Magnetic Order-Induced Polarization Anomaly of Raman Scattering in 2D Magnet Crl₃

Yujun Zhang,^{†,‡,||} Xiaohua Wu,^{‡,||} BingBing Lyu,[‡] Minghui Wu,[‡] Shixuan Zhao,[‡] Junyang Chen,[‡] Mengyuan Jia,[‡] Chusheng Zhang,[‡] Le Wang,[§] Xinwei Wang,[†] Yuanzhen Chen,^{‡,§} Jiawei Mei,^{‡,§} Takashi Taniguchi,[#] Kenji Watanabe,[#] Hugen Yan,[⊥] Qihang Liu,^{‡,§} Li Huang,[‡] Yue Zhao,^{*,‡,§} and Mingyuan Huang^{*,‡}

[†]School of Advanced Materials, Shenzhen Graduate School Peking University, Shenzhen 518055, China

[‡]Department of Physics, Southern University of Science and Technology, Shenzhen 518055, China

[§]Shenzhen Institute for Quantum Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China

[#]Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki 305-0044, Japan

¹State Key Laboratory of Applied Surface Physics and Department of Physics, Fudan University, Shanghai 200433, China

Supporting Information

ABSTRACT: The recent discovery of 2D magnets has revealed various intriguing phenomena due to the coupling between spin and other degrees of freedoms (such as helical photoluminescence, nonreciprocal SHG). Previous research on the spin-phonon coupling effect mainly focuses on the renormalization of phonon frequency. Here we demonstrate that the Raman polarization selection rules of optical phonons can be greatly modified by the magnetic ordering in 2D magnet CrI₃. For monolayer samples, the dominant A_{1g} peak



shows an abnormally high intensity in the cross-polarization channel at low temperatures, which is forbidden by the selection rule based on the lattice symmetry. For the bilayer, this peak is absent in the cross-polarization channel for the layered antiferromagnetic (AFM) state and reappears when it is tuned to the ferromagnetic (FM) state by an external magnetic field. Our findings shed light on exploring the emergent magneto-optical effects in 2D magnets.

KEYWORDS: 2D magnets, Raman spectroscopy, CrI₃, magneto-optical effect

T he discovery of 2D van der Waals magnets has attracted a lot of attention in both fundamental physics and potential applications.¹⁻⁹ Among these 2D magnetic materials, CrI_3 is the most intensively studied, where the weak interlayer AFM coupling can be manipulated by the magnetic field, electric field, doping, and pressure,¹⁰⁻¹⁵ leading to many interesting potential applications, such as magnetoresistive memories, spin filters,¹⁶⁻²⁰ and spin transistors.²¹ The recent experiment shows that the AFM bilayer CrI_3 exhibits giant nonreciprocal second-harmonic generation due to the inversion symmetry breaking induced by the layered AFM order,²² but how this magnetic ordering affects the inelastic light scattering is still unclear. Moreover, the Raman scattering in monolayer and other thin CrI_3 layers with a different magnetic ordering is elusive as well.

Raman spectroscopy is a versatile tool to probe magnetic materials and can provide information on energy, symmetry, and statistics of magnetic excitations, such as fluctuations of magnetic energy density (quasi-elastic scattering),^{23,24} magnons,^{25,26} and spinons.²⁷ It has been widely used in the study of magnetic phase transitions.²⁸ Besides the magnetic

excitations, Raman spectroscopy can be used to study the phonon behavior induced by magnetic order, including spinphonon coupling,²⁹ concomitant structural phase transition,³⁰ and Brillouin zone folding.^{9,31} In the study of recent 2D magnets, Raman spectroscopy was first used to study AFM order in 2D materials^{9,32–36} and subsequently used to probe the FM phase transition in $Cr_2Ge_2Te_6^{30}$ and CrI_3 .³⁷

In this work, we study the magneto-optical effect of CrI_3 thin layers by probing the phonon properties through polarized Raman spectroscopy. For the monolayer, the dominant Raman mode at about 128 cm⁻¹ displays an abnormally high intensity in the cross-polarization channel at low temperatures. Moreover, an abrupt intensity change in both parallel (XX) and cross (XY) polarization channels is observed with the spin flip driven by the external magnetic field. However, this peak (at about 129 cm⁻¹ for bilayer) is absent in the XY channel for the AFM bilayer and reappears when the bilayer is tuned to the

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FM state by a magnetic field. A new peak at around 127 cm^{-1} , presumably due to the Davydov splitting, can be observed in the AFM bilayer, though it is silent in the FM state due to the inversion symmetry changes. This anomalous polarization behavior cannot be explained by the lattice symmetry, and the magnetic ordering must have been taken into account. By group theory analysis, we highlight that the polarization selection rule of optical phonons can be greatly modified by the magnetic order. Furthermore, we also demonstrate that Raman spectroscopy can probe the magnetic order transitions in 3- and 4-layer CrI₃, and this polarization anomaly gets weaker as the number of layers increases.

We first investigated the Raman spectrum of CrI_3 monolayers as a function of temperature. Representative Raman spectra of a monolayer sample at 1.7 K are displayed in Figure 1a, with four Raman modes labeled as A_1 , A_2 , E_1 , and



Figure 1. Magnetic field dependence of the polarized Raman spectra for monolayer (1L) CrI₃. (a) Raman spectra of a monolayer CrI₃ sample in the parallel (XX, red) and cross-polarization channels (XY, blue) at low temperatures (1.7 K). The phonon modes are labeled as A_1 , E_1 , E_2 , and A_2 . The inset is the atomic structure of monolayer CrI₃, where Cr^{3+} is red and I⁻ is cyan, with the arrows indicating the vibrational mode associated with the A_2 peak. (b–e) Color plots of polarized Raman spectral intensity versus Raman shift and magnetic field as for monolayer CrI₃ in the XX (b and c) and XY channels (d and e), where the red arrows indicate the B field sweep direction: increasing (b and d) and decreasing (c and e) magnetic field. (f) Reflective magnetic circular dichroism (RMCD) (red) and the total intensity (from both XX and XY channels, blue) over a cycle of the magnetic field. Hysteresis can be observed for both RMCD and Raman intensity.

 E_2 , similar to previous studies.^{37–41} The dominant Raman peak A_2 only shows up in the XX channel above the critical temperature (T_C about 45 K),¹ as shown in Figure S1. After the sample is cooled down below T_C , this A_2 peak starts to show up in the XY channel, and its intensity is even higher than that of the XX channel at 1.7 K. Such polarization change indicates strong coupling between this phonon and the magnetic order. Note that this work mainly focuses on the behavior of this A_2 mode.

We next explored the effect of the applied out-of-plane magnetic field. Figure 1b–e shows the evolution of the Raman spectra of the monolayer sample from both XX and XY channels with an increasing (Figure 1b,d) and decreasing (Figure 1c,e) magnetic field. We can clearly see a sudden increase (decrease) of the intensities in both XX and XY channels at around 0.075 T (-0.075 T) with an increasing

(decreasing) magnetic field. We plot the total intensity (from both XX and XY channels) versus the magnetic field together with the reflective magnetic circular dichroism (RMCD) signal in Figure 1f, where the observed hysteresis loop is direct evidence showing the spin flip driven by the external magnetic field. The spin-direction-dependent Raman scattering may result from the resonant effect by using a 633 nm laser.¹⁵ The coercive field extracted from the Raman hysteresis loop (about 0.075 T) is less than that from the RMCD measurement (about 0.2 T), which is probably due to the higher laser power used in our Raman measurement (see details below).

The crystal structure of monolayer CrI_3 belongs to the D_{3d} point group, and the A_2 peak is assigned as an A_{1g} mode, associated with the symmetrical breathing mode between the upper and lower iodine layers as shown in the inset of Figure 1a.³⁹ From the selection rule based on lattice symmetry, the scattering signal should only appear in the XX channel. One possible reason for the appearance of the Raman signal in the XY channel is a new Raman mode with the same frequency as the A₂ mode, such as magnon.³⁷ We performed Raman measurements on the monolayer sample at a high magnetic field up to 8 T. However, no observable shift or splitting was detected for this mode, as shown in the Figure S2, suggesting a different origin. Given the fact that the intensities from the XX and XY channels show similar behaviors under a magnetic field, we conclude that they are associated with the same phonon mode. This assignment can be further verified by the group theory analysis.

On the basis of the group theory below, we demonstrate that the polarization selection rules of optical phonons can be modified when the crystal undergoes a transition from a paramagnetic to a magnetic state as the time-reversal symmetry is broken. The monolayer CrI₃ has the crystallographic symmetry $D_{3d} = \{e, 2C_3, 3C_2, i, 2S_6, 3\sigma_d\}$, and the Raman tensor of the A₂ mode is derived as eq 1a. If there is out-ofplane FM spin alignment, the corresponding magnetic point group is $D_{3d}(S_6) = \{e, 2C_3, 3RC_2, i, 2S_6, 3R\sigma_d\}$, where *R* is the time-reversal operator. According to the group theory, the Raman tensor of the optical phonon in the magnetically ordered state will have the same form as that of the optical magnon because they are constrained by the same symmetry. Therefore, the Raman tensor of this phonon mode will turn into eq 1b in the FM state.^{42,43}

$$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & c \end{pmatrix} \quad (1a) \qquad A_{g} = \begin{pmatrix} a & ib & 0 \\ -ib & a & 0 \\ 0 & 0 & c \end{pmatrix} \quad (1b)$$
(1)

where a-c are constants and *i* is $\sqrt{-1}$. Obviously, the imaginary antisymmetric terms in the Raman tensor caused by the magnetic order can account for the Raman scattering signal observed in the XY channel (for details, see Figure S3).

For the CrI₃ samples with two and more layers, we observed a new peak at the lower frequency side of the A₂ peak at the temperature below $T_{\rm C}$, which is consistent with a previous report.³⁷ Figure 2a,b show the evolution of the Raman spectra of a bilayer sample in the XX and XY channels, respectively, with an increasing magnetic field from -1.5 to 1.5 T. In the XY channel, we observe that the original A₂ peak (129 cm⁻¹) disappears and the split peak at about 127 cm⁻¹ emerges at B = -0.65 T. As the magnetic field increases, the situation is reversed at B = 0.65 T. As shown in Figure 2d, RMCD plots



Figure 2. Magnetic field dependence of the polarized Raman spectra for bilayer (2L) CrI₃. (a, b) Color plots of the polarized Raman spectral intensity versus Raman shift and an increasing magnetic field for bilayer CrI₃ in the XX and XY channels, respectively. In the XX channel, only the original A₂ peak at 129 cm⁻¹ can be resolved, and its intensity undergoes an abrupt change during the magnetic phase transition between the AFM and FM states; in the XY channel, the A₂ peak can be observed at the FM state but disappears at the AFM state, and the situation is reversed for the split peak at 127 cm⁻¹. (c) Raman spectra in the XY channel at B = -1.0, 0, and 1.0 T: line-cut profiles indicated by the purple, green, and red lines in panel b, respectively. (d) RMCD (red) and the ratio of the total intensity (blue) between the split and original A₂ peaks over a cycle of the magnetic field.

indicate that magnetic phase transitions occur at B = -0.65 T (from the spin-down FM state to the AFM state) and 0.65 T (from the AFM state to the spin up FM state), suggesting a correlation between the Raman polarization change and the magnetic phase transition. In the XX channel, only the original A_2 peak can be observed, and a clear intensity change can be resolved at the critical magnetic fields. We also performed the same measurement with a decreasing magnetic field, as shown in the Figure S4. No hysteresis is observed, which agrees with an AFM ground state of bilayer CrI₃.

Figure 2c shows the Raman spectra in the XY channel under the magnetic fields of -1.0, 0, and 1.0 T. The appearance of the Raman signal for the A_2 mode in both XX and XY channels when the bilayer is tuned to the FM state is similar to the behavior of the monolayer. It is also worth noting that the Raman intensity from the XY channel at 1.0 T is higher than that of the spectrum at -1.0 T, similar to the Raman intensity behavior observed on a monolayer as well. By plotting the ratio of the total intensity between the split and the original A_2 peaks (Figure 2d), the magnetic phase transition can be revealed clearly by Raman, as compared to RMCD measurements.

Recent theoretical and experimental studies show that the thin layer CrI_3 has the structure of the monoclinic phase (space group C2/m) other than the rhombohedral phase (space group $R\overline{3}$) for the bulk crystal at a low temperature,^{13,14,44,45} which contributes to the interlayer AFM coupling. Because the lateral interlayer translation breaks most of the symmetries in the monolayer, the CrI_3 bilayer only has the following symmetry: $C_{2h} = \{e, C_2, i, \sigma_h\}$. When the bilayer is at the AFM (FM) state,

the corresponding magnetic point group is $C_{2h}(C_2) = \{e, C_2, Ri, R\sigma_h\}$ ($C_{2h}(C_i) = \{e, RC_2, i, R\sigma_h\}$), and the Raman tensor of this phonon mode has the form of eq 2a (2b).^{42,43}

$$A = \begin{pmatrix} a & 0 & d \\ 0 & f & 0 \\ h & 0 & c \end{pmatrix} (2a) \qquad A_{g} = \begin{pmatrix} a & ib & d \\ ie & f & ig \\ h & ik & c \end{pmatrix} (2b)$$
(2b)

where a-h and k are constants. For van der Waals materials, the Raman spectra that originated from a single phonon process can usually be understood by their monolayer structure because the Van de Waals interaction between the layers is weak, and the lattice stacking order only has a small impact on the Raman spectrum. As a consequence, we have $f \approx a, e \approx -b$, and $d, h, g, k \approx 0$, and Raman tensor 2a (2b) turns into 1a (1b) (for details, see Figure S5). Consequently, for the AFM bilayer, the Raman scattering in the XY channel is prohibited but allowed for the FM bilayer, which is fully consistent with our experimental observation.

In comparison to the monolayer, there exists interlayer coupling in multilayer CrI_3 ; thus, the original A_{1g} mode of the monolayer splits into N modes in N-layer CrI_3 . Such splitting is termed as Davydov splitting.^{46,47} Given the facts of the spectrum weight transfer behavior and small frequency difference between the split and original A2 modes, we suggest that the split new peak at 127 cm^{-1} is originated from the Davydov splitting. To confirm our assignment, we performed the first-principles calculation within the density functional theory on bilayer CrI₃ to determine the frequencies of its vibrational modes (for details, see Figure S6). The calculated frequency difference between those two modes that originated from the A_2 mode is about 1.8 cm⁻¹, which agrees very well with our experimental value of 2.0 cm^{-1} . From the symmetry analysis, the A_2 mode (A_{1g}) splits into an A_g (Raman active) and a B_{μ} (Raman inactive) mode in bilayer CrI₃. With a layered AFM spin order, the B_{11} mode turns into a Raman active B mode due to the inversion symmetry breaking; as of the FM spin order, on the other hand, this mode turns into a Raman inactive A_u mode. Such mode assignments are in good agreement with our experimental findings that the split peak can only be observed in the AFM phase. Assuming a weak interlayer coupling, we can predict that this split peak can only show up in the XY channel (for details, see Figure S5).

The field-dependent measurements demonstrate that the Raman spectra of the monolayer and bilayer CrI₃ strongly depend on their magnetic ordering, making Raman spectroscopy a sensitive probe for layered magnetism. We then apply the Raman technique to investigate CrI₃ with an increasing number of layers. Figure 3a,b shows the Raman spectra from the XY channel for a trilayer (3L) and a four-layer (4L) sample at B = -2.0, -1.0, 0 (for 3L, two different spectra for increasing and decreasing magnetic fields), 1.0, and 2.0 T, along with the RMCD plots in the insets. For both samples, the split peak at around 126 cm⁻¹ is suppressed at the fully polarized FM state, and the intensity ratio between the split and original peaks changes with interlayer spin configurations. The 3L sample shows different Raman spectra at B = 0 T for the increasing and decreasing magnetic fields, originating from its FM ground states. Moreover, no hysteresis is observed for the 4L sample.

According to the previous group theory analysis, when the multilayer CrI_3 is tuned to the FM state, the polarization selection rule of the A_2 Raman mode is the same as that of the



Figure 3. Probing the magnetic order in trilayer (3L) and four-layer (4L) CrI_3 by Raman spectroscopy. (a, b) Raman spectra in the XY channel for 3L CrI_3 (a) and 4L CrI_3 (b) at different magnetic fields, where the magnetic order can be deduced from the RMCD plot (insets of panels a and b). The split peak at around 126 cm⁻¹ is suppressed at the fully polarized FM state, and the intensity ratio between the split and original A_2 peaks changes with the interlayer magnetic order.

monolayer, and the magnetic order induces the Raman scattering signal in the XY channel. To investigate the dimensional effect of this behavior, we plot the Raman spectra of fully polarized CrI_3 samples with different layers in both XX and XY channels in Figure 4. The Raman intensity ratio of this



Figure 4. Layer dependence of the polarized Raman spectra in the XX (red) and XY channel (blue) for 1-5 L CrI₃ at the spin-down FM state. The inset shows the Raman intensity ratio of the A₂ peak between the XY and XX channels as a function of the layer number. The intensity ratio decreases monotonically with the number of layers.

 A_2 mode between the XY and XX channel is extracted as a function of the number of layers in the inset. Assuming that the magnetic ordering only contributes to the Raman scattering signal in the XY channel, this intensity ratio decreases with the increasing layer number, which may indicate that this effect is related to the thermal fluctuation.

In summary, we demonstrate that the Raman spectrum depends strongly on the magnetic order in thin layer CrI_3 . The polarization properties of the Raman peak associated with the layer breathing mode cannot be explained by the lattice symmetry, and the magnetic-order-induced symmetry changes have to be considered. The sensitivity of the Raman spectrum to the magnetic order implies strong spin–lattice coupling in the CrI_3 thin layer, which results in anomalous polarization properties other than the renormalization of the phonon energy. In addition, this polarization anomaly is getting stronger with the thinner CrI_3 sample, which may indicate that the spin–lattice coupling is stronger in 2D magnets. A similar effect could be observed in other 2D magnetic materials.

METHODS

Sample Fabrication. Bulk CrI_3 crystals were grown by the chemical vapor transport method by using the recipe described in ref 48. Thin layer CrI_3 samples were mechanically exfoliated on Si substrates with a 285 nm thick SiO_2 layer. The flakes were then encapsulated by hBN flakes using a polymer-assisted transfer technique.¹¹ All of the above-mentioned fabrication processes were carried out inside a glovebox with an Ar atmosphere to avoid sample degradation by moisture and oxygen. The numbers of layers were initially estimated by optical contrast and later confirmed by both the atomic force microscopy (AFM) measurements and RMCD measurements.

Reflective Magnetic Circular Dichroism (RMCD). RMCD was performed in an autoDRY 2100 cryostat with a base temperature of 1.7 K. A HeNe laser at 633 nm was coupled to the cryostat by using free-space optics. The laser beam was first tuned by a chopper with a frequency of 800 Hz and then passed through a photoelastic modulator (PEM), which operated at 50.2 kHz with a maximum retardance of λ / 4. The modulated laser beam was focused onto the sample by a low-temperature objective with a power less than 5 μ W, and the reflected light was collected by the same objective and detected by a photodiode. The RMCD signal was given by the ratio of ac component at 50.2 kHz and 800 Hz (both measured by lock-in amplifiers).

Polarized Raman Spectroscopy. Polarized Raman spectroscopy was performed using a home-built microscope system in the backscattering geometry. A HeNe laser at 633 nm was used as the excitation laser, and the power was kept below 80 μW to avoid potential sample damage. The laser beam was focused onto the CrI₃ samples along the out-of-plane direction by a $40 \times$ low-temperature objective. The low temperature and magnetic field were provided by an AttoCube closed-cycle cryostat (autoDRY 2100). The scattering light was collected by the same objective and detected by a spectrometer with an 1800 groove/mm grating and a TE-cooled CCD. The excitation light passed through a linear polarizer, and a second polarizer was used for the scattered light to select the component either parallel (XX channel) or perpendicular (XY channel) with respect to the incident light polarization. For the measurement under a magnetic field, the polarizer on the scattered light beam was adjusted to compensate for the Faraday rotation angle caused by the low-temperature objective, and we polarized our zero-field cooled samples before taking the valid data to avoid the domain effect.

Please note that, during the finalizing stage of our manuscript, we are aware that two related works about the magneto-Raman of CrI_3 were reported by other researchers.^{49,50}

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.9b04634.

Temperature dependence of Raman spectrum of monolayer CrI_{3} , Raman spectrum of monolayer CrI_{3} under a high magnetic field, the polarization of the A_{2} mode in monolayer CrI_{3} , the polarized Raman spectra for bilayer CrI_{3} at a decreasing magnetic field, extended group theory analysis for bilayer CrI_{3} , and density functional theory calculation of Davydov splitting for bilayer CrI_{3} (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: huangmy@sustech.edu.cn. *E-mail: zhaoy@sustech.edu.cn.

ORCID ©

Xinwei Wang: 0000-0002-1191-8162 Yue Zhao: 0000-0002-9174-0519 Mingyuan Huang: 0000-0002-3901-6451

Author Contributions

^{II}Y.Z. and X.W. contributed equally. M.H. and Y.Z. conceived and initiated this project. L.W. and J.M. synthesized and characterized the bulk CrI₃ single crystals. T.T. and K.W. provided hBN crystals. S.Z., Q.L., and M.H. performed the group theory analysis. M.W. and L.H. conducted the DFT calculation. X.W., B.L., J.C., and C.Z. fabricated and characterized the few-layer samples. Y.Z. and M.J. performed the Raman and RMCD measurements. M.H., Y.Z., H.Y., Y.C., and X.W. analyzed the data. M.H. and Y.Z. wrote the paper, and all authors participated in the discussions of the results.

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Huang, B.; Clark, G.; Navarro-Moratalla, E.; Klein, D. R.; Cheng, R.; Seyler, K. L.; Zhong, D.; Schmidgall, E.; McGuire, M. A.; Cobden, D. H.; et al. Layer-Dependent Ferromagnetism in a van Der Waals Crystal down to the Monolayer Limit. *Nature* **2017**, *546* (7657), 270–273.

(2) Gong, C.; Li, L.; Li, Z.; Ji, H.; Stern, A.; Xia, Y.; Cao, T.; Bao, W.; Wang, C.; Wang, Y.; et al. Discovery of Intrinsic Ferromagnetism in Two-Dimensional van Der Waals Crystals. *Nature* **2017**, *546* (7657), 265–269.

(3) Gong, C.; Zhang, X. Two-Dimensional Magnetic Crystals and Emergent Heterostructure Devices. *Science* **2019**, 363 (6428), No. eaav4450.

(4) Burch, K. S.; Mandrus, D.; Park, J.-G. Magnetism in Two-Dimensional van Der Waals Materials. *Nature* **2018**, *563* (7729), 47.

(5) Gibertini, M.; Koperski, M.; Morpurgo, A. F.; Novoselov, K. S. Magnetic 2D Materials and Heterostructures. *Nat. Nanotechnol.* **2019**, *14* (5), 408–419.

(6) Deng, Y.; Yu, Y.; Song, Y.; Zhang, J.; Wang, N. Z.; Sun, Z.; Yi, Y.; Wu, Y. Z.; Wu, S.; Zhu, J.; et al. Gate-Tunable Room-Temperature Ferromagnetism in Two-Dimensional Fe3GeTe2. *Nature* **2018**, *563* (7729), 94.

(7) Fei, Z.; Huang, B.; Malinowski, P.; Wang, W.; Song, T.; Sanchez, J.; Yao, W.; Xiao, D.; Zhu, X.; May, A. F.; et al. Two-Dimensional Itinerant Ferromagnetism in Atomically Thin Fe3GeTe2. *Nat. Mater.* **2018**, *17* (9), 778–782.

(8) Bonilla, M.; Kolekar, S.; Ma, Y.; Diaz, H. C.; Kalappattil, V.; Das, R.; Eggers, T.; Gutierrez, H. R.; Phan, M.-H.; Batzill, M. Strong Room-Temperature Ferromagnetism in VSe2Monolayers on van Der Waals Substrates. *Nat. Nanotechnol.* **2018**, *13* (4), 289.

(9) Wang, X.; Du, K.; Fredrik Liu, Y. Y.; Hu, P.; Zhang, J.; Zhang, Q.; Owen, M. H. S.; Lu, X.; Gan, C. K.; Sengupta, P.; Kloc, C.; Xiong, Q.; et al. Raman Spectroscopy of Atomically Thin Two-Dimensional Magnetic Iron Phosphorus Trisulfide (FePS3) Crystals. 2D Mater. **2016**, 3 (3), 031009.

(10) Huang, B.; Clark, G.; Klein, D. R.; MacNeill, D.; Navarro-Moratalla, E.; Seyler, K. L.; Wilson, N.; McGuire, M. A.; Cobden, D. H.; Xiao, D.; et al. Electrical Control of 2D Magnetism in Bilayer CrI3. *Nat. Nanotechnol.* **2018**, *13* (7), 544–548.

(11) Jiang, S.; Shan, J.; Mak, K. F. Electric-Field Switching of Two-Dimensional van Der Waals Magnets. *Nat. Mater.* **2018**, *17* (5), 406–410.

(12) Jiang, S.; Li, L.; Wang, Z.; Mak, K. F.; Shan, J. Controlling Magnetism in 2D CrI3 by Electrostatic Doping. *Nat. Nanotechnol.* **2018**, *13* (7), 549–553.

(13) Song, T.; Fei, Z.; Yankowitz, M.; Lin, Z.; Jiang, Q.; Hwangbo, K.; Zhang, Q.; Sun, B.; Taniguchi, T.; Watanabe, K.; et al. Switching 2D Magnetic States via Pressure Tuning of Layer Stacking. *Nat. Mater.* **2019**, *18* (12), 1298–1302.

(14) Li, T.; Jiang, S.; Sivadas, N.; Wang, Z.; Xu, Y.; Weber, D.; Goldberger, J. E.; Watanabe, K.; Taniguchi, T.; Fennie, C. J.; et al. Pressure-Controlled Interlayer Magnetism in Atomically Thin CrI3. *Nat. Mater.* **2019**, *18* (12), 1303–1308.

(15) Seyler, K. L.; Zhong, D.; Klein, D. R.; Gao, S.; Zhang, X.; Huang, B.; Navarro-Moratalla, E.; Yang, L.; Cobden, D. H.; McGuire, M. A.; et al. Ligand-Field Helical Luminescence in a 2D Ferromagnetic Insulator. *Nat. Phys.* **2018**, *14* (3), 277.

(16) Song, T.; Cai, X.; Tu, M. W.-Y.; Zhang, X.; Huang, B.; Wilson, N. P.; Seyler, K. L.; Zhu, L.; Taniguchi, T.; Watanabe, K.; et al. Giant Tunneling Magnetoresistance in Spin-Filter van Der Waals Heterostructures. *Science* **2018**, *360* (6394), 1214–1218.

(17) Klein, D. R.; MacNeill, D.; Lado, J. L.; Soriano, D.; Navarro-Moratalla, E.; Watanabe, K.; Taniguchi, T.; Manni, S.; Canfield, P.; Fernández-Rossier, J.; et al. Probing Magnetism in 2D van Der Waals Crystalline Insulators via Electron Tunneling. *Science* **2018**, *360* (6394), 1218–1222.

(18) Song, T.; Tu, M. W.-Y.; Carnahan, C.; Cai, X.; Taniguchi, T.; Watanabe, K.; McGuire, M. A.; Cobden, D. H.; Xiao, D.; Yao, W.; et al. Voltage Control of a van Der Waals Spin-Filter Magnetic Tunnel Junction. *Nano Lett.* **2019**, *19* (2), 915–920.

(19) Kim, H. H.; Yang, B.; Li, S.; Jiang, S.; Jin, C.; Tao, Z.; Nichols, G.; Sfigakis, F.; Zhong, S.; Li, C.; et al. Evolution of Interlayer and Intralayer Magnetism in Three Atomically Thin Chromium Trihalides. *Proc. Natl. Acad. Sci. U. S. A.* **2019**, *116* (23), 11131–11136.

(20) Wang, Z.; Gutiérrez-Lezama, I.; Ubrig, N.; Kroner, M.; Gibertini, M.; Taniguchi, T.; Watanabe, K.; Imamoğlu, A.; Giannini, E.; Morpurgo, A. F. Very Large Tunneling Magnetoresistance in Layered Magnetic Semiconductor CrI 3. *Nat. Commun.* **2018**, *9* (1), 1–8.

(21) Jiang, S.; Li, L.; Wang, Z.; Shan, J.; Mak, K. F. Spin Tunnel Field-Effect Transistors Based on Two-Dimensional van Der Waals Heterostructures. *Nat. Electron.* **2019**, *2* (4), 159–163.

(22) Sun, Z.; Yi, Y.; Song, T.; Clark, G.; Huang, B.; Shan, Y.; Wu, S.; Huang, D.; Gao, C.; Chen, Z.; et al. Giant Nonreciprocal Second-Harmonic Generation from Antiferromagnetic Bilayer CrI3. *Nature* **2019**, 572 (7770), 497–501.

(23) Sandilands, L. J.; Tian, Y.; Plumb, K. W.; Kim, Y.-J.; Burch, K. S. Scattering Continuum and Possible Fractionalized Excitations in α -RuCl3. *Phys. Rev. Lett.* **2015**, *114* (14), 147201.

(24) Li, G.; Chen, X.; Gan, Y.; Li, F.; Yan, M.; Ye, F.; Pei, S.; Zhang, Y.; Wang, L.; Su, H.; et al. Raman Spectroscopy Evidence for Dimerization and Mott Collapse in α -RuCl3 under Pressures. *Phys. Rev. Mater.* **2019**, *3* (2), 023601.

(25) Blumberg, G.; Abbamonte, P.; Klein, M. V.; Lee, W. C.; Ginsberg, D. M.; Miller, L. L.; Zibold, A. Resonant Two-Magnon Raman Scattering in Cuprate Antiferromagnetic Insulators. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *53* (18), R11930–R11933.

(26) Lockwood, D. J.; Cottam, M. G.; So, V. C. Y.; Katiyar, R. S. Raman Scattering from One-Magnon Excitations in FeF2. J. Phys. C: Solid State Phys. 1984, 17 (33), 6009–6026.

(27) Nasu, J.; Knolle, J.; Kovrizhin, D. L.; Motome, Y.; Moessner, R. Fermionic Response from Fractionalization in an Insulating Two-Dimensional Magnet. *Nat. Phys.* **2016**, *12* (10), 912–915.

(28) Merlin, R.; Zeyher, R.; Güntherodt, G. Spin-Disorder-Induced Raman Scattering in Europium Chalcogenides. *Phys. Rev. Lett.* **1977**, 39 (19), 1215–1218.

(29) Lockwood, D. J.; Cottam, M. G. The Spin-phonon Interaction in FeF2 and MnF2 Studied by Raman Spectroscopy. *J. Appl. Phys.* **1988**, 64 (10), 5876–5878.

(30) Tian, Y.; Gray, M. J.; Ji, H.; Cava, R. J.; Burch, K. S. Magneto-Elastic Coupling in a Potential Ferromagnetic 2D Atomic Crystal. 2D *Mater.* **2016**, 3 (2), 025035.

(31) Güntherodt, G.; Bauhofer, W.; Benedek, G. Zone-Boundary-Phonon Raman Scattering in VI2 Due to Modulation of Exchange Interaction. *Phys. Rev. Lett.* **1979**, *43* (19), 1427–1430.

(32) Lee, J.-U.; Lee, S.; Ryoo, J. H.; Kang, S.; Kim, T. Y.; Kim, P.; Park, C.-H.; Park, J.-G.; Cheong, H. Ising-Type Magnetic Ordering in Atomically Thin FePS3. *Nano Lett.* **2016**, *16* (12), 7433–7438.

(33) Kim, K.; Lim, S. Y.; Lee, J.-U.; Lee, S.; Kim, T. Y.; Park, K.; Jeon, G. S.; Park, C.-H.; Park, J.-G.; Cheong, H. Suppression of Magnetic Ordering in XXZ-Type Antiferromagnetic Monolayer NiPS3. *Nat. Commun.* **2019**, *10* (1), 1–9.

(34) Sun, Y.-J.; Tan, Q.-H.; Liu, X.-L.; Gao, Y.-F.; Zhang, J. Probing the Magnetic Ordering of Antiferromagnetic MnPS3 by Raman Spectroscopy. J. Phys. Chem. Lett. **2019**, *10* (11), 3087–3093.

(35) Kim, K.; Lim, S. Y.; Kim, J.; Lee, J.-U.; Lee, S.; Kim, P.; Park, K.; Son, S.; Park, C.-H.; Park, J.-G.; et al. Antiferromagnetic Ordering in van Der Waals 2D Magnetic Material MnPS3 Probed by Raman Spectroscopy. 2D Mater. **2019**, *6* (4), 041001.

(36) Sandilands, L. J.; Shen, J. X.; Chugunov, G. M.; Zhao, S. Y. F.; Ono, S.; Ando, Y.; Burch, K. S. Stability of Exfoliated Bi2Sr2DyxCa1– xCu2O8+ δ Studied by Raman Microscopy. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2010**, *82* (6), 064503.

(37) Jin, W.; Kim, H. H.; Ye, Z.; Li, S.; Rezaie, P.; Diaz, F.; Siddiq, S.; Wauer, E.; Yang, B.; Li, C.; et al. Raman Fingerprint of Two Terahertz Spin Wave Branches in a Two-Dimensional Honeycomb Ising Ferromagnet. *Nat. Commun.* **2018**, *9* (1), 5122.

(38) Guo, K.; Deng, B.; Liu, Z.; Gao, C.; Shi, Z.; Bi, L.; Zhang, L.; Lu, H.; Zhou, P.; Zhang, L.; et al. Layer Dependence of Stacking Order in Nonencapsulated Few-Layer CrI3. *Sci. China Mater.* **2019**.

(39) Larson, D. T.; Kaxiras, E. Raman Spectrum of CrI3: An Ab Initio Study. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2018**, *98* (8), 085406.

(40) Webster, L.; Liang, L.; Yan, J.-A. Distinct Spin-Lattice and Spin-Phonon Interactions in Monolayer Magnetic CrI3. *Phys. Chem. Chem. Phys.* **2018**, 20 (36), 23546-23555.

(41) Ubrig, N.; Wang, Z.; Teyssier, J.; Taniguchi, T.; Watanabe, K.; Giannini, E.; Morpurgo, A.; Gibertini, M. Low-Temperature Monoclinic Layer Stacking in Atomically Thin CrI₃ Crystals. 2D *Mater.* **2020**, *7*, 015007.

(42) Cracknell, A. P. Scattering Matrices for the Raman Effect in Magnetic Crystals. J. Phys. C: Solid State Phys. 1969, 2 (3), 500-511.

(43) Anastassakis, E.; Burstein, E. Morphic Effects. V. Time Reversal Symmetry and the Mode Properties of Long Wavelength Optical Phonons. J. Phys. C: Solid State Phys. **1972**, 5 (17), 2468–2481.

(44) Jiang, P.; Wang, C.; Chen, D.; Zhong, Z.; Yuan, Z.; Lu, Z.-Y.; Ji, W. Stacking Tunable Interlayer Magnetism in Bilayer CrI3. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2019**, 99 (14), 144401.

(45) Sivadas, N.; Okamoto, S.; Xu, X.; Fennie, Craig. J.; Xiao, D. Stacking-Dependent Magnetism in Bilayer CrI3. *Nano Lett.* **2018**, *18* (12), 7658–7664.

(46) Luo, X.; Zhao, Y.; Zhang, J.; Xiong, Q.; Quek, S. Y. Anomalous Frequency Trends in MoS2 Thin Films Attributed to Surface Effects. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2013**, 88 (7), 075320.

(47) Song, Q. J.; Tan, Q. H.; Zhang, X.; Wu, J. B.; Sheng, B. W.; Wan, Y.; Wang, X. Q.; Dai, L.; Tan, P. H. Physical Origin of Davydov Splitting and Resonant Raman Spectroscopy of Davydov Components in Multilayer MoTe2. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2016**, 93 (11), 115409.

(48) McGuire, M. A.; Dixit, H.; Cooper, V. R.; Sales, B. C. Coupling of Crystal Structure and Magnetism in the Layered, Ferromagnetic Insulator CrI3. *Chem. Mater.* **2015**, *27* (2), 612–620.

(49) Huang, B.; Cenker, J.; Zhang, X.; Ray, E. L.; Song, T.; Taniguchi, T.; Watanabe, K.; McGuire, M. A.; Xiao, D.; Xu, X. Tuning Inelastic Light Scattering via Symmetry Control in 2D Magnet CrI₃; *ArXiv191001804 Cond-Mat*, 2019

(50) McCreary, A.; Mai, T. T.; Utermohlen, F.; Simpson, J. R.; Garrity, K. F.; Feng, X.; Shcherbakov, D.; Zhu, Y.; Hu, J.; Weber, D. Distinct Magneto-Raman Signatures of Spin-Flip Phase Transitions in CrI3; *ArXiv191001237 Cond-Mat*, 2019