Characterization of collective ground states in single-layer NbSe₂

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Layered transition metal dichalcogenides are ideal systems for exploring the effects of dimensionality on correlated electronic phases such as charge density wave (CDW) order and superconductivity. In bulk NbSe₂ a CDW sets in at $T_{CDW} = 33$ K and superconductivity sets in at $T_c = 7.2$ K. Below T_c these electronic states coexist but their microscopic formation mechanisms remain controversial. Here we present an electronic characterization study of a single two-dimensional (2D) layer of NbSe₂ by means of low-temperature scanning tunnelling microscopy/spectroscopy (STM/STS), angle-resolved photoemission spectroscopy (ARPES), and electrical transport measurements. We demonstrate that 3×3 CDW order in NbSe₂ remains intact in two dimensions. Superconductivity also still remains in the 2D limit, but its onset temperature is depressed to 1.9 K. Our STS measurements at 5 K reveal a CDW gap of $\Delta = 4$ meV at the Fermi energy, which is accessible by means of STS owing to the removal of bands crossing the Fermi level for a single layer. Our observations are consistent with the simplified (compared to bulk) electronic structure of single-layer NbSe₂, thus providing insight into CDW formation and superconductivity in this model strongly correlated system.

any-body electronic ground states can be sensitive to the spatial dimensions of a material¹⁻⁵. In transition metal dichalcogenide materials, for example, significant differences are expected in charge density wave and superconducting (SC) phases as dimensionality is reduced from a bulk three-dimensional (3D) material to a single-layer 2D material⁶⁻⁹. NbSe₂ is a model system in this regard, as it has been predicted to preserve its charge density wave (CDW) order in the single-layer limit, although with a significantly shortened CDW wavevector (q_{CDW} ; ref. 6). A metal to semi-metal transition has also been predicted for NbSe₂ when it is reduced to the 2D limit^{6,7,10}. Previous work has shown that the superconducting transition temperature for NbSe₂ decreases from its bulk value of $T_{\rm C} = 7.2 \,\rm K$ as the thickness is reduced¹¹⁻¹³, but no experimental studies have yet been performed that explore the interplay between NbSe2 superconductivity and CDW formation in the extreme 2D limit.

CDW behaviour in the 3D limit of NbSe₂, on the other hand, has been well studied, although the origin of the bulk CDW transition at $T_{\rm CDW} = 33$ K remains controversial. Recent experiments suggest that electron–phonon coupling plays a dominant role in triggering the CDW phase^{14–20}, thus casting doubt on mechanisms involving Fermi-surface nesting^{21–24} and saddle-point singularities^{25,26}. Critical experimental parameters associated with the CDW, such as the magnitude and location of the energy gap, also remain unclear.

Previous STS measurements on bulk NbSe₂ in the CDW phase have revealed an unexpectedly large gap-like structure having width $2\Delta \sim 70$ meV (refs 27,28), although a recent analysis of STS data suggests that the CDW energy gap is only $2\Delta \approx 24$ meV (ref. 18). In contrast, low-temperature angle-resolved photoemission spectroscopy (ARPES) measurements performed on bulk NbSe₂ show an anisotropic CDW energy gap at $E_{\rm F}$ with a width of only a few meV (ref. 17). In general, it is expected that a weak-coupling CDW derived from Fermi-surface nesting should open a small gap on the Fermi surface, whereas a strong-coupling CDW caused by electron-phonon coupling should open a larger gap away from the Fermi surface.

Here we report measurement of the electronic structure of single-layer NbSe₂ using a combination of scanning tunnelling microscopy/spectroscopy (STM/STS), ARPES and electronic transport techniques. This allows us to directly probe the electronic ground state of NbSe₂ in the 2D limit, enabling interrogation of the effects of dimensionality and interlayer coupling in this layered material. We observe a reduction in the number of Fermi-level-crossing bands from three (for bulk) to one in the single-layer limit. Despite this change in electronic structure, CDW order in single-layer NbSe₂ remains unchanged with respect to the bulk case. The simplified band structure of single-layer NbSe₂, however, allows unprecedented access to the NbSe₂ CDW energy gap by

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Figure 1 | **Structure of single-layer NbSe**₂ **on bilayer graphene. a**, Top and side view sketches of single-layer NbSe₂, including the substrate. **b**, Large-scale STM image of 0.9 ML of NbSe₂/BLG ($V_s = -100 \text{ mV}$, $I_t = 3 \text{ nA}$, T = 5 K). **c**-**e**, Atomically resolved STM images of single-layer NbSe₂ for different temperatures: T = 45 K ($V_s = +95 \text{ mV}$, $I_t = 53 \text{ pA}$) (**c**), T = 25 K ($V_s = -120 \text{ mV}$, $I_t = 70 \text{ pA}$) (**d**) and T = 5 K ($V_s = -4 \text{ mV}$, $I_t = 50 \text{ pA}$) (**e**). The FFT of the STM image of **e** is shown in the inset.

means of STS (observed here to be $2\Delta = 8 \text{ meV}$ centred at $E_{\rm F}$). Superconductivity in NbSe₂, on the other hand, is significantly suppressed in the 2D limit, showing an onset of superconducting fluctuations at 1.9 K and a broadened superconducting transition with a midpoint at 0.65 K consistent with a Kosterlitz–Thouless transition. The one Nb antibonding band⁶ that remains in the Fermi surface of single-layer NbSe₂ thus seems to play a critical role in the NbSe₂ CDW state, whereas the absent bands have a stronger influence on NbSe₂ superconductivity¹⁷. These results provide a window into the electronic structure of single-layer NbSe₂ and help to clarify the long-standing debate over NbSe₂ CDW formation.

Our experiments were carried out on high-quality submonolayer NbSe₂ films grown on epitaxial bilayer graphene (BLG) on 6H-SiC(0001), as sketched in Fig. 1a. The large-scale STM image in Fig. 1b shows the typical morphology of our single-layer NbSe₂ samples. Black regions correspond to the BLG substrate and the NbSe₂ layer is purple. The temperature dependence of the electronic ground state of single-layer NbSe₂ was measured by means of STM and electrical transport. Figure 1c–e shows STM topographic data for selected temperatures from T = 45 K to T = 5 K. At T = 45 K, well above the critical transition temperature for bulk NbSe₂ ($T_{CDW} = 33$ K), only the undistorted crystal structure is observed (Fig. 1c). At a lower temperature of T = 25 K, weak and spotty signatures of a superlattice are apparent (Fig. 1d). Here, small CDW patches surrounded by non-CDW regions can be seen. This is reminiscent of STM images of bulk NbSe₂ at temperatures close to the CDW transition temperature¹⁹. At T = 5 K, the 3×3

CDW superlattice is fully and uniformly developed for singlelayer NbSe₂ (Fig. 1e). Figure 2 shows the temperature-dependent electrical resistance of single-layer NbSe₂ on BLG, acquired using a four-point probe low-excitation dc method (see Supplementary Information). No signature of the CDW transition is seen in the temperature dependence of the resistivity. Previous temperaturedependent resistivity measurements^{19,29} for bulk NbSe₂ samples show a change in slope near the CDW onset temperature only for samples with large residual resistivity ratios. The absence of such a signature in the single-layer limit could be due to differences in the dominant electron scattering mechanism for bulk versus 2D samples. Importantly, a sharp downturn in the resistance begins at T = 1.9 K, indicative of the onset of superconducting fluctuations, the superconducting transition midpoint is at 0.65 K and the zero resistance point at 0.46 K, as shown inset. These data indicate that the trend of reduced superconducting transition temperature (T_c) with decreasing layer number in NbSe₂ (refs 11,12) continues down to the single-layer limit.

The alignment of the 3×3 CDW superlattice with the 1×1 atomic arrangement for single-layer NbSe₂ can be seen in Fig. 1e, similar to what has been seen previously in STM images of bulk NbSe₂ (refs 18,19,30). The 3×3 superlattice remains unchanged in our STM images, regardless of the orientation between the NbSe₂ layer and the BLG (see STM and LEED data in the Supplementary Information). This rules out the possibility that the 3×3 superlattice observed here in single-layer NbSe₂ is a moiré pattern (moiré patterns have been observed in MoSe₂/BLG (ref. 31)). A 3×3





Four-point probe measurement of the temperature-dependent resistance of single-layer NbSe₂/BLG on insulating SiC(0001). Inset shows expanded view of *R* versus *T* between 0.05 and 4 K.

moiré pattern formation requires a quasi-commensurate match between overlayer and substrate atomic lattices, which does not occur here as NbSe₂ has a much larger unit cell than graphene. The rotational disorder we find in single-layer NbSe₂ with respect to the BLG substrate indicates weak coupling between them (similar weak coupling has been demonstrated for epitaxial graphene grown on different metal substrates³²).

We experimentally determined the electronic structure of singlelayer NbSe₂ by means of a combination of STS and ARPES. Figure 3a shows a typical STM dI/dV spectrum of single-layer NbSe₂ taken over a large bias range. In the positive bias (empty state) region the most pronounced feature is the peak labelled C_1 at $V_s = 0.5$ V. For negative bias (filled states) we observe a very shallow asymmetric peak near $V_s = -0.2$ V (labelled V_1), below which the local density of states (LDOS) flattens out and does not rise again until the peak labelled V_2 at $V_s = -0.8$ V. This behaviour is very different from previous STS results obtained for bulk NbSe₂, which show much higher LDOS in the region -0.8 V < V < 0V (ref. 19). Figure 3b shows the ARPES data obtained from the same type of single-layer NbSe₂ sample as in Fig. 3a using *sp*-mixed polarized light. The measured electronic dispersion is energetically aligned with the dI/dVspectrum for comparison. Owing to rotational misalignment within



Figure 3 | **Electronic structure of single-layer NbSe₂ on bilayer graphene. a**, Wide-bias STM dl/dV spectrum acquired on single-layer NbSe₂/BLG showing several electronic features: V_{1-3} in the filled states and C_1 in the empty states (f = 403 Hz, $I_t = 100 \text{ pA}$, $V_{r.m.s.} = 5 \text{ mV}$, T = 5 K). **b**, Second-derivative *sp*-polarized ARPES dispersion of single-layer NbSe₂/BLG (T = 300 K) aligned in energy with the STM dl/dV curve shown in **a**. The dispersion exhibits angular integration due to the intrinsic rotational misalignment of NbSe₂ domains on the BLG substrate. The dotted and dot-dashed orange curves indicate bands from the Γ -K and Γ -M directions, respectively. The enhanced intensity near E_F is a well-known artefact of the second-derivative process and should not be confused with an electronic band. **c**,**d**, Predicted band structures and Fermi surfaces of bulk NbSe₂ (**c**) and single-layer NbSe₂ (**d**). The calculated band structures (DFT) have been adapted from ref. 6.

the NbSe₂ layer, the ARPES dispersion reflects a mixture of states with dominant intensity coming from the high-symmetry directions Γ -M and Γ -K. Two dispersive features can be seen crossing $E_{\rm F}$ (highlighted by the orange dashed lines). The ARPES spectrum also shows an energy gap over the range $-0.8 \, {\rm eV} < E < -0.3 \, {\rm eV}$, and below this several dispersive bands merge at the Γ point. In comparison, the ARPES spectrum for 5ML–NbSe₂ (see Supplementary Information) exhibits an additional Nb-derived band crossing the same energy range that is gapped for single-layer NbSe₂.

This experimental data is consistent with the changes in band structure that are predicted to occur when NbSe₂ is thinned down to a single layer⁶. The bulk NbSe₂ band structure (Fig. 3c) has three bands crossing $E_{\rm F}$ (two Nb-derived bands and one S-derived band), and exhibits no bandgap throughout our experimental energy range. Single-layer NbSe₂, on the other hand, has a much simpler predicted electronic structure (Fig. 3d), consisting of just one Nb-derived band crossing $E_{\rm F}$ away from the Γ point, as well as a bandgap from -0.4to -0.8 eV and valence bands below that. These predicted features can be seen in our experimental ARPES dispersion (Fig. 3b) which shows that states right below $E_{\rm F}$ are located away from the Γ point, there exists an energy gap between -0.3 and -0.8 eV, and there exist several valence bands below -0.8 eV. Our dI/dV spectroscopy (Fig. 3a) is also consistent with the predicted single-layer band structure. For example, the peak at C_1 is consistent with the high DOS associated with the top of the Nb-derived band at Γ above $E_{\rm F}$. We can also associate the shallow peak at V_1 with the Nb band right below $E_{\rm F}$. The flat dI/dV region seen between V_1 and V_2 is consistent with the predicted bandgap (the fact that the dI/dV does not reach zero is due to residual tunnelling into the BLG substrate), and the peaks at V_2 and V_3 are consistent with the lower-energy valence band structure^{6,33}. Overall, these features are very different from previous STS spectra obtained for bulk NbSe₂, which show much higher LDOS below $E_{\rm F}$ and no signs of a bandgap in the filled-state regions¹⁹. This is due to the additional electronic bands and resulting DOS expected in this energy range for bulk NbSe₂ as compared to single-layer NbSe₂ (Fig. 3c,d). This is also reflected in the additional band that can be seen in the ARPES spectrum of 5ML-NbSe₂ (Supplementary Information), which corresponds to a Nb bonding band (the blue band in Fig. 3c,d). The Se-derived band (green band in Fig. 3c,d) is typically not observed in ARPES owing to the high k_z dispersion.

To better understand the collective ground states of single-layer NbSe₂, we experimentally probed its low-energy electronic structure near $E_{\rm F}$ by means of STS. Figure 4 shows a typical low-bias dI/dV spectrum obtained for single-layer NbSe₂. This spectrum exhibits a striking energy gap feature centred at $E_{\rm F}$ that is not present in the calculated band structure of single-layer NbSe₂ (Fig. 3d). This feature, which is also not observed experimentally in bulk NbSe₂ (refs 18,27,28), exhibits a sharp dip at $E_{\rm F}$ bounded by two narrow peaks that sit on top of an asymmetric background. The dip at $E_{\rm F}$ does not reach all the way to zero, suggesting that it is not a full gap in the electronic structure. These STS features (including both wide-bias and low-bias spectra) were observed consistently for hundreds of dI/dV curves measured on several samples using a variety of different tip apexes. However, the width (2Δ) of the low-bias gap feature was found to exhibit some spatial variation, probably due to heterogeneity induced by the presence of defects at the NbSe₂/graphene interface (see Fig. 5c). Statistical analysis of data (257 curves) obtained at many different locations for T = 5 K yields an average gap value of $\Delta = 4.0$ mV with a standard deviation of 1 mV (the gap magnitude is defined as half the energy distance between the two peaks bracketing the gap). This value is in agreement with anisotropic gap-opening observed previously by low-temperature ARPES (ref. 17) at the Fermi surface near the K point in the band that is predicted to remain in the 2D single-layer limit of NbSe₂ (orange band in Fig. 3d).



Figure 4 | CDW gap of single-layer NbSe₂. Low-bias STM *dI/dV* spectrum acquired on single-layer NbSe₂/BLG showing the CDW gap (Δ) at *E*_F (*f*=871 Hz, *l*_t=100 pA, *V*_{r.m.s.}=0.6 mV, *T*=5 K). The dashed lines indicate the positions of the CDW coherence peaks.

To better understand the origin of the $E_{\rm F}$ gap feature of Fig. 4, we performed spatially resolved dI/dV mapping of single-layer NbSe₂ at different bias voltages near $E_{\rm F}$. Figure 5a,b shows dI/dV conductance maps of the same region taken at bias voltages outside $(V_{\rm b} = -26 \,\mathrm{mV})$ and inside $(V_{\rm b} = 3 \,\mathrm{mV})$ the low-bias gap region (Fig. 5c shows STM topography for this same region). The dI/dVconductance map taken at an energy outside of the gap (Fig. 5a) clearly shows the 3×3 CDW pattern, but the conductance map measured at an energy inside of the gap (Fig. 5b) shows no sign of the CDW. We Fourier analysed dI/dV maps taken at different voltages to obtain a more quantitative understanding of the energy dependence of CDW electronic features. Figure 5d shows the relative intensity of the resulting 3×3 peaks ($I_{3\times 3}$) in the FFTs normalized to the intensity of the 1×1 Bragg peaks (I_{Bragg}). This ratio $(I_{3\times3}/I_{\text{Bragg}}(E))$ is a measure of the strength of the CDW modulation on the density of states and would remain constant if the gap had a different origin, such as electronic correlations. As seen in Fig. 5d, $I_{3\times3}/I_{\text{Bragg}}$ has large amplitude at energies far from E_{F} , but shows a decrease of nearly two orders of magnitude very close to $E_{\rm F}$. Figure 5e shows a higher-resolution plot of the dip in $I_{3\times3}/I_{\rm Bragg}$ at $E_{\rm F}$ (boxed region in Fig. 5d). The decrease in the ratio $I_{3\times3}/I_{\rm Bragg}$ is seen to follow the energy dependence of the low-bias gap feature observed in dI/dV spectroscopy. This correlation of CDW intensity with gap energy dependence suggests that the gap is the result of CDW order. In particular, the diminishing CDW intensity for in-gap energies suggests that the residual LDOS within the gap arises from a portion of the Fermi surface that is not gapped by CDW order.

Our results allow us to draw some conclusions regarding different models of CDW formation in NbSe₂. First, we rule out recently proposed dimensionality effects on the CDW phase that were predicted for single-layer NbSe₂ but that are not observed here. This includes a predicted reduction of the CDW wavevector in the 2D limit⁶. We also rule out proposed Fermi-surface nesting mechanisms^{19,21,22,24} involving the inner pockets around Γ and K (blue band in Fig. 3c) as these bands are not present in the single-layer limit and the CDW remains unchanged. As saddle-point-based mechanisms of CDW formation^{23,26} involve the Fermi pockets that are still present in the



Figure 5 | **Spatially and energetically resolved CDW phase in single-layer NbSe₂. a,b**, Experimental conductance maps taken at $V_s = -26$ mV (**a**) and $V_s = +3$ mV (**b**) (f = 871 Hz, $I_t = 40$ pA, $V_{r.m.s.} = 0.6$ mV, T = 5 K). The FFT of each conductance map is shown as an inset, allowing identification of Bragg (1 × 1) and CDW (3 × 3) peaks. **c**, STM topograph of the same region where the conductance maps in **a** and **b** were acquired ($V_s = -17$ mV, $I_t = 40$ pA, T = 5 K). **d**, Logarithmic plot of the intensity of the 3 × 3 peaks ($I_{3 \times 3}$) in the FFT of the different conductance maps normalized by the Bragg peak intensity (I_{Bragg}) as a function of bias voltage. **e**, Linear scale zoom-in of the boxed region in **d**.

single-layer limit, we cannot rule them out based on fermiology. However, these mechanisms predict a CDW gap centred at an energy tens of meV away from $E_{\rm F}$, and thus are inconsistent with our observation that the CDW gap is centred at $E_{\rm F}$.

Our data also bring out some puzzling features concerning the CDW in NbSe₂. On the one hand, our observations that the gap is tethered to the Fermi energy, which is rather small, and that it correlates with the CDW amplitude are all consistent with the notion that the gap is the result of Fermi-surface nesting. On the other hand, our observation that the CDW modulation is observed in the LDOS at biases far exceeding the gap edges suggests that the CDW order is not a weak-coupling phenomenon arising from Fermi-surface nesting. This dual nature of the CDW gap imposes stringent constraints on any future theory of CDW formation in NbSe₂.

The suppression of the superconducting onset temperature in single-layer NbSe₂ is consistent with the trend previously observed¹¹⁻¹³, namely that the superconducting transition temperature decreases with sample thinning. Possible reasons for this include enhancement of thermally driven superconducting phase fluctuations, as well as weakening of the strength of Cooper pairing in two dimensions. Additional factors that may contribute to this weakening are the reduced screening of the Coulomb interaction¹² and the reduction of DOS at $E_{\rm F}$ for single-layer NbSe₂ arising from band reduction. It is likely that the electronic bands that are absent in single-layer NbSe₂ play a key role for thicker NbSe₂ films¹⁷.

Methods

Methods and any associated references are available in the online version of the paper.

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Author contributions

M.M.U. and A.J.B. conceived the work and designed the research strategy. M.M.U., A.J.B., Y.C., W.R. and M.T.E. measured and analysed the STM/STS data. Y.Z., H.R. and S.-K.M. performed the MBE growth and ARPES and LEED characterization of the samples. S.O., C.O.-A., M.M.U. and Y.C. carried out the transport experiments. H.-Z.T. and A.R. helped in the experiments. D.L. participated in the interpretation of the experimental data. Z.H. and Z.-X.S. supervised the MBE and sample characterization. A.Z. supervised the transport measurements. M.F.C. supervised the STM/STS experiments. M.M.U. wrote the paper with help from M.F.C. and A.Z. M.M.U. and M.F.C. coordinated the collaboration. All authors contributed to the scientific discussion and manuscript revisions.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to M.M.U. or M.F.C.

Competing financial interests

The authors declare no competing financial interests.

Methods

Single-layer NbSe2 was grown by molecular beam epitaxy (MBE) on epitaxial BLG on 6H-SiC(0001) at the HERS endstation of beamline 10.0.1, Advanced Light Source, Lawrence Berkeley National Laboratory (the MBE chamber had a base pressure of $\sim 2 \times 10^{-10}$ torr). We used SiC wafers with two different resistivities, $\rho \sim 300 \,\Omega$ cm (STM and ARPES experiments) and $\rho > 10^8 \,\Omega$ cm (transport and STM experiments). The morphology of the single-layer NbSe₂ was the same in both cases. The epitaxial BLG substrate was prepared by following the procedure detailed in refs 31,34. High-purity Nb and Se were evaporated from an electron-beam evaporator and a standard Knudsen cell, respectively. The flux ratio of Nb to Se was controlled to be \sim 1:30. The growth process was monitored by *in* situ RHEED and the growth rate was \sim 17 min per monolayer. During the growth the substrate temperature was kept at 600 K, and after growth the sample was annealed to 670 K. Low-energy electron diffraction (LEED) patterns were routinely taken after the growth to determine the quality of the sample (see Supplementary Information). Subsequent characterization by ARPES and core-level spectroscopy were performed in the analysis chamber (base pressure $\sim 3 \times 10^{-11}$ torr) of the 10.0.1 beamline. To protect the film from contamination and oxidation during transport through air to the ultrahigh vacuum scanning tunnelling microscopy (UHV-STM) chamber, a Se capping layer with a thickness of ~10 nm was deposited on the sample surface after growth. For subsequent STM and transport experiments the Se capping layer was removed by annealing the sample to $\sim 600 \,\mathrm{K}$ in the UHV STM system for 30 min. STM imaging and STS experiments were performed in an in-house-built UHV-STM operated at T = 5 K. STM differential

conductance (dI/dV) spectra were measured at 5 K using standard lock-in techniques. To avoid tip artefacts, the STM tip was calibrated by measuring reference spectra on the graphene substrate³¹. STM/STS data were analysed and rendered using WSxM software³⁵.

Four-probe contacts for transport measurements were placed on the sample by electron-beam evaporation of 6.5 nm Ti and 100 nm Au through a shadow mask onto exposed graphene portions of the NbSe₂ sample (with a Se capping layer, see Supplementary Information). The Se capping layer was then removed in UHV and resistance measurements were subsequently performed either *in situ* inside the STM chamber, or in a Quantum Design PPMS dilution refrigerator (employing a rapid transfer from the UHV chamber to the inert gas/vacuum PPMS chamber). Measurements were made using a Keithley 2602A SourceMeter unit and a Keithley 181 nanovoltmeter with a current bias of 100 nA. At each temperature point the voltage was measured at both 100 nA and -100 nA to remove thermoelectric voltages induced by the temperature difference between the sample and measurement electronics. The heating rate during measurement ranged from 1 K h⁻¹ to 60 K h⁻¹.

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