Tunable layered-magnetism–assisted magneto-Raman effect in a two-dimensional magnet CrI$_3$

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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 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 first-order A$_g$ phonon of the monolayer splits into an $N$-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 first-order to higher-order multiphonon scattering processes. Our results on the magneto-Raman effect of the first-order phonons in the multiplet and the higher-order multiphonons in $N$-layer CrI$_3$ demonstrate the rich and strong behavior of emergent magneto-optical effects in 2D magnets and underline the unique opportunities of spin–phonon physics in van der Waals layered magnets.

Significance

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 magneto-optical effects in CrI$_3$ are well understood, its recently discovered inelastic magneto-Raman effect remains to have case-specific interpretations varying 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 layered-magnetism–coupled phonon scattering mechanism that explains the rich magneto-Raman effect in CrI$_3$ of arbitrary thickness and elucidates the spin–phonon coupling physics in layered magnets.

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The authors declare no competing interest.

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placed onto SiO₂/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 × 10⁻⁵ mbar, and under an out-of-plane magnetic field (B⊥) up to 2.2 T.

We start with resolving in N-layer CrI₃ the interlayer coupling-induced split of the Aₜ mode of monolayer CrI₃ (20, 21). Fig. 1A shows Raman spectra in both parallel and crossed linear polarization channels taken at T = 10 K and B⊥ = 0 T on 1L to 4L CrI₃ (see full-range spectra in both channels and comparison to off-resonance 532-nm excitations in SI Appendix, section I and Figs. S1 and S2, respectively). It has been established for CrI₃ that the modes in the crossed channel in Fig. 1A correspond to antisymmetric Raman tensor (RAS) whereas those in the parallel channel are for symmetric Raman tensor of Aₜ symmetry (R₀) (19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19). We highlight three key observations that have not been reported in previous work (7, 16, 19).

![Fig. 1](image-url)

**Fig. 1.** (A) Raman spectra of 1L to 4L CrI₃ acquired in linear parallel (red) and crossed (blue) channels at 10 K. The solid curves are fits to the raw data (dots). The vertical bars underline individual spectra denote the fitted frequencies and Uᵢ (i = 1, . . . , N) labels the corresponding modes in N-layer CrI₃. (B) Plot of the fitted frequencies of the modes in A as a function of layer number N. Red solid circles and blue solid 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 U₀ along with the layered-AFM order to illustrate that Uₙ and M share the same parity and that Uₙ · M is maximized at i = N. The rectangular bar represents the atomic displacement amplitude and phase for individual layers, by its length and color (red and blue for opposite phase), respectively.

Following on previous work (7, 16, 19), 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 Aₜ mode splitting, we take a simple linear chain model of N-layer CrI₃, as introduced in few-layer transition metal dichalcogenides (24, 27).

\[
H = H₀ + \frac{1}{2} \sum_{i=1}^{N} k (u_{i+1} - u_i)^2, \quad \text{with} \quad H₀ = \sum_{i=1}^{N} \left( \frac{1}{2} m u_i^2 + \frac{1}{2} k \omega_i^2 \right),
\]

where \(H₀\) represents the original \(Aₜ\) mode at frequency \(\omega₀ = \sqrt{k₀/m}\) 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 \(\Omega_i(\omega₀, \omega)\) and their corresponding eigenmodes \(\tilde{U}_i\) (\(i = 1, 2, . . . , N\)) (i.e., Davydov splitting), with \(i = 1\) being the highest-frequency mode and \(i = N\) being the lowest-frequency mode. By choosing \(\omega₀ = 129.10 ± 0.10\) cm⁻¹ and \(\omega = 15.98 ± 0.55\) cm⁻¹, the calculated frequencies \(\Omega_i\) (solid lines with open diamonds) match well with all of the experimental values (red solid squares and blue solid circles), as highlighted by the fan diagram in Fig. 1B. See detailed calculations of \(\Omega_i\) and \(\tilde{U}_i\) in SI Appendix, section II and Tables S1 and S2.

Because N-layer CrI₃ 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., \(\tilde{U}_1 = (1,1, . . . , 1)/\sqrt{N}\)). In the parallel channel where only modes with even parity and symmetric Raman tensor \(R₀\) 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 \(U_i\) for \(N = 1\) and 2 and \(U_{i,3}\) for \(N = 3\) and 4 are observed in the linear parallel channel in Fig. 1A and B. In contrast to the structure of N-layer CrI₃, the layered-AFM order is centrosymmetric for odd \(N\) and noncentrosymmetric 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 \(Rₐₐ\) and can appear only 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 \(\tilde{U}_N\) always has the same parity as the layered AFM for any \(N\). The result in Fig. 1A and B corroborates with this prediction that \(U_i\) for \(N = 1, U_2\) for \(N = 2, U_{3,3}\) for \(N = 3, \text{and} U_{4,2}\) 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 \(\tilde{U}_i · M\) of the eigenmode vector \(\tilde{U}_i\) onto the
yielding the strongest coupling strength of state of 1L to 4L CrI3 in $A$ respectively, is further supported by their distinct temperature behavior (29) (red curves in Fig. 2). Critical temperature $T_c(M)$ of 2L CrI3 in the linear crossed channel (blue curves). Critical temperature $T_c(M)$ of 2L CrI3 in the linear crossed channel follows a smooth anharmonic decay (24 27) and the layered-AFM–coupled phonons of RAS 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$_2$Ge$_2$Te$_6$ (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 CrI3 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 increases only slowly below $T_C$, as illustrated by representative spectra taken at 70, 40, and 10 K in Fig. 2A. Such a behavior extends beyond the first-order phonons (Fig. 2A, Left) to the second- and third-order ones (Fig. 2A, Center 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 $I_0 + I\sqrt{T - T}$ (blue curves in Fig. 2B), in contrast to those in the linear parallel channel following a smooth anharmonic decay behavior (29) (red curves in Fig. 2B). As pictorially summarized in Fig. 2C, we propose that a multiphonon process (30, 31) leads to conventional first-, second-, and third-order phonon modes (red) in the linear parallel channel, and their coupling with the layered-AFM order results in the magnetic counterparts (blue) 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 to prevent any artifacts from the Faraday rotation of light from passing through optical components in a stray magnetic field. In this work, we focus on two representative thickneces, 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 and Fig. S3). We note that the mechanism described below is applicable for arbitrary N-layer CrI$_3$.

The 2L CrI$_3$ undergoes a layered-AFM to FM transition at a critical magnetic field $B_c = \pm 0.6$ T (5). Fig. 3A presents Raman spectra of first-order modes taken at $B_c = 0$ 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 ($I_0$ 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 ($I_0$) survives, and it shows giant Raman circular dichroism of $\pm 78\% \left(\frac{I_0 + U_2}{I_0 - U_2}\right)$. 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. 3B. Fig. 3E and F shows the magnetic field dependence of the second- and third-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 second order and $\pm 50\%$ for the third order. This observation suggests the participation of $U_1$ in the second- and third-order multiphonon process.
We refer to the layered-magnetism–phonon coupling that we have developed above to understand the magnetic field dependence of the two first-order modes (U1 and U2) of 2L CrI3. For each mode Ui, its Raman tensor R is composed of the conventional structural (Rc) and the layered-magnetism–assisted magnetic (Rm) contributions; i.e., R = Rc + Rm, where Rm is magnetic field independent and is present only for parity-even modes. Rs ∝ M is the magnetic origin and selects the zero-momentum component, and λi is the ratio of the magnetic to structural contribution for the ith mode that depends on microscopic parameters such as spin–orbit coupling. Here, M changes from (1, 1) to (±1, ±1) across the layered-AFM to FM transition at Bc = ±0.6 T with the fully polarized FM spin moments pointing upward/downward. Specifically, for the parity-even high-frequency mode of \( \tilde{U}_1 = \frac{1}{\sqrt{2}}(1, 1) \), \( R_s^1 = \begin{pmatrix} \rho_1 & 0 \\ 0 & -\rho_1 \end{pmatrix} \) at all magnetic fields and \( R_s^2 = \tilde{U}_1 \cdot \tilde{M} \begin{pmatrix} 0 & -a_1 \\ +a_1 & 0 \end{pmatrix} \) below \( B_c \) and \( \begin{pmatrix} 0 & +a_1 \\ -a_1 & 0 \end{pmatrix} \) above \( B_c = \pm 0.6 \) T (Fig. 3 C, Top and Bottom), whereas for the parity-odd low-frequency mode of \( \tilde{U}_2 = \frac{1}{\sqrt{2}}(1, -1) \), \( R_s^2 = 0 \) always and \( R_s^2 = \begin{pmatrix} 0 & -\sqrt{2}a_2 \\ +\sqrt{2}a_2 & 0 \end{pmatrix} \) below \( B_c \) and 0 otherwise (Fig. 3C, Middle), where \( \tilde{M} \) accounts for the broken time-reversal symmetry and \( a_1 \) stands for the Raman scattering strength of the \( \delta \)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 first-order modes of 2L CrI3 in LL and RR channels by tuning only \( \lambda_i \) and \( a_i \) (Fig. 3D).

Different from 2L CrI3, N-layer CrI3 (N > 2) undergoes two spin–flip transitions with increasing \( B_c \), one at \( B_c = \pm 0.7 \) T for spins in surface layers and the other at \( B_c = \pm 1.6 \) T for spins in interior layers (1, 2). For simplicity but without losing any generality, we pick 4L CrI3 and focus on measurements with the upward magnetic field and in the RR polarization channel. Fig. 4A shows Raman spectra of first-order modes taken at \( B_c = 0 \), 1, and 2 T, below \( B_c \), between \( B_c = 1 \) and \( B_c = 2 \), and above \( B_c = 2 \), respectively, at 10 K and in the RR channel. At 0 T, we can reliably resolve only three of the fourfold multiplet of 4L CrI3, namely, \( U_1 \), \( U_3 \), and \( U_2 \) as fitted by the red, orange, and blue Lorentzian profiles, respectively. This is because \( U_2 \) is spectrally so close to \( U_1 \) but has a much weaker intensity (Fig. 1A), thus getting overwhelmed by the strong \( U_1 \) in the RR channel. We observe both \( U_1 \) and \( U_3 \) decrease subsequently at 1 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 \( U_2 \) integrated intensity is shown in Fig. 4B, displaying the contrasting trends of \( U_1 \) to \( U_1 \) and \( U_3 \), and those of the second- and third-order modes are shown in Fig. 4E and F, closely mimicking that of \( U_1 \).

We carry out a similar analysis as we have done for 2L CrI3 above, but add an additional intermediate magnetic phase \( M = (1, 1, 1, 1) \) between the layered AFM of \( (1, 1, 1, 1) \) and the fully spin-polarized FM of \( (1, 1, 1, 1) \). While the structural contribution (Rs) is present only for parity-even modes, \( U_1 \) and \( U_3 \), and remains magnetic field independent, the layered-magnetism–coupled magnetic contribution (Rs) varies proportionally to \( \tilde{U}_1 \cdot \tilde{M} \) as \( M \) changes as a function of \( B_c \).
the modes that have finite coupling to every layered magnetic order and thus nonzero RAS, according to which the magnetic contribution of U₁ appears above B₁, that of U₃ emerges between B₁ and B₃, and U₂ is present only below B₃ (see the calculated magnetic field dependence of U₁, U₂, U₃, and U₄ in SI Appendix, Tables S6 and S7). By adjusting λ₁ and a₁, the ratio of the magnetic to structural contribution and the overall strength of the ith mode, we successfully show the consistency between the experimental and calculated magnetic field dependence of U₁,3,4 and predict that of U₂ despite its invisibility in our experiment (Fig. 4D).

In conclusion, we have established the Davydov splitting of the A₂ mode of a monolayer into an N-fold multiplet in N-layer CrI₃ and discovered, distinct from nonmagnetic few-layer atomic crystals (24–27), a unique layered-magnetism–assisted phonon scattering mechanism in the magnetic phases of CrI₃. We find this mechanism extends beyond first-order phonons to the multiphonon modes and further resolve the distinct magnetic field dependence for different first-order modes within the N-fold multiplet in N-layer CrI₃. 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 CrI₃ of arbitrary thickness.

Materials and Methods

Sample Fabrication. CrI₃ single crystals were grown by the chemical vapor transport method, as detailed in ref. 19. The 1L to 4L CrI₃ samples were exfoliated in a nitrogen-filled glovebox. Using a polymer-stamping transfer technique inside the glovebox, 1L to 4L CrI₃ flakes were then sandwiched between two few-layer hBN flakes and transferred onto SiO₂/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 40x 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 to 2.2 T.

Data Availability. All study data are included in this article and SI Appendix.

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