Topological Landscape of Competing Charge Density Waves in 2H-$NbSe_2$

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Despite decades of studies of the charge density wave (CDW) of 2H-$NbSe_2$, the origin of its incommensurate CDW ground state has not been understood. We discover that the CDW of 2H-$NbSe_2$ is composed of two different, energetically competing, structures. The lateral heterostructures of two CDWs are entangled as topological excitations, which give rise to a CDW phase shift and the incommensuration without a conventional domain wall. A partially melted network of topological excitations and their vertices explain an unusual landscape of domains. The unconventional topological role of competing phases disclosed here can be widely applied to various incommensuration or phase coexistence phenomena in materials.

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The competition of distinct periodicities or ordered phases is widely found in various material systems [1–4]. Periodically ordered phases in spin [5], charge [6–8], and orbital degrees of freedom [9] have also interacted with the underlying lattice periodicities, which result in commensuration-incommensuration phenomena and create domain-wall topological excitations [10,11]. Notable examples are Frenkel-Kontorova solitons in one-dimensional systems [12] and moiré structures in van der Waals layers [13,14]. In most of the cases, competitions between ordered phases and those between them and underlying lattices have been separately discussed. However, here we observe a unique case where those two phenomena, the competing phases and the incommensuration, are topologically entangled to exhibit an unusual landscape of domains of coexisting phases.

We pick up the charge density wave (CDW) in two-dimensional (2D) materials, which is one of the most extensively investigated topics in condensed matter physics together with superconductivity [15]. For most of the 2D CDW phases [16], ground states are commensurate with their atomic lattices, which would transit into incommensurate CDW phases with topological excitations (discommensurations or domain walls carrying a CDW phase shift [17]) through thermal excitation [18], doping [19,20], or pressure [21,22]. Topological excitations are believed to have crucial roles not only in the superconductivity emerging with the commensurate CDW order suppressed [19–22] but also in outstanding functionalities of CDW materials such as the ultrafast switching behavior [23] and the memrister operation [24]. Nevertheless, atomic structures of domain walls are largely unknown [25] and thus naturally microscopic mechanisms for the emerging superconductivity and functionalities have been elusive.

In one of the most widely investigated model systems of 2D CDW, 2H-$NbSe_2$, the intriguing nature of the incommensurate phase has become even a long term mystery. 2H-$NbSe_2$ undergoes a phase transition to the (3×3) CDW state at 33 K [7,8]. While the microscopic origin of the transition is still under debate, the CDW ground state has been reported to be intriguingly incommensurate as confirmed by electron microscopy [26], nuclear magnetic resonance [27], and recent scanning tunneling microscopy (STM) [28] experiments. However, none of these experiments identified the atomic structure of the discommensuration or the domain wall. Moreover, there is still ambiguity in the atomic structure of the commensurate CDW itself. In the early neutron scattering experiment, the CDW state was suggested to have a hexagonal symmetry [8] but later the electron microscopy clarified the symmetry as an orthorhombic one [26]. Three types of distinct CDW structures had been suggested in early theories [29,30] and their atomic structures together with possible magnetic orders were discussed by a very recent density functional theory (DFT) calculation [31].

In this work, we clarify the unconventional atomistic origin of the incommensurate CDW state in 2H-$NbSe_2$ using STM experiments and DFT calculations. The CDW state of 2H-$NbSe_2$ is divided by domains of two different CDW structures. Our DFT calculations and experimental results disclose atomic structures of the distinct CDW structures and their degenerate energies. The characteristic heterostructure of two CDW domains produces a phase shift for the discommensuration [17]. Such a topological role of two competing phases explains the unusual domain distribution observed in the experiment. This reveals a distinct mechanism of the CDW discommensuration and a unique case of topologically entangled domain formation, which might be considered not only in CDW systems but also in a wide variety of materials with incommensuration phenomena and competing phases including moiré structures in van der Waals layers [13,14].

Single crystal 2H-$NbSe_2$ is cleaved in high vacuum to obtain clean surfaces and transferred to the ultrahigh-vacuum

chamber equipped with a commercial cryogenic STM operating at 4.3 K. STM images were obtained using the constant current mode. Our DFT calculations were performed using the Vienna *ab initio* simulation package [32] with the projector augmented wave method [33,34] and the Perdew-Burke-Ernzerhof exchange correlation functional [35]. Single-layer structures of $NbSe_2$, inserted between 10 Å vertical vacuum, were calculated with a $(6 \times 6 \times 1)$ k-point mesh and a plane wave cutoff energy of 366.5 eV. The residual force criterion to terminate atomic relaxation is 0.01 eV/Å.

The STM topography of $2H$-$NbSe_2$ shows clearly the coexistence of two different CDW structures [Fig. 1(a)]. Hexagonally arrayed protrusions represent the top Se atoms of $NbSe_2$ and the (3×3) CCDW order is clear with periodic enhancements of protrusions. Bright triangular protrusions or Se trimers are conspicuous in one of the CDW domains. The other domain exhibits a structurally distinct CDW state with a single bright Se protrusion per each (3×3) unit cell. Figure 1(b) shows a detailed line profile across two CDW structures; the single big peak and two small ones for the CDW structure with monomer protrusions smoothly transform into two big peak structures which are parts of bright Se trimers. The coexisting CDW states is ubiquitous in our measurements over whole measured surfaces [Fig. 1(c)], different cleavages, crystals, and tunneling biases (see Fig. S1 in the Supplemental Material [36]). Moreover, the coexisting structures are noticeable in most of the STM images published previously although they have never been discussed explicitly [28,37]. These CDW structures exhibit an intriguing domain structure as shown in Fig. 1(c); the landscape of all-connected monomer and all-isolated trimer domains deviate certainly from a random heterogeneous domain mixture of competing phases. As revealed below, this unusual landscape has a topological origin.

We identify atomic structures of two CDW structures using STM images and DFT calculations (Fig. 2). As discussed in the previous literature, CDW maxima can locate on cation (Nb), anion (Se), or hollow sites to form different CDW structures [29,30] (see Fig. S2 in the Supplemental Material [36]). The cation-centered (CC) structure has hexagonal symmetry but the anion-centered (AC) and hollow-centered (HC) structures have orthorhombic symmetry [29,30]. Hexagonal symmetry is not consistent with the electron microscopy experiment [26] and the CC structures are not favorable in our calculation and comparison to STM images [36]. We thus just consider the

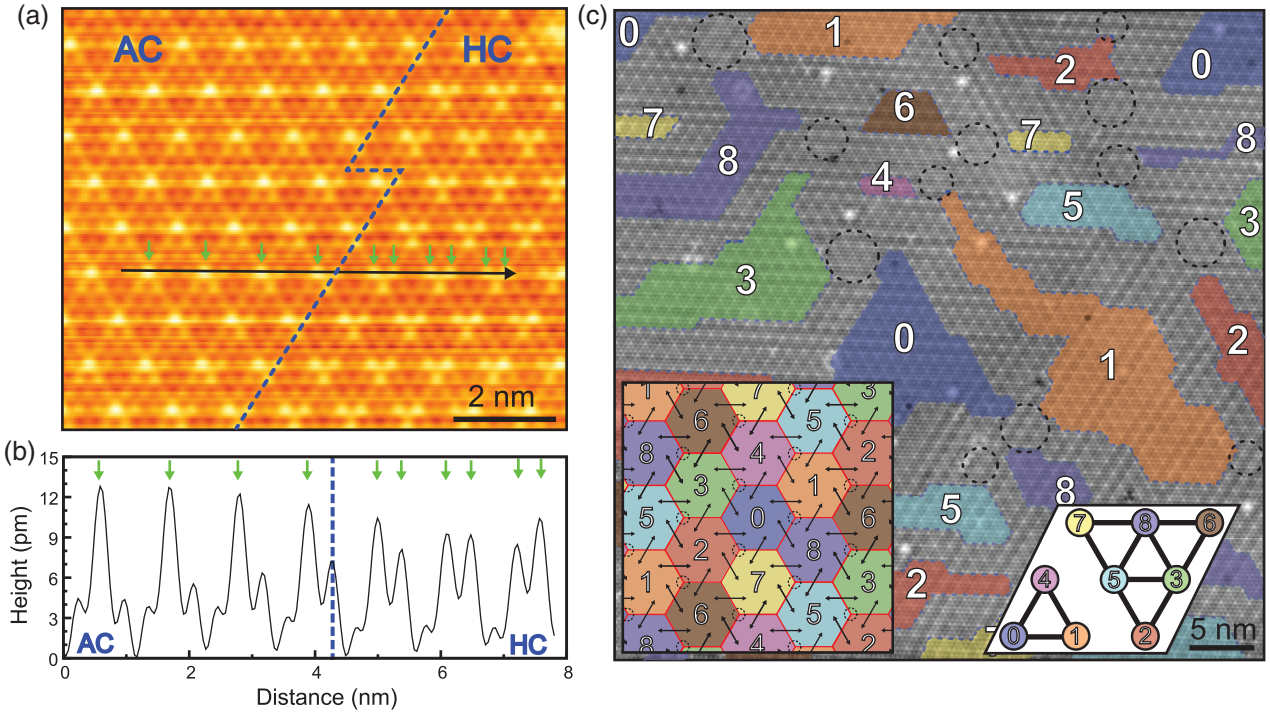

FIG. 1. (a) STM topography of the coexisting domains in $2H$-$NbSe_2$ at a sample bias of 100 mV. The blue dashed line separates two different domains. (b) Line profile along the black arrow in (a). Green arrows indicate the locations of bright topographic protrusions. (c) STM topography of HC CDW domains at 100 mV. Black dashed circles indicate the region of AC CDW dislocations as magnified in Fig. 4(b). The colors and numbers indicate particular HC CDW domains among nine translationally degenerate domains. These domains have to be connected properly in the ideal domain network shown in the insets. Different domains are identified by their relative translation as defined in the right inset within one CDW unit cell. The black arrows represent the directions of CDW translations among HC CDW domains.

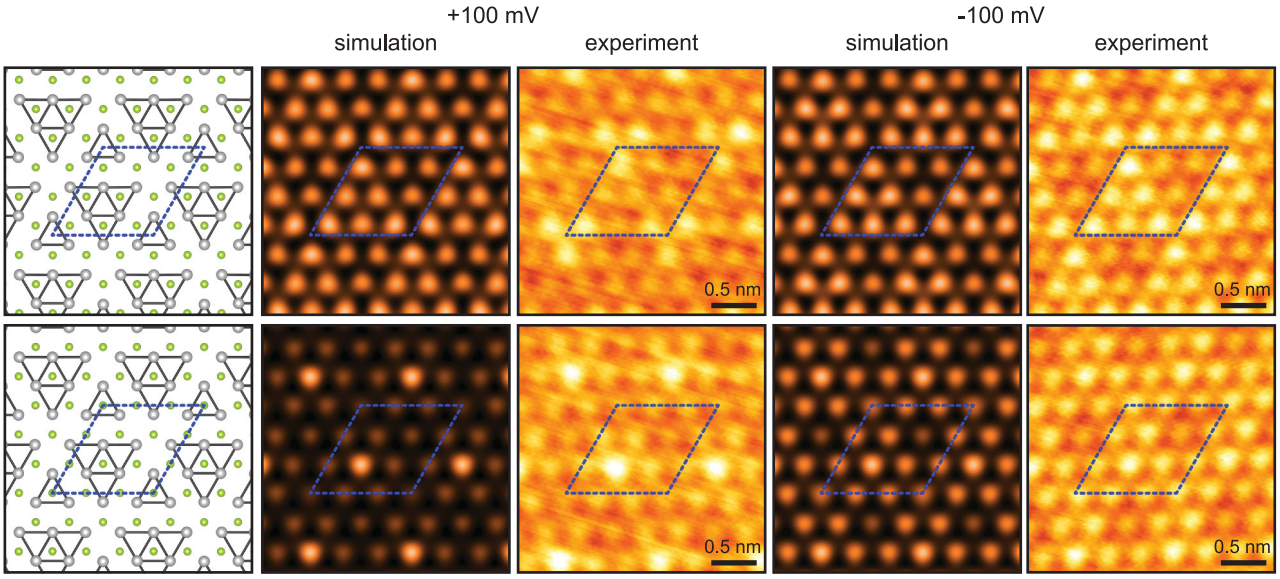

FIG. 2. Atomic structure models, simulated and experimental STM topographic images at two different biases of +100 and −100 mV of the HC (upper) and AC (lower) CCDW structures. The large gray (small green) balls represent Nb (Se) atoms in the structure model and the solid lines indicate short bonds for CDW distortions. The blue dashed lines indicate (3 × 3) CCDW unit cells.

latter two structures. In terms of Nb atom distortions relaxed in the corresponding DFT calculations, HC and AC CDW structures have similar units of a large triangle with six Nb atoms and a small triangle of a Nb trimer (Fig. 2). However, the HC structure has Nb triangles centered on the hollow sites while the AC structure's triangles are centered on Se atoms.

STM simulations of our (3 × 3) CDW structures reproduce well the local topographies. In the HC structure, the bright trimer protrusion of three Se atoms on the Nb trimer is well compared with the STM topography at 100 mV and the bright (dark) triangular protrusion of six (three) Se atoms is in good agreement with the experiment at −100 mV. In contrast, in the AC structure, the brightest protrusion made by the center Se atom of the Nb sextet agrees well with the STM topography at both biases. The HC structure has a 13 (17) meV energy gain per (3 × 3) unit cell compared with the AC (CC) structure. A very recent DFT study, considering only HC and CC structures, also reported a consistent result [31].

With these CDW atomic structures, we can clarify the structural origin of the CDW discommensuration. As a matter of fact, a translation between HC and AC structures cannot be defined due to the absence of a common reference as shown in Figs. 1(b) and 3 but one can define it between two HC domains sandwiching a stripe of an AC domain or vice versa. Figure 3 shows such a structure observed by STM and its schematic atomic structure. This kind of structures is found all over the surface [see Fig. 1(c)]. One of the Se atoms nearby the Nb trimer (small blue triangle) in the HC structure and the Se atom at the center of a Nb sextet (large red triangle) in the AC structure are superimposed to connect the domains. This structure is fully relaxed in the DFT calculation and produces the STM image [Fig. 3(c)], which is fully consistent with the observed one [Fig. 3(a)]. The AC domain between two HC domains and two domain boundaries between the HC and

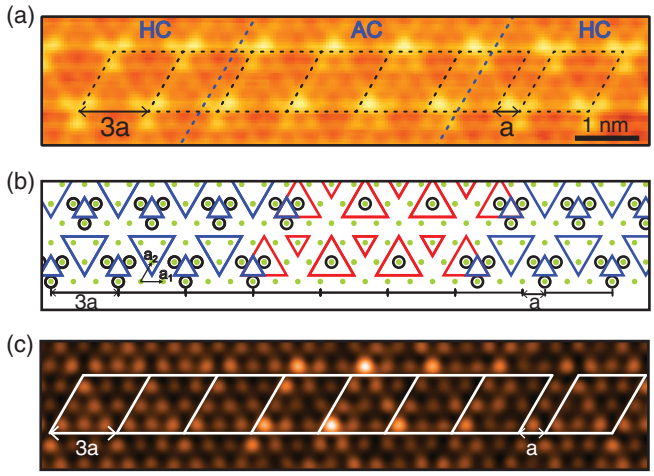

FIG. 3. (a) STM topography of a HC-AC-HC heterostructure in 2H-$NbSe_2$ at 100 mV. The blue dashed lines represent boundaries between HC and AC structures. The black dashed lines indicate (3 × 3) CDW unit cells showing a CDW translation between HC structures. (b) Schematic atomic and CDW configurations of the HC-AC-HC heterostructure. The blue and red lines indicate CDW distortions of Nb atoms in the HC and AC structures, respectively. The green dots represent Se atoms and black circles indicate the bright protrusions in STM. $\mathbf{a}_1$ and $\mathbf{a}_2$ are pristine lattice vectors to define the CDW translation, which is indicated for the HC structure at the bottom. (c) Simulated STM topography of the fully relaxed HC-AC-HC heterostructure at 100 mV. The white lines are drawn to indicate a CDW translation between HC structures.

AC structures together play the role of the discommensuration, which give rise to the translation of the HC CDW by a single unit cell of the pristine structure $\pm\mathbf{a}_1$. This corresponds to the phase shift of $(\mp(2\pi/3), 0, \pm(2\pi/3))$ [17,38–40] in the HC CDW order parameter [Figs. 3(a) and 3(b)].

Among domain walls in CDW materials, those of $2H$-$NbSe_2$ are unique. Most of CDW translations by discommensurations have been assumed between the same CDW structures with the translational degeneracy and is composed of well-isolated broken CDW clusters. While there are very few examples of CDW domain walls with their structures determined, the recent case in $1T$-TaS_2 shows such broken CDW clusters clearly [25]. In contrast to such an abrupt local change of structures, the present heterostructure for the CDW translation is a very smoothly connected structure [25], making it hard to be identified. More contrastingly, while the domain walls of $1T$-TaS_2 result in strongly localized in-gap states on the broken CDW clusters, the current HC-AC-HC heterostructure does not induce any strong electronic singularity (see Fig. S4 in the Supplemental Material [36]).

In fact, the idea of degenerate CDW structures and their possible role as the discommensuration was introduced as early as 1982 for the case of $2H$-$TaSe_2$ [30]. The main idea was that the two competing CDW structures in phase shifting heterostructures (HC-AC-HC in this work) can reduce the energy cost of conventional domain walls. While this idea did not find clear experimental evidence in $2H$-$TaSe_2$ yet, it is fully consistent with what we observed here. The only difference is that the previous theory considered only CC and AC domains, neglecting simply the HC structure [30]. The free energy consideration of the previous work does not depend on any structural details of the phases involved [30] so that it can equally be applied to the present case of HC and AC competing structures [36].

The discommensuration would ideally form a honeycomb lattice [10] as shown in the inset of Fig. 1(c) (see the Supplemental Material for a detailed explanation [36]). In the present system, this should correspond to hexagonal HC domains and the honeycomb network of the AC CDW stripes [Fig. 4(a)]. To form a honeycomb network, three AC CDW stripes should merge and the neighboring HC domains should have proper phase shifts [indicated by the domain numbering in Fig. 1(c)]. If the atomic structure of the HC-AC-HC discommensuration is put into this honeycomb network, the merging point of AC stripes is dictated to have two distinct structures: one with the dislocations (dashed circles) of AC CDW but the neighboring one without [Fig. 4(a) and also see Fig. S5 Supplemental Material [36]]. These correspond to a domain wall vortex and antivortex as dictated by the Z3 topology [11]. They are indeed observed in the STM topography; Fig. 4(b) shows two representative merging points of AC stripes and only one of them shows the dislocations at its core (dashed circles). While the experimentally observed domain distribution in Fig. 1 is largely disordered, it can be closely mapped into the ideal honeycomb network [36]. This network explains naturally why the HC and AC structures have distinct distributions of all isolated and all connected domains, respectively, and indicates the topological nature of the domain distribution as a partially melted network of topological excitations.

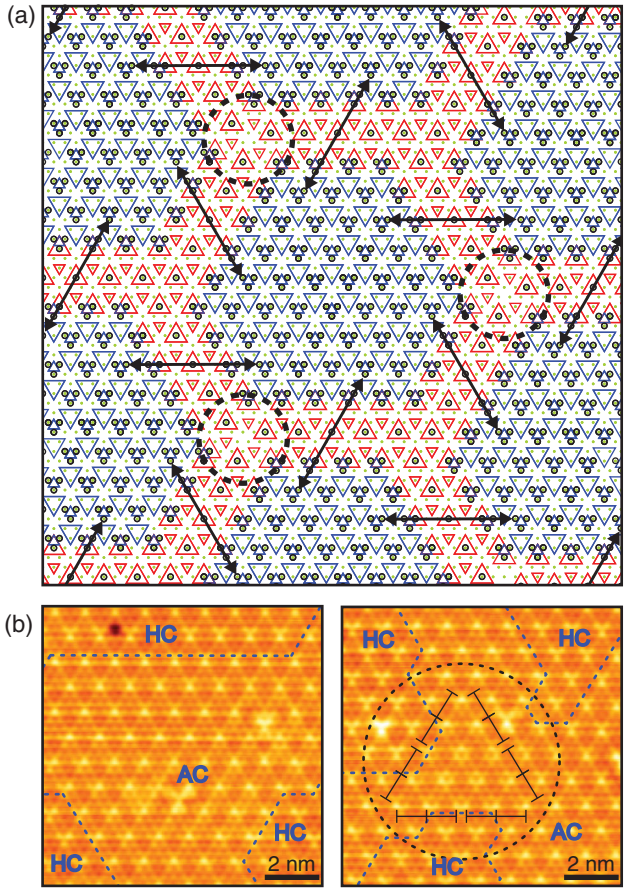

FIG. 4. (a) Atomistic schematics of an ideal honeycomb structure of the HC CDW domains and discommensurations which are composed of type I and II vertices. The black dashed circle denotes the region of AC CDW dislocation and the black arrows the directions of CDW translations among the HC CDW domains. (b) STM topography of type I (left) and II (right) vertices where three AC CDW stripe domains merge. Black dashed circle indicates the region of AC CDW dislocations. Black solid lines represent the dislocations among the AC structures.

In this work, the long-standing puzzle of the microscopic nature of the incommensurate CDW of $2H$-$NbSe_2$ is thereby solved [36]. The competition between HC and AC structures with a very small energy difference must be closely related to the quantum phase fluctuation observed very recently [1,2]. While the previous work suggested the 1Q phase as the source of the quantum fluctuation with the limited microscopic information, we very rarely observe the 1Q phase, and its origin in the inhomogeneous strain

[28] is not easily compatible with spontaneous quantum fluctuation. The concept of a topologically entangled competing phase and the discommensuration without a domain wall may find its application in various different materials systems with incommensuration phenomena.

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Note added in the proof.—A recent paper [41] showed that the energy difference between the HC and AC phases becomes much smaller in similar DFT calculations using a larger unitcell.

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