Structural, magnetic, and electrical properties of $Li_2Ir_{1-x}Ru_xO_3$

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The crystal structure, resistivity, and magnetic susceptibility of the $\text{Li}_2\text{Ir}_{1-x}\text{Ru}_xO_3$ (x = 0-1) polycrystals have been investigated. We found that the parent antiferromagnetic phase disappears for x > 0.2 and bond dimers appear in the averaged structure for x > 0.5 and likely fluctuate for much smaller x. Unexpectedly, this system remains insulating for all the doping levels, contrary to the predictions based on the one-band $j_{\text{eff}} = 1/2$ Kitaev-Heisenberg model. These results suggest that the honeycomb iridates doped with ruthenium are a unique 5*d*-orbital-based platform for studying the interplay of the charge, orbital, spin, and lattice degrees of freedom.

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A variety of insulating iridium oxides with open $Ir^{4+} 5d$ shells, such as honeycomb-lattice $(Li,Na)_2IrO_3$, square-lattice $(Sr,Ba)_2IrO_4$, hyperkagome-lattice $Na_4Ir_3O_8$, and pyrochlores $R_2Ir_2O_7$ (R = Y, Sm, Eu, and Lu), are a subject of recent intensive investigations. These iridates break the general expectation that open-shell 5*d* systems are wide-band weakly correlated metals, and are characterized as "spin-orbit Mott insulators" owing to the band-narrowing effect of strong spinorbit coupling (SOC) on the Ir 5*d* orbitals [1–3]. Explorations into what types of exotic phenomena can be developed from this novel type of Mott insulator have begun [4].

One particularly interesting question is how the magnetic and electric properties of these iridates evolve upon charge doping—will superconductivity emerge [5–12]? This was motivated by comparing the iridates to the layered cuprates in which high-temperature superconductivity develops when the "parent" antiferromagnetic (AFM) Mott insulating phase is suppressed by doping. Similarly, the layered iridates (Sr,Ba)₂IrO₄ (214) and (Li,Na)₂IrO₃ (213) exhibit long-range AFM ordered ground states as well [8,13–17]. In addition, both the 214 and 213 iridates have been widely modeled as effective one-band total angular momentum $j_{eff} = 1/2$ Mott insulators [1–4,18], comparable to the effective one-band spin S = 1/2Mott insulator modeling of the cuprates. Experimentally, Ru, La, or K doping was found to systematically drive (Sr,Ba)₂IrO₄ to a robust metallic state, although superconductivity is not yet within reach [5–7]. As for (Li,Na)₂IrO₃, the deviation of the observed AFM state from the predicted Kitaev spinliquid (KSL) state [18] seems to be remedied by including the Heisenberg exchanges, as the calculated magnon and single-hole spectra agree with the experiments [15,19–22]. Based on the one-band $j_{eff} = 1/2$ Kitaev-Heisenberg model, it was further predicted that the superconductive ground state would emerge with hole doping [10-12] but the experimental information is lacking.

In this Rapid Communication, we present experimental studies of $\text{Li}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_3$ (x = 0-1) polycrystals on crystal structure, resistivity, and magnetic susceptibility. Since a Ru

atom has one less outer shell *d* electron than an Ir atom, Ru substitution for Ir is generally regarded as hole doping [5]. The essential crystal structure is the honeycomb lattice of the Ir/Ru atoms [Fig. 1(a)]. In Li₂IrO₃ all the Ir-Ir bond lengths are almost the same [23], whereas in Li₂RuO₃ one third of the Ru-Ru bonds are significantly shortened below a metal-insulator transition at 540 K, forming ordered dimers attributed to the formation of molecular orbitals [24–26] or spin singlets [27]. It was anticipated that once the structural phase transition is suppressed, Li₂RuO₃ should be metallic [25]. As expected, we observed that the AFM order in Li₂IrO₃ and the bond-length alternation in Li₂RuO₃ are suppressed by doping the system away from the end members.

Surprisingly, we found that $\text{Li}_2\text{Ir}_{1-x}\text{Ru}_xO_3$ remains insulating for all the doping levels. This sharp contrast between the 213 and 214 iridate systems demonstrates that the fundamental physics of the doped iridates depends strongly on the lattice structure. For the honeycomb lattice, we attribute the hole induced breakdown of the $j_{\text{eff}} = 1/2$ picture to a quasimolecular-orbital Jahn-Teller instability, which reactivates the orbital degree of freedom (DOF) and leads to the large effects of electron-phonon (EP) coupling which cooperates with the electron-electron interaction to account for the persistent insulating character and bond dimerization.

Polycrystalline samples of $Li_2Ir_{1-x}Ru_xO_3$ were synthesized using a solid-state reaction method, as described previously [17,24]. RuO₂ was heated at 1000 K for 6 h and Li₂CO₃ was baked at 500 K for 5 h in air before use. Stoichiometric amounts of Li2CO3, RuO2, and anhydrous IrO2 were mixed, ground, and pelletized. Then, the pellets were placed in an alumina crucible which was covered by a lid and sintered at 975 °C for 24 h, followed by furnace cooling to room temperature. The resulting materials were mixed with 5% Li₂CO₃ in order to compensate the loss of Li₂CO₃ during heating treatment. The mixtures were reground, pelletized, and sintered at 975 °C for 48 h. This step was repeated several times until the final samples were pure $Li_2Ir_{1-x}Ru_xO_3$ without a trace of RuO₂. The structures of the samples were characterized by powder x-ray diffraction (XRD) using a Bruker diffractometer model D8 ADVANCE (a reflection mode with Cu $K\alpha$ radiation and a transmission mode with Mo $K\alpha$ radiation and capillary). Rietveld refinement of the XRD patterns was performed using the code TOPAS4 [28]. Electrical

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FIG. 1. (Color online) (a) Lattice parameters, (b) the β values, (c) the unit-cell volumes, and (d) Ir/Ru-Ir/Ru bond lengths at room temperature as a function of *x* for Li₂Ir_{1-x}Ru_xO₃. The insets schematically illustrate (a) the honeycomb lattice with 1/3 of shorter Ru-Ru bonds and (b) the regular honeycomb lattice with almost same Ir-Ir bonds. The thick solid lines represent short chemical bonds and the thin solid lines represent long chemical bonds.

transport with a four-probe configuration and high-temperature magnetization measurements were carried out in a Quantum Design physical property measurement system (PPMS-9). The low-temperature magnetization measurement was carried out in a Quantum Design magnetic property measurement system (MPMS).

At room temperature, Li2IrO3 and Li2RuO3 have a monoclinic symmetry with space groups C2/m and $P2_1/m$, respectively [23,24]. In order to determine where the structure is changed from C2/m to $P2_1/m$ with increasing x, the XRD patterns for the whole series are tried to be fitted by both crystallographic structures. We found [29] that when x is closed to 1, the patterns can only be fitted well by using the space group of $P2_1/m$; on the other hand, the space group of C2/m has a better fitting quality than $P2_1/m$ near the Li_2IrO_3 side. But in between, especially when x is near 0.5, the patterns can be fitted by using either of the structural models. From the values of the fit residuals (R_n) and R_{wp}), the crossover from $P2_1/m$ to C2/m happens at x = 0.5-0.6. The fitted lattice parameters, the unit-cell volume V_{cell} , and bond lengths between Ir/Ru and Ir/Ru as a function of x at room temperature are shown in Fig. 1. The a- and *b*-axial lattice parameters decrease with increasing *x* for both crystallographic structures; on the other hand, the c-axial lattice parameter slightly increases in general for the C2/mspace group and remains almost unchanged for the $P2_1/m$ space group [Fig. 1(a)]. For the values of the β angle, both of them decrease with x [Fig. 1(b)]. Figure 1(c) shows the change in volume of the unit cell as a function of x. It can be seen that the unit cell shrinks gradually with Ru doping, and the obtained values for the two structures are consistent. It can be ascribed to the slightly smaller ionic radius of Ru^{4+} (0.67 Å) than Ir^{4+} (0.68 Å).

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FIG. 2. (Color online) (a) Temperature dependence of reduced resistivity $\rho(T)/\rho(400 \text{ K})$ of the Li₂Ir_{1-x}Ru_xO₃ polycrystal. The $\rho(400 \text{ K})$ from x = 0 to x = 1 is 27.7, 18.1, 11.2, 8.6, 9.5, 7.8, 2.9, 4.4, 1.7, 7.9, and 8.3 Ω cm, respectively. The fits of $\rho(T)/\rho(400 \text{ K})$ curves (solid red lines) using (b) the thermal activation model for $x \leq 0.5$ and (c) the variable-range hopping model for $0.5 \leq x \leq 1.0$. (d) Fitted thermal activation energy and the characteristic temperature $T_0^{1/3}$.

The most important structural parameters are the bond lengths between Ir/Ru and Ir/Ru ions. Figure 1(d) shows the existence of two x regimes: With Ru doping, the shortest Ru-Ru bond length (Ru/Ir1-Ru/Ir4) decreases gradually for x > 0.5, before which the bond length is almost unchanged with x. On the other hand, the other two Ir/Ru-Ir/Ru bond lengths (Ir/Ru1-Ir/Ru2 and Ir/Ru1-Ir/Ru3) are nearly unchanged and the difference between these two bond lengths is within 3.3% for the whole series, compared with the 14% difference between Ir/Ru1-Ir/Ru2 and Ir/Ru1-Ir/Ru4 in Li₂RuO₃.

Regarding the electron transport properties, all of the temperature dependencies of resistivity $\rho(T)$ for the whole series show insulating behaviors [Fig. 2(a)]. In particular, the resistivity decreases monotonically as x increases, in sharp contrast with the decrease-then-increase behavior generally expected for charge doping between two insulating end members.

The insulating behaviors for both ending members Li₂IrO₃ and Li₂RuO₃ below 400 K are consistent with previous experimental results in the literature [17,24]. Quantitatively, the insulating behavior for $x \le 0.5$ follows the Arrhenius law $\rho = \rho_0 \exp(E_a/T)$ very well, where E_a is the thermal activation energy [Fig. 2(b)]. It is different from that of Na₂IrO₃, where the three-dimensional variable-range hopping (VRH) mechanism seems to dominate the resistivity behavior [13]. However, when $x \ge 0.5$, the behaviors of $\rho(T)$ start to deviate from Arrhenius law and crossover to the VRH region $(\rho = \rho_0 \exp[(T_0/T)^{1/(d+1)}]$, where T_0 is the characteristic temperature and *d* is the dimension of system) [Fig. 2(c)]. The fitting results for d = 2 are slightly better than those for d = 3, implying that the dimensionality of VRH might be two



FIG. 3. (Color online) (a) Temperature dependence of dc magnetic susceptibility $\chi(T)$ of the Li₂Ir_{1-x}Ru_xO₃ polycrystal between 2 and 400 K at H = 10 kOe with the zero field cooling (ZFC) mode. Inset: Enlarged part of $\chi(T)$ at low temperature for $0 \le x \le 0.3$. (b) Temperature dependence of $\chi(T)$ between 300 and 800 K at H = 10 kOe for $0.3 \le x \le 1$. (c) Fitted Weiss temperature θ , effective moment μ_{eff} of Ir/Ru, and transition temperature T_K at high temperature as a function of *x* for Li₂Ir_{1-x}Ru_xO₃.

dimensional. As shown in Fig. 2(d), the fitted E_a and $T_0^{1/3}$ generally decrease with Ru doping.

The magnetic susceptibility as a function of temperature $\chi(T)$ is shown in Fig. 3(a). For Li₂IrO₃, there is a drop at around 15 K, which is consistent with the result in literature and is ascribed to the AFM transition [17]. Fitting the $\chi(T)$ data between T = 150 and 400 K using the Curie-Weiss law,

$$\chi(T) = \chi_0 + C/(T - \theta), \tag{1}$$

we obtained that $\theta = -37.7(2)$ K and C = 0.6174(9) emu K/mol Oe. The Weiss temperature θ is close to the previously reported value [17]. Assuming the g factor equals

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2, the obtained value of C corresponds to an effective moment of $\mu_{eff} = 2.217(2)\mu_B$ for Li₂IrO₃, which is slightly larger than $1.83(5)\mu_B$ reported in Ref. [17]. This value suggests that the spin moment of Ir^{4+} is 1/2. The frustration factor $f = |\theta|/T_N \approx 2.48$. With increasing the content of Ru, the AFM transition is suppressed quickly [the inset of Fig. 3(a)]. When x = 0.1, T_N is shifted to about 3 K and $\theta = -28.6(1)$ K; thus the nominal value of f increases to about 9.5. With further increasing of Ru, the AFM transition becomes incomplete for x = 0.2 and cannot be observed for x > 0.3down to 2 K. It is tempting to attribute the enhancement of magnetic frustration and the suppression of the AFM order to the emergence of the KSL state in the way that Ru doping relatively promotes the Kitaev interaction to dominate the Heisenberg exchange interaction. For the lightly doped regime, this scenario seems compatible with the observed insulating character, as no quasiparticles were found in the KSL regime in recent studies of a single hole moving in the Kitaev-Heisenberg model [21,22], yet it is unlikely to apply to larger x. As shown in Fig. 3(c), the increase of Ru content changes the sign of the Weiss temperature θ from negative to positive around x = 0.4, while the fitted effective moment of Ir/Ru keeps getting smaller. This signals that a different mechanism starts taking over the low-energy physics.

This shift of physics becomes apparent in the other end member, Li₂RuO₃. As shown in Fig. 3(b), the $\chi(T)$ curve for x = 1 drops to a very small value around $T_K = 540$ K, leading to the nearly temperature-independent behavior [χ_0 in Eq. (1)] below 400 K. This is consistent with the dimerization of the Ru-Ru bonds [24-27]. Upon reducing the amount of Ru, the transition temperature T_K shifts to a lower temperature and the changes of $\chi(T)$ at T_K become smaller [Figs. 3(b) and 3(c)]. Finally, this anomaly cannot be observed at $x \sim 0.5$. These results are consistent with the above crystallographic data where the shortest Ir/Ru-Ir/Ru bond length increases gradually with decreasing x and it becomes comparable to the other two bonds at $x \sim 0.5$. Furthermore, we found $\chi_0(x) \approx$ αx , where $\alpha = 0.00111(9)$ emu/mol Oe for 0.1 < x < 0.8[29]. This means that the portion of the bond dimers increases with Ru doping and could exist (fluctuate) well below x = 0.5, generating electronic inhomogeneity.

Since $\operatorname{Ru}^{4+} 4d^4$ is a strong impurity scattering center to Ir^{4+} $5d^5$, it is reasonable to ask whether the Ir/Ru substitutional disorder leads to the Anderson localization in $\text{Li}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_3$. In a comparative study, we found [31] similar structural, magnetic, and electric behaviors in $Li_2Rh_{1-x}Ru_xO_3$ where Ru is a weak impurity scattering center to Rh, since they are nearest neighbors in the periodic table. The Ir/Ru (or Rh/Ru) disorder is thus unlikely the driving force for the persistent insulating behavior in these 213 systems, in accord with the fact that the Ru substitution for Ir can drive a robust metallic state in $Sr_2Ir_{1-x}Ru_xO_4$ (x = 0.5) [5]. Interestingly, there could exist an "intrinsic" source of strong disorder in A_2 IrO₃, namely, the A sites centered at the hexagons of the Ir sublattice could be partially occupied by Ir and vice versa [13,23,32]. It remains to be elucidated how the degree of the Li/Ir disorder is affected by the Ru substitution.

We emphasize that the strong bond dimerization points to the large effect of EP coupling, which was long recognized to be critical for the persistent insulating character of the Mott



FIG. 4. (Color online) Schematic plots of (a) an $(Ir,Ru)_6$ hexagon with six relevant t_{2g} orbitals in the tight-binding approximation and (b) the energy levels of the six quasimolecular orbitals formed by the six t_{2g} atomic orbitals on one hexagon [30] with electron filling corresponding to Li₂IrO₃ (left) and Li₂RuO₃ (right), rendering Li₂RuO₃ subject to the Jahn-Teller splitting of the half-filled doubly degenerate E_{2u} level.

insulators [33]. The different transport behaviors exhibited by the doped 213 and 214 iridates are reminiscent of the historic comparison of the doped nickelate La_{2-x}Sr_xNiO₄ that remains insulating and the doped cuprate $La_{2-x}Sr_xCuO_4$ that becomes metallic for x > 0.03 [34–36]. In the nickelate both $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals are active, while in the cuprate only the latter one is. The orbital DOF interplaying with the charge and spin DOF generally results in a synergy between electron-electron and EP interactions which reinforce each other to drive a stronger tendency to small polarons, domain walls, and charge-density waves in the nickelates than in the cuprates [37,38]. Likewise, charge ordering and large effects of EP coupling were often seen in the Jahn-Teller active manganites with degenerate $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals [39,40]. Here we argue that the essential physics underlying the persistent insulating character of $Li_2Ir_{1-x}Ru_xO_3$ is similarthe doped holes experience the orbital DOF and large effects of EP coupling—rather than the common one-band $j_{eff} = 1/2$ modeling with the EP interaction neglected.

In the following, we describe a possible origin of the hole induced breakdown of the $j_{\text{eff}} = 1/2$ picture employing the quasimolecular-orbital (QMO) concept recently proposed for A_2 IrO₃ [30]. As illustrated in Fig. 4(a), a peculiar feature of the Ir honeycomb lattice is that, although every Ir site contributes three 5*d* t_{2g} (*xy*, *yz*, *zx*) orbitals to the low-energy physics, only one t_{2g} orbital is relevant to a given Ir₆ hexagon in the tight-binding approximation. As a result, the hexagons could

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be approximately treated as independent building blocks of the lattice and the energy levels are determined by forming six molecular orbitals per hexagon [30]. The electron filling is ten electrons for Li₂IrO₃ and eight for Li₂RuO₃ [Fig. 4(b)]. In both cases, the highest occupied QMOs are twofold degenerate with the E_{2u} symmetry. They are fully and half occupied in Li₂IrO₃ and Li₂RuO₃, respectively. This leads to the Jahn-Teller instability in Li₂RuO₃ where the strong bond dimerization is now viewed as a different QMO Jahn-Teller distortion, but in Li_2IrO_3 such instability is absent and the $j_{\text{eff}} = 1/2$ local state can be stabilized. This local-hexagon picture provides a simple explanation for the bond dimerization and its persistence in a wide range of doping levels. It agrees with recent local structural x-ray measurements showing that disordered dimers survive at the nanoscale up to \sim 920 K [26] and also with the absence of bond dimerization in Li₂MnO₃ (where the E_{2u} QMOs are unoccupied) [41]. An intriguing implication of this picture is inhomogeneous deformation of the hexagons with charge disproportion among them in hole-doped Li₂IrO₃ systems.

Finally, it is noteworthy that there exist significant differences between Ru doping and ideal hole doping, because the Ru atom has considerably smaller SOC and larger Coulomb repulsion than the Ir atom. A_{1-x} IrO₃ with depletion of the A = Li or Na atoms between the Ir honeycomb layers could be such an ideal hole-doped 213 system that the variation of the Ir honeycomb lattice is minimal. It is thus urgent to use the A_{1-x} IrO₃ material to verify the above analysis.

In summary, we have studied the structural, magnetic, and electric properties of $\text{Li}_2 \text{Ir}_{1-x} \text{Ru}_x O_3$ polycrystals. We found that this system remains insulating for all the doping levels, contrary to the predictions based on the widely used $j_{\text{eff}} = 1/2$ Kitaev-Heisenberg model. Our analyses suggest that hole-doped honeycomb iridates are a unique 5*d*-orbitalbased platform for studying the interplay of the charge, orbital, spin, and lattice degrees of freedom, which warrants further investigation.

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