

Raman evidence for high-temperature $2a \times 2a$ charge density wave in disorder-W-intercalated NbSe₂

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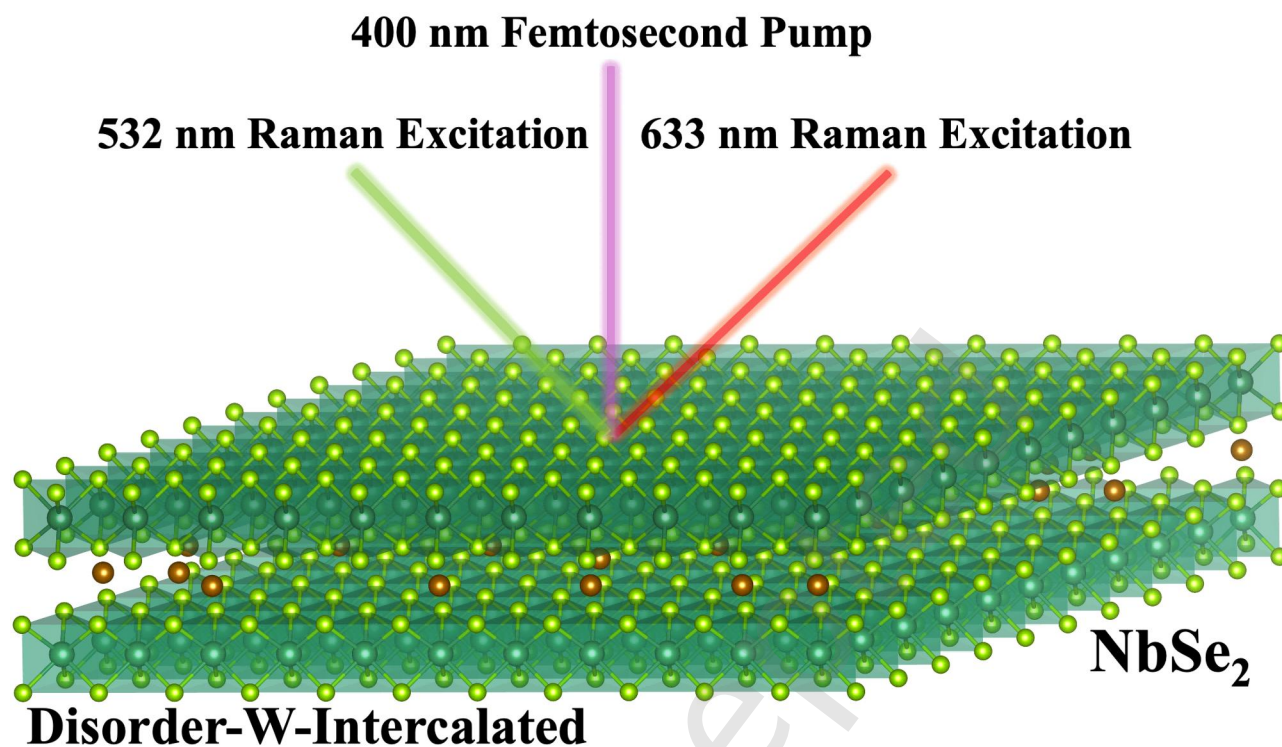
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Disordered tungsten intercalation in NbSe₂ induces a high-temperature $2a \times 2a$ charge density wave phase driven by selectively enhanced electron-phonon coupling. This finding demonstrates how intercalant-induced charge transfer can effectively tailor macroscopic quantum states in correlated materials.

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ABSTRACT: Correlated electron systems provide platforms for macroscopic quantum phenomena. We investigate lattice dynamics and ultrafast carrier relaxation in disorder-W-intercalated NbSe₂ using temperature-dependent Raman spectroscopy and transient absorption microscopy (TAM). Intercalation induces a $2a \times 2a$ superstructure accompanied by a localized vibrational mode of W atoms ($\sim 108 \text{ cm}^{-1}$) and a zone-folded phonon mode from M point ($\sim 156 \text{ cm}^{-1}$). Anharmonicity and thermal melting of the zone-folded mode provide evidence for that the $2a \times 2a$ superstructure relates to a high-temperature charge density wave (CDW), attributed to selectively enhanced electron-phonon coupling (EPC). Conversely, the two-phonon soft mode exhibits unusual temperature dependence, indicating the $3a \times 3a$ CDW transition temperature decreases from 35.6 K to 11.8 K. TAM results corroborate this suppression, as prolonged fast and slow relaxation time constants reflect structural disorder and charge redistribution. Our findings demonstrate charge transfer induced by disordered intercalation selectively modulates EPC, offering insights into tailoring quantum orders in correlated materials.

KEYWORDS: intercalation, $2a \times 2a$ superstructure, charge density wave, electron-phonon coupling, temperature-dependent Raman spectroscopy, femtosecond transient absorption microscopy

1 Introduction

Correlated electron systems host robust collective orders ranging from superconductivity and Mott insulators to charge density wave (CDW) phases, and have become a fertile playground for the manipulation of macroscopic quantum states, showing immense potential for quantum devices[1-5]. Among them, CDW phase has attracted particular attention and represents a fundamental manifestation of collective behavior in low-dimensional material, arising from the coupled reorganization of electronic states and the crystal lattice[6]. This state features a periodic modulation of charge density and a symmetry-breaking lattice distortion, reflecting the intimate interplay between electrons and phonons in reduced dimensions[6].

CDW was first described in 1D metallic systems by Peierls, where perfect Fermi surface nesting drives lattice instability (Kohn anomaly) via divergent electronic susceptibility[7]. However, such instability remains insufficient for higher-dimensional CDW phenomena[8-10]. In quasi-two-dimensional materials, the Fermi surface typically lacks perfect nesting required to sustain a purely electronic instability. Relevant experimental reports and theoretical calculations indicate that the CDW transition is dominated

by the cooperative interaction between electronic states and lattice degrees of freedom, depending on the strong momentum-dependent electron-phonon coupling (EPC), implying that the selective softening of phonon modes at specific wave vectors within the Brillouin zone (BZ) plays a decisive factor[9,11]. Therefore, the CDW transition can be understood as a coupled electronic-structural instability, rather than a purely electronic Peierls transition[11,12].

Layered transition-metal dichalcogenides (TMDs) represent a prototypical material family for exploring the complex nature of CDW physics in two dimension materials[13-15]. For example, 2H-NbSe₂ in a layered structure, in which a central plane of niobium atoms is covalently sandwiched between two hexagonal selenium planes in a trigonal prismatic coordination, exhibits a coexistence of commensurate $3a \times 3a$ CDW phase ($T_{\text{CDW}} \sim 33.5 \text{ K}$) and superconductivity ($T_{\text{c}} \sim 7.2 \text{ K}$) [16,17]. Despite lacking ideal Fermi-surface nesting conditions, NbSe₂ hosts the robust CDW phase driven by the anisotropic EPC, which induces an anomalous phonon softening at the wave vector $q \approx 2/3 \Gamma\text{-M}$ within BZ, facilitating the CDW instability and stabilizing symmetry-lowered lattice distortions[18,19]. Consequently, tuning and optimizing the CDW phase in NbSe₂ to achieve enhanced macroscopic quantum states and exploring the

underlying physical mechanisms have become a focal point of recent researches. The application of external pressure and mechanical strain are particularly prevalent strategies[20-22]. For example, Cao et al. reported that the CDW phase in NbSe₂ can be gradually suppressed with applied high pressure and disappears at ~ 3.7 GPa, which simultaneously enhances the superconductivity phase[22]. Gao et al. reported that CDW configuration in NbSe₂ can transform from the $3a \times 3a$ to $2a \times 2a$ phase upon applying $\sim 5\%$ - 6% uniaxial tensile strain[23]. However, these methods often involve high experimental costs and may cause irreversible sample damage.

Alternatively, intercalation engineering, inserting guest species into the van der Waals (vdW) gaps of TMDs (MxTMDs), offers a flexible and non-destructive strategy to tune the CDW phase by manipulate the electronic structure and lattice dynamics[18,24]. Conventionally, the modified physical properties in MxTMDs are discussed in the context of the induced ordered superstructures[25,26]. Specific stoichiometric intercalations (e.g., $x=1/4$ or $1/3$) of transition metals like Fe or Cr into TMDs not only result in long-range ordered superstructures (e.g., $2a \times 2a$ or $\sqrt{3}a \times \sqrt{3}a$), which fold BZ and impose new periodic potentials, but also effectively tune the CDW phase[27-29]. Notably, the intercalation of ordered foreign metal atoms into NbSe₂ typically suppresses the CDW phase[30-33]. For example, Luo et al. reported that ordered Cu intercalation can disrupt the out-of-plane coherence and effectively suppresses the CDW phase in NbSe₂[30]. Wadge et al. reported that Ni intercalation can significantly alter the Fermi surface topology of NbSe₂ and introduce a new electron pocket at the Γ point of BZ to suppresses the CDW phase[31]. Recent studies suggest that structural ordering may not be a prerequisite for macroscopic quantum states[34]. For instance, Tian et al. reported that charge doping in disordered Fe intercalated NbSe₂ can stabilize a new $2a \times 2a$ CDW phase and suppress the intrinsic $3a \times 3a$ one, challenging the traditional view that disorder always exclusively suppresses CDW phase[18]. This finding highlights that the decoupling of charge doping from structural periodicity can lead to electronic instabilities. Tungsten (W), a non-magnetic heavy transition metal, offers an ideal platform to investigate above effects but without the complexity of magnetic ordering. Previously reported transport measurements on W-intercalated NbSe₂ reveal the non-monotonic evolution of the superconducting transition temperature, which indicates the interplay between doping and electronic correlations. However, the microscopic impact of W intercalation on the lattice dynamics and EPC in NbSe₂ remains elusive.

Specifically, understanding how the structural ordering and charge transfer introduced by intercalation of W atoms in NbSe₂ modulate the phonon self-energy requires identifying spectroscopic signatures. In this work, we investigate the lattice dynamics and ultrafast carrier relaxation in disorder-W-intercalated NbSe₂ by combining temperature-dependent Raman spectroscopy (TDRS) and transient absorption microscopy (TAM). Disorder-W intercalation in NbSe₂ induces a high-temperature $2a \times 2a$ CDW phase, evidenced by the unconventional background anharmonic scattering

and the thermal quenching of a zone-folded phonon mode from the BZ M point. Simultaneously, the intrinsic low-temperature $3a \times 3a$ CDW in NbSe₂ is suppressed, driven by a weakened EPC. Ultrafast dynamics analysis reveals a prolongation of quasiparticle relaxation times, corroborating the structural disorder and charge redistribution upon intercalation. These results demonstrate that charge transfer induced by disordered intercalation can selectively modulate the EPC, providing a new perspective on tailoring correlated states in layered materials.

2 Experimental

Sample Fabrication

W_xNbSe₂ single crystals with different intercalation ratios ($x = 0, 0.05$, and 0.16) in lateral sizes of ~ 2 mm (Figure S1a) were synthesized via the chemical vapor transport method[35]. Pristine NbSe₂, W_{0.05}NbSe₂, and W_{0.16}NbSe₂ nanoflakes were prepared via mechanical exfoliation. The exfoliated nanoflakes were promptly stored in a vacuum container, and most subsequent characterizations were conducted under vacuum conditions to avoid ambient oxidation. For microstructural and elemental structural analyses, the nanoflakes were directly exfoliated onto standard copper grids. Concurrently, to eliminate substrate-induced signal interference and ensure high optical transmittance for subsequent optical measurements, the nanoflakes were deposited onto double-side polished sapphire (0001) substrates.

Characterization

X-Ray Diffraction Measurement

The crystal structure and phase purity of the pristine NbSe₂, W_{0.05}NbSe₂ and W_{0.16}NbSe₂ bulk single crystals were characterized using an X-ray diffractometer (MiniFlex 600, Rigaku, Japan). The obtained diffraction patterns were utilized to verify the crystallinity and lattice parameters.

Atomic Force Microscopy Measurement

The micromorphologies of the mechanically exfoliated pristine NbSe₂, W_{0.05}NbSe₂ and W_{0.16}NbSe₂ nanoflakes were initially screened and located using optical microscopy (CaiKang, China). Subsequently, to evaluate the surface flatness and determine the sample thickness, atomic force microscopy (Agilent 5500, USA) was employed in tapping mode. All acquired topographic images and height profiles were processed and analyzed using the WSxM software.

Transmission Electron Microscopy Measurement

The mechanically exfoliated pristine NbSe₂, W_{0.05}NbSe₂ and W_{0.16}NbSe₂ nanoflakes were transferred onto copper grids. Subsequently, high-resolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns were acquired using a transmission electron microscope (JEOL 2100F, JEOL, Japan).

Raman Spectroscopy Measurement

Raman scattering measurements were performed on the pristine NbSe₂, W_{0.05}NbSe₂ and W_{0.16}NbSe₂ samples using an Invia Qontor Raman Spectrometer (Renishaw, UK) equipped with 532 nm and 633 nm excitation lasers and an 1800 lines/mm grating, yielding a spectral resolution of ~ 0.5 cm⁻¹. To prevent laser-induced heating effects and sample damage, the incident laser power was strictly maintained below 1

mW. Temperature-dependent measurements were conducted using a programmable stage (THMS600, Linkam, UK), where the temperature was regulated by a liquid nitrogen cooling system combined with an internal heater, achieving a stability of ± 0.1 K. The measurements were carried out in the temperature range from 80 K to 550 K with a heating step of 10 K. At each temperature setpoint, the samples were equilibrated for 5 minutes prior to measurement to ensure thermal stability.

Transient Absorption Microscopy Measurements

Femtosecond transient absorption (TA) measurements were carried out using a Helios spectrometer (Ultrafast Systems). The laser source was a Coherent Astrella Ti: sapphire amplifier system (800 nm, 35 fs, 1 kHz) seeded by a Coherent Vitesse oscillator. The 400 nm pump pulses were generated via an optical parametric amplification (OPA) system. For the probe beam, a small fraction of the fundamental 800 nm pulses was focused into a sapphire plate to generate a white-light supercontinuum, which served as the probe source. The time delay between the pump and probe pulses was controlled by a motorized optical delay line. The sample was excited by a narrowband pump pulse (400 nm), and the subsequent differential absorption ($\Delta A = -\log(I(\lambda)_{\text{pumped}}/I(\lambda)_{\text{unpumped}})$) was monitored by a broadband probe pulse. Both the pump and probe beams were focused to a spot in diameter of approximately 2 μm , and the applied pump fluence was maintained at 2.23 mJ/cm².

3 Results and discussion

High structural integrity and phase purity of the single crystals are essential prerequisites for the current study. To verify the as-grown crystal quality of W_xNbSe_2 , X-Ray Diffraction (XRD) measurements were performed. The XRD patterns of as-grown NbSe_2 (blue curve) and $\text{W}_{0.16}\text{NbSe}_2$ (red curve) crystals are shown in Figure 1a (Figure S1b for $\text{W}_{0.05}\text{NbSe}_2$). The XRD pattern of pristine NbSe_2 shows four Bragg peaks at 13.91° , 28.26° , 43.06° and 58.67° , which correspond to the (002), (004), (006) and (008) crystal planes, respectively. The corresponding peaks for $\text{W}_{0.16}\text{NbSe}_2$ ($\text{W}_{0.05}\text{NbSe}_2$) are located at 13.76° (13.87°), 28.08° (28.16°), 42.87° (42.98°) and 58.45° (58.55°), which indicates that all the Bragg peaks shift to lower angles with increasing W intercalation amounts. The (002) peak shifts from 13.91° for NbSe_2 to 13.76° for $\text{W}_{0.16}\text{NbSe}_2$ as highlighted in Figure 1b. Thus, the c-axis lattice parameter expands from $12.62 \pm 0.03 \text{ \AA}$ ($x=0$) to $12.70 \pm 0.05 \text{ \AA}$ ($x = 0.16$), confirming that W atoms occupy the interstitial sites within the vdW gap of NbSe_2 rather than undergoing substitutional doping[35].

To investigate the local structure and elemental composition of the samples, Transmission Electron Microscopy (TEM) and Energy Dispersive Spectroscopy (EDS) were carried out

on the exfoliated NbSe_2 , $\text{W}_{0.05}\text{NbSe}_2$ and $\text{W}_{0.16}\text{NbSe}_2$ nanoflakes onto copper grids. High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) was employed to characterize the atomic structures of these nanoflakes. The low magnification TEM images in Figure S2 show the flat and uniform surface across the examined regions. Figures 1c and 1d show the EDS spectra of NbSe_2 and $\text{W}_{0.16}\text{NbSe}_2$ (Figure S1c for $\text{W}_{0.05}\text{NbSe}_2$), confirming the presence of W in $\text{W}_{0.16}\text{NbSe}_2$ ($\text{W}_{0.05}\text{NbSe}_2$). The atomic percentages of Nb and Se in pristine NbSe_2 are calculated from the integrated intensities for each element peak to be 32.8% and 67.2% (indicating the calculated formula of $\text{NbSe}_{2.05}$), while those of W, Nb and Se in $\text{W}_{0.16}\text{NbSe}_2$ are 5.1%, 31.6% and 63.3%, respectively, corresponding to the calculated formula of $\text{W}_{0.16}\text{NbSe}_{2.01}$, which aligns well with the composition of NbSe_2 and $\text{W}_{0.16}\text{NbSe}_2$. Additionally, the atomic ratio of $\text{W}_{0.05}\text{NbSe}_2$ calculated from Figure S1c also aligns well with its theoretical stoichiometry. The corresponding EDS elemental mappings in Figure S2 demonstrate the uniform elemental distribution within each nanoflake, indicating the high quality of the samples.

Figures 1e and 1f display the Selected Area Electron Diffraction (SAED) patterns from the STEM images in Figure S2 for NbSe_2 and $\text{W}_{0.16}\text{NbSe}_2$, respectively. The hexagonal lattices of the parent NbSe_2 with lattice vector q_1 are represented with golden circles. The extracted intensity profiles (in Figure S3) show that the average full width at half maximum (FWHM) of the corresponding parent hexagonal lattice spots increases from 0.069 1/nm for pristine NbSe_2 to 0.095 1/nm for $\text{W}_{0.16}\text{NbSe}_2$, which indicates that W atom intercalation introduces structural disorder. Moreover, the SAED pattern of $\text{W}_{0.16}\text{NbSe}_2$ exhibits additional spots at half q_1 positions highlighted by blue circles, indicating the occurrence of a new $2a \times 2a$ superstructure. Similar features are also observed in the SAED pattern of $\text{W}_{0.05}\text{NbSe}_2$ (Figure S1d). However, no discernible differences in lattice fringes can be observed in the corresponding High-Resolution Transmission Electron Microscopy (HRTEM) images (Figure S4). Such discrepancy is probably attributed to the significantly lower diffraction intensity of the superstructure spots relative to the fundamental lattice spots (Figure 1f), causing them to be obscured by the dominant parent lattice signals during HRTEM imaging. The new $2a \times 2a$ superstructure might be associated with periodic structural modulations involving minute atomic displacements, reminiscent of the intrinsic CDW phase characteristics observed in 2H-NbSe_2 [36]. Its concurrent emergence at low intercalation ratios ($x = 0.05$ and 0.16 , Figures 1f and S1d) indicates that the new phase in W_xNbSe_2 differs from traditional intercalant-ordered superstructures[18,36]

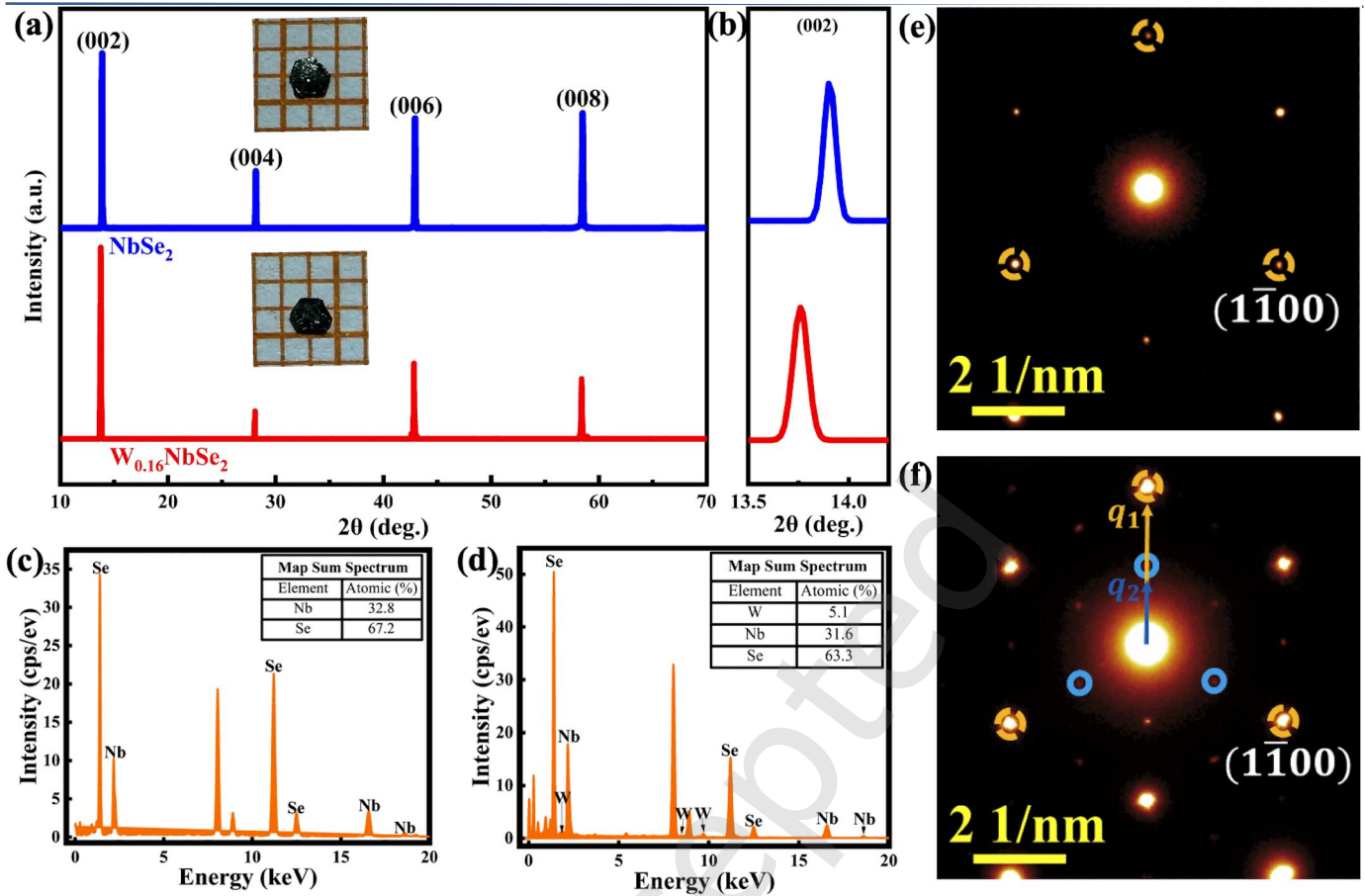


Figure 1. Characterization of NbSe₂ and W_{0.16}NbSe₂. (a) XRD patterns of NbSe₂ and W_{0.16}NbSe₂ single crystals, the insets display the photographs of the bulk single crystals; (b) Zoomed-in XRD patterns to highlight the shift of the (002) plane; EDS spectra of NbSe₂ (c) and W_{0.16}NbSe₂ (d) nanoflakes transferred onto copper grids, respectively; (e, f) SAED patterns of the NbSe₂ and W_{0.16}NbSe₂ nanoflakes.

Figures 2a and 2b show the Atomic Force Microscopy (AFM) images of large NbSe₂ and W_{0.16}NbSe₂ nanoflakes on double-side polished sapphire substrates with comparable thicknesses (120 nm VS 130 nm), respectively, which were used for the following optical measurements. The measured root-mean-square roughness (Rq) values are 0.29 nm and 0.26 nm, respectively, indicating the atomically flat surfaces and high quality of the nanoflakes.

To reveal the influence of W intercalation on the lattice vibrations, room-temperature Raman spectroscopy was performed. The 633 nm excitation induces a resonance enhancement of the A_{1g} mode, yielding Raman spectra with a relatively high signal-to-noise ratio[37]. However, the intensely enhanced A_{1g} signal almost completely masks the E_{2g} mode. Therefore, both 532 nm and 633 nm excitations were employed. Figure 2c presents the typical Raman spectra from NbSe₂ and W_{0.16}NbSe₂ nanoflakes, acquired at the blue spots indicated in Figures 2a and 2b. The peaks located at 228.6 cm⁻¹ and 237.3 cm⁻¹ in the blue spectrum (532 nm) of NbSe₂ are assigned to the A_{1g} and E_{2g} modes, respectively[38]. The broad feature centered at ~180 cm⁻¹ represents a CDW-related two-phonon mode (TPM), driven by second-order scattering of mixed intralayer and interlayer vibrations near the BZ edge[37,39]. The green spectrum (633 nm) mainly exhibits the resonance enhanced A_{1g} mode. The red spectrum (532 nm) of W_{0.16}NbSe₂ not only retains the A_{1g} , E_{2g} and TPM, but also exhibits a new broad incoherent scattering background at ~95 cm⁻¹ and a

distinct peak located at ~115 cm⁻¹. The TPM exhibits no obvious change upon intercalation. As shown in the zoomed-in regions in Figure 1d, the A_{1g} and E_{2g} modes in W_{0.16}NbSe₂ present blueshifts of 1.2 and 2.0 cm⁻¹ compared to those in NbSe₂, suggesting that the NbSe₂ layers are subjected to strong charge doping[35,38,42].

When foreign metal atoms are intercalated into TMDs, their spatial arrangement can be broadly categorized as either ordered superstructures or disordered distributions[45,46]. Here, the W intercalation ratios (0.05 and 0.16) are substantially lower than the specific stoichiometric ratios (e.g., $x = 1/4$ or $1/3$), which are typically required to stabilize long-range intercalant-ordered superlattices. If the observed $2a \times 2a$ superstructures originated from the ordered arrangement of W atoms, different intercalation concentrations would lead to distinct superlattices, which directly contradicts the experimental results that both W_{0.05}NbSe₂ and W_{0.16}NbSe₂ exhibit identical $2a \times 2a$ spots in their SAED patterns (Figures 1f and S1d). Combined with the absence of characteristic W-Se local vibrational modes (A_{1g} ~250 cm⁻¹, E_{2g} ~248 cm⁻¹) in the Raman spectra, the intercalated W atoms are not considered to form a long-range ordered superstructure[47]. Moreover, the broadened SAED spots of the parent NbSe₂ hexagonal lattice and the incoherent scattering observed in the Raman spectra indicate structural disorder. Therefore, the intercalated W atoms are proposed to randomly occupy the tetrahedral or octahedral sites within the vdW gaps of NbSe₂[18,27,48,49], as schematically shown in Figure 2e.

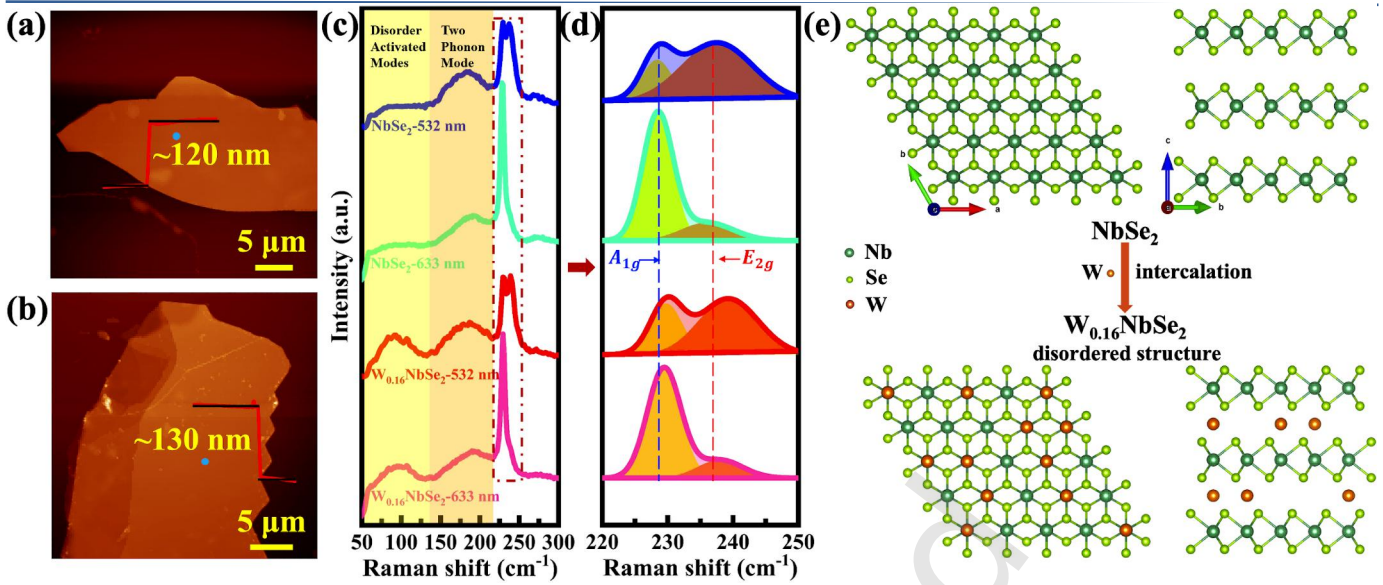


Figure 2. Raman-active modes in NbSe₂ and W_{0.16}NbSe₂. AFM images of the exfoliated NbSe₂ (a) and W_{0.16}NbSe₂ (b) nanoflakes on sapphire (0001); (c) typical Raman spectra in low frequency region from NbSe₂ and W_{0.16}NbSe₂ nanoflakes with different excitations and (d) zoomed-in highlighting the A_{1g} and E_{2g} modes of NbSe₂; (e) Schematic illustrations of the crystal structures for NbSe₂ and disorder-W-intercalated NbSe₂.

TDRS is a sensitive probe for tracking the thermal evolution of collective excitations and quantifying lattice anharmonicity across structural phase transitions[50,51]. To systematically investigate the effect of the intercalated W atoms on the phonon modes and on the CDW states of NbSe₂, TDRS measurements were performed in the temperature range from 80 to 550 K. Figure S5 shows the typical Raman spectra of NbSe₂ and W_{0.16}NbSe₂ nanoflakes measured at high (550 K), room (300 K) and low (80 K) temperatures with 532 nm and 633 nm excitations. At 550 K, the A_{1g} and E_{2g} modes belonging to NbSe₂ merged together for both samples. At 80 K, the Raman spectra from W_{0.16}NbSe₂ show four additional peaks, which are more obvious in polarized Raman spectra shown in Figure S6. The additional peak at ~95 cm⁻¹ is attributed to the broad incoherent scattering background[38,40,41], labeled as ISB. The additional peak at ~108 cm⁻¹ originates from the out-of-plane vibration mode of W atoms[38,42-44], and another peak is observed at ~156 cm⁻¹ which warrants further investigation; both peaks exhibit A_{1g} symmetry (Figure S6 and ESM Note 1) and are labeled as A₁ and A₂, respectively. The additional peak at ~193 cm⁻¹ is assigned to the intercalation-modulated two-phonon mode (MTPM)[32]. Additionally, the absence of crystalline W-Se vibrational modes further corroborates the disordered intercalation of W atoms[47].

Figure 3a displays the corresponding TDRS color maps from NbSe₂ (upper) and W_{0.16}NbSe₂ (lower) with the 633 nm excitation, from which the peak frequency and peak width (FWHM) were extracted via least-squares pseudo-Voigt deconvolution (a Gaussian-Lorentzian combination) and plotted in Figures 3b-e and S6. The fitting details are provided in the Supplementary Information (ESM Note 2 and 3). For W_{0.16}NbSe₂, the ISB becomes distinct sharpening and weakening as the temperature decreasing, and the A₁ mode becomes clear, which indicates a slight enhancement in the local structural order in W_{0.16}NbSe₂[52].

The temperature-dependence of the A_{1g} mode for pristine and intercalated samples was compared (Figure S7 and Table S2). The experimental data can be well fitted using Equations S8 and S11, revealing that the extracted EPC constant $\Gamma_0^{\text{e-ph}}$ decreases from 4.27 cm⁻¹ to 1.43 cm⁻¹, which indicates suppressed EPC at the BZ center, although the

decreased lattice anharmonicity constants require further investigation.

As shown in Figure 3b, the temperature-dependence of TPM in both pristine NbSe₂ and W_{0.16}NbSe₂ exhibits softening characteristics and deviates from a single critical exponent law, arising from the significant anharmonic interaction and EPC. Thus, the contribution from the phase transition must be taken into account. Based on the classic Cochran soft-mode theory, Scott derived the soft-mode evolution law for a one-dimensional harmonic oscillator under the mean-field approximation[53]. However, it fails to accurately describe the phase transition characteristics of 2H-NbSe₂. Wu et al. approximated the TPM of NbSe₂ in a Klemens-Landau model as the sum of the anharmonic thermal decay and the phase-transition-induced softening[54]. Accordingly, we obtained a good fit for TPM by incorporating the higher-order Balkanski phonon decay model (Equation S10).

$$\Delta\omega = A \left(1 + \frac{2}{e^x - 1} \right) + B \left(1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right) + E\omega_0'(T - T_c)^{\frac{1}{2}} \quad (1)$$

where E is the phase transition coupling parameter (related to EPC), ω_0' is the phonon frequency at 300 K and T_c is the phase transition temperature.

The TPM intrinsically involves a second-order scattering process of two phonons at wave vector $q \approx 2/3 \Gamma\text{-M}$ [55]. The BZ folding induced by the CDW formation maps off-center phonons ($q \approx 2/3 \Gamma\text{-M}$) to the BZ center, thereby freezing the TPM, which serves as a signature of the CDW phase transition[56,57]. For pristine NbSe₂, upon cooling towards T_{CDW}, the TPM shows a long-range softening, evidenced by a frequency redshift from ~209 cm⁻¹ at 550 K to ~158 cm⁻¹ at 80 K (Figure 3b red points). The experimental data can be well fitted using Equation 1 (represented by the red solid lines). The extracted fitting parameters are listed in Table S1. The parameters quantifying the self-energy renormalization recovery driven by EPC are determined to be E = 1.43 × 10⁻² K^{-0.5} and T_c = 35.6 K, which aligns well with the reported T_{CDW} of 33.5 K[39,54]. Moreover, the anharmonicity is dominated by the 3-ph decay process ($A \sim 18.88 \times 10^{-2} \text{ cm}^{-1}$) and causes a redshift, whereas the 4-ph contribution ($B \sim -2.56 \times 10^{-4} \text{ cm}^{-1}$) causes only a weak blueshift.

The MTPM in W_{0.16}NbSe₂ (pink in Figure 3b) exhibits a significantly suppressed softening amplitude, showing a frequency redshift from 208.2 cm⁻¹ at 550 K to 193.4 cm⁻¹ at

80 K, which indicates the suppression of the Kohn anomaly. The phase transition coupling parameter E and transition temperature T_c decrease to $1.09 \times 10^{-2} \text{ K}^{-0.5}$ and 11.8 K (in table S1), respectively, indicating the weakened EPC strength at the BZ wave vector $q \approx 2/3 \Gamma\text{-M}$ upon W intercalation, thereby effectively suppressing the intrinsic $3a \times 3a$ CDW fluctuations[18,19].

Figure 3c shows the temperature-dependence of the TPM peak width. Conventional phonon linewidths typically narrow upon cooling due to reduced thermal scattering. However, the TPM of NbSe₂ anomalously broadens upon cooling, which can be accounted for by the EPC-driven strong anharmonic interactions[55,56]. In contrast, the peak width of the MTPM in W_{0.16}NbSe₂ exhibits the opposite temperature dependence, which can be well fitted by Equation S11 ($\Gamma_0^{\text{e-ph}} \sim 1.19 \text{ cm}^{-1}$), indicating that the EPC-driven softening is weakened upon W intercalation, consistent with the above results.

The A_2 mode appears at $\sim 470 \text{ K}$ during cooling down from 550 K (Figure 3d) with a continuous intensity evolution (Figure 3a), suggesting that a potential second-order phase transition occurs. The aforementioned $2a \times 2a$ superstructure can induce BZ reconstruction and result in phonon modes folding from the M point to the central Γ point. According to the calculated phonon dispersion of NbSe₂ (Figure S8), the A_2 mode could be assigned to the folded phonon mode of the Σ_2 transverse optical branch at $\sim 154.4 \text{ cm}^{-1}$ at the M point[18,55,58]. This new $2a \times 2a$ structural phase transition can be attributed to the charge transfer induced by intercalated atoms. Tian et al. demonstrated that as electron doping exceeds threshold (0.625 e/cell) in Fe_xNbSe₂, charge transfer shifts Fermi level toward Van Hove singularity near M point to induce increase in density of states, which reshapes band structure and selectively enhances EPC at M point such that phonon softening drives $2a \times 2a$ CDW phase in NbSe₂[18]. Similarly, the intercalation of W into NbSe₂ induces charge transfer into the parent lattice. Wang et al. revealed that in W_xNbSe₂ the energy matching between W 5d and Se 4p orbitals facilitates electron transfer ($\sim 1.02 \text{ e/atom}$) into Se 4p orbitals, which enhances dielectric screening to inhibit Se-orbital polarization and suppresses original EPC channel essential for intrinsic $3a \times 3a$ phase[35]. Thus, the existence of the A_2 mode below 470 K implies that the $2a \times 2a$

superstructure may constitute a new CDW phase and exists stably within this temperature regime.

Such tuning mechanism appears to be governed primarily by disorder-intercalant-induced charge transfer and momentum-selective EPC, rather than by magnetism. The ordered intercalation of specific stoichiometric magnetic (e.g., Fe, Ni) or non-magnetic (e.g., Cu) metal atoms typically forms long-range ordered superlattices in NbSe₂, suppressing the intrinsic $3a \times 3a$ CDW through periodic potential scattering or Fermi surface alteration[30,31,42]. Conversely, disordered intercalated atoms (such as Fe or W) break these periodic constraints and act primarily as charge donors[18]. Regardless of the magnetic properties of the intercalated atoms, charge transfer reconstructs the electronic band structure and shifts the Fermi level toward the Van Hove singularity near the M point, which selectively enhances the momentum-dependent EPC at the M point and drives the emergence of a robust $2a \times 2a$ CDW phase.

The A_2 frequency exhibits a blueshift with temperature decreasing (Figure 3d red data), which can be fitted by Equation S8. Extracted parameters listed in table S2 reveal that the anharmonic scattering process is dominated by 4-ph process ($B \sim -1.07 \times 10^{-3} \text{ cm}^{-1}$) leading to blueshift (3-ph process ($A \sim 3.53 \times 10^{-2} \text{ cm}^{-1}$) causes redshift), which can be attributed to the specific lattice distortion induced by the $2a \times 2a$ CDW. The A_2 mode exhibits non-monotonic peak width evolution upon cooling (Figure 3d blue data), broadening from 550 K down to 200 K before narrowing towards 80 K, which reveals the interplay between thermal anharmonicity and EPC. The turning point at $\sim 200 \text{ K}$ indicates potential new electronic phase transition, which may be related to the $2a \times 2a$ CDW phase[18]. Such distinctive lattice dynamics provide direct microscopic evidence for previously identified $2a \times 2a$ superstructure being CDW phase.

The A_1 mode also exhibits a frequency blueshift with temperature decreasing (Figure 3e red data), which can be fitted by Equation S8. Extracted parameters listed in table S2 indicate the anharmonicity is dominated by 3-ph decay process ($A \sim -7.37 \times 10^{-2} \text{ cm}^{-1}$) causing blueshift (4-ph contribution ($B \sim 2.22 \times 10^{-4} \text{ cm}^{-1}$) leads to redshift). However, the peak width of A_1 mode narrows with temperature decreasing (Figure 3e blue data), which cannot be well fitted by Equation S11, warranting further investigation into its physical origin.

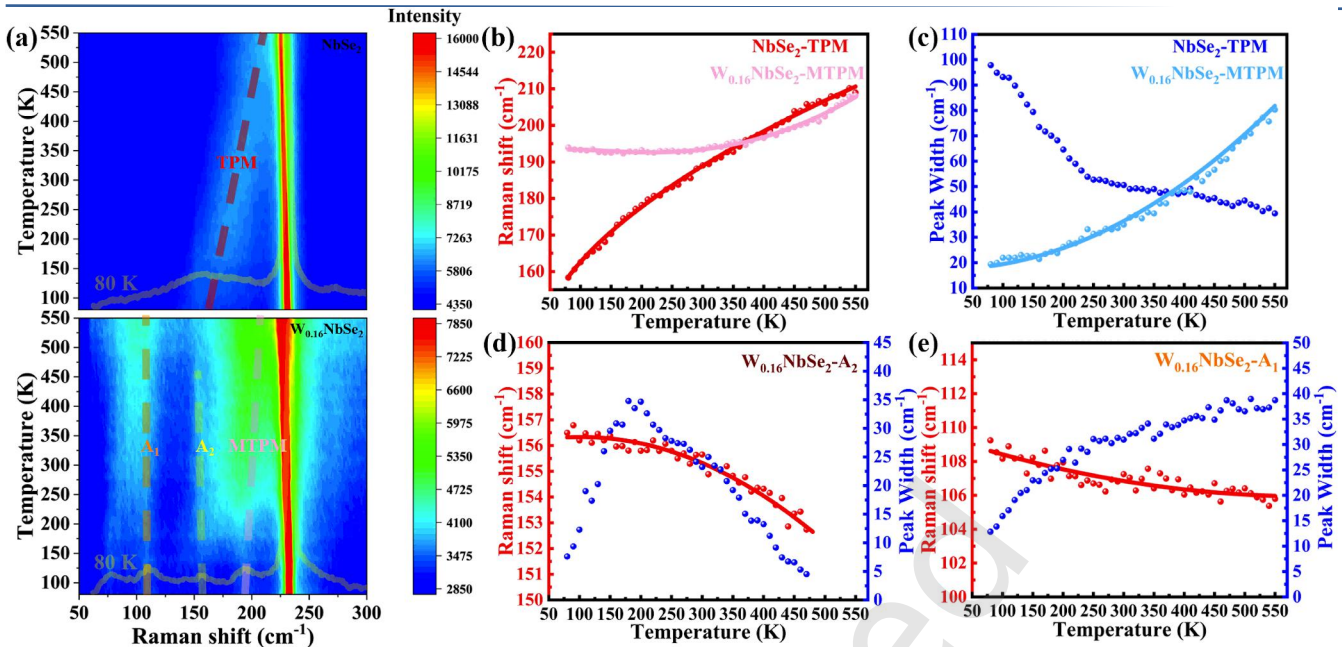


Figure 3. TDRS of NbSe₂ and W_{0.16}NbSe₂. (a) unpolarized TDRS color maps (80–550 K) of mechanically exfoliated NbSe₂ and W_{0.16}NbSe₂ nanoflakes with 633 nm excitation, with the Raman spectra at 80 K overlaid, the dashed lines trace the evolution of the TPM, A₁, A₂ and MTPM; temperature dependence of the peak frequency (b) and peak width (c) of the TPM in pristine NbSe₂ and the MTPM in W_{0.16}NbSe₂; temperature dependence of the peak frequency and peak width of the newly emerged A₂ (d) and A₁ (e) modes in W_{0.16}NbSe₂.

To further verify the W-intercalation-modulated lattice dynamics, ultrafast TAM was employed to investigate photocarrier dynamics in the pristine NbSe₂, W_{0.05}NbSe₂ and W_{0.16}NbSe₂ nanoflakes (Figures 4 and S9). Figures 4a and 4b display the 2D colormaps of ΔA plotted as a function of both probe wavelength and delay time for pristine NbSe₂ and W_{0.16}NbSe₂, respectively. The TA spectra reveal distinct features: a negative signal within 480–550 nm and a positive signal spanning 550–730 nm. The negative signal corresponds to ground state bleaching, resulting from the state-filling effect and Pauli blocking of photoexcited carriers in the conduction band, which inhibit the subsequent interband absorption of probe photons[59,60]. The positive signal arises from photoinduced absorption, where photogenerated free carriers absorb probe photons via intraband transitions, thereby opening a new absorption channel[60,61].

The kinetic traces of the spectral feature (~ 650 nm, positive signal) were extracted for quantitative analysis. As shown in Figures 4c, 4d and S9b, these dynamic curves can be well fitted by a biexponential decay function[62,63]:

$$\Delta A = A \exp\left(-\frac{t}{\tau_1}\right) + B \exp\left(-\frac{t}{\tau_2}\right) \quad (2)$$

where A and B represent the proportional coefficients of different components, t is the delay time between the pump light and the probe light, and τ_1 and τ_2 are the time constants corresponding to two different relaxation

processes. Photogenerated carriers are initially thermalized to a quasi-equilibrium state by electron-electron scattering on a femtosecond time scale[64,65], which is too fast to be detected by TAM. Subsequently, hot carriers dissipate energy to the lattice through electron-phonon scattering on a picosecond time scale (the fast relaxation process), leading to carrier cooling and a rise in lattice temperature[66–68]. Then, abundant non-equilibrium optical phonons accumulated within the lattice decay into acoustic phonons through phonon-phonon scattering to restore thermal equilibrium (the slow relaxation process), restricted by lattice anharmonicity and energy-momentum conservation[60,69,70].

The extracted parameters demonstrate that both τ_1 and τ_2 increase with the W atom intercalation content. Specifically, for pristine NbSe₂, W_{0.05}NbSe₂ and W_{0.16}NbSe₂, τ_1 increases from 0.49 ps to 1.04 ps and 4.80 ps, while τ_2 extends from 483.5 ps to 523.5 ps and 835.1 ps, as shown in Figure S9c. The increase in τ_1 signifies an inhibited electron-phonon cooling rate, while the prolonged τ_2 indicates hindered macroscopic thermal dissipation, reflecting the structural disorder and charge redistribution introduced by W intercalation. The TAM results confirm the enhanced free carrier density due to the charge transfer from intercalated W atoms to the NbSe₂ lattice and provide another direct evidence for the formation of $2a \times 2a$ CDW in W_xNbSe₂[60,71].

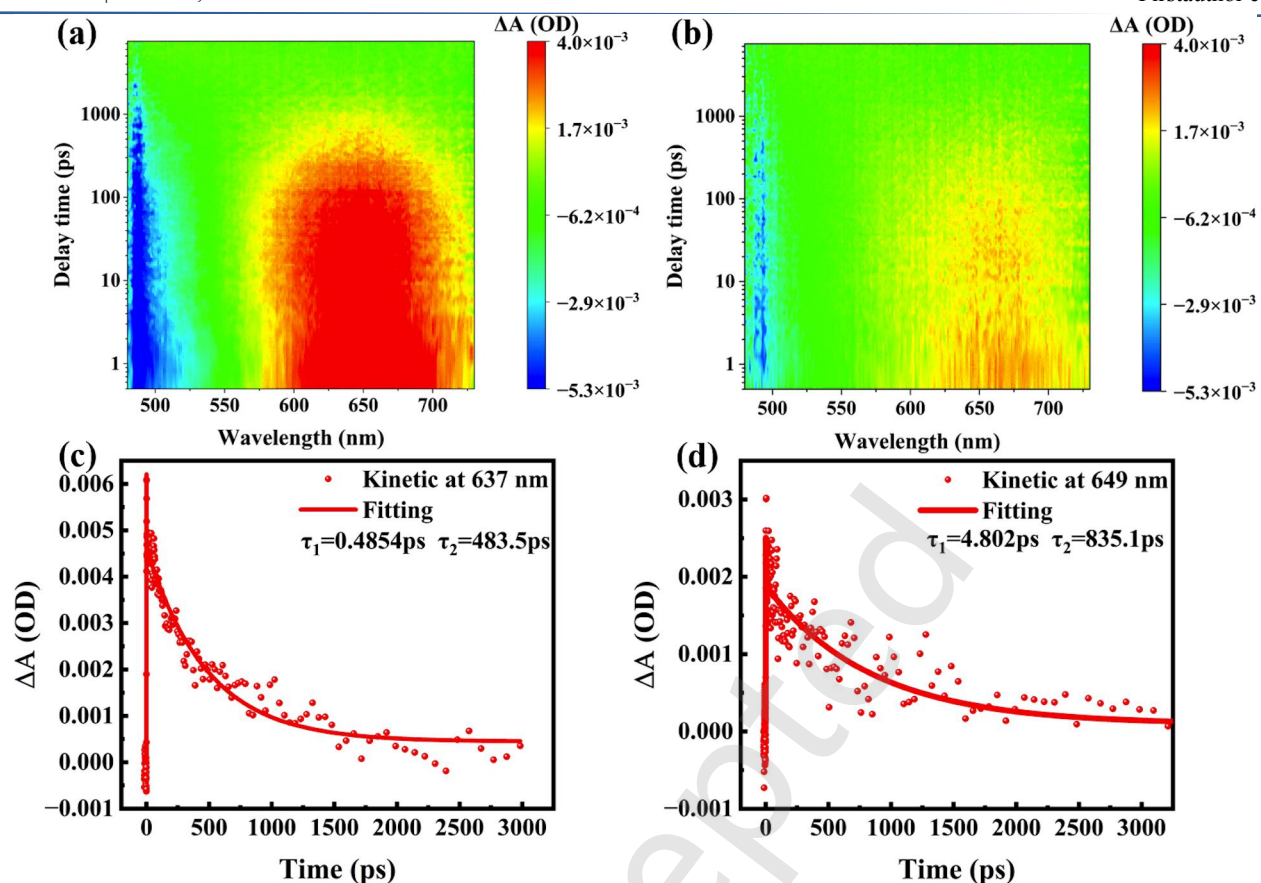


Figure 4. Ultrafast carrier dynamics in NbSe₂ and W_{0.16}NbSe₂. The two-dimensional transient absorption spectra of the original NbSe₂ (a) and W_{0.16}NbSe₂ (b) with the detection wavelength and pump-detection delay are plotted. For the carrier relaxation kinetics probed at 637 nm for pristine NbSe₂ (c) and 649 nm for W_{0.16}NbSe₂ (d), the solid red lines represent biexponential fitting results with the extracted time constants (τ_1 , τ_2) labeled in each panel; all measurements were performed with a 400 nm pump wavelength at a fluence of 2.23 mJ/cm².

4 Conclusions

In summary, we demonstrate that disordered W intercalation in NbSe₂ induces a new high-temperature 2×2 CDW phase, distinct from superstructures driven by atomic ordering. TDRS analysis reveals the unconventional background anharmonic scattering and thermal quenching of zone-folded phonon modes, consistent with the characteristics of a high-temperature CDW phase transition. Intercalant-induced charge transfer selectively enhances the EPC at the BZ M point, directly driving this lattice instability. Ultrafast dynamics results further corroborate this mechanism: the observed prolongation of carrier relaxation timescales confirms the structural disorder and charge transfer upon intercalation. These results indicate that charge transfer induced by disordered intercalation selectively modulates the EPC within the system, offering valuable insights for investigating and engineering EPC mechanisms and many-body interactions in correlated materials.

Furthermore, future investigations are required to fully establish the physical mechanisms of such CDW state, such as cross-sectional STEM on the distribution of W atoms in NbSe₂, temperature-dependent electrical transport measurements on the samples with continuous-gradient W concentration or with varying thickness for determining the CDW transition temperature, and so on.

Electronic Supplementary Material: Supplementary material (Section S1: Supplementary figures; Section S2: Supplementary Notes, including Polarization Dependence

and Raman Selection Rules of NbSe₂, Anharmonic Decay Models for Frequency Shift, and Peak width Broadening Mechanisms; Section S3: Supplementary Tables) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909127>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

Fangyan Ang: Conceptualization, Methodology, Data curation, Writing - original draft. Fengyu Li: Data curation, Formal analysis, Investigation. Jin Wang: Investigation, Validation. Zhiyi Liu: Validation, Resources. Bingce Liu: Software, Visualization. Wen Wan: Investigation, Resources. Yingwei Wang: Formal analysis. Haipeng Xie: Methodology. Han

Huang: Conceptualization, Funding acquisition, Supervision, Writing - review & editing. Jun He: Project administration, Supervision, Writing - review & editing. All the authors have approved the final manuscript.

Informed consent

Not applicable.

Ethics statement

Not applicable.

Use of AI statement

None.

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Electronic Supplementary Material

Raman evidence for high-temperature $2a \times 2a$ charge density wave in disorder-W-intercalated NbSe₂

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Section S1. Supplementary figures

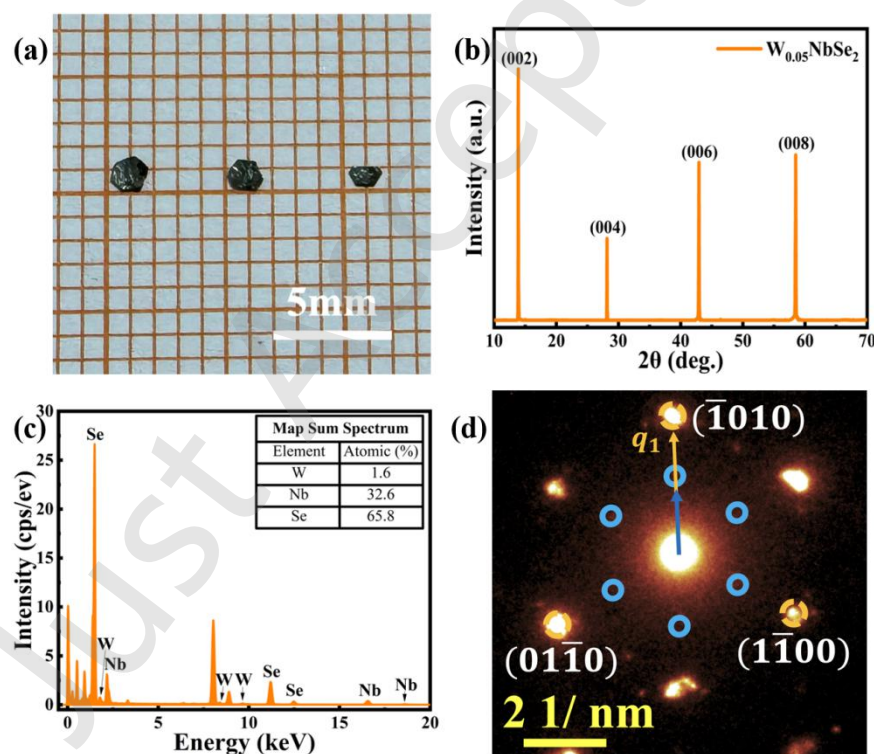


Figure S1. Characterization of $W_{0.05}NbSe_2$. (a) Optical photographs of the W_xNbSe_2 ($x = 0, 0.05$ and 0.16) single crystals synthesized via the CVT method; (b) XRD patterns of the $W_{0.05}NbSe_2$ single crystals; (c) EDS area spectra and (d) SAED pattern of the $W_{0.05}NbSe_2$ nanoflake transferred onto copper grids.

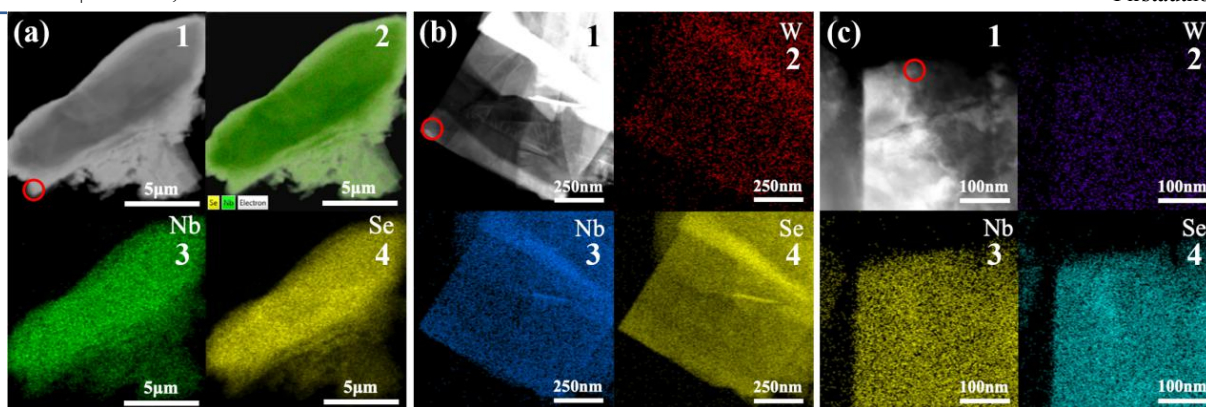


Figure S2. Morphology and elemental distribution of the pristine NbSe₂, W_{0.05}NbSe₂ and W_{0.16}NbSe₂ nanoflakes. Low-magnification HAADF-STEM images and the corresponding EDS elemental mappings of Nb, Se and W for the pristine NbSe₂ (a), W_{0.05}NbSe₂ (b) and W_{0.16}NbSe₂ (c) nanoflakes.

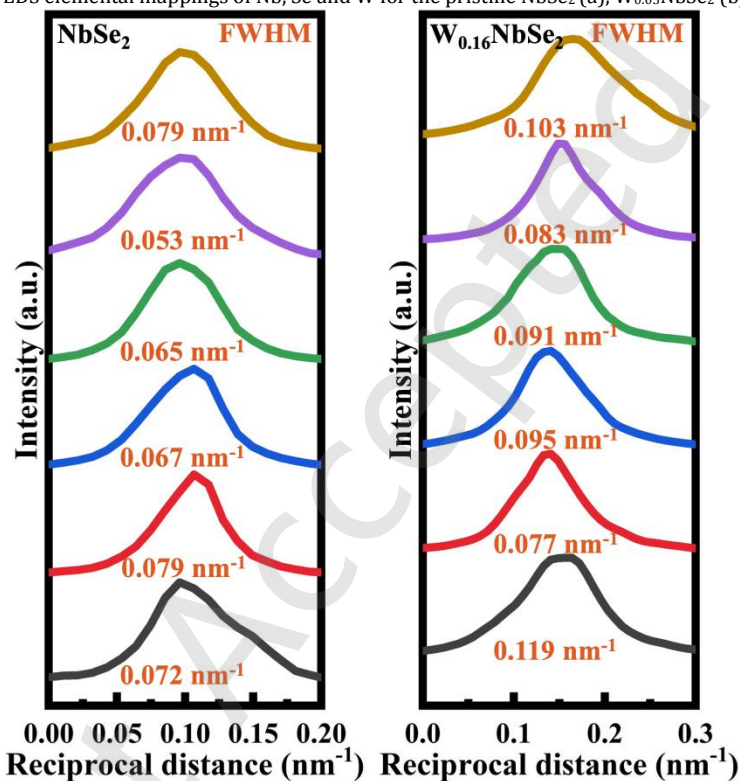


Figure S3. Normalized intensity profiles extracted from the main hexagonal lattice diffraction spots in the selected area electron diffraction (SAED) patterns of pristine NbSe₂ (left) and W_{0.16}NbSe₂ (right). The corresponding full width at half maximum (FWHM) values are labeled in orange for each profile (unit: nm⁻¹).

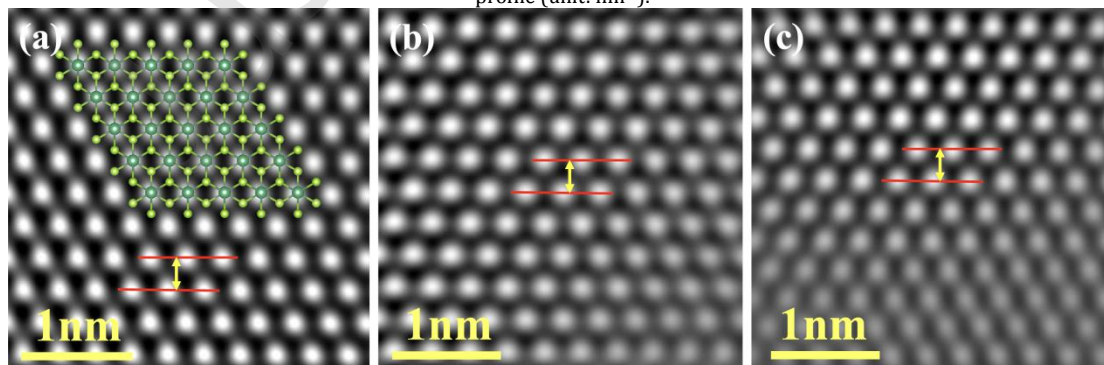


Figure S4. HRTEM characterization. HRTEM images of the pristine NbSe₂ (a), W_{0.05}NbSe₂ (b) and W_{0.16}NbSe₂ (c) nanoflakes, the parallel red lines in each panel indicate the in-plane lattice spacing.

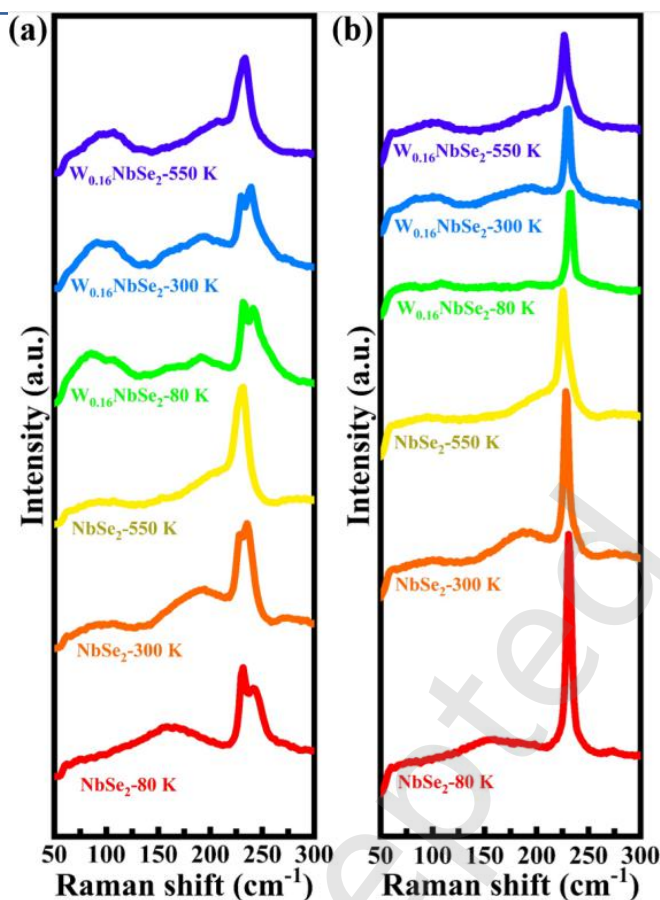


Figure S5. Unpolarized Raman spectra of NbSe₂ and W_{0.16}NbSe₂ nanosheets. Spectra measured at specific temperatures (80 K, 300 K and 550 K) under 532 nm (a) and 633 nm (b) excitation.

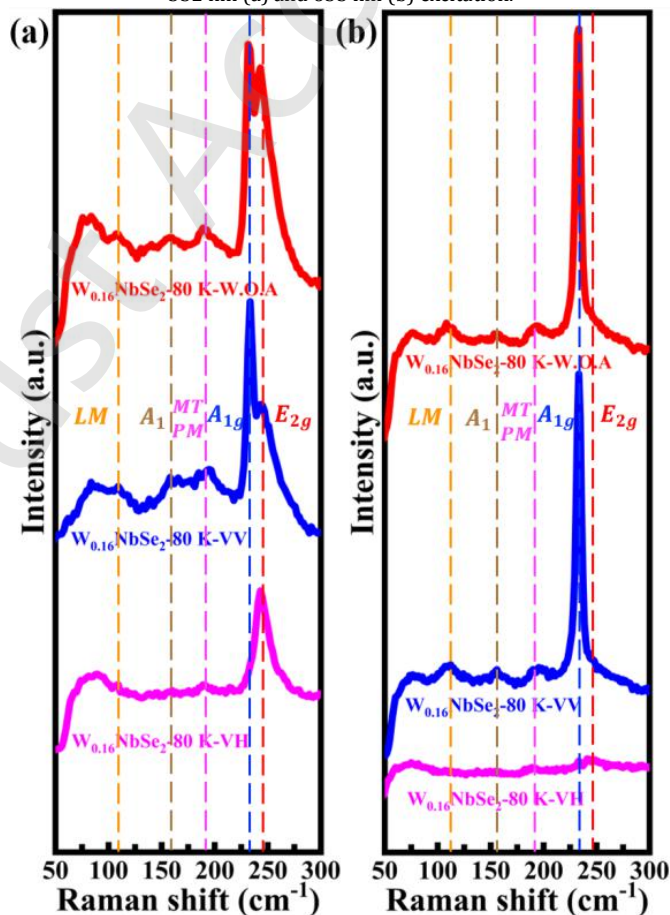


Figure S6. Polarized Raman spectra of W_{0.16}NbSe₂ measured at 80 K. Spectra acquired under 532 nm (a) and 633 nm (b) excitation in unpolarized (without analyzer, W.O.A), parallel-polarization (VV) and cross-polarization (VH) configurations, the dashed lines indicate the peak positions of the A₁, A₂, Modified Two-Phonon Mode (MTPM), A_{1g} and E_{2g} modes.

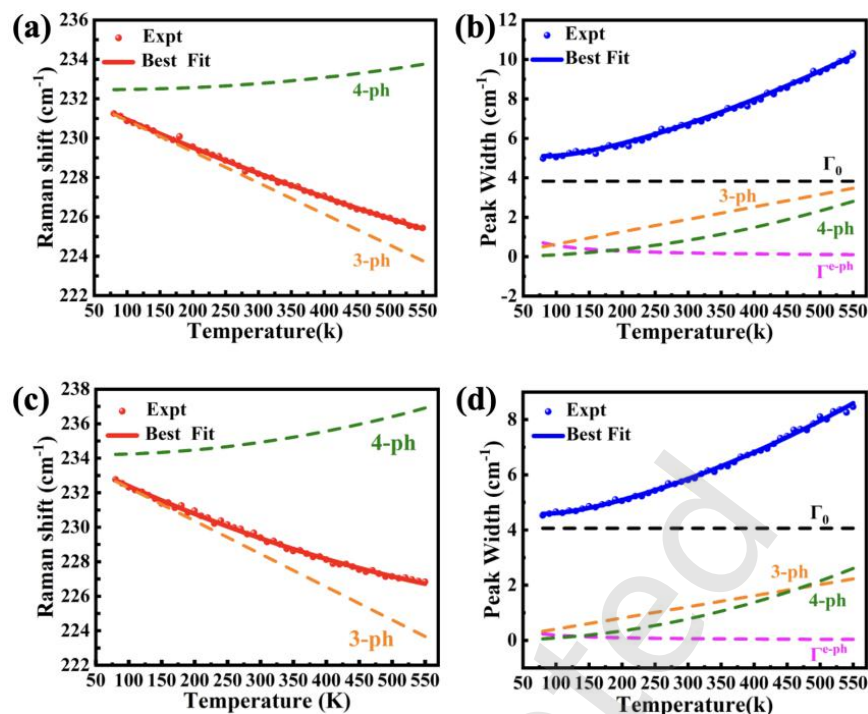


Figure S7. Temperature-dependent evolution and fitting of the A_{1g} mode. Raman shift and peak width as a function of temperature for pristine NbSe_2 (a, b) and $\text{W}_{0.16}\text{NbSe}_2$ (c, d), the solid lines represent the comprehensive fitting curves, while the dashed lines denote the decoupled theoretical contributions from multi-phonon scattering, static defect scattering, and electron-phonon coupling.

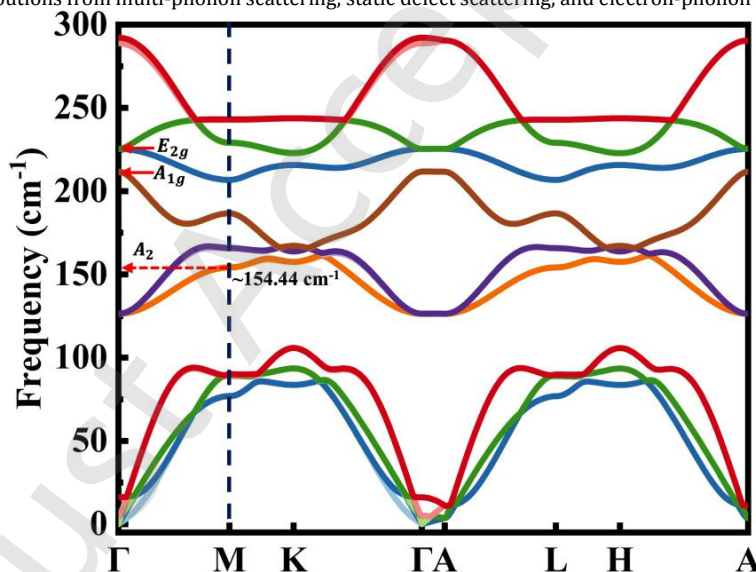


Figure S8. Calculated phonon dispersion curve of pristine NbSe_2 . The interatomic forces were evaluated using the MatterSim machine learning interatomic potential, and the phonon frequencies were subsequently calculated using Phonopy as implemented in the PhononBench platform[1]. The A_{1g} , E_{2g} and A_2 phonon modes are labeled.

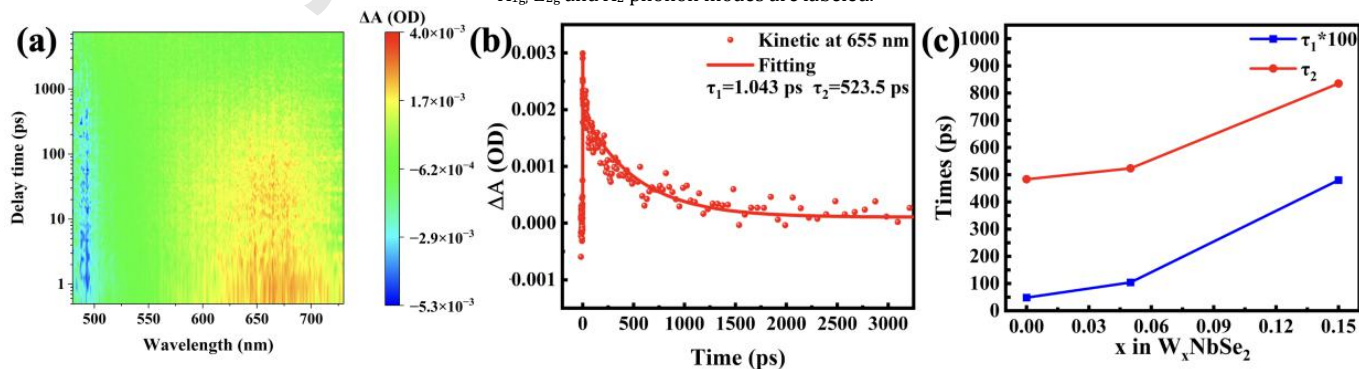


Figure S9. (a) 2D transient absorption spectra of $\text{W}_{0.05}\text{NbSe}_2$ plotted as a function of probe wavelength and pump-probe delay. (b) Carrier dynamics of $\text{W}_{0.05}\text{NbSe}_2$ probed at 655 nm, along with the corresponding fitted relaxation time constants. (c) The evolution of the carrier relaxation time constant of W_xNbSe_2 with intercalation concentration.

Section S2. Supplementary Notes

Note 1: Polarization Dependence and Raman Selection Rules of NbSe₂.

The theoretically observable Raman scattering intensity (I) for a given intrinsic lattice vibration is fundamentally determined by the polarization vector of the incident light (e_i), the polarization vector of the scattered light (e_s), and the Raman tensor (R) associated with the mode. This dependence is dictated by the universal formula:

$$I \propto (e_s^T \cdot R \cdot e_i)^2 \quad \#(1)$$

In the parallel-polarization configuration, the incident and scattered polarization vectors remain collinear. Defining the in-plane azimuthal angle θ as the angle between the incident polarization direction and a specific crystallographic axis, the vectors are given by $e_i = e_s = (\cos\theta, \sin\theta, 0)$. Based on group theory and crystal symmetry analysis, the Raman tensors for the primary Raman-active A_{1g} and E_{2g} modes of NbSe₂ can be respectively expressed as:

$$R_{A_{1g}} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \quad \#(2)$$

$$R_{E_{2g}} = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & 0 \\ 0 & 0 & b \end{pmatrix}, \begin{pmatrix} 0 & -c & 0 \\ -c & 0 & 0 \\ 0 & 0 & b \end{pmatrix} \quad \#(3)$$

By substituting the parallel polarization vectors into Equation S1, the Raman scattering intensities for the fully symmetric A_{1g} and the doubly degenerate in-plane E_{2g} modes are respectively deduced as:

$$I(A_{1g}) \propto \left((\cos\theta, \sin\theta, 0)^T \cdot \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \cdot (\cos\theta, \sin\theta, 0) \right)^2 = |a^2| \quad \#(4)$$

$$I(E_{2g}) \propto |c \cos^2\theta - c \sin^2\theta|^2 + |-2c \sin\theta \cos\theta| = |c^2| \quad \#(5)$$

These derivations explicitly demonstrate that under a parallel-polarization backscattering geometry, the polarized Raman intensities of both the A_{1g} and E_{2g} modes in pristine NbSe₂ are strictly independent of the in-plane azimuthal angle θ .

In the cross-polarization configuration, the polarization direction of the scattered light is strictly orthogonal to that of the incident light. Accordingly, the incident and scattered polarization vectors can be defined as $e_i = (\cos\theta, \sin\theta, 0)^T$ and $e_s = (-\sin\theta, \cos\theta, 0)^T$, respectively. By substituting these orthogonal polarization vectors into the Raman scattering intensity Equation S1, the theoretical scattering intensity for the A_{1g} mode is derived as:

$$I(A_{1g}) \propto \left((\cos\theta, \sin\theta, 0)^T \cdot \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix} \cdot (-\sin\theta, \cos\theta, 0) \right)^2 = 0 \quad \#(6)$$

This demonstrates that the phonon mode undergoes complete theoretical extinction under the cross-polarization configuration, with its Raman activity being completely suppressed.

For the E_{2g} mode, superimposing the orthogonal scattering contributions from its two tensor components yields:

$$I(E_{2g}) \propto |c \cos^2\theta - c (-\sin^2\theta)|^2 + |-2c \sin\theta \cos\theta|^2 = |c^2| \quad \#(7)$$

Unlike the A_{1g} mode, the Raman activity of the E_{2g} mode is not completely suppressed, yet its polarized Raman intensity remains independent of the in-plane azimuthal angle θ .

Note 2: Anharmonic Decay Models for Frequency Shift.

Generally, variations in vibrational frequency can be attributed to three contributions: thermal expansion ($\Delta\omega_V$), thermal expansion mismatch between the sample and the substrate ($\Delta\omega_D$), and anharmonic phonon-phonon coupling ($\Delta\omega_A$) [2-4]. The total frequency shift can be described as:

$$\Delta\omega = \omega(T) - \omega_0 = \Delta\omega_V + \Delta\omega_D + \Delta\omega_A \quad \#(8)$$

where ω_0 represents the phonon mode frequency at 0 K.

Compared to epitaxially grown films, mechanically exfoliated nanoflakes demonstrate negligible substrate interaction owing to the loose interface inherent in their van der Waals assembly[5,6]. Consequently, the $\Delta\omega_D$ term accounting for the thermal expansion mismatch between the sample and the substrate is neglected in this study.

The term $\Delta\omega_V$ is described by the following equation[7]:

$$\Delta\omega_V = \omega_0 \left(\exp \left(-n\gamma \int_0^T \alpha(T) dT \right) - 1 \right) \quad \#(9)$$

where n is the degeneracy of the optical phonon ($n(A_{1g})=1$; $n(E_{2g})=2$), $\alpha(T)$ is the thermal expansion coefficient ($6.6 \times 10^{-6} \text{ K}^{-1}$)[8], and γ is the Grüneisen parameter of the phonon. Based on relevant reports and order-of-magnitude calculations, $\Delta\omega_V$ is negligible within the temperature range of 80–550 K.

Experimentally, the Klemens anharmonic model, which considers only three-phonon scattering processes, failed to yield a satisfactory fit (see comparison in SI). Consequently, the Balkanski model was adopted to describe the anharmonic contribution, where $\Delta\omega_A$ is modeled by multi-phonon scattering involving both three-phonon and four-phonon decay processes[9,10]:

$$\Delta\omega_A = A \left(1 + \frac{2}{e^x - 1} \right) + B \left(1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right) \quad \#(10)$$

Here, A and B are the anharmonic constants for three-phonon and four-phonon processes, respectively, with $x = \hbar\omega_0/2k_B T$ and $y = \hbar\omega_0/3k_B T$.

Note 3: Peak width Broadening Mechanisms.

In an ideal defect-free crystal, phonon-phonon interactions arising from lattice anharmonicity constitute the dominant mechanism for Raman phonon decay. However, in charge density wave systems, electron-phonon coupling effects near the Fermi surface become non-negligible, further renormalizing the phonon self-energy and significantly modulating phonon decay dynamics. Therefore, the peak width broadening can be described as the sum of the residual peak width at 0 K, the electron-phonon coupling term, and the phonon interaction term[11,12]:

$$\Gamma(T) = \Gamma_0 + \Gamma^{\text{e-ph}}(T) + \Gamma^{\text{anh}}(T) \quad (11)$$

Γ_0 originates primarily from temperature-independent scattering mechanisms, including static scattering caused by lattice defects and impurities, as well as instrumental broadening due to the finite resolution of the spectrometer. $\Gamma^{\text{e-ph}}(T)$ and $\Gamma^{\text{anh}}(T)$ represent the contributions from electron-phonon coupling and phonon-phonon interactions, respectively.

2H-NbSe₂, as a layered metallic system where charge density waves coexist with superconductivity, exhibits strong electron-phonon coupling. This pronounced interaction profoundly influences the lattice dynamics, modulating the phonon lifetime of Raman vibrational modes. In NbSe₂, electron scattering channels near the Fermi surface play a pivotal role in phonon decay. The contribution can be formulated as the following simplified model[11,13]:

$$\Gamma^{\text{e-ph}}(T) = \Gamma_0^{\text{e-ph}} \left(\frac{1}{e^{-x} + 1} - \frac{1}{e^x + 1} \right) \quad (12)$$

$\Gamma_0^{\text{e-ph}}$ represents the phonon mode peak width at 0 K. The peak width contribution $\Gamma_0^{\text{e-ph}}$ induced by electron-phonon coupling depends directly on the electron occupation probability of states above and below the Fermi level. As the temperature rises, the thermal smearing of the Fermi surface leads to a decrease in occupied states below EF and an increase above it, thereby suppressing effective scattering channels and causing this peak width term to gradually decrease with increasing temperature. The anharmonic phonon interaction term can be expressed as[4,10,13]:

$$\Gamma^{\text{anh}}(T) = C \left(1 + \frac{2}{e^x - 1} \right) + D \left(1 + \frac{3}{e^y - 1} + \frac{3}{(e^y - 1)^2} \right) \quad (13)$$

In this formula, C and D are the anharmonic constants for three-phonon (3-ph) and four-phonon (4-ph) processes contributing to the peak width, respectively.

Section S3. Supplementary Tables

Table S1. Fitting parameters for the temperature dependence of the two-phonon soft mode peak position in W_xNbSe₂ nanosheets (x = 0 and 0.16)

x (W ratios)	mode	A (cm ⁻¹)	B (cm ⁻¹)	ω_0 (cm ⁻¹)	E (K ^{-0.5})	ω'_0 (cm ⁻¹)	T _c (K)
0	TPM	18.88×10^{-2}	-2.56×10^{-4}	138.65	1.42×10^{-2}	189.02	35.65
0.16	MTPM	-167.15×10^{-2}	127.21×10^{-4}	187.22	1.09×10^{-2}	193.39	11.84

Table S2. Fitting parameters for the temperature dependence of Raman peak position and peak width in W_xNbSe₂ nanosheets (x = 0 and 0.16)

x (W ratios)	mode	A (cm ⁻¹)	B (cm ⁻¹)	ω_0 (cm ⁻¹)	Γ_0 (cm ⁻¹)	$\Gamma_0^{\text{e-ph}}$ (cm ⁻¹)	C (cm ⁻¹)	D (cm ⁻¹)
0	A _{1g}	-20.29×10^{-2}	5.59×10^{-4}	232.49	3.83	4.27	8.43×10^{-2}	9.66×10^{-4}
0.16	A ₁	-7.37×10^{-2}	2.22×10^{-4}	109.49	—	—	—	—
	A ₂	3.53×10^{-2}	-1.07×10^{-3}	156.19	—	—	—	—
	A _{1g}	-24.92×10^{-2}	10.81×10^{-2}	234.21	4.07	1.43	5.45×10^{-2}	9.09×10^{-4}

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