Amplitude excitation and giant spin-lattice fluctuations in a pyrochlore ruthenate single crystal

Dirk Wulferding,1,2 Junkyeong Kim,3 Mi Kyung Kim,1,2 Yang Yang,4 Jae Hyuck Lee,1,2 Dongjoon Song,1,2 Dongjin Oh,1,2 Heung-Sik Kim,5 Li Ern Chern,6 Yong Baeck Kim,6 Minji Noh,2,7 Hyunyong Choi,2,7 Sungkyun Choi,8,9 Natalia B. Perkins,4 Changyoung Kim,1,2† and Seung Ryong Park3,‡

1Center for Correlated Electron Systems, Institute for Basic Science, Seoul 08826, Korea
2Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea
3Department of Physics, Incheon National University, Incheon 22012, Korea
4School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455, USA
5Department of Physics, Kangwon National University, Chuncheon 24311, Korea
6Department of Physics, University of Toronto, Toronto, ON M5S 1A7, Canada
7Institute of Applied Physics, Seoul National University, Seoul 08826, Korea
8Center for Integrated Nanostructure Physics, Institute for Basic Science, Suwon 16419, Korea
9Sungkyunkwan University, Suwon 16419, Korea

(Dated: April 27, 2022)

We uncover a wide temperature regime of enhanced spin-lattice fluctuations in single crystals of the pyrochlore ruthenate Nd₂Ru₂O₇. These fluctuations, prominent in Raman spectroscopy, yet elusive to thermodynamic probes, emerge below the Néel temperature and culminate in a new low-energy amplitude excitation with an order-parameter-like behavior at 3 meV. Concomitantly, an enormous phonon energy renormalization of ∆ωphon > 3 meV—a order of magnitude larger than those in related pyrochlore oxides—is observed. The unique two-fold symmetry of the low-energy mode, incompatible with the underlying crystal structure, raises the possibility of nematic order. Our study shines a light on instabilities in pyrochlore systems and on resulting symmetries and amplitude excitations that can be described within the Higgs mechanism.

Introduction.— Among correlated electron systems, 4d transition metal oxides (TMOs) provide exceptional platforms for exploring complex emergent phenomena due to their intricate interplay of spin and orbital degrees of freedom [1, 2]. Examples include spin fractionalization into Majorana fermions due to bond-dependent exchange frustration in Kitaev honeycomb magnets [2–6], unconventional superconductivity [7], spin-ice states with emergent magnetic monopoles and unique quantum electrodynamics [8, 11], and materials with topologically non-trivial electronic and magnon band structures [12–14], to name a few. Particularly, the family of 4d transition metal pyrochlore oxides exhibit a diverse array of exotic phenomena, driven by the interplay between geometrical frustration, electronic interactions, spin-orbit coupling, and lattice instabilities [13].

The diverse physical properties of these 4d TMO pyrochlores with the general chemical formula A₂M₂O₇ are determined by the choice of A-site ions and transition metal ions M. A₂Ru₂O₇ with a series of rare-earth elements (A = Nd, Y, Sm, Eu, Ho, Er, ...), in which Ru⁴⁺ ions (electron configuration 4d⁷) are expected to carry S = 1 spins according to Hund’s rule, are of special interest as candidate materials to study magnetic properties of frustrated spin-1 antiferromagnetism [15–19]. On another hand, the spin-orbit coupling favors a non-magnetic J = 0 ionic ground state of Ru⁴⁺, in which case the magnetic order can be only realized via the condensation of excited J = 1 triplet states [20]. In this case, we should expect strong phase and amplitude fluctuations of magnetic order and, perhaps, some critical behavior as, e.g., observed in the d⁸ Mott insulator Ca₂RuO₄ [21]. Yet, the lack of high quality single crystals of the A₂Ru₂O₇ series has hindered a systematic experimental exploration of their exact ground states and emergent magnetic anisotropies so far.

Here, we employ polarization-resolved Raman spectroscopy to study the symmetry and the temperature-dependence of magnetic and phonon excitations in high quality Nd₂Ru₂O₇ single crystals. Details about the single crystal synthesis of Nd₂Ru₂O₇, their thermodynamic characterization, symmetry analysis, and the Raman scattering experiments are given in the Supplementary Information. In our study we uncover an extended temperature range of coupled spin and lattice fluctuations together with the emergence of an anomalous, well-defined low energy excitation below the Néel temperature of the Ru ions. Our observations suggest that the Ru⁴⁺ spin configuration in the ground state of Nd₂Ru₂O₇, either due to the ordering of S = 1 [15] or due to condensation of the triplets [21], exists in close vicinity to quantum criticality separating it from a non-magnetic phase with zero total angular momentum and exhibits strong magnetic fluctuations.

Nd₂Ru₂O₇ consists of Ru⁴⁺ ions octahedrally coordinated by O²⁻ ions. Both Ru⁴⁺ and Nd³⁺ ions are arranged in interpenetrated pyrochlore lattices of corner-sharing Ru (Nd) tetrahedra. These two sublattices are magnetically coupled thus leading to rich magnetic behaviors. Below T_N = 147 K, Ru magnetic moments order
antiferromagnetically, although a dispute exists about
the nature of the ordering – while some experiments
point towards a long-range ordered state \[22, 23\], an
earlier neutron diffraction study on powder samples of
\(\text{Nd}_2\text{Ru}_2\text{O}_7\) suggested a spin-glass or short-range ordered
state \[24\]. It also found a significantly reduced magnetic
moment of about 1.18 \(\mu_B\), compared to the nominal value of
2 \(\mu_B\) expected for Ru\(^{3+}\) ions \[24\]. This indicates the
existence of competing interactions and, perhaps, partial
quenching of the magnetic moment by the antiparallel
alignment of the orbital and the spin moment due to
spin-orbit coupling similarly to \(\text{Ca}_2\text{RuO}_4\) \[25, 26\]. Just
below 2 K, a second magnetic transition marks the all-
in-all-out long-range order of Nd\(^{3+}\) spins \[24\], i.e., the
spins on Nd ions on half of the tetrahedra point toward
its center (all-in), while those on neighboring tetrahedra
point outward (all-out).

Magnetic excitation spectrum. – We focus on tem-
peratures above 5 K, therefore considering the Nd\(^{3+}\) spins
to be paramagnetic and thus assign any magnetic exci-
tations in our study to Ru ions. In Figs. 1(a) and 1(b)
we plot Bose-corrected Raman data obtained at 300 K
and at 5 K in two different scattering geometries, dis-
tinguishing between the three allowed symmetry chan-
els \(A_{1g}+T_{2g}\) and \(E_g\). In the energy range 33 meV –
90 meV these spectra are dominated by phonon modes,
which we will discuss in more detail below. Three low-
energy excitations emerge below \(T_N\) at 32 meV, 25 meV,
and 3 meV, marked by asterisks in Fig. 1(a). Since
one-magnon excitations in the energy range \(\approx 20 – 35\)
meV were observed in the related spin-1/2 pyrochlore
compound \(\text{Y}_2\text{Ir}_2\text{O}_7\) \[28\], as well as in Raman scattering
experiments from powder samples of \(\text{A}_2\text{Ru}_2\text{O}_7\) \((A = \text{Y},
\text{Sm}, \text{Eu}, \text{Ho}, \text{Er})\) \[29\], we assign the two higher-lying ex-
citations at 32 and 25 meV to one-magnon modes.

In contrast to these modes of weak scattering intensi-
ties, the peak at 3 meV (in the following referred to as
the A-mode) dominates the Raman spectra at low temperatures.
The angular dependence of its intensity, measured at
\(T = 5\) K, is plotted as a function of light polarization
within the \(ab\) plane with parallel polarization [inset of
Fig. 1(a)] and crossed polarization [inset of Fig. 1(b)].
Its low two-fold symmetry in the parallel polarization
and the modulation of the lobe’s amplitudes in the cross
polarization are at odds with expected \(A_1, T_2,\) or \(E\) irre-
ducible representations of the \(T_d\) lattice point group.

FIG. 1. Temperature dependence of magnetic modes. (a) and (b) Bose-corrected Raman intensity (Im\(\chi\)) measured at
5 K (blue curve) and 300 K (red curve) in the \(A_{1g}+T_{2g}\) \((\text{e}_\text{in} = \text{e}_\text{out} = [1\overline{1}0])\) and the \(E_g\) \((\text{e}_\text{in} = [1\overline{1}0], \text{e}_\text{out} = [1\overline{1}0])\) symmetry channels,
respectively. Arrows mark the \(T = 5\) K (blue curve) and 300 K (red curve) in the \(A_{1g}\) intensity of excitation
\(\mu\) at 2 meV. The blue circles in (g) show the intensity of quasi-elastic scattering. The dashed green line marks
one-magnon excitation at 25 meV (pale green diamonds). The solid red curve is a mean-field fit to the energy (see text for
details). The blue circles in (g) show the intensity of quasi-elastic scattering. The dashed green line marks \(T_N\).

(a) and (b) Bose-corrected Raman intensity (Im\(\chi\)) measured at
5 K (blue curve) and 300 K (red curve) in the \(A_{1g}+T_{2g}\) \((\text{e}_\text{in} = \text{e}_\text{out} = [1\overline{1}0])\) and the \(E_g\) \((\text{e}_\text{in} = [1\overline{1}0], \text{e}_\text{out} = [1\overline{1}0])\) symmetry channels,
respectively. Arrows mark the \(T = 5\) K (blue curve) and 300 K (red curve) in the \(A_{1g}\) intensity of excitation
\(\mu\) at 2 meV. The blue circles in (g) show the intensity of quasi-elastic scattering. The dashed green line marks
one-magnon excitation at 25 meV (pale green diamonds). The solid red curve is a mean-field fit to the energy (see text for
details). The blue circles in (g) show the intensity of quasi-elastic scattering. The dashed green line marks \(T_N\).
of the pyrochlore lattice (see Supplementary Information for a detailed symmetry analysis).

To trace the thermal evolution of low energy excitations including the A-mode, we show their temperature dependence in a color contour plot in Fig. 1(c). Note that the energy is plotted on a logarithmic scale to highlight the low energy range. As we approach \( T_N \) from the high temperature side, there is a continuous increase in a broadened spectral weight at the left shoulder of the phonon around 40 meV (see the green-colored background between 10-40 meV). Once \( T_N \) is reached and crossed, this spectral weight is transferred towards zero energies, forming an increasing quasi-elastic scattering signal. This signal can be well fitted by a Lorentzian lineshape centered at \( E = 0 \), as demonstrated in Fig. 1(d) for the temperatures 110-140 K. Such behavior is characteristic for a phase transition and originates from increasing zero energy density fluctuations of the order parameter, which diverge through a phase transition. Only below 100 K does the quasi-elastic scattering intensity decrease, giving rise to a second, massive excitation, marked by the pale red shaded area in Fig. 1(d) for a few selected temperatures. The peak position determined from the fit is shown with pale blue squares in Fig. 1(c). The full temperature evolution of the A-mode is given in the panels of Figs. 1(e)-(g), where we analyze frequency, line width, and intensity of this excitation. Fig. 1(g) additionally plots the intensity over temperature for the quasi-elastic signal for direct comparison. Interestingly, neither bulk magnetization, nor specific heat show any hint for an additional phase transition around 100 K (see Supplementary Figure 1). Despite the absence of a phase transition at 100 K, the dispersion of the A peak suggests that this mode may be related to some order parameter \( \phi \) lowering the crystalline symmetry of the pyrochlore lattice.

Comparing the thermal evolution of the A mode with that of the 25 meV excitation, we notice a fundamentally different behavior, as shown in Figs. 1(e)-(g) (green diamonds vs. red squares). The nearly temperature-independent energy of the 25 meV one-magnon candidate stands in stark contrast to the dramatic softening of mode A, which instead follows an order-parameter-like behavior that can be described by a critical exponent, i.e., \( \omega(T) = \alpha |T - T^*|^\beta \), with \( \alpha \) being a scaling factor, \( T^* = 97 \text{ K} \) the critical temperature, and \( \beta = 2/5 \) the critical exponent. Likewise, while the linewidth of the one-magnon mode at 25-meV remains close to constant over a wide temperature range and up to \( T_N \), the width of the A-mode broadens significantly with increasing temperature. Finally, the intensity of the 25-meV mode gradually drops off and approaches 0 around \( T_N \). The A-mode, instead, evidences a quick drop in intensity with increasing temperature and disappears around \( 2/3 T_N \). As detailed in the Supplementary, the thermal evolution of the 32 meV excitation mirrors that of the 25-meV one.

Considering the above, we refrain from assigning this low-energy A-mode to a one-magnon scattering process. Although its nature remains ambiguous, a plausible assumption is that – similarly to \( \text{Cs}_8\text{Ru}_4 \) \( ^{25} \) – the A-mode observed here is dominated by coherent amplitude fluctuations of soft magnetic moments. In this scenario, the Higgs mechanism can account for the observed excitation A. Within the same picture of soft magnetic moments, excitations at 25 and 32 meV can be assign to the transverse excitations of the order parameter (triplon condensate), i.e., one-magnon excitations.

**Phonon dynamics.** In the following, we will discuss the enhanced lattice dynamics, which persist in \( \text{Nd}_2\text{Ru}_2\text{O}_7 \) down to half of \( T_N \). In Fig. 2(a) we present the mid-energy range of the \( E_g \) symmetry channel, which is dominated by the \( E_g \) phonon at 40 meV. The arrows at 35 and 52 meV mark small leakage of phonons from the \( T_2g \) channel. With decreasing temperature phonons sharpen, shift in frequency, and gain in intensity. In particular, below \( T_N \) a moderate softening of the phonon frequency is observed, followed by a highly dynamical, fluctuating regime in which the phonon splits into a dominating low-energy mode and a weaker high-energy shoulder. Below \( \approx 75 \text{ K} \), the lattice dynamics resumes its rather static behavior.

Fig. 2(b) highlights the temperature-dependent lineshape of the \( E_g \) phonon, which is highly asymmetric and can be described by a Fano lineshape at room temperature, indicating a strong deviation from the conventional anharmonic behavior. In contrast, the 5 K spectrum evidences a nearly symmetric Lorentzian phonon lineshape. A detailed analysis of the phonon peak parameters, such as frequency, linewidth, intensity, and Fano asymmetry is presented in Figs. 2(c)-(f). Above \( T_N \) the temperature dependence of the phonon frequency \( \omega \) and linewidth \( \Gamma \) closely follows conventional cubic second-order anharmonic softening and broadening, respectively, as indicated by the solid red lines. The corresponding fitting functions are given by \( \omega(T) = \omega_0 - C \left( 1 + \frac{2}{\exp(\omega_0/2k_B T) - 1} \right) \), and \( \Gamma(T) = \Gamma_0 \left( \frac{1 + D}{\exp(\omega_0/k_B T) - 1} \right) \), where \( C \) and \( D \) are fitting parameters [30]. Once Ru ions start to order magnetically below \( T_N \), this anharmonic behavior is abruptly halted and replaced by an enormous energy softening, peak broadening, and a line splitting. Simultaneously, the intensity of the dominating line starts to increase monotonically, and its Fano asymmetry drops and approaches zero towards lowest temperatures. As the \( E_g \) phonon involves twisting motions of the RuO\(_6\) octahedra it is significantly susceptible to changes in the Ru-O-Ru bond angle. Therefore, it can be a sensitive local probe to the onset of magnetic order or even to an enhancement of spin-spin correlations. In particular, the dramatically enhanced linewidth signals the opening of an effective decay channel.

The appearance of an asymmetric Fano lineshape
FIG. 2. Evidence for giant spin-phonon coupling in Nd$_2$Ru$_2$O$_7$. (a) Color contour plot of the mid-energy range focusing on the thermal evolution of the E$_g$ channel. Arrows mark leakage of phonons from the T$_{2g}$ channel. (b) Phonon spectra of the E$_g$ channel measured at 5 K and at 300 K (symbols) together with asymmetric Fano fits to the dominating E$_g$ phonon mode (solid lines). (c)-(f) Temperature-dependence of the phonon parameters frequency, linewidth (FWHM), intensity, and Fano asymmetry for the E$_g$ phonon. The solid red lines are fits to the frequency and linewidth, corresponding to anharmonic softening and broadening, respectively (see text for details). Deviations from this anharmonic behavior are shaded in pale-green. $T_N$ and $T^*$ are marked by dashed lines. (g) Polarization plots for phonons of A$_{1g}$, T$_{2g}$ and E$_g$ symmetry measured in parallel (red circles) and in crossed (black squares) configuration at $T = 5$ K. The solid red and gray lines trace the theoretical rotational anisotropy following the respective Raman tensors. (h) The nematic order parameter $\eta(T)$ as extracted from the phonon frequencies shown in panel (c). (i) Sketch of the ionic displacement pattern of the doubly degenerate E$_g$ mode.

is generally ascribed to the interference of a discrete (phonon) mode with an underlying, broad continuum of excitations [31]. A similar temperature dependence has been observed in the all-in-all-out pyrochlore compound Cd$_2$Os$_2$O$_7$ [32], where it was related to a metal-insulator transition driven by spin-charge-lattice coupling. We recall that Nd$_2$Ru$_2$O$_7$ remains electrically insulating across the investigated temperature regime [22], therefore we rule out an electronic continuum as the origin. Instead, incoherent spin fluctuations of the paramagnetic phase are a natural candidate for the broad continuum, as reported in the pyrochlore iridate Eu$_2$Ir$_2$O$_7$ [33]. Upon passing through $T_N$, the spectral weight of the continuum is transferred towards quasi-elastic scattering and eventually to the low-energy amplitude mode. Thus, below 100 K the interference between the broad magnetic continuum and the 40 meV phonon mode disappears and the phonon approaches a symmetric Lorentzian lineshape at low temperatures. Moreover, the splitting of the E$_g$ phonon mode into two one-dimensional modes E$_{1g}^1$ and E$_{2g}^2$ below $T_N$ signals a lowering of symmetry below $T_N$. In fact, with the onset of the magnetic order the mirror symmetry is broken, which transforms the structure from Fd$\bar{3}$m to Fd$\bar{3}$ with two distinct E$_g$ Raman tensors (see Supplementary Information for details).

Therefore, we now turn to the symmetry of the amplitude excitation and of the phonons, as well as to the possibility of nematic order in Nd$_2$Ru$_2$O$_7$. Fig. 2(g)
shows polar plots of phonon intensities of different symmetry, measured at $T = 5$ K in parallel ($xx$, red circles) and crossed ($xy$, black squares) polarization [see Supplementary Fig. 2 for the full data set]. The experimental data for the $A_g$ and $T_{2g}$ modes matches their fits very well, which are denoted by solid lines and based on the respective Raman tensors given in the Supplementary. In contrast, the splitting of the $E_g$ phonon mode into $\omega_1$ and $\omega_2$ lowers the symmetry of the resulting branches observed in parallel polarization from 4-fold to 2-fold rotationally symmetric. Thus pointing towards a global distortion of the RuO$_6$ octahedra. In crossed polarization, these two branches still appear as 4-fold symmetric [see Fig. 2(g) and Supplementary Fig. S2(d)]. Both the splitting and the symmetry reduction are reminiscent of a nematic phase transition. In Fig. 2(h) we quantify the energy difference between $\omega_1$ and $\omega_2$ by introducing $\eta = (\omega_1 - \omega_2)/(\omega_1 + \omega_2)$, a parameter related to the nematic order parameter [34], and Fig. 2(i) sketches the ionic displacement patterns corresponding to the two-fold degenerate $E_g$ phonon mode. Upon distortion of the local octahedral environment, this two-fold degeneracy may be lifted, resulting in a splitting of the $E_g$ phonon. The temperature dependence of $\eta$ closely follows that of the $A$-mode, hence its sharpening at around 100 K may indicate the onset of nematic order. Also, the fact that the two-fold, distorted $E_g$ polar plot resembles the rotational symmetry of excitation $A$, as shown in Figs. 1(a) and 1(b), suggests a strong correlation between the amplitude (nematic) $A$-mode and lattice degrees of freedom of the RuO$_6$ octahedra. We can also rule out a significant misalignment of the crystal or contributions from (potentially existing) neighboring domains as sources for these distorted polar plots, since all other phonons closely follow their expected rotational symmetry and only the $E_g$ mode is affected. Previous studies on Nd$_2$Ru$_2$O$_7$ have not found any indication of a structural phase transition within our temperature range of interest, with experimental methods ranging from synchrotron and x-ray diffraction [22, 33], to neutron diffraction [27]. However, a pronounced, non-monotonic decrease in the Ru-O-Ru angle was observed between 150 K – 100 K [35]. This can indicate a gradual rearrangement of spins in a (short-ranged) antiferromagnet or a transition among two neighboring phases with decreasing temperature, accompanied by strong fluctuations and manifested by the observed entangled spin-lattice instabilities.

We uncover a wide temperature regime of coupled spin and lattice fluctuations in the pyrochlore ruthenate Nd$_2$Ru$_2$O$_7$ via Raman spectroscopy, which is elusive in other thermodynamic probes. A new low-energy excitation emerging out of these fluctuations with a distinct symmetry and peculiar temperature evolution might be interpreted as either strong amplitude fluctuations of soft magnetic moments or related nematic fluctuations. Future studies under extreme conditions, such as high pressure and magnetic fields, are envisaged to tune these fluctuations and further pinpoint the nature of the low-energy mode.

We acknowledge important discussions with Tae Won Noh and SungBin Lee. This work was supported by the Institute for Basic Science (IBS) (Grant Nos. IBS-R009-G2, IBS-R009-Y3) and by the NRF (Grant No. 2020R1A2C1011439). M.N. and H.C. were supported by the National Research Foundation of Korea (NRF) through the government of Korea (Grant No. NRF-2021R1A2C3005905, NRF-2020M3F3A2A03082472), and Scalable Quantum Computer Technology Platform Center (Grant No. 2019R1A5A1027055). L.E.C. and Y.B.K. are supported by the NSERC of Canada. S.C. acknowledges support by the Institute for Basic Science (IBS-R011-Y3-2021). Y.Y. and N.B.P. were supported by the National Science Foundation under Award No. DMR-1929311.

**SUPPLEMENTARY INFORMATION**

**Sample Growth.** Single crystals of Nd$_2$Ru$_2$O$_7$ were synthesized using the KF flux method [36]. Typical resulting crystals of about 30 $\times$ 30 $\times$ 30 $\mu$m$^3$ volume exhibit shiny triangular- and rectangular-shaped as-grown surfaces, corresponding to [111] and [100] facets.

**Raman Scattering.** Raman spectroscopic experiments have been carried out using a $\lambda = 532$ nm solid state laser (Cobolt Samba) with a spot diameter of about 10 $\mu$m and an incident laser power at the sample position below 0.35 mW to reduce local laser heating effects. The scattered light passed through a volume Bragg grating notch filter set (Optigrate) to discriminate the laser line and to access Raman signals with energies as low as 0.8 meV. The light was dispersed through a single-stage Horiba iHR 320 spectrometer onto a Horiba Synapse CCD. Where indicated, Bose-corrected Raman intensity $\text{Im}\chi(\omega)$ is plotted. It is related to the as-measured Raman intensity $I(\omega)$ via the fluctuation-dissipation theorem by $I(\omega) = [1 + n(\omega)]\text{Im}\chi$, where $n(\omega)$ is the Bose factor.

**Magnetic Susceptibility and Specific Heat.** In Supplementary Fig. S1(a) we show the magnetization curves measured at a magnetic field of 100 Oe in zero-field-cooled and field-cooled mode. Because of the small size of individual crystals these measurements were performed on a polycrystalline pellet of Nd$_2$Ru$_2$O$_7$, thereby averaging over random field directions. Measurements of the specific heat of a polycrystalline pellet with and without applied magnetic field are shown in Fig. S1(b). Both susceptibility and specific heat measurements mark a sharp, well-defined phase transition at the Néel temperature at 147 K, while lacking any signature for additional transitions around 100 K.

**Phonon Assignment and Selection Rules.**
Nd$_2$Ru$_2$O$_7$ crystallizes in the cubic, centro-symmetric space group $Fd3m$, with atoms occupying the following atomic positions: Nd – (0.5, 0.5, 0.5), Ru – (0, 0, 0), O1 – (0.3309, 0.125, 0.125), O2 – (0.375, 0.375, 0.375) [27]. These correspond to the Wyckoff positions: Nd – 16$c$, Ru – 16$b$, O1 – 8$d$, O2 – 48$f$ [24], which results in the six Raman-active modes $A_{1g}$ + $E_g$ + 4$T_{2g}$, and their corresponding Raman tensors

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$$

$$E_g^1 = \begin{pmatrix} -\sqrt{3}c & 0 & 0 \\ 0 & \sqrt{3}c & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad E_g^2 = \begin{pmatrix} c & 0 & 0 \\ 0 & c & 0 \\ 0 & 0 & -2c \end{pmatrix}$$

$$T_{2g}^1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}, \quad T_{2g}^2 = \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}, \quad T_{2g}^3 = \begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

To assign the Raman active phonon modes to their respective symmetries, and to highlight their anomalous behavior, we plot color contour maps of the angular dependent Raman response in parallel and crossed configurations for two different temperatures in Supplementary Fig. S2. Excitations of all three symmetries $A_{1g}$, $E_g$, and $T_{2g}$ are clearly distinguished at 300 K, following their expected behavior. One $T_g$ phonon remains obscured either due to a weak scattering intensity, or due to a (partial) overlap with another phonon mode. At 5 K (i.e., below $T_N$) the $E_g$ phonon clearly deviates from its 4-fold symmetry (clearly observed for $E_{in}$ // $E_{out}$) and instead follows a distorted 2-fold pattern. Strikingly, the newly emerged 3-meV excitation mimics this behavior. We note that the maximal subgroup of $Fd3m$ (No. 227) which can support such behavior is $Fd\bar{3}$ (No. 203). Even though the lowering of the symmetry increases the number of Raman-active modes to $A_g + 2E_g + 6T_g$, the Raman tensors for $Fd\bar{3}$ resemble the exact same form as those for $Fd3m$ except for the $E_g$ channels, which transform to

$$E_g^1 = \begin{pmatrix} b' + \sqrt{3}c' & 0 & 0 \\ 0 & b' - \sqrt{3}c' & 0 \\ 0 & 0 & -2b' \end{pmatrix}$$

$$E_g^2 = \begin{pmatrix} c' - \sqrt{3}b' & 0 & 0 \\ 0 & c' + \sqrt{3}b' & 0 \\ 0 & 0 & 0 \end{pmatrix}.$$ 

Hence at $T = 5$, the other phonon modes retain their selection rules, while both of the two distinct $E_g$ channels now becoming Raman-active. The Raman tensor of $E_g^1$ ($E_g^2$) describes the angular dependence of $\omega_1$ ($\omega_2$) as discussed in the main text. At $T = 5$ K we clearly identify $A_g$ (at 61.4 meV) and split $E_g$ (at 37.8 meV and 41.5 meV) modes, as well as three out of the six $T_g$ phonons (at 34.9 meV, 51.6 meV, and a faint one at 81.9 meV). Two additional candidates for $T_g$ phonons might be located around 150 meV, not shown here).

**Temperature dependence of one-magnon modes.** The full temperature dependence of the low-energy spectral range is displayed in Supplementary Fig. S3, focusing on the evolution of one-magnon excitations at 25 meV and 32 meV (marked by dashed black lines). In contrast to the $A$-mode at 3 meV, these two excitations show no discernible energy- or linewidth-dependence on temperature, and gradually decrease in intensity upon approaching $T_N$.

**Symmetry elimination of one-magnon origin of the $A$-mode.** Here we will show that the $A$-mode can not be understood as a one-magnon Raman response in any of the magnetically ordered phases of the phenomenological $S = 1$ model obtained by a mean-field approach in Refs. [13, 18]. Five possible spin configurations were identified for a reasonable set of the model parameters: all-in-all-out state, splayed ferromagnet, coplanar XY antiferromagnet (1) and (2), and non-coplanar
FIG. 4. Supplementary Fig. S2. Angular-dependent color contour plots of Raman spectra on the [100] surface of Nd$_2$Ru$_2$O$_7$ taken at $T = 300$ K in parallel (a) and crossed (b) polarization. (c) and (d) Corresponding color contour plots measured at $T = 5$ K.

FIG. 5. Supplementary Fig. S3. Temperature dependent Raman spectra recorded in parallel light polarization, containing the $A_{1g} + T_{2g}$ symmetry channel.
XY antiferromagnet. To compute the Raman response, we employ a simple London-Fleury approach [31], in which the Raman operator on the bond $\langle i,j \rangle$ is defined as $R_{\text{LF}} \sim \sum_{\langle i,j \rangle} e_{\text{in}} \cdot r_{ij} (e_{\text{out}} \cdot r_{ij}) \mathcal{H}_{ij}$ and the Raman intensity as $I(\omega) = \int d^4 e \text{exp}(i \omega \langle R_{\text{LF}}(t) R_{\text{LF}}(0) \rangle)$, where $r_{ij}$ is the vector indicating the bond $\langle i,j \rangle$, $\mathcal{H}_{ij}$ is the effective spin Hamiltonian on this bond, and $e_{\text{in}}$ ($e_{\text{out}}$) denotes the polarization of the incident (outgoing) light. The symmetry consideration allows us to decompose the Raman operator into different symmetry channels according to the irreducible representation of the point group symmetry of the ground state: $R_{\text{LF}} = \sum_{\langle i,j \rangle} \mathcal{R}_{ij} = \sum_{\alpha,\beta=x,y,z} \xi_{\alpha\beta} \left( \sum_{\langle i,j \rangle} \mathcal{R}_{ij}^{\alpha\beta} \right) = \sum_{i} \xi^T \mathcal{R}^T$, where $\xi_{\alpha\beta} \equiv (e_{\text{in}}^\alpha e_{\text{out}}^\beta + e_{\text{in}}^\beta e_{\text{out}}^\alpha) / 2$, $\mathcal{R}_{ij}^{\alpha\beta} \equiv \sum_{\langle i,j \rangle} \mathcal{R}_{ij}^{\alpha\beta} = \sum_{\langle i,j \rangle} r_{ij}^{\alpha\beta} \mathcal{H}_{ij}$, and $\Gamma$ labels the irreducible representation (irrep). According to the grand orthogonality theorem, $\langle \mathcal{R}^{T\nu}_1(t) \mathcal{R}^{T\nu}_1(0) \rangle \propto \delta_{\Gamma_1 \Gamma_\mu}$, therefore, the product of Raman operators from different irreps gives no Raman response.

Now we can analyze the symmetry of the Raman response state by state. The all-in-all-out state has $\mathcal{R}_{ij}^{(1)} = \mathcal{R}_{ij}^{(2)} = \mathcal{R}_{ij}^{(3)} = \mathcal{R}_{ij}^{(4)} = 0$, so in the insets of Figs. 1(a) and 1(b) of the main text, for comparison with the polarization dependence shown (the point group symmetry of the ground state: $\mathcal{R}_{ij}^{(1)} \propto \mathcal{R}_{ij}^{(2)} \propto \mathcal{R}_{ij}^{(3)} \propto \mathcal{R}_{ij}^{(4)}$, where $\xi_{\alpha\beta}^{(1)} = \xi_{\alpha\beta}^{(2)} = \xi_{\alpha\beta}^{(3)} = \xi_{\alpha\beta}^{(4)}$, $\mathcal{R}_{ij}^{(1)} \equiv \sum_{\langle i,j \rangle} \mathcal{R}_{ij}^{(1)} = \sum_{i} \xi^T \mathcal{R}^{T(1)}_i$, $\mathcal{R}_{ij}^{(2)} \equiv \sum_{\langle i,j \rangle} \mathcal{R}_{ij}^{(2)} = \sum_{i} \xi^T \mathcal{R}^{T(2)}_i$, $\mathcal{R}_{ij}^{(3)} \equiv \sum_{\langle i,j \rangle} \mathcal{R}_{ij}^{(3)} = \sum_{i} \xi^T \mathcal{R}^{T(3)}_i$, $\mathcal{R}_{ij}^{(4)} \equiv \sum_{\langle i,j \rangle} \mathcal{R}_{ij}^{(4)} = \sum_{i} \xi^T \mathcal{R}^{T(4)}_i$, and $\Gamma$ labels the irreducible representation (irrep). According to the grand orthogonality theorem, $\langle \mathcal{R}^{T\nu}_1(t) \mathcal{R}^{T\nu}_1(0) \rangle \propto \delta_{\Gamma_1 \Gamma_\mu}$, therefore, the product of Raman operators from different irreps gives no Raman response.

For the remaining four spin configurations, the Raman operator can be decomposed according to the irreducible representation of the $D_{2d}$ point group. Denoting $\langle \mathcal{R}^{A_1}(t) \mathcal{R}^{A_1}(0) \rangle = r_1$, $\langle \mathcal{R}^{B_1}(t) \mathcal{R}^{B_1}(0) \rangle = r_2$, and $\langle \mathcal{R}^{B_2}(t) \mathcal{R}^{B_2}(0) \rangle = r_3$, we obtain the Raman response in the parallel and in the crossed channel as

$$I^\parallel(\omega) \propto \frac{1}{8} (8 r_1^2 + 4 r_2^2 + r_3^2) + \frac{1}{8} (4 r_2^2 - r_3^2) \cos 4 \theta,$$

and

$$I^\perp(\omega) \propto \frac{1}{8} (4 r_2^2 + r_3^2) + \frac{1}{8} (-4 r_2^2 + r_3^2) \cos 4 \theta.$$
[21] S.-M. Souliou, J. Chaloupka, G. Khaliullin, G. Ryu, A. Jain, B. J. Kim, M. Le Tacon, and B. Keimer, Phys. Rev. Lett. 119, 067201 (2017).

[22] M. W. Gaultois, P. T. Barton, C. S. Birkel, L. M. Misch, E. E. Rodriguez, G. D. Stucky, and R. Seshadri, J. Phys.: Condens. Matter 25, 186004 (2013).

[23] S. Choi, et al., in preparation.

[24] M. Ito, Y. Yasui, M. Kanada, H. Harashina, S. Yoshii, K. Murata, M. Sato, H. Okumura, and K. Kakurai, J. Phys. Soc. Jpn. 69, 888 (2000).

[25] S.-M. Souliou, J. Chaloupka, G. Khaliullin, G. Ryu, A. Jain, B. J. Kim, M. Le Tacon, and B. Keimer, Phys. Rev. Lett. 119, 067201 (2017).

[26] A. Jain, M. Krautloher, J. Porras, G. H. Ryu, D. P. Chen, D. L. Abernathy, J. T. Park, A. Ivanov, J. Chaloupka, G. Khaliullin, B. Keimer, and B. J. Kim, Nat. Phys. 13, 633 (2017).

[27] S. T. Ku, D. Kumar, M. R. Lees, W.-T. Lee, R. Aldus, A. Studer, P. Imperia, S. Asai, T. Masuda, S. W. Chen, J. M. Chen, and L. J. Chang, J. Phys.: Condens. Matter 30, 155601 (2018).

[28] T. H. Nguyen, J. Son, S. Kim, H. Cho, C. H. Kim, Y. P. Wang, K. S. Burch, I.-S. Yang, J. Jeong, J.-G. Park, S. J. Moon, and T. W. Noh, Phys. Rev. Lett. 127, 267203 (2021).

[29] J. Lee, et al., in preparation.

[30] M. Balkanski, R. F. Wallis, and E. Haro, Phys. Rev. B 28, 1928 (1983).

[31] U. Fano, Phys. Rev. 124, 1866 (1961).

[32] T. M. H. Nguyen, L. J. Sandilands, C. H. Sohn, C. H. Kim, A. L. Wysocki, I.-S. Yang, S. J. Moon, J.-H. Ko, J. Yamaura, Z. Hiroi, and T. W. Noh, Nat. Commun. 8, 251 (2017).

[33] K. Ueda, R. Kaneko, A. Subedi, M. Minola, B. J. Kim, J. Fujioka, Y. Tokura, and B. Keimer, Phys. Rev. B 100, 115157 (2019).

[34] W.-L. Zhang, A. S. Sefat, H. Ding, P. Richard, and G. Blumberg, Phys. Rev. B 94, 014513 (2016).

[35] S.-W. Chen, S.-W. Fu, C.-W. Pao, J.-M. Lee, S.-A. Chen, S.-C. Haw, J.-F. Lee, C.-H. Liu, C.-K. Chang, Y.-C. Chuang, H.-S. Sheu, K.-T. Lu, S.-T. Ku, L.-J. Chang, and J.-M. Chen, Phys. Chem. Chem. Phys. 17, 23667 (2015).

[36] J. N. Millican, R. T. Macaluso, S. Nakatsuji, Y. Machida, Y. Maeno, and J. Y. Chan, Mater. Res. Bull. 42, 928 (2007).

[37] P. A. Fleury and R. Loudon, Phys. Rev. 166, 514 (1968).