Giant phonon anomalies in the proximate Kitaev quantum spin liquid $\alpha$-RuCl$_3$

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The Kitaev quantum spin liquid epitomizes an entangled topological state, for which two flavors of fractionalized low-energy excitations are predicted: the itinerant Majorana fermion and the $Z_2$ gauge flux. It was proposed recently that fingerprints of fractional excitations are encoded in the phonon spectra of Kitaev quantum spin liquids through a novel fractional-excitation-phonon coupling. Here, we detect anomalous phonon effects in $\alpha$-RuCl$_3$ using inelastic X-ray scattering with meV resolution. At high temperature, we discover interlaced optical phonons intercepting a transverse acoustic phonon between 3 and 7 meV. Upon decreasing temperature, the optical phonons display a large intensity enhancement near the Kitaev energy, $J_K$-8 meV, that coincides with a giant acoustic phonon softening near the $Z_2$ gauge flux energy scale. These phonon anomalies signify the coupling of phonon and Kitaev magnetic excitations in $\alpha$-RuCl$_3$ and demonstrates a proof-of-principle method to detect anomalous excitations in topological quantum materials.
In correlated quantum materials, the nature of electronic interactions and their ground state topology is intimately linked to the geometry of the underlying lattice. The low-energy excitations arising from pure electronic degrees of freedom inevitably interact with the crystal lattice, leaving behind their fingerprints in the phonon spectrum. Hitherto, the interactions of phonons with "conventional" quasiparticles of either Bose–Einstein or Fermi–Dirac statistics, such as magnons in magnets, phasons and amplitudons in density waves, and Bogoliubons in superconductors, have been explored extensively. In contrast, the coupling between phonons and fractional excitations, including spinons in one-dimensional magnets, and Majorana fermions (MFs) and $Z_2$ gauge fluxes that are thought to exist in the Kitaev quantum spin liquids (QSL), have remained elusive. The discovery of such fractional-excitation-phonon coupling (FPC) is of fundamental importance, as they carry key information of the intertwined quantum state. In particular, the coupling of phonons to the itinerant MFs has been predicted to play a pivotal role in the realization of the field-induced quantum thermal Hall effect in $\alpha$-RuCl$_3$, which is a signature of quantum entanglement in Kitaev-QSL.

Numerous studies have shown that the low-temperature phase of $\alpha$-RuCl$_3$ is a promising Kitaev-QSL candidate. As displayed in Fig. 1a, the edge-sharing Ru–Cl octahedra form an effective spin-1/2 honeycomb network. The destructive quantum-interference through the close-to-90° Ru–Cl–Ru bonds significantly suppresses the Heisenberg magnetic exchange interaction, yielding a dominant Ising-type interaction ($J$) perpendicular to the Ru–Cl–Ru plane. Figure 1c schematically depicts the phase diagram of $\alpha$-RuCl$_3$. At zero magnetic field, the low-energy excitations in the paramagnetic phase are primarily determined by the Kitaev term:

$$H = \sum_{\langle i,j \rangle} J_{ij}^K s_i^x s_j^x$$

Here $J_{ij}^K (y = X, Y, Z)$ is the bond-dependent coupling parameter, and $\langle i,j \rangle$ stands for nearest-neighbor pairs of spins at one of the $X$, $Y$, or $Z$ bonds. The two characteristic energy scales are shown in Fig. 1d for the isotropic limit ($J_{ij}^K = J_K$). Below the Kitaev temperature scale $T_K \sim J_K$, the low-energy excitations of Eq. (1) start to fractionalize into itinerant MFs and fluctuating $Z_2$ gauge fluxes. The former features a continuum that peaks broadly near $J_K$, while the latter is a local excitation with an energy around $0.065 J_K$. Below $T_N = 7 \, K$, non-Kitaev interactions such as remnant Heisenberg magnetic exchange couplings, stabilize zigzag antiferromagnetic order that is suppressed under magnetic field. Above $B \sim 7 \, T$, a quantized thermal Hall conductivity (red region in Fig. 1c) is observed, indicating strongly an entangled topological phase. However, unlike the quantum Hall effect of electrons, it has been theoretically predicted that the quantum thermal Hall effect can only be approximate and requires strong FPCs. Here we report experimental signature of the FPC in $\alpha$-RuCl$_3$ by uncovering two-types of phonon anomalies at zero magnetic field: a 35% enhancement of the phonon spectral weight near the Kitaev energy $J_K$, and a giant phonon softening of ~15% below 2 meV.
In $\alpha$-RuCl$_3$, $J_K$ is estimated to be 5–9 meV in the low-temperature phase below 150 K. The Majorana–phonon coupling is present, phonon anomalies are expected in the energy range shown in Fig. 2b. Moreover, a recent theoretical study of the pure Kitaev model predicts that the Majorana–phonon coupling is momentum dependent and peaks near the M and K point. To uncover the energy and momentum-dependent coupling between the optical phonons and the suggested MFs, we compare the temperature-dependent $\chi''(q, \omega)$ along the M–F2 path. A large spectral enhancement can be observed clearly in Fig. 3a–f. Near the M point, the peak intensity of P1 increases dramatically upon cooling from 300 K to 10 K. In contrast, the peak intensity of P2 is unchanged except the 10 K data at the M point. When approaching the $\Gamma_2$ point (towards larger $|q|$), the intensity enhancement first decreases near the crossing-point (P1 and P2 crossed at $q = 0.75$), but then reappears at P2, which is higher in energy near the $\Gamma_2$ point. Interestingly, we find that the spectral enhancement is different between the symmetry-related points $q = 0.45$ and $q = 0.55$. As we show in Fig. 2a, the transverse acoustic phonon starts to merge with the optical phonon near the M point. Since the acoustic phonon intensity is stronger at $q = 0.45$, the asymmetric intensity enhancement suggests that the Majorana–phonon coupling is larger on the acoustic mode than the optical mode near $\omega \sim J_K$. To quantitatively show the spectral enhancement effect, we extract the temperature-induced difference in the integrated phonon intensity, $\Delta \chi''(q, \omega_0) = \int_{\omega_{\text{min}}}^{\omega_{\text{max}}} \chi''(q, \omega, 10K) - \chi''(q, \omega, 300K) d\omega$, and plot $\Delta \chi''(q, \omega_0)$ as function of $\Delta E = \omega_0 - \omega_{\text{max}}$ in Fig. 3g. Here $\omega_0$ denotes the phonon peak position and $\omega_{\text{max}} = 7$ meV is the band-top energy of P1 and P2. Unlike the broad continuum observed in the spin correlation function, the $\Delta \chi''(q, \omega_0)$ decreases rapidly as $\omega_0$ moves away from $J_K$ (Fig. 3). It also shows strong momentum dependence with the enhancement occurring around the high-symmetry points M and $\Gamma_2$.
Fig. 3 Itinerant MF-phonon coupling near \( \omega \sim J_K \). a-f Spectra of the interlaced optical phonons at different reduced momentum transfer \( \mathbf{q} \). Here, we define \( \mathbf{q} = (0, 0, 0) \) and \( (0, 1, 0) \) as \( \Gamma_1 \) and \( \Gamma_2 \), respectively, where the M point is at \( \mathbf{q} = (0, 0.5, 0) \). The labels \( P_1 \) and \( P_2 \) denote the two optical phonon branches. Note the relative peak position of \( P_1 \) and \( P_2 \) switches at \( \mathbf{q} = (0, 0.75, 0) \). The temperature dependent \( \chi' (\mathbf{q}, \omega) \) shows a spectral weight enhancement at \( \omega \sim J_K \) at low temperature. In b we notice a shoulder on \( P_2 \) that may come from the acoustic mode. The drastic increase of \( \Delta \omega \) is softened by about 13% at \( \mathbf{q} = (0, 0.6, 0) \) between 10 and 300 K as a function of \( \Delta \omega = \omega_0 - \omega_{\max} \). Here \( \omega_0 \) is the phonon peak position, \( \omega_{\max} = 7 \) meV is the band top of the interlaced optical phonons. The drastic increase of \( \Delta \omega \) is fitted to an exponential function (dashed line). The vertical error bars in all panels represent one standard deviation based on Poisson counting statistics. The horizontal error bars in g denote the 2\( \sigma \) returned from the fitting algorithm that extract the spectral peak positions.

Fig. 9). This observation is in qualitative agreement with theoretical calculation that shows energy and momentum dependent Majorana–phonon coupling28 (spectrum near the K point with spectral peak at higher energy is shown in Supplementary Fig. 6). The observed phonon enhancement is also consistent with a recent study of frustrated magnetic systems, which predicts large IXS cross-section for magnetic excitations7. We note, however, a quantitative understanding of the energy and momentum-dependent optical phonon enhancement may require theoretical calculations beyond the pure Kitaev model.

We then turn to the transverse acoustic phonon near \( \Gamma_1 \). Figure 4a and b show the temperature-dependence of \( \chi' (\mathbf{q}, \omega) \) at \( \mathbf{q}_1 = (0, 0.1, 0) \) and \( \mathbf{q}_2 = (0, 0.15, 0) \), respectively. At \( \mathbf{q}_1 \), the phonon peak position gradually shifts to lower energies. In contrast, it remains nearly unchanged at \( \mathbf{q}_2 \). The softening-effect is confirmed by directly comparing the raw data, \( S(\mathbf{q}, \omega) \), at 10 and 300 K (Fig. 4c and d). The peak position is softened by about 13% at \( \mathbf{q}_1 \), which corresponds to \(-0.3\) meV shift in energy. Figures 4e and f show the relative peak shift \( \omega_0 (T)/\omega_0 (300 \text{ K}) \) at \( \mathbf{q}_1 \) and \( \mathbf{q}_2 \) as function of temperature. We find that the acoustic phonon softening at \( \mathbf{q}_1 \) becomes progressively stronger below 80 K, consistent with the thermal Hall effect in \( \alpha\text{-RuCl}_3 \) where the thermal Hall conductivity, \( \kappa_{xy} \), starts to increase. In Fig. 4e, we further show the phonon softening at \( \mathbf{q}_3 = (0, 0.05, 0) \). The error-bars returned from fittings are larger at \( \mathbf{q}_3 \), as the elastic intensity becomes stronger when approaching the Bragg peak. Interestingly, the relative phonon softening at \( \mathbf{q}_3 \) (-15%) is even larger when compared to \( \mathbf{q}_1 \). This suggests an enhanced renormalization for long wavelength acoustic phonons.

Discussion
The discovery of temperature and energy dependent phonon softening provides important information on the FPC in \( \alpha\text{-RuCl}_3 \). In the pure Kitaev model [Eq. (1)], quantum fractionalization occurs at \( T_K \sim J_K \sim 100 \text{ K} \), in agreement with our observations. Below \( T_K \), the dispersionless gauge flux excitation crosses the linear dispersing acoustic phonon near \( \omega = 0.065 J_K \sim 0.5 \text{ meV} \) and induces a phonon anomaly near this energy scale (Fig. 4g). The observation of enhanced phonon softening \( \omega (\mathbf{q}_1) = 2 \) meV and \( \omega (\mathbf{q}_2) = 1 \) meV as \( \omega \rightarrow 0.065 J_K \) is consistent with this picture, where the softening effect is expected to be significantly suppressed for \( \omega (\mathbf{q}) \gg 0.065 J_K \). Figure 4h depicts another scenario that attempts to explain the phonon-softening. Here, the acoustic phonon and the itinerant MFs possess nearly identical linear dispersions at \( \mathbf{q} \rightarrow 0 \). This enhances Majorana–phonon coupling that yields a renormalization of the phonon dispersion below \( T_K \). To justify this conjecture, we extract the acoustic phonon velocity \( v_{\text{ph}} \sim 10 \text{ meV A} \) \((h = 1)\), which is based on the room-temperature phonon dispersion shown in Fig. 2. In the isotropic limit16, the velocity of the itinerant MF is \( v_{\text{MF}} = \frac{\sqrt{2}}{4} J_K a \), where the in-plane lattice constant \( a = 5.9639 \text{ Å} \). Comparing \( v_{\text{ph}} \) and \( v_{\text{MF}} \) gives \( J_K \sim 6.2 \text{ meV} \), comparable to the experimental value. Besides the \( Z_2 \) gauge flux and MFs, in more realistic models with non-Kitaev interactions44,45, other fractional excitations may also be consistent with the observed phonon anomalies. It is important to note that the charge and magnetic excitations below 2 meV still remain unresolved in \( \alpha\text{-RuCl}_3 \). In particular, direct experimental evidence of \( Z_2 \) gauge flux is not well established yet. The observed acoustic phonon softening below 2 meV demonstrates a small energy scale in \( \alpha\text{-RuCl}_3 \) that strongly renormalizes the acoustic phonon spectrum and hence may be responsible for the quantized thermal Hall effect.

Finally, we discuss the possibility of magnon–phonon coupling. Below \( T_N \), a gapped magnon excitation between 2–7 meV was observed in \( \alpha\text{-RuCl}_3 \) by previous neutron studies19,21,22,37. However, as we show in Figs. 3 and 4, the phonon anomalies onset at \( T_K \), which is well above \( T_N \). More importantly, evidence of an enhanced
phonon softening is observed at ω = 1 meV (see q₁ in Fig. 4e and Supplementary Fig. 5), which is well below the magnon gap. Therefore, a magnon–phonon coupling is unlikely giving rise to the observed acoustic phonon softening. However, the magnon–phonon coupling may indeed be present in α-RuCl₃. As we show in Fig. 2, the P₂ phonon energy is the same as the magnon energy near the M point¹⁹,²¹,³⁸. Interestingly, the P₂ phonon intensity at the M point is enhanced at 10 K–Tₘ, supporting magnon–phonon coupling⁴⁶. In addition, strong anharmonicity is proposed in the magnon excitation of this material⁴⁷, which represents the break-down of the spin quasiparticles. Such excitations contain extremely broad features⁴⁷ that are contradictory to the well-defined energy scale of the phonon anomalies observed here.

Our discovery of two-types of phonon anomalies, i.e., the spectral enhancement in the optical phonon and the acoustic phonon coupled systems¹⁰. The ~13% phonon softening at q₁ and q₂ (red squares in e) corresponds to a ~0.3 meV phonon peak shift. This value is as large as some well-known electron-phonon coupled systems¹⁰. The blue diamonds in e represent the relative peak shifts at q₃ = (0, 0.05, 0) that show even larger softening-effect (~15% at 60 K), whereas q₂ displays negligible change as shown in f. This acoustic phonon anomaly, together with the spectral enhancement discussed in Fig. 3, present a full picture of the FPC in α-RuCl₃. g, h Schematically show two phonon coupling mechanisms. g The flatband of the Z₂ flux mode intercepts the acoustic phonon near ω ~ 0.065/kₘ. h The nearly identical dispersion of the itinerant MF and the acoustic phonon at q → 0 causes a phonon renormalization at low temperature. The error bars in a–d represent one standard deviation assuming Poisson count statistics. The error bars in e, f denote the 2σ returned from the fitting.

**Methods**

**Sample preparation and characterizations.** Millimeter-sized α-RuCl₃ crystals were grown by the sublimation of RuCl₃ powder sealed in a quartz tube under vacuum²². The growth was performed in a box furnace. After dwelling at 1060 °C for 6 h, the furnace was cooled to 800 °C at 4 °C/h. Magnetic order was confirmed to occur at 7 K by measuring magnetic properties and specific heat²¹.

**Inelastic X-ray scattering.** The experiments were conducted at beam line 30-ID-C (HERIX) at the Advanced Photon Source (APS). The highly monochromatic X-ray beam of incident energy E₀ = 23.7 eV (l = 0.5226 Å) was focused on the sample with a beam cross section of ~35 × 15 mm² (horizontal × vertical). The total energy resolution of the monochromatic X-ray beam and analyzer crystals was ΔE ~ 1.3 meV (full width at half maximum). The measurements were performed in transmission geometry. Typical counting times were in the range of 30–120 s per point in the energy scans at constant momentum transfer Q. H, K, L are defined in the trigonal structure with a = b = 5.9639 Å, c = 17.17 Å at the room temperature.

**Density functional theory calculations of phonon spectrum.** Phonon dispersions for α-RuCl₃ were calculated using with density functional perturbation theory (DFPT) and the Vienna Ab initio Simulation Package (VASP). The exchange-correlation potential was treated within the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof variety, where the kinetic energy cutoff was set to 400 eV. Integration for the Brillouin zone was done by using a Monkhorst-Pack k-point grids which is equivalent to 8 × 8 × 9.

**Data availability**

The data that support the findings of this study are available from the corresponding author on reasonable request.
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Author contributions

H.M. conceived and designed the study. H.L., A.S., G.F., D.G.M., J.K.K., H.N.L., M.P.M.D., and D.G.M. performed the IXS experiment. H.L. and H.M. analyzed the IXS data. T.T.Z., S.M., G.B.H., and S.O. performed the DFT calculations and theoretical analysis. J.Q.Y. and D.M. synthesized the high-quality single crystal samples. H.L., T.T.Z., M.P.M.D., and H.M. prepared the manuscript with inputs from all authors.
Competing interests
The authors declare no competing interests.

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