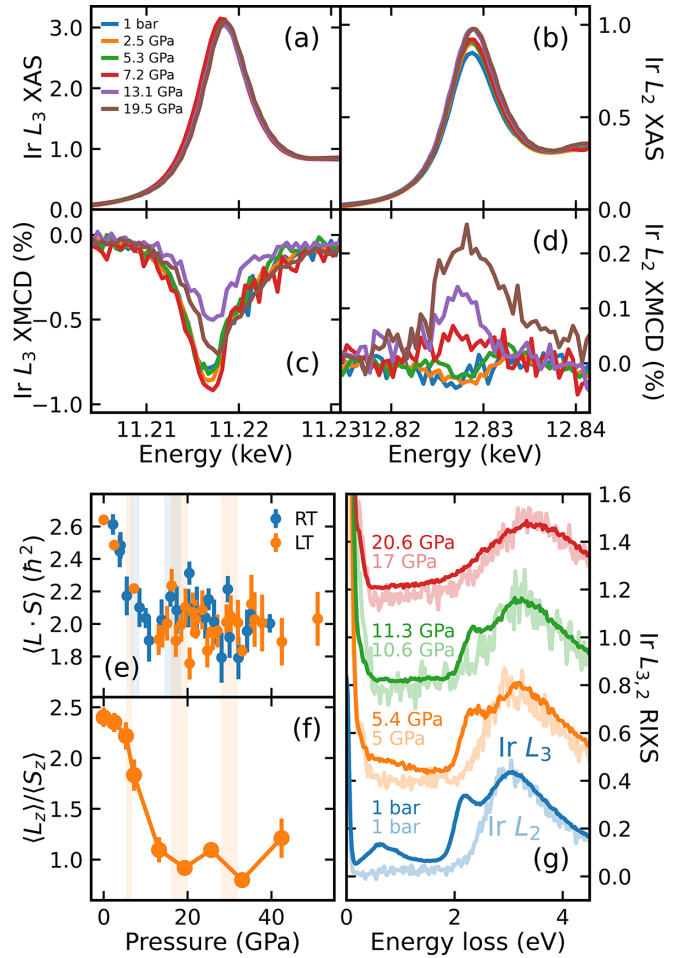


FIG. 2. Electronic properties of Cu_2IrO_3 across the dimerization transition. [(a)–(d)] Pressure dependence of the Ir $L_{3,2}$ XANES and XMCD spectra at low temperature ($1.5 \text{ K} < T < 15 \text{ K}$). Sum rules analysis of the XANES and XMCD yields the (e) average spin-orbit coupling and (f) orbital to spin moment ratio. (g) RIXS pressure dependence at the Ir L_3 (11.215 keV incident energy) and L_2 (12.821 keV) at room temperature. Vertical shaded areas in (e) and (f) correspond to the structural phase transition regions at RT (blue) and low temperature (orange) [20].

were grown as described in Ref. [13], and XMCD was collected using a magnetic field of 4 T. Experimental details are described in Appendix A. At ambient pressure, Cu_2IrO_3 displays the typical Ir^{4+} XANES and XMCD spectra at both 300 K and 1.5 K [Figs. 2(a)–2(d)], featuring large L_3/L_2 intensity ratio. Sum rules analysis reveals $\langle \mathbf{L} \cdot \mathbf{S} \rangle = 2.64(3) \hbar^2$ and $\langle L_z \rangle / \langle S_z \rangle = 2.4(1)$ [29–31], which is consistent with other honeycomb iridates [18,23,26,32] and, more generally, with $J_{\text{eff}} = 1/2$ Ir oxides [32–35].

RIXS measurements, however, point to a more complex picture, with meaningful differences in the orbital excitations among the honeycomb iridates. Na_2IrO_3 and $\alpha\text{-Li}_2\text{IrO}_3$ feature an exciton peak at $\sim 420\text{--}450 \text{ meV}$, and a pair of trigonal crystal field split $J_{\text{eff}} = 3/2$ peaks at about $720\text{--}830 \text{ meV}$ [36]. A markedly different excitation spectra is observed in $\text{Ag}_3\text{LiIr}_2\text{O}_6$, with theoretical modeling pointing to a substantially larger Ir-O hybridization, which is argued to

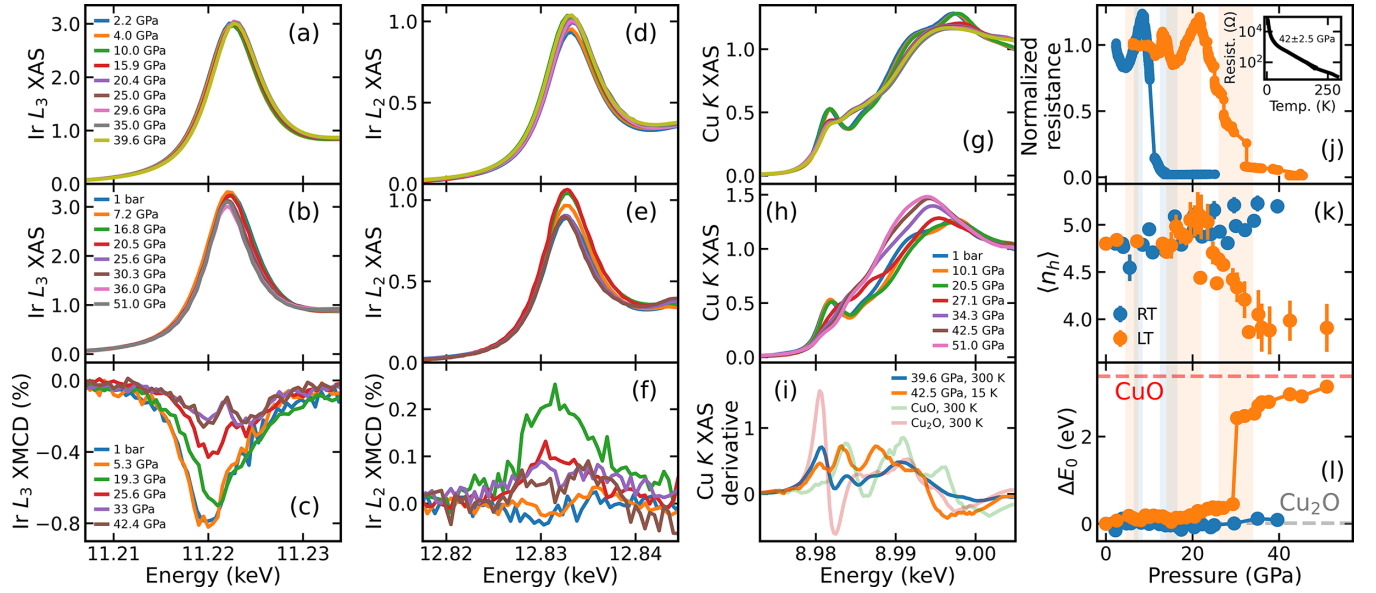


FIG. 3. Electronic properties of Cu_2IrO_3 across phases 3, 4, and 5. (a)–(c) and (d)–(f) display the pressure dependence of the room and low temperature XANES as well as low temperature XMCD taken at the Ir L_3 and L_2 edges, respectively. [(g) and (h)] Cu K -edge XANES at room and low temperature, respectively. Low temperature was kept between 1.5 and 15 K. (d) and (g) follow the same legend as (a). (i) Comparison between the Cu K -edge XANES derivative of Cu references (Cu_2^{1+}O and Cu^{2+}O) and Cu_2IrO_3 at room and low temperature taken at approximately the same pressure (corresponding to phases 3 and 5). (j) Resistance pressure dependence at room and low temperatures. The resistance was normalized to its value at ambient pressure (42 and 584 Ω at room and low temperatures, respectively). A substantial drop in resistance is seen near the onset pressure of phases 3 and 5. Inset: resistance temperature dependence upon warming at 42 ± 2.5 GPa showing that phase 5 remains insulating. [(k) and (l)] Number of $5d$ holes (n_h) and Cu K -edge shift at room and low temperatures extracted from XANES data. An electron transfer from Cu to Ir occurs only at the onset of phase 5. Vertical shaded areas in (j)–(l) correspond to the structural phase transition regions at RT (blue) and low temperature (orange) [20].

enhance magnetic frustration [18]. In Cu_2IrO_3 , a low energy peak near 0.6 eV is clearly observed at the Ir L_3 , but not at the L_2 , demonstrating the $J_{\text{eff}} = 1/2$ ground state [Fig. 2(g)]. However, while the spectra appears to be composed of three peaks, these are largely broadened compared to other honeycomb iridates [18,26,36,37]. Since measurements were done in powdered Cu_2IrO_3 , this suggests more dispersive J_{eff} excitations, which points to an increased delocalization of the $5d$ orbitals. Finally, compared to Cu_2IrO_3 and $\text{Ag}_3\text{LiIr}_2\text{O}_6$, $\text{H}_3\text{LiIr}_2\text{O}_6$ features electronic excitations that much closer resemble those of $\alpha - \text{Li}_2\text{IrO}_3$ [18,36,37], indicating the d -electron-based intercalation ion plays a key role in disrupting the Ir $5d$ orbital.

III. Ir-Ir DIMERS AND THE SUPPRESSION OF THE $J_{\text{eff}} = 1/2$ STATE IN PHASE 2

Pressure drives the onset of phase 2 at both room (6 ± 1.5 GPa) and low (7.5 ± 1 GPa) temperatures [Figs. 1(c) and 2(d)], featuring Ir-Ir structural dimers [20]. The emergence of phase 2 is closely correlated with a disruption of the $J_{\text{eff}} = 1/2$ state, as seen by the reduction of $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ and $\langle L_z \rangle / \langle S_z \rangle$ [Figs. 2(e) and 2(f)], as well as the suppression of the low energy excitation ($J_{\text{eff}} = 3/2$, < 1 eV) [Fig. 2(g)]. These results are similar to those observed at the dimerization of $\alpha -$ and $\beta - \text{Li}_2\text{IrO}_3$ [23–26,28,38]. However, contrary to Li_2IrO_3 [26,28], new low energy RIXS excitations are not seen in Cu_2IrO_3 , instead an increase in the incoherent continuum is observed [Fig. 2(g)]. Quasimolecular orbitals are likely also

stabilized in Cu_2IrO_3 , but the influence of hybridization with Cu $3d$ orbitals masks their low energy excitations. Notably, however, while the exact nature of the quasimolecular orbital cannot be determined, there is strong evidence for the persistent importance of spin orbit coupling (SOC). Both $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ and $\langle L_z \rangle / \langle S_z \rangle$ remain sizable. However, more strikingly, the RIXS excitation near 2.2 eV, which at ambient pressure is related to the SOC split t_{2g} band [36], not only persists at the Ir L_3 edge, but remains absent at the Ir L_2 [Fig. 2(g)]. These results are consistent with a picture that includes both large hopping between the dimerized Ir and large SOC, as described for other iridates [38–41]. Finally, an increase in resistance is observed in phase 2 at RT [Fig. 3(j)], consistent with a previous report [21], and in agreement with a larger band gap obtained from density functional theory (DFT) calculations [20].

IV. ELECTRONIC STRUCTURE OF PHASE 3

While the onset of phase 2 primarily affects the Ir $5d$ state, the Cu orbitals become more active at higher pressures. Curiously, the large reduction in interplanar distance (d) at the onset of phase 3 ($\Delta d/d \approx 8\%$, Fig. 8 and Ref. [20]) is not reflected in the Ir $L_{3,2}$ XANES, with no distinct changes to $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ or $5d$ occupation [Figs. 2(e) and 3(k)]. However, the RIXS excitation near 2.2 eV is largely suppressed in phase 3 [Fig. 2(g)], becoming indistinguishable from the intense continuum of excitations that develops in this phase and extends to zero energy loss. A similar increase in the

incoherent background is seen at the Ir L_2 RIXS [Fig. 2(g)]. These results suggest that the electronic structure of phase 3 features strongly hybridized Ir $5d$ -Cu $3d$ orbitals that destroy the quasimolecular orbitals of phase 2, and is consistent with the substantial drop in resistance [Fig. 3(j)]. The electrical resistance temperature dependence points to a possible metallicity near the onset of phase 3, with increasing semiconducting behavior at higher pressures (see Appendix B) [21], but, as shown in section VI, phase 3 is sensitive to the thermodynamic path, complicating the interpretation of these results. The nature of these orbitals is potentially interesting as $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ remains sizable, suggesting that, despite the collapse of the J_{eff} state and quasimolecular orbitals, SOC still plays an important role. No energy shift is observed in the Cu K -edge spectra, indicating that its modification is likely a structural response due to strongly modified interplanar O-Cu-O dumbbells, likely without an increase in the Cu coordination.

V. PHASE 5 NOVEL $\text{Ir}^{3+} - \text{Cu}^{1.5+}$ ELECTRONIC STATE

At low temperature, the onset of phase 5 is marked by a reduction in the Ir $L_{3,2}$ white line area and shift in the Cu K -edge energy (Fig. 3). Assuming that 80% of Ir are $4+$ at low pressures ($\langle n_h \rangle = 4.8$, where $\langle n_h \rangle$ is the number of $5d$ holes) [16], the reduction in the white line area implies $\langle n_h \rangle \sim 3.9$ above 30 GPa [Fig. 3(k)], i.e., an approximate Ir^{3+} valence state. The Cu valence can be extracted by the position of the absorption edge, which is defined as the maximum of the XANES first derivative. While the multifaceted Cu K edge of Cu_2IrO_3 largely complicates a quantitative analysis, a clear change in the first derivative is seen at the onset of phase 5 [Fig. 3(i)], leading to a discontinuous jump in position of the absorption edge [Fig. 3(l)]. Notably, the Cu K edge taken in phase 3 is very distinct, and features a lower energy edge [Fig. 3(i)]. The sharpness of this jump is artificial as the maximum moves from the first to the second peak in the XANES derivative [Fig. 3(i)]. Nevertheless, the increase in energy implies that Cu lost electrons, thus demonstrating a novel $\text{Cu} \rightarrow \text{Ir}$ electron transfer in Cu_2IrO_3 that occurs only in phase 5. The substantial difference in the electronic structure of phases 3 and 5 indicates that these phases likely feature distinct Cu environments, despite similar collapsed interplanar distances and stability pressure range.

The Ir^{3+} state implies that the nominal Cu valence is $1.5+$. Metallic electronic transport would be expected if this partial valence was only due to the delocalization of the Cu $3d$ bands. However, while a large drop in resistance is observed at pressures near the phase 5 onset, its temperature dependence points to a persistent electronic gap [inset of Fig. 3(j)]. Although the maximum of the Cu K -edge derivative shifts in phase 5, a sizable spectral weight is observed at the Cu^{1+} energy [Fig. 3(i)], indicating that the average $\text{Cu}^{1.5+}$ is formed by a mixture of $2+$ and $1+$ ions. The Ir^{3+} $5d^6$ orbital features fully occupied t_{2g} states, with a large octahedral crystal field ~ 3.5 eV, Fig. 2(g)]. Therefore, while increased Cu/Ir hybridization leads to a lower resistance in phase 5, the Ir^{3+} configuration combined with the Cu charge segregation results in the insulating behavior. Interestingly, this scenario is consistent with DFT calculations, despite phase 5 being different from the predicted crystal structure [20]. Finally,

the localized Cu^{2+} ions in phase 5 could drive magnetism. In fact, the small antiferromagnetic response of Cu_2IrO_3 at ambient pressure is attributed to the $\text{Cu}^{2+}/\text{Ir}^{3+}$ minority domains [13,16]. However, no XMCD signal was observed at the Cu K edge (Appendix F). While this suggests that Cu is not ferromagnetically ordered, it does not discard a possible antiferromagnetic state.

Copper delafossites feature a similar crystal structure pressure dependence to Cu_2IrO_3 , albeit with a triangular lattice [42]. Interestingly, while a pressure-driven interplanar collapse appears to be a general behavior in these compounds [43–47], only CuFeO_2 is known to feature a similar valence transition [43,44]. There is no established explanation for this behavior, but it suggests that the valence transition depends on the relative chemical potential of the related ions. This raises questions on the high-pressure behavior of other intercalated iridates. Recently, an unidentified structural transition was reported in $\text{Ag}_3\text{LiIr}_2\text{O}_6$ around 12–16.1 GPa at RT, which occurs concomitantly with a change in sign of the magnetoresistance [27]. This phenomenology is similar to that seen in Cu_2IrO_3 [21], and points to a potential valence instability.

VI. THERMODYNAMIC PATH DEPENDENCE OF THE HIGH-PRESSURE ELECTRONIC STRUCTURE

The dramatic temperature dependence of the high-pressure electronic structure of Cu_2IrO_3 led us to explore its thermodynamics through concomitant powder x-ray diffraction and Ir $L_{3,2}$ as well as Cu K -edge XANES collected at the HPCAT 16-BM-D beamline at the APS, ANL (see Appendix A for experimental details). Two temperature/pressure paths were taken: 1) pressure was applied at 300 K up to 38 GPa, followed by a nearly isobaric cool down to 14 K (pressure was maintained between 38 and 41 GPa), and low temperature decompression; 2) sample was cooled down to 14 K keeping the pressure below 5 GPa, then pressurized to 38.7 GPa at low temperature, followed by a nearly isobaric warm up to 300 K (pressure was kept between 38.7 and 43 GPa), and 300 K decompression. These different paths drive distinct sets of phase transitions. The compression in path 1) reproduces the phase transitions seen in our previous work [20], stabilizing phase 3 beyond ~ 18 GPa with collapsed interplanar distance [Fig. 4(a)]. High-pressure cool down preserves phase 3, which remains stable upon low temperature pressure release to at least 22.5 GPa. Path 2) again leads to the same set of reported low-temperature phases [Fig. 4(b)] [20]. Remarkably, phase 5 is also preserved upon warming up to 300 K. Pressure release at 300 K leads to a phase $5 \rightarrow 3$ transition at 27 ± 3 GPa, but no signs of phase 4. The dimerized phase 2 is also not detected on pressure release. The remarkable phase diagram of Cu_2IrO_3 is closely followed by the electronic structure [Figs. 4(c)–4(j)]. The $\text{Cu} \rightarrow \text{Ir}$ electron transfer occurs only within phase 5, with the reversal to the approximate $\text{Ir}^{4+}/\text{Cu}^{1+}$ configuration at the phase $5 \rightarrow 3$ transition, and the $J_{\text{eff}} = 1/2$ state features only in phase 1, again including on pressure release through path 2). These results highlight a strong electron-lattice coupling in Cu_2IrO_3 .

The RT phase diagram of Cu_2IrO_3 is not settled in the literature [20–22] (there is only one report on the low temperature structures [20]). While there is an overall agreement

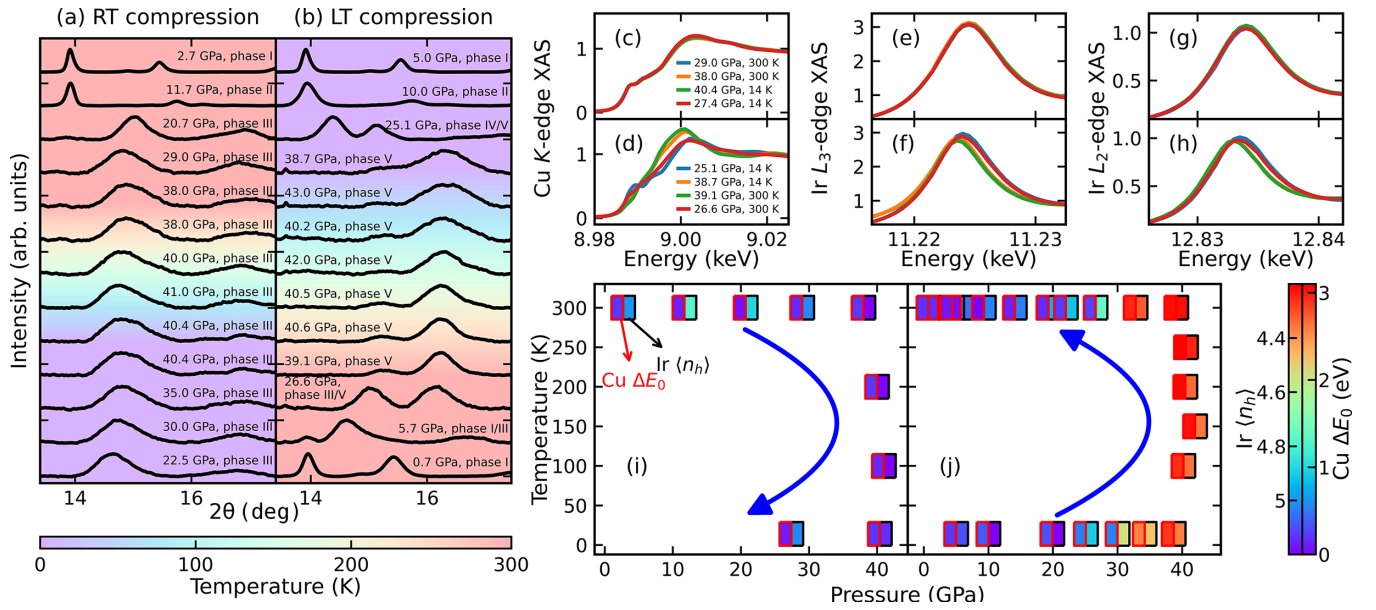


FIG. 4. Structural and electronic properties of Cu_2IrO_3 through two distinct thermodynamical paths. (a), (c), (e), and (g) display x-ray diffraction as well as Cu K and Ir $L_{3,2}$ -edge XANES measured while pressurizing at RT and depressurizing at 15 K, respectively, while (b), (d), (f), and (h) display the same measurements taken via the reverse path. [(i) and (j)] Number of $5d$ holes ($\langle n_h \rangle$) and the shift in Cu K-edge energy are shown for each path.

on the presence of a dimerized Ir-Ir and interplanar collapsed structures (phases 2 and 3), different critical and coexistence pressures have been reported. A key difference amongst these studies is the use of different pressure media, which likely leads to different hydrostaticity. The absence of phase 2 upon decompression from phase 5 further points to the importance of the non-hydrostatic shear in the phase stability of Cu_2IrO_3 , since decompression leads to large pressure gradients. The Cu_2IrO_3 growth method may also be relevant to the high-pressure phase stability, as recent developments have led to less structural disorder [48]. Additionally, our results suggest that previous transport measurements did not probe the properties of phases 4 or 5, as pressure was applied at RT [21,22]. Although our data [Fig. 3(j)] and theoretical calculations indicate that Cu_2IrO_3 is an insulator in phase 5, due to the distinct pressure media used in these measurements, concomitant electrical transport and x-ray diffraction measurements are needed to verify this result.

The processes that stabilize phases 3, 4, 5 remain an important open topic given their distinct electronic properties.

The absence of a phase $3 \rightarrow 5$ ($5 \rightarrow 3$) transition upon cooling (warming) at high pressure prevents determining whether one of these is the ground state. The onset of phase 4 at a similar pressure to phase 3 indicates that its presence is important in stabilizing phase 5. Both of these phases feature a collapsed interplanar distance, which is likely associated with modifications in the O-Cu-O dumbbells (note that this distance is nearly pressure-independent in phases 1 and 2) [20]. Such interplanar dumbbells typically feature strong low energy phonons [47,49]. Therefore it is likely that the stability of these phases is closely tied to the vibrational amplitude of the dumbbell phonons. This scenario implies that a similar phenomenology will occur in $\text{H}_3\text{LiIr}_2\text{O}_6$ and $\text{Ag}_3\text{LiIr}_2\text{O}_6$. Alternatively, low temperature might stifle the nucleation and growth of phase 3, stabilizing instead phase 4. It would be interesting to probe whether the speed of compression affects this transition [50] (in this work, we typically pressurized at a rate of ~ 50 GPa/h, stopping at each pressure point for about 10–30 min). Further exploration of the Cu_2IrO_3 thermodynamic landscape is needed, not only to clarify the

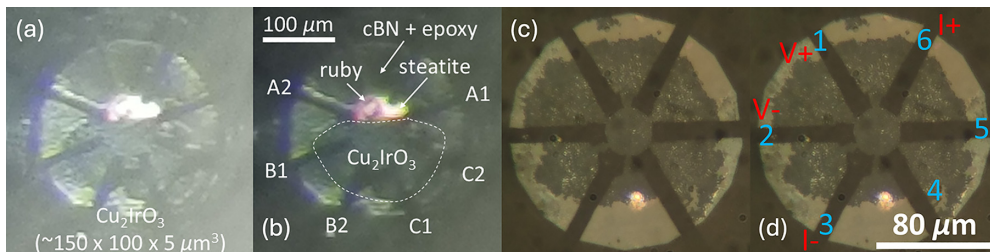


FIG. 5. Pictures of the sample configuration for Cu_2IrO_3 transport measurements. (a), (b) and (c), (d) are setup for room and low temperature compression measurements, respectively. (b) and (d) are the same as (a) and (c) but include details explaining the electrode configuration.

role and stability of phase 4, but also to search for novel phenomena.

VII. CONCLUSION

This work explored the pressure dependence of the electronic properties of Cu_2IrO_3 . At ambient pressure, an enhanced delocalization of $5d$ $J_{\text{eff}} = 1/2$ orbitals is observed, likely driven by hybridization with the in-plane Cu $3d$ orbitals. High-pressure data unveil a remarkable electronic phase diagram. The dimerized Ir-Ir bonds of phase 2 lead to a collapse of the $J_{\text{eff}} = 1/2$ state, likely stabilizing molecular orbitals with persistent J_{eff} character. Higher pressures lead to the collapse of the interplanar distances, and to large changes in the electronic structure. While the RT phase 3 feature dominant $\text{Ir}^{4+}/\text{Cu}^{1+}$ ions, the low temperature phase 5 stabilizes $\text{Ir}^{3+}/\text{Cu}^{1.5+}$. The insulating behavior of phase 5 appears to originate in a charge segregation of Cu^{1+} and Cu^{2+} , raising the prospect of antiferromagnetic order. A remarkable temperature dependence is seen at high pressures with phase 5 only being stabilized upon cold compression, but remaining stable upon warming to 300 K. The richness of the Cu_2IrO_3 phase diagram motivates further work. Additionally, it highlights the importance of investigating other intercalated iridates, and the role of the thermodynamic path in driving novel phenomena.

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APPENDIX A: EXPERIMENTAL DETAILS

1. X-ray spectroscopy

XANES and XMCD experiments were performed at the 4-ID-D beamline of the APS, ANL. Data were collected in transmission geometry at the Ir $L_{2,3}$ and Cu K edges as a function of pressure at room and low ($1.5 \text{ K} \leq T \leq 15 \text{ K}$)

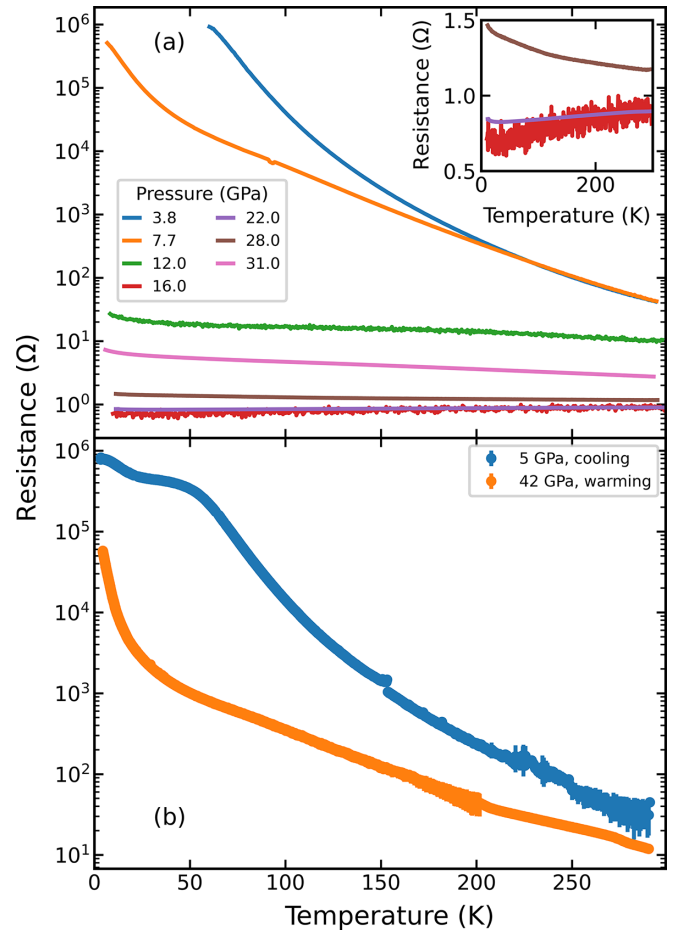


FIG. 6. Cu_2IrO_3 electrical transport temperature dependence at high pressure. (a) Pressure was always applied at room temperature, and electrical transport was measured on warming. (b) Data were collected on cooling at 5 ± 2 GPa (blue points), followed by compression at 15 K. Resistance was then measured at 42 ± 3 GPa on warming (orange points).

temperatures. A 4 T magnetic field was applied to the sample during XMCD scans. Magnetic field and temperature were controlled using a 6.5 T LHe cooled magnet system. For ambient pressure measurements, Cu_2IrO_3 powder was brushed onto Kapton tapes, which were then stacked to generate the desired absorption edge jump (~ 0.7). High pressure was generated using a CuBe cell fitted with a set of partially perforated plus mini anvils of 300 μm culet diameter [51]. Pressure was controlled *in situ* using He gas membranes. Ruby spheres were used as manometer [52]. Helium was used as pressure media and loaded using the GSECARS gas loading facility [53]. Monochromatic x-rays were generated using a Si(111) double crystal monochromator. The beam was focused to $100 \times 250 \mu\text{m}^2$ using a toroidal mirror, and further reduced to $50 \times 50 \mu\text{m}^2$ using slits. X-ray harmonics were rejected by both detuning the monochromator second crystal, and a Pd-coated flat mirror at 3.1 mrad. Circular x-ray polarization for XMCD measurements was obtained using a 500 μm diamond phase plate. Data analysis was performed using the Larch package [54].

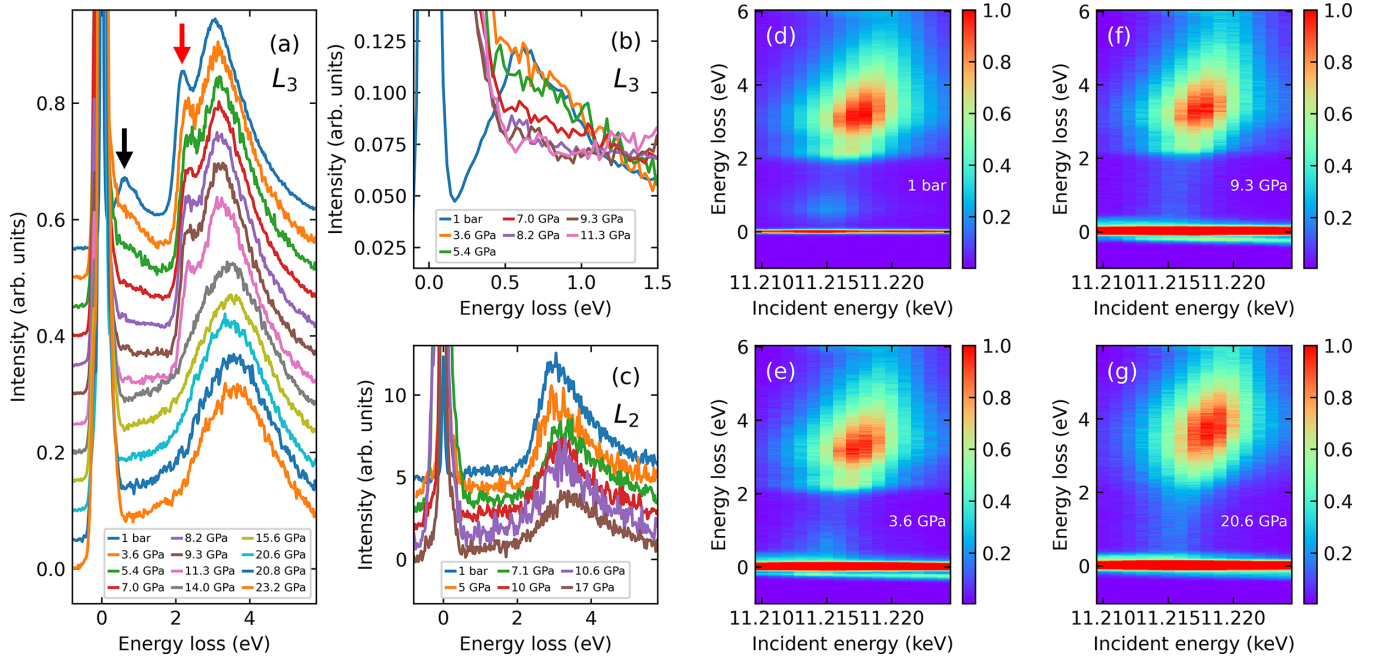


FIG. 7. Cu_2IrO_3 Ir $L_{3,2}$ RIXS pressure dependence at room temperature. (a) Inelastic signal collected using 11.215 keV incident x-ray energy. Note that the ambient pressure data were collected outside the pressure cell, hence the narrower elastic line. (b) The $J_{\text{eff}} = 1/2 \rightarrow 3/2$ excitation is strongly suppressed upon the onset of the dimerized phase 2. (c) RIXS signal from the Ir L_2 (12.821 keV). [(d)–(g)] Incident energy dependence of the Ir L_3 at selected pressures. While the $J_{\text{eff}} = 1/2 \rightarrow 3/2$ excitation is suppressed by pressure, a clear spectral weight remains around 11.215 keV up to at least 20.6 GPa.

2. Resonant inelastic x-ray scattering

RIXS was measured at the Ir $L_{2,3}$ as a function of pressure at room temperature. The experiments were performed at the MERIX instrument located at the 27-ID beamline of the APS, ANL. Incoming x-rays were monochromatized using a combination of high-heat-load diamond (111) and four bounce Si(400) monochromators, and focused to about $40 \times 25 \mu\text{m}^2$ (full width half maximum) in the horizontal and vertical directions at the sample position. Inelastic scattering was measured using a Rowland geometry with 2 m diameter, and employing Si(4 4 8) and Ge(0 6 10) spherical analyzers for the Ir L_3 and L_2 edges, respectively. This setup yielded a total RIXS resolution (full width half maximum) of 90.4 meV at the Ir L_3 , and 84.3 meV at the L_2 . Ambient pressure measurements were performed using a Cu_2IrO_3 pellet. High pressure was generated using a Princeton-type symmetric diamond anvil cell fitted with regular anvils of 300 μm culet diameter. Spurious signal from the diamond anvils can substantially affect the RIXS spectrum [55]. This contamination was reduced by using a gasket-in/gasket-out geometry in which both incoming and outgoing x-rays reach the sample through a Be gasket. Ruby fluorescence was used to calibrate pressure [52], and neon served as pressure media.

3. Temperature dependent concomitant x-ray spectroscopy and powder diffraction

Concomitant x-ray powder diffraction as well as Ir $L_{2,3}$ and Cu K -edge XANES were collected at the HPCAT 16-BM-D beamline of the APS, ANL. High pressure was generated

using Princeton-type symmetric cells fitted with a set of partially perforated and regular diamond anvils of 300 μm culet diameter. Both the Au lattice constant and ruby fluorescence were employed as pressure calibrants [52,56,57]. Diffraction was collected using x-ray wavelength $\lambda = 0.6888 \text{ \AA}$ ($E = 18 \text{ keV}$) in order to facilitate the XANES measurements taken at the Ir $L_{2,3}$ (12.284 keV and 11.214 keV) and Cu K (8.979 keV) edges. Measurements were performed using a LHe flow cryostat, with pressure applied in-situ through He gas membranes. Helium was used as pressure medium, and was loaded using the GSECARS gas loading facility [53]. The 2D images from the MAR3450 detector were converted to 1D diffractograms using the Dioptras software [58], which was also used to mask diamond Bragg peaks, as well as correct for the diamond and seat absorption. XANES was measured in transmission geometry using ion chambers to detect the incident and transmitted x-ray intensity.

4. Electrical transport

a. Room-temperature compression

A powdered Cu_2IrO_3 chunk was kept inside an argon-filled glove box with O_2 levels below 0.5 ppm. A sample with dimensions of approximately $150 \times 50 \times 5 \mu\text{m}^3$, as shown in Fig. 5, was placed in a gas membrane-based diamond anvil cell (ChicagoDAC from Almax-EasyLab) within one or two hours outside of the glove box, along with a ruby (20 μm in diameter) for pressure calibration [59]. A designer-diamond anvil with a 20 μm central flat, featuring eight symmetrically embedded tungsten electrodes, was used along with a 500 μm

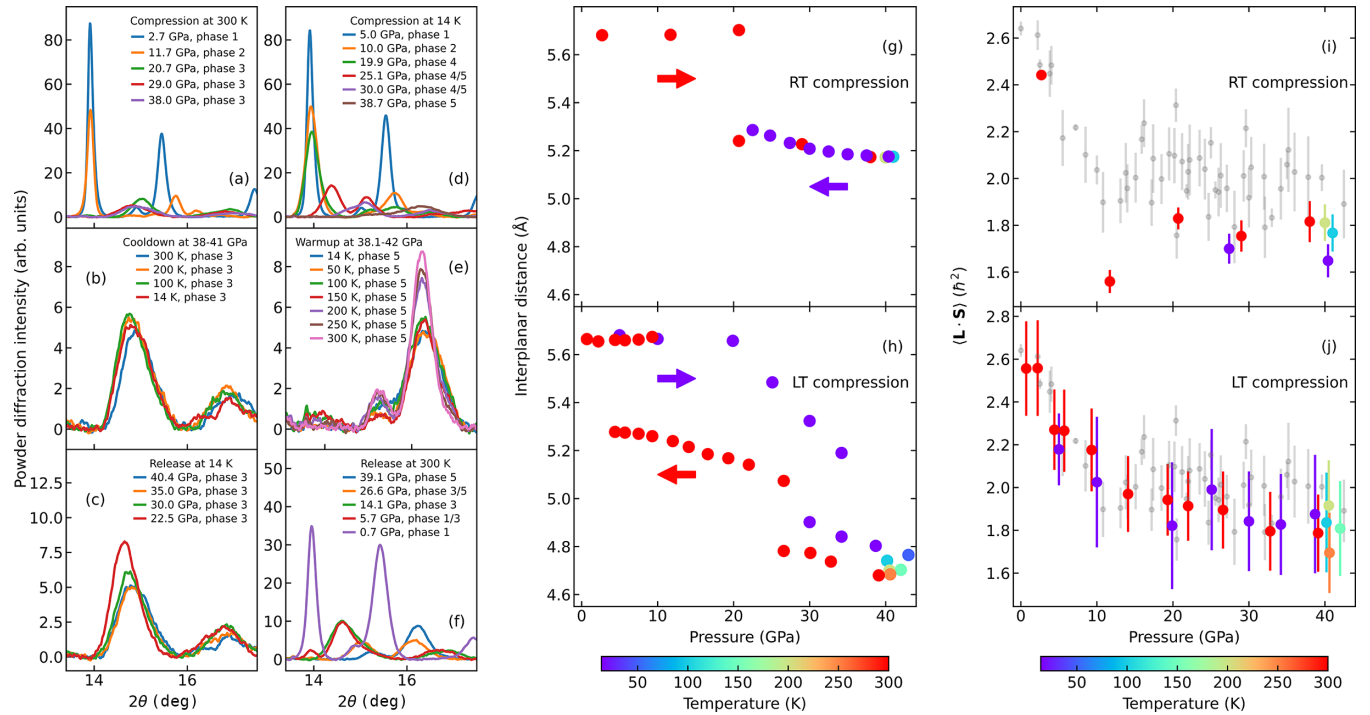


FIG. 8. Cu_2IrO_3 x-ray scattering and spectroscopy data taken through two thermodynamic routes. Room temperature compression (a), followed by nearly isobaric cooldown at 39 ± 1.5 GPa (b), then low temperature (14 K) pressure release (c). Low temperature (14 K) compression (d), followed by nearly isobaric warmup around 40 ± 2 GPa (e), then room temperature pressure release (f). [(g) and (h)] Pressure dependence of the interplanar distance extracted from the (002) reflection through the room and low temperature compression paths, respectively. [(i) and (j)] Ir 5d $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ measured through the same thermodynamic paths as in (g) and (h), respectively. The combined data taken through isothermal measurements at room and low temperature are shown in gray [same data as in Fig. 2(e)].

culet diameter anvil on the opposite side [60]. A 316 stainless steel metal gasket was pre-indented from approximately 150 μm to 25 μm in thickness, with a hole (~ 140 μm in diameter) filled with a cBN-epoxy mixture and soapstone (steatite), which acted as both an electrical insulator and a pressure-transmitting medium. After loading the sample, the cell was placed in a Physical Property Measurement System (PPMS) by Quantum Design. The electrode configuration used was B2: +V, C2: -V, A1: +I, B1: -I [Fig. 5(b)]. A current of 10 μA was used in all the measurements shown. Resistance was measured in a four-probe arrangement using a Keithley 6221 DC current source and a Keithley 2182a nanovoltmeter configured for “delta mode.” The instruments were set to voltage mode rather than resistance mode. The compliance voltage (maximum voltage allowed to read) was set to 10 V. The temperature was changed at a rate of approximately 1.5 K/min for each temperature sweep between pressure changes at room temperature.

b. Low-temperature compression

A gas-membrane-driven diamond anvil cell (OmniDAC from Almax-EasyLab) with two opposing diamond anvils (160 μm and 500 μm central flats) was used. One of these anvils was a designer-diamond anvil (160 μm central flat) with six symmetrically deposited tungsten microprobes encapsulated in high-quality-homoepitaxial diamond [60]. Stainless steel was used as gasket, as pre-indented to a thickness

of around 20 to 25 μm . A cBN-epoxy mixture along with steatite was used for insulation and as the pressure medium. A micro-sized Cu_2IrO_3 powder sample, with dimensions of approximately $140 \times 100 \times 5$ μm^3 , was then loaded into the diamond anvil cell within one or two hours outside of the glove box, along with a ruby (15 μm in diameter) for pressure calibration [59]. The cell screws were then used to secure the sample and apply an initial pressure of 3 GPa. After attaching the membrane to the cell, a small amount of helium gas pressure (0.3 bar) was added to the membrane, and the screws were removed.

The gas-membrane-driven diamond anvil cell was then placed inside a customized continuous-flow cryostat (Oxford Instruments). A home-built optical system, attached to the bottom of the cryostat, was used for the visual observation of the sample and measurement of the ruby fluorescence. Initially, the sample was cooled down to 3 K at 3 GPa. Pressure was then applied at approximately 15 K, reaching 45 GPa, and the sample was subsequently cooled down to 4 K and warmed up to room temperature while maintaining the pressure between 40–45 GPa. To reach the mega-ohm range at low temperatures, we used a 1 μA current source. A Keithley delta mode was employed in the same manner as in the room temperature compression experiment. We used a 100 V range in the voltage mode, which showed noise in the low resistance range below 1000 Ω . Upon warming from 200 K, we switched to a 10 V range, resulting in reduced noise. Further details of the nonhydrostatic high-pressure resistivity technique, includ-

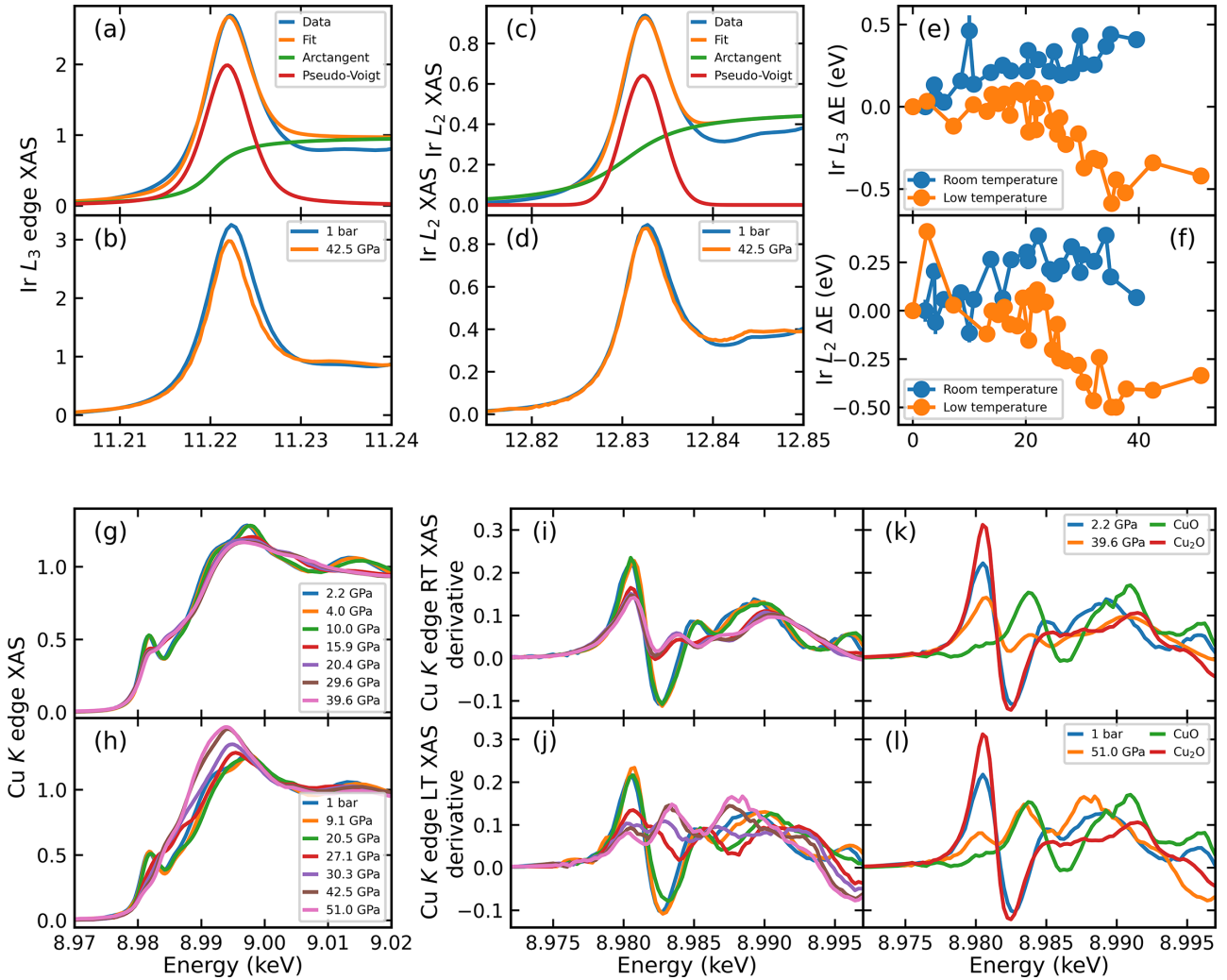


FIG. 9. Analysis of the Cu_2IrO_3 XANES data. [(a)–(d)] Example of the Ir $L_{3,2}$ fitting and pressure dependence. [(e) and (f)] Position of the white line of the Ir L_3 and L_2 edges extracted from fitting, respectively. [(g) and (h)] Cu K-edge XANES taken during room and low temperature compression, respectively. [(i) and (j)] First derivative of the data in (g) and (h), the absorption edge is defined as the energy of the maximum of the first derivative. (k) and (l) Comparison between the lowest and highest pressures of the data shown in (i) and (j) with data from Cu^{2+}O and Cu_2^{1+}O standards.

ing a photograph using a designer-diamond anvil, are provided in Ref. [61].

APPENDIX B: ADDITIONAL ELECTRICAL TRANSPORT DATA

Figure 6 displays the temperature dependent resistance measurements that were performed through both room and low (15 K) compression. The room temperature compression data [Fig. 6(a)] was binned to 0.5 K steps to improve noise level. The low temperature compression measurements employed a low precision temperature sensor, which resulted in digitized temperature steps with multiple resistance measurements per temperature. Fig. 6(b) shows the average of these measurements with error bar being the standard deviation.

The onset of phase 3 (14.5 ± 2 GPa) at room temperature leads to a sharp drop in resistance [Fig. 3(k)]. Remarkably, near that transition the temperature dependence suggests a

weakly metallic behavior [inset of Fig. 6(a)], but further compression leads to an increase in resistance and re-entry of an insulating/semiconducting state. This behavior is consistent with previous work [21]. However, given the complex dependence on the thermodynamic path presented in this work, it is unclear whether Cu_2IrO_3 retains phase 3 upon cool down near 15 GPa, and therefore whether it is truly metallic.

APPENDIX C: ADDITIONAL RESONANT INELASTIC X-RAY SCATTERING DATA

The full Ir $L_{3,2}$ RIXS dataset is presented in Fig. 7. The characteristic $J_{\text{eff}} = 1/2 \rightarrow 3/2$ excitation is clearly seen at the L_3 edge at ambient pressure, and, as expected, absent at the L_2 . Scattering from the high-pressure environment increases the width of the elastic peak, whose tail overlaps with the J_{eff} excitation. Nevertheless, a clear suppression of the excitation is seen across the dimerization transition, similar to data from

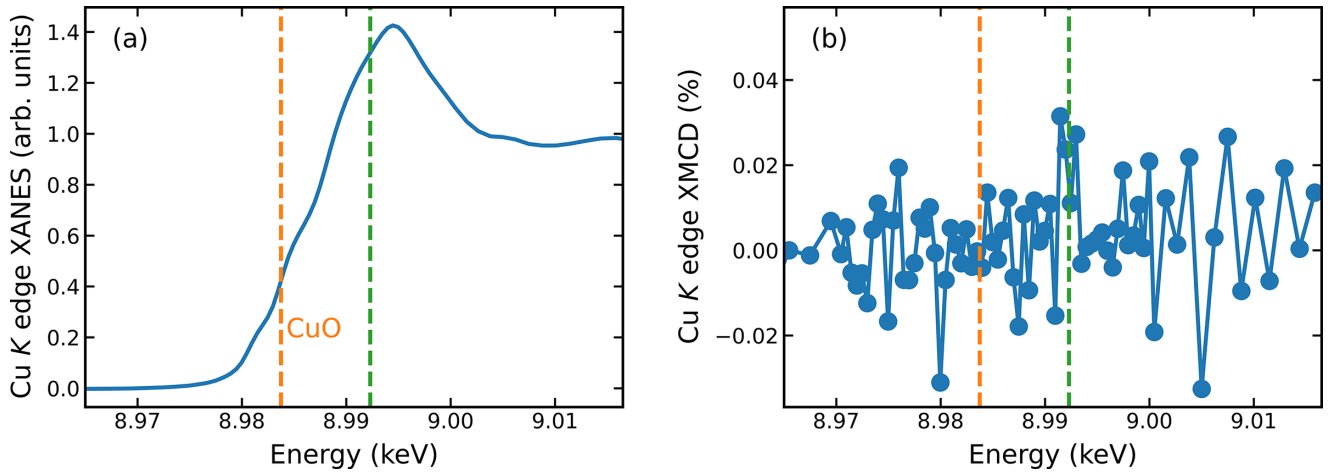


FIG. 10. Cu_2IrO_3 Cu K edge XANES (a) and XMCD (b) at 42.5 GPa and 1.6 K (phase 5). The orange dashed line corresponds to the absorption edge position for Cu^{2+} .

Li_2IrO_3 [26,28]. Interestingly, the peak near 2.2 eV [red arrow in Fig. 7(a)] only completely vanished around the onset of phase 3 (14.5 ± 2 GPa) [20], and leads to a substantial incoherent excitation continuum that is clearly seen in Fig. 7(g). The L_2 -edge data also show an increased continuum in phase 3 [Fig. 7(c)]. These results suggest that spin-orbit coupling remains relevant in the dimerized phase (albeit without a $J_{\text{eff}} = 1/2$ state), but it is quenched in phase 3, likely due to increased hybridization.

APPENDIX D: INTERPLANAR DISTANCE DEPENDENCE ON THE THERMODYNAMIC PATH AND RECOVERY OF $J_{\text{eff}} = 1/2$ STATE ON PRESSURE RELEASE

Further details of the structural transitions seen in Cu_2IrO_3 for different thermodynamic paths are presented in Fig. 8. Compression at both room and low temperature lead to the previously reported phase transitions [20]. This is further evidenced by the interplanar distance pressure dependence [Figs. 8(g) and 8(h)]. The onsets of both phases 3 and 5 are marked by an interplanar distance collapse, with the low temperature phase 5 displaying a shorter distance than the room temperature phase 3 [20]. The phase 5 to 3 transition observed on the cold-compression/warm-release pathway clearly demonstrate that phase 5 indeed has a smaller interplanar distance than phase 3, being thus correlated with their distinct Ir/Cu valence states. The strong electron-lattice coupling is also evident by the Ir $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ behavior [Figs. 8(i) and 8(j)], which includes a recovery of the $J_{\text{eff}} = 1/2$ state on pressure release.

APPENDIX E: X-RAY ABSORPTION SPECTROSCOPY DATA ANALYSIS

In order to employ the XANES and XMCD sum rules analysis at the Ir L -edges, the area of the XANES white line (peak near the absorption edge) must be extracted [29,30]. To this end, we fit the Ir $L_{3,2}$ XANES with a combination of arc-tangent step function and a pseudo-Voigt peak, an example of this fit is displayed in Figs. 9(a) and 9(b). In order to estimate systematic errors, we average the area of the pseudo-Voigt

with an integral of the data minus the step function, and use their difference as errors.

The Ir valence transition in phase 5 is demonstrated by the $\langle n_h \rangle$ extracted through the Ir $L_{3,2}$ XANES [Fig. 3(k)]. Such transition is also expected to shift the white line position to lower energies [32,35]. Figures 9(e) and 9(f) display the position of the Ir $L_{3,2}$ white line as a function of pressure. A clear shift is observed in both edges at the onset of phase 5, providing further evidence for the Ir^{3+} state.

The Cu K -edge position, defined as the absorption inflection point, is a signature of the Cu valence state, with the Cu_2^{1+}O and Cu^{2+}O edges at 8980.4 and 8983.7 eV, respectively [Figs. 9(k) and 9(l)]. While large changes in the XANES are seen at the onset of phase 3, the energy of the edge moves only slightly to higher energies ($\lesssim 0.1$ eV), remaining much closer to the Cu^{1+} reference [Figs. 9(g) and 9(k)]. In contrast, phase 5 leads to a clear shift in spectral weight to similar energies as seen in the Cu^{2+} reference [Figs. 9(h) and 9(l)]. But, notably, the Ir $4+ \rightarrow 3+$ transition [Fig. 3(k)] implies that Cu is nominally $1.5+$ due to the $2/1$ stoichiometry. It is unclear whether this Cu mixed valence state corresponds to distinct $\text{Cu}^{1+}/\text{Cu}^{2+}$ sites (as in a charge order insulator), or a semi-filled band (band insulator). However, the persistence of a clear peak near the $1+$ energy suggests that the former scenario is stabilized [Fig. 9(j)].

APPENDIX F: Cu K -EDGE X-RAY MAGNETIC CIRCULAR DICHROISM

As discussed in the manuscript and Appendix E, there is evidence for the charge segregation of Cu^{1+} and Cu^{2+} ions in phase 5. The $\text{Cu}^{2+} 3d^9$ orbitals have a local moment and could lead to magnetic order. In fact, the magnetic signal observed in Cu_2IrO_3 at low temperatures is likely due to the $\text{Cu}^{2+}/\text{Ir}^{3+}$ minority domains [13,16]. The K -edge XMCD signal is typically small ($\sim 0.1\%$ – 0.5% of the absorption jump) since it relies on the small orbital moment of the p valence states [62]. There is no clear expectation for the size of the XMCD signal for Cu^{2+} , since it typically orders antiferromagnetically, but ferromagnetic Cu metal normally yields an XMCD amplitude of $\sim 0.2\%$ [63]. Figure 10 shows Cu K -edge XMCD data taken

in phase 5 (42.5 GPa and 1.6 K) using the same setup described in Appendix A 1. No clear XMCD signal is observed at the $\sim 0.1\%$ level, suggesting that the Cu_2IrO_3 phase 5 is not ferromagnetic. A small peak is observed at roughly the

same energy as the white line (green dashed line in Fig. 10), which is consistent with the paramagnetic signal reported in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ [64]. However, given its small amplitude and narrow width ($\lesssim 2$ eV), it is unclear if it is a real signal.

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