Distinct magneto-Raman signatures of spin-flip phase transitions in CrI₃

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The discovery of 2-dimensional (2D) materials, such as CrI₃, that retain magnetic ordering at monolayer thickness has resulted in a surge of both pure and applied research in 2D magnetism. Here, we report a magneto-Raman spectroscopy study on multilayered CrI₃, focusing on two additional features in the spectra that appear below the magnetic ordering temperature and were previously assigned to high frequency magnons. Instead, we conclude these modes are actually zone-folded phonons. We observe a striking evolution of the Raman spectra with increasing magnetic field applied perpendicular to the atomic layers in which clear, sudden changes in intensities of the modes are attributed to the interlayer ordering changing from antiferromagnetic to ferromagnetic at a critical magnetic field. Our work highlights the sensitivity of the Raman modes to weak interlayer spin ordering in CrI₃.

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Magnetic van der Waals-bonded materials represent a rapidly growing research field, where these materials provide a solid-state platform to study a variety of exciting physics and potential applications of magnetism in two dimensions, including proximity effects, control using strain and gating, spin fluctuations, magnetic excitations, spintronics, and possible quantum spin liquids. One material of particular interest is chromium tri-iodide (CrI₃), a ferromagnet (FM) at bulk thicknesses below the Curie temperature (Tₘ) but with the remarkable property of layered antiferromagnetism (AFM) in thin multilayers. Although each individual layer is FM, the layers themselves are AFM coupled, and this effect persists for samples tens of layers thick. Furthermore, the interlayer spin arrangement in CrI₃ can be switched between AFM and FM by an electric field, applied pressure, and a magnetic field, providing tunability in potential devices.

Raman spectroscopy is a powerful technique to study a variety of phenomena in 2D quantum materials, including effects of strain, electron-phonon coupling, phase transitions, spin-phonon coupling, and magnetic excitations. In addition, the diffraction-limited spot size allows for the investigation of atomically thin samples and heterostructures using a non-contact probe. In this work, we collect temperature- and magnetic field-dependent Raman spectra on a thin (~10 layers) CrI₃ single crystal encapsulated in hexagonal boron nitride (hBN). Interestingly, at low temperature, increasing the magnetic field results in dramatic changes in the Raman spectra, indicating a magnetic field-induced phase transition when the interlayer spin arrangement changes from AFM to FM. By calculating the phonon dispersion of CrI₃ in both the FM and AFM state, we conclude the two modes that only appear in the AFM state are zone-folded phonons. This work validates magneto-Raman spectroscopy as a sensitive technique to probe interlayer magnetic ordering in quantum materials.

Results

Polarization-dependent Raman at zero magnetic field. A thin flake of CrI₃ (~7 nm from atomic force microscopy, or ~10 layers) was encapsulated between two 20 nm and 30 nm flakes of hBN using the dry transfer technique. In the ab plane, the CrI₃ crystals are arranged in a honeycomb lattice, where each chromium atom is bonded with six iodine atoms to form a distorted octahedron. At room temperature, bulk CrI₃ has a monoclinic structure (C2/m) but exhibits a crystallographic phase transition below 220 K to rhombohedral (R3) symmetry, where the main difference between the two structures is the stacking of the layers (see Supplementary Fig. 1). The bulk Tₘ is ~61 K, with the spins aligned perpendicular to the ab plane. Surprisingly, the magnetic behavior of thinner samples is very different; whereas the spins still align perpendicular to the ab plane, the interlayer magnetic stacking is AFM, as demonstrated through a variety of experimental techniques.

Raman spectra were collected with a triple grating spectrometer using an excitation laser wavelength of 632.8 nm and keeping the power below 150 µW (~1 µm spot size) at the sample to avoid heating. The laser polarization of the incoming εᵢ light makes an angle θ with respect to the b axis (Fig. 1a), and the scattered εᵣ light angle θ is changed from θ = 0° (parallel, xx) to θ = 90° (perpendicular, xy). As the crystallographic a- and b-axes are not known in our sample, the angle θ is arbitrary, yet constant angle in our experiments. Figure 1b shows the Raman spectra at T = 5 K in both the xx and xy polarization configurations. We confirm the monoclinic symmetry in our ~10 layer flake by resolving two peaks at 108 cm⁻¹ and 109 cm⁻¹ between xx (black, scaled by 0.5) and xy (red), unlike the doubly degenerate peak seen in the rhombohedral structure. Thus, we label the phonons using the irreducible representations of the 2/m point group, where only the A₆ and B₆ modes are Raman active. The density functional theory (DFT) calculated atomic displacements associated with these modes are shown in Supplementary Table 1.

Two modes appear below Tₘ in the xy configuration at 77 cm⁻¹ (9.5 meV) and 126 cm⁻¹ (15.6 meV), labeled P₀ and P₁ in Fig. 1b, respectively. These modes were previously attributed to one-magnon excitations since they appear in the magnetically ordered state and have their largest intensity in xy (inset of Fig. 1b, Supplementary Fig. 2), indicating B₆ symmetry. Instead, the bulk magnon dispersion at 5 K shows a low-energy magnon at Γ below 1 meV (8 cm⁻¹), similar to what was measured by recent FM resonance experiments and magnons at the M point of the Brillouin zone at ~9 meV and 15 meV. Furthermore, a recent Raman study of magnon excitations in FePS₃ showed it is possible for magnons to be present in both xx and xy in quasi-2D van der Waals magnets. Thus, the B₆ nature of P₀ and P₁ is not conclusive evidence that they are magnons.

Fig. 1 Crystal structure and Raman spectra of CrI₃. a Top and side views of two layers of CrI₃ with monoclinic structure and a schematic defining angles θ and φ with respect to the a- and b-crystal axes and the polarization vectors of the incoming εᵢ and scattered εᵣ light. The two CrI₃ layers are color-coded differently. b Raman spectra for both xx (black) and xy (red) polarization configurations at T = 5 K and B = 0 T. Spectra in xx were divided by two for clarity. Peaks that appear below Tₘ are highlighted with blue asterisks. Inset shows intensity as a function of εᵣ for P₀ and A₆ in a polar plot.
perpendicular to the ab plane (B ⊥ ab, Faraday geometry) on P₁ and P₂, as detailed in Fig. 2. Two spectral ranges from 65 cm⁻¹ to 90 cm⁻¹ (P₁, A₁) and 120 cm⁻¹ to 136 cm⁻¹ (P₂, A₆) are shown on different intensity scales (= a factor of 3:1, respectively) for clarity. At B = 0 T and in xy, P₁ and P₂ have strong intensities, whereas the two A₈ modes at slightly higher frequencies have minimum intensities as they are forbidden in the xy configuration. Increasing the magnetic field results in drastic changes in the Raman spectra, where P₁ and P₂ behave in the same fashion. Above ~1.6 T, the intensities of P₁ and P₂ abruptly start to vanish and A₁ and A₆ begin to appear in xy. By B = 2 T, P₁ and P₂ are absent in all polarization configurations, whereas A₁ and A₆ are no longer forbidden in xy. No further changes occur above 2 T, and no hysteresis was observed when the field was lowered back to 0 T. It should be noted that P₁ and P₂ do not show frequency shifts with magnetic field, suggesting they are not one-magnon processes with spins perpendicular to the ab plane.

Raman spectra were collected as the magnetic field was increased in finer steps up to 2 T. This is shown as a false-color map (Fig. 3a) and spectra (Fig. 3b) for the frequencies near P₁ and A₆, where six distinct magnetic field ranges are revealed. Upon close inspection, there is additional Raman scattering intensity, i.e., spectral weight, present between P₂ and A₆ = 128 cm⁻¹, although it cannot be discerned if the spectral weight is attributed to a single or multiple mode(s). No changes to P₂, A₆, or the spectral weight were observed in Range 1 from 0 T and 0.6 T. In Range 2 between 0.7 T and 0.8 T, the spectral weight between P₂ and A₆ appears to shift in frequency and intensity. The spectra are again stable through Region 3 from 0.8 T to 1.4 T, after which striking changes are seen in Regions 4 and 5. In Region 4, P₂ starts to decrease in intensity, the intensity of A₆ stays relatively constant, and the spectral weight shifts in frequency and increases in intensity. In Region 5, P₂ decreases in intensity until they disappear, whereas A₆ grows in intensity until B > 1.95 T (Region 6), when the phase transition is finally complete. It should be noted that experimental uncertainty, including instrumental drift and corrections for Faraday rotation

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in magneto-cryostat objective lenses, can lead to small changes in peak intensities (generally less than 5%) when comparing consecutively taken Raman spectra. The intensity changes being tracked in the field ranges in Fig. 3b, however, are more significant than any changes seen in the Ω point phonons (see Supplementary Fig. 3) and are thus outside of experimental uncertainty. Moreover, frequency shifts, such as those observed in the spectral weight between P₂ and A₆ in Regions 2 and 4, are significantly more reliable than intensity changes, generally reproducible to within one CCD detector pixel (~0.4 cm⁻¹ with He–Ne excitation herein). For fitted peaks (e.g., well-defined phonons), changes in the Raman shift frequency are even more precise (better than 0.1 cm⁻¹).

Recent magneto-tunneling measurements of few-layered CrI₃ observed large changes in the tunneling current at nearly the same magnetic field values where we observe marked changes in the Raman spectra, such as at 0.8 T and 2 T,¹¹,¹²,¹⁵,²⁵. These changes were attributed to the spin-filtering effect when the magnetic field is strong enough to change the interlayer spin arrangement from AFM to FM, and the effect was observed even for 20 nm thick samples (our sample is ~7 nm). The striking resemblance in the evolution with magnetic field values where we observe marked changes in the Raman spectra, such as at 0.8 T and 2 T,¹¹,¹²,¹⁵,²⁵ suggests it is most likely a result of the surface layers (adjacent to the hBN) flipping while the second, final jump is the flipping of the internal layers at ~2 T. This spin-flip phase transition is supported by the observation of the lower energy FM magnon for B > 6.5 T (Supplementary Fig. 4), which matches previous results on bulk, FM CrI₃,¹³,³⁸, and the lack of change in the Raman spectra between 2 T and 9 T (Supplementary Fig. 5). The 10 L sample remains monoclinic at high magnetic fields (Supplementary Fig. 6), demonstrating that a change in crystal structure is not the source of the evolution in the Raman spectra. In particular, the spectral weight present between P₂ and A₆ is extremely sensitive to the spin-flipping, displaying strong frequency shifts and intensity variations where the spin flips occur. The fact that the spectral weight does not shift in magnetic field in Regions 1 and 3, which are regions of stability, suggests its presence does not involve a one-magnon process. It is possible that the spectral weight results from the excitation laser wavelength (λ = 632.8 nm) being nearly resonant with the ligand-to-metal charge transfer transition,³⁷-⁴⁰ but the weak Raman signal at off-resonance excitation laser wavelengths makes this difficult to verify.

The polar plots for A₆, which track the intensity of A₆ as a function of angle θ, at various magnetic fields provide further evidence of the magnetic phase transition. As seen in Fig. 4a, the polar plot is rotated by ~35° at B = 2 T when compared with B = 0 T. This can be understood if we write the Raman tensor for the A₆ phonon with an induced magnetization m under applied magnetic field (B // ab) as

\[
R_{A_6, B // ab} = R_{A_6, m = 0} + m_z \cdot R_{A_6, m_z}
\]  

which separates the spin-independent and spin-dependent terms. The point group of CrI₃ requires that the total Raman tensor Rₐ₆ is symmetric under twofold rotation around the b axis (C₂ₓ). Thus, Rₐ₆, m = 0 and m_z · Rₐ₆, m_z must be symmetric under twofold rotation individually. As m_z itself is antisymmetric under C₂ₓ, then the form of Rₐ₆, m_z is required to also be antisymmetric under C₂ₓ such that their product is symmetric:

\[
R_{A_6, B // ab} = \begin{pmatrix}
\alpha & 0 & \beta \\
0 & \gamma & 0 \\
\beta & 0 & \delta
\end{pmatrix} + m_z \begin{pmatrix}
0 & 0 & \gamma \\
0 & 0 & \delta \\
0 & \delta & 0
\end{pmatrix}
\]  

Thus, for the B = 0 T case (AFM state) where there is no induced magnetization, the Raman tensor would be purely symmetric, and we would not expect to detect the A₆ phonon in xy polarization configurations. A magnetic field applied perpendicular to the ab plane that spin-polarizes the CrI₃ to the FM state, however, introduces off-diagonal tensor elements and breaks this expectation, causing the polar plot to rotate as seen in Fig. 4a. Assuming there are minimal changes between the monoclinic (C₂ₓ), 10 L CrI₃ and the hexagonal point group of the monolayer (D₃h), then β = α + Δ and δ = −(γ + Δ'), where Δ and Δ' are small corrections.

\[
R_{A_6, B // ab} = \begin{pmatrix}
\alpha & m_y & \beta \\
-m_y & \gamma & \alpha + \Delta \\
\beta & \alpha + \Delta & \alpha
\end{pmatrix}
\]  

Writing the matrices as in Eq. (3) makes it clear that when the magnetic field direction is flipped from Bₓ to −Bₓ, thus flipping the direction of the induced magnetization, the signs of the off-diagonal elements switch, resulting in the opposite rotation of the polar plot, exactly as we observed in Fig. 4b and Supplementary Fig. 7.

Figure 4c shows the angle of maximum intensity of the polar plot in 4a as a function of magnetic field is swept through the phase transition, where Regions 1–6 from Fig. 3 are marked with vertical dashed lines. Although Fig. 3 and magneto-tunneling results indicate that parts of the phase transition occur between Regions 2 and 4, there is no observable change in the maximum intensity of the polar plot in those field ranges. In Region 5, however, it increases to ~10° for B = 1.7 T and 1.8 T, and then finally to ~35° for 1.8 T and above. The lack of rotation of the polar plot between 0.7 T and 0.8 T reveals that not enough magnetization is induced in this field range to introduce the off-diagonal Raman tensors in Eq. (2).

The temperature dependence of the spin flips was investigated by tracking the intensity of P₂ as a function of magnetic field for different temperatures between T = 9 K and 26 K, as detailed in Fig. 4d. The intensity of P₂ is shown relative to the intensity of the combination peak A₆²/B₆² at ~115 cm⁻¹ at B = 0 T for each temperature, as this peak appears to remain constant with temperature and magnetic field (in the probed range). The spin-flip transition field, or the amount of magnetic field necessary to cause P₂ to disappear, decreases with increasing temperature. In addition, the distinct jumps from spin flips and flat plateaus observed in the intensity of P₂ smooth out for higher T. Further temperature dependence is analyzed in Supplementary Fig. 8. This behavior is consistent with a phase transition where there is a strong correlation between the temperature and magnetic field, which suggests that the magnetic field takes the transition temperature to zero. Although this behavior is akin to a quantum phase transition, there is no evidence yet of any quantum critical behavior in this material, but it is a very interesting avenue for future investigation.

**Magneto-Raman measurements of 10 L CrI₃ in Voigt geometry.** Finally, we investigated the directional dependence of the spin-flip phase transition by rotating the sample such that the applied magnetic field is parallel to the ab plane (B || ab, Voigt geometry). Figure 4e shows I(P₂)/I(A₆²/B₆²) for B || ab and at
measurements of the magneto-tunneling current when the magnetic field, where \( T \) is directed along the \( ab \) axis. Requiring that the total magnetic field components along the \( a \) axis, the polar plot would be expected. To test these predictions, we rotated the sample while the magnetic field was applied in the ab plane such that the magnetic field was pointed along two different crystal orientations \( \phi_1 \) and \( \phi_2 = \phi_1 + 90^\circ \). The polar plot of the intensity of \( A_6^g \) at \( B = 0 \) T and 7 T (in the spin-polarized state) are shown in Fig. 4f. Interestingly, for both orientations, in which either \( \phi_1 \) or \( \phi_2 \) must contain magnetic field components along the \( a \) axis, the polar plot of the intensity of \( A_6^g \) does not show the same rotation that was observed for spins pointing perpendicular to the ab plane in the spin-polarized state. This indicates that the off-diagonal elements \( y' \) and \( \delta' \) are negligible for magnetic fields pointing in the ab plane.

**Discussion**

Our data shows that \( P_1 \) and \( P_2 \), which appear (disappear) in the AFM (FM) state and are absent in bulk samples (Supplementary Fig. 10), are not one-magnon excitations, as their frequencies do not contain magnetic field components along the \( a \) axis, the polar plot would be expected. To test these predictions, we rotated the sample while the magnetic field was applied in the ab plane such that the magnetic field was pointed along two different crystal orientations \( \phi_1 \) and \( \phi_2 = \phi_1 + 90^\circ \). The polar plot of the intensity of \( A_6^g \) at \( B = 0 \) T and 7 T (in the spin-polarized state) are shown in Fig. 4f. Interestingly, for both orientations, in which either \( \phi_1 \) or \( \phi_2 \) must contain magnetic field components along the \( a \) axis, the polar plot of the intensity of \( A_6^g \) does not show the same rotation that was observed for spins pointing perpendicular to the ab plane in the spin-polarized state. This indicates that the off-diagonal elements \( y' \) and \( \delta' \) are negligible for magnetic fields pointing in the ab plane.

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not shift with applied magnetic field. After considering other theoretical models (see Supplementary Notes 1 and 2, Supplementary Tables 2–5, Supplementary Fig. 11), we conclude that P1 and P2 are actually zone-folded phonons owing to a doubling of the AFM unit cell in the c direction. This is illustrated in Fig. 5a, where the opposite spins of consecutive layers in the AFM configuration lead to a unit cell that is twice as large in the c direction compared to the FM configuration.

Using DFT, we calculated the phonon dispersions for monolayer, bulk CrI₃ in both the FM and AFM stacking configurations. The full phonon dispersions, Brillouin zone, and table of frequencies are given in Supplementary Figs. 12 and 13 and Supplementary Table 6. Figure 5b shows only the Raman-active phonons in the FM state (red, solid) and AFM state (blue, dotted) for frequencies near P1 and P2. In general, Raman spectroscopy is only sensitive to modes at the Γ point in the phonon dispersion due to conservation of momentum. Thus, phonons at the A point (in direction of k₃) in the FM state are not observed. However, the doubling of the unit cell in the AFM state leads to zone-folding, where the phonons at the A point in the Brillouin zone in the FM state fold back onto Γ in the AFM state and can be observed in Raman spectroscopy. Two pairs of modes with similar frequencies to P1/A₁ and P2/A₂ have an easily resolvable frequency splitting at Γ (highlighted Fig. 5b), with the zone-folded phonon (P1 or P2) between 2 cm⁻¹ and 4 cm⁻¹ lower in frequency than the original phonon (A₁ or A₂). Illustrations of these vibrations are shown in Fig. 5c, d, where the two layers vibrate in-phase for A₁ and out-of-phase for P1 and P2. In the bulk, P1 and P2 would have B₃ symmetry and would thus be Raman silent but infrared active. However, the breaking of inversion symmetry for an even number of layers in the AFM configuration would allow P1 and P2 to be Raman active with B symmetry (only seen in xy configurations). These zone-folded phonons would not shift in magnetic field and would be Raman-active (forbidden) in the AFM (FM) state, aligning with the observed behaviors of P1 and P2.

Even though the doubling of the unit cell is purely magnetic in nature, the observation of very strong zone-folded phonons that have similar intensity as the observed Γ point phonons reveals the strong coupling between magnetism and the lattice in atomically thin CrI₃. Of note, the origins of P1 and P2 as zone-folded phonons predict they would disappear for a monolayer sample (no zone-folding) or a sample with an odd number of layers because the AFM state preserves inversion symmetry with an odd number of layers. Recent work⁴¹,⁴² has shown P1 and P2 are not present in monolayers of CrI₃, yet data by Jin et al.³⁴ suggests the presence of P1 and P2 for odd layer thicknesses. One possibility is that the encapsulation of thin layers of CrI₃ in hBN breaks inversion symmetry naturally, leading to the presence of P1 and P2 in all thicknesses. Further studies as a function of layer thickness and encapsulation parameters are needed to elucidate the symmetry response of P1 and P2 for even vs. odd numbers of layers.

In conclusion, we utilized temperature-dependent, magneto-Raman spectroscopy to elucidate a magnetic phase transition in CrI₃ where the interlayer stacking changes from AFM to FM. Substantial changes in the Raman spectra are detected at specific magnetic field values due to spin flips of layers to a FM stacking state, indicating that Raman modes are extremely sensitive to this phase transition. Moreover, Raman scattering proves to be crucial to understanding the symmetry and frequency shifts of the modes. We deduce that the modes P1 and P2 are not high frequency magnons as previously concluded, but instead attribute the modes to zone-folded phonons using symmetry arguments, polarization-dependent Raman responses, and calculated phonon dispersions in the FM and AFM stacking configurations. This study paves the way for further use of magneto-Raman spectroscopy to investigate spin-flip phase transitions in 2D van der Waals magnets.

**Methods**

**Sample preparation and encapsulation.** Bulk CrI₃ crystals were grown by a chemical vapor transport technique using stoichiometric mixtures of Cr and I in a sealed evacuated quartz tube, as mentioned in other references⁵,²⁴. The phase of the obtained crystals were checked by X-ray diffraction. These crystals were then exfoliated onto Si/SiO₂ substrates in an Ar-filled glovebox having O₂ and H₂O concentrations of <0.1 ppm. hBN/CrI₃/hBN heterostructures were fabricated using a dry transfer technique detailed elsewhere⁵,²⁴. Specifically, PDMS (polydimethylsiloxane) was used as the polymer stamp.

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**Fig. 5 Unit cells, phonon dispersions, and normal modes for FM and AFM stacking.** a Comparing the unit cell for the FM and AFM stacked structures, where the AFM unit cell is doubled in the c direction. Chromium atoms are green, whereas iodine atoms are blue. b Calculated phonon dispersion showing the Raman-active modes in the FM (red, solid) and AFM (blue, dashed) stacking in bulk CrI₃ in the monoclinic crystal structure. In the AFM case, the doubling of the unit cell along the c direction in real space results in the A₁(Γ₃) point folding into Γ, such that the number of modes is doubled compared with the FM case. The Γ–A distance in the AFM case is half that of the FM case. Modes that correspond to P1, A½, P2, and A½ are highlighted and their atomic vibrations are shown in c and d.
Raman spectroscopy. A triple grating Raman spectrometer (Horiba JY T64000®, 1800 mm−1 grating) coupled to a liquid nitrogen cooled CCD detector was used to collect Raman spectra. The excitation wavelength was 632.8601 nm from a He-Ne laser and spectra were measured in the 180° backscattering configuration. Raman spectra as a function of temperature and magnetic field were collected using an attoDRY cryostat (Attocube Inc.), where the sample was zero-field cooled and studied with a magnetic field compatible objective (≤50, N.A. 0.82). Ultra-broadband polarizers and achromatic half wave plates were used to select and control polarization, including correcting for Faraday rotation in the objective under applied magnetic field. The laser power was ~150 µW to avoid local heating and integration times were ~12 min.

DFT phonon calculations. We performed DFT calculations14,15 with the Quantum Espresso code, using the GBRV ultrasoft pseudopotential set47,48. We used the vdW-df-ob86 exchange correlation functional49,50, which includes long range van der Waals interactions.

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**Author contributions**
A.M., T.T.M, J.R.S., R.V.A, and A.R.H.W conceived the project. Bulk CrI3 crystals were grown by Y.Z, J.H., D.W, J.E.G, and Z.M. Hexagonal boron nitride crystals were supplied by K.W. and T.T. Heterostructures were fabricated by D.S. and C.N.L. Raman measurements and analysis were carried out by A.M., T.T.M., J.R.S., R.V.A., and A.R.H.W. Theoretical analysis, including modeling, and numerical calculations, were carried out by F.G.U. and X.F., N.T., and Y.-M.L. Phonon DFT calculations were carried out by K.F.G. All authors contributed to the writing of the manuscript.

**Competing interests**
The authors declare no competing interests.

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