Lattice-Tuned Magnetism of Ru\(^{4+}(4d^4)\) Ions in Single-Crystals of the Layered Honeycomb Ruthenates: Li\(_2\)RuO\(_3\) and Na\(_2\)RuO\(_3\)

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We synthesize and study single crystals of the layered honeycomb lattice Mott insulators Na\(_2\)RuO\(_3\) and Li\(_2\)RuO\(_3\) with magnetic Ru\(^{4+}(4d^4)\) ions. The newly found Na\(_2\)RuO\(_3\) features a nearly ideal honeycomb lattice and orders antiferromagnetically at 30 K. Single-crystals of Li\(_2\)RuO\(_3\) adopt a honeycomb lattice with either C\(_2/m\) or more distorted P\(_2_1/m\) below 300 K, depending on detailed synthesis conditions. We find that Li\(_2\)RuO\(_3\) in both structures hosts a well-defined magnetic state, in contrast to the singlet ground state found in polycrystalline Li\(_2\)RuO\(_3\). A phase diagram generated based on our results uncovers a new, direct correlation between the magnetic ground state and basal-plane distortions in the honeycomb ruthenates.

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It has been of great interest to study interacting electrons on the honeycomb lattice in various contexts both experimentally (e.g. graphene) and theoretically (e.g. the Kitaev model). Studies of honeycomb materials have intensified in recent years [1-19] in part because strong spin-orbit coupling (SOC) along with other competing interactions and geometric frustration in the honeycomb iridates Na$_2$IrO$_3$ and Li$_2$IrO$_3$ favors a highly anisotropic Kitaev interaction[20] that stabilize exotic ground states such as topological spin-liquids[1]. It is now experimentally established that Na$_2$IrO$_3$ exhibits a peculiar zigzag magnetic order at $T_N=18$ K[5, 14, 15], and Li$_2$IrO$_3$ also orders at $T_N=15$ K but with a different ground state yet to be defined [3, 17, 21, 22, 23]. Indeed, for (Na$_{1-x}$Li$_x$)$_2$IrO$_3$ with $0 \leq x \leq 0.90$, the measured phase diagram demonstrates a dramatic suppression of $T_N$ at intermediate $x$ suggesting that the magnetic order in Na$_2$IrO$_3$ and Li$_2$IrO$_3$ is different; however, no spin liquid has been observed thus far[17].

Our pursuit of an understanding of the honeycomb iridates has led us to their ruthenate counterparts, Na$_2$RuO$_3$ and Li$_2$RuO$_3$. These materials feature Ru$^{4+}$(4d$^4$) ions and a weaker or “intermediate strength” SOC (~0.16 eV, compared to ~0.4 eV for Ir ions) [24]. The different d-shell filling and contrasting hierarchy of energy scales between the ruthenates and iridates provide a unique opportunity for a deeper understanding of the fundamental problem of interacting electrons on the honeycomb lattices. The magnetism of Ru$^{4+}$ ions as well as other heavy “d$^4$ ions” (such as Rh$^{5+}$(4d$^4$), Re$^{3+}$(5d$^4$), Os$^{4+}$(5d$^4$) and Ir$^{5+}$(5d$^4$)) is interesting in their own right, as emphasized recently[25]. Materials with heavy d$^4$ ions tend to adopt a low-spin state because larger crystal fields often overpower the Hund’s rule coupling. On the other hand, SOC with the intermediate strength may still be strong enough to impose a competing, singlet ground state or an angular
momentum J=0 state. Novel magnetic states may thus emerge when the singlet-triplet splitting (0.05-0.20 eV) becomes comparable to exchange interactions (0.05-0.10 eV) and/or non-cubic crystal fields\[25-27\]. This is evidenced in a recent study of materials containing 5d\(^4\) ions [28].

Up until now, no physical and structural properties of Na\(_2\)RuO\(_3\) have been investigated but a few experimental and theoretical studies of polycrystalline Li\(_2\)RuO\(_3\) have been reported in recent years [29-32]. In essence, polycrystalline Li\(_2\)RuO\(_3\) undergoes a structural phase transition near \(T_D=540\) K that features a change of space group from C2/m (No. 12) at high temperatures to P2\(_1\)/m (No. 11) at low temperatures. The low-temperature phase adopts a strongly distorted honeycomb lattice, which prompts a simultaneous dimerization that results in a singlet ground state [29]. The observation of dimerized zigzag chains has recently stimulated more investigations of Li\(_2\)RuO\(_3\)[30-32], in which the dimerization is attributed to orbital ordering [29], creation of valence bond crystal [30] and Jahn-Teller distortions [31], respectively. It is noted that all reported experimental results were culled from polycrystalline Li\(_2\)RuO\(_3\)[29, 31, 32].

Here we report structural, magnetic, and thermal properties of single-crystalLi\(_2\)RuO\(_3\) and Na\(_2\)RuO\(_3\). The newly found Na\(_2\)RuO\(_3\) with space group C2/m features a nearly ideal honeycomb lattice and orders antiferromagnetically below 30 K. It may serve as a reference for almost perfect honeycomb symmetry. On the other hand, single-crystal Li\(_2\)RuO\(_3\) adopts a less ideal honeycomb lattice with either C2/m or more distorted P2\(_1\)/m below 300 K but both phases exhibit a well-defined, though different, magnetic state, which sharply contrasts with the singlet ground state due to dimerization observed in polycrystalline Li\(_2\)RuO\(_3\)[28]. This work produces a phase diagram that uncovers a direct
correlation between the ground state and basal-planedistortions or lattice-tuned magnetismin all honeycomb ruthenates studied.(Both Li$_2$RuO$_3$ and Na$_2$RuO$_3$ are highly insulating; their transport properties are not included in this paper.)

Crystal Structures Single-crystals of Li$_2$RuO$_3$ and Na$_2$RuO$_3$ were synthesized using the self-flux method, which is described elsewhere [17]. For synthesis of single-crystal Li$_2$RuO$_3$ the mixed chemicals were first heated up to 1250 °C and then cooled to 900 °C at 2 °C/hour and finally room temperature at 50 °C/hour. In contrast, the polycrystalline Li$_2$RuO$_3$ was synthesized at much lower temperature of 950 °C. The different synthesis conditions may have important implications for the ground state of Li$_2$RuO$_3$. For more experimental details, see Supplemental Material [33]. Crystal structures on which the ground state so sensitively hinges require a close examination. Table 1 includes the lattice parameters of single-crystals Li$_2$RuO$_3$ and Na$_2$RuO$_3$ as well as those of polycrystalline Li$_2$RuO$_3$ and iridate counterparts for contrast and comparison. For the sake of discussion, single-crystal Li$_2$RuO$_3$ with C2/m and P2$_1$/m are labeled as Li$_2$RuO$_3$ (C) and Li$_2$RuO$_3$ (P), respectively. A major distinction between Li$_2$RuO$_3$ (C) and Li$_2$RuO$_3$ (P) is the number of unequal Ru-Ru bond distances, which measures distortions that in turn dictate the ground state. Li$_2$RuO$_3$ (C) features two bond distances, or a long and short one, L$_l$ and L$_s$, respectively, whereas Li$_2$RuO$_3$ (P) has three bond distances, i.e., L$_l$, L$_s$, and a medium bond distance, L$_m$. The basal-plane distortion is characterized by the bond difference ratio defined as (L$_l$-L$_s$)/L$_s$, which is shown in Table 1. Figs 1a and 1b. In general, honeycomb lattices with C2/m tend to have a larger a-axis lattice parameter and smaller ratio b/a(~/√3) than those with P2$_1$/m, thus less distorted. Figs. 1c and 1d demonstrate the lattice parameters of single-crystal and polycrystalline samples as a function of temperature. As
seen, no structural transition is discerned in the single crystals studied for the temperature range measured. In short, the structural differences between the polycrystalline \( \text{Li}_2\text{RuO}_3 \) and \( \text{Li}_2\text{RuO}_3 \) (C) or \( \text{Li}_2\text{RuO}_3 \) (P) are distinguished by the different space groups or by the difference in \( (L_l - L_s)/L_s \). It is clear that \( \text{Li}_2\text{RuO}_3 \) (P) is more distorted than \( \text{Li}_2\text{RuO}_3 \) (C) but much less distorted than the polycrystalline sample despite the same space group shared by both (Table 1).

### Table 1. Structural comparison between the honeycomb lattices at 100 K

| Compound                  | Space Group | \( a \) (Å)   | \( b \) (Å)   | \( b/a \) | \( (L_l - L_s)/L_s \) |
|---------------------------|-------------|---------------|---------------|-----------|------------------------|
| \( \text{Li}_2\text{RuO}_3 \) (Powder)* | P\(_2_1/m\) | 4.9210(2)     | 8.7829(2)     | 1.785     | 18.6%                  |
| \( \text{Li}_2\text{RuO}_3 \) (P) | P\(_2_1/m\) | 4.963(3)      | 8.766(6)      | 1.766     | 10.1%                  |
| \( \text{Li}_2\text{RuO}_3 \) (C) | C2/m        | 5.021(4)      | 8.755(6)      | 1.744     | 2.1%                   |
| \( \text{Na}_2\text{RuO}_3 \)       | C2/m        | 5.346(1)      | 9.255(2)      | 1.731     | 0.17%                  |
| \( (\text{Li}_{0.9}\text{Na}_{0.1})\text{IrO}_3 \) | C2/m        | 5.186(1)      | 8.964(2)      | 1.728     | 0.6%                   |
| \( \text{Na}_2\text{IrO}_3 \)       | C2/m        | 5.319(1)      | 9.215(2)      | 1.732     | 0.14%                  |

* Taken at 300 K

Physical Properties \( \text{Na}_2\text{RuO}_3 \) exhibits a sharp antiferromagnetic (AFM) transition at \( T_N=30 \) K, as shown in Fig. 2a. The magnetic anisotropy leads to a stronger out-of-plane magnetic susceptibility \( \chi_\perp \) than in-plane magnetic susceptibility \( \chi_\parallel \). The linearity illustrated in \( 1/\Delta\chi_\parallel \) (right scale in Fig. 2a) indicates that the data fit well with the Curie-Weiss law for \( 100 < T < 350 \) K, and yield the Curie-Weiss temperature \( \theta_{\text{CW}} = -137 \) K and effective moment \( \mu_{\text{eff}} = 2.45 \mu_\text{B}/\text{Ru} \) (Table 2). The frustration parameter defined as \( FP = |\theta_{\text{CW}}|/T_N \) is estimated to be 4.6. This value suggests a presence of modest frustration, comparable to that for its iridate counterpart.

The magnetic ordering is confirmed by the specific heat \( C(T) \) (Fig. 2b). However, an additional peak at \( T_{N2} = 26 \) K that is absent in \( \chi(T) \) is also seen in \( C(T) \). This behavior, which is reproducible, is remarkably similar to that observed in \( \text{Na}_2\text{IrO}_3 \) where an additional, weaker anomaly in \( C(T) \) is discerned at \( T^* = 21 \) K that is followed by the
zigzag order at $T_N = 18$ K [15, 17]. This two-step transition is discussed in context of the Kitaev-Heisenberg model on the hexagonal lattice [34]. A similar argument could be applied to Na$_2$RuO$_3$ although the origin of this magnetic behavior needs to be further investigated. The C(T) data also indicate that the entropy removal due to the two-step magnetic transition is small, less than 10% of Rln3 expected for an S=1 magnet. This implies that the magnetic ordering may not be fully developed perhaps in part because of the tendency of SOC to impose a singlet state. Application of magnetic field up to 14 T causes no visible changes in both C(T,H) and $\chi$(T,H).

The magnetic properties of both single-crystal Li$_2$RuO$_3$(C) and Li$_2$RuO$_3$(P) are examined for 1.7 < T < 900 K. Neither shows the singlet ground state observed in the polycrystalline Li$_2$RuO$_3$. Instead, Li$_2$RuO$_3$(C) displays paramagnetic behavior at T > 20 K with the magnetic susceptibility $\chi$ following the Curie-Weiβ law for 20 K < T $\leq$ 750 K (Fig.3a). Data fits to the Curie-Weiβ law yield an effective moment $\mu_{eff}$ = 2.77 $\mu_B$/Ru, consistent with that expected for an S=1 system, and a Curie-Weiβ temperature $\theta_{CW}$=-112 K. A signature for a long-range order near $T_N$=9K is evident in both $\chi$(T) and C(T)(Fig. 3b). A large frustration parameter, FP = $|$\theta$_{CW}$/T$_N$ = 12.4 suggests the presence of significant frustration (Table 2). Indeed, the two unequal Ru-Ru bondsmay favor a formation of zigzag chains along the a-axis (see schematic in the inset of Fig. 4) as the

| Compound                  | $T_N$ (K) | $\theta_{CW}$ (K) | FP   | $\mu_{eff}$ ($\mu_B$/Ru or Ir) |
|---------------------------|-----------|-------------------|------|-------------------------------|
| Li$_2$RuO$_3$ (P)         | ~5        | -58               | 11.6 | 1.46                          |
| Li$_2$RuO$_3$ (C)         | 9         | -112              | 12.4 | 2.77                          |
| Na$_2$RuO$_3$             | 30        | -137              | 4.6  | 2.45                          |
| (Li$_0.9$Na$_0.1$)$_2$IrO$_3$ | 7       | -18               | 2.6  | 1.95                          |
| Na$_2$IrO$_3$             | 18        | -119              | 6.6  | 1.76                          |

$FP$ stands for frustration parameter

Table 2. Physical parameters of the single-crystal honeycomb lattices
inter-chain interaction is weak due to the long Ru-Ru bond $L$. Therefore, no magnetic ordering occurs until below $T_N=9$ K when three-dimensional correlations are established.

For more distorted $\text{Li}_2\text{RuO}_3$ (P), a magnetically ordered state also takes place but at a lower temperature, $T_N=4$ K (Fig. 3c and 3d). Remarkably, the magnetic anisotropy is much stronger, and the magnitude of $\chi_\perp$ is significantly larger than that in $\text{Li}_2\text{RuO}_3$ (C), implying the importance of SOC. However, the temperature dependence of $\chi$ at high temperatures is much weaker than that for $\text{Li}_2\text{RuO}_3$ (C). The results suggest that $\text{Li}_2\text{RuO}_3$ (P) is “half-way” to dimerization as the lattice is more similar to that of the polycrystalline sample; the magnetic state eventually prevails below $T_N=4$ K because $\text{Li}_2\text{RuO}_3$ (P) is after all not as distorted as the polycrystalline $\text{Li}_2\text{RuO}_3$.

**Computational Results** Our LDA (local density approximation) calculations using the LMTO (linearized muffin-tin orbitals) method [35] and Wannier function projection method [36] show that the crystal-field splitting in the Ru $t_{2g}$ shell does not exceed 70 meV, indicating that the comparable SOC may play a significant role. However, the off-diagonal matrix elements of the Hamiltonian, hopping parameters, are even larger, $\sim 200$ meV, which is strong enough to form the quasi-molecular orbitals (QMOs) similar to those in Na$_2$IrO$_3$ where QMOs involve six Ir atoms arranged in a hexagon and each Ir atom belongs to three different QMOs, which dominate the formation of electronic structure [13]. The results of the optimization of the crystal structure performed in the GGA (generalized gradient approximation) calculations using the pseudopotential method [37] indicate that the nearly ideal honeycomb Na$_2$RuO$_3$ indeed corresponds to a minimum of the total energy for an AFM state. In addition, our GGA+U calculations show that a relatively small on-site Coulomb repulsion $U \sim 1.5$ eV is sufficient to
suppress the dimerization observed in polycrystalline Li$_2$RuO$_3$. The band structure of single-crystal Li$_2$RuO$_3$ strongly differs from that of both Na$_2$RuO$_3$ and Na$_2$IrO$_3$ on the LDA level (see SM Fig. 2[33]); and consequently, there is no sign of the QMOs. According to a recent study [30], when one of QMOs (of E$_2$u symmetry) is half-filled, the corresponding instability may induce the Jahn-Teller distortions (JTDs) that in turn lead to the dimerization. In less distorted single-crystal Li$_2$RuO$_3$, no sign of the JTDs is seen since the formation of the zigzag chains effectively removes the orbital degeneracy or JTDs. Therefore the zigzag chains constitute an alternative state to the dimerization when the JTDs are absent. However, both the zigzag chains and dimerized lattice cost certain elastic energy that tends to stabilize uniform structure, and the prevailing state sensitively depends on details of the band structure and bulk modulus of the system (see SM[33] for details).

Indeed, all relevant energies vigorously compete and critically bias their mutual competition to stabilize ground states. This explains that there exist nearly degenerate states in these materials, and the prevailing ground state critically depends on details of the structure, as illustrated in Fig. 4. The magnetic ordering systematically decreases with increasing $(L_1-L_0)/L_0$ and eventually vanishes at a critical value where the dimerization emerges, leading to the singlet ground state observed in polycrystalline Li$_2$RuO$_3$. All results strongly indicate a direct correlation between the ground state and basal-plan distortions. The newly found Na$_2$RuO$_3$ provides a reference for almost perfect honeycomb symmetry.

The absence of the dimerization in single-crystal Li$_2$RuO$_3$ cannot be due to either impurity or quality of the single crystals. In fact, the singlet ground state is unusually
resilient to heavy impurity doping and is even enhanced by 5% Na doping (see Fig. 3 in SM [33]) and survives up to 50% Ir substitution for Ru in the polycrystalline samples [31]. It is likely that the difference between the two forms of Li$_2$RuO$_3$ arises from different synthesis conditions, as discussed above, which might cause different degrees of site-disorder in the honeycomb network due to the similar ionic radius of Li and Ru, and/or slightly different stoichiometry (e.g. oxygen content) (see SM [33]). Hence, this work does not rule out the possibility that single-crystal Li$_2$RuO$_3$ having the same structural distortions and singlet ground state as polycrystalline Li$_2$RuO$_3$ may eventually form under certain synthesis conditions.

The work also offers the following general observations. Both Li$_2$RuO$_3$ and Li$_2$IrO$_3$ are more structurally distorted and behave with more complexities than their Na counterparts. SOC is expected to impose a J=0 state for Ru$^{4+}$(4d$^4$) ions (and a J$_{\text{eff}}$=1/2 state for Ir$^{4+}$(5d$^5$) ions) but the observed magnetic states in the honeycomb ruthenates as in many other ruthenates [25] indicate that SOC is not sufficient to induce a J=0 state. It is intriguing that all honeycomb ruthenates and iridates magnetically order in a similar temperature range (see SM-Fig. 4 [33]) despite the different role of SOC in them.

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Captions

Fig. 1. Diffraction images in the (h0l) plane of the single crystal Li$_2$RuO$_3$ with space group (a) P2$_1$/m and (b) C2/m. Insets: The corresponding honeycomb lattice and Ru-Ru bond distances. The temperature dependence of (c) the $a$-axis and (d) the ratio $b/a$ from our single crystal P2$_1$/m phase (blue), C2/m phase (purple), powder samples (red star), and powder data from Ref. 28 (black circles). Note that the sharp diffraction pattern clearly indicates the high quality of the single-crystal Li$_2$RuO$_3$.

Fig. 2. Single-crystal Na$_2$RuO$_3$: (a) The temperature dependence of the magnetic susceptibility for the basal plane $\chi_{||}(T)$ and out-of-plane $\chi_{\perp}(T)$ for single-crystal Na$_2$RuO$_3$; Right scale: $1/\Delta\chi_{||}$ where $\Delta\chi = \chi - \chi_{||}$ and $\chi_{||}$ is the temperature-independent contribution to $\chi$. (b) The temperature dependence of the specific heat $C(T)$ and $\chi_{\perp}(T)$ (right scale).

Fig. 3. Single-crystal Li$_2$RuO$_3$ (C): The temperature dependence of (a) the magnetic susceptibility $\chi_{||}(T)$ and $\chi_{\perp}(T)$ and $1/\Delta\chi_{\perp}$ (right scale) for $1.7 < T < 850$ K and (b) the specific heat $C(T)$ and $\chi_{\perp}(T)$ and $\chi_{\perp}(T)$ (right scale) at low $T$. Single-crystal Li$_2$RuO$_3$ (P): The temperature dependence of (c) $\chi_{||}(T)$ and $\chi_{\perp}(T)$ and $1/\Delta\chi_{\perp}$ (Inset) and (d) $\chi_{||}(T)$ and $\chi_{\perp}(T)$ and $d\chi_{\perp}/dT$ (right scale) at low $T$.

Fig. 4. The Neél temperature $T_N$ as a function of the bond distance ratio $(L_r - L_s)/L_s$ for all honeycomb ruthenates. Inset: a schematic of the honeycomb lattice featuring $L_r$.
and $L_{\alpha}$. 

![Fig. 1](image)

Fig. 1
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