Evolution of magnetism in single-crystal Ca$_2$Ru$_{1-x}$Ir$_x$O$_4$ (0≤$x$≤0.65)

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Evolution of magnetism in single-crystal $\text{Ca}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_4$ ($0 \leq x \leq 0.65$)


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We report structural, magnetic, transport, and thermal properties of single-crystal $\text{Ca}_2\text{Ru}_{1-x}\text{Ir}_x\text{O}_4$ ($0 \leq x \leq 0.65$). $\text{Ca}_2\text{RuO}_4$ is a structurally driven Mott insulator with a metal-insulator transition at $T_{\text{MI}} = 357$ K, which is well separated from antiferromagnetic order at $T_N = 110$ K. Substitution of a 5$d$ element, Ir, for Ru enhances spin-orbit coupling and locking between the structural distortions and magnetic moment canting. Ir doping intensifies the distortion or rotation of Ru/IrO$_6$ octahedra and induces weak ferromagnetic behavior along the $c$ axis. In particular, Ir doping suppresses $T_N$ but concurrently causes an additional magnetic ordering $T_{N2}$ at a higher temperature up to 210 K for $x = 0.65$. The effect of Ir doping sharply contrasts with that of 3$d$-element doping such as Cr, Mn, and Fe, which suppresses $T_N$ and induces unusual negative volume thermal expansion. The stark difference between 3$d$- and 5$d$-element doping underlines a strong magnetoelastic coupling inherent in the Ir-rich oxides.

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I. INTRODUCTION

The Coulomb interaction $U$ is generally comparable to the 4$d$ bandwidth $W$ in the 4$d$-based ruthenates, which leaves them precariously balanced on the border between metallic and insulating behavior, or on the verge of long-range magnetic order. A common characteristic of these materials is that underlying physical properties are critically linked to the lattice and orbital degrees of freedom and tend to exhibit a giant response to modest lattice changes. This is dramatically illustrated by Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$, where the former compound exhibits a prototypical p-wave superconducting state [1] that strongly contrasts with the more distorted structure (due to a smaller ionic radius $r_{\text{Ca}} < r_{\text{Sr}}$) and first-order metal-insulator transition, $T_{\text{MI}}$, observed for the latter compound [2,3].

Extensive investigations of $\text{Ca}_2\text{RuO}_4$ [4,5] have established that a strong cooperative Jahn-Teller distortion removes the degeneracy of the three Ru 2$g$ orbitals ($d_{x^2}, d_{y^2}, d_{z^2}$) via a transition to orbital order that, in turn, drives the metal-insulator transition at $T_{\text{MI}} = 357$ K [6–14]. Classic Mott insulators undergo simultaneous transitions to antiferromagnetic (AFM) order and an insulating state at $T_{\text{MI}}$. However, Ca$_2$RuO$_4$ undergoes AFM order at $T_N = 110$ K $\ll T_{\text{MI}}$ [2], and is therefore a highly interesting and unique archetype of a metal-insulator transition that is strongly coupled to a structural transition from a high-$T$ tetragonal to low-$T$ orthorhombic distortion and is not driven by AFM exchange interactions [2,3,6,12].

We recently observed that slight substitutions of a 3$d$ element $M$ ($M = \text{Cr}, \text{Mn}, \text{Fe}$) for Ru shifts $T_{\text{MI}}$, weakens the orthorhombic distortion, and induces either metamagnetism or magnetization reversal below $T_N$ [12–14]. Furthermore, $M$ doping for Ru produces substantial negative thermal expansion in Ca$_2$Ru$_{1-M}$O$_4$, with a total volume expansion ratio $\Delta V/V$ as high as 1% on cooling. The onset of the negative thermal expansion closely tracks shifts of $T_{\text{MI}}$ and $T_N$, and sharply contrasts with classic examples of negative thermal expansion that show no correlation with electronic properties. These unusual observations suggest a complex interplay between orbital, spin, and lattice degrees of freedom [12–14].

It is important to note Ru$^{4+}$($4d^{n+}$) ions tend to adopt a low-spin state or $S = 1$ state because relatively large crystal fields often overpower the Hund’s rule coupling [15]. On the other hand, the spin-orbit coupling (SOC) may be strong enough to impose a competing singlet, or an angular momentum, $J_{\text{eff}} = 0$, ground state [15,16]. Compared to 4$d$ ruthenates, 5$d$ iridates have stronger SOC ($\sim 0.4$ eV, compared to $\sim 0.16$ eV for Ru ions) [17], which compete vigorously with Coulomb interactions, noncubic crystalline electric fields, and Hund’s rule coupling [17–21]. A profound manifestation of this competition is the interesting “$J_{\text{eff}} = 1/2$ Mott state” that was recently observed in the layered iridates with tetravalent Ir$^{4+}$($5d^{n+}$) ions [18,19]. Therefore, substitution of Ir for Ru in 4$d$ ruthenates is expected to promote alternative magnetic behavior. Moreover, in light of the unique insulating state recently discovered in Sr$_2$IrO$_4$ [18], a comparison with its isostructural compound Ca$_2$IrO$_4$ would be desirable. However, the structural instability prevents the formation of the perovskitelike Ca$_2$IrO$_4$; the heavily Ir-doped Ca$_2$RuO$_4$ or Ca$_2$Ru$_{1-M}$Ir$_M$O$_4$ with $x$ up to 0.65 thus provides an alternative for comparison and contrast to the archetype $J_{\text{eff}} = 1/2$ insulator Sr$_2$IrO$_4$ that antiferromagnetically orders at 240 K [22].

In this paper, we report results of our study of single-crystal Ca$_2$Ru$_{1-x}$Ir$_x$O$_4$ with $0 \leq x \leq 0.65$. Our central findings are that increasing Ir substitution suppresses $T_N$ but simultaneously induces an additional magnetic order at a higher temperature, $T_{N2}$, which reaches as high as 210 K at $x = 0.65$. Ir doping also causes a dramatic increase in moment canting and the appearance of a weak ferromagnetic (FM) moment along the $c$ axis, along with enhanced magnetic anisotropy due to increased SOC. The increase in both $T_{N2}$ and $T_{\text{MI}}$ with increased Ir doping closely follows the enhanced Ru/IrO$_6$
octahedral rotation or reduced Ru/Ir-O-Ru/Ir bond angle. This study reveals that Ir doping enhances the coupling between the lattice and magnetic moment, sharply contrasting 3d-element doping that readily reduces such a coupling and orthorhombic distortions; it thus suppresses the AFM and insulating states. The pronounced difference illustrated in this study highlights a strong magnetoelastic coupling inherent in the SOC-driven iridates that dictates magnetic properties. This work also provides an important comparison to the extensively studied Sr2IrO4.

II. EXPERIMENT

Single crystals were grown using flux techniques described elsewhere [23]. The structures of Ca2Ru1−xIr4O4 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 [24]. All structures affected by absorption and extinction were corrected by comparison of symmetry-equivalent reflections using the program SADABS [24]. It needs to be emphasized that the single crystals are of high quality and there is no indication of any mixed phases or inhomogeneity in the single crystals studied. The standard deviations of all lattice parameters and interatomic distances are smaller than 0.1%. More detailed information is available in the Supplemental Material (SM) [25]. Chemical compositions of the single crystals were estimated using both single-crystal x-ray diffraction and energy dispersive x-ray (EDX) analysis (Hitachi/Oxford 3000). Magnetization, specific heat, and electrical resistivity were measured using the SQUID Magnetometer and/or a Physical Property Measurement System with 14-T field capability.

III. RESULTS AND DISCUSSION

Ca2RuO4 adopts a very peculiar distortion of the K2NiF4 prototype with a Pbc a (61) space group consisting of layers of RuO6 octahedra separated by Ca atoms [4,14]. Neighboring corner-shared octahedra tilt and rotate in an ordered manner; as a result, the Ru-O-Ru bond angle is severely distorted from 180°.

Substituting Ir4+ for Ru4+ preserves the crystal structure but results in a reduction in the a- and b-axis lattice parameters and an elongation in the c-axis lattice parameter, and eventually shrinks the unit cell volume V, as shown in Fig. 1(a). Compared to the parent compound Ca2RuO4, the c/a ratio increases, by 1.9% for x = 0.5 at 90 K, for example. The orthorhombic distortion also increases with increasing x; e.g., (b − a)/b = 0.0437465 for x = 0, and (b − a)/b = 0.0467 for x = 0.5 at 90 K. The decrease in the bond angle Ru/Ir-O1-Ru/Ir, θ, is a further manifestation of more distorted Ru/IrO6 octahedra for the Ir-doped compounds, sharply contrasting with that for a 3d-element doping [12–14]. The decrease in θ has important implications for magnetic and transport properties, as discussed below.

The magnetic susceptibility χ(T) of the parent compound Ca2RuO4 exhibits a sharp anomaly due to AFM ordering at TN = 110 K [see inset in Fig. 2(a)] [2]. Ir doping induces pronounced changes in the magnetic properties of single-crystal CaRu1−xIr3O4, as shown in Fig. 2. It suppresses TN but concurrently introduces an additional magnetic ordering TN2 at higher temperatures. For example, TN decreases to 80 K at x = 0.34 from 110 K at x = 0; at the same time, TN2...
emerges at 190 K, as shown in Fig. 2(a), \( T_{N2} \) signals a weak FM behavior along the \( c \) axis. The sizable hysteresis in isothermal magnetization along the \( c \) axis is consistent with the weak FM behavior, as shown in Figs. 2(b) and 2(c). Furthermore, there is a strong magnetic anisotropy that renders a much weaker magnetic response in the \( ab \) plane.

\( \text{Ca}_2\text{RuO}_4 \) has a canted AFM structure adapted to a Dzyaloshinskii-Moriya (DM) interaction on a distorted orthorhombic perovskite structure \([14,26-29]\). The spins are canted away from the \( ab \) plane toward the \( c \) axis; consequently the value of the susceptibility along the \( ab \) plane is lower than along the \( c \) axis [see inset in Fig. 2(a)]. The crystal and magnetic structures suggest that the easy axis for AFM order lies in the \( ab \) plane \([2,4]\). The susceptibility cusp at \( T_N = 110 \text{ K} \) for \( x = 0 \) indicates that the canted moments in successive layers interact antiferromagnetically. The enhanced distortions in Ir-doped compounds \( \text{CaRu}_{1-x}\text{Ir}_x\text{O}_4 \) having larger \( c/a \) ratios and smaller Ru/Ir-O1-Ru/Ir bond angles further reduce the symmetry and enhance the DM interaction. In contrast to the parent compound \( \text{Ca}_2\text{RuO}_4 \), the interlayer interaction in Ir-doped compounds drives the weak FM behavior observed along the \( c \) axis (see Figs. 2 and 3). Figure 2(d) shows a schematic picture of the moment configuration of \( \text{CaRu}_{1-x}\text{Ir}_x\text{O}_4 \). The net moments along the \( c \) axis for individual layers exhibit FM coupling due to canting. It is remarkable that the interlayer coupling changes from AFM coupling for the parent compound \( \text{Ca}_2\text{RuO}_4 \) to FM coupling for Ir-doped compounds.

Indeed, the evolution of the magnetic behavior is remarkably consistent with a theoretical proposal for the iridates that suggests an increased \( c/a \) ratio tends to result in a spin-flop transition to a collinear magnetic order along the \( c \) axis due to a strong magnetoelastic coupling \([30]\). That the increase in \( T_{N2} \) closely tracks the decrease in the Ir/Ru-O1-Ir/Ru bond angle \( \Theta \) also manifests the strong magnetoelastic coupling [Fig. 1(b)] \( \text{Ca}_2\text{RuO}_4 \).

It is now recognized that the 5d-based iridates have strong SOC that competes vigorously with Coulomb interactions, noncubic crystalline electric fields, and other relevant energies, leading to the \( J_{\text{tot}} = 1/2 \) state \([17-21]\). One profound result of this competition is that 5d iridates exhibit complex magnetic states with high critical temperatures, such as \( \text{Sr}_2\text{IrO}_4 \) \( (T_N = 240 \text{ K}) \) \([22]\), \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) \( (T_N = 285 \text{ K}) \) \([31,32]\), and \( \text{BaIrO}_3 \) \( (T_C = 183 \text{ K}) \) \([33,34]\). It is established that the magnetic moment and ordering temperature are closely associated with the Ir-O-Ir bond angle \( \Theta \) \([35]\). In particular, a recent study reveals that there is a perfect locking between the octahedral rotation and also magnetic moment canting angles that can persist even in the presence of large noncubic local distortions \([35,36]\). Since Ir doping further reduces \( \Theta \), it is not surprising that \( T_{N2} \) steadily rises with \( x \), as shown in Figs. 3(a) and 3(b); \( T_{N2} \) reaches 210 K for 65% of Ir doping, and would approach an even higher temperature for 100% of Ir doping or \( \text{Ca}_2\text{IrO}_4 \) according to the upward trajectory in Fig. 3(c) should perovskitelike \( \text{Ca}_2\text{IrO}_4 \) exist.

The temperature dependence of the electrical resistivity \( \rho(T) \) of \( \text{CaRu}_{1-x}\text{Ir}_x\text{O}_4 \) is shown in Fig. 4. It is clear that the metal-insulator transition increases from \( T_{\text{MI}} = 357 \text{ K} \) for \( x = 0 \) to \( T_{\text{MI}} = 369 \text{ K} \) for \( x = 0.016 \), and \( T_{\text{MI}} = 384 \text{ K} \) for \( x = 0.03 \), beyond which it is no longer well defined. (It is noted that the slope of the resistivity above \( T_{\text{MI}} \) is still slightly negative. The magnitude is a few orders of magnitude smaller and the temperature dependence is much weaker compared...
to those below $T_{MI}$; thus $T_{MI}$ qualifies for a metal-insulator transition.) The increase in $T_{MI}$ closely tracks the enhanced distortions of the Ru/ IrO$_6$ octahedra with reduced Ru/Ir-O1-Ru/Ir bond angle $\Theta$. This behavior contrasts with that of a 3$d$ transition-metal ion $M$ (Cr, Mn, Fe) that weakens the orthorhombic distortions, thus, the insulating state [12,13]. The resistivity data over the interval $220 < T < 290$ K fit an activated behavior with a gap of about 0.40 eV for $x = 0$, and 0.28 eV for the Ir-doped crystals. Variable-range hopping (VRH) model $[\rho \sim \exp(1/T)^{1/2}]$ fits were more successful for $x = 0$, suggesting Anderson localization is relevant in the parent compound. However, VRH fails to describe the resistivity of Ir-doped crystals.

The heat capacity $C(T)$ data for 0.016 $x \leq 0.65$ show weak or no anomaly at $T_N$ and $T_{N2}$, while the anomaly around $T_{MI}$ for $x = 0.016$ confirms that the metal-insulator transition involves a structural phase transition between the high-$T$ tetragonal to low-$T$ orthorhombic distortion [12,13], as shown in Fig. 5(a). Interestingly, the heat capacity of Sr$_2$IrO$_4$ also shows no corresponding anomaly at the magnetic ordering temperature 240 K, which is one of its signature features of the $J_{eff} = 1/2$ insulator [32]. Fitting the data to $C(T) = \gamma T + \beta T^3$ for $1.7 < T < 20$ K yields the Sommerfeld coefficient $\gamma$ for the electronic contribution to $C(T)$, 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 no substantial increase of $\gamma$ with Ir concentration [Fig. 5(b)].

The small values of $\gamma$ are consistent with the low electrical conductivity observed at low temperatures. The slight increase in $\gamma$ with increasing $x$ results from the moderate drop in activation gap for Ir-doped compounds.

IV. CONCLUSIONS

The substitution of Ir for Ru in CaRuO$_4$ enhances the SOC and intensifies the distortions of the Ru/IrO$_6$ octahedra. As a result, the metal-insulator transition rises and a pronounced weak ferromagnetic behavior occurs, which strengthens with increasing Ir concentration. The Ir-induced ordering temperature $T_{N2}$ reaches 210 K at $x = 0.65$, which is remarkably comparable to 240 K for Sr$_2$IrO$_4$ [22], along with the enhanced magnetic anisotropy due to SOC. The increase in both $T_{N2}$ and $T_{MI}$ with increased Ir doping closely follows the enhanced Ru/IrO$_6$ octahedral rotation or reduced Ru/Ir-Ir bond angle. More generally, the effect of Ir doping tends to strengthen the coupling between the lattice and magnetic moment whereas a 3$d$-element doping readily reduces such a coupling and the orthorhombic distortions, thus suppressing the AFM and insulating states and causing the unusual negative volume expansion as well. For comparison and contrast, the magnetic susceptibility for some representative 3$d$-element and Ir-doped Ca$_2$Ru$_{1-x}$M$_x$O$_4$ compounds including the parent compound Ca$_2$RuO$_4$.

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