Simultaneous Metal-Insulator and Antiferromagnetic Transitions in Orthorhombic Perovskite Iridate Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ Single Crystals

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Simultaneous metal-insulator and antiferromagnetic transitions in orthorhombic perovskite iridate

Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ single crystals

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The orthorhombic perovskite SrIrO$_3$ is a semimetal, an intriguing exception in iridates where the strong spin-orbit interaction coupled with electron correlations tends to impose an insulating state. We report results of our investigation of bulk single-crystal Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ or Ir-deficient, orthorhombic perovskite SrIrO$_3$. It retains the same crystal structure as stoichiometric SrIrO$_3$ but exhibits a sharp, simultaneous antiferromagnetic (AFM) and metal-insulator (MI) transition occurring in the basal-plane resistivity at 185 K. Above it, the basal-plane resistivity features an extended regime of almost linear temperature dependence up to 800 K but the strong electronic anisotropy renders an insulating behavior in the out-of-plane resistivity. The Hall resistivity undergoes an abrupt sign change and grows below 40 K, which along with the Sommerfeld constant of 20 mJ/mol K$^2$ suggests a multiband effect. All results including our first-principles calculations underscore a delicacy of the paramagnetic, metallic state in SrIrO$_3$ that is in close proximity to an AFM insulating state. The contrasting ground states in isostructural Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ and SrIrO$_3$ illustrate a critical role of lattice distortions and Ir deficiency in rebalancing the ground state in the iridates. Finally, the concurrent AFM and MI transitions reveal a direct correlation between the magnetic transition and formation of an activation gap in the iridate, which is conspicuously absent in Sr$_2$IrO$_4$.

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I. INTRODUCTION

It is now widely recognized that strong spin-orbit interaction (SOI) coupled with the electron-electron interaction (on-site Coulomb repulsion $U$) drives narrow-gap Mott insulating states in iridates [1–7]. The SOI is a relativistic effect proportional to $Z^4$ ($Z$ is the atomic number), and is approximately 0.4 eV in the iridates (compared to $\sim$20 meV in 3d materials), and splits the $t_{2g}$ bands into states with $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$, the latter having lower energy in the Ruddlesden-Popper series, Sr$_{n+1}$Ir$_{n}$O$_{3n+1}$ ($n = 1$ and 2; $n$ defines the number of IrO$_6$ layers in a unit cell) [1–7]. Since Ir$^{4+}$($5d^9$) ions provide five 5d electrons to bonding states, four of them fill the lower $J_{\text{eff}} = 3/2$ bands, and one electron partially fills the $J_{\text{eff}} = 1/2$ band where the Fermi level $E_F$ resides. The $J_{\text{eff}} = 1/2$ band is so narrow that even a reduced $U$ ($\sim$0.5 eV, due to the extended nature of 5d electron orbitals) is sufficient to open a small gap $\Delta$ supporting the insulating state in Sr$_{n+1}$Ir$_n$O$_{3n+1}$. The splitting between the $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$ bands narrows and the two bands progressively broaden and contribute to the density of states near the Fermi surface as the dimensionality (i.e., $n$) increases in Sr$_{n+1}$Ir$_n$O$_{3n+1}$. In particular, the 5d bandwidth $W$ of the $J_{\text{eff}} = 1/2$ band increases from 0.48 eV for $n = 1$ to 0.56 eV for $n = 2$ and 1.01 eV for $n = \infty$ [2,4,6]. Since the effects of the SOI and $U$ are largely local and remain essentially unchanged throughout the entire series, Sr$_{n+1}$Ir$_n$O$_{3n+1}$, the ground state evolves with decreasing $\Delta$ and increasing $W$, from a robust antiferromagnetic (AFM) insulating state for Sr$_2$IrO$_4$ ($n = 1$) to a paramagnetic semimetallic state for SrIrO$_3$ ($n = \infty$). That such a semimetallic state occurs in SrIrO$_3$ notwithstanding the presence of the strong SOI is of great interest both theoretically and experimentally [2,7–21]. It is conceived that the strong SOI reduces the threshold of $U$ for a metal-insulator (MI) transition [8,9]. More recently, theoretical studies have found that the stronger SOI requires a larger critical $U$ instead for a MI transition to occur in SrIrO$_3$ because of a protected Dirac node for given $U$ in the $J_{\text{eff}} = 1/2$ bands near the Fermi level due to a combined effect of the lattice structure and strong SOI [10,11]. In essence, small hole and electron pockets with a low density of states take place in SrIrO$_3$ and render a less effective $U$, which would otherwise drive a magnetic insulating state [10,11]. Indeed, tuning the relative strength of the SOI and $U$ effectively changes the ground state in the iridates, and the rare occurrence of a semimetallic state in SrIrO$_3$ provides a unique opportunity to closely examine the intricate interplay of the SOI, $U$, and lattice degrees of freedom. The correlation between the AFM state and MI transition in the iridates has been among the most discussed topics in recent years [7,22–24].

A good number of excellent studies of the orthorhombic perovskite SrIrO$_3$ have been conducted in recent years [2,13–21]. However, bulk orthorhombic perovskite SrIrO$_3$ forms only at high pressures and high temperatures [12,13], and almost all studies of SrIrO$_3$ so far are limited to samples...
in thin-film or polycrystalline form [2,13–21]. Little work on bulk single-crystal \( \text{SrIrO}_3 \) has been reported and critical information, such as anisotropies, magnetic properties, and their correlation with the electronic state, etc., is still lacking. (Note that single crystals of the \textit{hexagonal} \( \text{SrIrO}_3 \), which have been studied [25], are not part of this work.) In this paper, we report results of our study on bulk single crystals of the orthorhombic perovskite \( \text{Sr}_0.94\text{Ir}_0.78\text{O}_2.68 \) for an extended temperature range from 0.05 to 800 K. \( \text{Sr}_0.94\text{Ir}_0.78\text{O}_2.68 \) retains the very same crystal structure as stoichiometric \( \text{SrIrO}_3 \) but exhibits sharp, concurrent AFM and MI transitions at 185 K with a charge gap of 0.027 eV, sharply contrasting with stoichiometric \( \text{SrIrO}_3 \) that is paramagnetic and semimetallic. The electrical resistivity is highly anisotropic and features an extended regime of approximately linear in a basal-plane resistivity between 185 and 800 K. The Hall resistivity undergoes an abrupt sign change near 40 K (rather than at \( T_N = 185 \text{ K} \)), from holelike at high temperatures to electronlike at low temperatures, which along with a finite Sommerfeld constant of 20 mJ/mol K\(^2\) implies in-gap states. Our band structure calculations confirm a small energy gap and finite magnetic moment in an AFM insulating state as a result of the Ir deficiencies in \( \text{Sr}_0.94\text{Ir}_0.78\text{O}_2.68 \). This work underscores the delicacy of the metallic state that is in close proximity to an AFM insulating state that is highly sensitive to even slight lattice defects in \( \text{SrIrO}_3 \). The concurrent AFM and MI transitions provide clear evidence for a direct correlation between the magnetic transition and charge gap in \( \text{SrIrO}_3 \), which is absent in \( \text{Sr}_2\text{IrO}_4 \).

II. EXPERIMENTAL DETAILS

The single crystals studied were grown at ambient pressure from off-stoichiometric quantities of \( \text{SrCl}_2, \text{SrCO}_3 \), and \( \text{Ir}_2 \text{O}_3 \) using self-flux techniques. The mixed powders with a weight ratio of \( \text{Sr} \) to \( \text{Ir} \) being 4 to 1 were fired up to 1470 °C for 5 h and then slowly cooled down at a rate of 2 °C/h. The size of the single crystals is \( 1.0 \times 0.5 \times 0.5 \text{ mm}^3 \). The formation of nonstoichiometric \( \text{SrIrO}_3 \) single crystals at ambient pressure is consistent with recent observations that the orthorhombic perovskite phase can be stabilized at ambient pressure via chemical doping [13–16]. The crystal structure of single-crystal \( \text{Sr}_{0.94}\text{Ir}_{0.78}\text{O}_{2.68} \) was determined using a Rigaku x-ray diffractometer XtaLAB PRO equipped with a PILATUS 200K hybrid pixel array detector at the Oak Ridge National Laboratory. More than 20 crystals were carefully examined. Full data sets were collected from 100 to 260 K and the structures were refined using SHEXL-97 and FULLPROF software [26,27] (see Table I). Chemical compositions of single-crystal \( \text{Sr}_{0.94}\text{Ir}_{0.78}\text{O}_{2.68} \) were determined using energy dispersive x-ray analysis (EDX) (Hitachi/Oxford 3000) and x-ray diffraction discussed below. Magnetization, specific heat, and Hall and electrical resistivity were measured using either a Quantum Design MPMS-7 SQUID Magnetometer and/or Physical Property Measurement System with 14-T field capability. The Hall resistivity as function of temperature (or magnetic field) was determined by the difference between two sets of transverse resistivity data taken at a magnetic field with the same magnitude but opposite directions. Transport measurements were made with ac resistance bridges (Linear Research 700 and Lakeshore 370). The high-temperature resistivity was measured using a Displex closed cycle cryostat capable for a continuous temperature ramping from 9 to 900 K.

The electronic band structure calculations were performed using the full potential linearized augmented plane-wave method as implemented in the WIEN2K package. Local spin density approximation (LSDA) for the exchange-correlation potential was used. We utilized a LSDA + SOI + \( U(U = 3 \text{ eV}) \) scheme. The self-consistent calculations were considered converged when the difference in the total energy of the crystal does not exceed 0.01 mRy.

III. CRYSTAL STRUCTURE

The single-crystal \( \text{Sr}_{0.94}\text{Ir}_{0.78}\text{O}_{2.68} \) adopts an orthorhombic perovskite structure with space group \( \text{Pbnm} \) (No. 62), as shown in Fig. 1 and Table I. It has 3.12 Ir atoms, rather than 4, in a unit cell but its crystal structure is consistent with that of stoichiometric, orthorhombic perovskite \( \text{SrIrO}_3 \) reported in the literature [12–17]. The Ir and O deficiencies inevitably lead to proportionally smaller lattice parameters of \( \text{Sr}_{0.94}\text{Ir}_{0.78}\text{O}_{2.68} \) than those of \( \text{SrIrO}_3 \) with an approximate 2.5% decrease in volume (for the high-pressure bulk \( \text{SrIrO}_3 \) phase, \( a = 5.60075(5.58871) \text{ Å}, \ b = 5.57115(5.57245) \text{ Å}, \ c = 7.89601(7.88413) \text{ Å}, \) and \( V = 246.376(245.534) \text{ Å}^3 \) at 300 K (3 K) [17]). The Ir-O-Ir bond angles for in plane and out of plane are 161.1(3)° and 162.3(4)°, respectively. A close comparison with the data of the stoichiometric \( \text{SrIrO}_3 \) in Ref. [17] indicates that \( \text{Sr}_{0.94}\text{Ir}_{0.78}\text{O}_{2.68} \) has a larger in-plane rotation of \( \text{IrO}_6 \) octahedra, 9.45° (vs 8.75°) but a smaller out-of-plane tilt, 8.85° (vs 12°). The in-plane rotation is likely to have a greater impact on physical properties than the out-of-plane tilt. Note that the \( \text{IrO}_6 \) octahedra in \( \text{Sr}_2\text{IrO}_4 \) and \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) only rotate within the basal plane by about 12° without the out-of-plane tilt [28–31].

In addition, the crystal structure is also systematically examined in a temperature range of 100–260 K using FIG. 1. The crystal structure of perovskite \( \text{Sr}_{0.94}\text{Ir}_{0.78}\text{O}_{2.68} \). Legends: (green) Sr, (brown) Ir, and (red) O. Note there are 3.12 Ir atoms in a unit cell, as compared to 4 in \( \text{SrIrO}_3 \).
single-crystal x-ray diffraction. No lattice anomaly is discerned in this temperature range including 185 K where AFM and MI transitions occur, which is discussed below.

IV. EXPERIMENTAL RESULTS

A. Magnetic properties

One of the central features of Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ is that a robust AFM transition occurring at $T_N = 185$ K [Fig. 2(a)] is accompanied by a sharp MI transition. Fitting the $a$-axis magnetic susceptibility $\chi_a(T)$ in Fig. 2(a) to a Curie-Weiss law for 200–340 K yields the Curie-Weiss temperature $\theta_{CW} = +160$ K and the effective moment $\mu_{eff} = 0.19 \mu_B$/Ir. Like that of Sr$_2$IrO$_4$ and other related iridates [4,32,33], $\theta_{CW}$ shows a characteristic positive sign, despite the AFM ground state. $\mu_{eff}$ is finite but significantly smaller than that for other more insulating iridates (e.g., 0.4 $\mu_B$/Ir for Sr$_2$IrO$_4$) due to the more itinerant nature of the system discussed below. The isothermal magnetization $M(H)$ varies almost linearly with the magnetic field $H$ up to 7 T, as anticipated for an AFM ground state [see Fig. 2(b)]. The magnetic anisotropy is visible but weak, consistent with the nature of the orthorhombic perovskite. For comparison, the evolution of the AFM order in the Ruddlesden-Popper series Sr$_{n+1}$Ir$_n$O$_{3n+1}$ with $n = 1, 2$ and Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ ($n = \infty$) is illustrated in Fig. 2(c). $T_N$ for Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ is clearly lower than that for $n = 1$ (240 K) and $n = 2$ (285 K) but the low-temperature magnetic moment of Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ seems considerably stronger than that of $n = 2$ [right scale in Fig. 2(c)].

B. Electrical resistivity

The electrical resistivity $\rho(T)$ features a sharp MI transition at $T_N = 185$ K and an almost linear $T$ dependence of the $a$-axis $\rho_a$ for an extended regime of 185–800 K. Along the $c$ axis, the apparent electronic anisotropy leads to a much less metallic behavior or in which $\rho_c$, with much weaker temperature dependence above $T_N$, is more than one order of magnitude greater than $\rho_a$ despite the nearly isotropic structure [see Fig. 3(a)]. It is remarkable that the system exhibits a metallic character within the basal plane but insulating behavior out-of-plane above $T_N$. The $c$-axis $\rho_c$ fits perfectly an activation law, $\rho_c \sim \exp(\Delta / T)$, for 125 K $< T < 350$ K; an evident slope change at $T_N$ signals a significant widening of the activation gap $\Delta$ from 0.008 eV above $T_N$ to 0.027 eV below $T_N$ [see inset in Fig. 3(a)]. $\rho_c$ does not follow any power law below 125 K. The occurrence of the sharp MI transition at $T_N$ with the pronounced change of $\Delta$ clearly indicates a strong correlation between the AFM and MI transitions in this iridate. This behavior sharply contrasts with that of Sr$_2$IrO$_4$ in which such a correlation seems more intricate, unconventional, and still open to debate [22,23]. Furthermore, $\rho_a$ exhibits the metallic behavior above $T_N$, which would suggest a Slater transition; however, $\rho_c$ indicates that the insulating state already exists above $T_N$, which seems to be consistent with a Mott transition. This peculiar feature is absent in other iridates. In fact, the distinct temperature dependence of $\rho_a$ and $\rho_c$ above $T_N$ seems similar to that for so-called strange metals, which is observed in the ruthenates [34] and cuprates [35,36].

An extended regime of linear temperature resistivity is a classic signature of high-$T_C$ cuprates and the $p$-wave superconductor Sr$_2$RuO$_4$, Fe-based superconductors and many other correlated oxides [37], in which spin fluctuations play an important role in the electron scattering. Elementary Bloch-Grüneisen theory predicts $\rho(T) \sim T$ for $T \gg \theta_D$, in the case of electron-phonon scattering where Debye temperature $\theta_D = 343$ K for Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$. Resistivity saturation is anticipated when the mean free path $l$ of the quasiparticles becomes shorter than the lattice parameter $a$ (Mott-Ifjﬀe-Regel limit [38,39]), or for $\rho \sim 100–150$ $\mu$Ω cm (Mooij limit [40,41]). Here $\rho_a(T)$ for Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ is well above the Mott-Ifjﬀe-Regel or Mooij limits, and yet shows no sign of saturation up to 800 K. Furthermore, both $\rho_c(T)$ and $\rho_a(T)$ show an anomaly near $T^* = 40$ K that accompanies no corresponding magnetic anomaly. The origin of $T^*$ is unclear but closely related to the Hall resistivity discussed below.

For comparison and contrast, $\rho_a$ for Sr$_{n+1}$Ir$_n$O$_{3n+1}$ with $n = 1, 2$ and Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ ($n = \infty$) is presented in Fig. 3(b). $\rho_a$ decreases rapidly by as much as seven orders of magnitude at low temperatures as $n$ increases from $n = 1$ to $n = \infty$, and the ground state evolves from the insulating state at $n = 1$ to a much more metallic state at $n = \infty$, particularly above $T_N$.

C. Hall resistivity

The Hall resistivity $\rho_H(T)$ is linear in the magnetic field up to 7 T [see inset of Fig. 3(c)], $\rho_H(T)$ taken at $\mu_B H = 7$ T for Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ exhibits an abrupt change in temperature dependence near $T^*$, marking a drop in $\rho_H(T)$, thus a sign change from positive to negative with decreasing temperature, suggesting a multiband effect [Fig. 3(c)]. It appears that holes
as charge carriers predominate above \( T^* \) whereas electrons become overwhelming below \( T^* \). The sign change is probably due to a change with temperature of the mobilities (two-band model). A two-carrier type model \((p \text{ and } n)\) needs to be considered to adequately determine the carrier densities but a rough estimate using the Drude theory yields the carrier densities to be of the order of \( 10^{19} \text{ cm}^{-3} \). Sr\(_{0.94}\)Ir\(_{0.78}\)O\(_{2.68}\) is electron doped by 0.36 electrons per unit formula. It is likely that most of the electrons are trapped by disorder scattering and do not contribute to the Hall resistivity. It is also worth pointing out that the Hall resistivity of this compound is much larger than that in SrIrO\(_3\) [20,21], possibly suggesting a departure from the nearly compensated character of SrIrO\(_3\). This indicates that the severe off stoichiometry of this compound actually provides charge doping.

### D. Heat capacity

The specific heat \( C(T) \) was measured over an extended range, \( 0.05 \text{ K} < T < 250 \text{ K} \). A slope change in \( C(T) \) occurs near \( T_N \), confirming the magnetic phase transition [see Fig. 4(a)]. \( C(T) \) for \( 1 \text{ K} < T < 4 \text{ K} \) approximately fits the

![Figure 2](image2.png)

**FIG. 2.** (a) The temperature dependence at \( \mu_0 H = 0.5 \text{ T} \) of the magnetic susceptibility \( \chi \) for \( a \) axis, \( \chi_a \), and \( c \) axis, \( \chi_c \), and \( \chi_a^{-1} \) (right scale) for Sr\(_{0.94}\)Ir\(_{0.78}\)O\(_{2.68}\). (b) The isothermal magnetization \( M_a \) (blue) and \( M_c \) (red) up to 7 T. (c) The temperature dependence of \( \chi_a \) for Sr\(_{n+1}\)Ir\(_n\)O\(_{3n+1}\) with \( n = 1, 2, \) and \( \infty \). Note \( \theta_{CW} \) and \( \mu_{\text{eff}} \) are the Curie-Weiss temperature and effective moment, respectively.

![Figure 3](image3.png)

**FIG. 3.** The temperature dependence of (a) the \( a \)-axis resistivity \( \rho_a \) and the \( c \)-axis resistivity \( \rho_c \) for Sr\(_{0.94}\)Ir\(_{0.78}\)O\(_{2.68}\) (note that \( \rho_a \) is on a logarithmic scale on the right axis); (b) \( \rho_a \) for Sr\(_{n+1}\)Ir\(_n\)O\(_{3n+1}\) with \( n = 1, 2, \) and \( \infty \); and (c) the Hall resistivity \( \rho_H \) for Sr\(_{0.94}\)Ir\(_{0.78}\)O\(_{2.68}\). Inset in (a): \( \ln \rho_a \) vs \( T^{-1} \). Inset in (c): the magnetic field dependence of \( \rho_H \) at a few representative temperatures.
or tunneling of atoms in a double well potential can also measure of the density of states of the conduction states near $C$ term comes from the phonon contribution; $\gamma$ fields. (c) nonmetallic ground state, $\gamma$ arises from the electronic contribution to $\gamma$ for this iridate is 343 K but can also include a contribution $(\gamma T)^2$ for 100 $< T <$ 2 K before decreasing with increasing $H$. The origin of the unusual field dependence of $\gamma$ is unclear but it could be due to in-gap states and/or a field-induced magnetic order that shifts up to higher temperature with increasing $H$ [Fig. 4(b)]. It is not unusual for strongly correlated electron systems that the expression $\gamma T + (\gamma T)^2$ fit does not continue down to 0 K. This is common for heavy fermion compounds and implies a change of mechanism at very low temperatures.

V. BAND STRUCTURE

Our first-principles calculations for both Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ and stoichiometric SrIrO$_3$ using the LSDA + SOI+U method with $U = 3$ eV result in different band topologies [Figs. 5(a) and 5(b)]. The octahedral crystal field splits the bands into $t_{2g}$ and $e_g$-like orbitals. The bands closest to the Fermi level are $t_{2g}$ orbitals hybridized with $O$. The band structure for SrIrO$_3$ is in agreement with that reported in Ref. [10] [Fig. 5(b)].

For Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$, we use a supercell of Sr$_8$Ir$_6$O$_{22}$, which is sufficiently close to Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ and corresponds to two cells as shown in Fig. 5(c). There are three Ir ions in each cell with different local environments due to the O coordination and tilting and rotations of the octahedra. According to the calculations, the Ir and O deficiencies alter the IrO$_6$ octahedra, leading to three distinct Ir sites denoted by $A$, $B$, and $C$ in Fig. 5(c). For site $A$ the IrO$_6$ octahedra remain intact, and for site $B$ the IrO$_6$ octahedra remain but with a broken Ir-O-Ir bond along the $c$ or $z$ direction; for site $C$, the IrO$_6$ octahedra evolve to IrO$_3$ prisms because of a missing O [Fig. 5(c)]. Note that the tilting and rotations of Ir-O octahedra occur in all three sites. For site $A$, $J_{eff} = 3/2$ and $J_{eff} = 1/2$ states with a magnetic moment of 0.19 $\mu_B$/Ir are anticipated; for site $B$, the broken Ir-O-Ir bond along the $z$ direction renders a fully occupied $d_{xy}$ orbital (the lowest state) and half-filled $d_{yz}$ and $d_{xz}$ orbitals. Thus, as shown in Fig. 5(d), the electrons can easily hop between sites $A$ and $B$, which would explain metallic behavior in the basal plane. The $J_{eff} = 3/2$ and $J_{eff} = 1/2$ states arise from the combined effect of the SOI and the cubic crystalline electric field. The broken Ir-O-Ir bond gives rise to a tetragonal crystal field which is usually larger than a cubic one and competes with the SOI so that the $J_{eff} = 3/2$ and $J_{eff} = 1/2$ states are not formed at site $B$. Similarly, for site $C$ a tetragonal crystalline field develops and the $d_{yz}$ and $d_{xz}$ orbitals are fully occupied, which favors an insulating behavior along the $c$ direction, as indeed indicated in the electrical resistivity [Fig. 3(a)].

The band calculations [Fig. 5(a)] illustrate an insulating ground state in Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ that emerges from a metallic state in SrIrO$_3$ as the Ir and O deficiencies break some pathways of electron hopping along the $c$ axis in Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$. A narrow charge gap of 0.081 eV for Sr$_{0.94}$Ir$_{0.78}$O$_{2.68}$ is predicted, which
FIG. 5. Comparisons of the band structures calculations using LSDA + \( U + SO \) (\( U = 3 \) eV) for (a) \( Sr_{0.94}Ir_{0.78}O_{2.68} \) and (b) stoichiometric \( SrIrO_3 \); the Fermi level is at 0. Note that the energy range, \(-3.0–1.0 \) eV, is dominated by Ir 5\(d\) states whereas the 2\(p\) states of O are located below \(-2.0 \) eV. The crystal fields of the sites \(A\), \(B\), and \(C\) are different from one another and there is strong hybridization between them; the bands cannot be labeled distinctly in the figure. (c) The schematic structure for \( Sr_{0.94}Ir_{0.78}O_{2.68} \) illustrates three different Ir ion sites due to the nonstoichiometry: \(A(5d^5)\), \(B(5d^4)\), and \(C(5d^4)\) (see text), and (d) the corresponding 5\(d\) orbitals and electron hopping between the orbitals.

is somewhat larger but qualitatively consistent with 0.027 eV estimated from \( \rho_c \) below \( T_N \) or for \( 125 < T < 185 \) K.

In essence, the Ir and O deficiencies generate the three distinct Ir sites and it is these differences between them that induces the unexpected anisotropic resistivity [Fig. 3(a)], despite the near-cubic structure of \( Sr_{0.94}Ir_{0.78}O_{2.68} \). It is worth mentioning that the rotation of Ir\(_6\) octahedra within the basal plane is a structural signature of \( Sr_2IrO_4 \) and \( Sr_1Ir_2O_7 \) [28–31] and is critical to the AFM ground state [42]. The AFM state in \( Sr_{0.94}Ir_{0.78}O_{2.68} \) might be in part a result of the increased in-plane rotation of Ir\(_6\) octahedra, 9.45° (compared to 8.75° for \( SrIrO_3 \)), whereas the decreased out-of-plane tilt, which is absent in \( n = 1 \) and 2, may not be as critical in determining the ground state.

The supercell considered here is only a first-order approximation to the real compound. Normalizing \( Sr_{0.94}Ir_{0.78}O_{2.68} \) to 6 Ir ions we have 7.23 Sr atoms and 20.62 O atoms per supercell. This differs somewhat from \( Sr_8Ir_6O_{22} \) and it is therefore necessary to consider a much larger supercell to obtain a more precise band structure with the correct composition. On the other hand, this is only the average composition and one should allow for some fluctuations in the composition. A few details of the calculations need more clarity: No assumption that oxygen vacancies surround the Ir vacancies was made in the calculations. Instead, several possible states were assumed and optimized in order to identify the one having the lowest total energy. The atomic positions were optimized in the calculations. For site \( A \), Ir\(_6\) octahedra hardly change. For site \( B \), the broken Ir-O-Ir bonds along the \( c \) axis reduce the apical Ir-O bonds. For site \( C \), the oxygen vacancy changes the IrO\(_5\) prisms to trigonal bipyramidal.

VI. CONCLUSION

This work reveals the simultaneous AFM and MI transitions that illustrate a direct correlation between the AFM transition and charge gap in the iridate, which is conspicuously absent in \( Sr_2IrO_4 \). The contrasting ground states in isostructural \( Sr_{0.94}Ir_{0.78}O_{2.68} \) and \( SrIrO_3 \) highlight the critical role of the lattice degrees of freedom that along with the delicate interplay of the SOI and \( U \) needs to be adequately addressed both experimentally and theoretically. In particular, the elusive superconductivity in the iridates, despite the apparent similarities between the cuprates and iridates, might be in part due to the ultrahigh sensitivity to lattice distortions in the SOI-coupled iridates; the lattice dependence in the cuprates is much weaker since the SOI, which anchors physical properties to the lattice in general, is negligible.
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