Raman evidence for dimerization and Mott collapse in $\alpha$-RuCl$_3$ under pressures

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We perform Raman spectroscopy studies on $\alpha$-RuCl$_3$ at room temperature to explore its phase transitions of magnetism and chemical bonding under pressures. The Raman measurements resolve two critical pressures, about $p_1 = 1.1$ GPa and $p_2 = 1.7$ GPa, involving very different intertwining behaviors between the structural and magnetic excitations. With increasing pressures, a stacking order phase transition of $\alpha$-RuCl$_3$ layers develops at $p_1 = 1.1$ GPa, indicated by the new Raman phonon modes and the modest Raman magnetic susceptibility adjustment. The abnormal softening and splitting of the Ru in-plane Raman mode provide direct evidence of the in-plane dimerization of the Ru-Ru bonds at $p_2 = 1.7$ GPa. The Raman susceptibility is greatly enhanced with pressure increasing and sharply suppressed after the dimerization. We propose that the system undergoes Mott collapse at $p_2 = 1.7$ GPa and turns into a dimerized correlated band insulator. Our studies demonstrate competitions between Kitaev physics, magnetism, and chemical bondings in Kitaev compounds.

Introduction—The spin-orbit coupling always invigorates new vitality to the intertwines of magnetism and chemical bonds [1–5], and generates the bond-dependent Dzyaloshinskya-Moriya-type [2, 3] and Ising-type interactions [4]. While the former interactions yield non-trivial magnetic topology [6, 7], the latter terms on a honeycomb lattice provide a pathway to realize the Kitaev exactly solvable spin model [8–10]. The ground state of Kitaev spin model [8] represents a typical quantum paramagnetism dubbed quantum spin liquid, in which the spin degree of freedom does not freeze even at zero temperature [11]. Quantum spin liquid displays various patterns of long-range quantum entanglement [8, 12, 13] and supports the fractional excitations [14–20]. Kitaev interactions have been identified in layered honeycomb magnetic materials, such as $\alpha$-Li$_2$IrO$_3$[21] and $\alpha$-RuCl$_3$[22]. However, due to further non-Kitaev interactions, these materials have long-range magnetic orders at low temperatures [23–27]. To achieve the quantum spin liquid state, in-plane magnetic fields have been implemented to suppress the magnetic order in $\alpha$-RuCl$_3$, and the magnetic properties are consistent with theoretical expectations [28–36].

Pressure also promotes the breakdown of magnetic order in $\alpha$-RuCl$_3$ [37–40]. Above a critical pressure, the magnetic signal disappears [37–39]; however, the charge gap does not change significantly, and the system remains an insulating state [37]. A present debate is whether the phase transition under pressures involves the structural deformation due to chemical bondings. X-ray diffraction (XRD) measurements in Ref. [37] didn’t detect any crystal structural phase transition up to 150 GPa, and hence a new quantum magnetic disordered state was proposed. However, XRD measurements in Ref. [39] revealed a Ru-Ru bond dimerization of about 0.6 Å above a critical pressure, and supported a non-magnetic gapped dimerized state at high pressures. Ref. [40] reached a similar non-magnetic dimerized scenario in optical measurements. This is reminiscent of recent high-pressure investigations on the 2D Kitaev material $\alpha$-Li$_2$IrO$_3$ [41] and its 3D polymorph $\beta$-Li$_2$IrO$_3$ [42]. At high pressures, $\alpha$-Li$_2$IrO$_3$ dimerizes [41], while $\beta$-Li$_2$IrO$_3$ manifests the coexistence of dynamically correlated and frozen spins without structural deformation [42]. Raman spectrum simultaneously detects the lattice and magnetic excitations, and their mutual couplings [43, 44]. It is an exemplary experimental tool to study competition between spin-orbit couplings [45–48], magnetism [43, 44, 49, 50], and chemical bondings in Kitaev compounds [47, 51–54].

In this Letter, we perform Raman scattering measurements on $\alpha$-RuCl$_3$ to study the nature of the phase transitions under pressures. Measurements are carried out at room temperature if the temperature is not specified. From the evolution of the Raman spectra, we identify two characteristic pressures $p_1 = 1.1$ GPa and $p_2 = 1.7$ GPa for structural phase transitions. The inversion symmetry of the monoclinic $C2/m$ breaks at $p_1 = 1.1$ GPa and the system turns out to be trigonal $P3_1$12 owing to the stacking pattern changes of the $\alpha$-RuCl$_3$ layers. At $p_2 = 1.7$ GPa, the Ru in-plane Raman mode (161 cm$^{-1}$ at ambient pressure) softens and splits, indicating the dimerization of the Ru-Ru bonds. The Raman suscep-
FIG. 1. Evolution of the Raman spectra of the $\alpha$-RuCl$_3$ under different pressure at room temperature.

![Raman spectra](image)

FIG. 2. (a) The atomic displacements of Raman mode eigenvectors for 5 Raman active modes ($4E_g + 1A_{1g}$) in $\alpha$-RuCl$_3$ under ambient pressure. Only one represented mode is shown for the double degenerated $E_g$ modes. (b) Pressure dependence of the frequencies of the 5 dominate Raman peaks. $p_1 = 1.1$ GPa and $p_2 = 1.7$ GPa are two critical pressures.

bility is greatly enhanced with pressure increasing, mildly adjusts at $p_1 = 1.1$ GPa, and sharply suppressed after the dimerization at $p_2 = 1.7$ GPa. We conclude that the system undergoes the Mott collapse and turns out to be dimerized correlated band insulator with the pressure larger than $p_2 = 1.7$ GPa.

Experimental setup – High-quality single crystals of $\alpha$-RuCl$_3$ are grown from commercial RuCl$_3$ powder by chemical vapor transport method. We use the diamond anvil cell to apply hydrostatic pressures on the samples, and calibrate the value of pressures by the shift of the photoluminescence of Ruby. Raman spectrum measurement is conducted in the backscattering configuration with the light polarized in the basal plane. Light from a 633 nm and 488 nm laser is focused down to 3 µm with the power below 1 mW. Two ultra-narrow band notch filters are used to suppress the Rayleigh scattering light. The scattering light is dispersed by a Horiba iHR550 spectrometer and detected by a liquid nitrogen cooled CCD detector.

Raman spectral evolution – Figure 1 displays the evolution of the Raman spectra of $\alpha$-RuCl$_3$ with the pressure from ambient pressure to 9.4 GPa. The highest measured pressure is up to 24 GPa and the pressure process is reversible [55]. Here, we can identify two characteristic pressures, $p_1 = 1.1$ GPa and $p_2 = 1.7$ GPa, at which the dramatic change of Raman spectra implies the structural phase transitions. At ambient pressure, five Raman modes are clearly resolved at 116, 161, 268, 294, and 310 cm$^{-1}$. At $p_1 = 1.1$ GPa, three new Raman modes at 201, 290 and 363 cm$^{-1}$ appear. The original five modes evolves as following. For the mode at 116 cm$^{-1}$, a new mode splits out at the right side and the original mode disappears at $p_2 = 1.7$ GPa. A similar splitting can be identified for the mode at 161 cm$^{-1}$ at the same pressure, but the original mode remains after that. A splitting can be seen at the left side of the mode at 268 cm$^{-1}$ at $p_1 = 1.1$ GPa and the original peak disappears at $p_2 = 1.7$ GPa. No splitting behavior can be resolved for the mode at 294 cm$^{-1}$ and the intensity of the mode at 310 cm$^{-1}$ experiences a dramatic increasing after 1.7 GPa. After $p_2 = 1.7$ GPa, no sudden change is observed up to 24 GPa [55].

Raman phonon mode assignment – At ambient pressure, we perform Raman and IR measurements on exfoliated $\alpha$-RuCl$_3$ samples down to three atomic layers and no significant difference is observed [55]. Hence we can assign the Raman modes at ambient pressure according to the $D_{3d}$ point group of the single $\alpha$-RuCl$_3$ layer. From group theory, the irreducible representa-
tion of atomic displacement at the Γ point is \( \Gamma_{\text{opt}} = 2A_{1g} + 2A_{2g} + 4E_g + A_{1u} + 2A_{2u} + 3E_u \). Among them, Raman active modes are \( \Gamma_R = 2A_{1g} + 4E_g \). From the polarization measurement \([55]\) and previous Raman studies \([52]\), the first four modes are assigned as doubly degenerated \( E_g \) mode and the last mode as \( A_{1g} \) mode. Other two small Raman modes at 219 and 339 cm\(^{-1}\), can also be resolved by using 488 nm laser as the excitation light \([55]\).

We assign the Raman mode eigenvectors with the help of first-principle calculations \([55]\) and the atomic displacement of 5 Raman active modes are displayed in Fig. 2 (a). For the 4 \( E_g \) modes, the mode at 116 cm\(^{-1}\) is dominated by the twist of the Ru-Cl-Ru-Cl plane; the mode at 161 cm\(^{-1}\) is associated with Ru in-plane relative movement; the mode at 268 cm\(^{-1}\) is related to the Ru-Cl-Ru-Cl plane shearing, and the mode at 294 cm\(^{-1}\) is the Ru-Cl-Ru-Cl ring breathing mode. The \( A_{1g} \) mode at 310 cm\(^{-1}\) can be assigned as the symmetrical layer breathing mode. The other \( A_{1g} \) mode is the triangular distortion mode and the calculated frequency is about 149 cm\(^{-1}\), which is close to the frequencies of the \( A_{1g} \) modes observed in \( \text{CrCl}_3 \) \([54]\) and \( \text{FeCl}_3 \) \([56]\), 142 and 165 cm\(^{-1}\), respectively. Since there is no \( A_{1g} \) peak observed in this range, we believe that the triangular distortion mode is unresolved due to the small scattering cross section, other than the small Raman mode observed at 339 cm\(^{-1}\).

**Inversion symmetry breaking at \( p_1 = 1.1 \) GPa** – The main feature at \( p_1 = 1.1 \) GPa is the appearance of three new Raman modes at 201, 290 and 363 cm\(^{-1}\). The original five Raman modes at ambient pressure change slightly at \( p_1 \). According the group theory and the first-principle calculations of the single \( \alpha-\text{RuCl}_3 \) layer, we assign the mode at 201 cm\(^{-1}\) as an IR-active \( E_u \) mode, 290 cm\(^{-1}\) as an inactive \( A_{2g} \) mode, and 363 cm\(^{-1}\) as an IR-active \( A_{2u} \) mode which has the highest frequency and is related to the asymmetrical layer breathing \([55]\). The appearance of IR-active modes in Raman spectrum indicates the inversion symmetry breaking. To confirm this, the second harmonic generation (SHG) measurement is performed on pressured samples \([55]\). No SHG signal was detected before \( p_1 = 1.1 \) GPa, but SHG signal was detected at 1.4 GPa and higher pressure, which is consistent with inversion symmetry breaking at around \( p_1 = 1.1 \) GPa. Because of no significant change in other Raman modes, we can conclude that the inversion symmetry breaking is due to stacking pattern change of the \( \alpha-\text{RuCl}_3 \) layers.

**Dimerization transition at \( p_2 = 1.7 \) GPa** – As shown in Fig. 2 (b), almost all of the Raman modes show blue-shift with the pressure increasing, however, the Ru in-plane mode at 161 cm\(^{-1}\) displays anomalous red-shift and a large splitting at \( p_2 = 1.7 \) GPa. As shown in Fig. 2 (b), a split peak appears at around 171 cm\(^{-1}\) after 1.7 GPa and rapidly increases to 181 cm\(^{-1}\) at around 2.4 GPa. The the split peak has the higher frequency indicating that two Ru atoms move close to each other and form the dimerization state. By simply assuming that the distance of the nearest Ru atoms is inversely proportional with the frequency of the Ru in-plane mode, we can estimate that the Ru-Ru bond dimerization is about 0.5 Å at 2.4 GPa and increases with pressure.

The Ru-Ru dimerization in the \( \alpha-\text{RuCl}_3 \) layers splits all degenerated \( E \) modes into \( A + B \) modes. We do observe such a splitting for the twist mode at 116 cm\(^{-1}\), shearing mode at 268 cm\(^{-1}\) (it splits at lower pressure probably due to the interlayer interaction). We don’t detect the splitting for the ring breathing mode at 294 cm\(^{-1}\) probably due to its low intensity and the adjacent intensive layer breathing mode. By considering the normal modes of the split Ru in-pane mode, we can assign the high frequency one as \( A_g \) and the low frequency one as \( B_g \). As shown in Fig. 1, the \( A_g \) peak becomes much more intense than the \( B_g \) peak with pressure increasing. By using 488 nm laser as excitation light, the \( B_g \) peak even becomes unresolvable \([55]\). Similarly, the \( B_g \) peak of the split twist mode is the low frequency one and cannot be observed after the dimerization. For the shearing mode, the \( B_g \) peak is the high frequency one and disappears after the phase transition. In a summary, the softening and large splitting of the Ru in-plane mode provide a direct evidence of dimerization and the behaviors of other Raman modes are consistent with this picture.

**Magnetic breakdown from Raman susceptibility** – Raman spectroscopy also measures the magnetic response in the strong spin-orbit coupling system \([43, 45-47]\). The Raman intensity \( I(\omega) \) is proportional to the dynamical Raman tensor susceptibility, \( I(\omega) \propto \langle 1 + n(\omega) \rangle \chi''(\omega) \). Here \( \chi''(\omega) \) is the imaginary part of the correlation functions of Raman tensor, \( \chi(\omega) = \int_0^\infty dt \int d\mathbf{r} \langle \{ \tau(0,0), \tau(\mathbf{r},t) \} \rangle e^{-i\omega t} \). In general, we can expand the Raman tensor \( \tau(\mathbf{r}) \) in powers of spin-1/2 operators, \( \tau^{\alpha\beta}(\mathbf{r}) = \tau^{\alpha\beta}_0(\mathbf{r}) + \sum_\mu K^{\alpha\beta}_\mu S_\mu(\mathbf{r}) + \sum_{S'\neq S} M^{\alpha\beta}_{S'\delta}(\mathbf{r},\delta) S'_\mu S_\delta + ... \). The first term corresponds to Rayleigh scattering, the second and third term are linear and quadratic in the spin operators \( S_\mu \) and correspond to the one magnon \([43, 45, 46]\) and two-magnon process \([43, 45-48, 51]\), respectively. The complex tensor \( K \) determines the strength of the coupling of light to the spin system associated with spin-orbit coupling.

To extract the Raman susceptibility, we first get Raman tensor conductivity \( \chi''(\omega)/\omega \) for frequencies down to 15 cm\(^{-1}\), as shown in Fig. 3 (a) and then integrated over the frequency rang of 15-220 cm\(^{-1}\) to get the Raman susceptibility \( \chi_R \equiv \frac{2}{\pi} \int \frac{\chi''(\omega)}{\omega} d\omega \) in Fig. 3 (b), by using the Kramers-Kronig relation. The pressure dependent of \( \chi_R \) manifests a rapid increase with increasing the pressure and then a sharp drop to zero at \( p_2 = 1.7 \) GPa. The Raman susceptibility \( \chi_R \) contains the static spin susceptibility and multi-spin susceptibility (e.g., bond spin operators), corresponding to one-magnon and multi-magnon process, respectively. As we notice that the static mag-
Magnetic susceptibility $\chi_m$ of α-RuCl$_3$ at room temperatures changes little reported in Refs. [38, 40] before dimerization, we suspect that the increasing magnetic susceptibility $\chi_m$ and Raman susceptibility $\chi_R$ break down, implying the dimerized non-magnetic state.

The Raman spectra of the phonon modes at 116 cm$^{-1}$ and 161 cm$^{-1}$ display significant Fano asymmetry before $p_2 = 1.7$ GPa as shown in Fig. 3 (c). It captures the mutual couplings between the lattice and magnetic excitations. The full width at half maximum (FWHM) and the Fano asymmetry parameter $1/|q|$ measure the strength of the coupling between the lattice and magnetic excitations, as shown in Fig. 3 (d). We can see that the coupling between lattice and magnetic excitations increases with pressure and is completely suppressed after dimerization, consistent with the evolution of Raman susceptibility $\chi_R$ in Fig. 3 (b).

Discussions and conclusions– $\alpha$-RuCl$_3$ has a monoclinic $C2/m$ structure at room temperature at ambient pressure. At $p_1 = 1.1$ GPa, the inversion symmetry is breaking and the system probably turns into the trigonal $P3_112$ structure where the inter-layer interaction distorts the inversion symmetry. The structural transition at $p_1 = 1.1$ GPa is first-order type since the space group changes. The softening and big splitting of the Ru in-plane mode at $p_2 = 1.7$ GPa provide a direct evidence of dimerization. However, the softening is not complete, but a little. According the “little phonon softening” theory [57], the structural dimerization at $p_2 = 1.7$ GPa is a first-order transition. We suspect the system has the space group $C2$ after the dimerization. Dimerization brings the magnetic breakdown due to Mott collapse and the system remains insulating after dimerization. The schematic phase diagram is summarized in Fig. 4.

More remarks on the Mott collapse are needed here. At ambient pressure, $\alpha$-RuCl$_3$ is a spin-orbit Mott insulator with the Kitaev magnetism. Comparing to the iridates, $\alpha$-RuCl$_3$ has a larger electron correlation, but the effective $j_{\text{eff}} = 1/2$ and 3/2 bands near the Fermi surface are not well separated due to a smaller spin-orbit coupling. The mixing between the effective $j_{\text{eff}} = 1/2$ and 3/2 bands brings $\alpha$-RuCl$_3$ closer to a Mott transition. According to the first-principle calculations [59], when the on-site Coulomb interaction $U$ is introduced while fixing a paramagnetic state, the bands near the Fermi level take on a predominantly $j_{\text{eff}} = 1/2$ character and a band gap develops, suggesting a correlation-induced insulating phase. The pressure increases the band width, and hence the mixing between the effective $j_{\text{eff}} = 1/2$ and 3/2 bands. It would finally drive the system into a correlated band insulator via the Mott collapse. The Ru-Ru bond dimerization accelerates the Mott collapse process. Magnetism and chemical bondings is also studied the isostructural counterpart $\alpha$-MoCl$_3$ by the Raman scattering [58]. The spin-orbit coupling and quantum spin liquid physics brings more significant relativity and quantum effects in the studies of magnetism and chemical bonds [1].

In conclusions, we perform Raman studies on the relation between Kitaev magnetism and chemical bondings in $\alpha$-RuCl$_3$ under pressures. At the critical pressure $p_1 = 1.1$ GPa, $\alpha$-RuCl$_3$ undergoes the structural transition with the inversion symmetry breaking from the monoclinic $C2/m$ to the trigonal $P3_112$. due to differ-
ent layer stacking. At the critical $p_2 = 1.7$ GPa, Ru-Ru bonds in the $\alpha$-RuCl$_3$ dimerizes, and the system turns out to a correlated band insulator due to the Mott collapse.

Note added – During the preparation of our manuscript, similar results about the structural phase transition studied by XRD and infrared spectroscopy were reported by other researchers[39, 40].

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