Honeycomb-Structure RuI₃, A New Quantum Material Related to α-RuCl₃

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The layered honeycomb lattice material α-RuCl₃ has emerged as a prime candidate for displaying the Kitaev quantum spin liquid state, and as such has attracted much research interest. Here a new layered honeycomb lattice polymorph of RuI₃, a material that is strongly chemically and structurally related to α-RuCl₃ is described. The material is synthesized at moderately elevated pressures and is stable under ambient conditions. Preliminary characterization reveals that it is a metallic conductor, with the absence of long-range magnetic order down to 0.35 K and an unusually large T-linear contribution to the heat capacity. It is proposed that this phase, with a layered honeycomb lattice and strong spin–orbit coupling, provides a new route for the characterization of quantum materials.

1. Introduction

The quantum spin liquid (QSL) state is a highly uncommon state of matter in which long-range entangled spins remain entangled even near absolute zero temperature. QSLs can arise in some magnetic lattices due to strong bond-dependent competing spin anisotropy, yielding frustrated spin configurations on a single site, as described by the Kitaev model. The layered honeycomb lattice is an important potential host for this state, potentially leading to the so-called Kitaev QSL, which has recently attracted considerable attention both theoretically and experimentally. Materials with \( S = 1/2 \) spins arrayed on a honeycomb lattice and significant spin–orbit-coupling (SOC) are particularly good candidates for hosting this state. Ru(III) \((4d^7)\) compounds with layered honeycomb lattices are of interest in this context, as their five d electrons in the low spin state (due to the high energy splitting of the \( t_{2g} \) and \( e_g \) d orbitals in a large octahedral ligand field) and strong SOC will produce a local \( J_{\text{eff}} = 1/2 \) ground state, leading to the anisotropic interactions described by the Kitaev model and potentially to the QSL state. The electrically insulating honeycomb lattice material α-RuCl₃ has emerged as a good representative of this state.

α-RuCl₃, as a promising QSL candidate based on a 4d transition-metal-based honeycomb lattice, has been the subject of a great number of investigations. Its unconventional behavior, including an unusual magnetic excitation spectrum as well as the emergence of Majorana fermions, has been reported by magnetization, heat capacity, neutron scattering, and thermal transport measurements. Its ground state seems to be close to the ideal Kitaev QSL state, in spite of the magnetic ordering of α-RuCl₃ in zero applied magnetic field. In the meantime, the iodine-based version of RuCl₃, honeycomb-structured RuI₃ which until now has not been known to exist, has been the subject of several theoretical studies of its monolayer form. The structurally and chemically related compound RuI₃ has been reported, but studies have shown it to crystallize in a 1D chain structure instead of in honeycomb layers. Here, however, we report that RuI₃ in a honeycomb layered structure (α-RuI₃) can be made at moderately high pressures and is stable in ambient conditions. Preliminary characterization shows it to be a paramagnetic metal with a relatively high T-linear contribution to its heat capacity, in contrast to the insulating magnetic state of the chloride analog α-RuCl₃. The data suggest that α-RuI₃ may be a new kind of a metallic correlated electron material, and its strong chemical and structural analogy to α-RuCl₃ suggest that Kitaev interactions may significantly influence its magnetic and electronic properties.

2. Results and Discussion

To synthesize the layered honeycomb structure of RuI₃, commercially available amorphous RuI₃ powder (Alfa Aesar), was heated under a pressure of 6 GPa at 800 °C for 1 h. The resulting honeycomb-structure phase of RuI₃ is stable at ambient pressure for at least a few days in air before hydrating—appearing to be less hygroscopic than honeycomb-structure RuCl₃ powder. The vapor transport method was employed on postsynthesis samples in a quartz tube sealed under vacuum to purify the product, with the hot end at 300–350 °C and the cold end at ambient temperature. A small amount of chemical impurity, presumably present due to its presence in the starting material, was transferred to the cold end, and honeycomb-structure α-RuI₃ is maintained in the hot zone with no signs of decomposition or phase transformation. This suggests that layered-honeycomb-structure α-RuI₃ is stable for at least a few hours at 300–350 °C under a static vacuum.

The crystal structure of the material was determined by single-crystal X-ray diffraction (SXRD) at ambient temperature,
with single crystals picked from the postreaction samples. The material has a three-layer centrosymmetric rhombohedral symmetry structure, with a honeycomb-layer lattice in space group $R\bar{3}$ (No. 148, Figure 1). At 300 K the cell parameters are $a = 6.7913(6)$ Å and $c = 19.026(3)$ Å. The atomic coordinates are listed in Table 1, and further crystallographic data are presented in Tables S1–S3 (Supporting Information). A structural detail is that the normally empty interstitial sites (Ru$_2$, Wyckoff position 3$a$) in a three-layer honeycomb lattice appear to be occupied by a very small percentage of Ru atoms. Because diffraction experiments of the type typically performed are a time and positional average over the whole crystal, the very small partial occupancy of Ru at position 3$a$ is likely due to the presence of a small number of stacking faults,$^{[26]}$ such have often been observed in RuCl$_3$. Without constraints among the occupancy parameters in the structure refinement, the honeycomb material freely refines to the slightly Ru-deficient formula Ru$_{0.98(1)}$I$_3$; the ideal 6$c$ site of the honeycomb lattice is about 96% occupied while the ideally vacant 3$a$ site is about 2% occupied. Detailed structural study, especially by high-resolution electron microscopy, which can observe stacking faults or other structural errors, if present, may be of future interest.

Each Ru$_I$ octahedron in the $\alpha$-Ru$_I_3$ structure is close to an ideal geometry, with Ru–I bond lengths in a narrow range between 2.67 and 2.68 Å, and I–Ru–I bond angles of 86° to 92°. This suggests that distortions from ideal octahedral crystal fields are likely to be small. As shown in Figure 1C, each unit cell contains three honeycomb layers in the usual A B C rhombohedral geometry. The honeycomb layers are built of edge-sharing Ru$_I_6$ octahedra at a Ru–Ru distance of 3.9 Å. The distance between the layers is 6.3 Å. This interlayer separation is larger than those in $P3_121$ symmetry$^{[27]}$ $\alpha$-RuCl$_3$ (5.7 Å), suggesting that there will likely be weaker magnetic coupling between the Ru layers in $\alpha$-Ru$_I_3$ than is found in $\alpha$-RuCl$_3$.

No structural phase transition was observed for honeycomb-structure Ru$_I_3$ single crystals between 100 and 300 K.

In Figure 2, powder X-ray diffraction (XRD) confirms the consistency of the bulk product with the honeycomb structure observed by single-crystal diffraction. As shown in the inset, the layered nature of honeycomb lattice $\alpha$-Ru$_I_3$ can be straightforwardly seen by visual inspection of a scanning electron microscopy (SEM) image, while energy-dispersive X-ray (EDX) measurements verify the 1:3 Ru to I ratio and the uniform element distribution seen in the single-crystal XRD study. Our material is quite different from that previously reported for Ru$_I_4$, which was said to adopt a 1D chain structure ($\beta$-Ru$_I_3$)$^{[24,25,28]}$. The successful synthesis at a modestly high pressure of a new layered honeycomb phase of Ru$_I_3$, may be because the layered honeycomb lattice tends to be preferred under pressure, as the relative molar volumes of 1D chain $\beta$-Ru$_I_3$ and honeycomb structure $\alpha$-Ru$_I_3$ are 131.5 and 126.7 Å$^3$, respectively, i.e., that applied pressure drives the system toward a slightly more condensed phase (around 4% higher in density). This newly discovered Ru$_I_3$ phase will be of future interest due to its heavy-metal-based honeycomb lattice, which allows for the influence on potentially unusual physics of significant chemical factors such as the Ru–Cl versus Ru–I orbital hybridization, to be tested.

The elementary magnetic and electronic properties of $\alpha$-Ru$_I_3$ were characterized using a Quantum Design DynaCool Physical Property Measurement System (PPMS). Magnetic susceptibility (defined as $M/H$) was derived from the measured magnetization ($M$) on polycrystalline samples at temperatures between 1.8
and 300 K under a 1 kOe applied magnetic field \( (H) \). The result is shown in Figure 3A. Honeycomb-structured \( \alpha \)-RuI\(_3\) shows relatively weak paramagnetic behavior over a wide temperature range, along with a significant low temperature increase, with no 3D magnetic ordering features visible down to 1.8 K. The magnetization shows a linear dependence on the external field from \(-9\) to \(9\) T at 200 K (Figure 3A inset) and an S-shaped character at 2 K. Although an S-shaped character can be displayed by materials where a Brillouin function relationship between the available spins and the magnetization is present, that is not the case here (see the gray dashed curve in Figure 3A inset), where to explain the data the number of spins present would have to be more than is possible if all the Ru spins present in the material were to be isolated. Alternatively, if the S shaped character at 2 K is due to orphan spins (spins that do not participate in the bulk behavior of the magnetic system) then those spins would have to represent about 30% of the Ru spins in the system, an amount that is far outside of normal expectations.
and for which we have no evidence. The S shaped character of the $M$ versus $H$ curve at 2 K, if taken at face value, suggests that about $1/3$ of the total Ru spin are completely polarized by 9 T for $\alpha$-RuI$_3$, although the origin of the S shaped behavior may be less simply explained. Detailed magnetic study to higher applied magnetic fields of this new material may therefore be of future interest.

The heat capacity ($C_p$) was measured on a dense polycrystalline pellet of honeycomb-structure $\alpha$-RuI$_3$ between 0.35 and 10 K. No phase transition was observed. The $C_p$ versus $T$ curve is presented in Figure S1 (Supporting Information). Its decreasing trend with decreasing temperature turns nonlinear below 0.5 K. $C_p/T$ is plotted versus $T$ in the main panel of Figure 3B, while the plot at different applied magnetic fields is presented in Figure 3C. The total heat capacity of a quantum material ($C_{\text{total}}$) at low temperature can be described as the sum of electronic, magnetic, and phononic contributions, e.g., $C_{\text{total}} = C_{\text{electron}} + C_{\text{mag}} + C_{\text{phonon}}$, where electronic or other types of linear-$T$ contributions can contribute to $\gamma T$, and those of the phonons can be approximated by: $C_{\text{phonon}} = \beta_0 T^3 + \beta_1 T^5$. Thus by fitting the temperature range above, the values obtained are 0.0293, 0.00472, and $-1.2 \times 10^{-5}$ respectively for $\gamma$, $\beta_0$, and $\beta_1$. This result is distinctive compared to that seen for $\alpha$-RuCl$_3$ as a significant $\gamma T$ term is not observed in heat capacity fitting,[10] and it is also obviously larger than the common $T$ linear terms of insulating metal trihalides (for example, for layered material CrI$_3$, the linear-$T$ term is reported to be 1.17 mJ mol$^{-1}$ K$^{-2}$). The relatively large magnitude of the gamma term, $\gamma = 29.3$ mJ mol$^{-1}$ K$^{-2}$, is surprising and suggests that unconventional behavior may be present in this material at low temperature.

The upward tail visible in $C_p/T$ below about 700 mK is likely to be dominated by the nuclear Schottky anomaly from Ru, though that contribution may mask the presence of a very low temperature magnetic transition. This upturn has not been reported for $\alpha$-RuCl$_3$ or $\alpha$-RuBr$_3$,[31] but has on the other hand been reported for the well-defined Ru-based compounds La$_{1.5}$Ru$_6$O$_{19}$[32] and RuO$_2$,[33] for example. Taking this nuclear Schottky anomaly into consideration, a $\Delta T^2$ term would be added to $C_{\text{total}}$, as $C_{\text{total}} = AT^2 + \gamma T + \beta_0 T^3 + \beta_1 T^5$. A fit of $C_p/T$ to this equation (Figure S2, Supporting Information) gives $\gamma' = 33.2$ mJ mol$^{-1}$ K$^{-2}$, $\beta_0' = 4.54$ mJ mol$^{-1}$ K$^{-4}$, $\beta_1' = -0.0105$ mJ mol$^{-1}$ K$^{-6}$ and $A = 1.38$ mJ mol$^{-1}$ K. As shown in Figure 3C, the tail of the nuclear Schottky anomaly is not suppressed or shifted much by an applied field.[32] Thus the $\gamma T$ term, generally taken as an indication of the presence of a correlated electron state if significantly higher than 1, is on the order of 30 for both types of analysis. A clear suppression of the heat capacity below 3 K can be observed at applied magnetic fields higher than 3 T (Figure 3C). These features suggest that detailed study of the low temperature properties of $\alpha$-RuI$_3$ will be of future interest.

Preliminary resistivity measurements were conducted on an as-made dense pieces of polycrystalline RuI$_3$, directly from the high-pressure synthesis furnace. Metallic behavior was observed between 1.8 and 240 K (Figure 3B, inset) which differentiates this material significantly from $\alpha$-RuCl$_3$.[34–36] Multiple different as-made pieces were tested to rule out the possibility of random impurities or defects in the samples as the origin of the metallic behavior (Figure S3, Supporting Information). (Polycrystalline pellets pressed from loose powders show the kind of resistivity behavior seen for transport in poorly metallic samples disrupted by intergrain contacts, see Figure S3B, Supporting Information). A weak feature observed between about 260–280 K in the resistivity is not shown in the figures as in measurements on multiple samples it appears to depend on the presence of adsorbed water on the sample surface.

Finally, density functional theory based calculations of the electronic structure of $\alpha$-RuI$_3$ were performed with and without SOC and the Coulomb repulsion $U$ terms included ($U = 4$ eV, as employed for Ru d electrons based on the value used in such calculations for $\alpha$-RuCl$_3$[37] Lower values of $U$ also lead to a calculated metallic electronic structure.) The results are shown in Figure 4 along with comparison to the calculated electronic band structures of $\alpha$-RuCl$_3$. Both SOC- and non-SOC-calculated band structures of $\alpha$-RuI$_3$ support the observed metallic conductivity—the band structure shows obvious changes with both SOC and $U$ terms included, but the metallic state near the Fermi energy is maintained. In contrast, $\alpha$-RuCl$_3$ shows a semiconducting calculated band structure when both SOC and
U are included, consistent with experimental observations and previous reports. We have employed the most commonly adopted space group for α-RuCl₃ (P₃₁2₁)[3,39] but a calculation in the R₃ space group[40] for α-RuCl₃ is presented in Figure S4 (Supporting Information) to facilitate direct comparison with α-Ru₁₃. The result shows that α-RuCl₃ in space group R₃ is calculated to be a semiconductor, as it is in P₃₁2₁, consistent with experimental observations.

3. Conclusions
A new phase of Ru₁₃, displaying a layered honeycomb structure, is reported. Synthesized at moderate pressures, it is stable under ambient conditions in lab air. Preliminary characterization indicates that it differs from α-RuCl₃ in three primary ways despite the strong chemical and structural analogy of the phases: 1) it does not show any signs of long-range magnetic ordering down to 1.8 K under applied fields of 1000 Oe or to 0.35 K under zero field, 2) it has a surprisingly large linear-T contribution to the heat capacity, and 3) it is a metallic conductor. Our results suggest that Ru—I hybridization leads to a correlated metallic state in our material, while the Kitaev interactions may remain present. The spin-1/2 honeycomb lattice as well as the significant SOC of layered honeycomb lattice α-Ru₁₃ make it a viable candidate for further study as a quantum material. We argue that α-Ru₁₃ can serve as a new platform for exploring the behavior of a metallic compound for which the consequences of Kitaev spin interactions may be significant, especially when its properties are compared to those of insulating honeycomb RuCl₃ and recently described α-RuBr₃.[36]

4. Experimental Section
Amorphous Ru₁₃ starting material was purchased from Alfa Aesar (anhydrous, ≥ 99%). The powder was loaded in a boron nitride crucible which was then inserted into a pyrophillite cube assembly. The system was pressurized to 6 GPa using a cubic multianvil system (Rockland Research Corporation) and heated to 800 °C at 50 °C/min. Reciprocal space integrations were completed over a 8 × 8 × 2 Monkhorst–Pack k-point mesh. SOC effects were applied for both Ru and I atoms. Orbital potentials (U = 4 eV) were employed for Ru d electrons based on previous calculations for α-RuCl₃.[31] The structural parameters for Ru₁₃ were obtained from experiment, and the parameters for RuCl₃ were obtained from the ICSD.[27] With these settings, the calculated total energy converged to less than 0.1 meV per atom.

Note: One month after the submission of this paper to this journal and the manuscript was uploaded on arXiv for public view, a report on honeycomb-structured Ru₁₃ was posted by Nawa et al. (arXiv: 2109.12864[40]), with their sample prepared at 400 °C, 4 GPa, and the crystal structure refined using powder neutron diffraction. They reported the compound to be two-layered, in the R₃ space group, different from the three-layered R₃ structure that was observed. The different space group reported in their study can be due to the different synthesis conditions, which can lead to a different stacking sequence of the honeycomb layers, and is not surprising in layered compounds. This has often been seen in RuCl₃ for example.[8]

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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high-pressure synthesis, honeycomb layers, Kitaev quantum spin liquids, ruthenium iodide, ruthenium trihalide

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