Interlayer breathing and shear modes in NbSe2 atomic layers

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Abstract

Atomically thin NbSe2 is a metallic layered transition metal dichalcogenide with novel charge-density-wave (CDW) and superconductive phases. Properties of NbSe2 atomic layers are sensitive to interlayer coupling. Here we investigate the interlayer phonons of few-layer NbSe2 by ultralow-frequency Raman spectroscopy. We observe both the interlayer breathing modes and shear modes at frequencies below 40 cm\(^{-1}\) for samples of 2–15 layers. Their frequency, Raman activity, and environmental instability depend systematically on the layer number. We account for these results by a combination of linear-chain model, group theory and first-principles calculations. We find that, although NbSe2 has different stacking order from MoS2, MoSe2, WS2 and WSe2, they share the same crystal symmetry groups and exhibit similar Raman selection rules for interlayer phonons. In addition, the interlayer phonon modes evolve smoothly from \(T = 300\) to 8 K, with no observable response to the CDW formation in NbSe2. This finding indicates that the atomic registry between adjacent NbSe2 layers is well preserved in the CDW transition.

Introduction

Atomically thin transition metal dichalcogenide (TMD) niobium diselenide (NbSe2) has recently stimulated strong scientific interest due to its distinctive electronic and magnetic properties. In contrast to the more-studied group-VI TMD semiconductors, such as MoS2, MoSe2, WS2, and WSe2, bulk NbSe2 is a conductor, which exhibits charge density waves (CDWs) and superconductivity at transition temperature of \(T_{\text{CDW}} = 33.5\) K and \(T_C = 7.2\) K, respectively [1, 2]. Two-dimensional (2D) NbSe2 inherits these features, but their properties change significantly as the layer thickness approaches the monolayer (1L) limit. Recent research has reported distinct electronic band structure [3], strongly enhanced CDW order [4] and suppressed superconductivity in 1L NbSe2 compared to the bulk [3, 5]. Superconducting 1L NbSe2 also exhibits Ising pairing of spins due to broken inversion symmetry [5]. These thickness-dependent phenomena indicate that the interactions between the NbSe2 layers play a crucial role for a diverse set of material properties. It is therefore important to study the detailed characteristics of interlayer coupling in NbSe2 to thoroughly understand its rich physics.

The interlayer interactions in 2D materials are closely related to the layer stacking order. In this respect, the crystallographic structure of NbSe2 crystals is generally different from the common structure of MoS2, MoSe2, WS2 and WSe2 [6, 7]. According to the convention by Wilson and Yoffe [6], the position of the atoms in each TMD atomic plane can be specified by three points in a triangular lattice (a, b, c or A, B, C). The upper (lower) case denotes the chalcogen (metal) atoms. 1L NbSe2 has the same trigonal prismatic (H) structure as 1L MoS2 (denoted as AbA or equivalently AcA) (figure 1). As the layer number increases, however, the stacking order of NbSe2 layers differs subtly
from that of MoS₂. Multilayer MoS₂ exhibits the so-called 2Hc structure, which can be represented as (AbA BaB). In contrast, NbSe₂ exhibits the 2Ha structure (AcA BcB), in which the Nb atoms in all the layers are aligned vertically but the Se sublattice is rotated by 60° with respect to that of the neighboring layer [6, 7] (figure 1). It would be interesting to examine how this subtle stacking difference and the metallic nature of NbSe₂ may influence the interlayer interactions.

Raman spectroscopy is a powerful and non-destructive technique to investigate the interlayer interactions in 2D materials. In particular, recent research using ultralow-frequency Raman spectroscopy has revealed a set of interlayer phonon modes in NbSe₂ crystals with layer number N = 2–15 by using high-resolution ultralow-frequency Raman spectroscopy. We observe both the interlayer breathing modes and shear modes at frequencies below 40 cm⁻¹. The results allow us to directly extract the vertical and tangential interlayer force constants, which are important parameters for many thickness-dependent properties of NbSe₂. The frequency, Raman activity and environmental instability of the interlayer modes are found to evolve systematically with the layer number. We account for these observations by a combination of linear-chain model, group theory and first-principles calculations. In comparison to MoS₂, NbSe₂ exhibits similar interlayer coupling strength and Raman selection rules for the interlayer modes. Although NbSe₂ layers have different stacking order from MoS₂, our group-theory analysis shows that they share the same symmetry point groups and thus Raman selection rules for interlayer phonons. Therefore, the metallic nature and differing stacking order of the NbSe₂ layers do not significantly change the interlayer interactions of the material. In addition, we observe that the interlayer phonon modes in NbSe₂ evolve smoothly from room temperature to 8 K, well below the CDW transition temperature. This finding indicates that the atomic registry between adjacent NbSe₂ layers is well preserved in the CDW phase transition.

**Methods**

We prepared NbSe₂ samples with layer number N = 1–15 (denoted as 1L–15L) by mechanical exfoliation of high-quality bulk 2H-NbSe₂ crystals.Atomically thin samples were first deposited on silicone elastomer polydimethylsiloxane (PDMS) stamps, and afterward transferred onto Si/SiO₂ substrates [4]. The sample thickness was identified by the optical contrast (figure 2(a)) and further confirmed by the frequency of the interlayer Raman modes. To minimize the environmental effects, we covered some samples with hexagonal boron nitride (BN) flakes (thickness 10–20 nm) and stored all the samples in vacuum. We measured Raman spectra using a commercial Horiba

![Figure 1. Comparison of the crystal structure of bilayer NbSe₂ and MoS₂. (a) The schematic 2Ha structure of NbSe₂, with both the top and side views. The atom location can be specified by the a, b, c (or A, B, C) points of a triangular lattice, as denoted in the top view. The 2Ha structure can thus be represented as (AcA BcB), where the upper and lower cases denote the chalcogen and metal atoms, respectively. (b) The schematic 2Hc structure of MoS₂, as in panel a. Similar 2Hc structure also exists for MoSe₂, WS₂ and WSe₂.](image-url)
been reported in graphene and other TMD bilayers and CDW phenomena. In a simple model of two meters for the thickness-dependent superconductivity in the range of $10^{-5}$ cm.

**Figure 2**

Results and discussion

Figure 2(b) displays Raman spectra of 1L and 2L NbSe$_2$ in the range of 10–50 cm$^{-1}$, measured at room temperature in vacuum conditions. The 1L spectrum does not display any noticeable Raman feature in this range, but the 2L spectrum exhibits two distinctive peaks at 19.5 and 33 cm$^{-1}$. Because of their absence in the spectrum of 1L NbSe$_2$, we deduce that these two peaks arise from the interaction between the two NbSe$_2$ layers. Similar interlayer Raman features have been reported in graphene and other TMD bilayers. According to these prior studies, we attribute the 19.5 cm$^{-1}$ peak to the doubly degenerate interlayer shear (S) mode, and the 33 cm$^{-1}$ peak to the interlayer breathing (B) mode. These frequencies allow us to extract the coupling strengths between two NbSe$_2$ layers, which are important material parameters for the thickness-dependent superconductivity and CDW phenomena. In a simple model of two coupled layers, the interlayer mode frequency ($\omega$) is related to the monolayer mass density ($\mu$) and the interlayer force constant ($\kappa$) as $\omega^2 = 2\kappa/\mu$. From our measured frequencies, we estimate that $\kappa = 27$ and $78 \times 10^{18}$ N m$^{-3}$ for the shear and breathing modes in 2L NbSe$_2$, respectively. These values are very close to those in MoS$_2$ ($\kappa = 28$ and $87 \times 10^{18}$ N m$^{-3}$ for the shear and breathing modes, respectively) [23, 25, 26]. Therefore, the interlayer van der Waals forces are similar for the metallic NbSe$_2$ and the semiconducting MoS$_2$.

2H-NbSe$_2$ is known to be susceptible to the environment. To explore the effect of sample degradation on the interlayer modes, we compared the spectra of two 2L NbSe$_2$ samples. The first sample is exposed to the air for one day and the other is protected by a BN cap layer immediately after exfoliation. We find that the shear mode of the exposed sample exhibits a larger full width at half maximum (FWHM = 2.7 cm$^{-1}$) than that of the BN-capped sample (1.6 cm$^{-1}$) (figure 2(c)). The spectral broadening indicates higher defect density in exposed samples. However, we do not observe a shift of the mode frequency. We note that, while the BN cap layers help preserve the shear mode, they are found to suppress the breathing mode in some samples, possibly due to the damping of the vertical layer vibration. Similar suppression of the breathing mode has been observed in few-layer graphene due to the damping caused by surface adsorbates [11].

Figure 3(a) compares the Raman spectra of NbSe$_2$ samples with $N = 2$–15 layers to that of bulk NbSe$_2$, all measured at room temperature. In order to reveal the breathing modes more clearly, we used uncapped samples in all these measurements. For clarity, we removed the broad background by subtracting a smooth baseline for each spectrum. The multilayer samples exhibit two sets of interlayer modes: one shear mode that blueshifts with increasing $N$, and one layer breathing mode that redshifts with increasing $N$. Their thickness-dependent frequencies can be well described by a coupled-oscillators model with only nearest-layer coupling. In this simple model, the layers are treated as a linear chain of $N$ masses connected by constant springs. An $N$-layer system possesses $N-1$ normal modes with frequencies [11]:

$$\omega^{(N)} = \omega_0 \cos(n\pi/2N).$$

Here $n = 1, 2, \ldots N - 1$ is the mode index from high to low frequency, and $\omega_0$ is the shear (breathing) mode frequency of bulk NbSe$_2$ at the Brillouin zone center. For the shear mode, the bulk frequency can be directly
measured to be $\omega_0 = 28 \text{ cm}^{-1}$ (see the bulk spectrum in figure 3(a)). For the breathing mode that is Raman inactive in the bulk, we can deduce the bulk frequency to be $\omega_0 = \sqrt{2} \omega_1^{(1)} = 47 \text{ cm}^{-1}$ from the 2L frequency $\omega_1^{(1)} = 33 \text{ cm}^{-1}$. A direct comparison between theory and experiment shows that these modes correspond to the highest-frequency shear branch ($n = 1$) and the lowest-frequency breathing branch ($n = N - 1$) (figure 3(b)).

We further confirm our mode assignment by calculating the phonon frequencies in 1L, 2L and 3L NbSe$_2$ by density-functional theory (DFT). Our first-principles calculations were performed by using the Quantum ESPRESSO code with the Perdew–Wang [37] local density approximation exchange-correlation function (see supporting information). The open triangles in figure 3(b) indicate the predicted frequencies of the highest shear modes and lowest breathing modes for 2L and 3L NbSe$_2$. They agree with the measured values within 4 cm$^{-1}$. Given that NbSe$_2$ is a metallic system with complicated screening effects, such an agreement between theory and experiment is remarkable.

Prior comparative studies of ABA and ABC stacked 2D materials have shown that the Raman activity of the interlayer modes is highly sensitive to the stacking order [12, 38]. In particular, the highest-frequency shear modes can become Raman inactive as the stacking order changes from ABA to ABC stacking. From our results, however, we see that NbSe$_2$ exhibits the same Raman activity of interlayer modes as that in MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$, despite their different stacking order [11, 23, 34]. This observation contrasts with the reported stacking-dependent shear modes. To understand this behavior, we have analyzed the crystal symmetry of NbSe$_2$ with 2Ha structure and MoS$_2$ with 2Hc structure (see supplementary information). We find that although their detailed atomic configurations are different, the two 2H polytypes share the same symmetry point groups—$D_{3d}$ group with inversion symmetry for even layer number, and $D_{3h}$ group with mirror symmetry for odd layer number [7]. The phonons at the Brillouin zone center can be decomposed as:

\[
\Gamma_{D_{3d}} = \frac{3N}{2} (E_e + E_a + A_{1g} + A_{2e}) (N = \text{even}),
\]

\[
\Gamma_{D_{3h}} = \frac{3N+1}{2} E' + \frac{3N-1}{2} E'' + \frac{3N-1}{2} A_1' + \frac{3N+1}{2} A_2'' (N = \text{odd}).
\]

In our backscattering measurement geometry, there are a total of $N/2$ Raman active shear (breathing) modes and $N$ B modes. This selection rule is closely related to the mirror symmetry of the $D_{3h}$ group.

Figure 3. (a) Low-frequency Raman spectra of NbSe$_2$ with layer number $N = 2$–15 and bulk NbSe$_2$. For clarity the spectra are vertically displaced with the broad background removed by subtracting a smooth baseline. The green and red dashed lines highlight the shear (S) and breathing (B) modes, respectively. The 2L breathing mode is magnified by a factor of three for clarity. The orange curves in the 3L spectrum denote the fitted shear and breathing modes that overlap with each other. (b) Frequency of the shear and breathing modes as a function of layer number. The solid lines are the predicted phonon frequencies from the linear-chain model. The open triangles are the predicted phonon frequencies from DFT calculations. (c) The full width at half maximum (FWHM) of the shear and breathing Raman modes as a function of layer number.
modes with $E_g$ ($A_{1g}$) representation for even $N$, and
$(N - 1)/2$ Raman active shear (breathing) modes with $E''$ ($A_1'$) representation for odd $N$. By examining the
layer displacement patterns of these modes, we confirm that the highest-frequency shear modes and
the lowest-frequency breathing modes have the largest polarizability modulation and, hence, the highest
Raman activity. The different Raman activity between the breathing modes and shear modes arises from the
AB-like stacking order in NbSe$_2$, as explained in our
prior studies of few-layer graphene [11, 12]. Therefore,
the different stacking order of NbSe$_2$ does not change
the crystal symmetry, and the Raman behavior of
NbSe$_2$ still resemble those of few-layer graphene,
MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$.

In addition to the thickness-dependent frequency,
we have also examined the line width of the interlayer
modes as a function of layer number (Figure 3(c)). As
the NbSe$_2$ sample thickness increases from $N = 2$ to
15 layers, the breathing mode narrows from a line
width of 5 cm$^{-1}$ to 1 cm$^{-1}$. A major factor is the change
of phonon lifetime [11]. The breathing mode redshifts
dramatically from 34 to 5 cm$^{-1}$ as $N$ increases from 2
to 15 (Figure 3(b)). The reduced phonon energy at
higher layer number suppresses the anharmonic decay
into the acoustic phonons of lower energy. Conse-
quently, the breathing-mode phonons have a longer
lifetime and hence sharper Raman line for thicker
NbSe$_2$ samples. Similar narrowing behavior of
breathing modes has been observed in few-layer gra-
phene and TMDs [11, 23]. On the other hand, one may
expect an opposite (slightly broadening) behavior for
the shear mode that blueshifts moderately as $N$ incra-
ses, similar to that occurs in few-layer graphene [11].
However, our shear-mode spectra show a decrease of
line width from 2.7 to 1 cm$^{-1}$ as $N$ increases from 2 to
15 layers. This unexpected narrowing behavior is
attributed to environmental effects and sample degra-
dation. As shown in Figure 3(c), exposure to air broad-
eness considerably the shear mode of uncapped 2L
NbSe$_2$ samples. As the external environment predomi-
nantly affects the surface layer, its overall influ-
ence diminishes in thicker samples. To fully account
for the line width of the interlayer Raman modes, we
have to consider the competing contribution of pho-
non lifetime and surface degradation.

Finally, we comment on the possible influence of
CDWs on the interlayer phonon modes in NbSe$_2$. 
NbSe$_2$ hosts robust in-plane CDWs with $3 \times 3$ super-
cells at low temperature ($T_{CDW} = 33.5$ K) [1, 3, 39].
The origin and characteristics of these CDWs are an
on-going research topic. We have examined the influ-
ence of CDWs on the interlayer phonons by measur-
ing the Raman spectra of 2L NbSe$_2$ from $T = 300$ to
8 K (Figure 4). In this experiment, we used a BN-cap-
ped 2L sample to ensure high sample quality. In our
Raman results, the breathing mode is weak but

![Figure 4](image-url)
observable at $T > 100$ K (figures 4(a) and (b)). At $T < 100$ K, the breathing mode is overshadowed by a broad Raman band ($>30$ cm$^{-1}$). The shear mode remains prominent at all temperatures. It exhibits a slight blue shift in frequency as well as a decline of line width and intensity as the temperature decreases (figures 4(d)–(f)), which we attribute to the lattice contraction and the decrease of thermal fluctuation and phonon population at lower temperature, respectively. Notably, we observe the shear mode to evolve smoothly from $T = 300$ to 8 K, i.e., well below the bulk $T_{\text{CDW}}$ (33.5 K)—CDW formation does not cause a discontinuity in the frequency, line width, or intensity of the shear mode. Similar results are also found in the 4L and bulk NbSe$_2$, which are less sensitive to any surface degradation (figures S2 and S3 in the supporting information), as well as in a prior Raman study of few-layer NbSe$_2$ that displays broader shear mode features [4].

These observations indicate that the lattice match between two NbSe$_2$ layers is well preserved in the CDW transition. As the generation of shear restoring force requires rigorous atomic registry between adjacent layers, a slight interlayer lattice distortion can broaden, suppress or eliminate the shear mode, as demonstrated by recent Raman studies of twisted TMD layers [28, 33]. On one hand, our results imply that the lattice distortion caused by the CDW formation is very small, which causes negligible changes in the interlayer shear modes. On the other hand, our results suggest that the 3 × 3 CDW supercells in adjacent NbSe$_2$ layers align with one another (figure 4(c)), and the CDW patterns in different layers are vertically in phase. From an energetic point of view, vertically aligned CDWs, which minimize the interlayer lattice mismatch, are generally more stable than randomly aligned CDWs, which minimize the interlayer lattice mismatch in phase. From an energetic point of view, vertically aligned CDWs, which minimize the interlayer lattice mismatch, are generally more stable than randomly aligned CDWs, which minimize the interlayer lattice mismatch in phase.

In conclusion, we have investigated the interlayer breathing and shear modes in NbSe$_2$ atomic layers by ultralow-frequency Raman spectroscopy, group-theory analysis and DFT calculations. Although the layer stacking order of NbSe$_2$ differs from MoS$_2$, MoSe$_2$, WS$_2$ and WSe$_2$, it exhibits the same symmetry and Raman selection rules, as well as similar interlayer coupling strength and thickness dependence of interlayer phonon modes. These interlayer phonons in NbSe$_2$ are found to be insensitive to CDW transition. The information gained in our research should be useful to understand the thickness-dependent properties of NbSe$_2$. Moreover, the experimental technique established here can be applied to study a broad set of further properties of NbSe$_2$ and other TMDs, such as the superconducting phase at low temperature.

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