Decoupling of the Antiferromagnetic and Insulating States in Tb-Doped Sr$_2$IrO$_4$

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Decoupling of the antiferromagnetic and insulating states in Tb-doped Sr$_2$IrO$_4$

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Sr$_2$IrO$_4$ is a spin-orbit-coupled insulator with an antiferromagnetic (AFM) transition at $T_N = 240$ K. We report results of a comprehensive study of single-crystal Sr$_2$Ir$_{1-x}$Tb$_x$O$_4$ ($0 \leq x \leq 0.03$). This study found that a mere 3% ($x = 0.03$) of tetravalent Tb$^{4+}$ (4f$^7$) substituting for Ir$^{4+}$ (rather than Sr$^{2+}$) completely suppresses the long-range collinear AFM transition but retains the insulating state, leading to a phase diagram featuring a decoupling of the magnetic interactions and charge gap. The insulating state at $x = 0.03$ is characterized by an unusually large specific heat at low temperatures and an incommensurate magnetic state having magnetic peaks at (0.95,0,0) and (0.95,0,0) in the neutron diffraction, suggesting a spiral or spin-density-wave order. It is apparent that Tb doping effectively changes the relative strength of the spin-orbit interaction (SOI) and the tetragonal crystal electric field and enhances the Hund’s rule coupling that competes with the SOI, and destabilizes the AFM state. However, the disappearance of the AFM is accompanied by no metallic state chiefly because an energy level mismatch for the Ir and Tb sites weakens charge carrier hopping and causes a persistent insulating state. This work highlights an unconventional correlation between the AFM and insulating states in which the magnetic transition plays no critical role in the formation of the charge gap in the iridate.

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I. INTRODUCTION

Sr$_2$IrO$_4$ is a pseudospin-1/2 Heisenberg antiferromagnet (AFM) with a Néel temperature $T_N = 240$ K [1–4] and AFM exchange coupling approximately 0.1 eV [5]. This system is a prototype for physics driven primarily by a strong interplay of on-site Coulomb $U$ and spin-orbit interaction (SOI) [2–6]. The relativistic SOI proportional to $Z^2$ ($Z$ is the atomic number), is approximately 0.4 eV in the iridate (compared to $\sim 20$ meV in 3$d$ materials), and splits the $t_{2g}$ bands into bands with $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$, the latter having lower energy [2,3]. Since the Ir$^{4+}$ (5$d^5$) ions provide five 5$d$-electrons, 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 $U$ ($\sim 0.50$ eV) due to the extended nature of 5$d$-electron orbitals is sufficient to open a gap ($\leq 0.62$ eV) supporting a novel insulating state [2–8]. It has become increasingly clear that the new, delicate balance between the relevant energies renders the ground state extremely susceptible to even slight changes of chemical composition [9–12].

Sr$_2$IrO$_4$ is perhaps the most intensively studied iridate thus far. The distinct energy hierarchy featuring a strong SOI along with its structural and electronic similarities to those of the celebrated La$_2$CuO$_4$ ($K_2NiF_4$ type, one hole per Ir or Cu ion, pseudospin- or spin-1/2 AFM, etc.) has stimulated a surge of interest in the iridates in recent years. A growing list of theoretical proposals predicts, among many SOI-coupled phenomena, novel topological states and superconductivity via electron or hole doping [5,6,13–15]. A recent study of angle-resolved photoemission exhibits a temperature and doping dependence of Fermi arcs at low temperatures via in situ K doping in cleaved crystal surfaces of Sr$_2$IrO$_4$, a phenomenology similar to that of the high-temperature superconducting cuprates [16]. However, superconductivity characterized by zero resistivity and diamagnetism remains elusive despite extensive experimental efforts. Nevertheless, a growing body of experimental evidence has shown that even slight electron or hole doping at either Sr or Ir sites leads to a metallic state despite the sizable energy gap ($\sim 0.62$ eV) inherent in Sr$_2$IrO$_4$. Oftentimes, the AFM state vanishes upon the presence of the metallic state; however, there are exceptions in which the AFM state survives chemical doping at Sr sites and coexists with a doping-induced metallic state [9,10,17,18]. Furthermore, recent high-pressure studies of Sr$_2$IrO$_4$ suggest that the magnetic transition vanishes near 20 GPa [19] but the insulating state persists at high pressure up to 55 GPa [19,20], highlighting an unconventional correlation between the AFM state and the insulating gap. Indeed, a signature behavior of Sr$_2$IrO$_4$ is that transport properties exhibit no discernable anomaly corresponding to the AFM transition at $T_N = 240$ K [1,18,21], sharply contrasting that of other correlated materials and iridates, such as bilayered Sr$_2$Ir$_2$O$_7$ [22] and hexagonal BaIrO$_3$ [23]. It is not surprising that the unusual character of this SOI-coupled insulator has recently revitalized discussions of Mott, Mott-Hubbard, and Slater insulators, particularly the dependence of charge gap formation on magnetic interactions. 

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in Sr$_2$IrO$_4$ [24,25]. Clearly, a better understanding of the $J_{\text{eff}} = 1/2$ insulating state and its correlation with the AFM state in Sr$_2$IrO$_4$ needs to be established.

In this paper, we report results of a comprehensive study of slightly Tb-doped Sr$_2$IrO$_4$ or single-crystal Sr$_2$Ir$_{1-x}$Tb$_x$O$_4$ (0 ≤ $x$ ≤ 0.03). This study utilizes various tools including x-ray absorption near-edge structure (XANES) and x-ray absorption fine structure (XAFS) spectroscopy, neutron diffraction, and other probes to characterize structural, transport, thermal, and magnetic properties of these single crystals. The central finding of this study is that a mere 3% ($x = 0.03$) tetravalent Tb$^{4+}$($4f^7$) substituting for Ir$^{4+}$ (rather than Sr$^{2+}$) completely suppresses the long-range collinear AFM state but retains an insulating state, leading to a phase diagram featuring a decoupling of the magnetic interactions and charge gap. The insulating state at $x = 0.03$ exhibits an unusually large specific heat at low temperatures and accompanies an incommensurate magnetic state that is characterized by magnetic peaks at (0.95, 0, 0) and (0, 0.95, 0) in the neutron diffraction, suggesting a spiral or spin density wave order. Slight Tb doping effectively changes the relative strength of the SOI and the tetragonal crystal electric field (CEF), enhances the Hund’s rule coupling that competes with the SOI, and destabilizes the AFM state; however, there is no concurrent metallic state. This “disentanglement” of the charge and magnetic aspects of doped Mott insulators sharply contrasts with the conventional argument where a simultaneous suppression of the magnetic order and charge gap would be anticipated, as both are primarily driven by the same force, the Coulomb interaction [26].

II. EXPERIMENTAL DETAILS

The single crystals studied were grown from off-stoichiometric quantities of SrCl$_2$, SrCO$_3$, IrO$_2$, and Tb$_2$O$_7$ using self-flux techniques [1,9–11]. The size of the single crystals is as large as 2.0 × 2.0 × 0.2 mm$^3$. The structures of Sr$_2$Ir$_{1-x}$Tb$_x$O$_4$ were determined using a Nonius Kappa CCD x-ray diffractometer at the University of Kentucky and a Rigaku x-ray diffractometer equipped with a PILATUS 200 K hybrid pixel array detector at Oak Ridge National Laboratory. Full data sets were collected between 100 and 300 K, and the structures were refined using the SHELX97-97 programs [27] and FULLPROF software [28]. The chemical compositions of the single crystals were estimated using energy-dispersive x-ray (EDX) analysis (Hitachi/Oxford 3000). The error analysis

FIG. 1. (Color online) (a) A comparison of our XANES results for $x = 0.02$ and 0.03 with peaks for Tb$^{3+}$ and Tb$^{4+}$ ions reported in previous studies; (b) and (c) magnitudes and real parts of the complex Fourier transformation (FT) of the XAFS data (black line) and fits (red line). The XAFS data were fitted using FEFF6 theoretical standards generated with the known crystal structure of Sr$_2$IrO$_4$ at room temperature and placing Tb dopants at Ir sites. Dashed lines indicate the upper bound for the fitting range.
indicates that the error for the Sr and Ir atomic percentage is 0.1% and 3%, respectively, whereas this value for the Tb concentration is \( \sim 11\% \). An example of the EDX results with standard deviation is illustrated in the Supplemental Material [29]. Magnetization, specific heat, and electrical resistivity were measured using a Quantum Design MPMS-[7] superconducting quantum interference device (SQUID) magnetometer and/or a physical Property measurement system with [14]-T field capability.

X-ray absorption near-edge structure and x-ray absorption fine structure measurements were carried out at beamline [4]-ID-D of the Advanced Photon Source, Argonne National Laboratory at room temperature. XANES data at the Tb \( L_3 \) absorption edge were used to determine the Tb valence state by comparing the leading edge position to reference samples with known valence state: Tb\(_2\)O\(_7\) with Tb\(^{3.5+}\) (i.e., mixed valence with equal amounts of 3+ and 4+ states) and BaTbO\(_3\) with Tb\(^{4+}\). XANES and XAFS data were collected in fluorescence geometry due to the low Tb content. A four-element, energy-resolving silicon drift diode detector was used to measure the intensity of the Tb \( Lα_α \) emission as the x-ray energy was scanned through the Tb \( Lα \) absorption edge. Data were corrected for detector dead time. The reference compounds were in powder form while the Tb-doped samples were single crystals oriented in such a way that the electric field of the linearly polarized x rays was in the IrO\(_2\) plane of the tetragonal Sr\(_2\)IrO\(_4\) structure. XAFS data were collected to 13 Å\(^{-1}\) using the same fluorescence geometry. XAFS fits were done using theoretical standards computed with the FEFF6.0 code [30]. Prior to the fittings, simulations of XAFS data were done by placing Tb atoms at either Ir or Sr sites of the Sr\(_2\)IrO\(_4\) lattice to determine that Tb occupies Ir sites.

The neutron diffraction was carried out at Oak Ridge National Laboratory using the elastic diffuse scattering spectrometer (CORELLI) at the Spallation Neutron Source as well as triple-axis spectrometers HB1 and HB1A at the High Flux Isotope Reactor. CORELLI uses a semiblack beam with incident neutron energy ranging from 10 to 200 meV whereas the triple-axis spectrometers HB1 and HB1A utilize

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**FIG. 2.** (Color online) Determination of Tb site substitution by comparing XAFS data and simulations: Panels show XAFS data (black dots and lines) and simulations (red lines for Tb at Ir sites, green lines for Tb at Sr sites) for (a) the magnitude of the complex Fourier transform in real space, (b) the real part of the complex Fourier transform in real space, (c) XAFS in photoelectron momentum space, and (d) the back Fourier transform in photoelectron momentum space. Comparison of XAFS data and simulations: For Tb doping at Ir and Sr sites: Upper panels show data and simulations in real (Fourier-transformed space) while lower panels show data and simulations in photoelectron space. See text for additional details.
incidence energies of 13.50 and 14.64 meV, respectively. The temperature control was achieved via a closed-cycle refrigerator.

III. RESULTS AND DISCUSSION

Rare earth ions are nominally trivalent but there are a number of exceptions, and Tb is one of them. It can be trivalent Tb\(^{3+}\), tetravalent Tb\(^{4+}\), or mixed-valent. The trivalent Tb\(^{3+}\)(4\(^f^8\)) ion has a tendency to lose its eighth 4\(^f\) electron to become tetravalent Tb\(^{4+}\)(4\(^f^7\)). We therefore conducted XANES experiments to determine the valence state of Tb. The results are illustrated in Figs. 1(b) and 1(c) where the magnitudes and real parts of the complex Fourier-transformed XAFS data (black line) and fits (red line) are plotted, respectively. The local Tb-O, Tb-Sr, and Tb-Ir distances were found to be expanded by 0.10(1), 0.12(4), and 0.05(3) Å relative to the Ir-O, Ir-Sr, and Ir-Ir distances in the undoped structure of Sr\(_2\)IrO\(_4\). This is consistent with results from the XANES measurements where Tb is found to be in the tetravalent state (the ionic radius of Tb\(^{4+}\) shell is spherical and does not favor directional bonds.

We have based our conclusion that Tb dopants occupy Ir sites on the results of simulations of Tb XAFS data using FEFF 6.0 theoretical standards (Fig. 2). The simulations are remarkably different for Tb doping at Ir and Sr sites. It suffices to inspect the plots in Fig. 2 to conclude that Tb is...
located at Ir sites since the simulations in that case reasonably agree with the data even without carrying out any fittings. In contrast, the placement of Tb at Sr sites is inconsistent with the data. The local atomic environments around Ir and Sr sites are very different; hence XAFS can easily detect Tb site substitution. For example, for Tb at Ir sites the peaks in Figs. 2(a) are due to oxygen neighbors, Sr neighbors, and then Ir neighbors with increasing distance from the Tb site. In comparison, for Tb at Sr sites the first peak is due to oxygen neighbors, then Ir neighbors, and then Sr neighbors. As seen in these simulations in Fig. 2, placing Tb dopants at Ir sites yields perfect fits to the data by accommodating small distortions related to mismatch in ionic radii between Tb and Ir ions. The XAFS data cannot be fitted with a model in which Tb atoms replace Sr atoms.

A unique and important structural feature, which is absent in La$_2$CuO$_4$, is that Sr$_2$IrO$_4$ crystallizes in a reduced tetragonal structure (space-group I4$_1$/a) due to a rotation of the IrO$_6$ octahedra about the c axis by $\sim 11^\circ$, resulting in a larger unit cell by $\sqrt{2} \times \sqrt{2} \times 2$ [34–38]. This rotation corresponds to a distorted in-plane Ir-O-Ir bond angle $\theta$ critical to the electronic structure [9–12]. Slightly substituting Tb$^{4+}$ for Ir$^{4+}$ (up to 3%) retains the tetragonal crystal structure but causes significant changes in the lattice parameters and reduces structural distortions (Fig. 3). The initial decrease in the unit cell volume $V$ is unusual but it is followed by a sudden increase in $V$ at $x \approx 0.03$, which is anticipated by the increased bonding distances of Tb [Fig. 3(a)]. Similarly, the $c/a$ ratio decreases initially and then rises at $x \approx 0.03$, roughly tracking the changes in $V$. Hence, the variation of $V = (c/a)a^3$ with $x$ is predominantly driven by $(c/a)$, i.e., $c$. It is also remarkable that the rotation of IrO$_6$-octahedra inherent in Sr$_2$IrO$_4$ is considerably reduced so that the Ir-O-Ir bond angle $\theta$ increases almost linearly with $x$ from 156.47$^\circ$ at $x = 0$ to 160.05$^\circ$ at $x = 0.02$ before dropping to 158.60$^\circ$ at $x = 0.03$ [Fig. 3(b)]. These changes have important implications for magnetic properties because of the strong magnetoelastic coupling [21,36–40].

Impurities are expected to disrupt the itinerant order of the Ir spins, which is based on collective modes, and destroy the spin-density waves. Localized moments are much less susceptible to impurities. The tetravalent Tb$^{4+}$ density waves. Localized moments are much less susceptible spins, which is based on collective modes, and destroy the spin-susceptibility the long-range AFM transition temperature $T_N$ because of the strong magnetoelastic coupling [21,36–40].

Fig. 5. (Color online) (a) The temperature dependence of $\Delta \chi^{-1}$ for $0 \leq x \leq 0.03$. Inset: The Tb concentration $x$ dependence of the Curie-Weiss temperature $\theta_{\text{CW}}$ and effective moment $\mu_{\text{eff}}$. (b) The isothermal magnetization $M_a$ (blue) and $M_c$ (red) up to 14 T for $0 \leq x \leq 0.03$.
becomes larger than $M_c$ instead. $M(H)$ at low temperatures is considerably enhanced because of Tb doping. For example, $M_c$ extrapolated to $H = 0$ for $x = 0.03$ is approximately $0.25 \mu_B/\mu$ at $T = 1.8$ K, one order of magnitude stronger than $\sim 0.02 \mu_B/\mu$ for $x = 0$. The field dependence of $M(T,H)$ at 1.8 K is also suggestive of ferromagnetic (FM)-like behavior [see Fig. 5(b) as well as Fig. 4]. While for $x = 0$ $M$ saturates already at $\mu_0 H < 2$ T, for $x = 0.03$ the magnetization does not saturate at 14 T.

These changes in the magnetic state are corroborated by results of our neutron diffraction study, as shown in Fig. 6. With increasing $x$, a signature magnetic peak at (1,0,2) for the AFM state at $x = 0$ [37,38] becomes weakened at $x = 0.005$ [Fig. 6(a)] and eventually vanishes at $x = 0.03$. Note that the magnetic peak intensity at $x = 0.005$ decreases and the magnetic moment is reduced to 90% of that at $x = 0$. The disappearance of the sharp magnetic peak associated with the canted antiferromagnetic configuration at $x = 0$ is accompanied by an emergent incommensurate magnetic order with wave vectors $q_m = (0.95, 0, 0)$ and $(0, 0.95, 0)$. The incommensurate magnetic order becomes better defined at $x = 0.03$ when the higher-$T$ background is subtracted [inset of Fig. 6(b)]. The intensity of the new peaks is much weaker compared to those at $q = (1,0,2)$ for $x = 0$. The new peaks exhibit a clear temperature-dependence and evolve into a featureless background above 30 K.

The occurrence of the pair of peaks at $(0.95,0,0)$ and $(0, 0.95, 0)$ implies a possible spiral order with moments along the $c$ axis or an incommensurate spin-density wave as neutron diffraction probes only the moment component perpendicular to the momentum transfer. The spiral order along the $c$ axis agrees with the stronger $M_c$ at $x = 0.03$ [Fig. 5(b)] and is therefore the more likely scenario. It is likely that the magnetic moment of Tb ions, which tends to polarize the magnetic moment of surrounding Ir ions along with it, is ferromagnetically aligned along the $c$ axis or forms magnetic polarons. Generally, a $c$-axis alignment is more energetically favorable when the tetragonal crystal field effect (CFE) is enhanced [14], and specifically the significantly increased $c/a$ ratio at $x = 0.03$ [Fig. 3(b)] inevitably strengthens the tetragonal CEF, thus favoring the $c$-axis alignment for the Ir moments. In addition, the Hund’s rule coupling is also enhanced on the Tb sites, further increasing the tendency of a FM interaction along the $c$ axis. A strong competition between the in-plane AFM (due to Ir $5d$ electrons) and out-of-plane FM (due to Tb $4f$ electrons) interactions thus accounts for the disappearance of the canted AFM state at $x = 0.03$.

The $a$-axis and $c$-axis electrical resistivity, $\rho_a(T)$ and $\rho_c(T)$, are systematically reduced with $x$. $\rho_a(T)$ decreases by nearly four orders of magnitude at low temperatures from $\sim 10^9 \Omega \text{cm}$ at $x = 0$ to $\sim 10^5 \Omega \text{cm}$ at $x = 0.03$, as shown in Figs. 7(a) and 7(b). The reduction of $\rho_a(T)$ and $\rho_c(T)$ may be
a result of the increased Ir-O-Ir bond angle $\theta$, which makes electron hopping more energetically favorable. However, the insulating state remains at $x = 0.03$ with both $d\rho_a/dT$ and $d\rho_c/dT < 0$. Indeed, the ratio of $\rho(2\text{K})/\rho(300\text{K})$ for $\rho_0(T)$ merely drops by one order of magnitude, from $\sim 10^6$ at $x = 0$ to $\sim 10^5$ at $x = 0.03$; this ratio for $\rho_c(T)$ at $x = 0.03$ is 2500. A close examination of $\rho_a(T)$ and $\rho_c(T)$ reveals that $\rho$ for $x > 0$ follows a variable-range hopping (VRH) model, $\rho \sim \exp \left(1/T^{1/2}\right)$, for a remarkably wide temperature range, particularly for $x = 0.03$. To a lesser extent, $\rho$ for $x = 0$ also follows the VRH behavior [see the inset in Fig. 7(a) for $\rho_a(T)$], suggesting that the structural distortion may play a significant role. Nevertheless, the VRH behavior signals that Anderson localization, rather than thermal activation, dominates the hopping process with long-range Coulomb repulsions between carriers playing an important role in this regime [41–43]. Anderson localization, which is due to disorder in general, may be associated with an energy level mismatch for the Ir and Tb sites that ultimately weakens electron hopping and results in the persistent insulating state.

The specific heat $C(T)$ for $5 < T < 20\text{K}$ approximately fits a common expression, $C(T) = \gamma T + \beta T^3$, where the first term arises from the electronic contribution to $C(T)$ and the second term the phonon contribution; $\gamma$ is usually a measure of the density of states of the conduction states near the Fermi surface and effective mass and $\beta$ is related to the Debye temperature [see Fig. 8(a)]. It is therefore intriguing to have relatively large $\gamma$ in an insulator. The origin of a specific heat linear in $T$ could be two-level tunneling centers between two atomic positions (possibly for the O ions) due to light disorder in the material even for $x = 0$ [17,18,21,44,45]. The increase of $\gamma$ or $C(T)$ with $x$ despite the persistent insulating state [inset in Fig. 8(a)] is due to the Tb$^{3+}$ spins. Below 5 K, the pronounced upturn in $C(T)/T$ for $x > 0$ and its strong dependence on the magnetic field $H$ which is parallel to the c axis [see Fig. 8(b)] is likely due to the spin degrees of freedom of the Tb$^{3+}$. $S = 7/2$ states. The field-dependence of $C(T)/T$ exhibiting a peak that shifts up with increasing temperature when the field is increased [inset in Fig. 8(b)]. This behavior is consistent with weakly correlated Tb$^{3+}$ ions ($S = 7/2$) in a magnetic field. The zero-field entropy $S = \int [C(x = 0.03) - C(x = 0)](dT/T)$ is 0.63 J/mole K. Converted into the entropy per Tb$^{3+}$ spin, we obtain 2.53 $k_B$ which is only slightly larger than the entropy of an $S = 7/2$, i.e., $\ln(8)k_B = 2.08k_B$. 

![Graph](image1)

![Graph](image2)

![Graph](image3)
that suggests an unconventional correlation between the AFM and insulating states in which the magnetic transition plays no critical role in the formation of a charge gap in the iridate.

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[42] Nevill Mott, Metal-Insulator Transitions (Ref. [26]), p. 52.