

Supplementary Information

Chiral excitations and the intermediate-field spin-liquid regime in the Kitaev magnet α -RuCl₃

Anuja Sahasrabudhe,¹ Mikhail A. Prosnikov,² Thomas C. Koethe,¹ Philipp Stein,¹ Vladimir Tsurkan,^{3,4} Alois Loidl,³ Markus Grüninger,¹ Hamoon Hedayat,¹ and Paul H. M. van Loosdrecht¹

¹*Universität zu Köln, II. Physikalisches Institut, Zùlpicher Straße 77, Köln D-50937, Germany*

²*High Field Magnet Laboratory (HFML-EMFL), Radboud University, 6525 ED Nijmegen, The Netherlands*

³*University of Augsburg, 86159 Augsburg, Germany*

⁴*Institute of Applied Physics, MD 2028, Chisinau, Republic of Moldova*

1. Experimental details

High quality α -RuCl₃ samples were prepared using a vacuum sublimation method. The samples were not cleaved or polished, so as not to introduce stacking faults. The measurements were performed in Voigt geometry ($\mathbf{k} \perp \mathbf{B}$), with an in-plane magnetic field perpendicular to the honeycomb bond. A bath cryostat was used in the experiment. The sample was immersed in Helium gas to achieve a base temperature of 1.7 K. Raman spectra were measured with a 532 nm continuous wave laser. The incident laser power was limited to 10 μ W to reduce heating. The incident light was passed through a linear polarizer followed by a quarter wave plate (QWP) at 45 deg (-45 deg) to create left (right) circularly polarised light. The back-scattered light was passed through a second QWP at -45 deg (45 deg) and a vertical polarizer before the spectrometer to collect right (left) circularly polarised light. Fig. S1 shows a detailed sketch of the experimental setup. For every field, Raman spectra is measured in both helicity channels by rotating the quarter wave plates. The difference in the intensity is estimated by following the procedure described in section 4 and 5 of Supplementary Information.

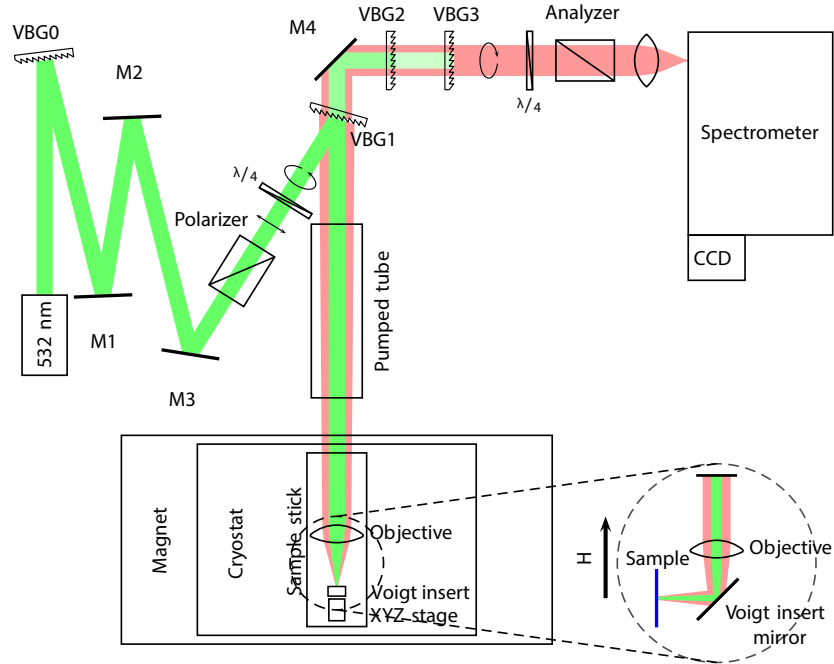


FIG. S1: Sketch of the magneto-optic setup used in the experiment. VBG: Volume Bragg Grating, M: Mirror

Sample quality

Stacking faults that result from the growth process yield different ordering temperatures. Crystals with ABCABC periodicity order at 7K, and those with ABAB periodicity order at 14K [1]. Using magnetic linear dichroism experiments, a clean phase transition at 7K is observed for our samples without any indication of a further phase transition. Furthermore, heat capacity measurements performed on our samples show one single phase transition at 7K.

Monoclinic space group

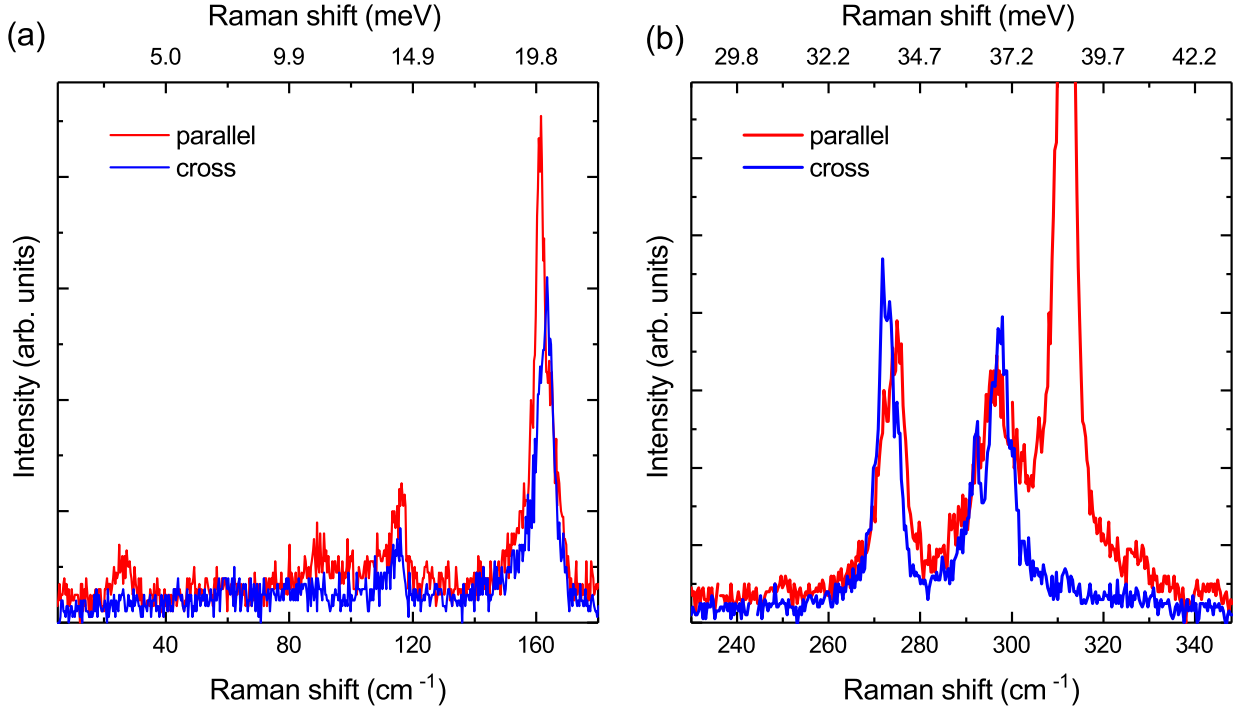


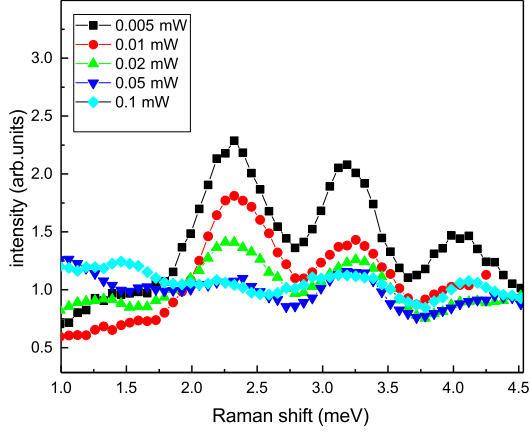
FIG. S2: Polarization resolved Raman spectra between (a) 10 cm^{-1} to 180 cm^{-1} (b) 230 cm^{-1} to 350 cm^{-1} . Splitting between the modes observed in the parallel and cross-polarization channel indicates broken 3-fold symmetry. The spectrum is measured at 4 K with $10\text{ }\mu\text{W}$ power to avoid heating.

In order to confirm the low-temperature crystal structure, Raman scattering was performed with linearly polarized light. The low-temperature ordered phase was verified by the presence of a magnon. Similar to a previous room-temperature measurement by TT. Mai *et al.* [2], we observe a splitting of about $1\text{-}2\text{ cm}^{-1}$ in the phonons, indicating a broken 3-fold symmetry and $C2/m$ monoclinic space group of the sample at 4 K (see Fig. S2).

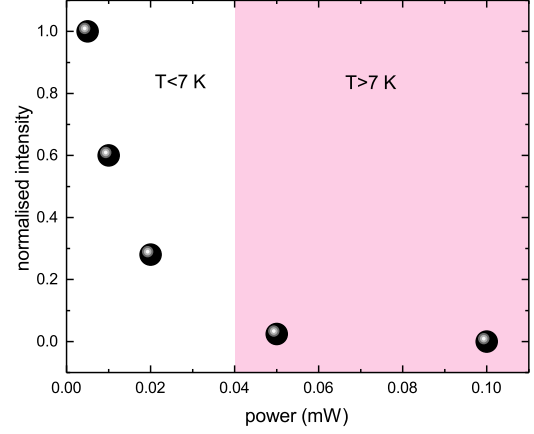
Power-temperature relation

At a base temperature of 1.7 K, at $B = 0$, two AFM magnons are observed at 2.3 and 3.2 meV. On increasing the power of the incident beam, the magnons melt into the multiparticle continuum (cf. Fig. S3a). The decrease in scattering intensity results from the heating induced by the probe beam. Above $40\text{ }\mu\text{W}$ the magnons are no longer

resolved, this indicates a local temperature of ~ 7 K (cf. Fig. S3b). For larger powers of the incident beam, the temperature is estimated using the ratio of anti-Stokes to Stokes intensity of the M1 mode at 30 T, which yields 25 K at $25 \mu\text{W}$ and 41 K at $1000 \mu\text{W}$. Based on these results, we estimate a temperature of ~ 3 K at $10 \mu\text{W}$ and ~ 13 K at $100 \mu\text{W}$.



(a) Change in AFM magnons with power.



(b) Integrated intensity of AFM magnons with power.

FIG. S3: Power dependence of AFM magnons for $B = 0$. $T_N = 7$ K is measured using magneto-optics [3].

2. Critical field B_c

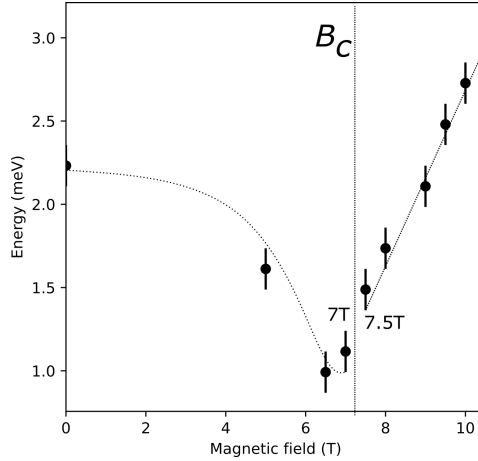


FIG. S4: Phase transition out of the ordered AFM phase. Below the critical field, the AFM magnon at 2.3 meV decreases in energy with increasing field. Above the critical field the energy of M1 shows a linear rise.

We track the energy of M1 in the magnetic field. At B_c , the M1 mode is connected to the 2.3 meV magnon (at $B = 0$ T) of the zigzag order, see Fig. S4. The energy of the magnon decreases with increasing magnetic field. The M1 mode, which is visible on quenching of the zigzag order evolves linearly above B_c (see Fig. S4). We observe a phase transition somewhere between 7 and 7.5 T. At 7.5 T the system is clearly out of the zigzag order (due to our limited field resolution, we refer to 7.5 T as B_c). The phase transition at 7.5 T (cf. Fig. S4) is consistent with the direction of the magnetic field perpendicular to the Ru-Ru bond [4, 5].

3. Helicity dependent scattering

Figure. S5 is a reference scan taken at 7.5 T in the IFR. It shows that the magnetic excitations and the multi-particle continuum are absent in the (co-circular) I_{++} and I_{--} geometries. The co-circular polarization geometry is characterised by Raman active A_g phonons (green and black lines).

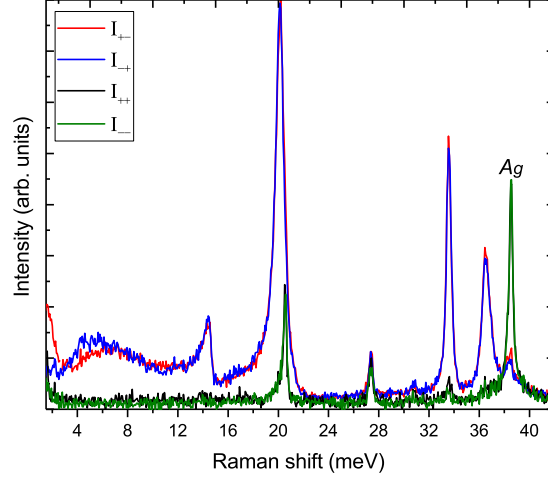


FIG. S5: polarization dependence at 7.5 T.

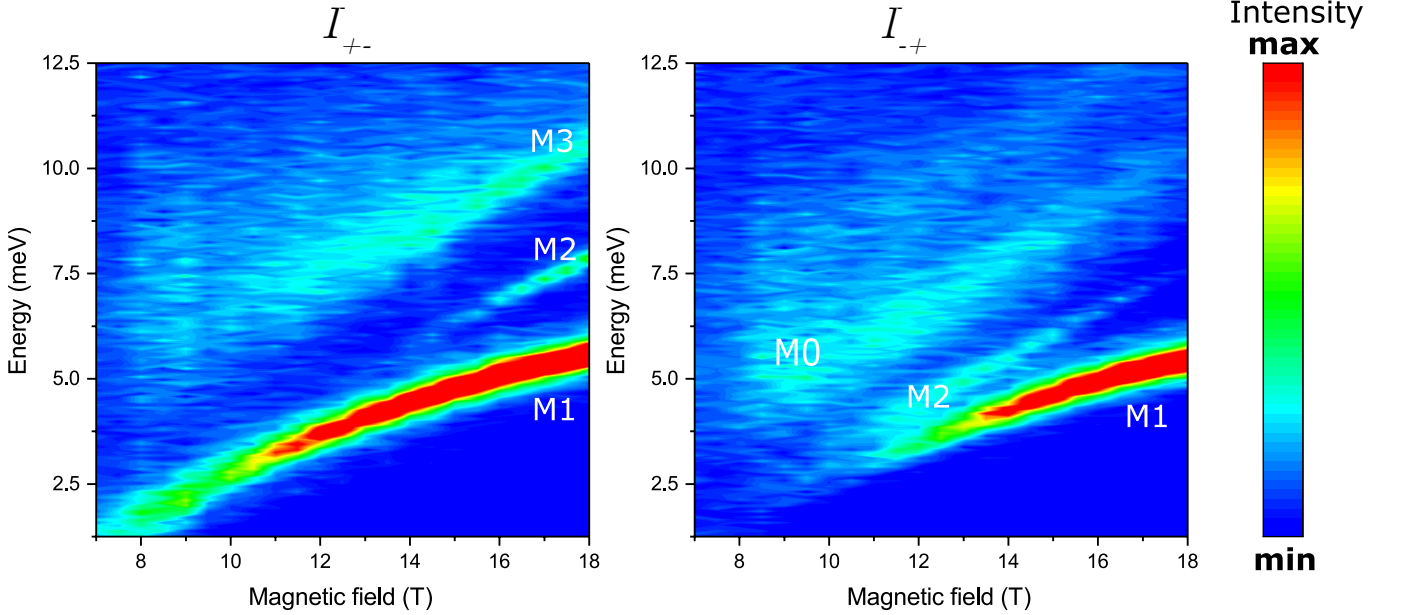


FIG. S6: Color plot shows the change in intensity and energy of excitations with the field, as observed in the I_{+-} and the I_{-+} channels. Both plots are constructed using the same color scale to compare the intensities.

Helicity dependent Raman scattering resolves the development of the magnetic excitations in two separate polarization channels - I_{+-} and I_{-+} . In the I_{+-} channel, M1 is visible immediately above the zigzag phase. In the I_{-+} channel, M1 only appears above 10.5 T. This shows that M1 is fully chiral in the field regime of 7.5 T to 10.5 T. M2 can be seen to interchange between the two channels at 15 T (cf. Fig. S6).

4. ROA of M1

In this section, we briefly define a procedure to extract the ROA of M1, especially for fields close to B_c , where a broad continuum is present beneath the mode. To find the ROA, areas obtained from fitting a Lorentzian peak are compared.

1. M1 as observed in the I_{+-} channel is fitted with a Lorentzian with a constant background (Fig. S7a).
2. The obtained fit is then subtracted from the I_{+-} spectrum to obtain the shape of the continuum (Fig. S7b).
3. The continuum is then subtracted from the I_{-+} spectrum, to reveal a peak if any in the I_{-+} channel. Two Lorentzians are then fitted to the obtained curve to obtain the integrated intensity of the peak corresponding to M1. For 9 T no peak is observed at the same energy as M1 (Fig. S7d). However, M1 is observed in the I_{-+} channel at 11.5T (Fig. S8).
4. Integrated intensities of M1 obtained from the fitting process in the two channels are I_{+-} and I_{-+} , and the ROA is calculated according to Eq. 1 of the main text.

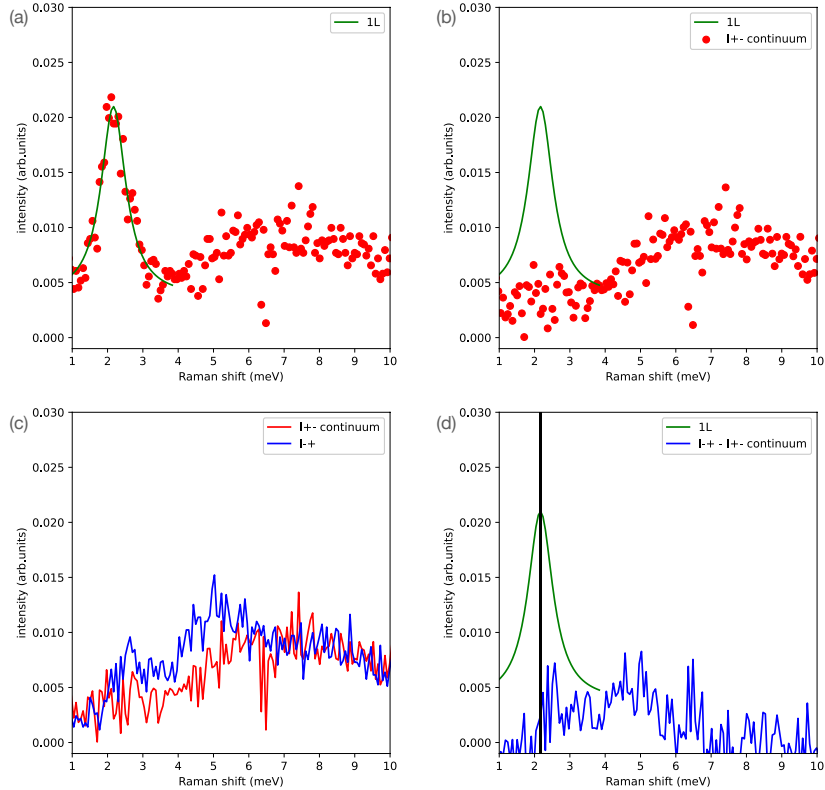


FIG. S7: Extracting ROA in the IFR. Example scan from IFR ($B = 9$ T). (a) In the I_{+-} channel, M1 is fitted with a Lorentzian. (b) Fitted Lorentzian is subtracted from the I_{+-} spectrum to obtain the shape of the continuum. (c) Shape of the continuum obtained from the I_{+-} channel is compared to the spectrum observed in I_{-+} . (d) Modes in I_{-+} obtained by subtracting the continuum obtained from the I_{+-} channel. At 9 T, no peak is observed at the same energy as M1, i.e the intensity of M1 in the I_{-+} channel is zero and ROA=1.

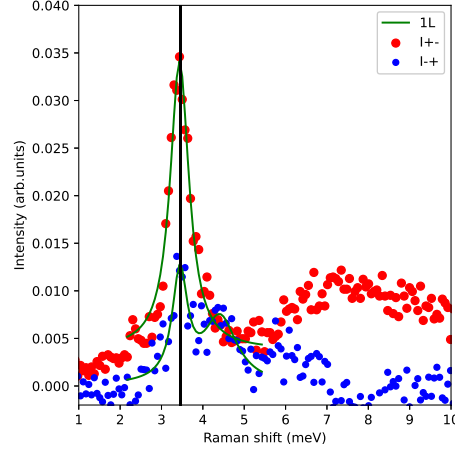


FIG. S8: Example spectra from the transition regime ($B = 11.5$ T). Integrated intensity of M1 is obtained by fitting the peaks in I_{-+} polarization with two Lorentzians.

5. Analysis for M0

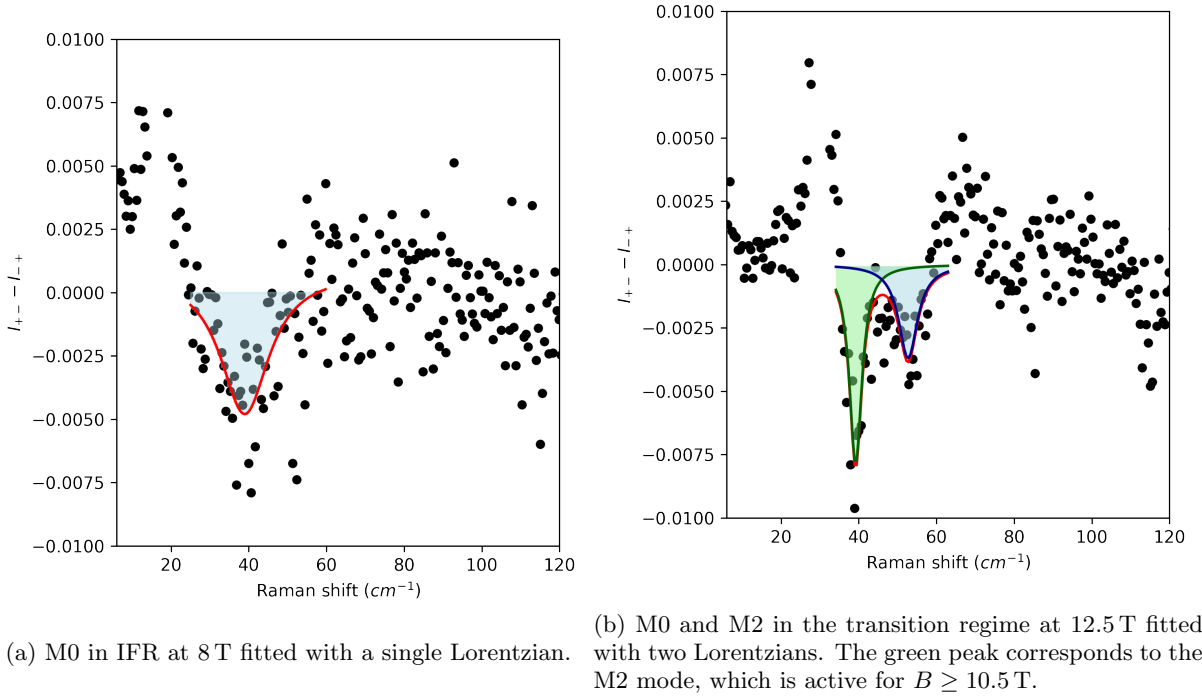


FIG. S9: Fits for $I_{+-} - I_{-+}$ in the intermediate field regime (a) and transition regime (b) to estimate the energy and intensity of M0.

In the ROA spectra, there appears a broad energy regime close to 5 meV which is consistently stronger in the I_{-+} channel. On taking the difference spectra $I_{+-} - I_{-+}$ a broad feature is revealed around 5 meV. This broad feature is fitted with a Lorentzian (see Fig. S9a). Fitting by a Lorentzian produces a decent fit with $\chi_r^2 = 1.233$ for an average y-error of 0.001 on the differential intensity. The peak energy using this fitting is found to be at (4.9 ± 0.1) meV. On increasing the field to 10.5 T, a new mode M2 starts to grow exclusively in the I_{-+} channel. Thereby, at $B = 10.5$ T

and above, the spectra in the vicinity of 5 meV cannot be fitted with a single Lorentzian and instead the spectra will have to be fitted by two Lorentzians (see Fig. S9b). Out of the two Lorentzians, the lower energy peak is identified as M2 and the higher energy peak is the M0 mode. A test fit to the data at 12.5 T yields $\chi_r^2 = 0.883$.

6. ROA in paramagnetic regime

We analyse the excitations for the C2/m space group, using Wyckoff positions from [6]. The Raman tensors in the linear basis are given as:

$$RA_g = \begin{pmatrix} b & 0 & d \\ 0 & c & 0 \\ d & 0 & a \end{pmatrix} \quad RB_g = \begin{pmatrix} 0 & a & 0 \\ a & 0 & e \\ 0 & e & 0 \end{pmatrix}$$

The Raman intensity is given by $I = |e_s^\dagger \cdot R \cdot e_i|^2$ with $e_s = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \\ 0 \end{pmatrix}$ and $e_+ = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \\ 0 \end{pmatrix}$ where R is the Raman tensor and $e_i(e_s)$ are the vectors of the incident(scattered) light. ROA is calculated as:

$$ROA = \frac{I_{+-} - I_{-+}}{I_{+-} + I_{-+}}$$

In cross-circular polarization geometry, this yields an intensity of $I_{+-}(B_g) = I_{-+}(B_g) = a^2$ for C2/m. Therefore $ROA(B_g) = 0$. The observation of pronounced ROA in the IFR, just above B_c , corroborates the particular character of the IFR. Its symmetry deviates from that of the paramagnetic phase.

7. High field regime

Figure S9 provides an overview of our Raman spectra measured in the different field regimes. As stated in the main text, we do not find any significant changes in ROA above 15 T.

References

- [1] H. B. Cao, A. Banerjee, J.-Q. Yan, C. A. Bridges, M. D. Lumsden, D. G. Mandrus, D. A. Tennant, B. C. Chakoumakos, and S. E. Nagler, Low-temperature crystal and magnetic structure of α -RuCl₃, Phys. Rev. B **93**, 134423 (2016).
- [2] T. T. Mai, A. McCreary, P. Lampen-Kelley, N. Butch, J. R. Simpson, J.-Q. Yan, S. E. Nagler, D. Mandrus, A. R. H. Walker, and R. V. Aguilar, Polarization-resolved Raman spectroscopy of α -RuCl₃ and evidence of room-temperature two-dimensional magnetic scattering, Phys. Rev. B **100**, 134419 (2019).
- [3] J. Wagner, A. Sahasrabudhe, R. Versteeg, L. Wysocki, Z. Wang, V. Tsurkan, A. Loidl, D. Khomskii, H. Hedayat, and P. H. van Loosdrecht, Magneto-optical study of metamagnetic transitions in the antiferromagnetic phase of α -RuCl₃, npj Quantum Materials **7**, 28 (2022).
- [4] A. Ponomaryov, L. Zviagina, J. Wosnitza, P. Lampen-Kelley, A. Banerjee, J.-Q. Yan, C. Bridges, D. Mandrus, S. Nagler, and S. Zvyagin, Nature of magnetic excitations in the high-field phase of α -RuCl₃, Physical Review Letters **125**, 037202 (2020).
- [5] C. Balz, L. Janssen, P. Lampen-Kelley, A. Banerjee, Y. H. Liu, J.-Q. Yan, D. G. Mandrus, M. Vojta, and S. E. Nagler, Field-induced intermediate ordered phase and anisotropic interlayer interactions in α -RuCl₃, Phys. Rev. B **103**, 174417 (2021).
- [6] R. D. Johnson, S. C. Williams, A. A. Haghighirad, J. Singleton, V. Zapf, P. Manuel, I. I. Mazin, Y. Li, H. O. Jeschke, R. Valentí, and R. Coldea, Monoclinic crystal structure of α -RuCl₃ and the zigzag antiferromagnetic ground state, Phys. Rev. B **92**, 235119 (2015).

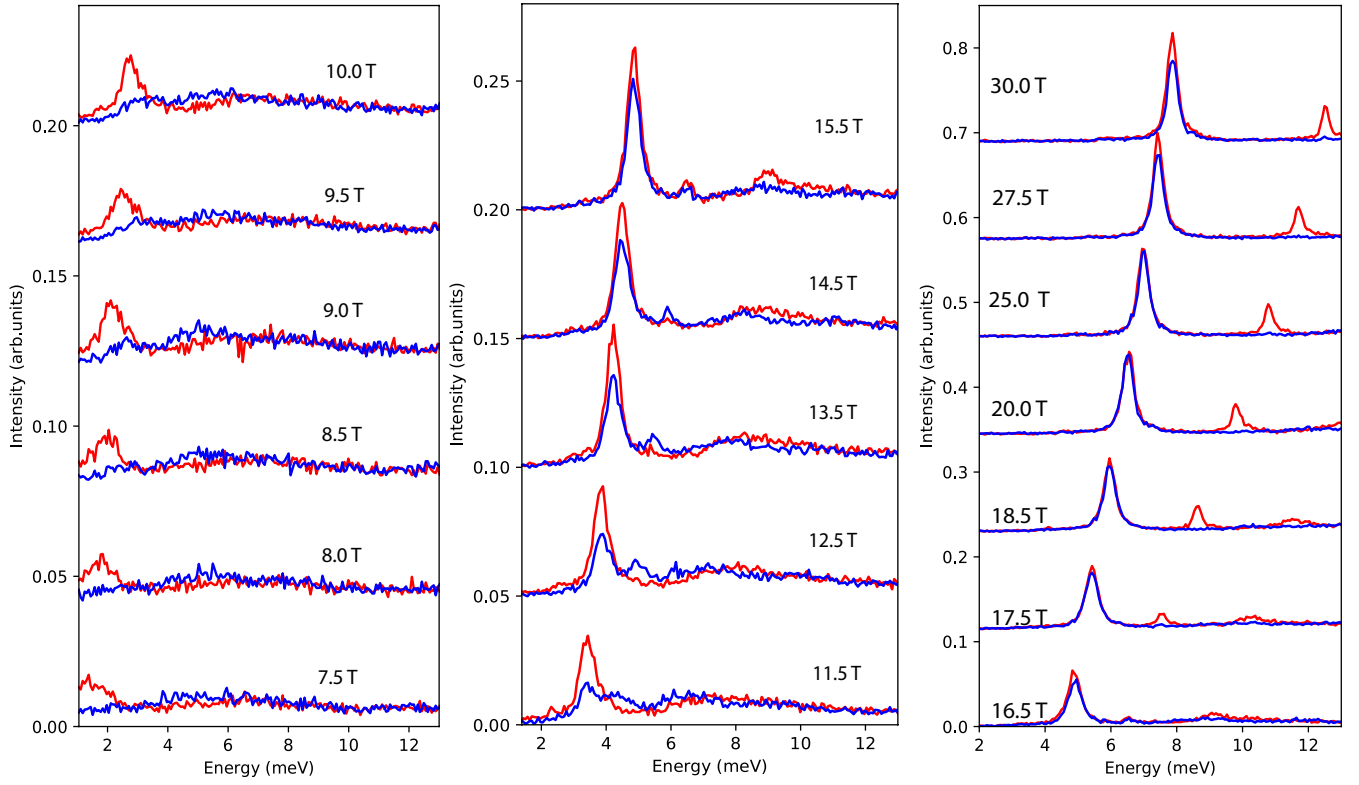


FIG. S10: Red and blue lines show the Raman spectrum as measured from 7.5 T to 30 T in the I_{+-} and the I_{-+} channel, respectively. For clarity, the spectra are plotted with a constant offset. The three boxes show the helicity dependence in the intermediate, the transition, and the high field regime.