From $J_{\text{eff}}=1/2$ Insulator to $p$-Wave Superconductor in Single-Crystal Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ ($0 \leq x \leq 1$)

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From $J_{\text{eff}} = 1/2$ insulator to p-wave superconductor in single-crystal Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ (0 $\leq x \leq 1$)

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I. INTRODUCTION

The 5d-electron-based iridates have continuously attracted considerable interest as they display unusual properties primarily resulting from a delicate interplay between strong spin-orbit coupling (SOC) and other competing energies such as Coulomb interactions, noncubic crystalline electric fields, and Hund’s rule coupling [1–3]. The $J_{\text{eff}} = 1/2$ insulating state is a manifestation of physics driven by such a new hierarchy of energies [1,2,4].

Among all the iridates studied, the single-layered Sr$_2$IrO$_4$ has been subjected to the most extensive investigations due to its $J_{\text{eff}} = 1/2$ insulating ground state, and similarities of its crystallographic, electronic, and magnetic structures to those of the undoped high-$T_C$ cuprate La$_2$CuO$_4$. However, IrO$_6$ octahedra in Sr$_2$IrO$_4$ rotate about the c axis by about 12$^\circ$; this distinct structural feature, which is absent in La$_2$CuO$_4$, critically affects the ground state of the iridate. Sr$_2$IrO$_4$ undergoes an antiferromagnetic (AFM) ordering at $T_N = 240$ K, and exhibits a canted magnetic structure that rigidly tracks the staggered rotation of the IrO$_6$ octahedra in Sr$_2$IrO$_4$ [5–8].

It is useful to first compare Sr$_2$IrO$_4$ with its isostructural 4d-based counterparts Sr$_2$RhO$_4$ and Sr$_2$RuO$_4$. Their underlying structural and physical properties are listed in Table I for contrast and comparison. Both Sr$_2$IrO$_4$ and Sr$_2$RhO$_4$ crystallize in a reduced tetragonal structure with space group $I4_1/acd$ due to a rotation of the IrO$_6$ or RhO$_6$ octahedra about the c axis by $\sim 12^\circ$ or $\sim 9^\circ$, respectively, resulting in an unit cell expanded by $\sqrt{2} \times \sqrt{2} \times \sqrt{2}$, as compared to the undistorted cell [9,10]. Despite the structural similarity, Sr$_2$RhO$_4$ is a paramagnetic (PM) correlated metal, sharply contrasting with the magnetic insulator Sr$_2$IrO$_4$ [5,6,9,11,12], owed chiefly to the weaker SOC ($\sim 0.15$ eV), compared with the SOC ($\sim 0.4$ eV) for Sr$_2$IrO$_4$, which renders a smaller splitting between the $J_{\text{eff}} = 1/2$ and $J_{\text{eff}} = 3/2$ bands [1,13]. On the other hand, Sr$_2$RuO$_4$ adopts an ideal tetragonal structure without the rotation of RuO$_6$ octahedra and supports a p-wave superconducting state [14]. Indeed, the impact of the SOC strongly depends on the detailed band structure near the Fermi surface $E_F$, the Coulomb interactions, and the lattice distortions [15–18], and this in part explains differences between the superconducting Sr$_2$RuO$_4$ and metallic Sr$_2$RhO$_4$ which is very close to the borderline of a metal-insulator transition.

In our previous work, we tuned the ground state by substituting Rh for Ir in Sr$_2$IrO$_4$, in an attempt to reduce the SOC [13]. This chemical substitution generates a rich phase diagram for Sr$_2$Ir$_{1-x}$Rh$_x$O$_4$ (0 $\leq x \leq 1$), where a robust metallic state is not fully established until x approaches 1 due in part to a variation of the valence state of Rh with x [13,19,20]. As a natural extension of this study, we have extended our investigation to Ru-doped Sr$_2$IrO$_4$ or Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$. There have been several studies on structural, transport, and magnetic properties of Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ based on polycrystalline samples [21–24]. These studies certainly reveal valuable information about the system. However, given the nature of the layered crystal structure of Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$, single-crystal samples are indispensable to fully and adequately address intrinsic properties of these materials.

In this paper, we report a thorough investigation of structural, transport, and magnetic properties of single-crystal Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ with 0 $\leq x \leq 1$. Ru doping induces a structural phase transition from a distorted tetragonal structure with space group $I4_1/acd$ to a more ideal one with $I4/mmm$ near $x = 0.50$. It is this structural change that marks a concurrent phase transition from the AFM insulating state ($x < 0.50$) to a Ru-doping induced PM metallic state ($x > 0.50$). We also make a comparison between Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ and Sr$_2$Ir$_{1-x}$Rh$_x$O$_4$, highlighting important similarities and differences.

II. EXPERIMENT

The single crystals of Sr$_2$Ir$_{1-x}$Ru$_x$O$_4$ were grown from off-stoichiometric quantities of SrCl$_2$, SrCO$_3$, IrO$_2$, and RuO$_2$ using self-flux techniques. Similar technical details are described elsewhere [4,6,25,26]. The structures of the crystals were determined using a Nonius Kappa CCD x-ray diffractometer at 90 K. Structures were refined by full-matrix least squares
using the SHELX-97 programs [27]. All structures affected by absorption and extinction were corrected by comparison of symmetry-equivalent reflections using the program SADABS [27]. It needs to be emphasized that the single crystals are of high quality and there is no indication of any mixed phases in all the doped single crystals studied. The presence of any mixed phases or inhomogeneity in the single crystals would not allow any converging structural refinements. The standard deviations of all lattice parameters and interatomic distances are smaller than 0.1%. Chemical compositions of the single crystals were estimated using both single-crystal x-ray diffraction and energy-dispersive x-ray analysis (Hitachi/Oxford 3000). Magnetization and electrical resistivity were measured using either a Quantum Design MPMS-7 superconducting quantum interference device (SQUID) magnetometer and/or a physical property measurement system with 14-T field capability.

III. RESULTS AND DISCUSSION

The Ru ion tends to be tetravalent Ru⁴⁺ in perovskite ruthenates [3]. Substituting Ru⁴⁺ (4d⁵) for Ir⁴⁺(5d⁵) in Sr₂IrO₄ changes the crystal structure and adds holes to the t₂g bands. We first examine changes of the crystal structure in Sr₂Ir₁₋ₓRuₓO₄. Sr₂IrO₄ crystallizes in a distorted tetragonal structure with reduced space-group symmetry 14/1/acd due to a rotation of the IrO₆ octahedra about the c axis by ~12° with the lattice parameters a = b = 5.4773(8) Å and c = 25.76(5) Å at T = 90 K. This rotation corresponds to a distorted in-plane Ir-O1-Ir bond angle θ (=156.474° at T = 90 K). In sharp contrast, Sr₂RuO₄ crystallizes in the ideal K₂NiF₄ structure with space group 14/mmm featuring 180° Ru-O1-Ru bonds in the basal plane or no rotation of RuO₆ octahedra [10]. With increasing x, Ru doping initially weakens and eventually eliminates the structural distortions with a decrease in the lattice parameters on the a and c axes and the ratio of c/a, as shown in Fig. 1. More importantly, a structural transition from 14/1/acd to 14/mmm occurs near x = 0.50. The Ir/Ru-O1-Ir/Ru bond angle θ, reflecting the rotation of the octahedra about the c axis, increases with x and becomes 180° abruptly near x = 0.50, the structural transition [see Fig. 2(a)]. The in-plane bond length Ir/Ru-O1 shortens correspondingly with a sudden shortening at the structural transition as well; it then levels off with further increasing x, as shown in Fig. 2(b). On the other hand, the Ir/Ru-O2 bond length, which is more closely associated with the lattice parameter on the c axis, initially decreases with x, and then shows a sudden increase at x = 0.50 before decreasing again with further increase of x [see Fig. 2(c)]. For contrast and comparison, we also illustrate the lattice parameters of Sr₂Ir₁₋ₓRhₓO₄ [see Figs. 2(d)–2(f)]. Apparently, all the bond angles and bond lengths for Rh-doped samples show only slight changes with increasing x, sharply contrasting with those in the Ru-doped Sr₂IrO₄.

![FIG. 1. (Color online) Ru concentration x dependence at T = 90 K of the lattice parameters of the a axis (a), the c axis (b), and the c/a ratio (c). Inset: Representative single-crystal Bragg diffraction peaks for the [001] direction; note the highly ordered crystal structure of Sr₂Ir₁₋ₓRuₓO₄. The shaded area indicates the region where the structural phase transition occurs.](image)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>SOC (eV)</th>
<th>Exemplary phenomena</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr₂IrO₄</td>
<td>I4₁/acd</td>
<td>~0.40</td>
<td>Antiferromagnet / Jₐₐ = 1/2 insulator</td>
</tr>
<tr>
<td>Sr₂RhO₄</td>
<td>I4₁/acd</td>
<td>~0.16</td>
<td>Paramagnet/metal</td>
</tr>
<tr>
<td>Sr₂RuO₄</td>
<td>I4/mmm</td>
<td>~0.15</td>
<td>Paramagnet/p-wave superconductor at low T</td>
</tr>
</tbody>
</table>

TABLE I. Comparison for Sr₂IrO₄, Sr₂RhO₄, and Sr₂RuO₄ [3].
The increased anisotropy in $\rho(T)$ suggests a two-dimensional nature of the electronic structure and is qualitatively consistent with the changes in the in-plane and out-of-plane Ir/Ru-O bond lengths [Figs. 2(b) and 2(c)]. It is remarkable that the resistivity exhibits no discernible effect due to disorder in $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$. In contrast, for Rh substitution the system always remains in proximity to the insulating state. Each Ru atom adds one hole, which gives rise to a higher density of states near $E_F$, more importantly, Ru doping drives a structural phase transition to an ideal tetragonal structure with no octahedral distortion, and thus enhances the electron hopping and supports a more robust metallic state in $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$ when $x$ approaches 1. Under these circumstances disorder in the alloy plays a less relevant role, in contrast to the situation in Rh-doped $\text{Sr}_2\text{IrO}_4$ in which Anderson localization dominates a wide range of Rh doping [13]. Nevertheless, the transport properties of $\text{Sr}_2\text{IrO}_4$ change more drastically with Ru doping, and this trend was observed and briefly discussed when compared to that of Rh-doped $\text{Sr}_2\text{IrO}_4$. The availability of additional single-crystal samples with more different Ru doping levels enables a more comprehensive study of $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$, leading to a rich phase diagram (Fig. 7) discussed below.

The temperature-dependent magnetization $M(T)$ data for representative compositions of single crystals of $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$ are presented in Fig. 4. There is a kink in $M(T)$ for $x = 0$ at 100 K that is attributed to a possible rearrangement of the magnetic order and is closely associated with the magnetoresistivity [30], the magnetoelectric effect [4], and unusual muon responses [31]. Ru doping suppresses the AFM transition $T_N$ from 240 K at $x = 0$ to zero at $x = 0.49$. It needs to be pointed out that the AFM transition $T_N$ for $0.40 < x < 0.49$ becomes less well defined; however, a close

FIG. 2. (Color online) On the left panel, the Ru concentration $x$ dependence at $T = 90$ K of (a) the Ir/Ru-O1-Ru/Ir bond angle $\theta$, (b) the in-plane Ir/Ru-O1 bond length, and (c) the out-of-plane Ir/Ru-O2 bond length. The shaded area indicates the region where the structural phase transition occurs. For comparison, the right panel shows the Rh concentration $x$ dependence of (d) the Ir/Rh-O1-Ir/Rh bond angle $\phi$, (e) the in-plane Ir/Rh-O1 bond length, and (f) the Ir/Rh-O2 bond length. The data for Rh doping are obtained from the crystals used in Ref. [13]. The insets show the definition of the bond angle Ir/Ru-O1-Ir/Ru, and the bond lengths Ir/Ru-O1 and Ir/Ru-O2.

FIG. 3. (Color online) The temperature dependence of the resistivity $\rho(T)$ (a),(b) in the $ab$ plane and (c),(d) along the $c$-axis for representative compositions $x = 0, 0.17, 0.36, 0.49, 0.58, 0.65, 0.74$, and 0.92. The arrows indicate the minimum of $\rho_a(T)$ defining $T^*$. The temperature-dependent magnetization $M(T)$ data for representative compositions of single crystals of $\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4$ are presented in Fig. 4. There is a kink in $M(T)$ for $x = 0$ at 100 K that is attributed to a possible rearrangement of the magnetic order and is closely associated with the magnetoresistivity [30], the magnetoelectric effect [4], and unusual muon responses [31]. Ru doping suppresses the AFM transition $T_N$ from 240 K at $x = 0$ to zero at $x = 0.49$. It needs to be pointed out that the AFM transition $T_N$ for $0.40 < x < 0.49$ becomes less well defined; however, a close
examination indicates that the $T_N$ is not completely suppressed to zero until $x = 0.49$. Nevertheless, it is reasonably close to the classical (i.e., spin-only) two-dimensional site percolation threshold of $x = 0.41$ [32]. It is also noted that the AFM state vanishes at $x = 0.16$ in Rh-doped Sr$_2$IrO$_4$ or Sr$_2$Ir$_{1-x}$Rh$_x$O$_4$ [13]. The rapid suppression of the AFM state is attributed to a varying valence state of Ir and Rh ions and a change in the relative strength of SOC, tetragonal electric field effects, and Hund’s rule coupling, which competes with the SOC and prevents the occurrence of the $I_{eff} = 1/2$ state [13,19].

We analyzed the magnetic data using the Curie-Weiss law $\chi = \chi_0 + C/(T - \theta_{CW})$ (where $\chi_0$ is a temperature-independent constant, $\theta_{CW}$ the Curie-Weiss temperature, and $C$ the Curie constant) and then used $\chi_0$ to obtain $\Delta \chi = \chi - \chi_0 = C/(T - \theta_{CW})$ and $\Delta \chi^{-1}$ vs $T$, as shown in Fig. 5(a). Here, $C = (N_A/3k_B)\mu_{eff}^2$, with $N_A$ being Avogadro’s number and $k_B$ the Boltzmann constant. The effective magnetic moment $\mu_{eff}$ per formula unit is then derived from $C$, as shown in Fig. 5(b). Note that the temperature range for the fit depends on $x$, but a high-temperature interval is used in every case. $\mu_{eff}$ remains essentially unchanged initially and then increases rapidly when $x > 0.49$, peaking at $x = 0.58$ before decreasing with further increasing $x$. The peak happens in the doping range where the structural phase transition takes place [see Figs. 2(a)–2(c)]. The Ru doping dependence of $\mu_{eff}$ is qualitatively consistent with the results in an earlier study on polycrystalline samples [21]. The Curie-Weiss temperature $\theta_{CW}$ tracks $T_N$ for $0 \leq x < 0.49$, and then changes its sign from positive to negative as $x$ increases further, as shown in Fig. 5(c). It is remarkable that the abrupt change in $\theta_{CW}$ also occurs in the range of the structural phase transition, echoing the sudden jump of $\theta_{CW}$ for 0.49, and then changes its sign from positive to negative where no long-range order exists. Since $\theta_{CW}$ measures the strength of the magnetic interaction, such a large absolute value of $\theta_{CW}$ in a system without magnetic ordering implies a strong magnetic frustration, which may primarily result from a competition between the AFM (Ir 5$d$ electrons) and ferromagnetic (Ru 4$d$ electrons) coupling.

Ru doping affects the magnetic anisotropy as well. The $c$-axis magnetization $M_c$ becomes stronger than the $a$-axis magnetization $M_a$, especially at low temperatures, with increasing $x$ (see Fig. 6 as well as Fig. 4). This behavior is absent in Rh-doped Sr$_2$IrO$_4$ but is observed in Ca$_2$Ru$_{1-x}$Ir$_x$O$_4$ due to the strong interaction between Ru 4$d$ and Ir 5$d$ electrons [33]. For $x = 0$, $M_c$ is larger than $M_a$ because the magnetic moment lies within the basal plane [7]. Upon Ru doping, $M_c$ becomes larger than $M_a$ at low temperatures initially and then throughout the entire temperature range measured for $x > 0.58$ (see Fig. 6). This change suggests a spin flop from the basal plane to the $c$ axis due to Ru doping. Interestingly, Rh doping (up to $x = 0.12$) rearranges the in-plane magnetic configuration without any $c$-axis magnetic component [13].

The above evolution of the transport and magnetic properties closely follows the changes in the lattice properties. As illustrated in Figs. 2(a) and 2(b), Ru doping results in an increase in the Ir/Ru-O1-Ir/Ru bond angle and a decrease in the in-plane Ir/Ru-O1 bond length, which inevitably enhance the $d$-orbital overlap or electron hopping. These lattice changes along with added holes and reduced SOC explain the drastic decrease in the electrical resistivity (Fig. 3) and the vanishing AFM state.

FIG. 5. (Color online) (a) The temperature dependence of magnetic susceptibility $\Delta \chi^{-1}$ for the representative compositions $x = 0.17, 0.40, 0.58$, and 0.74. The Ru concentration $x$ dependence of (b) the magnetic effective moment $\mu_{eff}$, and (c) $T_N$ and $\theta_{CW}$. Note the varying temperature intervals for the fit.
The phase diagram is the structural phase transition from a distorted $I4_1/acd$ to a more ideal $I4_1/mmm$ tetragonal structure near $x = 0.50$; this structural phase transition accompanies a magnetic transition from the canted-antiferromagnetic-insulating (CAF-I) to the paramagnetic-metal (PM-M) ground state. All results indicate that the Ru$^{4+}(4d^4)$ substituting for Ir$^{4+}(5d^5)$ adds holes into the $t_{2g}$ bands and reduces SOC but it is the lattice degrees of freedom that primarily drive the rich phase diagram. Remarkably, this phase diagram contrasts with that of Rh-doped Sr$_2$IrO$_4$ (Fig. 5 in Ref. [13]) in which the AFM state vanishes more rapidly (at 16% Rh doping) but the insulating state is much more resilient to Rh doping, in part because of the rotation of RhO$_8$ octahedra in Sr$_2$RhO$_4$ that leads to a band folding and narrowing, giving rise to nearly degenerate states close to the Fermi level [17] and because of the varying valence state of both Rh and Ir that causes the Anderson localization [13,19,20].

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