On the charge and magnetic ordering in monolayer NbSe$_2$: a first principles study

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Monolayer NbSe$_2$ has recently been shown to be a 2-dimensional superconductor, with a competing charge-density wave (CDW) order. This work investigates the electronic structure of monolayer NbSe$_2$ based on first principles calculations, focusing on charge and magnetic orders in connection to the superconductivity. It is found that decreased screening in the monolayer NbSe$_2$ with a perfect lattice exhibits magnetic instability, which is removed by the formation of CDW. Two energetically competitive but distinct $3\times3$ CDW structures are revealed computationally, which have a significant impact on the Fermi surface. The relations of the potential CDW phases with experimental structure and the coexisting superconductivity are discussed.

Layered transition metal dichalcogenides (TMDCs) MX$_2$, where M is a transition metal and X is a chalcogen, are a remarkable class of materials displaying a multitude of correlation effects, ranging from CDW, magnetic ordering to superconductivity. In recent years, TMDCs have become available in monolayer forms [1–5]. In particular, monolayer niobium diselenide, NbSe$_2$, has an extraordinarily rich phase diagram with respect to temperature. In the bulk form, NbSe$_2$ is one of the first materials found to host coexisting CDW and superconducting orders [6, 7]. In the monolayer limit, superconductivity again coexists with the CDW order, with a superconducting $T_c = 1.9$ K compared with the bulk value 7 K. A commensurate charge-density wave (CDW) transition was found at 145 K [1], with CDW vector $q = \frac{1}{3}a^*$, corresponding to a structural reconstruction within a $3\times3$ supercell. In the monolayer limit, on the other hand, it is well known that screening is significantly reduced compared to the bulk counterpart, leading sometimes to dramatically enhanced electronic correlation. Indeed, previous first principles calculations suggest possible antiferromagnetic order in monolayer NbSe$_2$ in the absence of CDW order [9, 10]. The above observations indicate that the correlations arising from lattice and interaction are both important in monolayer NbSe$_2$.

On account of such multi-correlated nature, the interplay of different correlation effects, and therefore possible phases of monolayer NbSe$_2$, are yet to be clarified, which requires treating different instabilities on the same footing. One aim of the present paper, therefore, is to analyze the equilibrium atom arrangement in the CDW phase of monolayer NbSe$_2$, and at the same time, the competition between the CDW and magnetic instabilities. It is revealed that the formation of CDW phase eventually suppresses the magnetic instability, providing clarification to the vagary regarding the absence of magnetic order in monolayer NbSe$_2$. A second objective of this paper is to understand the electronic structure of monolayer NbSe$_2$, in the eventual low-temperature CDW phase. A Brillouin zone unfolding scheme is devised to compare the Fermi surface of the CDW phase to that of the symmetric lattice phase. Whereas the monolayer NbSe$_2$ with symmetric lattice has three Fermi circles, at $\Gamma$, $K$ and $K'$, respectively, the CDW order leaves them partially or fully gapped. The extensive obliteration of the computed Fermi surface leads to an explanation for the disappearance of the magnetic instability, and potentially, for the lower-than-bulk superconducting $T_c$ for monolayer NbSe$_2$.

![Figure 1](image-url) (a) Top and side views of crystal structure of monolayer NbSe$_2$ without CDW. Distributions of the Nb atoms in the triangle CDW phase (b) and the star CDW phase (c). The solid gray bonds between the adjacent Nb atoms indicate that their distances were shortened after CDW transition. The rhombuses bounded by dashed lines in (b) and (c) denote $3\times3$ CDW supercells.

The structure of the monolayer NbSe$_2$ without CDW, isolated from the bulk phase $2H$-NbSe$_2$, forms a 2-
dimensional hexagonal lattice in the 2-dimensional space group $P6_{3}m2$, as shown in Fig. 1(a). It is composed of three layers of atoms, with a Nb layer sandwiched between Se layers. Each Nb atom sits inside a trigonal prismatic cage formed by six nearest-neighbor Se atoms. Nb atoms form a perfect hexagonal closest packing structure, with the shortest Nb-Nb separation $a = 3.474$ Å according to our calculations [11]. This non-CDW phase of monolayer NbSe$_2$ is found to be unstable below $T_{CDW}$ [12] and exhibits pronounced soft phonon mode around $q = \frac{1}{3}a^*$ in our calculations, indicating a strong structural instability to the formation of a 3$\times$3 supercell.

Density-functional theory (DFT) calculations were performed, within the generalized gradient approximation (GGA), parameterized by Perdew, Burke, and Ernzerhof (PBE) to investigate the crystal structure, electronic structure and lattice dynamics of monolayer NbSe$_2$ in non-CDW and CDW phase [1] [14]. The Kohn-Sham electronic density of states, averaged over an energy window, and $A$ the area of a supercell. The energy window is set to $\Delta = -4$ meV. The simulated STM topography, $z = z(x, y)$, is subsequently determined by the implicit equation, $\rho_{\text{avg}}(x, y, z) = \rho_0$, where the iso-density value $\rho = 6.3 \times 10^{-4} e/Å^2$ is used to best match the experimental STM topography [1]. Since the tunneling current is proportional to local density of states, $z(x, y)$ can be interpreted semiquantitatively as the topography revealed in a constant-current STM topographical scan.

When the structure of monolayer NbSe$_2$ is relaxed in a 3$\times$3 supercell, the CDW indeed forms, which can be characterized by a reconstruction of the Nb atomic layer, with concomitant displacements of Se atoms. Besides, we also examine the lattice stabilities of the three reconstructed CDW phases under different in-plane lattice constants and using different types of exchange-correlation functionals, which give rise to similar results as described in the supplemental material [11]. Using the fully relaxed in-plane lattice constant $a = 3.474$ Å, two 3$\times$3 CDW reconstructions are found to be important, referred to herein as triangle and star phases (see supplemental material for details [11]). Fig. 1(b) displays the triangle phase, where the Nb atoms are grouped into large and small triangular clusters, consisting of six and three Nb atoms respectively within a 3$\times$3 supercell. The star phase is characterized by overlapping star-shaped clusters, as displayed in Fig. 1(c), which is similar to bulk 2$H$-NbSe$_2$ in CDW state [2] [15].

The topography of monolayer NbSe$_2$ in the CDW phase, which may be revealed by scanning-tunneling microscopy (STM), is simulated. We compute the local electronic density of states, averaged over an energy window below the Fermi level

$$\rho_{\text{avg}}(r) = \frac{A}{\Delta} \sum_{n} \int_{\mu - \Delta}^{\mu} d\varepsilon \int \frac{d^2k}{(2\pi)^2} \psi_{nk}(r) \psi_{nk}(r) \delta(\varepsilon - \varepsilon_{nk}),$$  \hspace{1cm} (1)

where $\psi_{nk}(r)$ is the Kohn-Sham wavefunction of the $n$th band at wavevector $k$, $\mu$ the Fermi energy, $\Delta$ the width of the energy window, and $A$ the area of a supercell. The energy window is set to $\Delta = -4$ meV. The simulated STM topography, $z = z(x, y)$, is subsequently determined by the implicit equation, $\rho_{\text{avg}}(x, y, z) = \rho_0$, where the iso-density value $\rho = 6.3 \times 10^{-4} e/Å^2$ is used to best match the experimental STM topography [1]. Since the tunneling current is proportional to local density of states, $z(x, y)$ can be interpreted semiquantitatively as the topography revealed in a constant-current STM topographical scan.

The simulated STM topographies of monolayer NbSe$_2$ in the triangle (a) and star (b) CDW phase. The colors in the map represent the height function $z(x, y)$ as mentioned in the main text, where $x$ and $y$ are in-plane coordinates. The height of Nb layer was set to be $z = 0$. The red triangles in (a) and (b) indicate the dominant features of the corresponding topography within a 3$\times$3 CDW supercell bounded by white dashed lines. Top view of the configurations of the triangle (c) and star (d) CDW phase. The Se atoms with blue circles in (c) and (d) are corresponding to the dominant STM signals marked by the red triangles in (a) and (b) respectively as mentioned above.

The simulated STM topographies of the triangle and star CDW phases are displayed in Fig. 2. The STM topography is dominated by top Se atoms (see Fig. S2 [11]), despite that the electronic states around the Fermi level arise mostly from the d-orbitals of Nb atoms. Furthermore, the dominant STM feature of the triangle phase is contributed by the three Se atoms on the top of the large triangular cluster, shown as a red triangle as displayed in Figs. 2(a) and 2(c) (marked with three blue circles). Similarly, the star phase can be also characterized by similar red triangles as displayed in Fig. 2(b), attributable to the three top-layer Se atoms, indicated by blue circles in Fig. 2(d).

Comparing with the experimental STM topography shown in Fig. 1(e) of the reference [8], which shows an array of small triangles, we find that the sim-
culated STM topographies of triangle and star phases are both consistent with the experiment. Owing to the similarity of STM patterns and energies (see supplemental material [11]) of the triangle and star phases, we are unable to suggest which CDW is more likely to occur in the actual monolayer NbSe$_2$.

In the monolayer limit, the screening is substantially reduced compared to bulk material, giving rise to stronger interaction between electrons. It is then expected that monolayer material is more prone to developing magnetic order even with a non-magnetic bulk counterpart. Previous first principles investigations [9, 10] indicate that the most stable state of monolayer NbSe$_2$ without CDW order is antiferromagnetic in a 4 × 1 supercell. The issue, however, remains with whether the magnetic order coexists or competes with the CDW order, both of which are known to modify the Fermi surface and consequently the susceptibility. Therefore, in order to quantify the magnetic instability, we analyse the spin susceptibility of monolayer NbSe$_2$, obtained from tight-binding models based upon Wannier functions extracted from the Kohn-Sham band structures [17].

The general form of noninteracting susceptibilities reads [18]:

$$\chi_{st}^{\alpha \beta}(q, \omega) = -\frac{1}{N} \sum_{k, \mu \nu} \left[ f(E_{\nu}(k + q)) - f(E_{\mu}(k)) \right] \times \frac{a_{\mu}^{s}(k) a_{\nu}^{t}(k + q) a_{\nu}^{s}(k + q) a_{\mu}^{t}(k + q)}{\omega - E_{\nu}(k + q) - E_{\mu}(k) + i0^+}. \quad (2)$$

where $s, t, p, q$ denoting orbital index, $N$ is the number of lattice sites, and $a_{\mu}^{s}(k) = \langle s | \mu k \rangle$, is the amplitude of the $\mu$th band at crystal momentum $k$ on the $s$th Wannier orbital, obtained by diagonalizing the tight-binding Hamiltonian. The static one-loop spin susceptibility is given by $\chi_{S}(q, \omega = 0) = \chi_{S}(q, \omega = 0)$. In our non-spin-polarized DFT calculations of 3×3 supercells of monolayer NbSe$_2$, with and without (triangle or star) CDW and in-between, the manifold of 9 bands around the Fermi level are predominantly formed by Nb $d_{z^2}$ orbitals, which are well separated from all other bands. Therefore, these bands are used to construct 9-band tight-binding Hamiltonians.

In order to assess how the magnetic instability evolves as the CDW is developing, we calculated the spin susceptibilities $\chi_{S}(q)$ of a series structures interpolated between the non-CDW and CDW phases. Here, the atom positions of an interpolated supercell is given by $r(\alpha) = (1 - \alpha) r_0 + \alpha r_c$, where $\alpha$ corresponds to the amplitude of CDW distortions, and $r_0$ and $r_c$ are the positions of atoms in state without and with CDW distortions, respectively. Figs. 3(a)-3(b) show the calculated $\chi_{S}(q, \omega = 0)$ for different $\alpha$ in 3 × 3 supercells. When $\alpha = 0$, corresponding to non-CDW phase, the spin susceptibility peaks at around $\mathbf{M}$ and $\mathbf{K}$, which indicates magnetic instability, to the formation of a magnetic supercell. This is consistent with a spin-polarized calculation, leading to a magnetic configuration as shown in Fig. 3(c) [9]. It can be clearly seen that with the increase of $\alpha$, the spin susceptibilities generally decrease for both of the triangle and star CDW, suggesting that as the CDW order forms the magnetic order may eventually disappear. However, the spin susceptibilities of star phase are slightly larger than that of the triangle phase, which indicates that their magnetic behaviors may be different when CDW distortions set in.

![FIG. 3. Calculated noninteracting static spin susceptibilities $\chi_{S}(q, \omega = 0)$ in 3 × 3 supercells for different $\alpha$ when the CDW distortions are triangle-like(a) and star-like(b). (c) The calculated spin configurations in antiferromagnetic non-CDW phase. The high magnetic moment($\pm 0.41\mu_B$ per Nb atom) and low magnetic moment($\pm 0.12\mu_B$ per Nb atom) are denoted by long and short arrows, respectively.](image)

Our spin spiral calculations (see supplemental material for details [11]) suggest that the non-CDW phase of monolayer NbSe$_2$ possesses an antiferromagnetic magnetic ground state as depicted in Fig. 3(c), which is in agreement with previous predictions [9]. According to our spin susceptibility calculations above, this magnetic order may eventually be suppressed or even killed by CDW. As a confirmation, we computed the total energy of a 12 × 3 supercell to include in both magnetic and CDW orders. We used the interpolation method described above to get a series structures with different values of $\alpha$ and carried out both non-spin-polarized and spin-polarized calculations for each kind of CDW.

Figs. 4(a)-4(b) show the calculated total energies, and Figs. 4(c)-4(d) show the calculated magnetic moments of Nb atoms at various values of $\alpha$ for the triangle and star CDW, respectively. It is found that for both kinds of CDW, when an antiferromagnetic order is imposed, the total energy increases with the increase of $\alpha$. Meanwhile, the magnetic moments are suppressed, which indicates
a competition between CDW and SDW (spin-density wave). However, things are slightly different for triangle and star CDW. For triangle CDW, it is found that when $\alpha < 0.6$, magnetic phase, which has a collinear magnetic order as shown in Fig. 4(c), has lower energy than the non-magnetic phase as displayed in Fig. 4(a). As $\alpha$ increases, the difference of total energy between magnetic and non-magnetic calculations decreases gradually. At about $\alpha = 0.6$, the energetic advantage of magnetic phase disappears, beyond which the CDW order suppresses the magnetic order completely, which can be verified from the zero magnetic moments when $\alpha > 0.6$, as shown in Fig. 4(c).

For star CDW, although as $\alpha$ increases, the difference of total energies between magnetic and non-magnetic calculations decreases gradually, the magnetic order remains, as shown in Figs. 4(b) and 4(d). The general trend of the magnetic phases’ energies in the two kinds of CDW is also consistent with our previous spin susceptibility calculations. Based on the results above, we then conclude that without CDW, monolayer NbSe$_2$ favors antiferromagnetic order in a $4 \times 1$ supercell. When the CDW order sets in, the magnetic order is suppressed by the triangle CDW whereas the star CDW may coexist with magnetism.

To investigate the influence of CDW on electronic structure of monolayer NbSe$_2$, band structures and Fermi surfaces of the non-CDW and CDW phases were computed using a $3 \times 3$ supercell and unfolded to the (larger) primitive Brillouin zone of the non-CDW NbSe$_2$, by a weight factor measuring the tranformation of wavefunctions under primitive lattice translations (see supplemental material for details [11]).

As shown in Fig. 5(a), the Fermi surface of the non-CDW phase consists of three inequivalent circles (white lines), centered at $\Gamma$, $K$ and $K'$ points, respectively. After CDW transition, they are partially or fully gapped due to the lattice distortion. Fig. 5 displays the unfolded Fermi surfaces of the non-CDW phase (a), triangle CDW phase (b), and star CDW phase (c), respectively. It is evident that the triangle phase develops more extensive gapping on the Fermi surface compared to the star phase. Both of the triangle and star CDW phases show significant partial gapping along the Fermi surface encircling $\Gamma$, which appears to be more extensive for the triangle phase. Remarkably, while the $K$, $K'$-centered Fermi circles are only partially gapped in the star phase, they are almost completely obliterated in the triangle phase. The computed electronic density of states also show the consistent results. As displayed in Fig. 5(d), the density of states of star phase at the Fermi level exhibits slight decrease, compared with that of the non-CDW phase. In contrast, the triangle phase shows a more pronounced reduction of the Fermi density of states, corresponding to the more extensive CDW gap on the Fermi surface.

The modification of the Fermi surface also provides a microscopic insight into the interplay between CDW, SDW and superconductivity. In the non-CDW phase with the intact Fermi surface, there exist electronic instabilities which can potentially trigger CDW or SDW. In the presence of the CDW along with the modification of Fermi surface, the SDW instability was subdued as discussed above. It suggests that the electronic states triggering SDW are also responsible for the CDW insta-
bility, which are removed from Fermi surface when the CDW forms.

In summary, our calculations reveal that the formation of CDW in monolayer NbSe$_2$ suppresses the magnetic instability of the initiating lattice. Two possible CDW phases are identified computationally, which have similar STM topographical features in our simulation. The formation of CDW gap on the Fermi surface, as visualized from our band unfolding scheme, should also have an important impact on superconductivity. It is expected that the extent of CDW gap is inversely related to the superconducting $T_c$. The Fermi gapping is substantially more extensive in the triangle phase, in comparison with the bulk-like star phase. In view of the substantially lower $T_c$ of the monolayer NbSe$_2$ compared to the bulk and our computational observation that the star CDW phase remains magnetic, these results potentially favor the hypothesis that the triangle CDW might actually form.

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SUPPLEMENTAL MATERIALS

S1. GEOMETRY STRUCTURES OF THE CDW PHASES AND THEIR LATTICE STABILITIES

This part mainly reports the details of the geometry structures and lattice stabilities of the triangle, triangle* and star CDW phases obtained at $a = 3.474$ Å as supplemental information of the main text. Three types of reconstructed structures were obtained. Two of the structures are characterized by triangular clusters (the triangle and triangle* phase). Fig. S6(a) displays the triangle phase, where the Nb atoms are grouped into large and small triangular clusters, consisting of six and three Nb atoms respectively within a 3×3 supercell. The shorten Nb-Nb pairs after CDW transition can be classified as three types according to their distances marked by gray bonds with different thicknesses as illustrated in Fig. S6(a) and the corresponding distances were listed in Table S1. This structure exhibits the lowest total energy.

The distributions of Nb atoms between the phases of triangle and triangle* are very similar as shown in Figs. S6(a)-S6(b). The only difference lies in the distance of the bond I as listed in Table S1. In detail, among the shorten pairs of Nb-Nb, the bond I are the shortest in triangle phase but the largest in triangle* phase, which exhibits a slightly higher total energy as listed in Table S1. Interestingly, both of the two phases are likely to be local minimums of the potential energy surface according to the simulated results of lattice dynamics [Figs. S6(d)-S6(e)] and nudged elastic band (NEB) [1][3][Fig. S6(g)]. As a further confirmation, phonon spectrum was computed [4–6] to ensure the obtained structures are free of soft phonon modes. In detail, as shown in Figs. S6(d)-S6(e), the soft mode presenting in the non-CDW phase is completely removed in both triangle and triangle* phases. Furthermore, the transition
energy barrier between the two phases was computed. As displayed in Fig. S6(g), the energy barrier is only 7 meV, indicating that the structural transition inbetween is rather easy.

Another reconstructed structure, star phase, was displayed in Fig. S6(c). The star-shape clusters are grouped into two alternative units bounded by I type of Nb-Nb as shown in Fig. S6(c). The Nb layer can be viewed as composed of two sublattices owing to the modulation on Nb-Nb nearest-neighbour bonds. A continuous net of Nb forms a honeycomb lattice, with each of the bipartite sites decorated by a hexagonal cluster. The other sublattice is composed of an isolated Nb. It is easy to find that the displacements of Nb atoms in star phase are much smaller than that in the triangle phase by comparing the lengths of the magenta arrows in Fig. S6(c) with Figs. S6(a)-S6(b). In contrast to the triangle and triangle* phases, the star phase is likely to be a metastable structure as shown in Figs. S6(f) and S6(h).

TABLE S1. Nb-Nb distances (Å) and related total energies (meV per chemical formula) of the non-CDW phase and the three CDW phases regarding the triangle, triangle* and star phase at the fully relaxed in-plane lattice constant 3.474 Å using PBE. The pairs of Nb-Nb indexed I - III for the three CDW phases were shown in Figs. S6(a)-S6(c).

| Configuration | Nb-Nb I (Å) | Nb-Nb II (Å) | Nb-Nb III (Å) | E (meV/ C.F.) |
|---------------|------------|--------------|---------------|---------------|
| Triangle      | 3.33       | 3.37         | 3.41          | 0             |
| Triangle*     | 3.42       | 3.38         | 3.40          | 0.3           |
| Star          | 3.36       | 3.43         | 3.46          | 2.4           |
| Non-CDW       | 3.47       | 3.47         | 3.47          | 3.7           |

TABLE S2. Related total energies of non-CDW and the three CDW phases under different lattice constants computed using LDA and PBE.

| Lattice constant (Å) | Functional | Phase | E (meV/ C.F.) |
|----------------------|------------|-------|---------------|
| 3.47 a               | PBE        | Triangle | 0             |
|                      |            | Triangle* | 0.3           |
|                      |            | Star     | 2.4           |
|                      |            | Non-CDW  | 3.7           |
| 3.399 a              | LDA        | Triangle | 0.7           |
|                      |            | Triangle* | 0             |
|                      |            | Star     | 2.9           |
|                      |            | Non-CDW  | 3.3           |
| 3.458 a              | PBE        | Triangle | 0             |
|                      |            | Triangle* | 0.1           |
|                      |            | Star     | 2.4           |
|                      |            | Non-CDW  | 3.5           |
| 3.458 a              | LDA        | Triangle | 0.05          |
|                      |            | Triangle* | 0             |
|                      |            | Star     | 1.8           |
|                      |            | Non-CDW  | 3.4           |

The lattice constants 3.399 and 3.474 Å are obtained by fully relaxation of the lattices using LDA and PBE respectively. 3.458 Å is the lattice constant of bulk 2H-NbSe₂ [2].

We carefully examine the lattice stabilities of the triangle, triangle* and star CDW phases under the in-plane lattice constants of 3.399, 3.474 and 3.458 Å using different types of exchange-correlation functional including LDA, PBE. The values 3.399 and 3.474 Å are the fully relaxed lattice constants using LDA and PBE, respectively. The value 3.458 is the in-plane lattice constant of bulk 2H-NbSe₂ reported in the reference [2]. The related total energies are listed in Table S1. It is found that all the three CDW phases exist regardless of the lattice constants and exchange-correlation functional being used. Furthermore, it is reasonable that the total energies of the three CDW phases are found to
be lower than that of the non-CDW phase. In detail, the triangle and triangle* phase exhibit similar total energies, which are slightly lower than that of the star phase. In particular, the related total energies of the triangle, triangle* and star phase are 0, 0.3 and 2.4 meV per chemical formula respectively at the lattice constant \( a = 3.474 \) Å.

### S2. THE STM TOPOGRAPHY

In the calculations of the STM topographies for the CDW phases, non-self-consistent calculations was carried out with a denser \( k \)-grid \( 48 \times 48 \) after self-consistent calculations. Fig. S7 displays the computed STM topography of monolayer NbSe\(_2\) in the triangle and star CDW phases. They are similar to the STM topography displayed in Figs. 2(a) and 2(b) in the main text but with different colorbars. By comparing the STM signals within the \( 3 \times 3 \) CDW supercell (bounded by white dashed lines) in Figs. S7(a) and S7(b) to the atomic positions within the corresponding supercells (bounded by black dashed lines) in Figs. 2(c) and 2(d) in the main text, one can find that the STM signal is dominated by Se atoms.

![Fig. S7. Computed STM topography of monolayer NbSe\(_2\) in the triangle (a) and star (b) CDW phases. The colors in the map represent the height function \( z(x, y) \) as mentioned in the main text, where \( x \) and \( y \) are in-plane coordinates. The height of Nb layer was set to be \( z = 0 \).](image)

### S3. DETAILS OF SPIN SPIRAL CALCULATIONS

In order to examine the magnetic ground state(s) suggested by the spin susceptibility calculations, spin spiral calculations were carried out to determine the magnetic order of monolayer NbSe\(_2\) in non-CDW phase. As depicted in Fig. S8(b), we shall restrict ourselves to a consideration of spin spiral structures of the form \(^8\)

\[
\begin{align*}
m_{j,x} &= m_j \sin \theta \cos \phi \\
m_{j,y} &= m_j \sin \theta \sin \phi \\
m_{j,z} &= m_j \cos \theta \\
\phi &= \mathbf{q} \cdot (\mathbf{r}_j + \mathbf{t}_n)
\end{align*}
\]

where \( m_{j,x}, m_{j,y}, m_{j,z} \) denote the three components of atomic magnetic moments, the \( \mathbf{t}_n \) are the lattice translations, the \( \mathbf{r}_j \) are position vectors of atoms within the unit-cell, the \( m_j \) is the magnetic moment of the \( j \)th atom, and \( \mathbf{q} \) is the vector of the spiral order. Although crystal with spin spiral magnetic order loses its translation symmetry, a generalized Bloch theorem allows us to compute the energy of a supercell with spiral magnetic order using and at the computational cost of a primitive cell. This allows us to quickly and accurately survey the energies for different \( \mathbf{q} \)'s.

As shown in Fig. S8(c), the calculated total energy reaches minima at \( \mathbf{q} = (\mathbf{a}^*/4, 0) \) (and other equivalent \( \mathbf{q} \) vectors, \( \mathbf{a}^* \) and \( \mathbf{b}^* \) are reciprocal lattice vectors of primitive cell), indicating a possible magnetic ground state in a \( 4 \times 1 \) supercell. Subsequently, the spiral magnetic order is imposed on \( 2 \times 1 \) and \( 2 \times 2 \) supercells, which allows spin modulation within a supercell. Fig. S8(d) shows the total energy with respect to spiral vectors in \( 2 \times 1 \) supercell, the minima appear at \( \mathbf{q} = (\mathbf{a}^*/4, 0) \) (the reciprocal lattice vector in \( \mathbf{a} \) direction of \( 2 \times 1 \) supercell is half of the primitive
cell). The results for $2 \times 2$ supercell are shown in Fig. S8(e), the spiral vectors for the lowest total energy are $(a^*/4, 0)$ as well. Based on the results of our spin spiral calculations, we infer that a magnetic ground state may appear in a $4 \times 1$ supercell, which are consistent with the magnetic instability indicated by our previous spin susceptibility calculations. We then did a magnetic calculation in a $4 \times 1$ supercell to finally determine the magnetic order. Fig. 3(c) in the main text shows our calculated antiferromagnetic spin configurations, which is the most stable state in the non-CDW phase, in agreement with previous predictions [9].

FIG. S8. (a) $2 \times 2$ supercell of monolayer NbSe$_2$. $a$ and $b$ are lattice vectors of primitive cell. (b) A schematic diagram of spin spiral structures. (c)-(e): Spin spiral calculated total energy with respect to spin spiral vectors in $1 \times 1$, $2 \times 1$, and $2 \times 2$ supercells, respectively. Here $a^*$ and $b^*$ are reciprocal lattice vectors of primitive cell. For supercells, the total energy with respect to spin spiral vectors are drawn in corresponding reciprocal cell of their own primitive lattice. The relationship of size between reciprocal cells of different supercells is depicted as well.

S4. UNFOLDING ELECTRONIC STRUCTURES

In the unfolding calculations for the non-CDW and CDW phases of monolayer NbSe$_2$, $3 \times 3$ CDW supercells are adapted, each containing 27 atoms in total. The Fermi surfaces are computed on a $96 \times 96$ $k$-grid and subsequently unfolded to the primitive Brillouin zone (PBZ) of the non-CDW phase using unfolding technique [10]. In light of this method, the electronic bands in supercell Brillouin zone are unfolded to PBZ with a weight function $W_{KJ}(G) = 1/N \sum_{j=1}^{N} \langle KJ|\hat{T}(r_j)|KJ \rangle e^{-i(K+G) \cdot r_j}$ which measures the degree of the Bloch symmetry belonging to a primitive cell, that an eigenstate of a supercell possess. The supercell contains $N$ primitive cells. $|KJ \rangle$ donates an eigenstate of the supercell with a band index $J$ and a wavevector $K$. $G$ is a reciprocal lattice vector of the supercell, connecting $K$ to a wavevector $k$ in the PBZ as $k = K + G$. $\hat{T}(r_j)$ is the translation corresponding to the $j$th primitive cell in the supercell.

FIG. S9. Unfolded band structures of the non-CDW phase (a), the triangle CDW phase (b), and the star CDW phase (c), respectively. The sizes of the dots in (a)-(c) denote corresponding unfolding weights $W_{KJ}$. The Fermi levels were aligned.

Fig. S9 displays the electronic band structures of non-CDW phase (a), the triangle CDW phase (b), and the star CDW phase (c) of monolayer NbSe$_2$, respectively. The unfolded band structure of the non-CDW phase agrees perfectly with the one directly computed with a primitive cell. The sizes of the red dots are uniform and the corresponding
unfolding weights $W_{k,J} = 1$. The most prominent changes of the electronic states after the CDW transition are located in the following three regions: $-2 \sim -2.5$ eV, $-0.8 \sim -1.6$ eV and around the Fermi level. Some parts of the electronic states are removed compared to that of the non-CDW phase, especially near the momenta at $2/3\Gamma M$, $1/3MK$, $1/3\Gamma$ and $2/3K\Gamma$. Despite the above changes, the band structures of the CDW phases coincide with that of the non-CDW phase approximatively, indicating that the shapes of the band structures remain virtually unchanged and there exist negligible energy shifts for each band in the presence of CDW.

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