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ABSTRACT

Layered materials enable the assembly of a new class of heterostructures where lattice-matching is no longer a requirement. Interfaces in these heterostructures therefore become a fertile ground for unexplored physics as dissimilar phenomena can be coupled via proximity effects. In this article, we identify an unexpected photoluminescence (PL) peak when MoSe_2 interacts with TiSe_2 . A series of temperature-dependent and spatially resolved PL measurements reveal that this peak is unique to the TiSe_2 - MoSe_2 interface, is higher in energy compared to the neutral exciton, and exhibits exciton-like characteristics. The feature disappears at the TiSe_2 charge density wave transition, suggesting that the density wave plays an important role in the formation of this new exciton. We present several plausible scenarios regarding the origin of this peak that individually capture some aspects of our observations but cannot fully explain this feature. These results therefore represent a fresh challenge for the theoretical community and provide a fascinating way to engineer excitons through interactions with charge density waves.

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I. INTRODUCTION

Two-dimensional (2D) material interfaces in van der Waals (vdW) heterostructures provide a fascinating playground to explore proximity effects.¹ The relaxation of lattice constraints on heterostructure assembly allows for the arbitrary stacking of 2D materials.² These interfaces may, in some cases, support emergent states absent from the parent compounds, with superconductivity in twisted bilayer graphene and moiré excitons in transition metal dichalcogenides (TMDs) serving as remarkable examples.^{3–6} Many studies of vdW heterostructures incorporate semiconducting TMDs

as an active component. This commonality is due to the availability of high-quality samples, well-established exfoliation procedures,^{7,8} and the existence of tightly bound 2D excitons.⁹

The zoology of excitons in monolayer (ML) semiconductors is vast: Neutral (X^0) and charged excitons or trions (X^- or X^+),^{9–12} neutral and charged biexcitons,^{13–16} and dark exciton states^{17–20} have all been observed and exhaustively studied in semiconducting TMDs. The 2D nature of TMD excitons also renders them highly sensitive to the local dielectric environment,^{21–26} allowing for a remote, contact-free probe of interface characteristics in vdW

heterostructures. For instance, semiconductor hetero-bilayer and homo-bilayer heterostructures exhibit new photoluminescence (PL) emission peaks from interlayer excitons and splitting of exciton peaks due to the moiré potential.^{5,27–30} Proximity effects between 2D magnets and semiconductors lead to large valley splittings,^{31,32} and magnetic manipulation of exciton PL energy, intensity, and selection rules.^{1,33–35} Exotic correlated insulating states such as Wigner crystals and Mott insulators in twisted TMD semiconductor heterostructures are also observable in PL spectra.^{36–38} However, there have been no studies exploring the impact of similar electron correlated phases such as charge density waves (CDWs)³⁹ on PL in vdW heterostructures.

Here, we investigate optical signatures of interlayer coupling between the semiconductor MoSe₂ and the putative excitonic insulator 1T-TiSe₂,^{40–43} which hosts a commensurate $2 \times 2 \times 2$ CDW state below 200 K. We find that the CDW alters the manifold of optically active excitons at the TiSe₂–MoSe₂ interface, which results in a new PL peak above X⁰. This feature, referred to as H1, appears in the MoSe₂ PL spectrum with a linewidth comparable to X⁰. While lower-energy PL sidebands are relatively common in TMDs due to phonon replicas and exciton localization,^{44–48} these observations are the first such detection of a higher-energy PL sideband. Detailed temperature-dependent, power-dependent, and spatially resolved

PL measurements on multiple heterostructures demonstrate that H1 has an origin consistent with a native exciton state rather than a localized exciton or defect state. However, H1 disappears at the TiSe₂ CDW temperature, which suggests that these two phenomena are closely linked. We have identified multiple plausible scenarios and discuss them in detail, although none are able to explain all aspects of our observations. Interactions between excitons and CDWs provide a fresh challenge to the theoretical community and a novel method for engineering excitons in 2D materials.

II. RESULTS

A. Optical characterization of vdW heterostructures

The optical microscope images of two TiSe₂–MoSe₂ vdW heterostructures termed sample 1 and sample 2, respectively, are presented in Figs. 1(a) and 1(b). These samples are assembled by a modified viscoelastic method⁴⁹ that incorporates atomic force microscope (AFM) cleaning.⁵⁰ The black dashed line outlines the ML–MoSe₂ flake in each sample. Representative low-temperature (5 K) PL spectra taken on (black) and off (red) the interface are shown in Figs. 1(c) and 1(d) for the two samples. Emission from the MoSe₂ X⁻ (≈ 1.62 eV) and X⁰ (≈ 1.65 eV) states agrees with prior observations in both energy and linewidth.^{11,18,51–53} The interface PL

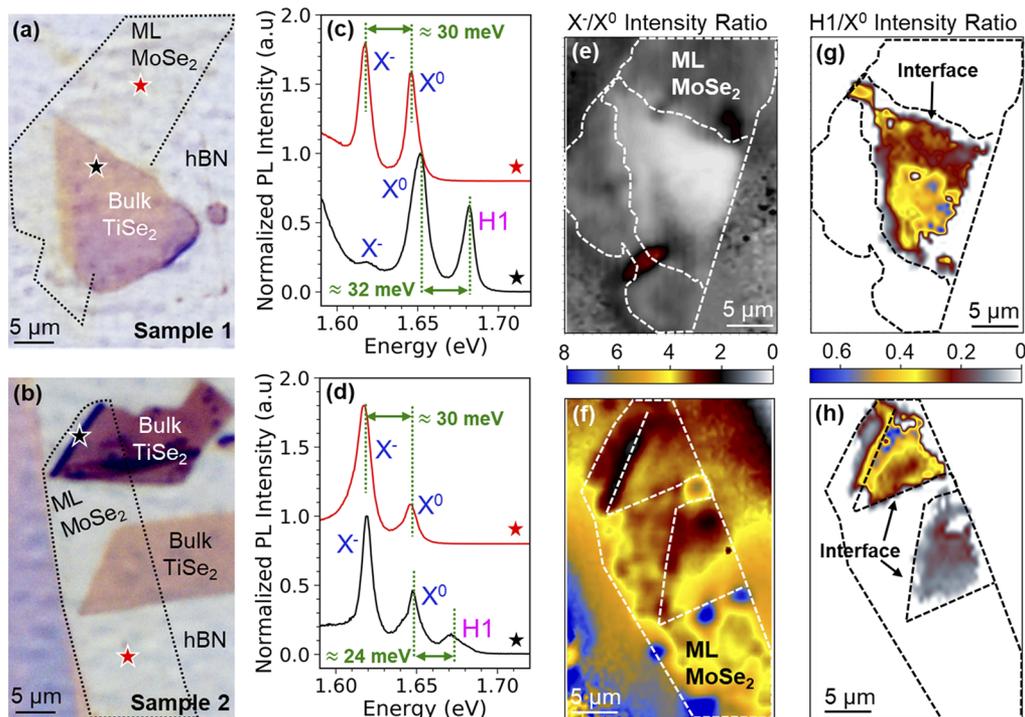


FIG. 1. Optical microscope images of TiSe₂–MoSe₂ vdW heterostructures: (a) sample 1 and (b) sample 2. The black dotted line outlines the ML–MoSe₂ layer. 5 K PL spectra taken on (black) and off (red) the interface for (c) sample 1 and (d) sample 2. These locations are denoted by red and black stars in panels (a) and (b), respectively. In addition to the X⁰ and X⁻ emission observed in ML–MoSe₂, the H1 PL peak appears at ≈ 1.68 eV on the interface. Spatially mapped X⁻/X⁰ integrated intensity ratio across the interface showing variations in the X⁻ intensity for (e) sample 1 and (f) sample 2. Spatially mapped H1/X⁰ integrated intensity ratio across the interface showing changes in the H1 intensity in (g) sample 1 and (h) sample 2. The ratio X⁻/X⁰ correlates with changes in the H1/X⁰ intensity at the interface.

spectra contain a previously unobserved feature, referred to as H1, at ≈ 1.68 eV. H1 is comparable to X^0 in both intensity and linewidth for sample 1, while being weaker and broader in sample 2.

The 5 K PL spectra also show the evidence of an anticorrelation between H1 and X^- . Spatially resolved PL maps of the interface allow us to explore this behavior further and connect it to interface quality by examining the integrated intensity ratios X^-/X^0 [Figs. 1(e) and 1(f)] and $H1/X^0$ [Figs. 1(g) and 1(h)]. H1 and $X^0 + X^-$ integrated intensities are plotted separately in Fig. S1 of the [supplementary material](#). For sample 1, the ratio of X^-/X^0 [Fig. 1(e)] varies between 1 and 2 over most of the MoSe_2 flake with a notable jump at the crack on the bottom left quadrant of the map. On the heterostructure itself, this ratio plummets to well below 1, indicating the absence of free charges that can participate in trion formation. The connection of the X^-/X^0 ratio to charge transfer is well established in numerous reports^{11–13,54} and, since the transfer efficiency is exponentially dependent on distance, can be used as a proxy for interlayer spacing. MoSe_2 tends to be *n*-type as-exfoliated, and TiSe_2 band alignment suggests that it will act as an electron acceptor.⁵⁵ Therefore, the near absence of X^- emission on the sample 1 overlap region suggests good

coupling between the TiSe_2 – MoSe_2 flakes. For sample 2, the X^-/X^0 ratio [Fig. 1(f)] is larger on the MoSe_2 flake, varying between 3 and 6, which may originate from unintentional doping during the heterostructure fabrication process. On the TiSe_2 – MoSe_2 overlap, we observe a reduction in the X^- intensity co-localized with H1 but smaller than in sample 1. From this, we suggest that interlayer coupling is weaker in sample 2, which could be due to contaminants or partial oxidation of the TiSe_2 flake. The remaining analyses will therefore focus on sample 1, unless otherwise noted.

B. Temperature and power dependence of H1

In this section, we discuss temperature- and power-dependent PL measurements on and off the TiSe_2 – MoSe_2 interface. [Figure 2\(a\)](#) shows a temperature-dependent PL intensity map from 5 to 265 K taken on the interface in sample 1. A similar dataset for sample 2 is included in the [supplementary material](#) (Fig. S2). Here, the 5 K PL emission spectrum is the same as in [Fig. 1\(c\)](#) with prominent, sharp emission from X^0 and H1, heavily reduced X^- emission, and a broad feature originating from defects. With increasing temperature, PL from defect excitons and X^- decreases and becomes unobservable

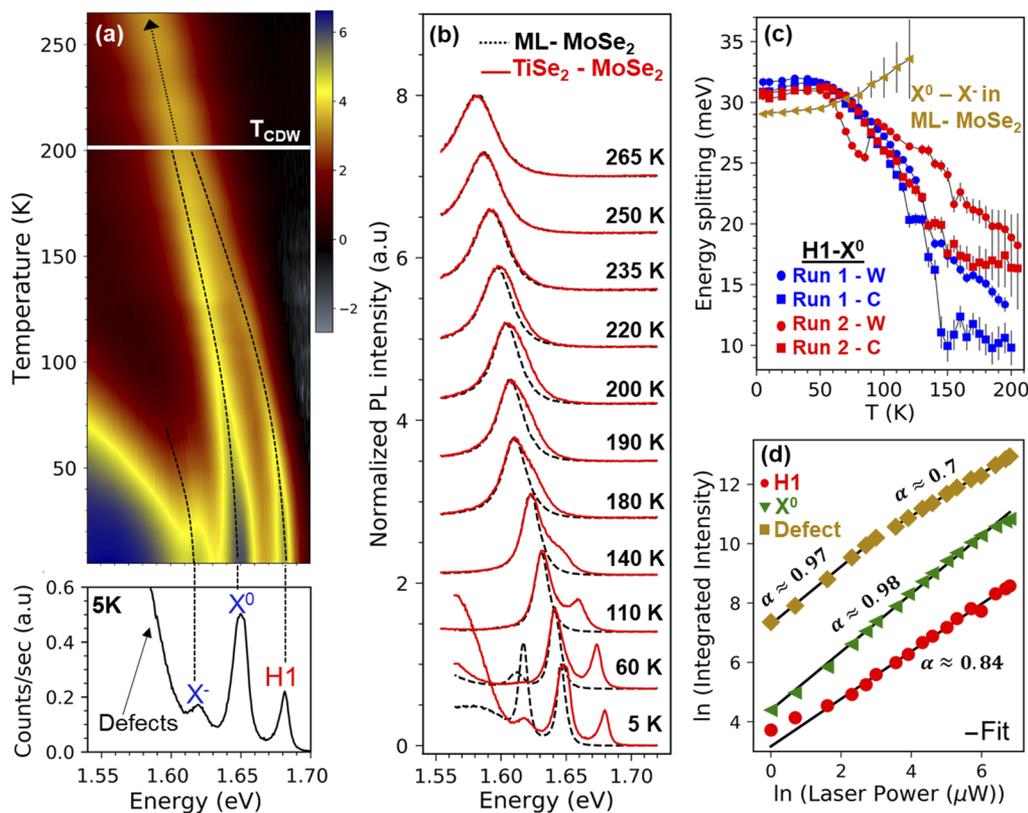


FIG. 2. (a) Temperature-dependent PL map on the TiSe_2 – MoSe_2 interface of sample 1. The dashed lines are guides to the eye, and the 5 K PL spectrum beneath the map labels the optical transitions. T_{CDW} for bulk TiSe_2 is indicated by the horizontal white line. (b) Line shape analysis of PL spectra taken on (red) and off (black) the TiSe_2 – MoSe_2 interface. The interface spectra have been shifted to align the X^0 emission energies between the two curves. (c) Energy separation between H1 and X^0 vs temperature for two separate runs (red, blue), each consisting of a warming (W, circles) and cooling (C, squares) curve. $1-\sigma$ error bars from fits to the PL spectra are included. $X^0 - X^-$ is included for ML-MoSe_2 to illustrate the difference from H1. (d) Log–log plot of the PL integrated intensity vs excitation laser power. The solid black lines are power-law fits to the data.

for $T > 70$ K in agreement with prior studies.^{56–59} Both X^0 and H1 are visible at elevated temperatures but are difficult to distinguish above ≈ 190 K. We obtain a better understanding through the analysis of the PL line shape for ML–MoSe₂ and TiSe₂–MoSe₂. Figure 2(b) compares PL spectra at selected temperatures taken on (red curve) and off (black curve) the TiSe₂–MoSe₂ interface. The presence of the TiSe₂ capping layer causes X^0 to blueshift due to the different dielectric constant.^{25,26} To facilitate comparison, we eliminate this shift by adjusting the energy axis of the TiSe₂–MoSe₂ spectrum so that the X^0 PL peaks overlap. The energy shift amounts to ~ 1 – 3 meV across the entire temperature range. H1 is visible as a weak shoulder of X^0 between 190 and 220 K. Above these temperatures, the PL line shape on and off the interface is identical, indicating that the driving mechanism behind H1 has dissipated. We also fit each PL spectrum to a sum of Lorentzian functions and extract the temperature-dependent peak parameters for H1, X^0 , and X^- . The energy splitting, H1– X^0 , is shown in Fig. 2(c) over two cooling and warming runs that extend up to 200 K. In both cases, the energy separation between H1 and X^0 decreases with temperature until 200 K after which it is difficult to obtain a reliable fit.

The temperature window of 190–220 K is apparently crucial to H1 and is known to be important for TiSe₂. Bulk 1T–TiSe₂ undergoes a $2 \times 2 \times 2$ commensurate-CDW transition in the range of $T_{CDW} \approx 200$ – 210 K, as observed in a variety of optical and electronic measurements.^{39,60–62} The CDW transition opens a bandgap at the TiSe₂ M point in the Brillouin zone (BZ) with an associated order parameter well described by the Bardeen–Cooper–Schrieffer (BCS) model.⁶² The observed correlation of H1 with T_{CDW} suggests a close relationship between H1 in MoSe₂ and the CDW in TiSe₂.

Power-dependent PL measurements provide further insight into the nature of H1, as presented for sample 1 in Fig. 2(d) and for sample 2 in the supplementary material (Fig. S2). The PL intensity generally scales with power as $I_{PL} \propto P^\alpha$, where I_{PL} is the integrated PL intensity and P is the excitation power. The exponent $\alpha \approx 1$ for free excitons and >1 for multiexcitons.¹⁶ Localized exciton states exhibit a more complicated behavior. At low powers, $\alpha \sim 1$ but then becomes sublinear as the localized states are saturated.⁵⁹ These behaviors are observed in Fig. 2(d) where we plot the natural logarithms of I_{PL} and P . The linear fits to these data allow for the extraction of α . We find that both X^0 and H1 have an $\alpha \approx 1$, with the value for H1 being somewhat lower, suggesting free exciton characteristics. As expected, the defect band first exhibits $\alpha \approx 1$ at low powers and then shows signs of saturation with $\alpha \approx 0.7$. While α for H1 is lower than would be expected for a free exciton, the absence of saturation is more consistent with this interpretation.

C. CDW phase at the TiSe₂–MoSe₂ interface

Raman spectroscopy can probe the square of the CDW order parameter directly since the intensity of the symmetry-forbidden modes appears in the second order of the ionic displacements of the high-symmetry positions. Raman measurements performed at the TiSe₂–MoSe₂ interface in the range of 5–265 K are shown in Fig. 3(a). The 5 K Raman spectra show the CDW modes at E_g^{CDW} (70 cm^{-1}) and A_g^{CDW} (108 cm^{-1}), as well as normal TiSe₂ lattice modes at 132 and 200 cm^{-1} of E_g and A_{1g} symmetry, respectively.^{63,64} The MoSe₂ A_{1g} mode is also visible at 245 cm^{-1} and is related to out-of-plane vibrations.⁶⁵ Figure 3(b) plots the

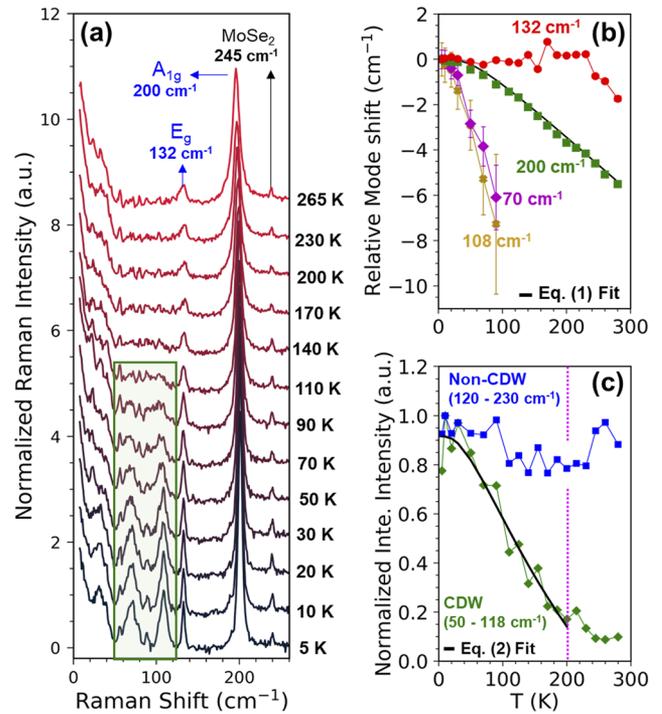


FIG. 3. (a) Temperature-dependent Raman spectra taken on the TiSe₂–MoSe₂ interface in sample 1. (b) Shift in the observed TiSe₂ Raman modes relative to the 5 K value. 1 - σ error bars from spectral fitting are included. The solid black line is fit to Eq. (1) that accounts for optical phonon decay processes. (c) Normalized integrated Raman intensity of the CDW modes (green diamonds) and lattice modes (blue squares) vs temperature. The dotted magenta line indicates T_{CDW} . The solid black line is a fit to Eq. (2).

temperature-dependent shifts of all TiSe₂ modes relative to their frequency at 5 K. The 135 cm^{-1} mode is largely unaffected by temperature changes, blueshifting slightly as temperature is lowered and then stabilizing. The 200 cm^{-1} mode is insensitive to the CDW transition, and its anharmonicity can be understood by a combination of optical phonon decay and temperature-dependent changes in the lattice constants.⁶⁶ This is described by the following equation [solid black line in Fig. 3(b)]:

$$\Delta(\omega(0), T) = \omega_0 + A \left(1 + \frac{2}{e^x - 1} \right). \quad (1)$$

Here, $x = \hbar\omega_B/2k_B T$, ω_0 is the 0 K harmonic frequency, and A represents the anharmonic contributions to the frequency of the 200 cm^{-1} optical mode as it decays into two acoustic phonons. The obtained value for $A = -1.85$ cm^{-1} is within the ballpark of similar phonon anharmonicity studies done on TMDs.^{67,68}

The CDW modes at 70 and 109 cm^{-1} redshift and broaden with increasing temperature. These modes are unresolved above $T = 100$ K, which is well below T_{CDW} . This behavior is commonly attributed to quantum fluctuations of the density wave.⁶⁹ Integrating the Raman intensity over the spectral range encompassing the CDW modes allows us to monitor the CDW up to the transition temperature [Fig. 3(c)]. Thermal melting of the CDW is expected to

follow a temperature dependence consistent with the BCS treatment where the order parameter $\Delta(T)$ can be given as⁷⁰

$$\frac{\Delta^2(T)}{\Delta^2(0)} \propto \tanh^2\left(\alpha_{\text{BCS}}\sqrt{1 - \frac{T}{T_{\text{CDW}}}}\right), \quad (2)$$

where α_{BCS} is a constant determined by BCS theory but in practice can vary between materials. This model fits the integrated intensity data well up to T_{CDW} , as shown in Fig. 3(c).

III. DISCUSSION

Investigations into the properties of 2D excitons in TMDs have covered remarkable ground over the past decade.^{9,10,71–73} Despite these remarkably comprehensive studies, no observations of vdW heterostructures have shown PL satellites above X^0 . Therefore, we explore here three possible mechanisms that could be responsible for H1.

Before proceeding with the analysis of potential microscopic interpretations of the new peak, we summarize key experimental observations. First, H1 lies 25–32 meV above X^0 with an intensity that differs between samples (Fig. 1). Second, within a single sample, the relative intensity of H1 to X^0 is temperature independent

[Fig. 4(a)]. Third, the energy difference between H1 and X^0 follows the CDW order parameter Δ^2 . We illustrate this in Fig. 4(c) by overlaying neutron scattering data from Ref. 61, the energy separation H1– X^0 , and the integrated intensity of the TiSe₂-CDW Raman features. Fourth, the intensity ratio H1/ X^0 decreases with increasing laser power [Fig. 4(b)]. Finally, H1 and X^- are spatially anti-correlated (Fig. 1).

A. Mechanism I: Activation of forbidden/dark excitons

Semiconducting TMDs host numerous dark exciton states where optical recombination is forbidden by momentum conservation or symmetry. Density functional theory (DFT) calculations of MoSe₂ suggest that a finite-momentum dark exciton lies 30 meV above X^0 .⁷⁴ This indirect exciton is formed from an electron residing at the $Q(Q')$ valley and a hole at the $K(K')$ valley [Fig. 4(e)]. The indirect exciton has not been observed experimentally in PL, but resonant Raman measurements offer some evidence for dark excitons above X^0 .⁷⁵ While the energy of this exciton matches the energy of H1, a viable mechanism is required to provide the missing momentum needed for optical recombination of this dark state. Mechanism I explores how the interface between TiSe₂ and MoSe₂

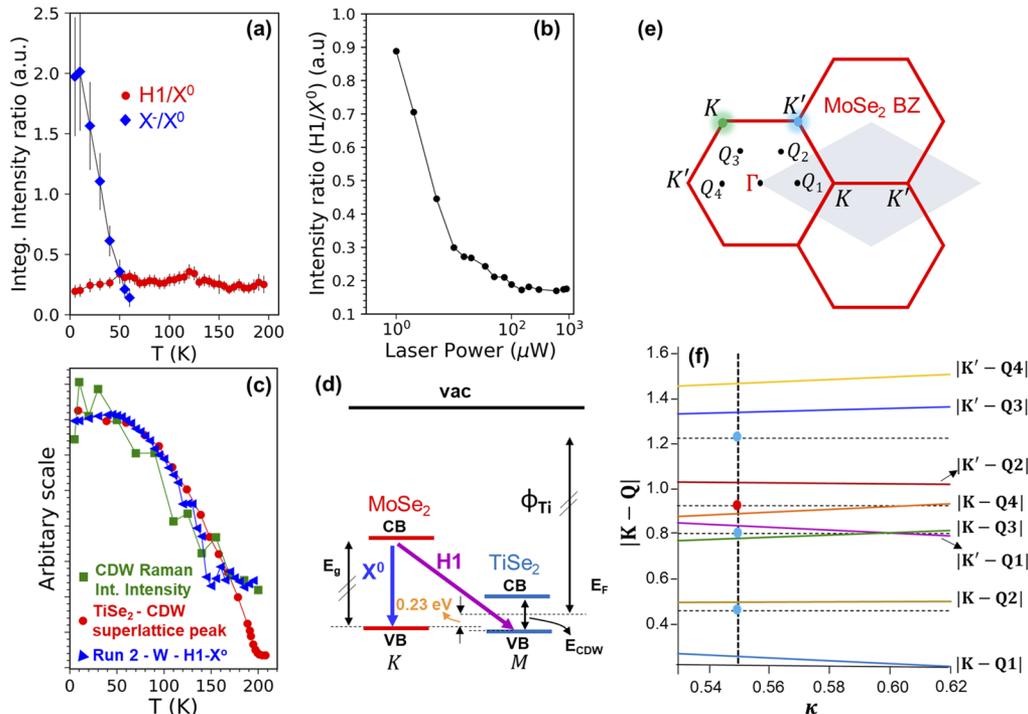


FIG. 4. (a) PL integrated intensity ratios H1/ X^0 (red circles) and X^-/X^0 (blue diamonds) vs temperature. (b) H1/ X^0 integrated intensity ratio vs the laser power (lin–log scale). (c) Overlay of the energy separation between H1 and X^0 for sample 1, the integrated Raman intensity of the CDW modes, and the TiSe₂ CDW superlattice peak extracted from neutron scattering data in Ref. 61, all versus temperature. (d) A schematic of a type-II band alignment at the TiSe₂–MoSe₂ interface leading to an interlayer exciton. (e) Brillouin zones for the MoSe₂ lattice and the corresponding reciprocal lattice unit cell (gray). (f) Lengths of the scattering vectors $|\mathbf{K} - \mathbf{Q}|$ in units of the MoSe₂ reciprocal lattice vectors (colored solid lines) compared to the length of the reciprocal lattice vectors of the undistorted (red dot) and CDW (blue dots) lattice in TiSe₂. The horizontal dashed lines are guides to the eye. The vertical dashed line is drawn to pass through $\kappa = 0.55$ to facilitate the comparison with the magnitude of the MoSe₂ wavevectors $|\mathbf{K} - \mathbf{Q}|$ and the smallest reciprocal lattice vector (dots) in TiSe₂.

could potentially activate such dark states by introducing a new spatial periodicity that violates quasimomentum conservation.

MoSe₂ and TiSe₂ form an incommensurate superstructure for most stacking configurations, which, formally, implies a full relaxation of quasimomentum conservation. In order to illustrate this, consider the MoSe₂ Bloch wave functions at the TiSe₂-MoSe₂ overlap. We assume that there is no hybridization between MoSe₂ and TiSe₂ wave functions, which is reasonable due to their large spatial separation. The quasimomentum can then be defined by the MoSe₂ lattice alone, and the Bloch functions are $\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{\mathbf{g}} a_{\mathbf{k}+\mathbf{g}} \exp[i(\mathbf{k} + \mathbf{g}) \cdot \mathbf{r}]$, where \mathbf{g} is a MoSe₂ reciprocal lattice (r.l.) vector and $a_{\mathbf{k}+\mathbf{g}}$ are the Bloch coefficients. The presence of the TiSe₂ lattice and CDW can be thought of as a periodic “defect” for MoSe₂ that enables scattering between the K and Q points. The matrix element of the associated potential for Bloch states is $\langle \psi_{\mathbf{Q}} | V(\mathbf{r}) | \psi_{\mathbf{K}} \rangle$, where \mathbf{K} is a wavevector for any of the K -equivalent points and \mathbf{Q} is a wavevector for any of the Q -equivalent ones [Fig. 4(e)]. $V(\mathbf{r})$ is the effective TiSe₂ defect potential, which can be expanded in the TiSe₂ r.l. vectors \mathbf{t} . Note that the lattice parameter for TiSe₂ is 7.8% larger than MoSe₂ so that if we measure the reciprocal space in units of $2\pi/a_{\text{MoSe}_2}$, then for Mo, the first r.l. vectors will be $\mathbf{g}_{1,2} = \{\sqrt{3}/2, \pm 1/2\}$; $\mathbf{g}_3 = \mathbf{g}_1 + \mathbf{g}_2$. For TiSe₂, the equivalent r.l. vectors $\mathbf{t}_{1,2,3}$ will be shorter by 7.8%.

Using the expansion of $V(\mathbf{r})$, we obtain

$$\begin{aligned} \langle \psi_{\mathbf{Q}} | V(\mathbf{r}) | \psi_{\mathbf{K}} \rangle &= \sum_{\mathbf{t}} \langle \psi_{\mathbf{Q}} | v_{\mathbf{t}} e^{i\mathbf{t} \cdot \mathbf{r}} | \psi_{\mathbf{K}} \rangle \\ &= \sum_{\mathbf{t}, \mathbf{g}, \mathbf{g}'} \left\langle a_{\mathbf{K}+\mathbf{g}} e^{i(\mathbf{K}+\mathbf{g}) \cdot \mathbf{r}} v_{\mathbf{t}} e^{i\mathbf{t} \cdot \mathbf{r}} a_{\mathbf{Q}+\mathbf{g}'}^* e^{-i(\mathbf{Q}+\mathbf{g}') \cdot \mathbf{r}} \right\rangle \\ &= \sum_{\mathbf{t}, \mathbf{K}, \mathbf{Q}} a_{\mathbf{K}} a_{\mathbf{Q}}^* v_{\mathbf{t}} \left\langle e^{i(\mathbf{K}-\mathbf{Q}+\mathbf{t}) \cdot \mathbf{r}} \right\rangle \\ &= \sum_{\mathbf{t}, \mathbf{K}, \mathbf{Q}} a_{\mathbf{K}} a_{\mathbf{Q}}^* v_{\mathbf{t}} \delta(\mathbf{K} - \mathbf{Q} + \mathbf{t}). \end{aligned}$$

In the last line, the summation goes over all equivalent K and Q points. While, in principle, in an infinite lattice, one can always find a triad $\mathbf{K}, \mathbf{Q}, \mathbf{t}$ wavevectors that closely satisfies the condition $|\mathbf{K} - \mathbf{Q} + \mathbf{t}| = 0$, the coefficients $v_{\mathbf{t}}$ and, to lesser extent, $a_{\mathbf{g}}$ rapidly decay (the form factor effect), and so this scattering process can only be efficient if $|\mathbf{t}|$ is small.

Determining if the TiSe₂ “defect” potential can enable $K \rightarrow Q$ scattering requires matching $|\mathbf{t}|$ and $|\mathbf{K} - \mathbf{Q}|$. We have carried out DFT calculations of the TiSe₂-MoSe₂ heterostructure to determine how this position is altered by interlayer coupling. The location of the Q valley is $\kappa = |\mathbf{Q} - \Gamma|/|\mathbf{K} - \Gamma|$, which are clustered around 0.55 ± 0.05 for multiple DFT runs. The magnitude of the smallest scattering vectors $\mathbf{K} - \mathbf{Q}$ is $(1 - \kappa)/\sqrt{3}$, $(1 + \kappa)/\sqrt{3}$, $(\sqrt{1 - \kappa + \kappa^2})/\sqrt{3}$, $(\sqrt{1 + \kappa + \kappa^2})/\sqrt{3}$, $(2 - \kappa)/\sqrt{3}$, and $(\sqrt{4 - 2\kappa + \kappa^2})/\sqrt{3}$, where the first two values correspond to scattering from Q to K or K' , while the next two values correspond to scattering from Q' to K or K' , and the last two to scattering into the next BZ. For $\kappa = 0.55$, in units of $2\pi/a_{\text{MoSe}_2}$, these are 0.260, 0.895, 0.501, 0.785, 0.832, and 1.033, respectively. At the same time, the smallest vector of the r.l. of TiSe₂ without the CDW is $t_1 = 0.928(2\pi/a_{\text{Mo}})$.

In Fig. 4(e), we present the magnitude of the scattering wavevector $|\mathbf{K} - \mathbf{Q}|$ between different K and Q points vs κ in MoSe₂. These are compared to the r.l. vectors of TiSe₂ in the normal (blue

dots) and CDW (red dot) phases. The smallest TiSe₂ r.l. vector can only match one of the $|\mathbf{K} - \mathbf{Q}|$ values if κ is 0.607, which is far outside our DFT predictions. In the $2 \times 2 \times 2$ CDW phase of TiSe₂, the magnitude of the r.l. vectors (τ_i) are shortened to $\tau_1 = t_1/2$; $\tau_2 = t_1\sqrt{3}/2$; $\tau_3 = t_1$; $\tau_4 = \sqrt{7}/2t_1$. We find that particularly $\tau_2 = 0.804$ is close to the magnitude of one of the $\mathbf{K} - \mathbf{Q}$ vectors. This is shown by the red dot in Fig. 4(e). The mismatch is less than $0.019(2\pi/a_{\text{Mo}})$ and is reduced to zero for $\kappa = 0.59$, a value within the range of the DFT calculations.

Therefore, we conclude that the CDW potential opens a new $K \rightarrow Q$ scattering channel. This would enable optical recombination of an indirect, finite-momentum exciton, resulting in the appearance of a new PL line at the same energy as H1.⁷⁴ Future calculations taking into account the effect of the CDW-exciton coupling may be able to assess this scenario quantitatively, but such calculations are outside our current capabilities. This result explains the emission energy of H1, its disappearance at T_{CDW} , and its anticorrelation with X^- . However, this mechanism would also imply H1- X^0 (barring unrelated phenomena) to be T -independent and the H1/ X^0 intensity ratio to follow Δ^2 . Our observations indicate just the opposite [Figs. 4(a) and 4(c)]. Furthermore, this mechanism cannot explain the decrease in the H1/ X^0 intensity ratio with excitation power in Fig. 4(b).

B. Mechanism II: Interlayer 2D TiSe₂-MoSe₂ exciton

Another intriguing possibility is the formation of an interlayer exciton by an electron in MoSe₂ and a hole in the TiSe₂ layer, as shown in Fig. 4(d). This is only possible due to the opening of the CDW bandgap in the low-temperature regime but is inconceivable in the normal metallic phase. The intensity of such an exciton will be defined by (T -independent) interlayer tunneling, and the position will be, roughly, given by $E_c(\text{MoSe}_2) - E_F(\text{TiSe}_2) - E_{\text{CDW}}(\text{TiSe}_2)/2$. The energy gap, E_{CDW} , is proportional to the order parameter Δ^2 , and its value is unclear: Experiments cite different numbers, and most angle-resolved photoemission spectroscopy studies find the top of the valence band to be separated from the Fermi level (i.e., half the bandgap) by 50–75 meV,^{62,76} qualitatively consistent with the H1- X^0 separation, and roughly following Δ^2 .

For this scenario to be realized, the top of the Mo valence band at K should fall inside the CDW gap in TiSe₂ (or, equivalently, within a few tens of meV from the TiSe₂ Fermi energy, E_F , in the metallic phase). Our standard DFT calculations using a supercell with 2×2 periodicity in TiSe₂ and $\sqrt{7} \times \sqrt{39}$ in MoSe₂ (Ti₁₆Mo₁₉) show that E_F is about 230 meV above the MoSe₂ valence band. This is illustrated in Fig. 4(d) and detailed in Sec. S3 of the [supplementary material](#). Hence, while this naturally explains all five experimental observations it also requires an assumption that the DFT calculations of the band alignment are off by 100–150 meV, which may be reasonable once the electronic correlations that drive the CDW formation and the details of the vdW interface are properly included.

C. Mechanism III: Exciton-phonon and exciton-plasmon interaction

Exciton formation and recombination can, in principle, be assisted through coupling to a variety of bosonic excitations. Again focusing on the activation of a dark finite-momentum exciton, the

lowest energy phonon with the appropriate momentum has an energy of ~ 10 meV⁷⁷ so that the corresponding PL energy should be shifted down (phonon-assisted emission) from the momentum dark exciton energy. This would suggest that H1 is a phonon replica of a higher-energy exciton, either symmetry forbidden or momentum-indirect. However, this mechanism is unlikely considering that it is intrinsic to MoSe₂ and cannot explain the role of the TiSe₂ CDW. In principle, interlayer coupling could allow TiSe₂ phonons to create exciton–phonon replicas in MoSe₂. H1 should in this case emerge at higher temperature if TiSe₂ phonons are involved, and the replica would show additional temperature dependence compared to X⁰, in contradiction with our observation.^{78–80} An additional possibility regarding the activation of a finite-momentum exciton by coupling to TiSe₂ is the presence of a distinct low-energy plasmon. A curious aspect of the TiSe₂–CDW transition is the presence of a low-energy plasmon, which has been claimed as evidence of the excitonic insulator mechanism,⁸¹ although this claim was later disputed.⁸² This plasmon was measured to have an energy of $\hbar\omega_{pl}(q) \approx 50$ meV at $T = 17$ K with $q = 0$. This excitation was found to soften with temperature, reaching $\hbar\omega_{pl} \approx 35$ meV at $T = 185$ K. The plasmon is only present in the CDW phase, so it is tempting to associate it with the H1 PL line.

Signatures of exciton–plasmon interaction in PL have attracted considerable attention recently.^{83–86} While these papers consider excitons and plasmons spatially coexisting in the same material, the theory is equally applicable to spatially separated MoSe₂ excitons and TiSe₂ plasmons, as long as they are coupled by the Coulomb interaction. In principle, two mechanisms are possible (see Sec. S4 of the [supplementary material](#) for a detailed discussion): The exciton Green function can be renormalized by a virtual process of emission and absorption of a plasmon or a process with either emission or absorption of a real plasmon. The former process shifts the exciton line E_X up by a fixed amount, which in the first approximation can be expressed as $E_X^2 - E_{X0}^2 \approx 4|\mathcal{M}|^2 E_{X0} \hbar\omega_{pl} / (E_{X0}^2 - (\hbar\omega_{pl})^2) \approx 4|\mathcal{M}|^2 \hbar\omega_{pl} / E_{X0}$, where E_{X0} is the position of X⁰ in the absence of exciton–plasmon coupling and \mathcal{M} is the exciton–plasmon coupling constant. However, one would expect the coupling constant to vary spatially, so instead of two lines one would observe a broad manifold starting at E_{X0} and ending at around $E_{X0} + 2|\mathcal{M}|^2 \hbar\omega_{pl} / E_{X0}$, in contradiction with the experiment. The other mechanism preserves the main line and adds two satellites, shifted down and up by around ω_{pl} . The intensity of the upper peak is roughly temperature independent, and the intensity of the lower peak is proportional to the population of thermally or extrinsically excited plasmons. We do not observe the lower satellite at all, and the upper satellite, H1, only loses its intensity with temperature [Fig. 2(b)] and with the laser power [Fig. 4(b)], in obvious contradiction with the assumed physics.

D. Summary of possible mechanisms

We have presented here three speculative scenarios by which a new feature may appear in the PL of a TiSe₂–MoSe₂ heterostructure. While none can fully capture the entire scope of our observations, we conclude that the dark exciton and interlayer exciton interpretations are the most likely explanations for H1. While the plasmon model is exciting due to its connection to TiSe₂ excitonic-insulator physics, it appears less likely to be important for this particular heterostructure.

IV. CONCLUSION

We have discovered the presence of a new exciton-like peak in TiSe₂–MoSe₂ heterostructures using temperature-dependent PL spectroscopy. The H1 emission feature is localized to the heterostructure interface and correlated with T_{CDW} in TiSe₂. We have presented multiple scenarios that could explain the origin of this feature. The most plausible explanations of H1 are, presently, (1) an interlayer TiSe₂–MoSe₂ exciton and (2) the brightening of momentum dark excitons by the CDW potential. These results are the first demonstration of exciton engineering via proximitized CDWs and provide the 2D theoretical community with a fresh challenge to understand the microscopic mechanisms underlying CDW–exciton interactions.

V. GROWTH OF TMD MATERIALS

MoSe₂ crystals were grown by the chemical vapor transport (CVT) method using polycrystalline MoSe₂ powder (≈ 1 g) and SeBr₄ transport agent (≈ 0.1 g). The source and growth zones in a vacuum-sealed 20 cm long quartz ampoule were kept at 980 and 890 °C, respectively, for seven days. The procedure for CVT-grown TiSe₂ crystals is outlined in Ref. 39.

VI. SAMPLE PREPARATION, ASSEMBLY, AND AFM “NANO-SQUEEGEE”

Bulk-hBN flakes were mechanically exfoliated and transferred on O₂ plasma cleaned Si/SiO₂ substrates. MLs of 2H–MoSe₂ obtained through mechanical exfoliation were subsequently transferred on an identified hBN flake. For both materials, the transfer process was done using the PDMS-based dry viscoelastic stamping method.⁴⁹ This method has been known to leave polymer residues between the interface of two TMDs deposited during the transfer process but has proven to be optimal for fabricating heterostructures.⁷ To create clean interfaces, an AFM-based “nano-squeegee” procedure was employed.⁵⁰ This involves the use of a standard AFM tip to push out polymer residues deposited between the two TMDs in a vertical heterostructure. We were able to use the same method to also remove surface residues present on the ML–MoSe₂ flake, using a 7 N/m spring constant tip and a contact force of 140 nN. Bulk TiSe₂ is then brought into contact with the sample using the same dry-transfer technique as done for ML–MoSe₂. The sample was additionally vacuum annealed at 200 °C for 5 h to improve coupling.

VII. EXPERIMENTAL SETUP

Low-temperature PL and Raman measurements were carried out on a confocal microscope setup with 532 nm laser excitation focused through a 0.42 NA, 50× long working-distance objective to achieve a spot diameter of 2.4 μ m. The light is collected in a back-scattering geometry, with the collection fiber-coupled to a 500 mm focal length single spectrometer integrated with a liquid-N₂ cooled charge-coupled device detector. The samples were placed under vacuum and cooled in a closed cycle He-cooled cryostat (Montana Instruments Corporation) with a variable temperature range from 4 to 300 K. Raman measurements on the TiSe₂–MoSe₂ interface were carried out using the same setup; however, the excitation path included a collection of Bragg grating

notch filters enabling the acquisition of data within 15 cm^{-1} of the laser line. The excitation wavelength used for Raman measurements was 532 nm, and the laser power was kept at $300\text{ }\mu\text{W}$ pre-objective. Spatially resolved and temperature-dependent PL measurements were done using the same laser wavelength, while the power was kept within $150\text{ }\mu\text{W}$ pre-objective.

SUPPLEMENTARY MATERIAL

Additional spatially resolved PL measurements of samples 1 and 2, temperature and power-dependent measurements of sample 2, DFT calculations of the $\text{TiSe}_2\text{-MoSe}_2$ heterostructure, and a theoretical model of exciton-plasmon coupling are included in the [supplementary material](#).

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Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- I. Žutić, A. Matos-Abiague, B. Scharf, H. Dery, and K. Belashchenko, "Proximitized materials," *Mater. Today* **22**, 85–107 (2019).
- A. K. Geim and I. V. Grigorieva, "Van der Waals heterostructures," *Nature* **499**, 419–425 (2013).
- R. Bistritzer and A. H. MacDonald, "Moiré bands in twisted double-layer graphene," *Proc. Natl. Acad. Sci. U. S. A.* **108**, 12233–12237 (2011).
- Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras, and P. Jarillo-Herrero, "Unconventional superconductivity in magic-angle graphene superlattices," *Nature* **556**, 43–50 (2018).
- K. Tran, G. Moody, F. Wu, X. Lu, J. Choi, K. Kim, A. Rai, D. A. Sanchez, J. Quan, A. Singh, J. Embley, A. Zepeda, M. Campbell, T. Autry, T. Taniguchi, K. Watanabe, N. Lu, S. K. Banerjee, K. L. Silverman, S. Kim, E. Tutuc, L. Yang, A. H. MacDonald, and X. Li, "Evidence for moiré excitons in van der Waals heterostructures," *Nature* **567**, 71–75 (2019).
- H. Yu, G. B. Liu, J. Tang, X. Xu, and W. Yao, "Moiré excitons: From programmable quantum emitter arrays to spin-orbit-coupled artificial lattices," *Sci. Adv.* **3**, e1701696 (2017).
- R. Frisenda, E. Navarro-Moratalla, P. Gant, D. Pérez De Lara, P. Jarillo-Herrero, R. V. Gorbachev, and A. Castellanos-Gomez, "Recent progress in the assembly of nanodevices and van der Waals heterostructures by deterministic placement of 2D materials," *Chem. Soc. Rev.* **47**, 53–68 (2018).
- M. Onodera, S. Masubuchi, R. Moriya, and T. Machida, "Assembly of van der Waals heterostructures: Exfoliation, searching, and stacking of 2D materials," *Jpn. J. Appl. Phys., Part 1* **59**, 010101 (2020).
- G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, "Colloquium: Excitons in atomically thin transition metal dichalcogenides," *Rev. Mod. Phys.* **90**, 021001 (2018).
- T. Mueller and E. Malic, "Exciton physics and device application of two-dimensional transition metal dichalcogenide semiconductors," *npj 2D Mater. Appl.* **2**, 29 (2018).
- J. S. Ross, S. Wu, H. Yu, N. J. Ghimire, A. M. Jones, G. Aivazian, J. Yan, D. G. Mandrus, D. Xiao, W. Yao, and X. Xu, "Electrical control of neutral and charged excitons in a monolayer semiconductor," *Nat. Commun.* **4**, 1474 (2013).
- Z. Li, T. Wang, S. Miao, Z. Lian, and S.-F. Shi, "Fine structures of valley-polarized excitonic states in monolayer transitional metal dichalcogenides," *Nanophotonics* **9**, 1811–1829 (2020).
- Z. Li, T. Wang, Z. Lu, C. Jin, Y. Chen, Y. Meng, Z. Lian, T. Taniguchi, K. Watanabe, S. Zhang, D. Smirnov, and S.-F. Shi, "Revealing the biexciton and trion-exciton complexes in BN encapsulated WSe_2 ," *Nat. Commun.* **9**, 3719 (2018).
- Z. Ye, L. Waldecker, E. Y. Ma, D. Rhodes, A. Antony, B. Kim, X.-X. Zhang, M. Deng, Y. Jiang, Z. Lu, D. Smirnov, K. Watanabe, T. Taniguchi, J. Hone, and T. F. Heinz, "Efficient generation of neutral and charged biexcitons in encapsulated WSe_2 monolayers," *Nat. Commun.* **9**, 3718 (2018).
- S.-Y. Chen, T. Goldstein, T. Taniguchi, K. Watanabe, and J. Yan, "Coulomb-bound four- and five-particle intervalley states in an atomically-thin semiconductor," *Nat. Commun.* **9**, 3717 (2018).
- M. Barbone, A. R.-P. Montblanch, D. M. Kara, C. Palacios-Berraquero, A. R. Cadore, D. De Fazio, B. Pingault, E. Mostaani, H. Li, B. Chen, K. Watanabe, T. Taniguchi, S. Tongay, G. Wang, A. C. Ferrari, and M. Atatüre, "Charge-tunable biexciton complexes in monolayer WSe_2 ," *Nat. Commun.* **9**, 3721 (2018).
- C. Robert, B. Han, P. Kapuscinski, A. Delhomme, C. Faugeras, T. Amand, M. R. Molas, M. Bartos, K. Watanabe, T. Taniguchi, B. Urbaszek, M. Potemski, and X. Marie, "Measurement of the spin-forbidden dark excitons in MoS_2 and MoSe_2 monolayers," *Nat. Commun.* **11**, 4037 (2020).
- Z. Lu, D. Rhodes, Z. Li, D. V. Tuan, Y. Jiang, J. Ludwig, Z. Jiang, Z. Lian, S.-F. Shi, J. Hone, H. Dery, and D. Smirnov, "Magnetic field mixing and splitting of bright and dark excitons in monolayer MoSe_2 ," *2D Mater.* **7**, 15017 (2019).
- E. Malic, M. Feierabend, S. Brem, D. Christiansen, F. Wendler, A. Knorr, and G. Berghäuser, "Dark excitons in transition metal dichalcogenides," *Phys. Rev. Mater.* **2**, 014002 (2018).
- X.-X. Zhang, T. Cao, Z. Lu, Y.-C. Lin, F. Zhang, Y. Wang, Z. Li, J. C. Hone, J. A. Robinson, D. Smirnov, S. G. Louie, and T. F. Heinz, "Magnetic brightening and control of dark excitons in monolayer WSe_2 ," *Nat. Nanotechnol.* **12**, 883–888 (2017).
- W.-t. Hsu, J. Quan, C.-y. Wang, L.-s. Lu, M. Campbell, W.-h. Chang, L.-J. Li, X. Li, and C.-K. Shih, "Dielectric impact on exciton binding energy and quasiparticle bandgap in monolayer WS_2 and WSe_2 ," *2D Mater.* **6**, 025028 (2019).
- M. Florian, M. Hartmann, A. Steinhoff, J. Klein, A. W. Holleitner, J. J. Finley, T. O. Wehling, M. Kaniber, and C. Gies, "The dielectric impact of layer distances on exciton and trion binding energies in van der Waals heterostructures," *Nano Lett.* **18**, 2725–2732 (2018).
- S. Borghardt, J.-S. Tu, F. Winkler, J. Schubert, W. Zander, K. Leosson, and B. E. Kardynał, "Engineering of optical and electronic bandgaps in transition

- metal dichalcogenide monolayers through external dielectric screening,” *Phys. Rev. Mater.* **1**, 054001 (2017).
- ²⁴A. V. Stier, N. P. Wilson, G. Clark, X. Xu, and S. A. Crooker, “Probing the influence of dielectric environment on excitons in monolayer WSe₂: Insight from high magnetic fields,” *Nano Lett.* **16**, 7054–7060 (2016).
- ²⁵A. Raja, A. Chaves, J. Yu, G. Arefe, H. M. Hill, A. F. Rigosi, T. C. Berkelbach, P. Nagler, C. Schüller, T. Korn, C. Nuckolls, J. Hone, L. E. Brus, T. F. Heinz, D. R. Reichman, and A. Chernikov, “Coulomb engineering of the bandgap and excitons in two-dimensional materials,” *Nat. Commun.* **8**, 15251 (2017).
- ²⁶A. Raja, L. Waldecker, J. Zipfel, Y. Cho, S. Brem, J. D. Ziegler, M. Kulig, T. Taniguchi, K. Watanabe, E. Malic, T. F. Heinz, T. C. Berkelbach, and A. Chernikov, “Dielectric disorder in two-dimensional materials,” *Nat. Nanotechnol.* **14**, 832–837 (2019).
- ²⁷Y. Jiang, S. Chen, W. Zheng, B. Zheng, and A. Pan, “Interlayer exciton formation, relaxation, and transport in TMD van der Waals heterostructures,” *Light: Sci. Appl.* **10**, 72 (2021).
- ²⁸A. T. Hanbicki, H.-J. Chuang, M. R. Rosenberger, C. S. Hellberg, S. V. Sivaram, K. M. McCreary, I. I. Mazin, and B. T. Jonker, “Double indirect interlayer exciton in a MoSe₂/WSe₂ van der Waals heterostructure,” *ACS Nano* **12**, 4719–4726 (2018).
- ²⁹B. Miller, A. Steinhoff, B. Pano, J. Klein, F. Jahnke, A. Holleitner, and U. Wurstbauer, “Long-lived direct and indirect interlayer excitons in van der Waals heterostructures,” *Nano Lett.* **17**, 5229–5237 (2017).
- ³⁰N. Zhang, A. Surrente, M. Baranowski, D. K. Maude, P. Gant, A. Castellanos-Gomez, and P. Plochocka, “Moiré intralayer excitons in a MoSe₂/MoS₂ heterostructure,” *Nano Lett.* **18**, 7651–7657 (2018).
- ³¹T. Norden, C. Zhao, P. Zhang, R. Sabirianov, A. Petrou, and H. Zeng, “Giant valley splitting in monolayer WS₂ by magnetic proximity effect,” *Nat. Commun.* **10**, 4163 (2019).
- ³²L. Ciorciaro, M. Kroner, K. Watanabe, T. Taniguchi, and A. Imamoglu, “Observation of magnetic proximity effect using resonant optical spectroscopy of an electrically tunable MoSe₂/CrBr₃ heterostructure,” *Phys. Rev. Lett.* **124**, 197401 (2020).
- ³³B. Scharf, G. Xu, A. Matos-Abiad, and I. Žutić, “Magnetic proximity effects in transition-metal dichalcogenides: Converting excitons,” *Phys. Rev. Lett.* **119**, 127403 (2017).
- ³⁴D. Zhong, K. L. Seyler, X. Linpeng, R. Cheng, N. Sivadas, B. Huang, E. Schmidgall, T. Taniguchi, K. Watanabe, M. A. McGuire, W. Yao, D. Xiao, K. C. Fu, and X. Xu, “Van der Waals engineering of ferromagnetic semiconductor heterostructures for spin and valleytronics,” *Sci. Adv.* **3**, e1603113 (2017).
- ³⁵G. Xu, T. Zhou, B. Scharf, and I. Žutić, “Optically probing tunable band topology in atomic monolayers,” *Phys. Rev. Lett.* **125**, 157402 (2020).
- ³⁶Y. Zhou, J. Sung, E. Brutschea, I. Esterlis, Y. Wang, G. Scuri, R. J. Gelly, H. Heo, T. Taniguchi, K. Watanabe, G. Zaránd, M. D. Lukin, P. Kim, E. Demler, and H. Park, “Bilayer Wigner crystals in a transition metal dichalcogenide heterostructure,” *Nature* **595**, 48–52 (2021).
- ³⁷E. Liu, T. Taniguchi, K. Watanabe, N. M. Gabor, Y.-T. Cui, and C. H. Lui, “Excitonic and valleytronic signatures of correlated states at fractional fillings of a moiré superlattice,” *Phys. Rev. Lett.* **127**, 037402 (2020).
- ³⁸S. Miao, T. Wang, X. Huang, D. Chen, Z. Lian, C. Wang, M. Blei, T. Taniguchi, K. Watanabe, S. Tongay, Z. Wang, D. Xiao, Y.-T. Cui, and S.-F. Shi, “Strong interaction between interlayer excitons and correlated electrons in WSe₂/WS₂ moiré superlattice,” *Nat. Commun.* **12**, 3608 (2021).
- ³⁹A. A. Balandin, S. V. Zaitsev-Zotov, and G. Grüner, “Charge-density-wave quantum materials and devices—New developments and future prospects,” *Appl. Phys. Lett.* **119**, 170401 (2021).
- ⁴⁰K. Rossnagel, L. Kipp, and M. Skibowski, “Charge-density-wave phase transition in 1T-TiSe₂: Excitonic insulator versus band-type Jahn–Teller mechanism,” *Phys. Rev. B* **65**, 235101 (2002).
- ⁴¹T. Pillo, J. Hayoz, H. Berger, and F. Lévy, “Photoemission of bands above the Fermi level: The excitonic insulator phase transition,” *Phys. Rev. B* **61**, 16213–16222 (2000).
- ⁴²H. Cellier, C. Monney, F. Clerc, C. Battaglia, L. Despont, M. G. Garnier, H. Beck, P. Aebi, L. Patthey, H. Berger, and L. Forró, “Evidence for an excitonic insulator phase in 1T-TiSe₂,” *Phys. Rev. Lett.* **99**, 146403 (2007).
- ⁴³D. J. Campbell, C. Eckberg, P. Y. Zavalij, H.-H. Kung, E. Razzoli, M. Michiardi, C. Jozwiak, A. Bostwick, E. Rotenberg, A. Damascelli, and J. Paglione, “Intrinsic insulating ground state in transition metal dichalcogenide TiSe₂,” *Phys. Rev. Mater.* **3**, 053402 (2019).
- ⁴⁴M. He, P. Rivera, D. Van Tuan, N. P. Wilson, M. Yang, T. Taniguchi, K. Watanabe, J. Yan, D. G. Mandrus, H. Yu, H. Dery, W. Yao, and X. Xu, “Valley phonons and exciton complexes in a monolayer semiconductor,” *Nat. Commun.* **11**, 618 (2020).
- ⁴⁵E. Liu, J. van Baren, C.-T. Liang, T. Taniguchi, K. Watanabe, N. M. Gabor, Y.-C. Chang, and C. H. Lui, “Multipath optical recombination of intervalley dark excitons and trions in monolayer WSe₂,” *Phys. Rev. Lett.* **124**, 196802 (2020).
- ⁴⁶S. Brem, A. Ekman, D. Christiansen, F. Katsch, M. Selig, C. Robert, X. Marie, B. Urbaszek, A. Knorr, and E. Malic, “Phonon-assisted photoluminescence from indirect excitons in monolayers of transition-metal dichalcogenides,” *Nano Lett.* **20**, 2849–2856 (2020).
- ⁴⁷Z. Li, T. Wang, C. Jin, Z. Lu, Z. Lian, Y. Meng, M. Blei, S. Gao, T. Taniguchi, K. Watanabe, T. Ren, S. Tongay, L. Yang, D. Smirnov, T. Cao, and S.-F. Shi, “Emerging photoluminescence from the dark-exciton phonon replica in monolayer WSe₂,” *Nat. Commun.* **10**, 2469 (2019).
- ⁴⁸Z. Li, T. Wang, S. Miao, Y. Li, Z. Lu, C. Jin, Z. Lian, Y. Meng, M. Blei, T. Taniguchi, K. Watanabe, S. Tongay, W. Yao, D. Smirnov, C. Zhang, and S.-F. Shi, “Phonon-exciton Interactions in WSe₂ under a quantizing magnetic field,” *Nat. Commun.* **11**, 3104 (2020).
- ⁴⁹A. Castellanos-Gomez, M. Buscema, R. Molenaar, V. Singh, L. Janssen, H. S. J. van der Zant, and G. A. Steele, “Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping,” *2D Mater.* **1**, 011002 (2014).
- ⁵⁰M. R. Rosenberger, H.-J. Chuang, K. M. McCreary, A. T. Hanbicki, S. V. Sivaram, and B. T. Jonker, “Nano-‘Squeeze’ for the creation of clean 2D material interfaces,” *ACS Appl. Mater. Interfaces* **10**, 10379–10387 (2018).
- ⁵¹O. A. Ajayi, J. V. Ardelean, G. D. Shepard, J. Wang, A. Antony, T. Taniguchi, K. Watanabe, T. F. Heinz, S. Strauf, X.-Y. Zhu, and J. C. Hone, “Approaching the intrinsic photoluminescence linewidth in transition metal dichalcogenide monolayers,” *2D Mater.* **4**, 031011 (2017).
- ⁵²J. Wierzbowski, J. Klein, F. Sigger, C. Straubinger, M. Kremser, T. Taniguchi, K. Watanabe, U. Wurstbauer, A. W. Holleitner, M. Kaniber, K. Müller, and J. J. Finley, “Direct exciton emission from atomically thin transition metal dichalcogenide heterostructures near the lifetime limit,” *Sci. Rep.* **7**, 12383 (2017).
- ⁵³J. Jadczyk, J. Kutrowska-Girzycka, P. Kapuściński, Y. S. Huang, A. Wójs, and L. Bryja, “Probing of free and localized excitons and trions in atomically thin WSe₂, WS₂, MoSe₂ and MoS₂ in photoluminescence and reflectivity experiments,” *Nanotechnology* **28**, 395702 (2017).
- ⁵⁴E. Liu, J. van Baren, Z. Lu, M. M. Altaïry, T. Taniguchi, K. Watanabe, D. Smirnov, and C. H. Lui, “Gate tunable dark trions in monolayer WSe₂,” *Phys. Rev. Lett.* **123**, 027401 (2019).
- ⁵⁵C. Zhang, C. Gong, Y. Nie, K.-A. Min, C. Liang, Y. J. Oh, H. Zhang, W. Wang, S. Hong, L. Colombo, R. M. Wallace, and K. Cho, “Systematic study of electronic structure and band alignment of monolayer transition metal dichalcogenides in van der Waals heterostructures,” *2D Mater.* **4**, 015026 (2016).
- ⁵⁶R. Sharma, J. Pandey, K. R. Sahoo, K. S. Rana, R. K. Biroju, W. Theis, A. Soni, and T. N. Narayanan, “Spectroscopic correlation of chalcogen defects in atomically thin MoS₂(1-x)Se_{2x} alloys,” *J. Phys. Mater.* **3**, 045001 (2020).
- ⁵⁷T. Verhagen, V. L. P. Guerra, G. Haider, M. Kalbac, and J. Vejpravova, “Towards the evaluation of defects in MoS₂ using cryogenic photoluminescence spectroscopy,” *Nanoscale* **12**, 3019–3028 (2020).
- ⁵⁸M. Tangi, M. K. Shakfa, P. Mishra, M.-Y. Li, M.-H. Chiu, T. K. Ng, L.-J. Li, and B. S. Ooi, “Anomalous photoluminescence thermal quenching of sandwiched single layer MoS₂,” *Opt. Mater. Express* **7**, 3697 (2017).
- ⁵⁹S. Tongay, J. Suh, C. Ataca, W. Fan, A. Luce, J. S. Kang, J. Liu, C. Ko, R. Raghunathanan, J. Zhou, F. Ogletree, J. Li, J. C. Grossman, and J. Wu, “Defects activated photoluminescence in two-dimensional semiconductors: Interplay between bound, charged and free excitons,” *Sci. Rep.* **3**, 2657 (2013).
- ⁶⁰K. Sugawara, Y. Nakata, R. Shimizu, P. Han, T. Hitosugi, T. Sato, and T. Takahashi, “Unconventional charge-density-wave transition in monolayer 1T-TiSe₂,” *ACS Nano* **10**, 1341–1345 (2016).
- ⁶¹F. J. Di Salvo, D. E. Moncton, and J. V. Waszczak, “Electronic properties and superlattice formation in the semimetal TiSe₂,” *Phys. Rev. B* **14**, 4321–4328 (1976).

- ⁶²P. Chen, Y.-H. Chan, X.-Y. Fang, S.-K. Mo, Z. Hussain, A.-V. Fedorov, M. Y. Chou, and T.-C. Chiang, "Hidden order and dimensional crossover of the charge density waves in TiSe_2 ," *Sci. Rep.* **6**, 37910 (2016).
- ⁶³D. L. Duong, G. Ryu, A. Hoyer, C. Lin, M. Burghard, and K. Kern, "Raman characterization of the charge density wave phase of 1T-TiSe_2 : From bulk to atomically thin layers," *ACS Nano* **11**, 1034–1040 (2017).
- ⁶⁴C. S. Snow, J. F. Karpus, S. L. Cooper, T. E. Kidd, and T.-C. Chiang, "Quantum melting of the charge density wave state in 1T-TiSe_2 ," *Phys. Rev. Lett.* **91**, 136402 (2003).
- ⁶⁵P. Tonndorf, R. Schmidt, P. Böttger, X. Zhang, J. Börner, A. Liebig, M. Albrecht, C. Kloc, O. Gordan, D. R. T. Zahn, S. Michaelis de Vasconcelos, and R. Bratschkitsch, "Photoluminescence emission and Raman response of monolayer MoS_2 , MoSe_2 , and WSe_2 ," *Opt. Express* **21**, 4908 (2013).
- ⁶⁶M. Balkanski, R. F. Wallis, and E. Haro, "Anharmonic effects in light scattering due to optical phonons in silicon," *Phys. Rev. B* **28**, 1928–1934 (1983).
- ⁶⁷J. Joshi, I. R. Stone, R. Beams, S. Krylyuk, I. Kalish, A. V. Davydov, and P. M. Vora, "Phonon anharmonicity in bulk $\text{T}_d\text{-MoTe}_2$," *Appl. Phys. Lett.* **109**, 031903 (2016).
- ⁶⁸L. Su, Y. Zhang, Y. Yu, and L. Cao, "Dependence of coupling of quasi 2-D MoS_2 with substrates on substrate types, probed by temperature dependent Raman scattering," *Nanoscale* **6**, 4920–4927 (2014).
- ⁶⁹G. Grüner, *Density Waves in Solids* (CRC Press, 1994).
- ⁷⁰P. Wölfle, "Theory of sound propagation in pair-correlated Fermi liquids: Application to $^3\text{He-B}$," *Phys. Rev. B* **14**, 89–113 (1976).
- ⁷¹K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, "Atomically thin MoS_2 : A new direct-gap semiconductor," *Phys. Rev. Lett.* **105**, 136805 (2010).
- ⁷²S. Shree, I. Paradisanos, X. Marie, C. Robert, and B. Urbaszek, "Guide to optical spectroscopy of layered semiconductors," *Nat. Rev. Phys.* **3**, 39–54 (2021).
- ⁷³D. Unuchek, A. Ciarrocchi, A. Avsar, K. Watanabe, T. Taniguchi, and A. Kis, "Room-temperature electrical control of exciton flux," *Nature* **560**, 340–344 (2018).
- ⁷⁴T. Deilmann and K. S. Thygesen, "Finite-momentum exciton landscape in mono- and bilayer transition metal dichalcogenides," *2D Mater.* **6**, 035003 (2019).
- ⁷⁵L. P. McDonnell, J. J. S. Viner, P. Rivera, X. Xu, and D. C. Smith, "Observation of intravalley phonon scattering of 2s excitons in MoSe_2 and WSe_2 monolayers," *2D Mater.* **7**, 045008 (2020).
- ⁷⁶C. Monney, E. F. Schwier, M. G. Garnier, N. Mariotti, C. Didiot, H. Beck, P. Aebi, H. Cercellier, J. Marcus, C. Battaglia, H. Berger, and A. N. Titov, "Temperature-dependent photoemission on 1T-TiSe_2 : Interpretation within the exciton condensate phase model," *Phys. Rev. B* **81**, 155104 (2010).
- ⁷⁷T. M. Project, "Materials data on MoSe_2 by materials project," (Lawrence Berkeley National Lab. (LBNL), Berkeley, CA, 2020).
- ⁷⁸H. Shibata, "Negative thermal quenching curves in photoluminescence of solids," *Jpn. J. Appl. Phys., Part 1* **37**, 550–553 (1998).
- ⁷⁹J. Huang, T. B. Hoang, and M. H. Mikkelsen, "Probing the origin of excitonic states in monolayer WSe_2 ," *Sci. Rep.* **6**, 22414 (2016).
- ⁸⁰S. S. Lin, B. G. Chen, W. Xiong, Y. Yang, H. P. He, and J. Luo, "Negative thermal quenching of photoluminescence in zinc oxide nanowire-core/graphene-shell complexes," *Opt. Express* **20**, A706 (2012).
- ⁸¹A. Kogar *et al.*, "Signatures of exciton condensation in a transition metal dichalcogenide," *Science* **358**, 1314–1317 (2017).
- ⁸²C. Lian, Z. A. Ali, and B. M. Wong, "Charge density wave hampers exciton condensation in 1T-TiSe_2 ," *Phys. Rev. B* **100**, 205423 (2019).
- ⁸³D. Van Tuan, B. Scharf, I. Žutić, and H. Dery, "Marrying excitons and plasmons in monolayer transition-metal dichalcogenides," *Phys. Rev. X* **7**, 041040 (2017).
- ⁸⁴D. Van Tuan, B. Scharf, Z. Wang, J. Shan, K. F. Mak, I. Žutić, and H. Dery, "Probing many-body interactions in monolayer transition-metal dichalcogenides," *Phys. Rev. B* **99**, 085301 (2019).
- ⁸⁵B. Scharf, D. Van Tuan, I. Žutić, and H. Dery, "Dynamical screening in monolayer transition-metal dichalcogenides and its manifestations in the exciton spectrum," *J. Phys.: Condens. Matter* **31**, 203001 (2019).
- ⁸⁶D. Van Tuan, B. Scharf, I. Žutić, and H. Dery, "Intervalley plasmons in crystals," *arXiv:1901.02567* (2019).