

# Cu<sub>2</sub>IrO<sub>3</sub>: A New Magnetically Frustrated Honeycomb Iridate

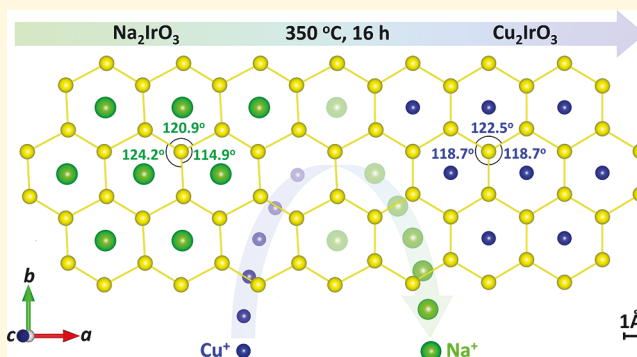
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## Supporting Information

**ABSTRACT:** We present the first copper iridium binary metal oxide with the chemical formula Cu<sub>2</sub>IrO<sub>3</sub>. The material is synthesized from the parent compound Na<sub>2</sub>IrO<sub>3</sub> by a topotactic reaction where sodium is exchanged with copper under mild conditions. Cu<sub>2</sub>IrO<sub>3</sub> has the same monoclinic space group (C2/c) as Na<sub>2</sub>IrO<sub>3</sub> with a layered honeycomb structure. The parent compound Na<sub>2</sub>IrO<sub>3</sub> is proposed to be relevant to the Kitaev spin liquid on the basis of having Ir<sup>4+</sup> with an effective spin of 1/2 on a honeycomb lattice. Remarkably, whereas Na<sub>2</sub>IrO<sub>3</sub> shows a long-range magnetic order at 15 K and fails to become a true spin liquid, Cu<sub>2</sub>IrO<sub>3</sub> remains disordered until 2.7 K, at which point a short-range order develops. Rietveld analysis shows less distortions in the honeycomb structure of Cu<sub>2</sub>IrO<sub>3</sub> with bond angles closer to 120° compared to Na<sub>2</sub>IrO<sub>3</sub>. Thus, the weak short-range magnetism combined with the nearly ideal honeycomb structure places Cu<sub>2</sub>IrO<sub>3</sub> closer to a Kitaev spin liquid than its predecessors.



## INTRODUCTION

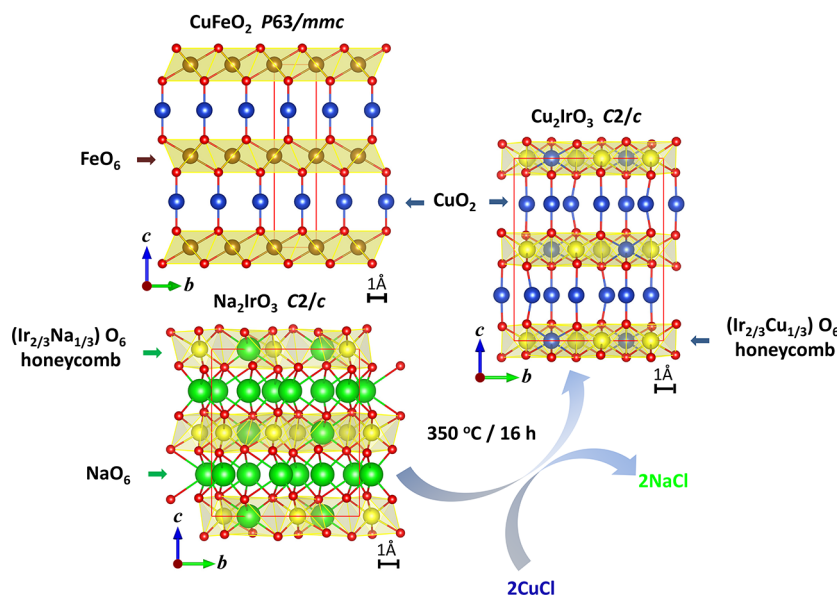
The intricate relation between lattice structure and magnetism is a fascinating area of research in materials chemistry.<sup>1</sup> Geometric frustration is known to suppress magnetic ordering in triangular, pyrochlore, and Kagomé lattices.<sup>1</sup> The complete suppression of magnetic order in a  $S = 1/2$  system gives rise to a quantum spin liquid.<sup>2,3</sup> In a seminal work, Kitaev proposed an intriguing theoretical model for quantum spin liquids by placing  $S = 1/2$  Fermions onto a honeycomb geometry.<sup>4</sup> The *Kitaev model* is based on a bond-dependent ferromagnetic (FM) interaction  $S_i^x S_j^x$ , where  $i$  and  $j$  are neighboring sites at 120° and the bond dependence is imposed by  $\gamma = x, y, z$ . The special commutation relations between the Pauli matrices,  $S_i^x = \frac{\hbar}{2} \sigma_i^x$ , frustrate this interaction and give rise to a spin liquid. The Kitaev model received more appreciation after the discovery of honeycomb iridates Na<sub>2</sub>IrO<sub>3</sub> and Li<sub>2</sub>IrO<sub>3</sub>.<sup>5,6</sup> Both of these materials contained Ir<sup>4+</sup> in an octahedral crystal field with effective  $S = 1/2$  placed onto a honeycomb lattice, satisfying the basic requirements of the Kitaev model. However, both compounds showed robust antiferromagnetic (AFM) order at 15 K, therefore failing to become true spin liquids.<sup>6,7</sup> The AFM order was explained as a result of two competing interactions on the honeycomb lattice:<sup>5</sup>  $\mathcal{H}_{ij}^x = -KS_i^x S_j^x + JS_i \cdot S_j$ . The  $K$  term is the famous Kitaev FM interaction corresponding to the spin liquid. The  $J$  term is a conventional Heisenberg AFM interaction corresponding to the AFM order. The relative

magnitude of the two terms tunes magnetism from a Kitaev limit (spin liquid) to a Heisenberg limit (AFM order). The long-range AFM order in Li<sub>2</sub>IrO<sub>3</sub> and Na<sub>2</sub>IrO<sub>3</sub> shows they are closer to the Heisenberg limit. Nearly a decade of research failed to produce another alkali honeycomb iridate due to the large ionic radii of K, Rb, and Cs. We now present a new honeycomb iridate made not with another alkali but with a transition metal. We first describe the chemistry pathway to make metastable Cu<sub>2</sub>IrO<sub>3</sub> with copper in the 1+ state. We then reveal a near-ideal honeycomb structure and a lack of magnetic ordering down to 2.7 K, suggesting an unprecedented proximity to the Kitaev limit.

Structurally, A<sub>2</sub>IrO<sub>3</sub> honeycomb iridates are derivatives of the ABO<sub>2</sub> delafossite system which has two polytypes: the bilayer hexagonal (2H) polytype known as the CuFeO<sub>2</sub> structure and the trilayer rhombohedral (3R) polytype known as the AgFeO<sub>2</sub> structure.<sup>8</sup> The structural parent of the honeycomb iridate, Na<sub>2</sub>IrO<sub>3</sub>, is the bilayer delafossite CuFeO<sub>2</sub> with space group  $P6_3/mmc$ . CuFeO<sub>2</sub> has layers of edge-sharing FeO<sub>6</sub> octahedra stacked along [001] and linked with linear CuO<sub>2</sub> dumbbells.<sup>9</sup> Two structural modifications occur in transition from CuFeO<sub>2</sub> (space group  $P6_3/mmc$ ) to Na<sub>2</sub>IrO<sub>3</sub> (space group  $C2/c$ ). First, within each layer, FeO<sub>6</sub> octahedra are replaced by (Ir<sub>2/3</sub>Na<sub>1/3</sub>)O<sub>6</sub> octahedra. Every sodium atom is surrounded by

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**Figure 1.** Structural and chemical relations between  $\text{CuFeO}_2$ ,  $\text{Na}_2\text{IrO}_3$ , and  $\text{Cu}_2\text{IrO}_3$ . The structure of  $\text{Cu}_2\text{IrO}_3$  consists of edge-sharing  $(\text{Ir}_{2/3}\text{Cu}_{1/3})\text{O}_6$  octahedra in honeycomb layers, similar to  $\text{Na}_2\text{IrO}_3$ , and copper dumbbells between the layers, similar to  $\text{CuFeO}_2$ . The exchange reaction occurs according to eq 1 at moderate temperatures. Sodium atoms are replaced by copper atoms both between the layers and within the honeycomb layers.

six iridium atoms, whereas every iridium has three nearest neighbor iridium atoms. This arrangement gives rise to a planar honeycomb structure which accommodates two Ir for each Na. To emphasize the honeycomb ordering, the structural formula of  $\text{Na}_2\text{IrO}_3$  can be written as  $\text{Na}_3(\text{NaIr}_2)\text{O}_6$ .<sup>10</sup> The second structural modification occurs between the layers where  $\text{CuO}_2$  dumbbells in  $\text{CuFeO}_2$  are replaced by distorted  $\text{NaO}_6$  octahedra in  $\text{Na}_2\text{IrO}_3$  (Figure 1).<sup>11</sup> Historically, the crystalline and the magnetic structures of  $\text{Na}_2\text{IrO}_3$  have been tuned by either substituting the iridium with other transition metals<sup>12</sup> or by the isovalent substitution of  $\text{Na}^+$  with  $\text{Li}^+$ .<sup>13,14</sup> We succeeded to fully substitute  $\text{Na}^+$  by  $\text{Cu}^+$  through a topotactic reaction between  $\text{Na}_2\text{IrO}_3$  and  $\text{CuCl}$  to make the new honeycomb iridate  $\text{Cu}_2\text{IrO}_3$  (Figure 1). Structural refinement shows that  $\text{Cu}_2\text{IrO}_3$  crystallizes in the  $\text{C2/c}$  space group with honeycomb layers of edge-sharing  $(\text{Ir}_{2/3}\text{Cu}_{1/3})\text{O}_6$  octahedra similar to  $\text{Na}_2\text{IrO}_3$ , but these layers are linked by the  $\text{CuO}_2$  dumbbells as in  $\text{CuFeO}_2$  (Figure 1). The formation of  $\text{CuO}_2$  dumbbells is due to the eclipsed stacking of adjacent layers which aligns oxygen atoms in a linear coordination with the interlayer copper atoms. As a result,  $\text{Cu}_2\text{IrO}_3$  acquires a hybrid structure between  $\text{Na}_2\text{IrO}_3$  and  $\text{CuFeO}_2$ . Chemical analyses indicate the absence of sodium in the structure, confirming a complete exchange of sodium with copper, even from within the honeycomb layer.

## EXPERIMENTAL SECTION

**Synthesis.** The new copper iridate  $\text{Cu}_2\text{IrO}_3$  was obtained through a metathesis reaction between sodium iridate ( $\text{Na}_2\text{IrO}_3$ ) and copper(I) chloride ( $\text{CuCl}$ , Alfa Aesar, 99.999%). To synthesize  $\text{Na}_2\text{IrO}_3$ , a well-ground homogeneous mixture of sodium carbonate ( $\text{Na}_2\text{CO}_3$ , Alfa Aesar, 99.5%, dried at 120 °C for 24 h) and iridium oxide ( $\text{IrO}_2$ , Alfa Aesar, 99%) was prepared with the mole ratio of 1.15:1 and total mass of 300 mg. The mixture was placed in a covered alumina crucible and transferred to a muffle furnace. Preparation of the reaction mixture was carried out inside an argon-filled glovebox with  $\text{O}_2$  and  $\text{H}_2\text{O}$  content <0.1 ppm. The crucible was heated at 3 °C/min to 800 °C, annealed at 800 °C for 48 h, then cooled at 10 °C/min to 600 °C, and quenched

into the antechamber of the glovebox to avoid decomposition.<sup>11</sup> The resulting sample contained 1–2% of  $\text{IrO}_2$  impurity and was purified by successive cycles of adding 5–10 mol % of  $\text{Na}_2\text{CO}_3$ , grinding, and annealing at 825 °C for 24 h. The ion exchange was performed by mixing  $\text{Na}_2\text{IrO}_3$  and  $\text{CuCl}$  in the mole ratio 1:3 or 1:2.05 with no difference in the final product. The mixture with total mass of 150–300 mg was pelletized, placed in a covered alumina crucible, and sealed under vacuum in a quartz tube. The tube was slowly heated at 1 °C/min to 350 °C, kept at that temperature for 16 h, then cooled to room temperature at the same rate. In order to remove the excess of  $\text{CuCl}$  and  $\text{NaCl}$ , samples were subsequently ground into fine powders and washed five times with ammonium hydroxide ( $\text{NH}_4\text{OH}$ , Alfa Aesar, 28%) and twice with deionized water. After being washed, all samples were dried at room temperature under vacuum for 1 h.  $\text{Cu}_2\text{IrO}_3$  was found to be stable in air with no changes of color or X-ray diffraction pattern after 3 weeks at ambient conditions.

**X-ray Diffraction.** Powder X-ray diffraction (PXRD) was performed using a Bruker D8 ECO instrument in the Bragg–Brentano geometry with a copper X-ray source ( $\text{Cu K}\alpha$ ), a nickel filter to absorb the  $\text{K}\beta$  radiation, and with two 2.5° Soller slits after the source and before the LYNXEYE XE 1D energy-dispersive detector. Rietveld refinement on the PXRD pattern was performed using the FullProf suite.<sup>15</sup> Peak shapes were modeled with the Thompson–Cox–Hastings pseudo-Voigt profile convoluted with axial divergence asymmetry.

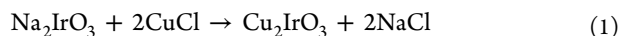
**Electron Microscopy, Optical Spectroscopy, and Thermogravimetric Analysis.** Energy-dispersive X-ray spectroscopy (EDXS) was performed using an EDAX detector installed on a JEOL JSM 6340F field emission scanning electron microscope (FESEM). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed using the Agilent model 5100 VDV spectrometer operating in axial mode. For quantitative analysis with ICP-OES, sodium and copper standards with five different concentrations were made from  $\text{NaCl}$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  dissolved in deionized water. The experimental uncertainties were calculated by a propagation of error analysis using a linear direct calibration plot.<sup>16</sup> Thermogravimetric analysis (TGA) was performed using a NETZSCH analyzer (model STA 449 F1 Jupiter) to determine the oxygen content of  $\text{Cu}_2\text{IrO}_3$ . The sample was heated to 500 °C at 1 °C/min under a 20 mL/min flow of 5%  $\text{H}_2/\text{Ar}$  gas mixture to provide a reducing environment.

**Physical Property Measurements.** Magnetization in powder specimens was measured as a function of field and temperature by zero

field cooling and field cooling in a 7 T Quantum Design MPMS3. A low background brass holder was used to mount the powder material, and the measurements were performed in the DC mode. Four-probe resistivity measurements and heat capacity measurements on pressed pellets of  $\text{Cu}_2\text{IrO}_3$  were performed in a Quantum Design Dynacool system.

## RESULTS AND DISCUSSION

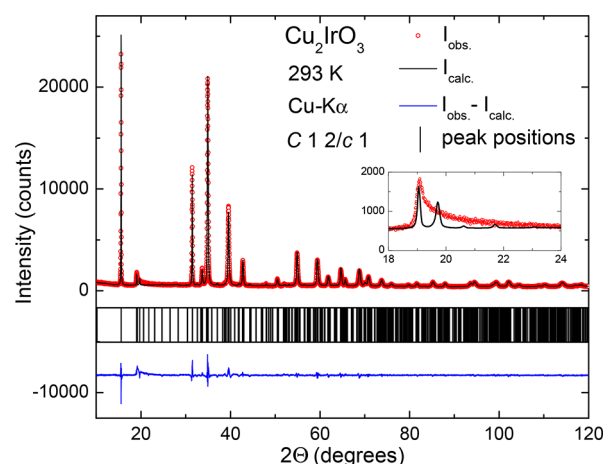
**Chemical Composition.** The synthetic goal was to completely replace  $\text{Na}^+$  with  $\text{Cu}^+$  in sodium iridate according to



In the first trial, we used 50% excess of  $\text{CuCl}$  and set the temperature to 400 °C to ensure a complete exchange. Later experiments revealed that lower temperatures (350 °C) and less excess  $\text{CuCl}$  (5%) worked equally well. The low temperature and the short duration of the exchange reaction prevented structural collapse, while copper atoms replaced sodium atoms. We tried solid-state synthesis from  $\text{CuO}$  and  $\text{IrO}_2$  at high temperatures (700–900 °C) without success, which confirmed that topotactic reaction under mild conditions is the preferred method for making copper iridate (Figure 1). EDXS analysis on multiple samples confirmed the ratio  $\text{Cu}/\text{Ir} = 2:1$ . The sodium peak at 1.041 keV was absent in the EDXS spectrum (Supporting Information). To confirm the absence of sodium from the structure, the sample was dissolved in hot concentrated hydrochloric acid (37%) and subjected to ICP-OES analysis using five standards each for sodium and copper. The solution was found to contain  $0.099 \pm 0.070$  ppm sodium and  $28.8 \pm 0.3$  ppm copper, which confirmed negligible sodium content within the experimental uncertainty. The oxygen content of the material was confirmed with thermogravimetric analysis by placing 19.83 mg of the sample in an alumina pan and heating it to 500 °C at 1 °C/min under the reducing environment of 5%  $\text{H}_2/\text{Ar}$  mixture. The mass loss began at 380 °C and ended after 100 min. The sample was then cooled, and the mass loss was measured to be 2.60 mg corresponding to  $\Delta m/m = 13.11\%$ . Considering the formula  $\text{Cu}_2\text{IrO}_3$ , the expected  $\Delta m/m = 13.07\%$  was in excellent agreement with the observed value.

**Crystal Structure.** Figure 2 shows the PXRD pattern of  $\text{Cu}_2\text{IrO}_3$  indexed in the space group  $\text{C}2/c$ , which is common among derivatives of the delafossite structure such as  $\text{Na}_2\text{IrO}_3$ ,  $\text{CuNi}_{2/3}\text{Sb}_{1/3}\text{O}_2$ , and  $\text{CuCo}_{2/3}\text{Sb}_{1/3}\text{O}_2$ .<sup>10,11</sup> After an initial profile matching with the  $\text{C}2/c$  space group, we naturally tried to draw atomic coordinates from the same model as the parent compound,  $\text{Na}_2\text{IrO}_3$ , where honeycomb layers of  $(\text{Ir}_{2/3}\text{Na}_{1/3})\text{O}_6$  are stacked by  $\text{NaO}_6$  octahedra (Figure 1). The  $\text{Na}_2\text{IrO}_3$  model did not provide a good fit. We then took atomic positions from  $\text{CuNi}_{2/3}\text{Sb}_{1/3}\text{O}_2$  where honeycomb layers of  $(\text{Ni}_{2/3}\text{Sb}_{1/3})\text{O}_6$  are stacked by  $\text{CuO}_2$  dumbbells<sup>10</sup> (Figure 1). The  $\text{CuNi}_{2/3}\text{Sb}_{1/3}\text{O}_2$  model provided an excellent starting point for our refinement with the atomic positions listed in Tables 1 and 2. The  $c$ -axis in  $\text{Cu}_2\text{IrO}_3$  is larger than in  $\text{Na}_2\text{IrO}_3$  (11.51 Å versus 10.77 Å), but the monoclinic angles are nearly the same (99.03° versus 99.50°).<sup>11</sup> Therefore,  $\text{Cu}_2\text{IrO}_3$  has larger interlayer spacing,  $d = \frac{c}{2} \sin \beta$ , with more 2D character.

The size broadening of the peaks was refined using spherical harmonics based on the  $2/m$  Laue class. The region from 19 to 24° in Figure 2 shows asymmetric line broadening known as the Warren line shape,<sup>17</sup> which is common among the delafossite-type layered structures.<sup>18</sup> It is modeled as a number



**Figure 2.** Room temperature powder X-ray diffraction pattern of  $\text{Cu}_2\text{IrO}_3$ . Experimental data are shown in red, Rietveld refinement in black, and the difference between observation and calculation in blue. Asymmetric broadening due to stacking faults in the range of 18–24° is magnified in the inset. Standard parameters for the Rietveld refinement and the Wyckoff positions are given in Tables 1 and 2.

**Table 1.** Crystallographic Data for  $\text{Cu}_2\text{IrO}_3$  Obtained at Room Temperature Using  $\text{Cu K}\alpha$  Radiation with  $\lambda = 1.5406$  Å<sup>a</sup>

| unit cell parameters  |                | refinement parameters  |      |
|-----------------------|----------------|------------------------|------|
| space group           | $\text{C}2/c1$ | parameters             | 26   |
| $a$ (Å)               | 5.39331(5)     | $R_{\text{Bragg}}$ (%) | 8.83 |
| $b$ (Å)               | 9.31118(9)     | $R_{\text{F}}$ (%)     | 10.5 |
| $c$ (Å)               | 11.51269(6)    | $R_{\text{P}}$ (%)     | 19.6 |
| $\beta$ (deg)         | 99.02916(1)    | $R_{\text{WP}}$ (%)    | 19.1 |
| $V$ (Å <sup>3</sup> ) | 570.982(5)     | $R_{\text{exp}}$ (%)   | 8.06 |
| $Z$                   | 8              | $\chi^2$               | 5.6  |

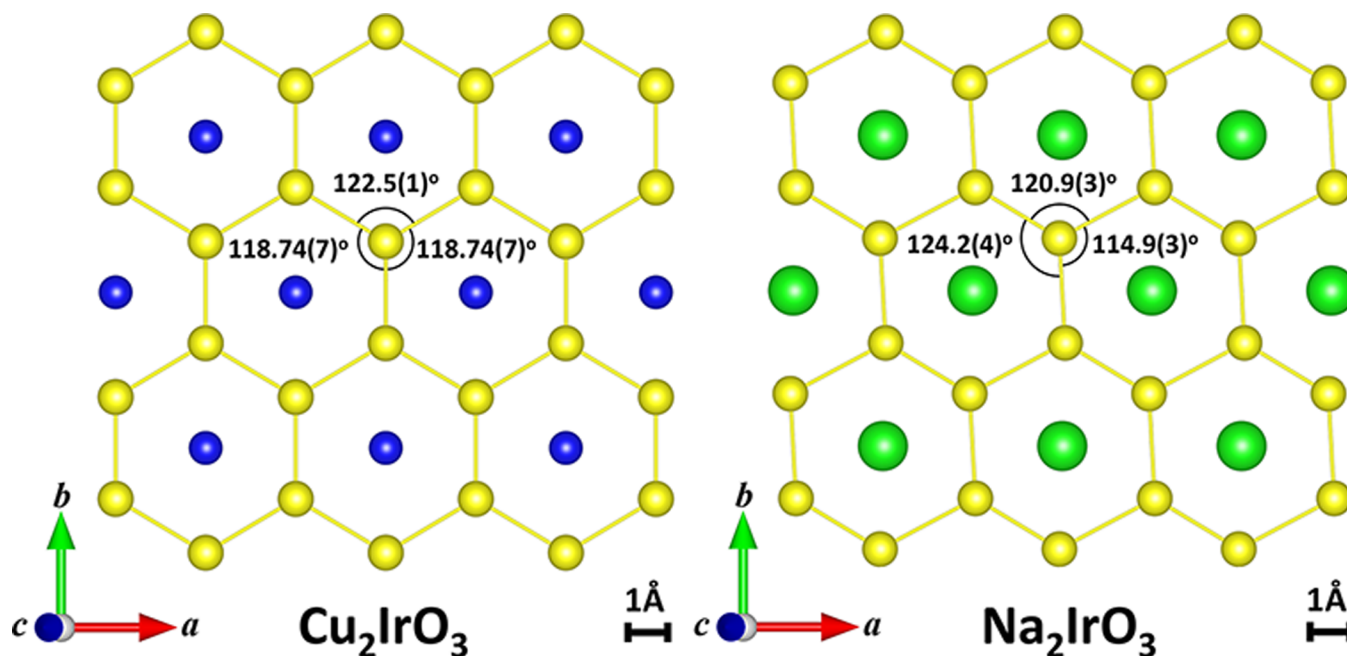
<sup>a</sup>Unit cell dimensions and refinement parameters are reported. The region of stacking faults, between 18 and 24°, artificially increases the  $R$  factors (Figure 2). Excluding this region yields  $R_{\text{WP}} = 13.5$ ,  $R_{\text{exp}} = 7.78$ , and  $\chi^2 = 3$ .

**Table 2.** Wyckoff Sites, Atomic Coordinates, and Site Occupancies in the Crystal Structure of  $\text{Cu}_2\text{IrO}_3$ <sup>a</sup>

| atom | site | $x$      | $y$      | $z$      | occupancy |
|------|------|----------|----------|----------|-----------|
| Ir1  | 8f   | 1/4      | 0.079(4) | 0        | 0.81(1)   |
| Cu1  | 8f   | 1/4      | 0.079(4) | 0        | 0.18(9)   |
| Ir2  | 4d   | 3/4      | 1/4      | 0        | 0.37(8)   |
| Cu2  | 4d   | 3/4      | 1/4      | 0        | 0.62(2)   |
| Cu3  | 4e   | 0        | 3/4      | 1/4      | 1         |
| Cu4  | 4e   | 0        | 0.455(7) | 1/4      | 1         |
| Cu5  | 4e   | 0        | 0.080(5) | 1/4      | 1         |
| O1   | 8f   | 0.949(9) | 3/4      | 0.090(8) | 1         |
| O2   | 8f   | 0.940(6) | 0.420(7) | 0.078(0) | 1         |
| O3   | 8f   | 0.932(6) | 0.084(8) | 0.091(6) | 1         |

<sup>a</sup>The Debye–Waller (thermal) factors are reasonably low with  $B_{\text{iso}} = 1.0$  Å<sup>2</sup> for copper and oxygen atoms and  $B_{\text{iso}} = 0.9$  Å<sup>2</sup> for iridium atoms.

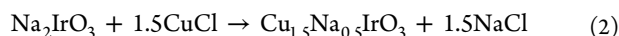
of small peaks merged together due to variations in the stacking of the honeycomb order from one plane to the next, known as stacking faults. An analysis of the Warren line shape yields about 10% stacking faults in the sample (Supporting Information). Similar patterns are observed in related layered materials including  $\text{Na}_2\text{IrO}_3$ ,<sup>11</sup>  $\text{CuCo}_{2/3}\text{Sb}_{1/3}\text{O}_2$ ,<sup>10</sup> and



**Figure 3.** Planar view of the honeycomb ordering in  $\text{Cu}_2\text{IrO}_3$  (left) and  $\text{Na}_2\text{IrO}_3$  (right) to compare the Ir–Ir–Ir bond angles between the two materials in the same space group ( $C2/c$ ). Yellow, blue, and green spheres represent Ir, Cu, and Na, respectively. Ir–Ir–Ir bond angles are closer to the ideal  $120^\circ$  in  $\text{Cu}_2\text{IrO}_3$  compared to  $\text{Na}_2\text{IrO}_3$  beyond the margin of error. The  $C2/c$  structure of  $\text{Na}_2\text{IrO}_3$  is taken from ref 11.

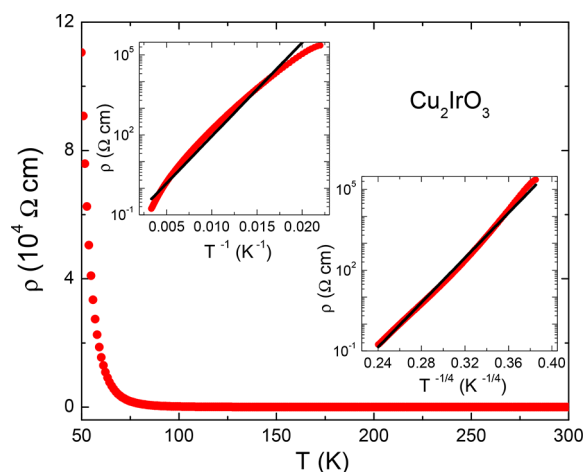
$\text{NaCo}_{2/3}\text{Sb}_{1/3}\text{O}_2$ .<sup>19</sup> Figure 3 compares the honeycomb ordering, in the  $a$ – $b$  plane, between  $\text{Na}_2\text{IrO}_3$  and  $\text{Cu}_2\text{IrO}_3$ . The Ir–Ir–Ir bond angles in  $\text{Cu}_2\text{IrO}_3$  are closer to  $120^\circ$  than in  $\text{Na}_2\text{IrO}_3$ . The more 2D character and the more ideal bond angles bring  $\text{Cu}_2\text{IrO}_3$  in closer proximity to the geometry of the Kitaev model.<sup>5</sup>

In a recent study,<sup>20</sup> similar mild conditions were applied to  $\text{Na}_2\text{IrO}_3$  to exchange the interlayer sodium atoms but without exchanging the intralayer atoms:



The product has the same honeycomb layers as  $\text{Na}_2\text{IrO}_3$ , but the layers are stacked with copper dumbbells similar to the  $\text{Cu}_2\text{IrO}_3$ . The significance of the present work is to demonstrate that sodium can be exchanged with copper even inside the octahedral cages within the honeycomb layer.

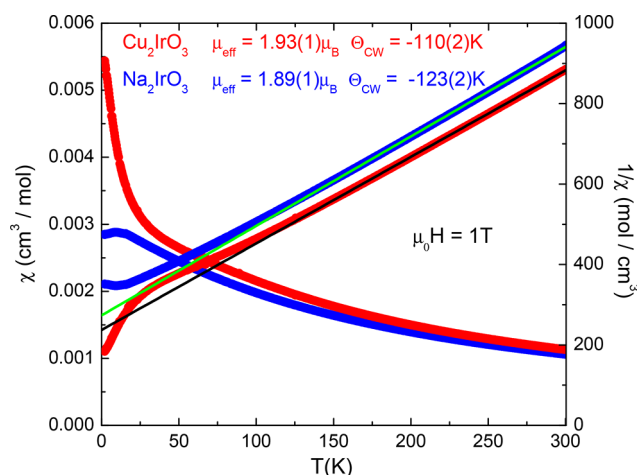
**Resistivity.** Figure 4 shows the temperature dependence of resistivity in  $\text{Cu}_2\text{IrO}_3$  from 50 to 300 K. The top left inset shows a poor fit to the Arrhenius expression  $\rho \propto \exp(E_g/k_B T)$ , where  $E_g$  is the energy gap. In a typical insulator,  $E_g$  is temperature-independent and much larger than  $k_B T$ , so  $\log(\rho)$  scales linearly with  $T^{-1}$ . If the energy gap is temperature-dependent, a different behavior known as variable-range hopping (VRH) appears, where  $\rho \propto \exp(E_g/k_B T^{1/(D+1)})$  in  $D$  dimensions.<sup>21,22</sup> The bottom right inset of Figure 4 shows a better fit to the 3D VRH expression,  $\rho \propto \exp(E_g/k_B T^{1/4})$ . A linear fit of  $\log(\rho)$  to  $T^{-1/4}$  indicates a “pseudogap”  $E_g = 825$  meV in  $\text{Cu}_2\text{IrO}_3$ , the same order of magnitude as the optical gap measured in  $\text{Na}_2\text{IrO}_3$  (340 meV).<sup>23</sup> Photoemission and spectroscopy experiments will be required for accurate evaluation of the optical gap in  $\text{Cu}_2\text{IrO}_3$ . A similar VRH behavior is observed in the parent compound  $\text{Na}_2\text{IrO}_3$ .<sup>6</sup> As previously explained for  $\text{Sr}_2\text{IrO}_4$ ,  $\text{Ir}^{4+}$  has five electrons in the  $t_{2g}$  manifold with effective spin of  $1/2$ . Strong spin–orbit coupling opens a gap in the  $t_{2g}$  manifold and drives the system toward a Mott insulator.<sup>24</sup> It is not clear why spin–orbit driven Mott



**Figure 4.** Resistivity plotted as a function of temperature in  $\text{Cu}_2\text{IrO}_3$  showing insulator behavior. The top left inset shows that  $\log(\rho)$  does not scale linearly with  $T^{-1}$ . The bottom right inset shows that  $\log(\rho)$  scales better with  $T^{-1/4}$ .

insulators have a VRH instead of a conventional Arrhenius behavior.

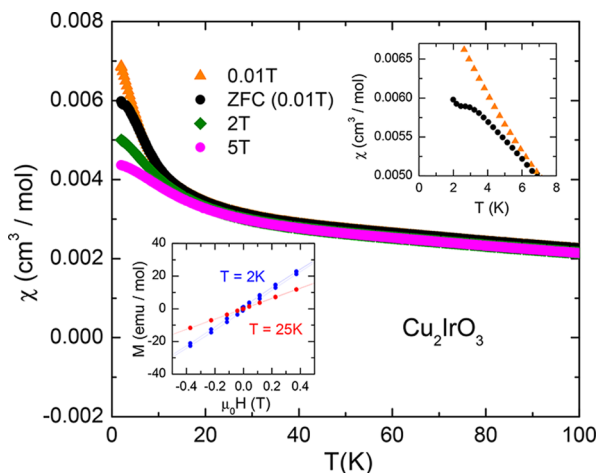
**Magnetization.** Figure 5 shows the magnetic susceptibility (left y-axis) and the inverse susceptibility (right y-axis) as a function of temperature from 2 to 300 K in both  $\text{Na}_2\text{IrO}_3$  and  $\text{Cu}_2\text{IrO}_3$ . The susceptibility data for both samples fit to the expression  $\chi = \frac{C}{T - \Theta_{\text{CW}}}$  where the Curie–Weiss temperature  $\Theta_{\text{CW}}$  is related to the magnetic exchange coupling and the Curie constant  $C$  is related to the effective magnetic moment,  $\mu/\mu_B = \sqrt{3k_B C/N}$ , with Avogadro number  $N$  and Boltzmann constant  $k_B$ . Our data on  $\text{Na}_2\text{IrO}_3$  are consistent with previous reports.<sup>5,6,25</sup> The resulting magnetic moment  $\mu_{\text{eff}} = 1.93(1)\mu_B$  in  $\text{Cu}_2\text{IrO}_3$  is nearly identical to  $1.89(1)\mu_B$  in  $\text{Na}_2\text{IrO}_3$  and close to the expected moment  $1.73 \mu_B$  from  $\text{Ir}^{4+}$  with effective



**Figure 5.** Molar magnetic susceptibility (left y-axis) and inverse susceptibility (right y-axis) as a function of temperature in  $\text{Cu}_2\text{IrO}_3$  (red) and  $\text{Na}_2\text{IrO}_3$  (blue). The effective magnetic moment and the Curie–Weiss temperature are reported on the figure from the Curie–Weiss fit in the range of 150–300 K. Fitting errors were evaluated by varying the fitting range.

$S = 1/2$ . Figure 5 shows that  $\chi(T)$  above 100 K is almost identical between  $\text{Cu}_2\text{IrO}_3$  and  $\text{Na}_2\text{IrO}_3$ , with comparable  $\Theta_{\text{CW}}$  and  $\mu$ . However, below 100 K, the two curves differ.  $\text{Na}_2\text{IrO}_3$  shows a clear peak at 15 K due to a long-range AFM order, but  $\text{Cu}_2\text{IrO}_3$  maintains the Curie–Weiss behavior until 2.7 K.

Figure 6 shows that  $\text{Cu}_2\text{IrO}_3$  orders at 2.7 K, much lower than  $T_N = 15$  K in  $\text{Na}_2\text{IrO}_3$ . The ratio  $f = |\Theta_{\text{CW}}|/T_N$ , known as

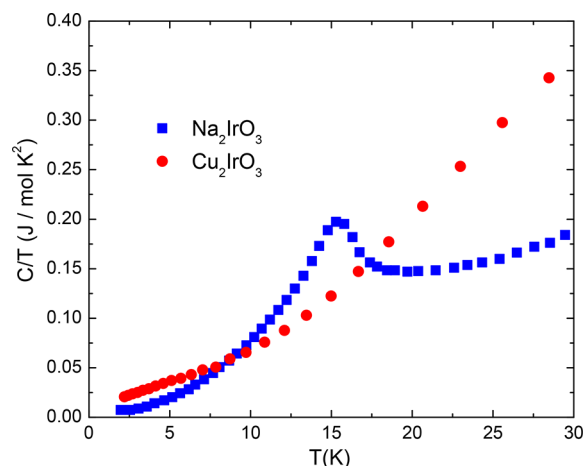


**Figure 6.** Molar susceptibility plotted as a function of temperature below 100 K to focus on the magnetic ordering. Top inset shows that  $\text{Cu}_2\text{IrO}_3$  orders at 2.7 K with zero field cooling, but the order disappears in a weak magnetic field. The Curie tail below 10 K is suppressed by increasing field. Bottom inset shows a very small hysteresis at 2 K, which disappears at 25 K.

the frustration index,<sup>1</sup> is a rough measure of magnetic frustration. In  $\text{Na}_2\text{IrO}_3$ , the order of magnitude difference between  $|\Theta_{\text{CW}}| = 123$  K and  $T_N = 15$  K gives rise to  $f = 8.2$ . In  $\text{Cu}_2\text{IrO}_3$ , the frustration index increases significantly to  $f = 40$ , showing that the new copper iridate is even more frustrated than its parent compound and, therefore, is closer to a Kitaev spin liquid.<sup>5,26</sup> Two structural reasons could explain this: (a) the bond angles in the honeycomb layer of  $\text{Cu}_2\text{IrO}_3$  are closer

to the ideal  $120^\circ$  than in  $\text{Na}_2\text{IrO}_3$  (Figure 3), and (b) the  $c$ -axis of  $\text{Cu}_2\text{IrO}_3$  is larger than that of  $\text{Na}_2\text{IrO}_3$  (Table 1). Figure 6 shows that the transition in  $\text{Cu}_2\text{IrO}_3$  is weak; it is observable only by zero field cooling, disappears in the presence of a small field, and shows a small hysteresis. Such behavior could indicate a spin glass transition<sup>27</sup> with short-range (local) correlations instead of a long-range antiferromagnetic order.

**Heat Capacity.** Figure 7 compares the heat capacity in  $\text{Cu}_2\text{IrO}_3$  with  $\text{Na}_2\text{IrO}_3$ .<sup>6</sup> The robust long-range AFM order is



**Figure 7.** Heat capacity divided by temperature as a function of temperature in  $\text{Cu}_2\text{IrO}_3$  (red circles) compared to  $\text{Na}_2\text{IrO}_3$  (blue squares, from ref 6).  $\text{Na}_2\text{IrO}_3$  shows a clear peak at the AFM transition  $T_N = 15$  K. Such a peak is absent from the transition in  $\text{Cu}_2\text{IrO}_3$  at 2.7 K.

marked by a peak at  $T_N = 15$  K in the heat capacity of  $\text{Na}_2\text{IrO}_3$ . At this temperature, there is no evidence for magnetic ordering in  $\text{Cu}_2\text{IrO}_3$ . The heat capacity shows no sharp peak even at 2.7 K, where the weak order is observed in magnetic susceptibility. However,  $\text{Cu}_2\text{IrO}_3$  exhibits a broad feature around 5 K, which could be evidence for short-range spin glass correlations.<sup>27</sup> In the Supporting Information, a  $T^3$  lattice estimate is used to reveal a negligible entropy release ( $<5\% R \ln(2)$ ), near the transition, confirming the lack of long-range magnetic order. Curiously, in the limit of  $T \rightarrow 0$ ,  $C/T$  approaches zero much slower in  $\text{Cu}_2\text{IrO}_3$  than in  $\text{Na}_2\text{IrO}_3$ , which may be due to the proximity to the spin liquid phase. Our interpretation is that the FM Kitaev interaction in  $\text{Cu}_2\text{IrO}_3$  is stronger than that in  $\text{Na}_2\text{IrO}_3$  due to more favorable geometry of the honeycomb layers. In this scenario, the Kitaev interaction wins over the AFM Heisenberg interaction, which means  $\text{Cu}_2\text{IrO}_3$  is closer to a Kitaev spin liquid than  $\text{Na}_2\text{IrO}_3$ . Further experiments such as NMR and neutron scattering are required to establish the true nature of magnetism in  $\text{Cu}_2\text{IrO}_3$ .

## CONCLUSIONS

We demonstrate that it is possible to completely substitute all sodium atoms in  $\text{Na}_2\text{IrO}_3$  with copper atoms through a topotactic reaction under mild conditions. The resulting material,  $\text{Cu}_2\text{IrO}_3$ , is the first copper iridium binary metal oxide and a new member of  $\text{A}_2\text{IrO}_3$  honeycomb iridates. Structurally,  $\text{Cu}_2\text{IrO}_3$  has honeycomb layers in a  $C2/c$  unit cell similar to  $\text{Na}_2\text{IrO}_3$ , but the layers are linked by linearly coordinated  $\text{CuO}_2$  dumbbells similar to  $\text{CuFeO}_2$ .  $\text{Cu}_2\text{IrO}_3$  is an insulator with VRH behavior similar to  $\text{Na}_2\text{IrO}_3$ . From the Curie–Weiss analysis, iridium is in the 4+ oxidation state,

relevant to the Kitaev model and necessary for a spin liquid phase.  $\text{Cu}_2\text{IrO}_3$  shows a weak magnetic order at 2.7 K with a frustration index of 40, which is an order of magnitude larger than  $\text{Na}_2\text{IrO}_3$ . The absence of a peak in the heat capacity data, the large frustration index, and the sensitivity of the magnetic transition to an external field are evidence for proximity to a quantum spin liquid. The structure of  $\text{Cu}_2\text{IrO}_3$  provides a nearly perfect geometry for the Kitaev model with bond angles closer to the ideal  $120^\circ$  and a larger interlayer spacing compared to that of  $\text{Na}_2\text{IrO}_3$ .

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b06911.

Crystallographic data for  $\text{Cu}_2\text{IrO}_3$  (CIF)

Additional details and figures as described in text (PDF)

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### Notes

The authors declare no competing financial interest.

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