Layer dependence of stacking order in nonencapsulated few-layer CrI₃

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ABSTRACT Long-range magnetic orders in atomically thin ferromagnetic CrI₃ trigger new fascinating physics and application perspectives. The physical properties of two-dimensional (2D) ferromagnetism CrI₃ are significantly influenced by interlayer spacing and stacking order, which are sensitive to the hydrostatic pressure and external environments. However, there remains debate on the stacking order at low temperature. Here, we study the interlayer coupling and stacking order of non-encapsulated 2–5 layer and bulk CrI₃ at 10 K by Raman spectroscopy; demonstrate a rhombohedral stacking in both antiferromagnetic and ferromagnetic CrI₃. The opposite helicity dependence of A₈ and E₈ modes arising from phonon symmetry further validates the rhombohedral stacking. An anomalous temperature-dependent behavior is observed due to spin-phonon coupling below 60 K. Our study provides insights into the interlayer coupling and stacking orders of 2D ferromagnetic materials.

Keywords: ferromagnetic 2D materials, Ising ferromagnet, spintronics, magneto-optical

INTRODUCTION

Since the discovery of two ferromagnetic atomically thin CrI₃ and Cr₂Ge₂Te₆ in 2017, intrinsic ferromagnetism in two-dimensional (2D) van der Waals (vdW) materials, maintaining long-range magnetic orders at the atomic monolayer limit, has received increasing attention [1–7]. 2D vdW ferromagnetic materials as spin-filters have been integrated into vdW heterostructures, demonstrating giant tunneling magnetoresistance towards the next-generation information transfer and data storage technologies [8–10]. Among 2D ferromagnetic materials, CrI₃ is of particular interest. Bulk CrI₃ is ferromagnetic below the Curie temperature (Tₘ), but few-layer CrI₃ displays striking layer-dependent magnetism. Each individual layer is ferromagnetic; however, adjacent layers are antiferromagnetically coupled together and could become a layered antiferromagnet when thinned down to a few atomic layers [1]. The interlayer magnetic state can be switched between ferromagnetic and antiferromagnetic by electric gating or electrostatic doping [11–14] and pressure [15,16].

In a vdW material and heterostructures, a tiny change of lattice constant and interlayer coupling between adjacent layers can drastically influence their physical properties. Bulk CrI₃ adopts the monoclinic stacking at room temperature, while transfers to rhombohedral stacking at ~210 K. Bulk and encapsulated few-layer CrI₃ with rhombohedral stacking have been reported to be ferromagnetic below ~61 K [17,18]. However, recent experiments demonstrate that the BN-encapsulated bi- and few-layer CrI₃ and CrCl₃ belong to monoclinic structure (point group C₅h (2/m)) rather than rhombohedral structure at low temperature [19,20], and some theoretical proposals demonstrate that the antiferromagnetic coupling is associated with monoclinic layer stacking [21]. Thus, there is still a debate on the stacking order of CrI₃ at low temperature.

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A complete understanding of the low-temperature lattice structure and stacking order is crucial for 2D vdW ferromagnetic materials. Raman spectroscopy is a powerful tool to study the crystal structures, lattice vibration and shift and interlayer coupling [22–28]. In this study, we investigate the layer, polarization and helicity dependencies of Raman features of non-encapsulated 2–5 layer and bulk CrI\(_3\) at 10 K, demonstrating that few-layer and bulk CrI\(_3\) are rhombohedral phase at low temperature, including antiferromagnetic bilayer CrI\(_3\). The peak intensities of \(E^3_\text{g}\) and \(E^4_\text{g}\) mode are independent of the polarization angle, while the intensities of \(A^3_\text{g}\) and \(A^3_\text{g}\) show a two-fold polarization dependence. The polarization-resolved Raman spectra demonstrate that the \(A^3_\text{g}\) and \(E^4_\text{g}\) features show opposite helicities in which the \(A^3_\text{g}\) mode maintains the helicity of incident light; however, the \(E^4_\text{g}\) mode reverses it. Under cooling, the \(A^3_\text{g}\) and \(E^4_\text{g}\) modes shift to higher frequencies; remarkably, a spin-phonon coupling takes place and causes an anomalous behavior for the Raman feature below \(\sim 60\) K.

**EXPERIMENTAL METHODS**

**Sample preparation**

Few-layer CrI\(_3\) was mechanically exfoliated from a bulk crystal onto polydimethylsiloxane films and was then directly transferred onto SiO\(_2\)/Si substrates, which was then loaded into the cold head for optical measurements in a glove box filled with Ar.

**Optical measurements**

The Raman signals were recorded using a Witec Alpha 300R Plus confocal Raman microscope with a closed cycle optical cryostat (10 K) and a 7 T magnetic field. A power-stabilized 633 nm HeNe laser was modulated by photelastic modulator (PEM) and coupled to the Witec Raman system. The modulated beam was directed through a non-polarizing beamsplitter cube to the sample, housed in a closed-cycle cryostat at 10 K. An out-of-plane magnetic field was applied in Faraday geometry. The reflected beam passed through the same non-polarizing beamsplitter cube, non-PM multimode fiber onto a photodetector, where lock-in detection measured the reflected intensity at \(f_{\text{PEM}}\) (50 kHz). A long working distance 50× objective (NA = 0.45) was used for the Raman and reflective magnetic circular dichroism (RMCD) measurements. The Raman signals were coupled into the spectrometer with an 1800 and 600 g mm\(^{-1}\) grating. 1/4L waveplate and polarization analyzer were used for the polarization-resolved Raman measurements. The power of a 514 nm laser was measured to be approximately 2 mW, and the typical integration time was 30 s.

**RESULTS AND DISCUSSION**

**Layer dependence of magnetic order**

In 2D ferromagnetic CrI\(_3\), the Cr\(^{3+}\) ions in each layer are coordinated by six nonmagnetic I\(^-\) ions to form an octahedral geometry, which further share edges to build a honeycomb network (Fig. 1a). Bulk CrI\(_3\) crystals undergo a phase transition to a rhombohedral structure (space group \(R3\), Fig. 1b) at \(\sim 210–220\) K from a monoclinic structure (space group \(C2/m\), Fig. 1c) at room temperature [17]. Fig. 1d shows the non-encapsulated CrI\(_3\) with 2–6 layers on SiO\(_2\) (300 nm)/Si substrates, which are \(\text{in situ}\) loaded into cold head with an optical window in the glove box. The different numbers of layers can be identified through the optical contrast. Our experimental optical contrast results shown in Fig. 1e (red circles) are consistent with the reported experimental and calculated results from Xu et al. [1] (solid blue line in Fig. 1e). Bulk CrI\(_3\) crystals show distinct ferromagnetism below \(\sim 65\) K (Fig. 1f).

Fig. 2 shows the RMCD signal in atomically-thin CrI\(_3\) at 10 K. RMCD signals from a bilayer CrI\(_3\) flake approach zero when applied magnetic fields \(\pm 0.65\) T, indicating antiferromagnetic behavior (Fig. 2a). In bilayer CrI\(_3\), the two layers have opposite magnetic orientation and nearly compensate for the intrinsic magnetocrystalline anisotropy each other; therefore, the net magnetization disappear and 2-layer (2L) CrI\(_3\) is antiferromagnetic [1,2]. However, striking hysteresis is observed in 3L and 4L CrI\(_3\) flakes (Fig. 2b, c). In 3L CrI\(_3\), the magnetizations of the three layers are oriented to the same direction, while the magnetization of one layer is opposite with the other three in 4L CrI\(_3\). Thus, the net magnetization of 3L CrI\(_3\) is stronger than that of 4L CrI\(_3\).

**Layer dependence of stacking order**

The stacking order and crystal structures of non-encapsulated few-layer CrI\(_3\) can be identified by polarized Raman spectroscopy. The polarization selection rules were performed on a 2–5 layer (2L, 3L, 4L and 5L) and bulk CrI\(_3\) at 10 K using a confocal Raman microscope system with a backscattering geometry (Fig. 3a–d). The incident and scattered light are along the \(-Z\) and +Z direction, respectively. The polarization configuration of
the incident and scattered light are parallel (XX) or perpendicular (XY) to each other. The feature at ~103 and 128 cm$^{-1}$ is only present in the parallel configuration (XX), while the Raman peaks at ~107 and ~238 cm$^{-1}$ appear for both parallel and perpendicular configurations (XX and XY). The Raman scattering intensities $I$ are proportional to $|e_s \cdot R \cdot e_i|^2$, where $e_i$ and $e_s$ are the polarization unit vectors of the incident and scattered light, respectively [26,29,30]. $R$ is the Raman tensor of the Raman-active vibrational modes as predicted by group theory.

We consider both the rhombohedral (point group, $C_{3v}$) and monoclinic phase (point group, $C_{2h}$). The scattered light polarization has an angle of $\theta$ with that of the incident light, which is parallel to the $x$-axis. Thus, $e_i = (1, 0, 0)$ and $e_s = (\cos \theta, \sin \theta, 0)$, and $\theta = 0^\circ$ and $90^\circ$ under the XX and XY polarization configuration.

In rhombohedral structure, Raman active modes are the $A_g$ and $E_g$ modes and the corresponding Raman tensors are given by [31].
Taking $e_i$, $e_s$ and $R$ to $I \propto |e_s \cdot R \cdot e_s|^2$, the Raman intensities of $A_g$ and $E_g$ are

$$I_{A_g}(R) \propto a^2 \cos^2 \theta,$$

$$I_{E_g}(R) \propto c^2 \cos^2 \theta + c d \sin(2\theta) + d^2 \sin^2 \theta,$$

$$I_{E_g}(R) = \frac{1}{2} c^2 \cos^2 \theta - c d \sin(2\theta) + d^2 \sin^2 \theta. \quad (2)$$

The $E_g$ modes are degenerated. All $E_g$ modes contribute to a peak at the same frequency, so the Raman intensities of $E_g$ modes can be expressed as

$$I_{E_g}(R) = \frac{1}{2} I_{E_g}(R) + \frac{1}{2} I_{E_g}(R) = c^2 + d^2; \quad (3)$$

as a constant, and the $E_g$ modes are independent of the polarization, which can be detected in any polarization configuration. In contrast, the $A_g$ modes show striking two-fold polarization dependence, which can be observed only in parallel polarization configuration.

In monoclinic structure, the symmetry is lowered and the $E_g$ modes split to an $A_g$ and a $B_g$ mode. Thus, only the $A_g$ and $B_g$ modes are active and corresponding Raman tensors are given by

$$A_g(M) : \begin{pmatrix} a & 0 & d \\ 0 & b & 0 \\ d & 0 & c \end{pmatrix}, \quad B_g(M) : \begin{pmatrix} 0 & e & 0 \\ e & 0 & f \\ 0 & f & 0 \end{pmatrix}. \quad (4)$$

The Raman intensities of $A_g$ and $B_g$ can be expressed as

Figure 3 Layer dependence of the stacking orders in CrI$_3$ at 10 K. Raman spectra of 2L (a), 3L (b), 4L (c) and bulk CrI$_3$ (d) in the parallel (XX, blue curve) and perpendicular (XY, red curve) polarization selection channels. (e) Polarization angle dependence of Raman intensity in 2–5 layer and bulk CrI$_3$. The Raman features at ~107 and ~234 cm$^{-1}$ are degenerated $E_g$ and $E_g$ mode for the Rhombohedral phase, whose intensities are independent of the polarization angle; in contrast, the $A_g$ and $A_g$ modes at ~103 and 128 cm$^{-1}$ show distinct a two-fold polarization dependence.
Thus, the Raman intensities of $A_g$ and $B_g$ modes have opposite two-fold dependence on polarization angle in the monoclinic phase.

Therefore, group theory predicts that the Raman scattering intensity is zero for $A_g$ modes under the perpendicular ($XY$) configuration in both the rhombohedral and monoclinic stacking [30]. However, only for rhombohedral phase, there remain the polarization-independent $E_g$ modes that have nonzero Raman intensities under the parallel ($XX$) and perpendicular ($XY$) configurations. The polarization angle dependences of the features at ~103, ~107, ~128 and ~234 cm$^{-1}$ of non-encapsulated 2–5 layer and bulk CrI$_3$ are shown in Fig. 3e. The Raman intensities of the peaks near 103 and 128 cm$^{-1}$ have a two-fold pattern versus polarization angle; in contrast, the modes at ~107 and ~234 cm$^{-1}$ are independent of the polarization angle. Therefore, the non-encapsulated 2–5 layer and bulk CrI$_3$ are rhombohedral phase rather than monoclinic phase; and the peaks at ~103, ~107, ~128 and ~234 cm$^{-1}$ are assigned to the $A_g^2$, $E_g^3$, $A_g^3$ and $E_g^4$ modes, respectively [18].

To further validate the rhombohedral stacking of CrI$_3$ at low temperature, the helicity selection rules were studied at 10 K (Fig. 4). Fig. 4a shows a schematic of the experimental optical setup. The linearly polarized light passes through a 1/4$\lambda$ waveplate and transfers to circularly polarized incident $e_i = E_0 e^{i(kz-wt)}(x \pm iy)$. The incident and scattered light are along opposite direction, and thus, the scattered light $e_s = E_0 e^{i(kz-wt)}(x \mp iy)$ and $E_0 e^{i(kz-wt)}(x \pm iy)$ under the same ($\sigma^+\sigma^-$) and opposite ($\sigma^+\sigma^+$) circular polarization configuration, respectively.

The Raman intensities of the $A_g$ modes in rhombohedral phase can be expressed as

$$I_{A_g}^{\sigma^+\sigma^+}(R) \propto a^2, \quad I_{A_g}^{\sigma^-\sigma^-}(R) = 0.$$  \hspace{1cm} (6)

On the contrary, the Raman intensities of the $E_g$ modes can be expressed as

$$I_{E_g}^{\sigma^+\sigma^+}(R) \propto c^2 + d^2.$$  \hspace{1cm} (7)

As shown in Equations (6, 7), the $A_g$ modes maintain the helicity of incident light; however, the $E_g$ modes re-
verse it. In contrast, for monoclinic phase with lower symmetry, both the $A_g$ and $B_g$ modes reverse the helicity of incident light, in which the Raman intensities of $A_g$ and $B_g$ modes are given by

$$I_{A_g}^{e+e-}(M) \propto 0, \quad I_{A_g}^{e+e+}(M) \propto a^2,$$
$$I_{B_g}^{e+e+}(M) \propto 0, \quad I_{B_g}^{e+e-}(M) \propto e^2. \quad (8)$$

The polarization-resolved Raman spectra were obtained under excitation by a left-handed circularly polarized light at 2.41 eV (σ+). Remarkably, the Raman features of 2L, 3L and 4L CrI$_3$ at ~128 cm$^{-1}$ have the same helicity as the incident photon, whereas the peaks at ~234 cm$^{-1}$ switch the helicity (Fig. 4b and c). The striking opposite polarization dependence of helicities of the two Raman modes is shown in Fig. 4d. The experimental data are in agreement with the predicted rhombohedral phase results. The helicity-dependent experimental results further validate that the peaks at ~128 and ~234 cm$^{-1}$ are assigned to the $A_g^3$ and $E_g^4$ modes, respectively, consistent with above polarization-resolved Raman results. With increasing magnetic field, the helicity selection behaviors show no detectable changes (Fig. 4c), indicating that this is independent of the external magnetic field. The helicity selection behaviors are only attributed to the symmetric Raman tensors. Thus, 2–5 layer and bulk 2D ferromagnetic CrI$_3$ have rhombohedral stacking order.

**Temperature dependence of the Raman features**

To better understand the lattice dynamics, the temperature dependence of the Raman features was determined in 2L, 3L and 6L CrI$_3$ flakes. Since the transition from the monoclinic phase to the rhombohedral phase occurs at around 210–220 K in CrI$_3$ [17], we focus on investigating the Raman features below 200 K. Fig. 5a–c show the normalized Raman intensity maps of the 2L, 3L and 6L CrI$_3$ with decreasing temperatures from 200 to 10 K. The $A_g^3$ and $E_g^4$ modes simultaneously blueshift to higher frequencies with decreasing temperatures, which are attributed to the phonon anharmonic decay and lattice contraction. The shifts of the $A_g^3$ modes are ~1.4, ~0.9 and ~0.8 cm$^{-1}$ for the 2L, 3L and 6L CrI$_3$, and the $E_g^4$ modes show shifts of ~2.9, ~2.9 and ~2.4 cm$^{-1}$, respectively.

![Figure 5](image_url)

**Figure 5** Temperature dependence of the $A_g^3$ and $E_g^4$ Raman modes. (a–c) Normalized Raman intensity maps of the 2L, 3L and 6L CrI$_3$ as a function of temperature. The Raman features shift to higher frequencies with decreasing temperatures. (d–i) The linewidths of the $A_g^3$ and $E_g^4$ Raman features as a function of temperature as extracted from Fig. 3a, b. The sudden increases in the linewidths indicate the occurrence of spin-phonon coupling.
The linewidths for the $A_g^3$ and $E_g^4$ modes are extracted to investigate the spin-phonon coupling behavior. Fig. 5d–i show the linewidths of the $A_g^3$ and $E_g^4$ modes of 2L, 3L and 6L CrI$_3$ with decreasing temperature from 200 to 10 K. The temperature dependence of the linewidths is predicted by phonon-phonon coupling [32], which is given by
\[
\Gamma_i(T) = \Gamma_i,0 (1 + 2\lambda_{\text{ph-ph}} / (\exp(h\omega_0 / 2k_B T) - 1)),
\]
where the $\Gamma_i,0$ and $\omega_0$ are the zero temperature limits of the linewidth and phonon energy, obtained by extrapolating the experimental results to 0 K. The $\lambda_{\text{ph-ph}}$ represents the phonon-phonon coupling constant. Above 60 K ($\sim T_C$), the linewidths of the $A_g^3$ and $E_g^4$ modes monotonically decrease as the temperature decreases (solid lines in Fig. 5d–i). However, the linewidths deviate from the expected tendency below 60 K. In particular, the $A_g^3$ ($E_g^4$) modes of the 2L (6L) CrI$_3$ exhibit distinct deviation behavior (Fig. 5d–i), which indicates that a new scattering mechanism contributes to the anomalous phonon behavior. The $T_C$ of few-layer CrI$_3$ is $\sim$65 K (Fig. 1f) [3]. The emerging long-range magnetic order is anticipated to result in the abrupt change in the linewidth originating from spin-phonon coupling. We briefly discuss the mechanism of spin-phonon coupling. The total Hamiltonian of lattice in crystals is expressed as
\[
H = H_{\text{ion}} + H_{\text{electron}} + H_{\text{e-ph}}.
\]
In the presence of magnetic orders, an additional Hamiltonian term is given by
\[
H_{\text{spin}} = -\sum_{ij} J_{ij} \langle S_i S_j \rangle,
\]
where $J_{ij}$ is the spin-phonon coupling constant and $\langle S_i S_j \rangle$ is spin correlation function [33]. In 2D layered CrI$_3$ materials, the electron-phonon coupling was not observed, thus the Hamiltonian $H_{\text{e-ph}}$ was neglected and only phonon-phonon coupling was considered. Thus, the total potential energy of a Raman active mode consists of “lattice” and “spin” contributions; corresponding Hamiltonian of Raman modes is expressed as
\[
H = H_{\text{ion}} + H_{\text{electron}} + H_{\text{spin}} = H_{\text{lattice}} + H_{\text{spin}}.
\]
Therefore, the spin-phonon exchange interaction takes place in the ferromagnetic phase at low temperature, resulting in the deviation of linewidth.

**CONCLUSION**

In summary, we demonstrated a comprehensive understanding of stacking order of 2D ferromagnetic CrI$_{3p}$, including layer, polarization and temperature dependence of $A_g$ and $E_g$ modes. The non-encapsulated 2–5 layer and bulk CrI$_3$ are rhombohedral stacking order at 10 K, rather than monoclinic structure. The spin-phonon coupling occurs below $\sim$60 K, resulting in the deviation of linewidth. Zero-momentum spin wave features close to the $A_g$ mode in frequency have been observed [34]. This work highlights the potential to manipulate spin waves through spin-phonon and magnetoelectric coupling in new ferromagnetic 2D materials to produce novel spintronic devices [35].

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**Author contributions** Peng B developed the concept, designed the experiment and prepared the manuscript. Cheng Y synthesized the CrI₃ crystal. Deng B, Guo K, Liu Z, Gao C and Shi Z prepared the CrI₃ samples and performed the Raman measurements. Bi L, Zhou P, Zhang L, Lu H and Zhang I. contributed to mechanism of Raman scattering.

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