

**IrSr<sub>2</sub>Sm<sub>1.15</sub>Ce<sub>0.85</sub>Cu<sub>2.175</sub>O<sub>10</sub>: A reentrant spin-glass material**

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A new iridium-containing layered cuprate material, Ir<sub>0.825</sub>Sr<sub>2</sub>Sm<sub>1.15</sub>Ce<sub>0.85</sub>Cu<sub>2.175</sub>O<sub>10</sub>, has been synthesized by conventional ambient-pressure solid-state techniques. The material's structure has been fully characterized by Rietveld refinement of high-resolution synchrotron x-ray diffraction data; tilts and rotations of the IrO<sub>6</sub> octahedra are observed as a result of a bond mismatch between in-plane Ir–O and Cu–O bond lengths. DC-susceptibility measurements evidence a complex set of magnetic transitions upon cooling that are characteristic of a reentrant spin-glass ground-state. The glassy character of the lowest-temperature ( $T_g = 10$  K) transition is further confirmed by AC-susceptibility measurements, showing a characteristic frequency dependence that can be well fitted by the Vogel-Fulcher law and yields a value of  $\frac{\Delta T_f}{[T_f \Delta \log(\omega)]} = 0.015(1)$ , typical of dilute magnetic systems. Electronic transport measurements show the material to be semiconducting at all temperatures, so that the CuO<sub>2</sub> planes are underdoped with no evidence of a transition to a superconducting state. Negative magnetoresistance is observed when the material is cooled below 20 K, and the magnitude of this magnetoresistance is seen to increase upon cooling to a value of  $MR = -9\%$  at 8 K.

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**I. INTRODUCTION**

The layered cuprates have attracted much scientific interest in recent years. The 1212- and 1222-layered cuprates have been well studied and have the general formulas  $MA_2RECu_2O_{8-\delta}$  and  $MA_2RE_2Cu_2O_{10-\delta}$ , respectively, where  $M$  is commonly a transition or p-block metal,  $A$  is an alkaline earth ion, and  $RE$  is a rare earth or mixture of rare-earth ions. The  $\delta$  signifies the oxygen nonstoichiometry, which is dependent on synthesis conditions,  $M$  oxidation state, and the Ln:Ce ratio,<sup>1</sup> a key tool for controlling the oxidation state of the copper planes and inducing superconductivity. The flexibility of this structural motif has led to an explosion of new materials, including analogues incorporating  $M$ -site ions varying from: first-row transition metals such as Cu, Fe, and Co;<sup>2–4</sup> second-row transition metals such as Ru;<sup>5</sup> third-row transition metals such as Ta, Hg, as well as p-block elements such as Ga and Tl.<sup>6,7</sup>

This wide variation in chemical composition leads to an equally wide diversity of electronic properties. As well as superconductivity, the fine electronic balance in many of these materials leads to novel and unexpected phenomena. The ruthenocuprates have received much attention for the observation of simultaneous weak ferromagnetism and superconductivity, two properties thought incompatible.<sup>8</sup> When underdoped, the ruthenocuprates have also been shown to display a sizeable low-temperature magnetoresistance.<sup>9–12</sup> Surprisingly, this magnetoresistance is found to be tunable from negative to positive values as  $\langle r_A \rangle$ , the mean  $A$  site (R<sub>1.1</sub>Ce<sub>0.9</sub>) cation radius, decreases in a series of RuSr<sub>2</sub>R<sub>1.1</sub>Ce<sub>0.9</sub>Cu<sub>2</sub>O<sub>10– $\delta$</sub>  ( $R = \text{Nd, Sm, Eu, and Gd}$  with Y) samples.<sup>13</sup> This lattice effect is further evidenced from studies of Ru<sub>1– $x$</sub> Ta <sub>$x$</sub> Sr<sub>2</sub>Nd<sub>0.95</sub>Y<sub>0.15</sub>Ce<sub>0.9</sub>Cu<sub>2</sub>O<sub>10</sub> materials;  $MR_{9T}$  (4 K) increases from  $-28\%$  to  $-49\%$  as  $x$  increases from 0 to 0.2, which further expands the unit cell.<sup>12</sup>

In an attempt to broaden this library of layered cuprates and search for further novel properties, we have experimented with the substitution of alternative transition metals into the 1222-layered structure. The large spin-orbit interaction in the

heavy-transition metals has been recently proposed to lead to exotic physics in a number of iridate systems. These exotic physics range from topological Fermi-arc states in Sr<sub>2</sub>IrO<sub>4</sub><sup>14</sup> to long-range order in Na<sub>2</sub>IrO<sub>3</sub><sup>15</sup> and even a proposed three-dimensional quantum spin liquid ground state in the frustrated hyperkagome lattice compound Na<sub>4</sub>Ir<sub>3</sub>O<sub>8</sub>.<sup>16</sup> The possibility of such unusual physical phenomena makes iridium-containing cuprates an obvious synthetic target.

Synthesis of several 1212-type iridocuprates by high pressure have previously been reported,<sup>17–19</sup> but this approach limits both sample volume and ease of compositional variation so that superconductivity has not yet been observed in the 1212 iridocuprates. The 1222-type iridocuprates have not previously been synthesized. While Ir<sup>5+</sup>-containing double perovskites, having the electronic configuration [Xe]4f<sup>14</sup> 5d<sup>4</sup> (where [Xe] is the xenon core), have found no contribution of the Ir ion to the magnetic properties,<sup>20</sup> the  $J = 1/2$  Ir<sup>4+</sup> ion ([Xe]4f<sup>14</sup> 5d<sup>5</sup>) has been seen to magnetically order in related double-perovskite materials.<sup>21</sup>

In this paper we report the ambient-pressure synthesis, structural characterization, and properties of the novel 1222-type iridocuprate, Ir<sub>0.825</sub>Sr<sub>2</sub>Sm<sub>1.15</sub>Ce<sub>0.85</sub>Cu<sub>2.175</sub>O<sub>10</sub>. While the sample is not found to be superconducting under these synthetic conditions, a complex temperature dependence to the magnetization, studied using both AC- and DC-susceptibility measurements, suggests reentrant spin glass behavior, likely due to disordered occupation of Cu<sup>3+</sup>, Ir<sup>4+</sup>, and Ir<sup>5+</sup> ions across the nominally IrO<sub>2</sub> layer. Low-temperature negative magnetoresistance is also observed upon cooling below 20 K.

**II. EXPERIMENTAL**

The sample of Ir<sub>0.825</sub>Sr<sub>2</sub>Sm<sub>1.15</sub>Ce<sub>0.85</sub>Cu<sub>2.175</sub>O<sub>10</sub> was prepared by standard solid-state techniques. A stoichiometric mixture of IrO<sub>2</sub>, SrCO<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and CuO powders were combined by thorough grinding in an agate mortar. Prior to use, the Sm<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> reagents were calcined at 800°C for 12 h to remove any absorbed moisture and CO<sub>2</sub>. The mixture

was pressed into a 10-mm pellet, loaded into a ceramic alumina crucible, and placed in a muffle furnace before heating to 800°C for 10 h. The pellet was then reground, repelleted, and transferred to a tube furnace. The sample was then heated under flowing oxygen to 1020°C at a rate of 5°C/min, allowed to dwell for 14 h, and cooled at the same rate before regrinding and repeating this oxygen firing a further two times. Care was taken with furnace calibration and sample positioning as the synthesis was found to be extremely sensitive to the firing temperature. As little as  $\pm 10^\circ\text{C}$  was found to lead to dramatically increased impurity formation. However, the magnetic and electronic properties described below are completely reproducible with repeated synthesis using the parameters described above. Room temperature laboratory x-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer. Data were collected over the range  $5^\circ < 2\theta < 100^\circ$ , with a step size of  $0.02^\circ$ . The profiles could all be indexed on a tetragonal  $I4/mmm$  symmetry space group as previously reported for other members of the 1222-layered cuprate family.<sup>1,3</sup>

### III. RESULTS AND DISCUSSION

#### A. Synchrotron x-ray diffraction

To confirm phase purity and refine the crystal structure, high-resolution synchrotron x-ray diffraction data was collected on a sample of  $\text{Ir}_{0.825}\text{Sr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10}$ . A pattern was collected at 290 K on beamline ID31, ESRF. A wavelength of  $\lambda = 0.40002 \text{ \AA}$  was used, and the sample was contained in a 0.5-mm-diameter borosilicate glass capillary mounted on the axis of the diffractometer, about which it was spun at  $\sim 1 \text{ Hz}$  to improve the powder averaging of the crystallites. Diffraction patterns were collected over the angular range  $2^\circ < 2\theta < 50^\circ$  and rebinned to a constant step size of  $0.002^\circ$  for each scan. The high-angle regions of the pattern were scanned several times to improve the statistical quality of the data. The Rietveld refinement program GSAS was used to refine the structure.<sup>22</sup> The data and refinement

fits can be seen in Fig. 1(a). This led to the refined lattice parameters and atomic positions seen in Table I.

While not detectable by laboratory x-ray diffraction, the higher resolution and increased flux of the synchrotron data showed the presence of impurity peaks that could be confidently assigned to the minor impurity phases  $\text{Sr}_3\text{IrCuO}_6$ ,  $\text{Sr}_2\text{CeIrO}_6$ , and unreacted  $\text{Sm}_2\text{O}_3$ . The small volume fractions of these impurities are not expected to effect the bulk property measurements and so do not change the conclusions of the measurements discussed later in this paper as these materials do not exhibit magnetic transitions coincident with the transitions reported. The structure can be described as alternating layers of nominally  $\text{IrO}_2$ ,  $\text{SrO}$ ,  $\text{CuO}_2$ ,  $\text{Sm/Ce}$ ,  $\text{O}_2$ ,  $\text{Sm/Ce}$ ,  $\text{CuO}_2$ ,  $\text{SrO}$ , and  $\text{IrO}_2$ , respectively [Fig. 1(b)]. Results from Rietveld refinement of the synchrotron x-ray diffraction data are displayed in Tables I and II. As with all compounds of the 1222 structure type, occupation of the rare-earth site by Sm and Ce ions is found to be fully disordered.<sup>1,3</sup>

Attempts to refine the Ir occupation of the  $2a$  Wyckoff site lead to a preference for reduced occupation. Site vacancies are unlikely, due to electrostatic arguments, leaving the possibility of mixed occupation of the site by both Ir and a weaker scatterer. Consideration of the available cations leaves Cu as the most likely candidate, primarily due to similarities in ionic radii ( $0.54$  and  $0.57 \text{ \AA}$  for  $\text{Cu}^{3+}$  and  $\text{Ir}^{5+}$ , respectively)<sup>23</sup> and preferred octahedral coordination environments. Refinement of mixed Ir/Cu occupation leads to a substitution of  $17.5(5)\%$  Cu onto the nominally Ir site. There is no evidence of cation disorder within the  $\text{CuO}_2$  planes.

Particular attention was paid to the refinement of oxygen positions as these define the octahedral rotation and tilting. While ordered tilting of nominally  $\text{IrO}_6$  octahedra is not symmetry allowed within the  $I4/mmm$  space group, refinements of the apical and equatorial oxygens of the octahedra, O(1) and O(3), respectively, found unphysical thermal displacement parameters when placed on the high-symmetry  $4e$  and  $4c$  Wyckoff sites. There was no evidence of weak superstructural peaks, which would indicate a change in symmetry due to

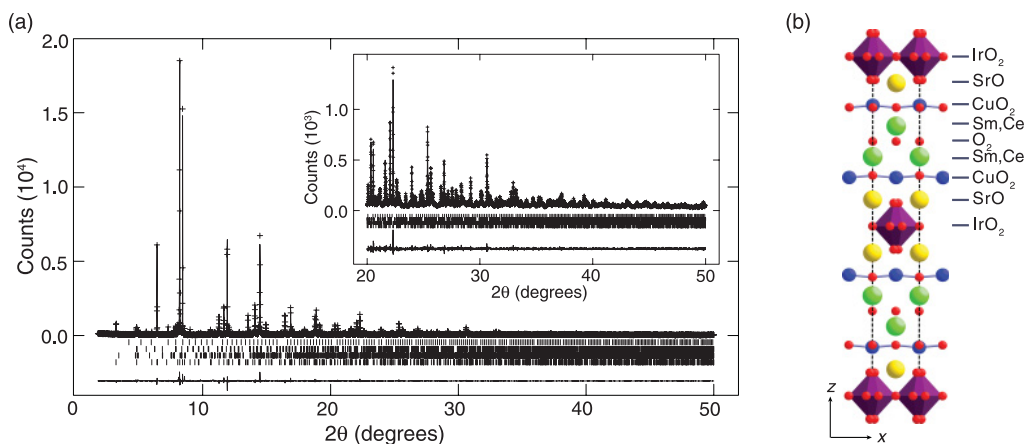


FIG. 1. (Color online) (a) Synchrotron x-ray diffraction pattern and Rietveld refinement fit to data collected on  $\text{Ir}_{0.825}\text{Sr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10}$ . The crosses show the collected pattern, the upper line is the refined fit, the lower line is the difference, and the tick marks denote reflection positions for  $\text{Sr}_3\text{IrCuO}_6$ ,  $\text{Sr}_2\text{CeIrO}_6$ ,  $\text{Sm}_2\text{O}_3$ , and  $\text{Ir}_{0.825}\text{Sr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10}$ , from top to bottom, respectively. The final goodness-of-fit parameter,  $\chi^2 = 1.849$ . The inset shows a blow-up of the high-angle region, again displaying an excellent fit to the data. (b) The crystal structure of nominally  $\text{IrSr}_2(\text{Sm,Ce})_2\text{Cu}_2\text{O}_{10}$  showing alternating layers of  $\text{Sr}_2\text{IrO}_6$ ,  $(\text{Sm,Ce})_2\text{O}_2$  and  $\text{CuO}_2$  common to all 1222-type materials.

TABLE I. Refined structural parameters for Ir<sub>0.825</sub>Sr<sub>2</sub>Sm<sub>1.15</sub>Ce<sub>0.85</sub>Cu<sub>2.175</sub>O<sub>10</sub> in the space-group *I4/mmm* from Rietveld refinement of synchrotron x-ray diffraction data.

<i>a</i> (Å)	<i>c</i> (Å)	Volume (Å <sup>3</sup> )	<i>R</i> <sub>wp</sub>	<i>R</i> <sub>p</sub>	χ <sup>2</sup>			
3.85647(2)	28.2347(2)	424.378(4)	0.1009	0.077	1.849			
Atom(s)	Wyckoff site	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> <sub>iso</sub> (Å <sup>2</sup> )	<i>U</i> <sub>11</sub> (Å <sup>2</sup> ) <sup>a</sup>	<i>U</i> <sub>33</sub> (Å <sup>2</sup> ) <sup>a</sup>
Ir, Cu	2 <i>a</i>	0	0	0	0.825(5), 0.175(5)	–	0.0030(3)	0.0037(4)
Sr	4 <i>e</i>	0.5	0.5	0.07839(5)	1	–	0.0103(3)	0.0135(6)
Sm, Ce	4 <i>e</i>	0.5	0.5	0.20486(2)	0.575, 0.425	–	0.0049(3)	0.0050(3)
Cu	4 <i>e</i>	0	0	0.14347(7)	1	–	0.0044(3)	0.0082(7)
O(1)	16 <i>m</i>	0.952(3)	0.952(3)	0.0685(4)	0.25	0.014(4)	–	–
O(2)	8 <i>g</i>	0	0.5	0.1499(3)	1	0.010(1)	–	–
O(3)	8 <i>j</i>	0.870(3)	0.5	0	0.5	0.015(3)	–	–
O(4)	4 <i>d</i>	0	0.5	0.25	1	0.011(2)	–	–

<sup>a</sup>All of the anisotropically refined sites have  $U_{11} = U_{22} \neq U_{33}$ ,  $U_{12} = U_{13} = U_{23} = 0$ .

ordered tilting/rotations of the IrO<sub>6</sub> octahedra. An improved fit and physically reasonable thermal displacement parameters were found by splitting the sites as shown in Table I. The refined positions of the split oxygen sites indicate both a disordered rotation and tilting of the IrO<sub>6</sub> octahedra of 14.6(3)° and 7.6(6)°, respectively. Similar tilts and rotations of the RuO<sub>6</sub> octahedra are observed in RuSr<sub>2</sub>GdCu<sub>2</sub>O<sub>8</sub><sup>5</sup> and RuSr<sub>2</sub>Gd<sub>2-x</sub>Ce<sub>x</sub>Cu<sub>2</sub>O<sub>10-δ</sub>.<sup>1</sup>

Attempts to refine the occupation of these oxygen sites resulted in stable but nonunique solutions, likely due to correlations with both site positions and thermal parameters. As a result, the O(1) and O(3) positions were fixed to complete occupancy. Additionally, oxygen site O(4), residing within the rare-earth block, refined to complete occupancy and so was fixed at unity. This oxygen position is most commonly found to accommodate oxygen vacancies in the 1222-type structures,<sup>1,24</sup> but due to the relatively high Ce content in this material, vacancies are not required for charge balancing.

Bond valence analysis, using the program ValList,<sup>25</sup> of the Cu (4*e*) site results in an average bond valence parameter

of 2.45. While this value is larger than would be expected for typical Cu<sup>2+</sup> coordination, it is typical of layered ruthenocuprate materials<sup>1</sup> and cannot be taken as evidence for increased hole doping of the CuO<sub>2</sub> plane. Consideration of the Cu–O bond distances 2.155(11) Å and 1.9368(7) Å for Cu–O(1) and Cu–O(2), respectively, find them to be comparable to those of the 1222 ruthenocuprates, where, for example, values of 2.157(5) and 1.9236(3) Å, respectively, are reported in the closely related compound RuSr<sub>2</sub>Gd<sub>1.3</sub>Ce<sub>0.7</sub>Cu<sub>2</sub>O<sub>10</sub>.<sup>1</sup> Due to the mixed occupation, as well as possible mixed valency of the nominally Ir (2*a*) site, bond valence analysis cannot be confidently performed. The Ir–O bond lengths give values of 1.972(11) and 1.992(3) Å for Ir–O(1) and Ir–O(3), respectively. These values are again similar to those of the ruthenocuprates, unsurprisingly due to the similar ionic radii of the two ions (0.57 and 0.565 Å for octahedral Ir<sup>5+</sup> and Ru<sup>5+</sup>, respectively),<sup>24</sup> leading to comparable octahedral coordination environments. The observed rotations and tilts of the IrO<sub>6</sub> octahedra, therefore, arise due to the bond mismatch between in-plane Ir–O(2) and Cu–O(2).

## B. DC-SQUID magnetometry

To probe the bulk magnetic properties of this new material, measurements of magnetization versus both field and temperature were performed using a Quantum Design MPMS-XL magnetometer. Measurements against temperature were performed in the range  $2 < T < 300$  K after cooling both in zero-field (ZFC) and in field (FC) using an applied field of  $H_{DC} = 100$  Oe. Isothermal measurements against field were made across the range  $-7 < H < 7$  T at temperatures of  $T = 2, 60, \text{ and } 200$  K.

Two distinct magnetic transitions are evidenced by the  $\chi$  versus  $T$  measurements (Fig. 2): a broad feature, seen in the inset of Fig. 2 and labeled as  $t_2$ , centered at 120 K that shows clear divergence between ZFC and FC datasets; and a sharp increase in susceptibility upon cooling through 8 K, labeled as  $t_3$ , with further ZFC-FC bifurcation. Inspection of a plot of  $\chi^{-1}$  versus  $T$  [Fig. 2(b)] shows that ZFC and FC splitting is also observed above  $t_2$  and is persistent up to 300 K. This splitting evidences history dependence to the magnetization that can be explained by the presence of ferromagnetic clusters in an otherwise paramagnetic state.

TABLE II. Selected refined bond lengths and angles for IrSr<sub>2</sub>Sm<sub>1.15</sub>Ce<sub>0.85</sub>Cu<sub>2</sub>O<sub>10-δ</sub>. The ranges of the O(1)–Cu–O(2) angle results from the disordered tilts of the IrO<sub>6</sub> octahedron.

Bond(s)	Length (Å)	Angle (°)
Ir–O(1) × 2	1.972(11)	–
Ir–O(3) × 4	1.992(3)	–
Ir–O(3)–Ir	–	150.8(6)
Sr–O(1) × 4	3.001(18)	–
Sr–O(1) × 8	2.754(2)	–
Sr–O(1) × 4	2.482(18)	–
Sr–O(2) × 4	2.806(5)	–
Sr–O(3) × 4	3.302(8)	–
Sr–O(3) × 4	2.653(6)	–
Sm/Ce–O(2) × 4	2.487(4)	–
Sm/Ce–O(4) × 4	2.3188(4)	–
Cu–O(1) × 4	2.155(11)	–
Cu–O(2) × 4	1.9368(7)	–
Cu–O(2)–Cu	–	169.2(4)
Cu–O(1)–Ir	–	165.4(10)
O(1)–Cu–O(2)	–	90.5(4)–100.3(4)

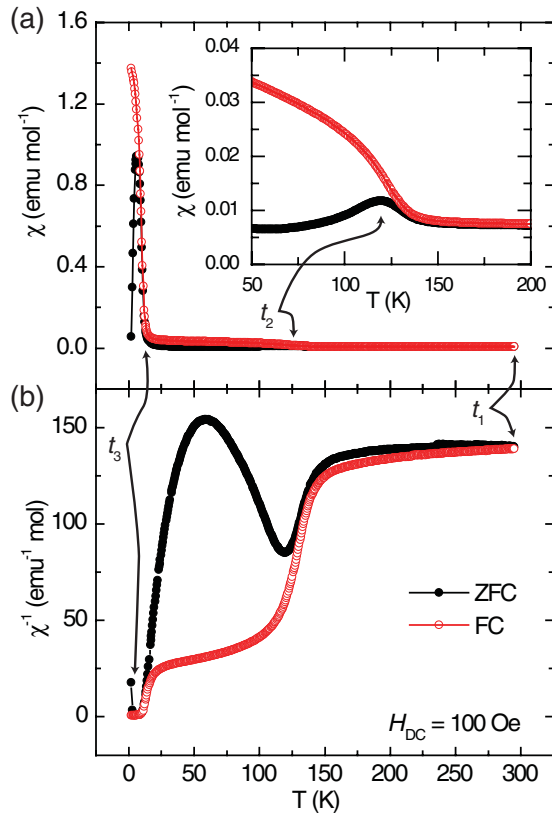


FIG. 2. (Color online) (a) The temperature variation of the magnetic susceptibility showing both zero-field-cooled (black closed circles) and field-cooled (red open circles) datasets. Transitions are evident at 125 and 10 K. Inset is an expansion highlighting the transition evident at 125 K. (b) A plot of inverse susceptibility vs. temperature, clearly showing the ZFC-FC separation, which is persistent up to 300 K.

This history dependence is further confirmed by the  $H$  versus  $T$  measurements seen in Fig. 3. At 200 K a very weak hysteresis is observed but dominated by the linear paramagnetic contribution. Below  $t_2$ , at 60 K, the hysteresis loop increases in size, and below  $t_3$  becomes much more evident. At 2 K the loop takes an unconventional shape known as a wasp-waist that has previously been assigned to disorder in the magnetic exchange.<sup>26</sup>

This complex type of magnetic behavior is commonly observed in reentrant spin-glasses (RSGs).<sup>27</sup> Upon cooling a reentrant spin-glass there is an initial onset of partial order at  $t_1$  ( $>300$  K in  $\text{Ir}_{0.825}\text{Sr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10}$ ), where ferromagnetic clusters are formed in the otherwise paramagnetic state. The size of these clusters grows upon cooling until an ordering transition is observed at  $t_2$ . As the material is cooled further, a third, disordering, spin-glass transition is seen at  $t_3$ .

### C. AC-SQUID magnetometry

To further probe the low-temperature transition,  $t_3$ , frequency-dependent AC-susceptibility measurements were performed, again using a Quantum Design MPMS-XL magnetometer. A drive field of  $H_{ac} = 3.5$  Oe was used, and measurements were performed at frequencies spanning several

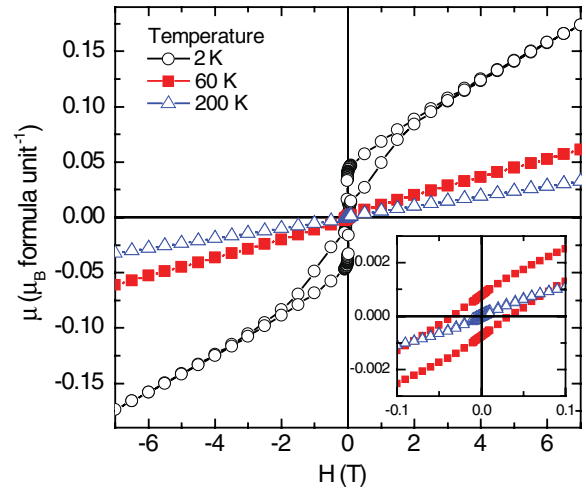


FIG. 3. (Color online) A plot of isothermal hysteresis loops at selected temperatures. The 2 K loop shows an unconventional wasp-waist shape usually assigned to exchange disorder, and the inset is a blow-up of the low-field region showing a small hysteresis is still present up to 200 K.

decades. The temperature dependence of the real and imaginary components to the susceptibility,  $\chi'$  and  $\chi''$ , respectively, can be seen in Fig. 4. A peak is observed in both components, which shows frequency dependence in the peak position as well as magnitude.

The peaks in  $\chi'$  were fitted with a Gaussian function to obtain the frequency dependence of the transition temperature,  $T_f$ , taken as the peak maximum. This frequency dependence of  $T_f$  can be seen in Fig. 5. For spin-glass transitions,  $T_f$  is expected to follow the Vogel-Fulcher law,  $\omega = \omega_0 e^{-E_a/k_B(T_f - T_0)}$ , where  $\omega$  is the AC-frequency,  $E_a$  is the activation energy of the spin glass,  $\omega_0$  is the characteristic frequency for spin freezing usually in the range  $10^8$ – $10^{15}$ , and  $T_0$  is the Vogel-Fulcher temperature.<sup>28</sup> Fits to the Vogel-Fulcher law gave excellent agreement with the experimental data, as can be seen in Fig. 5, and resulted in the following refined parameters:  $\omega_0 = 5.2 \times 10^{15}$  Hz;  $\frac{E_a}{k_B} = 65.1(3)$  K, and  $T_0 = 7.748(8)$  K. The excellent agreement of this fit is strong evidence that  $t_3$  is a spin-glass transition, strengthening the hypothesis that the complex set of magnetic transitions seen in  $\text{Ir}_{0.825}\text{Sr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10}$  can be assigned to reentrant spin-glass behavior.

Another consideration in the designation of spin glasses is the calculation of  $\Delta T_f/[T_f \Delta \log(\omega)]$ .<sup>28</sup> In canonical spin glasses this value falls in the range 0.005–0.28 with  $\text{Ir}_{0.825}\text{Sr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10}$  having a value of 0.015(1), in line with typical dilute magnetic systems such as PdMn and NiMn having 0.013 and 0.018, respectively.<sup>29,30</sup> Competition in magnetic exchange between antiferromagnetic and ferromagnetic interactions is the origin of the RSG phenomenon and this competition is presumably a consequence of the presence of  $\text{Ir}^{4+}$ ,  $\text{Ir}^{5+}$ , and  $\text{Cu}^{3+}$  within the *nominally*  $\text{IrO}_2$  plane for  $\text{IrSr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10-\delta}$ . These competing interactions lead to frustrations between the spins so that below 9.6 K ( $T_f$ ) a breakdown of the higher-temperature ferromagnetic state occurs and a disordering spin-glass transition is observed. Furthermore, such RSG behavior has not been previously

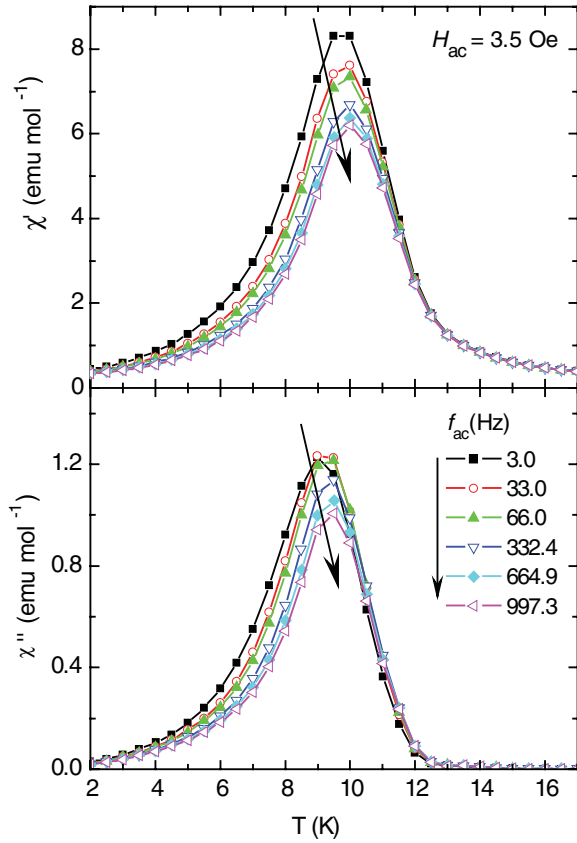


FIG. 4. (Color online) The temperature variation of the real,  $\chi'$ , and imaginary,  $\chi''$ , components of the AC susceptibility across the low-temperature transition,  $t_3$ . At higher frequencies, the peak is seen to diminish in magnitude and shift to higher temperatures.

evidenced in the CuO<sub>2</sub> plane of the many underdoped cuprates reported, so that it seems most likely that the origin of the RSG is in the IrO<sub>2</sub> slab.

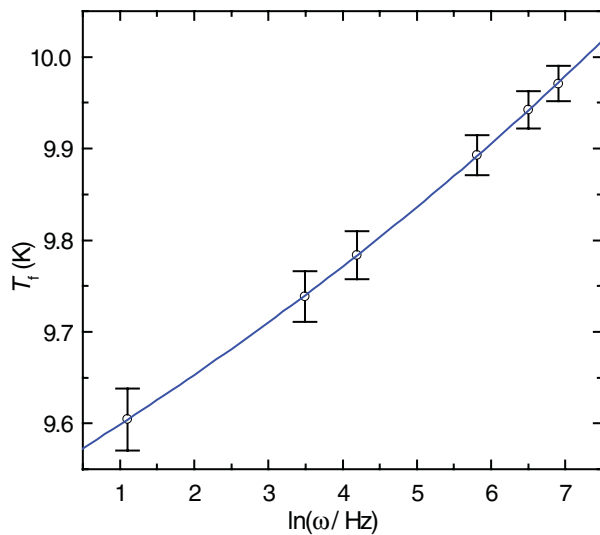


FIG. 5. (Color online) A plot of the fitted peak position,  $T_f$ , vs. the natural log of the AC-measurement frequency,  $\omega$ . The solid line shows a fit to the Vogel-Fulcher law, in excellent agreement with the data, indicative of spin-glass behavior.

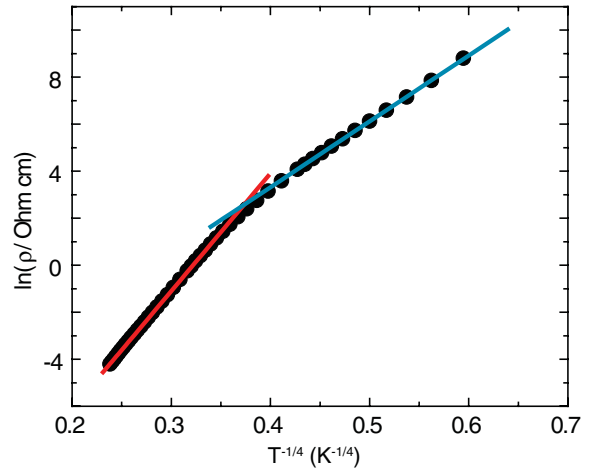


FIG. 6. (Color online) A plot of the resistivity,  $\rho$ , vs.  $T^{-1/4}$ . Linear behavior is indicative of three-dimensional variable-range hopping. A change in slope indicates a change in the electronic localization length, seen upon cooling below 80 K.

#### D. Electron-transport measurements

The electronic transport properties of a sintered ceramic bar of Ir<sub>0.825</sub>Sr<sub>2</sub>Sm<sub>1.15</sub>Ce<sub>0.85</sub>Cu<sub>2.175</sub>O<sub>10</sub> were investigated using a quantum design physical property measurement system (PPMS). The resistivity of the bar was measured, using the four-point probe technique, as a function of temperature in the range  $4 < T < 350$  K in both zero applied field and with a 7 T applied field. Additionally, an isothermal measurement of the resistivity was made at 8 K, sweeping the field range  $0 < H < 9$  T.

The resistivity measurements in zero field found the material to be semiconducting ( $\rho_{290\text{ K}} = 0.019 \text{ } \Omega\cdot\text{cm}$ ), and there was no evidence of superconductivity, which suggests that the CuO<sub>2</sub> planes are underdoped (i.e., that the oxidation state of Cu  $< 2.05$ <sup>31</sup>). It can be seen in Fig. 6 that between 350 K and 65 K there is an excellent fit to Mott three-dimensional variable-range-hopping [ $\rho = \rho_0 \exp(T_0/T)^{1/4}$ , where  $\rho$  is the measured resistivity,  $T$  is the temperature, and  $T_0$  is a fitted localization temperature].<sup>32</sup> Upon cooling below 70 K, there is a distinct change in slope of the linear fits so that  $T_0 = 6.25 \times 10^6$  K and  $6.2 \times 10^5$  K in the high- and low-temperature regions, respectively. This indicates a change in electronic localization length upon cooling [ $T_0 = \lambda \alpha^3 / k_B N(E_F)$ , where  $T_0$  is the degree of electronic disorder,  $\lambda$  is a dimensionless constant,  $\alpha^{-1}$  is equal to the localization length,  $k_B$  is the Boltzmann constant, and  $N(E_F)$  is the density of localized states at  $E_F$ ].

Using measurements of the resistivity measured in both zero field,  $\rho_{H=0}$ , and in a 7 T field,  $\rho_{H=7}$ , the temperature-dependent magnetoresistance can be calculated. Magnetoresistance is commonly defined as the percentage change in resistance upon application of a field,  $MR_{H=7\text{ T}} = 100 \times \left( \frac{\rho_{H=7} - \rho_{H=0}}{\rho_{H=0}} \right)$ . At high temperatures, no discernable magnetoresistive effects are observed. Upon cooling below 20 K, a negative magnetoresistance is observed, which increases in magnitude upon cooling (Fig. 7). The isothermal field sweep at 8 K, shown in the inset of Fig. 7, confirms the magnetoresistive effect and gives a maximum value of  $MR = -8\%$  at  $H = 9$  T. The magnetic

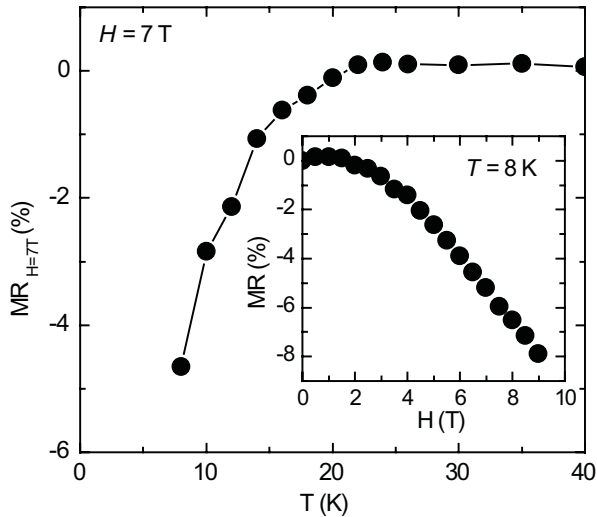


FIG. 7. The temperature variation of the  $MR$  ( $H = 7$  T) showing an increase in negative magnetoresistance upon cooling below 25 K. The inset shows  $MR$  variation with field at 8 K.

transitions reported here originate in the  $\text{IrO}_2$  layer, whereas the observed electronic properties arise in the  $\text{CuO}_2$  plane. As such, the magnetic and electronic transitions appear to be discrete from one another. Previous magnetotransport studies of the 1222 ruthenocuprates<sup>9–13</sup> show that the charge transport is dominated by magnetopolarons—small ferromagnetic regions surrounding each Cu hole within a matrix of antiferromagnetically ordered  $\text{Cu}^{2+}$  spins.<sup>33</sup> An applied magnetic field cants the Ru spins into a ferromagnetic arrangement, which induces partial ferromagnetism in the  $\text{CuO}_2$  planes, thereby increasing the mobility of the magnetopolarons, giving the observed, negative  $MR$ s.<sup>13</sup> Magnetopolaron hopping is a thermally activated process, leading to a characteristic exponential rise in  $-MR$ <sup>34</sup> below the Cu spin transition  $T_{\text{Cu}}$ .<sup>9</sup> The fact that a similar temperature variation of the  $-MR$  is observed for  $\text{Ir}_{0.825}\text{Sr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10}$  below 20 K suggests that the magnetic  $\text{IrO}_2$  planes have a similar influence on the magnetotransport within the  $\text{CuO}_2$  layer; variable field neutron diffraction on an isotopically enriched sample containing  $^{154}\text{Sm}$  will be necessary to investigate this further. Hence, it seems that low-temperature negative magnetoresistance is a common feature of the metalocuprates ( $M\text{Sr}_2\text{Ln}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10-\delta}$ ;  $M = \text{Ir}, \text{Ru},$ <sup>11–14</sup>  $\text{Co}$ <sup>35</sup>). It would

also appear that the RSG behavior in the  $\text{IrO}_2$  planes is less effective at enhancing this magnetopolaron mobility than the weak ferromagnetism in the  $\text{RuO}_2$  plane of  $\text{RuSr}_2\text{Ln}_{1-x}\text{Ce}_x\text{Cu}_2\text{O}_{10-\delta}$ , where magnetoresistances of up to  $-49\%$  have been reported.<sup>9,12,13</sup>

#### IV. CONCLUSIONS

In summary, we report the synthesis of the new 1222-iridocuprate material  $\text{Ir}_{0.825}\text{Sr}_2\text{Sm}_{1.15}\text{Ce}_{0.85}\text{Cu}_{2.175}\text{O}_{10}$ . High-resolution structural studies using synchrotron x-ray diffraction show the material to crystallize in the space-group  $I4/mmm$ , common to the 1222 cuprates. The structural refinement finds there to be a disordered tilting and rotation of the *nominally* Ir octahedra as well as partial Cu substitution onto the Ir site. Magnetic property measurements of both AC and DC susceptibility show a complex temperature dependence that is characteristic of a reentrant spin glass ground state. This behavior is likely due to the disordered occupation of magnetically active  $\text{Cu}^{3+}$  and  $\text{Ir}^{4+}$  in an otherwise diamagnetic lattice of  $\text{Ir}^{5+}$  on the Ir site, leading to frustrated exchange interactions. Electronic transport measurements find the material to be semiconducting at all measured temperatures, and resistivity measurements in an applied field find an increase in the magnitude of negative magnetoresistance upon cooling below 20 K. The features observed in the magnetic property and electronic transport measurements are not obviously concomitant, highlighting the distinctly different origins of the phenomena as coming from the  $\text{IrO}_2$  and  $\text{CuO}_2$  planes, respectively. Future work will concentrate on the synthesis of superconducting Ir-1222 material. The results reported herein suggest that the  $\text{CuO}_2$  planes are underdoped but with appropriate chemical substitutions (such as  $\text{Sr}^{2+} \leftrightarrow \text{Sm}^{3+}$ ) and/or annealing under high oxygen pressure it should be possible to oxidize some of the  $\text{Cu}^{2+}$  and induce superconductivity. This novel iridocuprate would then be an ideal material for further study of the interaction between discrete (ferro)magnetic and superconducting planes.

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<sup>1</sup>A. C. McLaughlin, J. P. Attfield, U. Asaf, and I. Felner, *Phys. Rev. B* **68**, 014503 (2003).

<sup>2</sup>G. V. M. Williams and J. L. Tallon, *Physica C* **258**, 41 (1996).

<sup>3</sup>L. Rukang, Z. Yingjie, Z. Daoyuang, X. Chen, Q. Yitai, C. Zuyao, and Z. Guien, *J. Alloy Compd.* **185**, 45 (1992).

<sup>4</sup>A. C. McLaughlin, D. Morrice, and F. Sher, *J. Solid State Chem.* **178**, 2274 (2005).

<sup>5</sup>A. C. McLaughlin, W. Zhou, J. P. Attfield, A. N. Fitch, and J. L. Tallon, *Phys. Rev. B* **60**, 7512 (1999).

<sup>6</sup>S. Adachi, K.-I. Kubo, S. Takano, and H. Yamauchi, *Physica C: Superconductivity* **191**, 174 (1992).

<sup>7</sup>M. H. Eder and G. Gritzner, *Supercond. Sci. Technol.* **18**, 87 (2005).

<sup>8</sup>I. Felner, U. Asaf, Y. Levi, and O. Millo, *Phys. Rev. B* **55**, R3374 (1997).

<sup>9</sup>A. C. McLaughlin, F. Sher, and J. P. Attfield, *Nature (London)* **436**, 829 (2005); **437**, 1057(E) (2005).

<sup>10</sup>A. C. McLaughlin, F. Sher, S. A. J. Kimber, and J. P. Attfield, *Phys. Rev. B* **76**, 094514 (2007).

<sup>11</sup>A. C. McLaughlin and J. P. Attfield, *J. Magn. Magn. Mater.* **310**, 1961 (2007).

<sup>12</sup>A. C. McLaughlin, L. Begg, A. J. McCue, and J. P. Attfield, *Chem. Comm.* **22**, 2273 (2007).

- <sup>13</sup>A. C. Mclaughlin, L. Begg, C. Harrow, S. A. J. Kimber, F. Sher, and J. P. Attfield, *J. Am. Chem. Soc.* **128**, 12364 (2006).
- <sup>14</sup>D. Pesin and L. Balents, *Nature Physics* **6**, 376 (2010).
- <sup>15</sup>X. Liu, T. Berlijn, W. G. Yin, W. Ku, A. Tsvetik, Young-June Kim, H. Gretarsson, Yogesh Singh, P. Gegenwart, and J. P. Hill, *Phys. Rev. B* **83**, 220403 (2011).
- <sup>16</sup>Y. Okamoto, M. Nohara, H. Aruga-Katori, and H. Takagi, *Phys. Rev. Lett.* **99**, 137207 (2007).
- <sup>17</sup>M. Hervieu, G. Van Tendeloo, C. Michel, C. Martin, A. Maignan, and B. Raveau, *J. Solid State Chem.* **115**, 525 (1995).
- <sup>18</sup>S. J. Dos Santos Garcia, A. M. Arevalo-Lopez, J. Fernandez-Sanjulian, M. A. Alario-Franco, and D. Frost, *High Pressure Res.* **30**, 17 (2010).
- <sup>19</sup>S. J. Dos Santos Garcia, M. H. Aguirre, R. Saex Puche, and M. A. Alario-Franco, *J. Solid State Chem.* **179**, 1296 (2006).
- <sup>20</sup>D. Harada, M. Wakeshima, and Y. Hinatsu, *J. Solid State Chem.* **145**, 356 (1999).
- <sup>21</sup>D. Harada, M. Wakeshima, Y. Hinatsu, K. Ohoyama, and Y. Yamaguchi, *J. Phys.: Condens. Matter* **12**, 3229 (2000).
- <sup>22</sup>A. C. Larson and R. B. Von Dreele, Los Alamos National Laboratory Report LAUR 86 (2004).
- <sup>23</sup>R. D. Shannon, *Acta. Cryst.* **A32**, 751 (1976).
- <sup>24</sup>C. S. Knee, B. D. Rainford, and M. T. Weller, *J. Mater. Chem.* **10**, 2445 (2000).
- <sup>25</sup>A. S. Wills, *Valist* (Program available from [www.ccp14.ac.uk](http://www.ccp14.ac.uk)).
- <sup>26</sup>L. Tauxe, T. A. T. Mullender, and T. J. Pick, *J. Geophys. Res.* **101**, 571 (1996).
- <sup>27</sup>I. Mirebeau, S. Itoh, S. Mitsuda, T. Watanabe, Y. Endoh, M. Hennion, and R. Papoular, *Phys. Rev. B* **41**, 11405 (1990).
- <sup>28</sup>J. A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor and Francis, London, 1993).
- <sup>29</sup>C. A. M. Mulder, A. J. Dytneveldt, H. W. M. van der Linden, B. H. Verbeek, J. C. M. van Donge, G. J. Nieuwenhuys, and J. A. Mydosh, *Phys. Lett. A* **83**, 74 (1981).
- <sup>30</sup>R. M. Roshko and W. Ruan, *J. Magn. Magn. Mater.* **104–07**, 1613 (1997).
- <sup>31</sup>A. Fukuoka, A. Tokiwa-Yamamoto, M. Itoh, R. Usami, S. Adachi, and K. Tanabe, *Phys. Rev. B* **55**, 6612 (1997).
- <sup>32</sup>N. F. Mott, *Phil. Mag.* **19**, 835 (1969).
- <sup>33</sup>E. L. Nagaev, *JETP Lett.* **6**, 18 (1967).
- <sup>34</sup>P. Majumdar and P. Littlewood, *Phys. Rev. Lett.* **81**, 1314 (1998).
- <sup>35</sup>G. Harlow and A. C. Mclaughlin (unpublished).