Ground-State Tuning of Metal-Insulator Transition by Compositional Variations in BaIr\(_{1-x}\)Ru\(_x\)O\(_3\) (0 ≤ \(x\) ≤ 1)

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Ground-state tuning of metal-insulator transition by compositional variations in BaIr\(_{1-x}\)Ru\(_x\)O\(_3\) (0 ≤ x ≤ 1)

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Hexagonal BaIrO\(_3\) is a magnetic insulator driven by the spin-orbit interaction (SOI), whereas BaRuO\(_3\) is an enhanced paramagnetic metal. Our investigation of structural, magnetic, transport, and thermal properties reveals that substitution of Ru\(^{4+}\) (4\(d^4\)) ions for Ir\(^{4+}\) (5\(d^5\)) ions in BaIrO\(_3\) reduces the magnitudes of the SOI and a monoclinic structural distortion and rebalances the competition between the SOI and the lattice degrees of freedom to render an evolution from a magnetic insulating state to a robust metallic state. The central findings of this paper are as follows: (1) light Ru doping (0 < x ≤ 0.15) prompts simultaneous, precipitous drops in both the magnetic ordering temperature \(T_N\) and the electrical resistivity, and (2) heavier Ru doping (0.41 ≤ x ≤ 0.9) induces a robust metallic state without any long-range magnetic order. All results suggest a critical role of the lattice degrees of freedom in determining the ground state in the heavy transition-metal oxides.

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I. INTRODUCTION

A unique feature of the 5\(d\) iridates is that a strong spin-orbit interaction (SOI) competes vigorously with Coulomb interactions, noncubic crystalline electric fields, and Hund’s rule coupling [1–5]. The relative strengths of these interactions stabilize new exotic ground states that provide a fertile ground for studying new physics. In particular, it is now recognized that strong SOI can drive novel narrow-gap Mott insulating states in iridates. The SOI is a relativistic effect that is proportional to \(Z^2\) (Z is the atomic number), is approximately 0.4 eV in the iridates (compared to ~20 meV in 3\(d\) 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. Since the Ir\(^{4+}\) (5\(d^5\)) ions provide five \(5d\) valence electrons, four of them fill the lower \(J_{\text{eff}} = 3/2\) bands, and one electron partially occupies the \(J_{\text{eff}} = 1/2\) band in which the Fermi level \(E_F\) resides. The \(J_{\text{eff}} = 1/2\) band is so narrow that even a reduced \(U\) (~0.50 eV due to the extended nature of 5\(d\)-electron orbitals) is sufficient to open a gap (~0.62 eV) that induces a novel insulating state, which is contrary to expectations based upon the relatively large unsplit 5\(d\) bandwidth [1–3,6].

Adopting a distorted hexagonal structure with both face-sharing and corner-sharing IrO\(_6\) octahedra, BaIrO\(_3\) is particularly unique in that it exhibits a simultaneous onset of weak ferromagnetic transition due to a canted antiferromagnetic structure and charge-density wave (CDW) orders with Néel temperature \(T_N = 183\) K, comparable to that of other iridates, such as 240 K for Sr\(_2\)IrO\(_3\) [7] and 285 K for Sr\(_2\)Ir\(_2\)O\(_7\) [8], and a temperature-driven transition from a bad metal to an insulating ground state [9–11]. The ground state of BaIrO\(_3\) is extremely sensitive to lattice contractions that can be tuned by light doping or the application of hydrostatic pressures [4,12,13]. The extraordinary delicacy of the ground state in BaIrO\(_3\) implies a critical balance among orbital, electronic, and lattice degrees of freedom [4,14]. The hexagonal structure of BaIrO\(_3\) is similar to that of nine-layered rhombohedral BaRuO\(_3\), which exhibits a crossover from metallic to insulating behavior and enhanced paramagnetism with decreasing temperature [15,16]. However, a monoclinic distortion extant in BaIrO\(_3\) at room temperature and 90 K generates twisting and buckling of the cluster trimers (see Fig. 1) that give rise to two one-dimensional (1D) zigzag chains along the \(c\) axis and a two-dimensional layer of corner-sharing IrO\(_6\) octahedra on the \(ab\) plane [9,12,17–19].

Although BaIrO\(_3\) and BaRuO\(_3\) have similar structures, they exhibit sharply contrasting physical properties, which underscore the critical role SOI (~0.4 eV for iridates and ~0.15 eV for ruthenates) [3], and the lattice degrees of freedom can play in determining the ground state in iridates. In this paper, substituting Ru\(^{4+}\) (4\(d^4\)) for Ir\(^{4+}\) (5\(d^5\)) in single-crystal BaIr\(_{1-x}\)Ru\(_x\)O\(_3\) (0 ≤ x ≤ 1) reduces the magnitude of the SOI, the structural distortions, and adds holes to the \(t_{2g}\) bands. The overall effect of Ru doping is to lower \(E_F\) and move the system away from the Mott instability toward a more robust metallic state. The emerging metallic state with delocalized electrons also accompanies a decrease in \(T_N\).

II. EXPERIMENT

The single crystals of BaIr\(_{1-x}\)Ru\(_x\)O\(_3\) were grown by conventional flux methods similar to earlier reports [9,15] using BaCl\(_2\) as a self-flux. Crystals were grown in platinum crucibles using IrO\(_2\) (99.98%, Alfa Aesar), RuO\(_2\) (99.98%, Alfa Aesar), BaCO\(_3\) (99.99%, Alfa Aesar), and anhydrous BaCl\(_2\) (99.5%, Alfa Aesar). Starting powders were placed in a Pt crucible with a Pt lid, and this assembly was then put in an alumina crucible with a cover. The mixtures were heated up to 1480 °C and then cooled to 1350 °C at a rate of 5 °C per hour before cooling down to room temperature. The ratio of the sample to flux remains at 1:8 throughout the entire series of BaIr\(_{1-x}\)Ru\(_x\)O\(_3\). The crystals have a hexagonal surface and a visible layered texture along the \(c\) axis as
The atomic parameters for BaIr1 data were collected after a field cooling procedure at the top and bottom octahedra of the trimers and the schematic of the parameters and interatomic distances are smaller than 0.1%. The inset in (a) shows a representative single crystal of BaIr1 with (a) 0 ≤ x ≤ 0.15 and (b) 0.42 ≤ x ≤ 1. The data were collected after a field cooling procedure at μ0H = 0.1 T. The inset in (a) shows a representative single crystal of BaIr1-xRu1-xO3 with x = 0. The inset in (b) shows an enlarged χc(T) for x = 0.15.

III. RESULTS AND DISCUSSION

The two end members BaIrO3 and BaRuO3 both have nine-layer rhombohedral phases with different space groups as shown in Figs. 1(a) and 1(b). The C2/m(12) space group of BaIrO3 features three face-sharing IrO6 octahedra forming Ir3O12 trimers that are corner and face shared via IrO6 octahedra (containing Ir1 and Ir3 sites) to form 1D chains along the c axis [12,16–19] [see Fig. 1(a)]. A monoclinic distortion generates twisting and buckling of the trimers (tilted ~12° relative to each other), which gives rise to two 1D zigzag chains along the c axis and a two-dimensional layer of corner-sharing IrO6 octahedra on the ab plane. Substituting Ru4+ for Ir4+ preserves the monoclinic structure in the entire doping range (x ≤ 0.90) except for x = 1 as shown in Table I. It results in a nearly uniform reduction in lattice parameters a-c axes and the unit-cell volume V. This behavior is expected because the ionic radius of Ru4+ (0.620 Å) is slightly smaller than that of Ir4+ (0.625 Å). In addition, the Ir/Ru-O-Ir/Ru bond angle θ increases linearly with increasing Ru concentration x and eventually reaches 180° for x = 1 (i.e., BaRuO3), indicating a significantly less distorted lattice. BaRuO3 or x = 1 exhibits a similar crystal structure with the R3̅m (166) space group as shown in Fig. 1(b). Three RuO6 octahedra share faces in a partial chain, facilitating direct Ru-Ru d-orbital interactions between the octahedra. Each of these triple units or trimers of the octahedra shares corners with its neighbors along the hexagonal axis via nearly 180° bond angles that favor superexchange coupling [Fig. 1(b)].

Ru doping induces pronounced changes in a wide range of physical properties of single-crystal BaIr1-xRu1-xO3. Representative data for the c-axis magnetic susceptibility χc(T) that shows the weak magnetic transition at Tc is depressed from 183 K for x = 0 to 145 K for x = 0.04 and vanishes for x ≥ 0.41 is presented in Fig. 2.

The magnetic anisotropy also decreases with Ru additions as shown in Fig. 3. Magnetic anisotropy is in general a result of SOI; Ru doping weakens the SOI, therefore, leading to a smaller magnetic anisotropy. Furthermore, Hund’s rule coupling competes with the SOI and thus weakens the relative strength of the SOI. With increasing x, the c-axis susceptibility χc(T) becomes relatively stronger and larger than the basal-plane susceptibility χab(T) [see Figs. 3(b) and 3(c)]. This change suggests a spin flop from the basal plane to the c axis due to Ru doping. For x = 1, the basal-plane χab(T) is larger than χc(T) again [see Fig. 3(d)]. Similar phenomena were also observed in Ca2Ru1−xIr1-xO4 [22] and Sr2Ir1−xRu1-xO4 [23]. This behavior could be due to the strong interaction between Ru 4d and Ir 5d electrons.

It is already established that the bond angle θ is critical to the electronic and magnetic structures of iridates [4]. As shown in Fig. 4(a), θ increases linearly with increasing x and...
TABLE I. The crystal structure and refinement details of BaIr_{1-x}Ru_{x}O_{3} at 90 K for x = 0, 0.10, 0.63, and 1 and at 240 K for x = 0.82 and 0.90. The diffractometer is a Nonius Kappa CCD, and the absorption correction is a multiscan SADABS. The Ir/Ru-O_{2}-Ir/Ru bond angle is defined in Fig. 1.

<table>
<thead>
<tr>
<th>x = 0</th>
<th>x = 0.10</th>
<th>x = 0.63</th>
<th>x = 0.82</th>
<th>x = 0.90</th>
<th>x = 1</th>
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<td>(90 K)</td>
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<td>(240 K)</td>
<td>(240 K)</td>
<td>(90 K)</td>
</tr>
</tbody>
</table>

Crystal data

- Crystal system, space group
  - Monoclinic, C12/m1(12)
  - Monoclinic, C12/m1(12)
  - Monoclinic, C12/m1(12)
  - Monoclinic, C12/m1(12)
  - Trigonal, R\bar{3}m (166)

- a-c (Å)

- β (deg) 103.411(1), 103.3402(9), 102.8574(9), 102.939(5), 102.882(4), NA

- V (Å³) 849.10(6), 842.25(3), 824.57(3), 838.28(8), 837.26(7), 615.40(3)

- Z 12, 12, 12, 12, 12, 9

- Bond angle (deg) 161.671(1), 163.678(0), 174.296(1), 175.1(3), 176.1(1), 180.0

Data collection

- Number of measured, independent, and observed [I > 4\sigma(I)] reflections
  - 6066,398,350, 7075,396,369, 7210,398,353, 14459,1643,1525, 14071,1769,1633, 7256,401,398

- R_{int} 0.021, 0.031, 0.035, 0.027, 0.038, 0.025

- R[F^2 > 4\sigma(F^2)] 0.016,0.035,1.05, 0.02,0.049,1.15, 0.025,0.069,1.17, 0.067,0.1847,1.085, 0.0720.205,1.024, 0.02,0.035,1.09

- wR[F^2], S 0.016,0.035,1.05, 0.02,0.049,1.15, 0.025,0.069,1.17, 0.067,0.1847,1.085, 0.0720.205,1.024, 0.02,0.035,1.09

- R_{int} 0.021, 0.031, 0.035, 0.027, 0.038, 0.025

eventually reaches an ideal 180° for x = 1. The increase in \( \theta \) directly enhances the electron hopping and favors a more metallic state with a concurrent decrease in \( T_N \) [see Fig. 4(b)]. Indeed, the evolution from the insulating to the itinerant state upon Ru doping is clearly illustrated in the electrical resistivity \( \rho(T) \). For x = 0, both the ab plane and the c axis \( \rho_{ab}(T) \) and \( \rho_{c}(T) \) exhibit a sharp kink at \( T_N = 183 \) K, consistent with previous results in which the energy gap is estimated to be 0.1 eV [9,17]. With Ru doping, both \( \rho_{ab}(T) \) and \( \rho_{c}(T) \) decrease rapidly (see Fig. 5). It is noted that the metallic behavior at higher temperatures for x = 0.04 [see Fig. 5(b)] does not seem to follow the general trend displayed by other compositions although the behavior is highly reproducible.

![FIG. 3. The magnetic susceptibilities \( \chi(T) \) on the ab plane and along the c axis for representative compositions (a) x = 0, (b) x = 0.10, (c) x = 0.82, and (d) x = 1, respectively. The magnetization was measured after field cooling at \( \mu_0H = 0.1 \) T.](image)

![FIG. 4. The Ru concentration \( x \) dependence of (a) the Ir/Ru-O_{2}-Ir/Ru bond angle \( \theta \) and (b) \( T_N \). The inset: schematic of the Ir/Ru-O_{2}-Ir/Ru bond angle \( \theta \). Note that \( \theta \) increases linearly with increasing \( x \).](image)
FIG. 5. The temperature dependence of the resistivity $\rho(T)$ for representative compositions (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.15$, (d) $x = 0.41$, (e) $x = 0.63$, (f) $x = 0.82$, (g) $x = 0.90$, and (h) $x = 1$. The vertical arrows indicate the kink that corresponds to the weak magnetic transition at $T = T_N$. The origin of this brief occurrence of the metallic state is yet to be understood. Nevertheless, dilute Ru substitutions for Ir result in a reduced $\rho(T)$ and an emerging metallic state for $x > 0.15$. For $x = 1$ or BaRuO$_3$, a broad upturn in $\rho_{ab}(T)$ at low temperatures might be a result of a pseudogap formation and 1D-CDW fluctuations according to Ref. [16].

The temperature dependence of the specific heat $C(T)$ for various $x$’s is given in Fig. 6(a). Fitting the data to $C(T) = \gamma T + \beta T^3$ for $7 < T < 17$ K yields the Sommerfeld coefficient $\gamma$ for the electronic contribution to $C(T)$ [see Fig. 6(b)], which serves as a measure of the electronic density of states at the Fermi level $N(E_F)$ and the effective mass of the carriers. There is a substantial increase in $\gamma$ with dilute Ru concentration; in particular, $\gamma$ reaches 11.75 mJ mol$^{-1}$ K$^{-2}$ for $x = 0.04$ and 15.09 mJ mol$^{-1}$ K$^{-2}$ for $x = 0.15$, compared to $\gamma = 2.34$ mJ mol$^{-1}$ K$^{-2}$ for the parent compound ($x = 0$). The $\gamma$ for $0.04 \leq x \leq 0.15$ in which the metallic state is not fully developed is unexpectedly high, and this is likely due to spin fluctuations existent in the system. Nevertheless, $N(E_F)$ and $\gamma$ eventually decrease with $x$ as shown in Fig. 6(b). In the case of BaRuO$_3$, the smaller values reflect pseudogap formation due to the CDW instability [16].

IV. CONCLUSIONS

We have investigated the structural, magnetic, transport, and thermal properties of BaIr$_{1-x}$Ru$_x$O$_3$. Ru doping rebalances the competition among the SOI, electron correlations, and the lattice degrees of freedom to generate a metallic state for $x > 0.15$. The Ru doping alters the relative strength of the SOI that dictates the ground state, which, in turn, affects the band gap near $E_F$. Unlike the situation in Sr$_2$IrO$_4$ that features an unconventional correlation between the magnetic transition and the charge gap, the evolution of the ground state in BaIr$_{1-x}$Ru$_x$O$_3$ appears to indicate a strong coupling between the magnetic order and the metal-insulator transition. All results suggest the critical role of lattice degrees of freedom that, along with the SOI, dictate the ground state of the heavy transition-metal oxides.

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