

PAPER

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Polytypism and unexpected strong interlayer coupling in two-dimensional layered ReS_2 [†]

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Anisotropic two-dimensional (2D) van der Waals (vdW) layered materials, with both scientific interest and application potential, offer one more dimension than isotropic 2D materials to tune their physical properties. Various physical properties of 2D multi-layer materials are modulated by varying their stacking orders owing to significant interlayer vdW coupling. Multilayer rhenium disulfide (ReS_2), a representative anisotropic 2D material, was expected to be randomly stacked and lack interlayer coupling. Here, we demonstrate two stable stacking orders, namely isotropic-like (IS) and anisotropic-like (AI) N layer ($N > 1$) ReS_2 are revealed by ultralow- and high-frequency Raman spectroscopy, photoluminescence and first-principles density functional theory calculation. Two interlayer shear modes are observed in AI-NL- ReS_2 while only one shear mode appears in IS-NL- ReS_2 , suggesting anisotropic- and isotropic-like stacking orders in IS- and AI-NL- ReS_2 , respectively. This explicit difference in the observed frequencies identifies an unexpected strong interlayer coupling in IS- and AI-NL- ReS_2 . Quantitatively, the force constants of them are found to be around 55–90% of those of multilayer MoS_2 . The revealed strong interlayer coupling and polytypism in multi-layer ReS_2 may stimulate future studies on engineering physical properties of other anisotropic 2D materials by stacking orders.

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1. Introduction

Two dimensional (2D) van der Waals (vdW) layered materials have attracted great interest, due to their excellent physical properties and remarkable device prospects.^{1–4} Anisotropic 2D materials, such as black phosphorus (BP),^{5–8} SnSe ,^{9,10} rhenium disulfide (ReS_2)¹¹ and rhenium diselenide (ReSe_2),¹² have one more degree of freedom than isotropic materials, *e.g.* graphene and MoS_2 ,¹³ to deliver various physical properties. This unique feature of anisotropic 2D materials promote them to be more promising materials for future applications in electronic, optoelectronic and thermoelectric devices.^{7,10,11} So far, anisotropic 2D materials can be divided into two categories in terms of their structure. One category has strongly buckled honeycomb sheets with ‘troughs’ running along the y -axis (b direction), typical examples of which are BP and SnSe .^{5,9,14} The other one lies in disordered 1T'-structures, unlike the

commonly seen highly symmetric 1T- or 2H-structure in transition metal dichalcogenides (TMDs), *e.g.* MoS_2 , WSe_2 .¹⁵ These 1T'-structures usually have extra in-plane metal-metal bonds or charge density wave states and representative materials are ReS_2 ,¹⁶ ReSe_2 ¹² and WTe_2 .^{17,18}

Interlayer interaction, mostly driven by vdW interactions, plays an important role in varying physical properties of multi-layered materials.^{13,19–21} For example, MoS_2 undergoes a direct to indirect bandgap transition from monolayer to bilayer owing to interlayer coupling.¹³ Moreover, it is also a result of interlayer electronic hybridization that the bandgap of BP increases from ~ 0.3 eV of the bulk form to 1.5–2.0 eV of the monolayer.²² Therefore, artificially made stacking orders, rather than the regular order found in natural 2D materials, may significantly affect the properties of 2D materials.^{21,23,24} For instance, the twisted bilayer graphene (BLG) emerges as pairs of singularities in the density of states in comparison with the Bernal-stacked BLG.^{23,25,26} In light of this, we believe that understanding the interlayer coupling and layer stacking are of essential importance before stacking them to build 2D heterostructures for both device application and basic physical research.²⁷

Anisotropic multilayer ReS_2 was previously found to be randomly stacked and lacked interlayer coupling.^{11,16,28} As a consequence, bulk ReS_2 exhibits monolayer behavior due to electronic and vibrational decoupling in bulk ReS_2 .¹⁶ Here, we

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successfully identified two stable, an anisotropic-like (AI) and an isotropic-like (IS), stacking orders in multilayer ReS_2 by Raman and photoluminescence (PL) spectroscopies and density functional theory (DFT) calculations. However, these two orders show fairly different lattice vibrational and electronic properties, which is, we believe, superior to the previously found electronic and vibrational decoupling. Particularly, two low-frequency rigid-layer shear (C) modes are observed in the AI-stacked bilayer (AI-2L- ReS_2), nevertheless, the IS-stacked bilayer (IS-2L- ReS_2) exhibits an isotropic feature that only one C mode is observed. The different numbers of observed C modes in AI- and IS-2L- ReS_2 suggest significant interlayer couplings between the ReS_2 layers. Indeed, the coupling strength, as the experimental or theoretical force constant suggested, is around 55–90% of that of multilayer MoS_2 . Moreover, these two stacking orders of ReS_2 also lead to appreciable differences in their high-frequency Raman modes and PL spectra. These results, namely the significant interlayer coupling and polymorphism, in multi-layer ReS_2 open the possibility of further understanding the role of stacking in other anisotropic 2D materials.

2. Results and discussion

Fig. 1(a) shows the crystal structure of monolayer ReS_2 , whose unit cell contains four formula units consisting of two categories of rhenium (Re) atoms together with four categories of sulfur (S) atoms. Each Re in monolayer ReS_2 has six neighboring S sites, and the Re atoms are sandwiched by the S

atoms at both sides. Unlike 2H TMDs such as MoS_2 and WSe_2 , ReS_2 crystals exhibit a distorted CdCl_2 -type lattice structure,²⁹ owing to Peierls distortion.³⁰ Four adjacent Re atoms are bonded together to form a zigzag chain,³¹ oriented along the direction of lattice vector $\mathbf{a}$ (see Fig. 1(a)). Fig. 1(b) shows two 2L ReS_2 flakes, SA and SB. The atomic force microscopy (AFM) topographic images shown in Fig. 1(b) reveal the thicknesses of flakes SA and SB to be 2.0 and 2.1 nm, respectively, which are about 0.7 nm larger than the expected thickness (1.4 nm) of 2L ReS_2 . This discrepancy is most likely ascribed to the instrumental offset for absolute values. Indeed, the thickness (~ 0.7 nm) of 1L ReS_2 was measured to be 1.4 nm as demonstrated in Fig. S1.† Although the SA and SB flakes are identified as 2L ReS_2 , they exhibit nonidentical optical contrast [see Fig. 1(c)], suggesting that 2L ReS_2 can crystallize in different crystal structures, in contrast to previous reports.^{11,16,28}

The bulk and 1L ReS_2 belong to the C_i space group. The unit cell of 1L ReS_2 comprised 12 atoms with 36 normal vibrational modes. In principle, for the N-layer (NL) ReS_2 with a unit cell of 12N atoms, 36N modes are expected. The Γ phonons of 1L ReS_2 can be expressed by the irreducible representations of C_i as follows: $\Gamma = 18(A'' + A')$, where three A'' are acoustic modes, the other A'' are infrared active, all the 18 A' modes are Raman active. The Raman spectrum of 1L ReS_2 has been studied by several groups^{16,28,32} and 18 A' modes are already observed. As depicted in the Fig. S2 in the ESI,† more than 18 Raman modes are observed in the Raman spectra of flakes SA and SB in the range of 100–450 cm^{-1} , similar for each type of sample. This similarity of Raman spectra

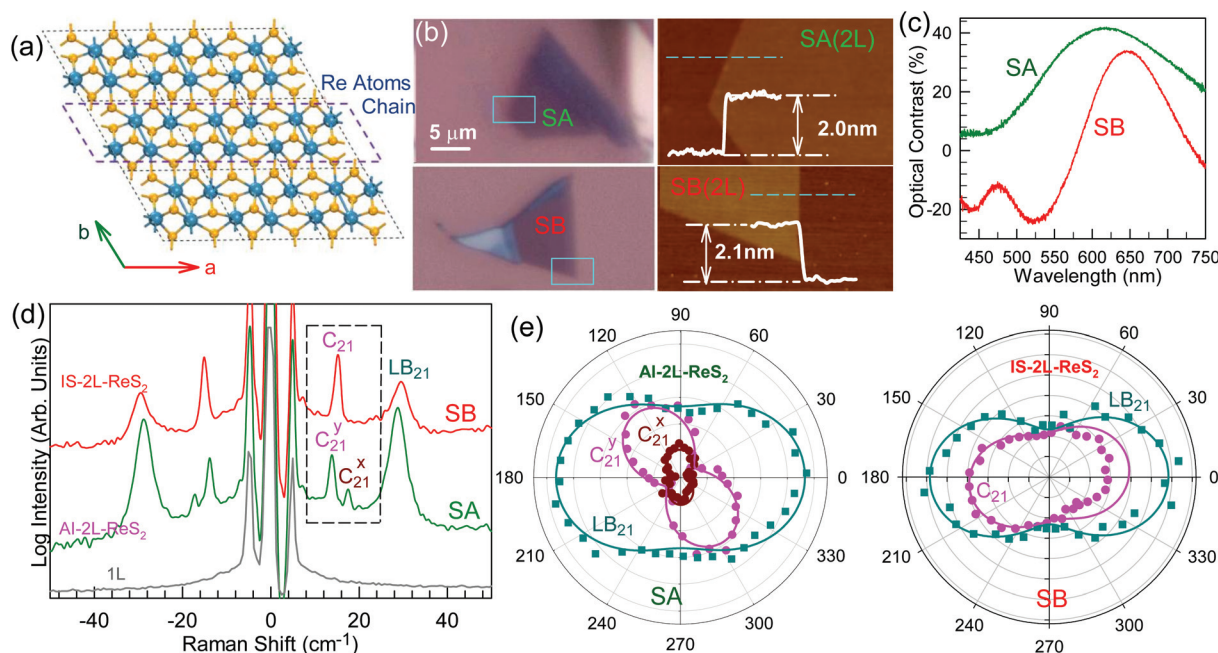


Fig. 1 (a) Crystal structure of 1L ReS_2 with 3×3 unit cells. The Re atom chain along the $\mathbf{a}$ direction is marked by the dashed frame. (b) Optical images of two ReS_2 flakes (SA and SB) on a 90 nm SiO_2/Si substrate and the corresponding AFM images within the square frames of the two flakes. The height profiles indicate that both SA and SB flakes are 2L- ReS_2 . (c) Optical contrast of the flakes SA and SB. (d) Stokes/anti-Stokes Raman spectra of the flakes SA and SB in the ULF region. (e) The intensities of the C and LB modes for the flakes SA and SB as a function of laser polarization angle. Circles and squares are experimental data and solid curves are the trends based on the symmetry analysis.

indicates that the SA and SB flakes share a nearly identical in-plane atomic structure and the difference in optical appearance, most likely, originates from interlayer coupling.

Interlayer vibration modes were usually adopted to characterize interlayer coupling^{4,12,19,33} and stacking orders^{21,23,24,26,34} of multilayer flakes of 2D materials. In particular, the shear (C) modes are very sensitive with the stacking condition.²³ For example, in the AB-stacked bilayer graphene (BLG),¹⁹ the C mode resides at 32 cm⁻¹, but it cannot be observed in the twisted bilayer graphene (tBLG),²³ due to the mismatch of periodicity between the two twisted layers. However, the twisting interface in twisted multilayer graphenes (MLG) does not substantially modify the frequency of the layer breathing (LB) modes because of the nearly unchanged interlayer distance after twisting.²⁶ On the other hand, the LB modes of the twisted 2L-MoS₂ slightly soften from that of the AB-stacked 2L-MoS₂,³⁵ due to the twisting induced increase of the interlayer distance.^{35,36} For in-plane isotropic 2D materials, such as MLG¹⁹ and multilayer MoS₂,^{33,37} the C mode is doubly degenerate. However, in an anisotropic 2D material, such as BP,^{14,38} the C modes are non-degenerated and named as C^x and C^y. For an NL 2D flake, there are $N - 1$ pairs of C modes and $N - 1$ LB modes. We denote the C and LB modes with the highest frequency, respectively, as C^x_{N1}, C^y_{N1} and LB_{N1}, and those with the second highest frequency as C^x_{N2}, C^y_{N2} and LB_{N2}.

Ultralow-frequency (ULF) Raman spectroscopy¹⁹ was used to further investigate the interlayer coupling and the stacking orders of ReS₂ flakes SA and SB, as shown in Fig. 1(d). Three peaks are located at 13.8, 17.5 and 28.7 cm⁻¹ in flake SA. However, only two peaks are observed at 15.1 and 29.3 cm⁻¹ in flake SB. There is no ULF mode in the 1L ReS₂ flake whose optical image is shown in Fig. S1,† further confirming that the flake is monolayer due to the absence of the C and LB modes.¹⁹ Because of the fact that LB vibration is usually stiffer

than the shear vibration in layered materials, we assign the mode with the highest frequency in flakes SA and SB as the LB₂₁ mode, these modes at 13.8 and 17.5 cm⁻¹ in flake SA as C^y₂₁ and C^x₂₁, respectively, and the mode at 15.1 cm⁻¹ in flake SB as C₂₁. These two C modes found in the SA flake manifest its anisotropic-like feature, similar to the BP case.^{14,38} However, only one C mode is observed in the SB flake, suggesting its isotropic-like character, like the case of multilayer MoS₂ or MLG.^{19,33} Each of these C and LB modes shows polarization dependence on the mode intensity, as depicted in Fig. 1(e), which is directly resulted from its low crystal symmetry (C_i) even in the presence of the isotropic-like C mode in the SB flake of 2L-ReS₂.

Both the optical contrast and measured frequencies of interlayer vibration modes indicate that the SA and SB flakes are 2L-ReS₂ with different structural symmetries or layer stacking orders. As shown in Fig. 1(a), the formed Re-Re bond in a unit cell is almost oriented parallel to the **b** direction, and the top S atom bonding with these two Re atoms are in the forward side of the **a** direction. This Re-S-Re triangle can be adopted to illustrate the structural symmetry of NL ReS₂, as shown in the left panels of Fig. 2(a) and (b). There may be many stacking orders for 2L-ReS₂. Since the multilayer samples are exfoliated ones, they tend to adopt the AA-stacking of the bulk crystal. The *c*-axis of the bulk crystal is tilted with respect to the *a*-*b* plane, therefore, the AA-stacked bilayer of ReS₂ looks similar to the AB-stacked bilayer of other TMDs, as illustrated in the right panels of Fig. 2(a) and (b). Given the geometry of the bottom layer, the Re-Re bond of the top layer has three possible orientations, namely with angles of 0°, 60° and 120° to that of the bottom layer. In each orientation, there are four possible relative positions of the two Re-Re bonds of both layers, totally 12 stacking configurations were considered (see Fig. S3† for details).

Among these configurations, our density functional theory calculations reveal that the AI-2L-ReS₂ is the most stable

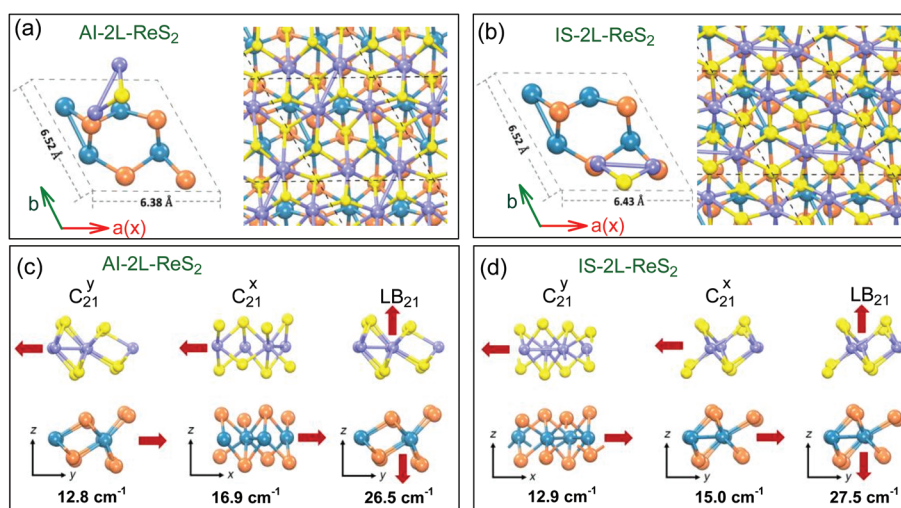


Fig. 2 (a and b) Stacking schematic diagrams and top view of crystal structure of the AI-stacked (a) and IS-stacked (b) 2L-ReS₂. The rotation axes are labeled by red dot-dashed lines. (c and d) Atomic displacement schematics of three ULF interlayer modes in AI-stacked (c) and IS-stacked (d) 2L-ReS₂ obtained from the DFPT calculation. The corresponding frequencies are marked.

configuration [see Fig. 2(a), referenced to 0 eV] where the Re–Re bond of the bottom layer (dark blue line) is along the b axis and that of the top layer (purple line) is oriented 60° to the b axis. The lattice constants of this configuration are 6.38 ($|a|$) and 6.52 ($|b|$) Å, respectively. Fig. 2(b) shows the structure of IS-2L-ReS₂, which is the second stable configuration (97 meV less stable) where each Re–Re bond is parallel to the a or b axis. Although the projection of these two bonds appears symmetric, the bilayer geometry is not exactly identical along the a and b axes, as supported by the fully relaxed lattice constants of 6.43 ($|a|$) and 6.52 ($|b|$) Å.

Fig. 2(c) illustrates the vibrational displacements for modes C_{21}^y , C_{21}^x and LB_{21} of AI-2L-ReS₂ with the associated frequencies of $\text{Pos}(C_{21}^y) = 12.8 \text{ cm}^{-1}$, $\text{Pos}(C_{21}^x) = 16.9 \text{ cm}^{-1}$ and $\text{Pos}(LB_{21}) = 26.5 \text{ cm}^{-1}$, respectively. The absolute values and the difference of 4.1 cm^{-1} between the two C modes of AI-2L-ReS₂ are very closed to the measured values of 13.8, 17.5, 28.7 and 3.7 cm^{-1} . We thus prefer to assign the SA flake as configuration AI-2L-ReS₂, which is supported by the results of IS-2L-ReS₂. The theoretical frequencies of these three modes for IS-2L-ReS₂ are 12.9, 15.0 and 27.5 cm^{-1} , respectively [see Fig. 2(d)], where the C mode difference is 2.1 cm^{-1} , only half that of AI-2L-ReS₂, which is comparable with the full width at half maximum (FWHM) of $1.3\text{--}1.9 \text{ cm}^{-1}$ for the C mode, leading to it most likely not being distinguishable by experiment and measured as one peak sitting at 15.1 cm^{-1} of the SB flake. In terms of the LB mode, it is 1.0 cm^{-1} stiffer in

IS-2L-ReS₂, consistent with the measured 0.6 cm^{-1} larger LB frequency of 29.3 cm^{-1} for the SB flake. In addition, if the assessment is correct, the 97 meV more stable AI-2L-ReS₂ shall result in over 90% of the observations being the SA flake. Indeed, we found over 80% of the exfoliated 2L-ReS₂ samples showing two C modes. All these results compellingly confirm the assessment of the stacking order for the SA (AI-2L-ReS₂) and SB (IS-2L-ReS₂) flakes.

Rigid layer modes of NL ReS₂ ($N > 2$) were further measured by ULF Raman spectroscopy. We found two categories of the ULF Raman spectra for each NL-ReS₂ that exhibit different spectral features in terms of mode number and peak position. Analogous to the bilayer case, these two categories correspond to the AI- and IS-stacking configurations and are denoted as AI-NL-ReS₂ and IS-NL-ReS₂ ($N > 1$), respectively, as depicted in Fig. 3(a) and (b), respectively, together with the data from 1L ReS₂ presented for comparison. The linear chain mode (LCM) can be used to describe the N-dependent interlayer mode frequency where only the nearest-neighbor interlayer interaction is considered.¹⁹ The frequency of $N - 1$ LB modes of in NL ReS₂ can be given as follows:³³

$$\text{Pos}(LB_{N,N-j}) = \sqrt{2}\text{Pos}(LB_{21}) \sin(j\pi/2N), \quad (1)$$

where j is an integer, $j = N - 1, N - 2, \dots, 2, 1$. The above equation can also be applied to the C modes in the AI-NL-ReS₂ ($N > 1$) by replacing $\text{Pos}(LB_{N,N-j})$ with $\text{Pos}(C_{N,N-j}^y)$ and

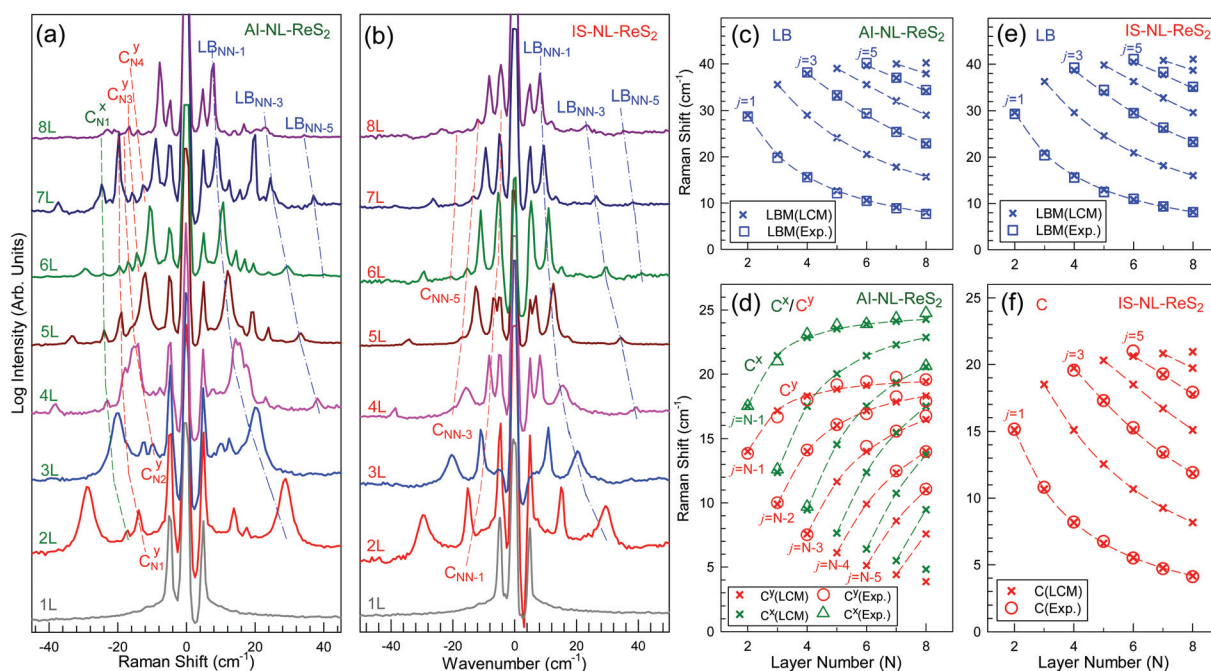


Fig. 3 (a and b) Stokes/anti-Stokes Raman spectra in the C and LB peak region for AI-stacked (a) and IS-stacked (b) 2–8L ReS₂ along with that of 1L ReS₂. The dashed lines are guides to the eye. (c and d) Positions of LB (c) and C (d) modes as a function of N for AI-stacked 2–8L ReS₂. The blue open squares, green open triangles and red open circles are the experiment data. The crosses are the theoretical data based on LCM. The index of each branch observed in the experiment is labeled. (e and f) Positions of LB (e) and C (f) modes as a function of N for IS-stacked 2–8L ReS₂. The blue open squares and red open circles are the experimental data. The crosses are the theoretical data based on LCM. The index of each branch observed in the experiment is labeled.

$\text{Pos}(C_{N,N-j}^x)$, and the C modes in the IS-NL-ReS₂ by replacing $\text{Pos}(\text{LB}_{N,N-j})$ with $\text{Pos}(C_{N,N-j}^y)$. Once the frequencies of the interlayer modes of 2L ReS₂ are determined, those in NL ReS₂ can be predicted. As demonstrated in Fig. 3(a) for the AI-NL-ReS₂, the LB_{NN-1} , LB_{NN-3} and LB_{NN-5} branches are marked by the blue dash-dotted lines, and the C_{N1}^x , C_{N1}^y , C_{N2}^y , C_{N3}^y , C_{N4}^y branches are marked by the green or red dashed lines, respectively. The prominent interlayer mode branches (C_{NN-1} , C_{NN-3} , C_{NN-5} , LB_{NN-1} , LB_{NN-3} , LB_{NN-5}) of IS-NL-ReS₂ are also demonstrated in the Fig. 3(b). The spectral feature is quite complex and peak fitting is necessary for certain AI-NL-ReS₂ to identify some interlayer modes, as depicted in Fig. S4 in the ESI† for AI-3L-ReS₂ and AI-4L-ReS₂. All the experimental $\text{Pos}(\text{C})$ and $\text{Pos}(\text{LB})$ of AI-NL-ReS₂ are summarized in Fig. 3(c) and (d), and those for IS-NL-ReS₂ in Fig. 3(e) and (f), respectively. All of them are in good agreement with the theoretical results based on LCM.

As shown in Fig. 3(c) and (e), the observed LB branches for AI- and IS-stacking configurations in NL ReS₂ are $j = 1, 3$ and 5. The interlayer mode in each branch of $j = 1, 3$ or 5 decreases in frequency with increasing N , which is also true for the C branches in IS-NL-ReS₂. However, the observed C branches in AI-NL-ReS₂ are $j = N - 1$ for C^x and $j = N - 1, N - 2, N - 3$ and $N - 4$ for C^y . It may result from the different symmetries and electron-phonon couplings between the AI- and IS-stacking orders.²³ Fig. 3(c-f) indicates that the N-dependent $\text{Pos}(\text{C})$ and $\text{Pos}(\text{LB})$ in AI- and IS-NL-ReS₂ can be explained by the LCM.

Given the measured or calculated frequencies, we move to the interlayer coupling strength for further discussion. We take ReS₂ bilayers as prototypes. The interlayer force constant, reflecting the coupling strength, can be deduced from the mode frequency of the C and LB modes of 2L-ReS₂ by formulae $\alpha_C = (2\pi^2 c^2) \mu \text{Pos}^2(C_{21})$ and $\alpha_{\text{LB}} = (2\pi^2 c^2) \mu \text{Pos}^2(\text{LB}_{21})$, where α_C and α_{LB} are the interlayer shear and breathing force constants per unit area, μ is atomic mass per unit area, and $\text{Pos}(C_{21})$ and $\text{Pos}(\text{LB}_{21})$ are the frequencies of the C and LB modes of

2L-ReS₂, respectively.³³ The experimentally derived α_C of AI-2L-ReS₂ along the x and y axes are $\sim 90\%$ and 55% to those of 2L-MoS₂,³³ respectively, significantly anisotropic in the basal plane, and α_{LB} in 2L-ReS₂ is about 76% to that in 2L-MoS₂. For the IS-2L-ReS₂, α_C is about 67% of that in 2L-MoS₂. Our results show compelling evidence of significant interlayer coupling in AI- and IS-NL-ReS₂, which are comparable with those in multilayer MoS₂.

Evolution of N-dependent high-frequency Raman modes is also governed by interlayer interaction in 2D materials.⁴ We summarized the optical Raman spectra of AI- and IS-NL-ReS₂ up to 8L from a range of 120–250 cm⁻¹ in Fig. 4(a) and (b), respectively, together with that of 1L ReS₂ for comparison. The appearance, namely the number and position of modes, does not significantly change with N increasing from 1L to 8L. The relative intensity between different modes is usually sample dependent, owing to specific intensity dependence of each on laser polarization. The peaks at $\sim 161, 213, 235$ cm⁻¹ do not appreciably move with respect to N for both AI- and IS-NL-ReS₂. However, as marked by the dashed lines in Fig. 4(a) and (b), the ma and mb peaks have different N-dependent evolution tendencies in AI- and IS-NL-ReS₂. In particular, the ma mode of 1L ReS₂ softens in AI-stacked NL-ReS₂ while it stiffens for IS-stacked ones. Unlike the ma mode, the mb mode stiffens in AI-stacked multilayers but almost remains unmoved for all IS-stacked samples. Consequently, $\text{Pos}(\text{mb}) - \text{Pos}(\text{ma})$ increases from 16.7 cm⁻¹ of 1L ReS₂ to 20.6 cm⁻¹ of AI-8L-ReS₂, but decreases to 13.3 cm⁻¹ of IS-8L-ReS₂, as plotted in Fig. 4(c). Therefore, $\text{Pos}(\text{mb}) - \text{Pos}(\text{ma})$ can be used to identify N and the stacking order, similar to the case of few-layer MoS₂.⁴

The inset in Fig. 4(c) shows the vibrational displacements of the ma and mb modes which are A_g-like out-of-plane and E_g-like in-plane modes analogous to those in MoS₂.³⁹ It was found that the intra-layer mode is usually stiffened by the interlayer vdW coupling and softened by the long-range

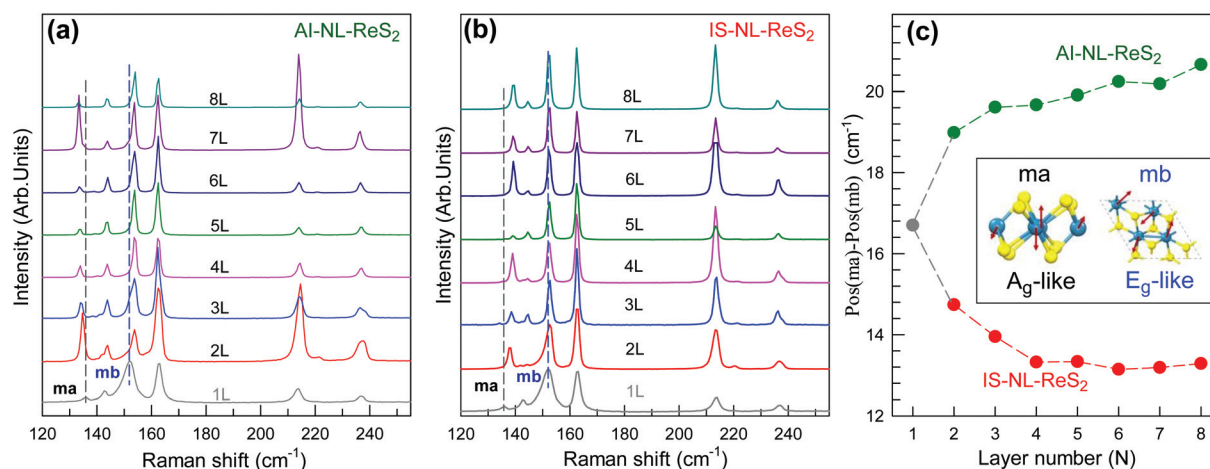


Fig. 4 (a and b) Raman spectra of AI-stacked (a) and IS-stacked (b) 2–8L ReS₂ in the range of 120–250 cm⁻¹, together with that of 1L ReS₂ for comparison. The dashed lines are guides to the eye. (c) $\text{Pos}(\text{mb}) - \text{Pos}(\text{ma})$ as a function of N for AI-stacked (green circles) and IS-stacked (red circles) 2–8L ReS₂. The inset shows the atom displacement of the modes ma and mb, which are indicated in (a) and (b).

Coulomb screening.³⁹ The overall strength between the two interactions determines the mode to be eventually stiffened or softened with increasing N . Both the vdW interaction and long-range Coulomb screening are sensitive to the stacking order. The calculated frequencies of the ma and mb modes of 1L ReS₂, AI-2L-ReS₂ and IS-2L-ReS₂ by DFPT are summarized in Table S1.† The calculated Pos(mb)–Pos(ma) increases from 18.5 cm^{−1} of 1L ReS₂ to 19.1 cm^{−1} of AI-2L-ReS₂ and decreases to 13.4 cm^{−1} for IS-2L-ReS₂, consistent with the experimental trend. Therefore, the calculated and experimental Pos(mb)–Pos(ma) values in 1L- and 2L-ReS₂ further confirm that significant interlayer coupling exists in NL ReS₂ and is different between the two stacking orders.

Optical transitions of AI- and IS-NL-ReS₂ are measured by PL spectra, as shown in Fig. 5(a), and the PL spectrum of 1L ReS₂ is plotted in the grey curve revealing its bandgap of 1.61 eV. In general, for a certain N , the PL spectrum of AI-NL-ReS₂ (green solid curves in Fig. 5(a)) exhibit weaker intensity and higher energy in comparison with that of IS-NL-ReS₂. The PL profile of AI-NL-ReS₂ is similar to that of 1L ReS₂ and with a full width at half maximum (FWHM) of about 160 meV. However, it is narrower in IS-NL-ReS₂ showing a sharper peak

at the peak center. These different PL features can be adopted as a gauge to distinguish the IS-stacked NL ReS₂ from the AI-stacked ones. The PL peak positions of NL ReS₂ decreases from 1.57 eV of 2L to 1.52 eV of 8L for AI-NL-ReS₂ while it decreases from 1.58 eV of 2L to 1.51 eV of 8L for IS-NL-ReS₂, as summarized in Fig. 5(b). Theoretical calculation shows a similar trend in that the optical transition energy of 1L ReS₂ of 1.55 eV drops to 1.53 and 1.43 eV for the AI- and IS-stacked bilayers, and further to 1.42 eV of AI-8L-ReS₂ and 1.36 eV of IS-8L-ReS₂. The calculated band structures indicate that 1L ReS₂ and both AI- and IS-NL-ReS₂ are direct bandgap semiconductors, corresponding to the valence-to-conduction transition at the Γ point of the Brillouin zone, as shown in Fig. 5(c). They are thus comparable with the experimentally measured PL spectra and theoretically calculated bandgaps. Note that the experimentally measured values are the transition energy between band centers of two highest valence bands and two lowest conduction bands at the Γ point, but not the band gap between valence maximum and conduction minimum, we therefore plotted the averaged theoretical gaps between the band centers of the two valence bands and two conduction bands in Fig. 5(b). The only exception of experiment–theory

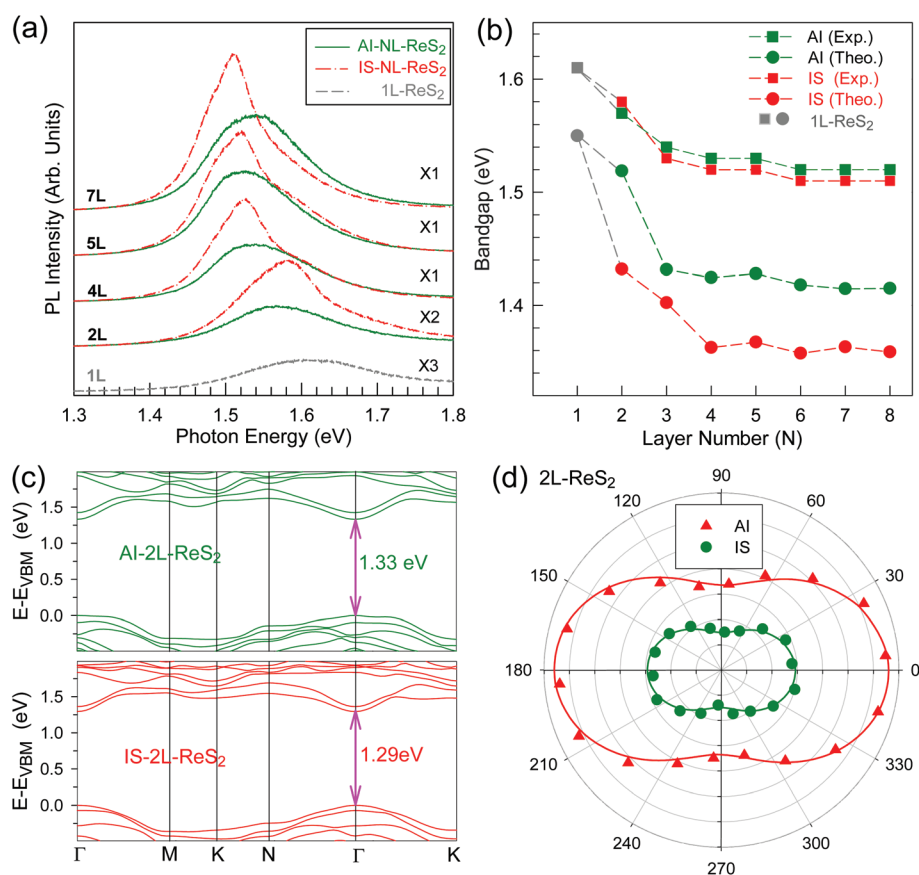


Fig. 5 (a) PL spectra of 2L, 4L, 5L and 7L ReS₂ with AI (green curve) and IS (red curve) stacking ways. (b) Evolution of optical transition energies of AI-stacked (green) and IS-stacked (red) NL-ReS₂ as a function of N . The peak energies are extracted from PL spectra (square) and also revealed by DFT calculation (circle). (c) Band structures of AI-stacked (top panel, green solid curves) and IS-stacked (bottom panel, red solid curves) 2L-ReS₂, respectively, where the corresponding minimum of valence-to-conduction transition is marked. (d) The polarization dependence of the PL intensity of AI-stacked (green) and IS-stacked (red) 2L-ReS₂.

comparison is in 2L-ReS₂ where the experimental transition energy of AI-2L-ReS₂ is smaller than that of IS-2L-ReS₂, but the calculation predicts the opposite. Standard DFT is widely known to underestimate the bandgap of semiconductors and does not consider exciton binding energy that is of importance in 2D layered structures. In terms of TMDs, standard DFT predicts reasonable bandgaps because of an error cancellation by the underestimation and lack of exciton binding energy. In thinner flakes, *e.g.* 2L-ReS₂, the role of exciton binding energy is more pronounced than those of thicker flakes. We thus argue that this experiment–theory discrepancy in 2L-ReS₂ is, most likely, a consequence of different exciton binding energies of AI- and IS-2L-ReS₂. Fig. 5(d) shows the polarized PL intensities of both AI- and IS-2L-ReS₂, the shapes of which are comparably ascribed to the similar in-plane crystal structures. The N-dependent PL peaks also indicate that the interlayer coupling in multi-layer ReS₂ is significant for both stacking orders.

3. Conclusions

In conclusion, two stable stacking orders (AI and IS) in the 2L ReS₂ have been identified by ultralow-frequency Raman spectroscopy and the first-principles calculation, which identifies a significant interlayer coupling in 2L ReS₂, in a different from than previously believed for non-interlayer-interaction. According to N-dependent frequency evolution of the C and LB modes, the AI and IS stacking orders also exist in multi-layer ReS₂ and the corresponding N-dependent frequency of C and LB modes can be predicted by the linear chain model. The N-dependent high-frequency Raman modes and PL spectra further confirm the existence of the AI- and IS-stacking orders in multi-layer ReS₂. The isotropic interlayer shear coupling with the appearance of one C mode, Pos(mb)–Pos(ma) and peak profile are key features in distinguishing IS-stacked NL-ReS₂ from AI-stacked ones. This study paves the way to exploring interlayer coupling, layer stacking, electronic and optical properties of other anisotropic 2D materials.

4. Methods

4.1. Sample

The ReS₂ flakes were prepared on Si/SiO₂ substrates from a bulk crystal (2D semiconductors Inc.) by the standard micro-mechanical exfoliation method.¹

4.2. Optical contrast

A micro-Raman confocal system and a $\times 50$ objective with a numerical aperture of 0.45 were used in the optical contrast measurement. A tungsten-halogen lamp was used as a light source. The optical contrast is defined as $1 - R_F(\lambda)/R_{Sub}(\lambda)$, where $R_{Sub}(\lambda)$ and $R_F(\lambda)$ are the reflected light intensities from the SiO₂/Si bare substrate and the ReS₂ flake deposited on SiO₂/Si substrate, respectively, dependent on the wavelength (λ) of the light source.

4.3. Raman and photoluminescence spectroscopy

Raman and PL spectra were measured at room temperature using a Jobin-Yvon HR800 micro-Raman system equipped with a liquid-nitrogen-cooled charge couple detector (CCD), a $\times 100$ objective lens (numerical aperture = 0.90) and several gratings. The excitation wavelengths were 502 nm from an Ar⁺ laser and 633 nm from a He–Ne laser. The 1800 lines per mm grating was used in the Raman measurement, which enables one to have each CCD pixel to cover 0.60 cm^{-1} at 502 nm. A typical laser power of 0.3 mW was used to avoid sample heating. The laser plasma lines were removed using a BragGrate bandpass filter. Measurements down to 5 cm^{-1} were enabled by three BragGrate notch filters with optical density 4 and with a FWHM of 5 cm^{-1} .

4.4. Density functional theory calculation

Density functional theory calculations were performed using the generalized gradient approximation for the exchange–correlation potential, the projector augmented wave method^{40,41} and a plane-wave basis set as implemented in the Vienna *ab initio* simulation package (VASP).⁴² Phonon-related properties were calculated with VASP based on density functional perturbation theory (DFPT).⁴³ The energy cut-off for the plane-wave basis was set to 700 eV for all calculations. A 2×2 supercell containing two ReS₂ layers and a vacuum layer of 16 Å was adopted to consider the distorted lattice with a k -mesh of $7 \times 7 \times 1$ to sample the first Brillouin zone of few-layered ReS₂. van der Waals interactions were considered at the vdW-DF^{44,45} level with the optB86b exchange functional (optB86b-vdW)^{46,47} for geometry optimization, which was found to be more accurate in describing the structural properties of layered materials.^{26,48–50} The shape (in-plane lattice parameters) of each supercell was fully optimized and all atoms in the supercell were allowed to relax until the residual force per atom was less than 0.001 eV Å^{-1} . In the electronic band structure calculations, the lattice constants were kept fixed to the 2L values for multilayers, and the residual forces of all atoms in each supercell were fully relaxed to less than 0.01 eV Å^{-1} .

Note: While finalizing this manuscript, we became aware of two preprints reporting the low-frequency Raman spectra of ReS₂.^{51,52}

Author contributions

P.-H. T. conceived the research. X.-F. Q., and W. S. prepared the samples. X.-F. Q., J.-B. W., X. Z. and P.-H. T. performed Raman and PL measurements and experimental data analysis. L.-W. Z., J.-S. Q., J.-B. W., P.-H. T. and W. J. performed theoretical analysis. J.-B. W., X.-F. Q., L.-W. Z., W. J. and P.-H. T. wrote the manuscript, which all authors read and commented on.

Competing financial interests

The authors declare no competing financial interests.

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