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Tunable layered-magnetism-assisted magneto-Raman effect in a two-dimensional magnet CrI_3

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Author Contributions

Liuyan Zhao, Rui He, and Wencan Jin conceived the idea and designed the experiment. Zhipeng Ye, Gaihua Ye, and Laura Rojas took the experimental data under the guidance of Liuyan Zhao, Rui He, and Wencan Jin. Wencan Jin, Xiangpeng Luo, Kai Sun, and Liuyan Zhao analyzed the data and performed the calculations of phonon mode split and magnetism-phonon coupling. Bowen Yang, Fangzhou Yin, and Hyun Ho Kim fabricated thin films of CrI_3 under the guidance of Adam W. Tsen. Shangjie Tian, Yang Fu, and Shaohua Yan grew bulk CrI_3 single crystals. Wencan Jin, Xiangpeng Luo, Rui He, and Liuyan Zhao wrote the manuscript.

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Abstract

We used a combination of polarized Raman spectroscopy experiment and model magnetism-phonon coupling calculations to study the rich magneto-Raman effect in the two-dimensional (2D) magnet CrI_3. We reveal a novel layered-magnetism-assisted phonon scattering mechanism below the magnetic onset temperature, whose Raman excitation breaks time-reversal symmetry, has an antisymmetric Raman tensor, and follows the magnetic phase transitions across critical magnetic fields, on top of the presence of the conventional phonon scattering with symmetric Raman tensors in N-layer CrI_3. We resolve in data and by calculations that the 1^{st}-order A_g phonon of monolayer splits into a N-fold multiplet in N-layer CrI_3 due to the interlayer coupling ($N \geq 2$) and that the phonons within the multiplet show distinct magnetic field dependence because of their different layered-magnetism-phonon coupling. We further find that such a layered-magnetism-phonon coupled Raman scattering mechanism extends beyond 1^{st}-order to higher-order multi-phonon scattering processes. Our results on magneto-Raman effect of the 1^{st}-order phonons in the multiplet and the higher-order multi-phonons in N-layer CrI_3 demonstrate the rich and strong behavior of emergent magneto-optical effects in 2D magnets and underlines the unique opportunities of new spin-phonon physics in van der Waals layered magnets.

Significance Statement

The two-dimensional (2D) magnetic semiconductor CrI_3 hosts a variety of strong and tunable magneto-optical effects and allows for the development of novel magneto-optical devices. While the elastic magnetic-optical effects in CrI_3 are well understood, its recently discovered inelastic magneto-Raman effect remains to have case-specific interpretations that vary upon the thickness of CrI_3. We perform comprehensive Raman measurements on 2D CrI_3 with polarization, temperature, layer number, and magnetic field dependence. We resolve a Davydov-split-induced N-fold multiplet in N-layer CrI_3 and reveal the distinct magneto-Raman behaviors of individual phonons within the multiplet. Our results discover a novel layered-magnetism-coupled phonon scattering mechanism that explains the rich magneto-Raman effect in CrI_3 of arbitrary thickness and elucidates the new spin-phonon coupling physics in layered magnets.

Main Text

Two-dimensional (2D) CrI_3 of few-layer form features a layered-antiferromagnetic (AFM) order where the spins align along the out-of-plane direction ferromagnetically within each layer and antiferromagnetically between adjacent layers (1-5). It undergoes a layered-AFM to FM phase transition upon applying a moderate magnetic field (1-7), or electric field (8-10), or electrostatic doping (11), or hydrostatic pressure (12, 13). The strong coupling between spin and charge degrees of freedom in 2D CrI_3 allows magneto-optical effects manifested in a variety of ways including large magneto-optical Kerr effect (5) and magnetic circular dichroism (8-13), spontaneous helical photoluminescence (14), giant nonreciprocal second harmonic generation (15), and anomalous magneto-optical Raman effect (7, 16-19). All of these magneto-optical effects can be tuned across the layered-AFM to FM phase transition, making 2D CrI_3 a promising candidate for applications in magnetic sensors, optical modulation, and data storage.

Among all magneto-optical effects in CrI_3, magneto-optical Raman effect is of particular interest for two reasons. First, among all known magnets, the largest magnetism-induced optical rotation is observed for the linearly polarized, inelastically scattered light off the A_g phonon mode (~ 129

cm^{-1}) in the FM phase of CrI_3 (16). Second, different phonon modes exhibit distinct magneto-optical behavior that the A_g mode emerges whereas its neighboring strongest antisymmetric mode (~ 127 cm^{-1}) disappears in the linear crossed polarization channel across the layered-AFM to FM transition (7, 16-18). However, the physical origin of magneto-optical Raman effect remains elusive with diverse proposals ranging from Davydov-split for bilayer CrI_3 (16, 18), zone-folded phonon for few-layer CrI_3 (17) and coupled magnetism-phonon scattering for bulk CrI_3 (7), none of which can be trivially generalized to explain CrI_3 of arbitrary thickness.

In this work, we systematically examine the magneto-optical Raman effect for N-layer CrI_3 (N = 1 – 4) by performing polarization, temperature, and magnetic field dependent micro-Raman spectroscopy measurements and unambiguously identify the layered-magnetism-assisted phonon scattering as the origin applicable for CrI_3 of any thickness. N-layer CrI_3 crystalline flakes were exfoliated from high-quality CrI_3 single crystals, sandwiched between hexagonal boron nitride (hBN) thin flakes, and then placed onto SiO_2/Si substrates inside a high-purity (> 99.999%) nitrogen-filled glovebox. Micro-Raman spectroscopy measurements in the backscattering geometry were carried out with a 633 nm excitation laser resonant with the charge-transfer transition (14), inside a vacuum cryostat at a base pressure lower than 7×10^{-7} mbar, and under an out-of-plane magnetic field ($B_\perp$) up to 2.2 T.

We start with resolving in N-layer CrI_3 the interlayer coupling-induced split of the A_g mode of monolayer CrI_3 (20, 21). Figure 1*A* shows Raman spectra in both parallel and crossed linear polarization channels taken at T = 10 K and $B_\perp$ = 0 T on 1 – 4L CrI_3 (see full-range spectra in both channels and comparison to off-resonance 532nm excitations in *SI Appendix*, section I, Figures S1 and S2, respectively). It has been established for CrI_3 that the modes in the crossed channel in Fig. 1*A* correspond to antisymmetric Raman tensor (R_{AS}) whereas those in the parallel channel are for symmetric Raman tensor of A_g symmetry (R_S) (19). We highlight three key observations that are new as compared to previous work (7, 16-19, 22, 23) and summarize them in Fig. 1*B* with fitted mode frequencies v.s. N. First, the number of modes increases proportional to the number of layers (with an exception for N = 3 that is explained in *SI Appendix*, section II). Second, the highest frequency remains constant while the lowest frequency decreases with increasing N, leading to a greater frequency separation between them. Third, the parallel and crossed channels show modes of the same frequencies for odd N whereas they select modes with distinct frequencies for even N.

To interpret the A_g mode splitting, we take a simple linear chain model of N-layer CrI_3, as introduced in few-layer transition metal dichalcogenides (24-27),

$$H = H_0 + \frac{1}{2}\sum_{i=2}^{N} k(u_{i-1} - u_i)^2, \text{ with } H_0 = \sum_{i=1}^{N}\left(\frac{1}{2}m\dot{u_i}^2 + \frac{1}{2}k_0 u_i^2\right),$$

where H_0 represents the original A_g mode at frequency $\omega_0 = \sqrt{k_0/m}$ within individual layers, u_i represents the displacement field in the i^{th} layer, and k stands for the coupling constant between adjacent layers, equivalent to a coupling frequency $\omega = \sqrt{k/m}$. Diagonalizing H leads to N nondegenerate eigenfrequencies $\Omega_i(\omega_0, \omega)$ and their corresponding eigenmodes $\vec{U}_i$ (i = 1, 2, …, N) (*i.e.*, Davydov-splitting), with i = 1 being the highest frequency mode and i = N being the lowest frequency mode. By choosing $\omega_0 = 129.10 \pm 0.10$ cm^{-1} and $\omega = 15.98 \pm 0.55$ cm^{-1}, the calculated frequencies Ω_i (solid lines with open diamonds) match well with all the experimental values (ruby filled squares and royal filled circles), as highlighted by the fan-diagram in Fig. 1*B*. See detailed calculations of Ω_i and $\vec{U}_i$ in *SI Appendix*, section II, Tables S1 and S2.

Because N-layer CrI_3 is structurally centrosymmetric, its N calculated eigenmodes have alternating parities, with the highest-frequency mode always parity-even as a result of equal, in-phase atomic displacement between layers (*i.e.*, $\vec{U}_1 = (1,1,\dots,1)/\sqrt{N}$). In the parallel channel where only modes with even parity and symmetric Raman tensor R_S can be detected, we expect to see every other mode starting with the highest frequency one (i = 1, 3, 5, …). This expectation is indeed consistent with our data that U_1 for N = 1 and 2 and $U_{1,3}$ for N = 3 and 4 are observed in the linear parallel channel in Fig. 1*A* and *B*. In contrary to the structure of N-layer CrI_3, the layered-AFM order is centrosymmetric for odd N and non-centrosymmetric for even N. Therefore, it should couple to parity-even phonon modes for odd N and parity-odd phonons for even N to make the coupled layered-AFM-phonon entity parity-even and thus Raman-active. Due to the broken time-reversal symmetry from the magnetism, this layered-AFM-assisted phonon scattering corresponds to antisymmetric Raman tensor R_{AS} and can only appear in the linear crossed channel. We anticipate observing in the linear crossed channel every other mode from the lowest-frequency one (i = N, $N-2$, $N-4$, …), because $\vec{U}_N$ always has the same parity as the layered-AFM for any N. The result in Fig. 1*A* and *B* corroborates with this prediction that U_1 for N = 1, U_2 for N = 2, $U_{3,1}$ for N = 3, and $U_{4,2}$ for N = 4 are present in the linear crossed channel. The coupling efficiency between a phonon mode and the layered-AFM order can be evaluated by the projection $\vec{U}_i \cdot \vec{M}$ of the eigenmode vector $\vec{U}_i$ onto the pseudo-vector (*i.e.*, axial vector) for the layered-AFM $\vec{M} = (1, -1, .., (-1)^{N-1})$ with $+1$ for spin up and -1 for spin down in a single layer. In particular, for any $N > 1$, the lowest-frequency mode $\vec{U}_N$ features out-of-phase atomic displacement between adjacent layers and matches best the pattern of alternating spin orientations in the layered-AFM state (Fig. 1*C*), yielding the strongest coupling strength of $\vec{U}_i \cdot \vec{M}$ and thus the most intense signal among the modes in the linear crossed channel (Fig. 1*A*). See the computed $\vec{U}_i \cdot \vec{M}$ in the layered-AFM state of 1–4L CrI_3 in *SI Appendix*, Table S3.

So far we have established the physical origin of the *N*-fold multiplet for *N*-layer CrI_3 as a combined effect of Davydov-splitting and layered-AFM-phonon coupling, leading to the conventional phonons of R_S in the linear parallel channel (24-27) and the layered-AFM-coupled phonons of R_{AS} in the linear crossed channel (7, 19). We note that a magnetism-induced symmetric E_g phonon mode splitting was previously reported in 2D $Cr_2Ge_2Te_6$ (28). Here, the structural and magnetic nature of modes in the linear parallel and crossed channel, respectively, is further supported by their distinct temperature dependence in these two channels. Taking 2L CrI_3 as an example, the crossed channel signal emerges below the magnetic transition temperature $T_C = 45$ K whereas the parallel channel signal is present above T_C and only increases slowly below T_C, as illustrated by representative spectra taken at 70 K, 40 K, and 10 K in Fig. 2*A*. Such a behavior extends beyond the 1st-order phonons (Fig. 2*A*, left) to the 2nd and 3rd-order ones (Fig. 2*A*, middle and right, respectively). For all three orders, the temperature dependence of integrated intensity (I.I.) in the linear crossed channel fits well with an order parameter-like function $I_0 + I\sqrt{T_C - T}$ (royal curves in Fig. 2*B*), in contrast to those in the linear parallel channel following a smooth anharmonic decay behavior (29) (ruby curves in Fig. 2*B*). As pictorially summarized in Fig. 2*C*, we propose that a multi-phonon process (30, 31) leads to conventional 1st, 2nd, and 3rd-order phonon modes (ruby) in the linear parallel channel, and their coupling with the layered-AFM order results in the magnetic counterparts (royal) in the linear crossed channel.

We then proceed to explore the magnetic field dependence of the layered-magnetism-assisted phonon modes in *N*-layer CrI_3. From here on, we chose circularly polarized light to perform Raman measurements for preventing any artifacts from the Faraday rotation of light passing through optical components in stray magnetic field. In this work, we focus on two representative thicknesses, 2L and 4L CrI_3, having one and two critical magnetic transitions, respectively (Raman spectra of 3L CrI_3 at 0 T in *SI Appendix*, section II, Figures S3). We note that the mechanism described below is applicable for arbitrary *N*-layer CrI_3.

2L CrI_3 undergoes a layered-AFM to FM transition at a critical magnetic field $B_c = \pm 0.6$ T (5). Figure 3*A* presents Raman spectra of 1st-order modes taken at $B_\perp = 0$ T and $\pm$ 1.4 T, below and above B_c, respectively, at 10 K in both LL and RR channels, where LL(RR) stands for the polarization channel with the incident and scattered light being left(right)-hand circularly polarized. At 0 T, both modes (U_1 and U_2) of 2L CrI_3 are present in Raman spectra that are identical in LL and RR channels. At $\pm$1.4 T, only the high-frequency mode (U_1) survives, and it shows giant Raman circular dichroism of $\pm$ 78% $\left(\frac{I.I._{LL}-I.I._{RR}}{I.I._{LL}+I.I._{RR}}\right)$. See the comparison of selection rules between linear and circular polarization bases for 2L CrI_3 in *SI Appendix*, Table S5. The magnetic field dependence of the U_2 integrated intensity clearly shows its disappearance at B_c, whereas that of U_1 increases (decreases) abruptly in the LL (RR) channel at B_c, as shown in Fig. 3*B*. Figures 3*E* and *F* show the magnetic field dependence of the 2nd and 3rd-order modes of 2L CrI_3. Both of them mimic the magnetic field dependence of U_1 with a reduction of circular dichroism above B_c, $\pm$ 71% for the 2nd-order and $\pm$ 50% for the 3rd-order. This observation suggests the participation of U_1 in the 2nd and 3rd-order multi-phonon process.

We refer to the layered-magnetism-phonon coupling that we have developed above to understand the magnetic field dependence of the two 1st-order modes (U_1 and U_2) of 2L CrI_3. For each mode U_i, its Raman tensor R^i is composed of the conventional structural ($\mathrm{R}_\mathrm{S}^\mathrm{i}$) and the novel layered-magnetism-assisted magnetic (R_AS^i) contributions, *i.e.*, $\mathrm{R}^\mathrm{i} = \mathrm{R}_\mathrm{S}^i + \lambda_i \mathrm{R}_\mathrm{AS}^i$, where R_S^i is magnetic field independent and is only present for parity-even modes, $\mathrm{R}_\mathrm{AS}^i \propto \vec{U}_i \cdot \vec{M}$ reflects the magnetic origin and selects the zero-momentum component, and λ_i is ratio of the magnetic to structural contribution for the *i*th mode that depends on microscopic parameters such as spin-orbit-coupling. Here, $\vec{M}$ changes from $(1,-1)$ to $(\pm 1, \pm 1)$ across the layered-AFM to FM transition at $B_c = \pm 0.6$ T with the fully polarized FM spin moments pointing upwards/downwards. Specifically, for the parity-even high-frequency mode of $\vec{U}_1 = \frac{1}{\sqrt{2}}(1,1)$, $\mathrm{R}_\mathrm{S}^1 = \begin{pmatrix} a_1 & \cdot \\ \cdot & a_1 \end{pmatrix}$ at all magnetic fields and

$\mathrm{R}_{\mathrm{AS}}^{1} = \vec{U}_1 \cdot \vec{M} \begin{pmatrix} \cdot & -a_1 \mathbb{i} \\ +a_1 \mathbb{i} & \cdot \end{pmatrix} = 0$ below B_c and $\begin{pmatrix} \cdot & \mp\sqrt{2} a_1 \mathbb{i} \\ \pm\sqrt{2} a_1 \mathbb{i} & \cdot \end{pmatrix}$ above $B_c = \pm\, 0.6$ T (Fig. 3*C*, top and bottom), whereas for the parity-odd low-frequency mode of $\vec{U}_2 = \frac{1}{\sqrt{2}}(1, -1)$, $\mathrm{R}_{S}^{2} = 0$ always and $\mathrm{R}_{\mathrm{AS}}^{2} = \begin{pmatrix} \cdot & -\sqrt{2} a_2 \mathbb{i} \\ +\sqrt{2} a_2 \mathbb{i} & \cdot \end{pmatrix}$ below B_c and 0 otherwise (Fig. 3*C*, middle), where $\mathbb{i} = \sqrt{-1}$ to account for the broken time-reversal symmetry and a_i stands for the Raman scattering strength of the i^{th} mode (see the calculated magnetic field dependence of U_1 and U_2 in *SI Appendix*, tables S4 and S5). This model faithfully reproduces the magnetic field dependence of both 1$^{\text{st}}$-order modes of 2L $\mathrm{CrI_3}$ in LL and RR channels by tuning only λ_i and a_i (Fig. 3*D*).

Different from 2L $\mathrm{CrI_3}$, *N*-layer $\mathrm{CrI_3}$ ($N > 2$) undergoes two spin-flip transitions with increasing $B_\perp$, one at $B_{c1} = \pm 0.7$ T for spins in surface layers and the other at $B_{c2} = \pm 1.6$ T for spins in interior layers (1, 2). For simplicity but without losing any generality, we pick 4L $\mathrm{CrI_3}$ and focus on measurements with the upwards magnetic field and in the RR polarization channel. Figure 4*A* shows Raman spectra of 1$^{\text{st}}$-order modes taken at $B_\perp = 0$ T, 1 T, and 2 T, below B_{c1}, between B_{c1} and B_{c2}, and above B_{c2}, respectively, at 10 K and in the RR channel. At 0 T, we can only reliably resolve three out of the 4-fold multiplet of 4L $\mathrm{CrI_3}$, namely, U_1, U_3, and U_4 as fitted by the ruby, honey, and royal Lorentzian profiles, respectively. This is because U_2 is spectrally so close to U_1 but has a much weaker intensity (Fig. 1*A*), thus getting overwhelmed by the strong U_1 in the RR channel. We observe both U_1 and U_4 decrease subsequently at 1 T and 2 T to finite and zero intensity respectively, whereas U_3 increases at 1 T and then decreases at 2 T. The detailed magnetic field dependence of the U_1, U_3, and U_4 integrated intensity is shown in Fig. 4*B*, displaying the contrasting trends of U_3 to U_1 and U_4, and those of the 2$^{\text{nd}}$ and 3$^{\text{rd}}$-order modes are shown in Figs. 4*E* and *F*, closely mimicking that of U_1.

We carry out a similar analysis as we have done for 2L $\mathrm{CrI_3}$ above, but add an additional intermediate magnetic phase $\vec{M} = (1, -1, 1, 1)$ between the layered-AFM of $(1, -1, 1, -1)$ and the fully spin polarized FM of $(1,1,1,1)$. While the structural contribution ($\mathrm{R}_{\mathrm{S}}^{i}$) is only present for parity-even modes, U_1 and U_3, and remains magnetic field independent, the layered-magnetism-coupled magnetic contribution ($\mathrm{R}_{\mathrm{AS}}^{i}$) varies proportionally to $\vec{U}_i \cdot \vec{M}$ as $\vec{M}$ changes as a function of $B_\perp$. Figure 4*C* lists the modes that have finite coupling to every layered magnetic order and thus nonzero R^i_{AS}, according to which the magnetic contribution of U_1 appears above B_{c1}, that of U_3 emerges between B_{c1} and B_{c2}, and $U_{2,4}$ only present below B_{c2} (see the calculated magnetic field dependence of U_1, U_2, U_3, and U_4 in *SI Appendix*, Tables S6 and S7.). By adjusting λ_i and a_i, the ratio of the magnetic to structural contribution and the overall strength of the i^{th} mode, we successfully show the consistency between the experimental and calculated magnetic field dependence of $U_{1,3,4}$ and predict that of U_2 despite its invisibility in our experiment (Fig. 4*D*).

In conclusion, we have established the Davydov-splitting of the A_g mode of monolayer into a *N*-fold multiplet in *N*-layer CrI_3 and discovered, distinct from non-magnetic few-layer atomic crystals (24-27), a unique layered-magnetism-assisted phonon scattering mechanism in the magnetic phases of CrI_3. We find this mechanism extends beyond 1st-order phonons to the multi-phonon modes, and further resolve the distinct magnetic field dependence for different 1st-order modes within the *N*-fold multiplet in *N*-layer CrI_3. Our calculations based on the combination of Davydov-splitting and layered-magnetism-phonon coupling successfully explain the selection rules for individual split modes and capture the rich behavior of their distinct magnetic field dependence, effective for 2D CrI_3 of arbitrary thickness.

Materials and Methods

Sample fabrication CrI_3 single crystals were grown by the chemical vapor transport method, as detailed in Ref.(19). 1–4L CrI_3 samples were exfoliated in a nitrogen-filled glovebox. Using a polymer-stamping transfer technique inside the glovebox, 1–4L CrI_3 flakes were then sandwiched between two few-layer hBN flakes and transferred onto SiO_2/Si substrates for Raman spectroscopy measurements.

Micro-Raman spectroscopy Micro-Raman spectroscopy measurements were carried out using a 633 nm excitation laser. The incident beam was focused by a 40× objective down to ~3 μm in diameter at the sample site, and the power was kept at 80 μW. The scattered light was collected by the objective in a backscattering geometry, then dispersed by a Horiba LabRAM HR Evolution Raman spectrometer, and finally detected by a thermoelectric cooled CCD camera. A closed-cycle helium cryostat is interfaced with the micro-Raman system for the temperature-dependent measurements. All thermal cycles were performed at a base pressure that is lower than 7×10^{-7} mbar. In addition, a cryogen-free magnet is integrated with the low temperature cryostat for the magnetic field-dependent measurements. In this experiment, the magnetic field was applied along the out-of-plane direction and covered a range of 0 – 2.2 Tesla.

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Figure Captions

Figure 1 (*A*) Raman spectra of 1 – 4L CrI_3 acquired in linear parallel (ruby) and crossed (royal) channels at 10 K. The solid curves are fits to the raw data (dots). The vertical bars underneath individual spectra denote the fitted frequencies and U_i (i = 1, …, *N*) labels the corresponding modes in *N*-layer CrI_3. (*B*) Plot of the fitted frequencies of the modes in (*A*) as a function of layer number *N*. Ruby filled circles and royal filled squares correspond to modes extracted from the linear parallel and crossed channels, respectively. Solid curves with open diamonds are fits to the Davydov-split frequencies calculated from the linear chain model. (*C*) Atomic displacement of the lowest frequency mode U_N along with the layered-AFM order to illustrate that $\vec{U}_i$ and $\vec{M}$ share the same parity and that $\vec{U}_i \cdot \vec{M}$ is maximized at i = *N*. The rectangular bar represents the atomic displacement amplitude and phase for individual layers, by its length and color (ruby and royal for opposite phase), respectively.

Figure 2 (*A*) 1st, 2nd, and 3rd order Raman spectra of 2L CrI_3 in the linear parallel (ruby) and crossed (royal) channels at selected temperatures of 70 K, 40 K, and 10 K. Spectra are vertically offset for clarity. 1st order spectra show raw data points and fitting curves, and 2nd and 3rd spectra are raw spectra. (*B*) Temperature dependence of integrated intensity (I.I.) of 1st, 2nd, and 3rd order Raman modes in the parallel (ruby circles) and crossed (royal squares) channels. Solid curves are fits to the anharmonic decay model in the parallel channel (ruby curves) and the order parameter-like function $I_0 + I\sqrt{T_C - T}$ in the crossed channel (royal curves). Critical temperature T_C = 45 K is marked by a dashed vertical line in each panel. (*C*) Schematic illustration of the single to multi-phonon scattering (ruby) and its layered-AFM-assisted counterpart (royal). The springs with one to three windings represent 1st to 3rd-order process.

Figure 3 (*A*) Raman spectra of 2L CrI_3 in co-circularly polarized channels, LL (ruby) and RR (royal), in selected out-of-plane magnetic field ($B_\perp$) of 1.4 T, 0 T, and -1.4 T. Dots are raw data points and solid curves are fitting curves. (*B*) Magnetic field dependence of integrated intensities (I.I.) of the two modes of 2L CrI_3, U_1 and U_2, in both LL (ruby circles) and RR (royal squares) channels. (*C*) List of phonon modes in 2L CrI_3 that have finite coupling strength $\vec{U_i} \cdot \vec{M}$ for individual magnetic orders at $B_\perp$ above and between B_c = $\pm$0.6 T, the critical magnetic field for the layered-AFM to FM transition. (*D*) Calculated $B_\perp$ dependence of U_1 and U_2 of 2L CrI_3. (*E*) 2^{nd} and 3^{rd}-order Raman modes (raw spectra) acquired in the same condition as (a). (*F*) $B_\perp$ dependence of I.I. of 2^{nd} and 3^{rd}-order modes of 2L CrI_3.

Figure 4 (*A*) Raman spectra of 4L CrI_3 in the RR channel in selected $B_\perp$ of 0 T, 1 T and 2 T. Grey dots are raw data points and black curves are fits to multiple Lorentzian function. Lorentzian profiles in ruby, honey, and royal correspond to U_1, U_3, and U_4 modes of 4L CrI_3. (*B*) $B_\perp$ dependence of I.I. of U_1 (ruby circles), U_3 (honey squares), and U_4 (royal diamonds). Vertical dashed lines mark the critical magnetic fields for spin-flip transitions, B_{c1} = 0.7 T and B_{c2} = 1.6 T.(*C*) List of phonon modes in 4L CrI_3 that have finite coupling strength $\vec{U_i} \cdot \vec{M}$ for magnetic orders below B_{c1}, between B_{c1} and B_{c2}, and above B_{c2}. Dash emerald box marks U_2 that is not observed in (*A*) due to its weak intensity and closeness to U_1. Solid boxes of ruby, honey, and royal color highlight U_1, U_3, and U_4, respectively. (*D*) Calculated $B_\perp$ dependence of U_1 (ruby), U_2 (emerald), U_3 (honey), and U_4 (royal) of 4L CrI_3. (*E*) and (*F*) $B_\perp$ dependence of 2^{nd} and 3^{rd}-order modes of 4L CrI_3.