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Probing interlayer interaction via chiral phonons in layered honeycomb materials

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Abstract

Van der Waals (vdWs) interaction plays a significant role in controlling the physical properties of layered materials. Typically, the vdWs interlayer interaction can be calculated by density functional theory or experimentally characterized by quantum capacitance measurement. Here, we report the probing of the interlayer interaction in layered honeycomb materials via chiral phonons. Through helicity-resolved Raman measurements, we observed a reduced chirality of the Raman G mode with increasing layer numbers. We introduced new interlayer coupling terms into the traditional Raman G mode tensor to simulate the reduced phonon chirality in Raman spectra. Our Raman tensor calculation results agree with the experiments well, suggesting that the interlayer interaction can significantly influence the lattice vibration. Our demonstration provides a new perspective for characterizing the interlayer interactions in vdWs layered materials with honeycomb lattice structure.

I. Introduction

Van der Waals (vdWs) materials[1], assembling the layered materials bonded by the vdWs interlayer interaction, provided an emerging platform for investigating both the fundamental physics[2-5] and the device applications [6-9]. The interlayer interaction plays a critical role in controlling the physical properties of vdWs materials. For example, the band structure of the MoS_2 experiences a direct-to-indirect bandgap transition from monolayer MoS_2 to its multilayer counterpart due to the interlayer interaction[10,11]. Moreover, the bandgap of black phosphorus (BP) can be tuned from around 2.0 eV in monolayer BP to 0.3 eV in its bulk limit[12,13], leading to photoluminescence emission from visible to mid-infrared[14-16]. The strength of the interlayer interaction can be estimated by theoretical calculations utilizing the density functional theory[17], which has been demonstrated in many layered materials, e.g. graphene[18,19], transitional metal dichalcogenides[20,21] and hexagonal boron nitride (hBN)[22]. Experimentally the direct probe of interlayer interaction has been demonstrated through the low-frequency Raman spectroscopy[23-25]. Quantum capacitance measurements has also been applied to investigate the interlayer coupling strength, which is limited to few-layer graphene [26,27]. Therefore, it is desirable to develop other complementary approaches to experimentally characterize the strength of interlayer interactions.

In this letter, we report a new strategy for probing the interlayer interaction via chiral phonons in layered honeycomb materials. The phonons in graphene exhibit distinct chiral properties due to its unique valley phonon scattering processes and the conservation of the pseudoangular momentum (PAM). Remarkably, the Raman G mode exhibits reduced phonon chirality with increasing layer number, evidenced by the decreasing polarization degree of the Raman signal in helicity-resolved measurements. This observation suggests that the interlayer interaction plays a crucial role in the lattice vibration in layered honeycomb graphene lattice and therefore, influences the phonon chirality. We introduced interlayer coupling terms to the fundamental Raman tensor to account for the effect of coupling. The calculated evolution of the phonon chirality versus the layer number based on the new Raman tensor agrees with the experimental results. The same layer number dependent phonon chirality was further observed in the Raman G mode of honeycomb hBN, further confirming the validity of our theory.

II. Helicity-resolved Raman spectrum in Graphene Layers

Graphene flakes with different layer numbers were directly deposited onto 90 nm SiO_2/Si substrate using the mechanical exfoliation method. Fig. 1a shows the optical micrograph of graphene flakes used for Raman spectrum measurements. The layer numbers of the monolayer and few-layer graphene were first identified by the optical contrast (Fig.1b)[28,29], which shows a monochromatically linear increase with layer numbers. The unpolarized Raman spectra further confirmed the layer numbers (Fig. 1c), which agreed with previous Raman studies well[30,31]. To investigate the Raman D mode arising from the defects which was absent in the pristine graphene, we introduced defects into monolayer graphene through oxygen plasma etching (See Methods). The unpolarized Raman spectrum of the etched monolayer graphene exhibits prominent Raman D mode emission, which it is absent in pristine graphene (Fig. 1d)[32,33].

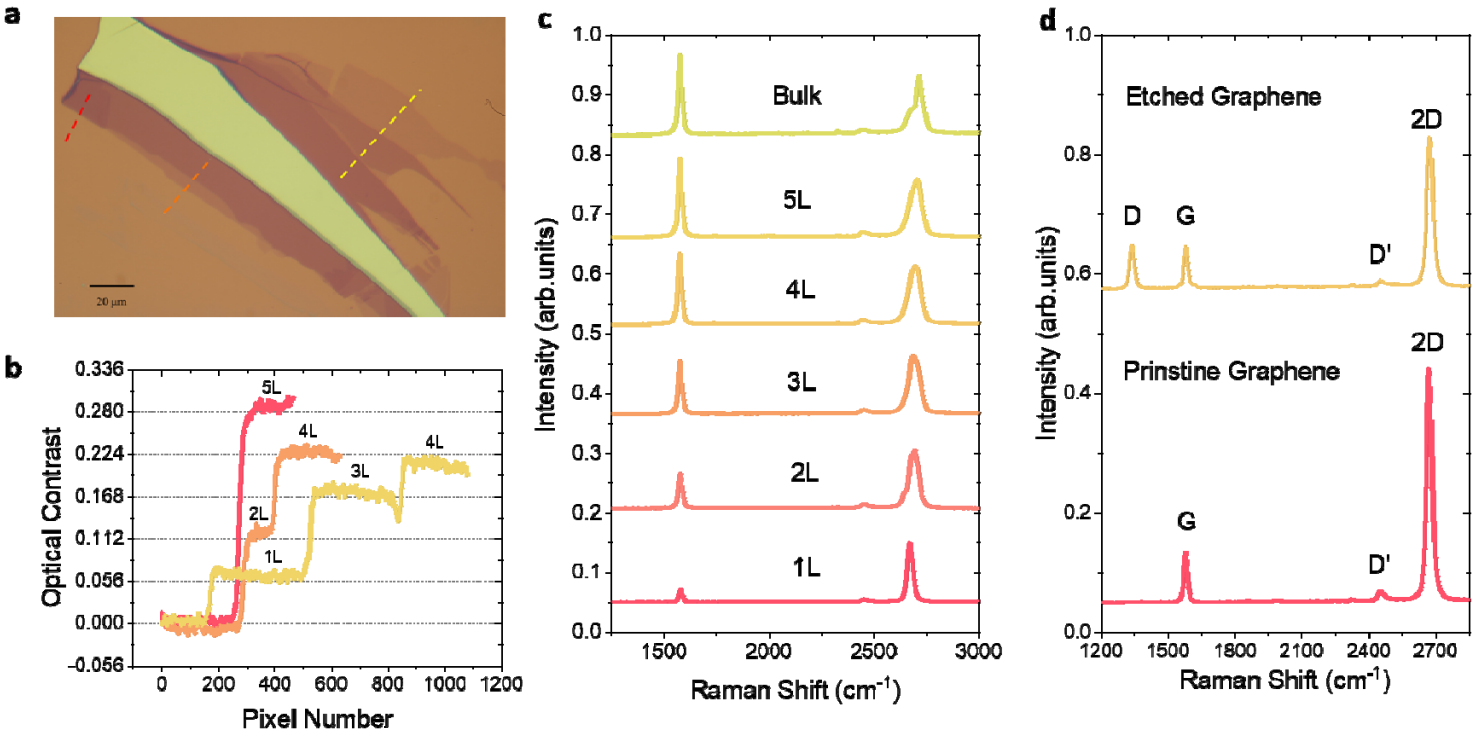

Figure 1. (a) Optical micrograph of graphene flakes. (b) Optical contrast of graphene flakes measured along the lines in (a). (c) Unpolarized Raman spectra of few-layer (1L to 5L) and thin-film (>100L) graphite. (d) Unpolarized Raman spectra of etched monolayer graphene and pristine monolayer graphene.

The helicity-resolved Raman measurement was performed in a home-made optical measurement system as illustrated in Fig. S1. The graphene flakes with different layer numbers were excited with either left (σ-) or right (σ+) circularly polarized laser and left and right circularly polarized component of Raman emissions were detected respectively (see Methods). We first investigated the chirality of the Raman modes in monolayer graphene at room temperature. Under σ+ excitation with photon energy of 2.33 eV, only σ- emissions of Raman G mode were detected while σ+ emissions completely vanished, indicating that the Raman G mode perfectly switched the helicity of the incident photons (Fig. 2a), which is consistent with previous observation[34,35]. This perfect Raman chirality was also preserved under the excitation photon energy of 1.94 eV (Fig. S2) or σ- excitation polarization (Fig. S3). In contrast, as shown in Figs. 2b and 2c, the Raman D and 2D modes in monolayer graphene showed no such chirality, evidenced by the insignificant difference between σ+ and σ- component of the Raman signal under σ+ excitation.

The distinct chiral properties between graphene Raman G, D and 2D modes can be attributed to their unique phonon scattering processes subject to the conservation of pseudoangular momentum (PAM) between graphene valleys. The Raman G mode arises from the intravalley scattering of excitation photons by a doubly degenerate phonon mode at highly symmetric Brillouin zone center (Γ point) [36], where the phonon mode acquires a PAM of ± 1 [37]. Since the intravalley scattering process requires the conservation of PAM, the variation of the PAM between the excitation photons and the emitting Raman photons should be equal to the PAM of the involved phonons. Therefore, the left (right) circularly polarized incident photons can only emits a right (left)-handed phonons, leading to the switching of the helicity of the Raman photons as illustrated in Fig. 2d [37]. On the contrary, the Raman 2D mode arises from the second order Raman process in the vicinity of the K and K′ points where intervalley scattering is involved [36]. The excited electrons in K valley are first scattered to K′ valley and then scattered back to K valley by emitting a phonon in both scattering processes (Fig. 2e). Since the phonons involved in these two processes have the opposite chirality, the emitted Raman photons will exhibit the same helicity as the incident photons, leading to the non-chirality of the Raman 2D mode. The Raman D mode involves the similar electron-phonon scattering processes to the 2D mode, while one of the scattering processes between K and K′ valleys is enabled by defects

instead of the phonons as illustrated in Fig. 2e. In equilibrium, the phonon-involved scattering processes can occur either from K to K' valley or K' to K valley. Since the phonons involved in these two processes acquire the opposite PAM, the Raman D modes exhibit no chirality.

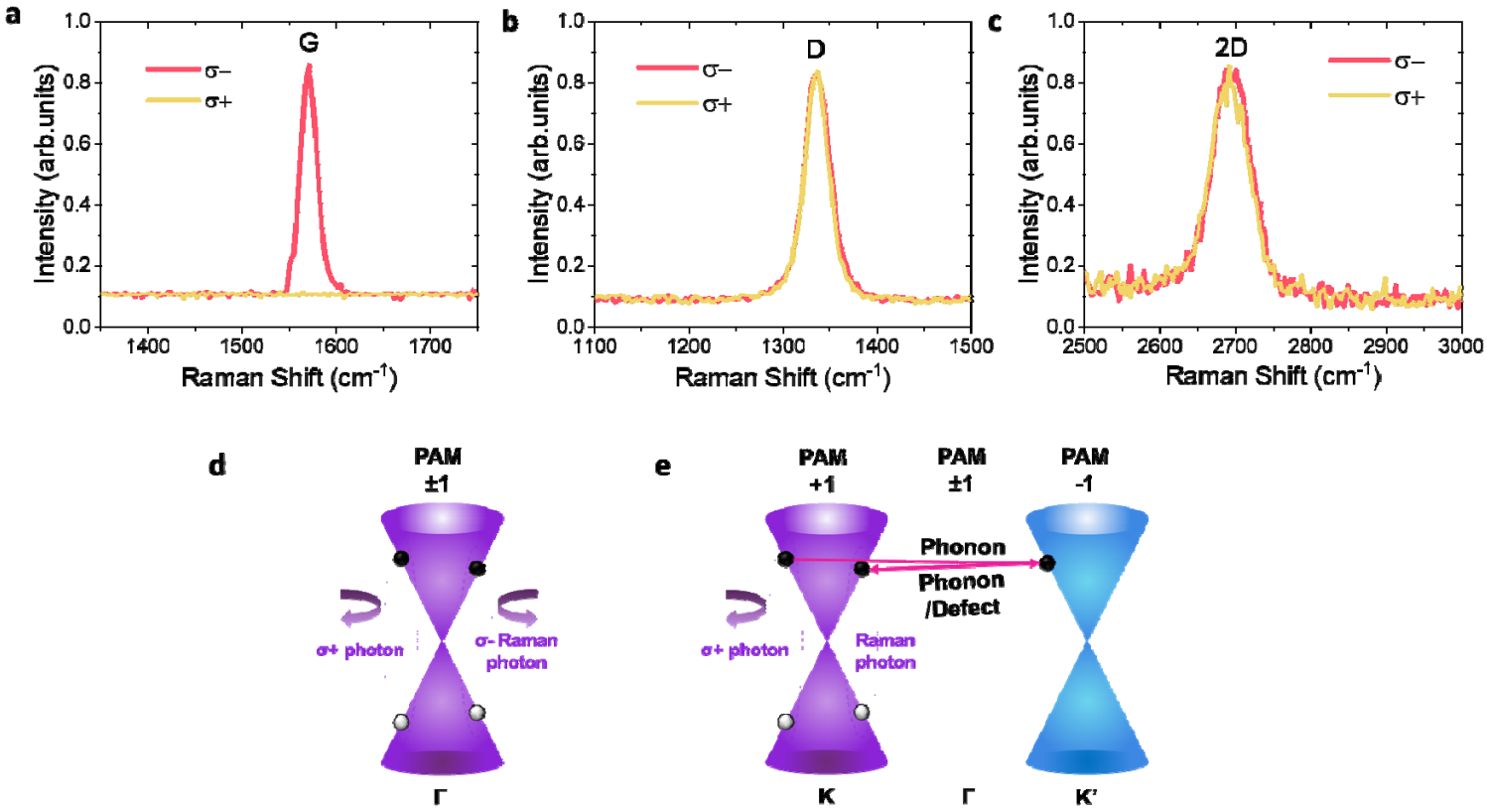

Figure 2. Helicity-resolved Raman spectra of Raman (a) G, (b) D and (c) 2D modes in monolayer graphene with excitation photon energy of 2.33 eV at room temperature. Schematic illustration of the valley phonon scattering processes and corresponding variation of PAM for Raman (d) G, (e) D and 2D modes in monolayer graphene.

We then performed helicity-resolved Raman spectrum measurements on pristine 2-5L graphene and thin-film graphite (> 100L) under the excitation photon energy of 2.33 eV. The Raman 2D mode exhibits no chirality regardless of the layer number, as illustrated in Fig. 3a. Figure 3b shows the polarization resolved Raman G mode spectra for graphene thicker than monolayer. As illustrated in Fig. 2a, in monolayer graphene, under σ+ excitation, the σ+ component of Raman G mode emission is completely absent. Here, a minor σ+ is observed starting from 2L graphene and the intensity increases as graphene becomes thicker. We extracted the Raman intensities of

σ+ (I_{min}) and σ- component (I_{max}) respectively and calculated the polarization degree (P) of the Raman G mode using $P=(I_{max}-I_{min})/(I_{max}+I_{min})$.

In Figure 3c, the polarization degree (P) is plotted against the layer number of graphene, which decreases sharply from 100% in monolayer graphene to 87.1% in bilayer graphene. It further decreases monotonously and approaches its bulk limit of 80.8%, as shown in Fig. 3c. Similar phenomenon was observed when the excitation photon energy was 1.94 eV (Fig. S4). The layer dependence of the polarization degree suggests that interlayer interaction among graphene layers significantly influences the phonon chirality.

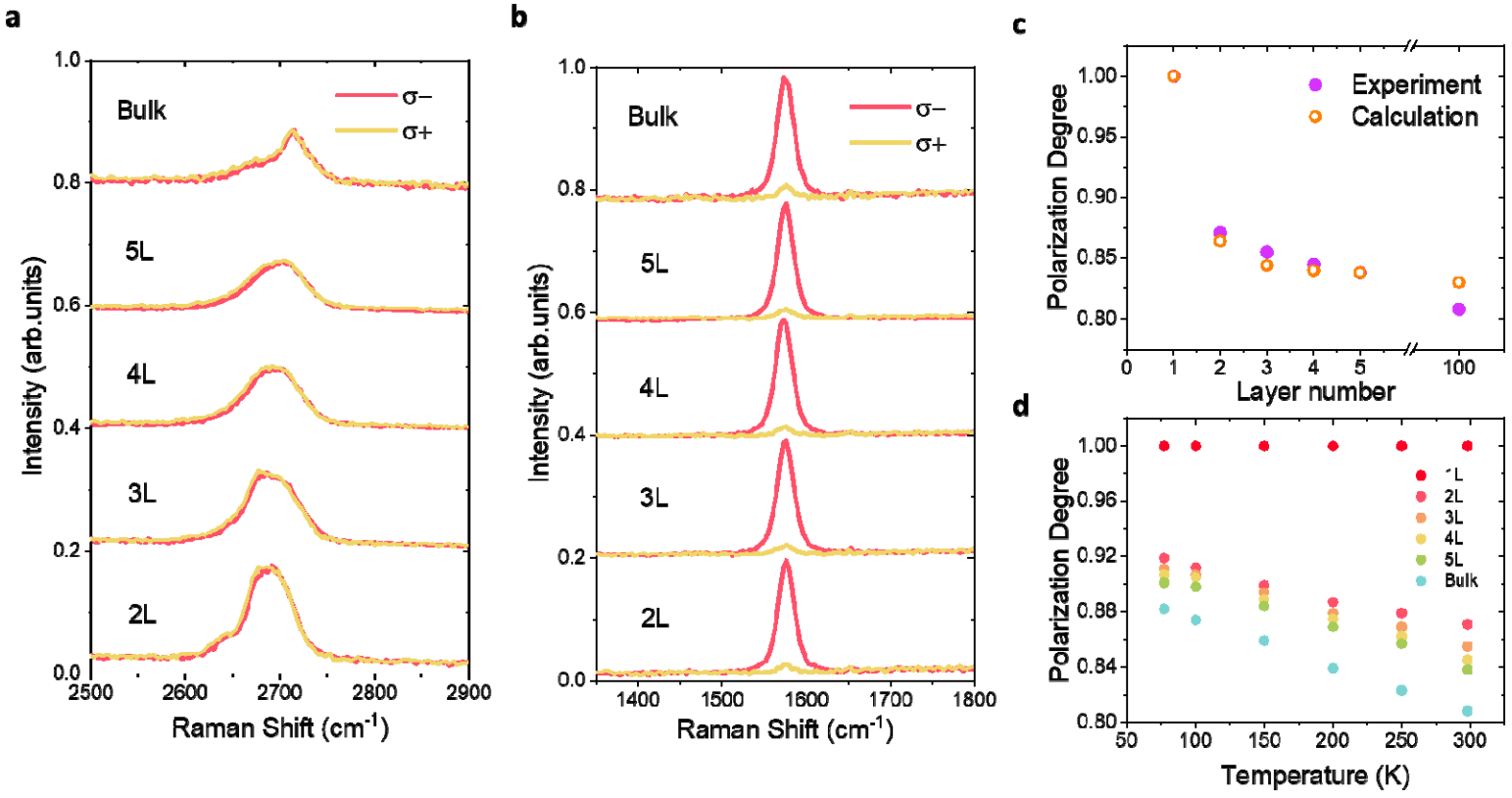

Figure 3. Helicity-resolved Raman spectra of Raman (a) 2D and (b) G modes in 2L-5L graphene and thin-film (>100L) graphite with excitation photon energy of 2.33 eV at room temperature. (c) Layer number dependence of the polarization degree for graphene Raman G mode. (d) Temperature dependence of polarization degree for Raman G mode in 2L-5L graphene and thin-film graphite.

III. Establishment of Novel Raman Tensors for Graphene Layers

To further understand the mechanism of the layer number dependent phonon chirality induced by interlayer interaction, we calculated the polarization degree in multilayer graphene based on symmetry analysis using Raman tensors. Here we first discuss the Raman G modes of monolayer graphene. At Γ point, the monolayer graphene belongs to the D_{6h} point group where the Raman G mode can be described as E_{2g} representations according to the symmetry analysis, corresponding to the Raman tensor A [38], where

$$A = \begin{vmatrix} a_{11} & a_{12} & a_{11} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = \begin{vmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \text{ or } A = \begin{vmatrix} a_{11} & a_{12} & a_{11} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} = \begin{vmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{vmatrix}$$

The left ($|\sigma_-\rangle$) and right ($|\sigma_+\rangle$) circularly polarized wave-vectors are defined as

$$|\sigma_-\rangle = \frac{1}{\sqrt{2}} (1 \quad i \quad 0)^T \text{ and}$$

$$|\sigma_+\rangle = \frac{1}{\sqrt{2}} (1 \quad -i \quad 0)^T, \text{ respectively.}$$

The normalized Raman intensity for different excitation/detection configuration can be calculated as $\left|\sigma_i^\dagger A \sigma_j\right|^2$, where both i and j can be "-" or "+". For excitation/detection configuration with the same polarization ($i = j$), the Raman signal completely vanishes as $I_{min} = \left|\sigma_i^\dagger A \sigma_j\right|^2 = 0$. In contrast, for excitation/detection configuration with the opposite polarization where $i \neq j$, the Raman intensity reaches its maximum as $I_{max} = \left|\sigma_i^\dagger A \sigma_j\right|^2 = \mathrm{d}^2$.

Furthermore, we established the Raman tensor for Raman G mode in bilayer graphene by adding an additional interlayer hopping term[39,40], which can be represented by a 6×6 matrix R.

$$R = \begin{vmatrix} A & B \\ B & A \end{vmatrix}$$

Here A matrix is the same as that in monolayer graphene and B is the matrix representation of the interlayer coupling term, which is defined as

$$B = \begin{vmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{vmatrix}$$

The matrix element t_{ij} $(i,j=1,2,3)$ is defined as the interlayer coupling coefficient between the adjacent graphene layers where $t_{ji}=t_{ij}$ due to the symmetry. The left and right circularly polarized wave-vectors are also extended to be compatible with the Raman tensor, which are defined as

$$|\sigma_-\rangle = \frac{1}{\sqrt{2}}(1 \quad i \quad 0 \quad 1 \quad i \quad 0)^T \text{ and}$$

$$|\sigma_+\rangle = \frac{1}{\sqrt{2}}(1 \quad -i \quad 0 \quad 1 \quad -i \quad 0)^T, \text{ respectively.}$$

Similarly, $\left|\sigma_i^\dagger A \sigma_j\right|$ is used to calculate the Raman intensity under the different excitation/detection polarization configurations. For excitation/detection configuration with the same polarization, the Raman intensity is

$$I_{min} = \left|\sigma_+^\dagger A \sigma_+\right|^2 = \left|\sigma_-^\dagger A \sigma_-\right|^2 = (t_{11}+t_{22})^2$$

which is non-vanishing in contrast to that in monolayer graphene. While for excitation/detection configuration with the opposite polarization, the Raman intensity is

$$I_{max} = \left|\sigma_+^\dagger A \sigma_-\right|^2 = \left|\sigma_-^\dagger A \sigma_+\right|^2 \approx 4d^2$$

Therefore, the polarization degree of Raman G mode in bilayer graphene is

$$P_2 = \frac{I_{max}-I_{min}}{I_{max}+I_{min}} = \frac{4d^2-(t_{11}+t_{22})^2}{4d^2+(t_{11}+t_{22})^2}$$

According to the Raman tensor calculation, the polarization degree in bilayer graphene will not be perfect (100%) due to the existence of the interlayer interaction coefficient. However, since the interlayer coupling coefficient t_{ij} should be significantly smaller than the fundamental Raman tensor term d, the polarization degree will not decrease significantly, evidenced by the low intensity Raman signal under excitation/detection configuration with the same polarization. The polarization degree of the Raman G mode in trilayer and multilayer graphene were calculated accordingly, where

$$P_3 = \frac{I_{max}-I_{min}}{I_{max}+I_{min}} = \frac{4d^2-(t_{11}+t_{22}+t_{44}+t_{55})^2}{4d^2+(t_{11}+t_{22}+t_{44}+t_{55})^2}$$

$$P_n = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = \frac{4d^2 - (t_{11} + t_{22} + t_{44} + t_{55} + t_{77} + t_{88} + \cdots + t_{3n-5,3n-5} + t_{3n-4,3n-4})^2}{4d^2 + (t_{11} + t_{22} + t_{44} + t_{55} + t_{77} + t_{88} + \cdots + t_{3n-5,3n-5} + t_{3n-4,3n-4})^2}$$

The detailed calculation process was provided in Supplementary Information VI. Here, t_{3n-5} and t_{3n-4} represents the interlayer coupling coefficient between the adjacent n layers, which decays significantly with the increasing n. Therefore, in multilayer graphene, the polarization degree of the Raman G mode will decrease with increasing layer numbers, which is consistent with our measurements.

To further verify the established model, we calculated the polarization degree by deducting the value of interlayer coupling coefficient t_{ii}. The value of the $(t_{11} + t_{22})^2$ was directly extracted from the helicity-resolved Raman spectrum in bilayer graphene, which exhibits a polarization degree of 87.1%. Therefore, the value of interlayer coupling coefficient in the adjacent graphene layers was determined as $(t_{11} + t_{22})^2 = 0.3d^2$. Since we assume that the interlayer interaction in graphene layers is contributed by dipole-dipole interaction which decays with the distance by $1/r^3$[41], the interlayer coupling coefficient in adjacent three layers can be estimated as

$$(\mathrm{t}_{44} + \mathrm{t}_{55})^2 = \frac{1}{8}(t_{11} + t_{22})^2 = 0.0375d^2$$

Therefore, the calculated polarization degree of the Raman G mode in trilayer graphene is 84.4%, which agrees well with our experimental result (85.5%). Similarly, we can further deduct the interlayer coupling coefficient in adjacent n layers, which gives

$$(t_{3n-5,3n-5} + t_{3n-4,3n-4})^2 = \frac{1}{(n-1)^3}(t_{11} + t_{22})^2.$$

Then when n is very large, we have

$$(t_{11} + t_{22} + t_{44} + t_{55} + t_{44} + t_{55} + \cdots + t_{3n-5,3n-5} + t_{3n-4,3n-4})^2 = 0.36d^2.$$

Therefore, the calculated polarization degree of the Raman G mode in thin-film graphite should be 83.0%, which also agrees well with the experimental results (80.8%). The evolution of the polarization degree against the layer number from Raman tensor calculation is also plotted in Fig. 3c together with the experimental results. It is clear that our model captures the impact of interlayer coupling on the phonon chirality.

IV. Temperature dependence of the phonon chirality

We further investigated the temperature dependence of the polarization degree in graphene Raman G mode. In monolayer graphene, the perfect phonon chirality was preserved at all temperatures, as illustrated in Fig. 3d. Moreover, Figure 3d also shows the degree of polarization as a function of the temperature for multilayer graphene. In general, the degree of polarization decreases as the temperature increases. The temperature dependence of the polarization degree indicates the role of interlayer phonon-phonon interaction, which suppresses the degree of phonon polarization. Reduced temperature can freeze the lattice vibration and therefore, suppress the interlayer phonon -phonon interaction in multilayer graphene and facilitates the preservation of the phonon chirality. We applied the same model to simulate the evolution of the polarization degree against the layer number at 77K (See Supplementary Information VII). The calculated polarization degree also agrees with the experimental results well (Fig. S5).

V. Helicity-resolved Raman spectrum in hBN Layers

In addition, we performed helicity-resolved Raman measurements on another 2D honeycomb material, hexagonal boron nitride (hBN). Monolayer hBN on SiO_2/Si substrate was transferred from hBN on copper grown by chemical vapor deposition (See method). We also prepared thin-film hBN (> 100L) by mechanical exfoliation from bulk crystal. Figure 4a shows the unpolarized Raman E_{2g} mode measurements. The Raman E_{2g} mode peaks at 1368.5 cm^{-1} and 1366 cm^{-1} for monolayer and bulk hBN, respectively, consistent with previous reports [42,43]. We then performed the helicity-resolved Raman measurements in both monolayer and thin-film hBN under 2.33 eV σ+ excitation at room temperature. The perfect phonon chirality was only preserved in monolayer hBN as shown by the top panel of Fig. 4b. For thin-film hBN, a clear σ+ peak was observed (lower panel of Fig. 4b). The temperature dependence of the polarization degree in hBN Raman E_{2g} modes for both monolayer and thin-film hBN is plotted in Fig. 4c. The phonon chirality remains perfect at all temperatures in monolayer hBN, while the degree of polarization decreases at elevated temperature in thin-film hBN. The layer number and temperature dependent chiral Raman modes in hBN further illustrate the role of the interlayer phonon-phonon interactions, which can affect the lattice vibration in 2D honeycomb lattice.

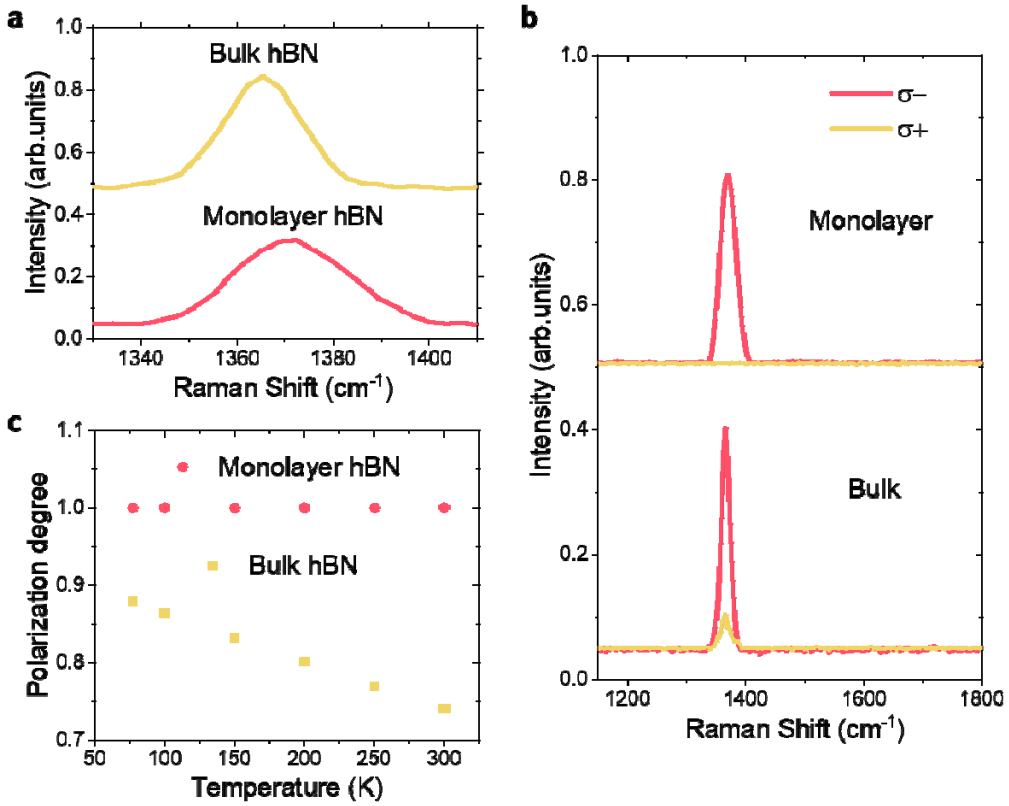

Figure 4. (a) Unpolarized Raman spectra of monolayer and bulk hBN. (b) Helicity-resolved Raman spectra of monolayer and bulk hBN with excitation photon energy of 2.33 eV at room temperature. (c) Temperature dependence of polarization degree for Raman G mode in monolayer and bulk hBN.

VI. Discussion

Previously, the circular polarization of the Raman emission has also been investigated in monolayer and few-layer transitional metal dichalcogenides (TMDs)[38]. The Raman emission due to out-of-plane relative motion of only chalcogen atoms (OC) mode has the same polarization state of the excitation photons. In contrast, the Raman emission due to in-plane relative motion of transition metal and chalcogen atoms (IMC) mode exhibits opposite circular polarization if compared with the circular polarization of the excitation photons. Remarkably, the circular polarization of Raman emission due to the OC modes remains perfect regardless of the layer number, while it becomes imperfect for Raman emission due to the IMC modes in multilayers. This observation suggests that the in-plane vibration modes are less robust to

interlayer interactions compared with the out-of-plane vibration modes in TMDs. In graphene and hBN, the Raman active G mode is only contributed by the in-plane lattice vibrations, while the out-of-plane lattice vibration modes are Raman inactive [43,44]. Although it is not feasible to investigate the impact of interlayer coupling on out-of-plane modes in graphene and hBN using Raman scattering, our observation of the imperfect and layer-dependent phonon chirality of the Raman G mode is consistent with the previously reported results on the IMC modes in TMDs [38].

VII. Conclusion

In conclusion, here we report a comprehensive investigation on the vdWs interlayer interactions in honeycomb lattice via chiral phonons. The interlayer interaction plays an important role in lattice vibrations of the honeycomb lattice and therefore, affects the phonon chirality, evidenced by the decreasing polarization degree of Raman G modes with increasing layer number and temperature. We further established a new method to construct the tensor for Raman G modes in multilayer 2D honeycomb lattice by introducing the interlayer coupling coefficients, which characterizes the strength of the interlayer interaction. The layer dependent phonon chirality extracted from Raman tensor calculation agrees with the helicity-resolved Raman measurement results well. Our observations provide a new perspective to probe the interlayer interaction in vdWs materials and heterostructures with unique honeycomb lattice symmetry.

Methods

Sample Preparation.

Monolayer and few-layer graphene flakes were mechanically exfoliated to the 90 nm SiO_2/Si substrate and then were identified under an optical microscope. The Raman D peak in graphene was introduced through gentle oxygen plasma (plasma power: 10W, oxygen flow: 10 sccm, duration: 1s). Large area CVD monolayer hBN on copper (2x2 inches) was purchased from HQ graphene. Firstly, a 400 nm-thick PMMA layer was spin-coated onto the hBN/copper surface. Secondly, the PMMA/hBN/copper was floated on the $FeCl_3$ solvent with copper layer downside for 30 mins to etch off the copper substrate. Then the PMMA/hBN layer was washed with DI

water and was picked up by the 90 nm SiO_2/Si substrate. Finally, the PMMA layer was washed out by acetone.

Optical Measurements.

The helicity-resolved Raman measurements were performed in a micro-optical measurement system as shown in Fig. S1. A combination of a linear polarizer and a broadband quarter-wave plate was used to generate the left/right circularly polarized excitation, which was focused onto the sample by a 40× microscope objective. The backscattered Raman signal was first depolarized by the same quarter-wave plate, then the left/right circularly polarized component of the signal was analyzed by a combination of broadband half-wave plate and a linear polarizer. The Raman signal was further collected and analyzed by an Andor Sharmock SR750 Spectrometer equipped with an iDus 420 series CCD camera. The sample was mounted in Janis ST-500 Microscopy Cryostat for both room temperature and low temperature measurements. Two continuous solid-state lasers with excitation photon energies of 1.90 eV and 2.33 eV were used as the excitation sources.

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Figure captions

Figure 1. (a) Optical micrograph of graphene flakes. (b) Optical contrast of graphene flakes measured along the lines in (a). (c) Unpolarized Raman spectra of few-layer (1L to 5L) and thin-film (>100L) graphite. (d) Unpolarized Raman spectra of etched monolayer graphene and pristine monolayer graphene.

Figure 2. Helicity-resolved Raman spectra of Raman (a) G, (b) D and (c) 2D modes in monolayer graphene with excitation photon energy of 2.33 eV at room temperature. Schematic illustration of the valley phonon scattering processes and corresponding variation of PAM for Raman (d) G, (e) D and 2D modes in monolayer graphene.

Figure 3. Helicity-resolved Raman spectra of Raman (a) 2D and (b) G modes in 2L-5L graphene and thin-film (>100L) graphite with excitation photon energy of 2.33 eV at room temperature. (c) Layer number dependence of the polarization degree for graphene Raman G mode. (d) Temperature dependence of polarization degree for Raman G mode in 2L-5L graphene and thin-film graphite.

Figure 4. (a) Unpolarized Raman spectra of monolayer and bulk hBN. (b) Helicity-resolved Raman spectra of monolayer and bulk hBN with excitation photon energy of 2.33 eV at room temperature. (c) Temperature dependence of polarization degree for Raman G mode in monolayer and bulk hBN.

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