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# The magnetic and crystal structures of Sr<sub>2</sub>IrO<sub>4</sub>: A neutron diffraction study

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We report a single-crystal neutron diffraction study of the layered Sr<sub>2</sub>IrO<sub>4</sub>. This work unambiguously determines the magnetic structure of the system, and reveals that the spin orientation rigidly tracks the staggered rotation of the IrO<sub>6</sub> octahedra in Sr<sub>2</sub>IrO<sub>4</sub>. The long-range antiferromagnetic order has a canted spin configuration with an ordered moment of 0.208(3)  $\mu_B$ /Ir site within the basal plane; a detailed examination of the spin canting yields 0.202(3) and 0.049(2)  $\mu_B$ /site for the *a*-axis and the *b*-axis, respectively. It is intriguing that forbidden nuclear reflections of space group *I*4<sub>1</sub>/*acd* are also observed in a wide temperature range from 4 K to 600 K, which suggests a reduced crystal structure symmetry. This neutron scattering work provides a direct, well-refined experimental characterization of the magnetic and crystal structures that are crucial to the understanding of the unconventional magnetism exhibited in this unusual magnetic insulator.

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The 5*d*-based iridates have continuously provided a fertile playground for the studies of novel physics driven by the spin-orbit interaction (SOI). It is believed that SOI (0.4 - 1 eV), which is proportional to  $Z^4$  ( $Z$  is the atomic number), plays a critical role in the iridates, and rigorously competes with other relevant energies, particularly the on-site Coulomb interaction  $U$  (0.4 - 2.5 eV), which is significantly reduced because of the extended nature of the 5*d* orbitals. A new balance between the competing energies is therefore established in the iridates and drives exotic quantum phases. Recent experimental observations and theoretical proposals for the iridates have captured the intriguing physics driven by SOI:  $J_{\text{eff}} = 1/2$  Mott state,<sup>1-4</sup> superconductivity,<sup>5,6</sup> correlated topological insulator with large gaps,<sup>7,8</sup> spin liquid in hyperkagome structure,<sup>9</sup> Weyl semimetal with Fermi arcs,<sup>10</sup> Kitaev mode,<sup>11,12</sup> and three dimensional (3*D*) spin liquid with Fermionic spinons.<sup>13</sup>

Among all the iridates studied, the single layer Sr<sub>2</sub>IrO<sub>4</sub> has been subjected to the most extensive investigations owing to its structural and electronic similarities to the undoped high- $T_C$  cuprates such as La<sub>2</sub>CuO<sub>4</sub>. This magnetic insulator was proposed to be an effective  $J_{\text{eff}} = 1/2$  Mott-Hubbard state arising from SOI.<sup>1,3</sup> Although the insulating ground state has been established by angle-resolved photoemission spectroscopy<sup>1</sup> and resonant x-ray scattering (RXS) measurements,<sup>3</sup> some critical insights into the crystal and magnetic structure remain conspicuously elusive. For example, the strong SOI limit  $J_{\text{eff}} = 1/2$  ground state scenario has been recently challenged by the x-ray absorption spectroscopy,<sup>14</sup> the time-resolved optical studies,<sup>15</sup> and theory<sup>16</sup>. The nature of the weak ferromagnetism arising from the canted antiferromagnetic (AFM) order is not fully characterized experimentally. This is primarily due to the lack of large single crystals and the strong absorbing cross section of the Ir ions that prevent a comprehensive neutron study.

Here, we report the results of a neutron diffraction investigation of single-crystal Sr<sub>2</sub>IrO<sub>4</sub>. The central findings of this work are the following: (1) The magnetic and crystal structures are completely determined; (2) The system undergoes an antiferromagnetic transition at 224(2) K with an ordered moment of 0.208(3)  $\mu_B$ /Ir site and a canted spin configuration within the basal plane; and (3) The spin orientation is intimately associated with the rotation of the IrO<sub>6</sub> octahedra, which results in 0.202(3) and 0.049(2)  $\mu_B$ /Ir site for the *a*-axis and the *b*-axis, respectively. In addition, nuclear reflections incompatible with the previously reported space group (SG) are observed and indicate a possible lowering of the structural symmetry.

The Sr<sub>2</sub>IrO<sub>4</sub> single crystal studied ( $2 \times 2 \times 1\text{mm}^3$ , mass=8 mg) was grown using self-flux techniques.<sup>17</sup> Because the iridium is highly neutron absorbing, the equal-dimensional shaped crystal simplifies the necessary absorption correction.<sup>18</sup> The neutron diffraction measurements were carried out at the HB1A, HB1 triple axis spectrometers, and the HB3A four circle diffractometer at the High Flux Isotope Reactor at the Oak Ridge National Laboratory. For the measurements using triple axis spectrometers, the crystal was aligned in the (*h*, 0, *l*), (*h*, *h*, *l*), (0, *k*, *l*) and other scattering planes to probe various magnetic reflections. A close-cycle refrigerator and high temperature furnace were employed to monitor the *T* dependence of the magnetic and nuclear reflections.

Sr<sub>2</sub>IrO<sub>4</sub> was reported to crystallize in a tetragonal structure (SG *I*4<sub>1</sub>/*acd*, No. 142) with  $a = b = 5.484 \text{ \AA}$ , and  $c = 25.83 \text{ \AA}$  at 4 K.<sup>19,20</sup> With reflection conditions compliant with the *I*4<sub>1</sub>/*acd* symmetry, we have collected 137 nuclear reflections of Sr<sub>2</sub>IrO<sub>4</sub> using HB3A for structure refinements. The most prominent features of the crystal structure are the elongation of the IrO<sub>6</sub> octahedra along the *c*-axis (2.055  $\text{\AA}$  for the out-of-plane distance compared to 1.981  $\text{\AA}$  in-plane one), and the rotation of

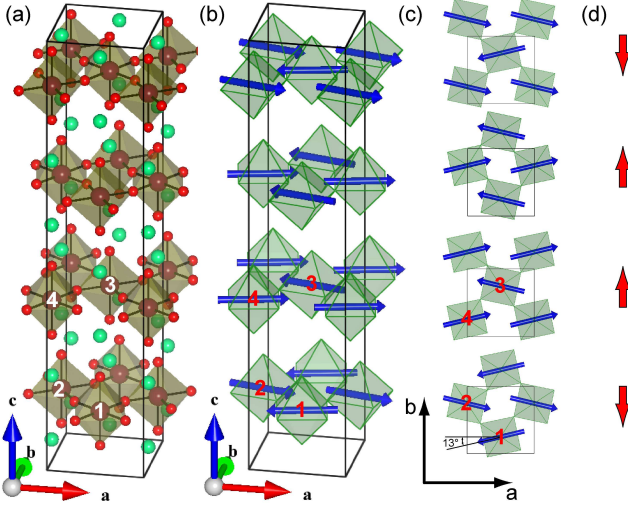


FIG. 1. (Color online) (a) The crystal structure of  $\text{Sr}_2\text{IrO}_4$  with SG  $I4_1/acd$  (setting 2). Each  $\text{IrO}_6$  octahedron rotates  $11.8^\circ$  about the  $c$ -axis. The Ir atoms of the nonprimitive basis are labeled as 1,2,3, and 4 plus the body centering translation  $(1/2,1/2,1/2)$ . (b) The refined magnetic structure from single-crystal neutron diffraction measurements. (c) The same spin configuration projected on the basal planes. (d) The net moment projected along the  $b$ -axis for individual layers.

the octahedra with respect to the  $c$ -axis about  $11.8(1)^\circ$  at 4 K. This leads to a  $\sqrt{2} \times \sqrt{2}$  expansion of unit cell in the basal plane compared to the higher symmetry  $\text{Sr}_2\text{RuO}_4$  [Figure 1(a)].

The anti-translation in combination with the body centering dictates a  $(1,1,1)$  magnetic propagation vector, as discussed previously.<sup>16,21</sup> Figure 2(a) displays the  $T$  dependence of the Bragg intensity ( $I_B \propto |M_s|^2$ ,  $M_s$  is the order parameter) of the magnetic reflection  $(1,0,2)$ . The intensity vanishes around  $T_N = 224(2)$  K and is consistent with the magnetization measurement.<sup>17</sup> Fitting the order parameter to the power law scaling function  $I_B \approx |t|^{2\beta}$ , where  $t = 1 - T/T_N$  is the reduced temperature, leads to the critical exponent  $\beta = 0.18(1)$ . It apparently deviates from the  $\beta = 0.325$  expected for a 3D Heisenberg spin system. Figs. 2(b)-2(c) illustrate the wavevector scans within and perpendicular to the basal plane at several temperatures. In both cases, the line-shape of the magnetic scattering evolves into a Gaussian profile below  $T_N$ , signaling the formation of long range magnetic order. Our observation is in accord with the RXS studies indicating that a short range Heisenberg spin fluctuation occurs only in a paramagnetic state.<sup>22</sup>

A quantitative characterization of the magnetic structure and moment size of the  $\text{Ir}^{4+}$  ions can be obtained by a comprehensive survey of the magnetic reflections in conjunction with the model calculation. Figure 3 shows the neutron diffraction scans at selected reflections. The disappearance of the scattering above  $T_N$  and decrease in intensity at large momentum transfer indicate their magnetic nature. Different from the early RXS stud-

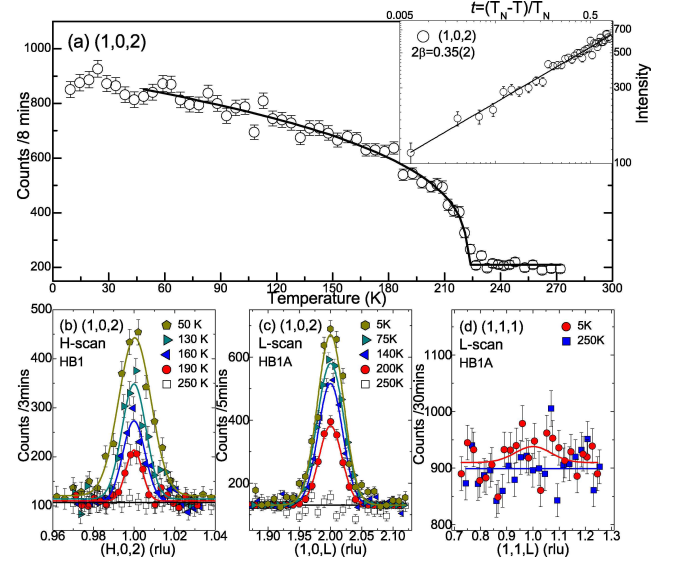


FIG. 2. (Color online) (a) The  $T$  dependence of the magnetic  $(1,0,2)$  reflection. Inset shows the intensity versus the reduced temperature ( $t = |1 - T/T_N|$ ) on logarithmic scale. The wavevector scan along (b) the  $[H,0,0]$  and (c) the  $[0,0,L]$  directions for the  $(1,0,2)$  peak at selected temperatures that probe the in-plane and out-of-plane correlations. (d) Similar wavevector scans for the magnetic  $(1,1,1)$  reflection above and below  $T_N$ . Note that the counting statistics is ten times compared to those of the strong reflection  $(1,0,2)$  peak.

TABLE I. Basis vectors (BVs) for the SG  $I4_1/acd$  with magnetic propagation vector  $\mathbf{k}=(1,1,1)$ . The decomposition of the magnetic representation is  $\Gamma_{\text{mag}} = 2\Gamma_1^2 + 2\Gamma_2^2 + 2\Gamma_3^2 + 2\Gamma_4^2$ . The atoms of the nonprimitive basis are located at 1: $(1/2,1/4,1/8)$ ,2: $(0,3/4,1/8)$ ,3: $(1/2,3/4,3/8)$ ,4: $(0,1/4,3/8)$  (Figure 1). For clarity, only the in-plane BVs are listed.

IR	BV	atom	component			IR	BV	atom	component		
			$m_a$	$m_b$	$m_c$				$m_a$	$m_b$	$m_c$
$\Gamma_1$	$\psi_1$	1	1	0	0	$\Gamma_2$	$\psi_5$	1	1	0	0
		2	1	0	0			2	1	0	0
		3	1	0	0			3	-1	0	0
		4	1	0	0			4	-1	0	0
	$\psi_2$	1	0	1	0		$\psi_6$	1	0	1	0
		2	0	1	0			2	0	1	0
		3	0	-1	0			3	0	1	0
		4	0	-1	0			4	0	1	0
	$\psi_3$	1	1	0	0		$\psi_7$	1	1	0	0
		2	-1	0	0			2	-1	0	0
		3	1	0	0			3	-1	0	0
		4	-1	0	0			4	1	0	0
	$\psi_4$	1	0	1	0		$\psi_8$	1	0	1	0
		2	0	-1	0			2	0	-1	0
		3	0	-1	0			3	0	1	0
		4	0	1	0			4	0	-1	0

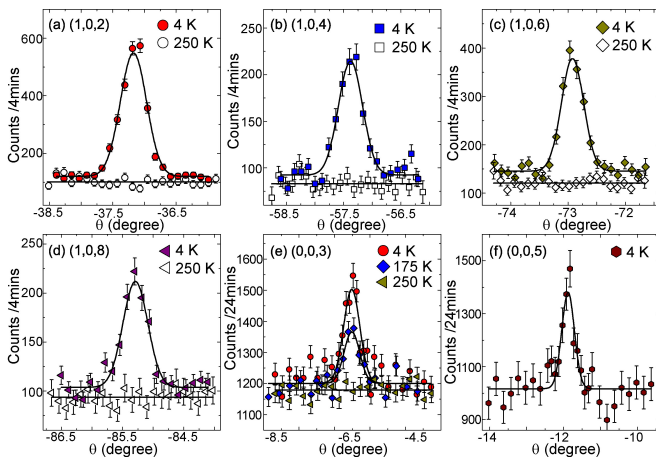


FIG. 3. (Color online) Selected rocking scans at 4 K and 250 K for the (a) (1,0,2), (b) (1,0,4), (c) (1,0,6), (d) (1,0,8), (e) (0,0,3), and (f) (0,0,5) magnetic reflections. The weaker (0,0,2n+1) are measured with much longer counting time.

ies where the magnetic reflections are present only at (0,1,4n+2) and (1,0,4n),<sup>3</sup> our neutron diffraction shows additional Bragg peaks at (0,1,4n) and (1,0,4n+2) positions. The nearly identical intensity at equivalent wavevectors (1,0,2) and (0,1,2) indicates the crystal has equally populated magnetic domains. Note that the structural refinement with the same sample cannot determine whether the system is structurally twinned.<sup>23</sup> The presence of both type of reflections strongly suggests that they originate from the twinned crystallographic domains. According to the Landau theory, the symmetry properties of the magnetic structure can be described by only one irreducible representation (IR). With Ir ions located at the 8a Wyckoff positions for the SG  $I4_1/acd$  and the propagation wavevector  $q_M = (1,1,1)$ , the magnetic representation can be decomposed into  $\Gamma_{\text{mag}} = 2\Gamma_1^2 + 2\Gamma_2^2 + 2\Gamma_3^1 + 2\Gamma_4^1$ , where  $\Gamma_1, \Gamma_2$  are the two-dimensional IRs with basis vectors lying in the  $ab$  plane,  $\Gamma_3, \Gamma_4$  are the one-dimensional IRs with moments pointing parallel the  $c$ -axis. Since the magnetic susceptibility suggests that the spin easy axis lies in the basal plane,<sup>17</sup> we exclude spin configurations associated with  $\Gamma_3$  and  $\Gamma_4$  in the analysis. Table I lists the basis vectors of IRs  $\Gamma_1$  and  $\Gamma_2$ . In particular, the spin structure based on linear combination of  $\psi(2)$  and  $\psi(3)$  of  $\Gamma_1$  has a (+-+-) configuration along the  $a$ -axis (or the M4 structure described in Refs. 16 and 21) and (++--) along the  $b$ -axis for the labeled Ir ions in Figure 1. In contrast, the linear combination of  $\psi(5)$  and  $\psi(8)$  in  $\Gamma_2$  gives (++--) along the  $a$ -axis and (+-+-) along the  $b$ -axis (the M3 configuration). These spin structures derived from representation analysis using BasIreps program<sup>24</sup> are in accord with the results from previous neutron powder diffraction.<sup>21</sup>

Table II compares the expected intensities for the two relevant spin models and the experimental observations. The M4 and M3 configurations each have distinct distributions of magnetic scattering intensities.<sup>26</sup> For example,

TABLE II. Comparison of observed and calculated magnetic intensities from two symmetry compatible spin models. To get the scale factor, separate sets of nuclear reflections were collected at HB3A with incident neutron wavelength of 1.5424 and 1.003 Å, respectively. Additional 37 nuclear reflections were collected at HB1A for intensity normalization.<sup>25</sup>

reflection	observation	M4 model	M3 model
(0,0,3)	$0.26 \pm 0.03$	0.25	0.25
(0,0,5)	$0.20 \pm 0.03$	0.20	0.20
(1,1,1)	$0.08 \pm 0.07$	0.08	0.08
(0,1,2)	$6.80 \pm 0.17$	6.99	1.05
(0,1,6)	$4.72 \pm 0.32$	4.50	2.73
(1,0,2)	$6.99 \pm 0.18$	6.99	1.05
(1,0,4)	$2.33 \pm 0.22$	2.48	5.81
(1,0,6)	$4.72 \pm 0.32$	4.51	2.73
(1,0,8)	$2.56 \pm 0.32$	2.28	3.01
(1,0,14)	$0.88 \pm 0.21$	0.54	0.48
(1,0,16)	$0.18 \pm 0.09$	0.24	0.26
(1,2,0)	$1.53 \pm 0.36$	1.76	0.43
(1,2,4)	$1.14 \pm 0.23$	1.46	0.52
(1,2,8)	$0.85 \pm 0.12$	0.82	0.45

the collinear structure with  $a$ -axis (+-+-) components produces the strongest scattering at the (0,1,2) reflection and gives zero intensity at the (1,0,0) Bragg point. However, the (++--) collinear state associated with the M3 configuration will generate the strongest scattering at the (1,0,0) peak which is not observed experimentally. The neutron diffraction results shown in Table II clearly support the M4 spin configuration and confirm the previous neutron diffraction work on the powder sample.<sup>21</sup> To test whether there are additional canted moments along  $b$ -axis with (++--) configuration within  $\Gamma_1$ , we probed the scattering at the expected (0,0,2n+1) reflections. Figures 3(d)-3(e) display the scans at the (0,0,3) and (0,0,5) Bragg peaks. Although much weaker, the magnetic scattering is clearly present at low  $T$  and confirms the staggered AFM order propagating along the  $c$ -axis. A total of 14 magnetic reflections combined with 137 nuclear reflections allow an accurate determination of the spin structure and the associated moment. Using the M4 spin model and the magnetic form factor for  $\text{Ir}^{4+}$ ,<sup>27</sup> we have obtained  $m_a = 0.202(3) \mu_B$  along the  $a$ -axis and  $m_b = 0.048(2) \mu_B$  along the  $b$ -axis, yielding a total moment of  $0.208(3) \mu_B/\text{Ir}^{4+}$  site. This value is smaller than  $0.36(6) \mu_B$  from a recent single crystal neutron scattering study<sup>28</sup> but quite consistent with the powder neutron diffraction results in which the upper limit of the moment does not exceed  $0.29(4) \mu_B$ .<sup>21</sup> The magnetic configuration in Figs. 1(b)-1(d) show that spins projected along the  $b$ -axis have a staggered  $\downarrow\uparrow\uparrow\downarrow$  pattern along the  $c$ -axis, with Ir spins deviating  $13(1)^\circ$  away from the  $a$ -axis [see Fig. 1(d)]. This spin canting rigidly tracks the staggered octahedral rotation, as illustrated in previous RXS

study.<sup>1</sup> This remarkable correlation proves the existence of strong magnetoelastic coupling in the iridate, which is also suggested in experimental studies of transport and magnetic properties of the system.<sup>4,29</sup>

Theoretically, the spin Hamiltonian in the strong SOI limit includes the isotropic coupling ( $J$ ) and the Dzyaloshinsky-Moriya interaction ( $D$ ) caused by the lattice distortion.<sup>11</sup> The spin canting is governed by the ratio of  $D$  and  $J$ , and is solely determined by the lattice distortion. This explains the relatively large spin canting in the  $5d$  system compared to that in  $\text{La}_2\text{CuO}_4$  where SOI is insignificant ( $\text{SOI} \propto Z^4$ ,  $Z=29$  and  $77$  for Cu and Ir, respectively). The measured magnetic moment is much smaller than  $1 \mu_B$  conventionally anticipated for a  $S = 1/2$  system, but is similar to those of other iridates, such as  $\text{Na}_2\text{IrO}_3$  and  $\text{BaIrO}_3$  where the saturated moment is less than 20% of  $1 \mu_B/\text{Ir}$ .<sup>17,30</sup> The significantly reduced moment might be attributed to the strong hybridization of the Ir  $5d$  orbital with the ligand oxygen  $2p$  orbital because of the large spatial extend of  $5d$  wavefunctions, or the axial distortion of  $\text{IrO}_6$  octahedra away from the cubic symmetry.<sup>16,21</sup> Although the latter has been invoked to explain the reduced moment, it is inconsistent with the branching ratio (BR) obtained from the x-ray absorption spectrum.<sup>31,32</sup> The reduced  $\langle \mathbf{S} \cdot \mathbf{L} \rangle$  caused by the decreased moment makes the corresponding BR values far too small compared to the measured one. It was argued that the moment value and BR are irreconcilable using only one  $t_{2g}$  electron and  $j = 5/2$ . For instance, Laguna-Marco *et al.* have shown in a multi-electron simulation in  $\text{BaIrO}_3$  that  $J_{\text{eff}} = 1/2$  accounts for only half of  $\langle \mathbf{S} \cdot \mathbf{L} \rangle$  required in BR to match the experimental determined value, while the remaining half is induced by spin-orbit mixing of  $t_{2g}$  and  $e_g$  states.<sup>33</sup>

The observation of the magnetic  $(0, 1, 4n + 2)$  and  $(1, 0, 4n)$  indicates either the breakdown of the tetragonal symmetry of the system, or a weak coupling between the magnetic and lattice degrees of freedom. To understand the possible structural origin of the anomalous magnetic behavior, we have surveyed extensively in reciprocal space and observed the presence of nuclear reflections (*odd*  $h, 0, \textit{odd}$   $l$ ) that are not allowed in SG  $I4_1/acd$ . Similar behavior is also observed in a recent single crystal neutron diffraction work.<sup>28</sup> Fig. 4(b) shows the rocking scans of the  $(0,1,1)$  reflection at selected temperatures. The intensity continuously decreases upon warming and shows no sign of transition up to 600 K. The reduction in intensity cannot be accounted by the thermal vibration of the elements (Debye-Waller factor). The lack of anomaly near  $T_N$  is also consistent with the transport,<sup>17,34</sup> thermodynamic<sup>29</sup>, and optical conductivity studies.<sup>2,15</sup> Scans across other Bragg peaks of  $(1,0,1)$  and  $(1,0,5)$  display similar violation of the required ( $h = 2n, 0, l = 2n$ ) reflection condition. Although it cannot be completely ruled out that the forbidden peaks might be due to the structural defects such as oxygen vacancies commonly observed in oxides, the systematically enhanced intensities of these forbidden peaks

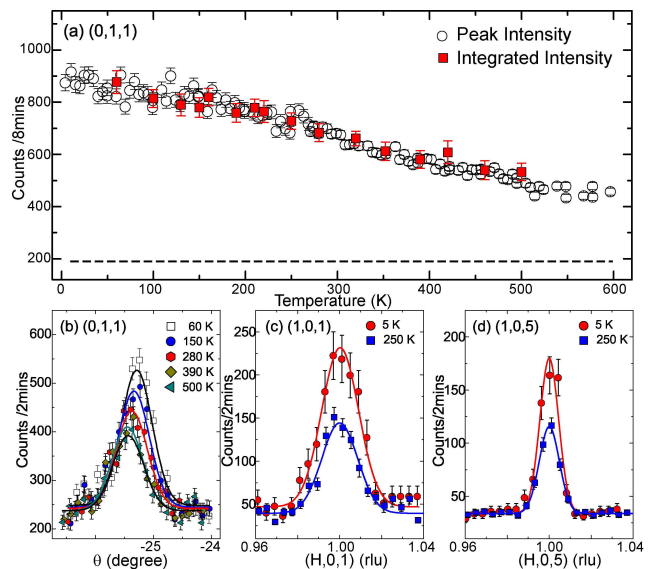


FIG. 4. (Color online) (a) The  $T$  dependence of the structural  $(0,1,1)$  reflection. Open circles are the peak intensity, solid squares integrated intensity. Dashed line is the background derived from the Gaussian fit to the rocking scan. (b) The rocking scans of the  $(0,1,1)$  peak at  $T=60, 150, 280, 390,$  and  $500$  K. The wavevector scans along the  $[1,0,0]$  direction for (c) the  $(1,0,1)$  and (d) the  $(1,0,5)$  reflections at  $5$  K and  $250$  K.

with isovalent Rh-doping<sup>35</sup> suggest it is an intrinsic property. If the observed forbidden peaks arise from the reduced crystal symmetry, they would lead to possible nonisomorphic subgroups of either  $I4_1/a22$  (No. 98) or  $I4_1/a$  (No. 88) due to the absent  $c$ - and  $d$ -glide planes. The absence of scattering across the  $(1,1,0)$  reflection further rules out the SG of  $I4_1/a22$ . Such observation of reduced structural symmetry that persists at a much higher temperature than  $T_N$ , implies the formation of a crystallographic template for the low- $T$  spin structure that changes the tetragonal symmetry. This observation is certainly intriguing and the origin of it remains to be understood.

It is established that the magnetic and electronic properties are highly susceptible to slight impurity doping for either Sr, Ir or oxygen.<sup>4,29,36–38</sup> For example, doping Mn results in a spin-flop transition with moments aligning along the  $c$ -axis.<sup>36</sup> The remaining  $J_{\text{eff}} = 1/2$  state revealed by RXS measurement suggests its robustness against the alternation of spin structure. On the other hand, replacing Ir with isovalent  $\text{Rh}^{4+}$  leads to a rich phase diagram of metal-insulator transition tuned by SOI.<sup>37</sup> The transition was explained by the effective reduction of the splitting between the  $J_{\text{eff}} = 1/2$  and  $J_{\text{eff}} = 3/2$  bands due to the reduced SOI; this in turn alters the relative strength of the SOI and the crystal electric field (CEF) that dictates the magnetic state. This notion is also consistent with recent theoretical proposal that the change of CEF associated with the underlying structure could be critical to determine the magnetic

ground states. The present single-crystal neutron diffraction unambiguously determines the magnetic structure and proves the rigid coupling of the spin canting with the rotation of the  $\text{IrO}_6$  octahedra. These findings finally fill the longstanding hiatus of our understanding of the magnetic properties in  $\text{Sr}_2\text{IrO}_4$ , an archetype of the  $J_{\text{eff}} = 1/2$  insulators.

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