The novel two-dimensional honeycomb layered Cu₃LiRu₂O₆ exhibits Pauli-like paramagnetic and Mott variable range hopping semiconduction behaviors, which contradict the large specific-heat Sommerfeld coefficient for metals, and indicate a possible spin-excitation induced nonmetallic metal. This nonmetallic feature can be significantly suppressed by pressure toward producing a bad-metal state, as reflected by the temperature-dependent resistivity response up to 35 GPa.

Materials based on delafossite modified structures have exhibited interesting physical properties and important applications, such as photocatalytic activity, thermoelectric behavior, use as transparent conductors, and in measurement-based quantum computation. The crystal structure of delafossite ABO₂ consists of two-dimensional (2D) edge-sharing BO₆ octahedral planes separated by intercalated linear-dumbbell A-cations. It can be modified to A₂BO₃- or A₃A'B₂O₆-types when intralayer disordering is introduced. Recently, exotic physical phenomena have been manifested in modified delafossites with 4d/5d transition metals at the B-site, particularly because of strong spin-orbit coupling (SOC) that coexists with other competing interactions and geometrical frustration inherent in the honeycomb layers. Mott and metal–insulator transitions have been reported in modestly frustrated A₂RuO₃ (A = Li, Na), while highly anisotropic Kitaev interactions rooted in the difference in electron configuration and SOC between Ru⁴⁺ (4d¹, S = 1) and Ir⁴⁺ (5d¹, S = 1/2) have been proposed in the iridates Na₂IrO₃ and Li₂IrO₃. Exotic low-energy excitations have been observed in the random Kitaev magnet Cu₃IrO₆. A quantum spin liquid state has, for the first time, been discovered in the quaternary 3R-delafossite A₃A'B₂O₆-type H₂LiIr₂O₆, which suggests that the electronic and magnetic properties of delafossite can be generally tuned by cationic substitution.

In the modified delafossite A₃A'B₂O₆, a higher degree of complication arises when two types of cations are ordered in the triangular layer, as in the quaternary 3R-delafossite A₃MB₂O₆. In comparison with ABO₂ delafossite, the lattice disorder in A₃MB₂O₆ disturbs the periodic potential and thus interferes with the electron waves, and makes the materials highly 2D in nature. This scenario can lead to dramatic changes in physical properties, as observed in ruthenate-based modified delafossites, implying that the electronic and magnetic properties of modified delafossites can be refined by substitution of the inter- and/or intra-layer cations, and are worthy of further exploration. In this work, we prepared a novel modified delafossite, Cu₃LiRu₂O₆, via a topotactic soft chemical synthesis from Li₃RuO₃ (Fig. S1, ESI†), and studied its crystal structure, magnetic response, specific heat, and pressure-dependent resistivity in detail.

The crystal structure determination of modified delafossite is challenging due to its complicated layer-stacking fault. Refinements of the synchrotron powder X-ray diffraction (SPXD) data of Cu₃LiRu₂O₆ were carried out in C2/m (no. 12, as in Ag₃LiRuO₆ and Ag₃LiMnO₆) and C2/c (no. 15, as in Cu₃LiIr₂O₆ and Cu₃IrO₃) respectively. An acceptable goodness of fit was observed in both cases, but the C2/m model gave better agreement overall (Fig. 1, Rwp/Rp = 5.65/6.92%) than the C2/c (Fig. S2 (ESI†), Rwp/Rp = 6.82/9.43%) model.
Therefore, the $C2/m$ cell ($a = 5.2085(2)$ Å, $b = 9.0236(2)$ Å, $c = 6.0267(2)$ Å, $\beta = 106.59(1)^{\circ}$, $V = 271.42(2)$ Å$^3$, $Z = 2$) was used to describe the crystal structure of Cu$_3$LiRu$_2$O$_6$. As can be seen in Fig. 1, an asymmetric broad feature (Warren-line shape)\(^{22}\) of the peaks appears around 8–11 degrees, which is characteristic of a 2D structural order with stacking faults in the $c$ direction, as further corroborated by the streaked diffraction peaks in the selected-area electron diffraction (SAED) patterns (Fig. S3 (ESI†)). Both BVS (Table S2, ESI†) and X-ray absorption near-edge spectroscopy (XANES, Fig. S9 and S10, ESI† in Tables S1 and S2 (ESI†)) studies imply Ru$^{4+}$ and Cu$^{+}$ dominated valence in Cu$_3$LiRu$_2$O$_6$.

Fig. 2 shows the magnetization curves of Cu$_3$LiRu$_2$O$_6$ at different magnetic fields ($H_{0}$ = 0.1, 1, 5 T). Unlike the strongly AFM ($T_N$ = 15 K) spin coupling in Cu$_3$LiIr$_2$O$_6$,\(^{16}\) no evidence for long-range magnetic order or spin freezing was detected down to 2 K in Cu$_3$LiRu$_2$O$_6$; instead the susceptibility remains subtly increased. The susceptibility of Cu$_3$LiRu$_2$O$_6$ is slightly decreased in the studied temperature range 2–200 K, signaling the absence of such a weak Curie–Weiss term in Cu$_3$LiRu$_2$O$_6$, resembling those of LaNiO$_3$,\(^{24}\) BaNbO$_3$,\(^{25}\) and Sr$_2$V$_2$O$_7$.\(^{26}\) Note that the molar magnetic susceptibility as a function of the magnetic field was investigated at 2 K, which veers away from a straight line, indicating the presence of ferromagnetic impurities in Cu$_3$LiRu$_2$O$_6$ (inset of Fig. 2a).

Fig. 1 Rietveld refinement of the SXPD data for the Cu$_3$LiRu$_2$O$_6$ in $C2/m$ structure at RT. The inset shows the crystal structure viewed along the [100] direction, Cu$_1$, gray spheres; Cu$_2$, blue spheres; (Li/Ru)O$_6$ octahedra, green.

\[ r(T) \approx \frac{C}{T - \theta} \]

\[ r = \rho \propto T^{-\frac{1}{4}} \]

\[ T_0 = 113 \text{ K}, \Theta_S = 633 \text{ K} \]
by the dotted line. As can be seen, the application of an 8 T external magnetic field has a marginal effect and only modifies \( C(T) \) slightly at low temperatures. The \( C(T) \) data below 10 K are replotted in Fig. 3b in the form of \( C/T \) versus \( T^2 \), and a linear model \( C/T = \gamma + \beta T^2 \) was applied to extract the linear specific-heat coefficient \( \gamma \), and the Debye temperature \( \Theta_D = (12 \pi^2 n R / 5 b)^{1/3} \), where \( n = 12 \) is the number of atoms in the formula unit, and \( R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \) is the ideal gas constant. Interestingly, we observe large linear specific-heat Sommerfeld coefficients \( \gamma = 41.7(5) \text{ and } 47.9(4) \text{ mJ mol}^{-1} \text{ K}^{-2} \) for 0 and 8 T, respectively, suggesting metallic behavior, which contradicts the VRH semi-conducting resistivity behavior shown in Fig. 2b. Although the presence of magnetic Ru\(^{4+} \) ions might give rise to a magnetic contribution to specific heat at low temperature, the observation of nearly temperature-independent magnetic susceptibility and the perfect overlap of ZFC/FC for \( \chi(T) \) rules out the presence of localized moments and spin-liquid or spin-glass states. In this regard, Cu\(_3\)LiRu\(_2\)O\(_6\) may belong to the novel family of nonmetallic metals, as reported for Lu\(_2\)Rh\(_2\)O\(_7\)\(^{27}\) and FeCrAs, considering their common features.\(^{28–31}\)

Nonmetallic metals present three common features: a triangular magnetic lattice and a temperature-independent Pauli paramagnetic response, large Sommerfeld coefficient \( \gamma \), and a gap in the density of states (negative slope of the \( \rho(T) \) curve).\(^{27–30}\) The triangular motifs enable geometric magnetic frustration, which corresponds to the corner-sharing tetrahedral sublattice in the pyrochlore Lu\(_2\)Rh\(_2\)O\(_7\), the distorted Kagome Cr-network in FeCrAs, and the honeycomb Ru-layer in Cu\(_3\)LiRu\(_2\)O\(_6\). A hidden spin-liquid state\(^{29}\) or Hund’s metal\(^{32}\) behavior is proposed by researchers to explain the nonmetallic behavior in Cu\(_3\)LiRu\(_2\)O\(_6\). The inset shows the \( T \)-dependence of specific heat \( C/T \) for Cu\(_3\)LiRu\(_2\)O\(_6\). The temperature dependence of specific heat from 0 to 35 GPa is shown in Fig. 4. Apparently, the nonmetallic state in Cu\(_3\)LiRu\(_2\)O\(_6\) can be achieved up to 35 GPa, the highest pressure in the present study, as shown in the inset to Fig. 4, where resistance \( R \) decreases at higher pressure (9–28 GPa) but starts to increase when the pressure is above 28 GPa, as discovered in other 4d/5d-transition metal oxides.\(^{38}\) The temperature-dependent \( R \)-dependence of specific heat in the higher-pressure region (inset to Fig. 4) cannot be well fitted or explained by any thermal activation model, indicating that the sample enters a conductive or a bad-metal state. Further investigations are needed to examine whether much higher pressures are required to drive Cu\(_3\)LiRu\(_2\)O\(_6\) into a true metallic state.\(^{39}\)

For materials with competing ground states, pressure is a powerful tool with which to refine the balance between SOC, Coulomb repulsion, and crystal field interactions for novel phenomena, as observed in layered ruthenates and iridates.\(^{36,37}\) The resistivity decreases gradually with increasing pressure over the whole temperature range. At RT, the resistivity is \~10 times smaller (0.01(1) \( \Omega \) cm) at 11 GPa than that (0.09(1) \( \Omega \) cm) at 0 GPa. The resistivity is significantly reduced at lower temperatures and higher pressures, being three orders of magnitude smaller (1.62(1) \( \Omega \) cm) at 11 GPa than that at 0 GPa (\~3000 \( \Omega \) cm) at 10 K. All observed resistivity behaviors can be well explained by Mott’s VRH mechanism, as shown in the inset to Fig. 2b, where the slope that reflects the Mott activation energy, \( T_0 \), decreases gradually with increasing pressure. The reduction in \( T_0 \) with pressure may be attributed to the intrinsic suppression of the band gap under pressure, in addition to an improvement in the grain connection for the studied polycrystalline sample. The schematic temperature- and pressure-dependent resistivity phase diagram is shown in Fig. 4. Apparently, the nonmetallic state in Cu\(_3\)LiRu\(_2\)O\(_6\) can be strongly suppressed under pressure. However, a true metallic state cannot be achieved up to 35 GPa, the highest pressure in the present study, as shown in the inset to Fig. 4, where resistance \( R \) keeps decreasing at higher pressure (9–28 GPa) but starts to increase when the pressure is above 28 GPa, as discovered in other 4d/5d-transition metal oxides.\(^{38}\) The temperature-dependent \( R \)-dependence of specific heat in the higher-pressure region (inset to Fig. 4) cannot be well fitted or explained by any thermal activation model, indicating that the sample enters a conductive or a bad-metal state. Further investigations are needed to examine whether much higher pressures are required to drive Cu\(_3\)LiRu\(_2\)O\(_6\) into a true metallic state.\(^{39}\)

In summary, we have prepared a new modified delafossite-type Cu\(_3\)LiRu\(_2\)O\(_6\) via a soft topotactic reaction, and extensively characterized its crystal structure and physical properties.
Both magnetic susceptibility and specific heat measurements on Cu₃LiRu₂O₆ demonstrate strong electron correlations, giving temperature-independent Pauli-like paramagnetic behavior and a large Sommerfeld coefficient, γ. However, resistivity measurements show that Cu₃LiRu₂O₆ is insulating at room temperature and follows Mott variable range hopping semiconducting behavior to low temperature. The contradiction suggests that Cu₃LiRu₂O₆ is a nonmetallic metal, probably attributable to spin excitation. Temperature-dependent resistivity measurements up to 35 GPa reveal that the nonmetallic state in Cu₃LiRu₂O₆ can be significantly suppressed by pressure, indicating a possible distortion, as reflected by the differences between Cu₃LiRu₂O₆ radii, electron configuration of the constituent TM, and lattice parameters. As a result, the resultant properties can be very subtly affected by ionic radii, electron configuration of the constituent TM, and lattice distortion, as reflected by the differences between Cu₃LiRu₂O₆ and Li₃LiRu₂O₆ (Li₂RuO₆). A large Sommerfeld coefficient, $g\gamma$, temperature-independent Pauli-like paramagnetic behavior and a large Sommerfeld coefficient, $g\gamma$.

Conflicts of interest
There are no conflicts to declare.

Notes and references