First-principles study of charge and magnetic ordering in monolayer NbSe$_2$

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(Received 26 November 2017; published 2 February 2018)

Monolayer NbSe$_2$ has recently been shown to be a two-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. 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 × 3 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.

DOI: 10.1103/PhysRevB.97.081101

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 charge-density wave (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 at 145 K [1], with CDW vector $q = \frac{1}{2}a^*$. In the monolayer limit, superconductivity again coexists with the CDW order, with a superconducting $T_c = 1.9$ K [8] compared with the bulk value 7 K. A commensurate CDW transition was found at 145 K [1], with CDW vector $q = \frac{1}{2}a^*$, corresponding to a structural reconstruction within a 3 × 3 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 multicoordinated 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 Rapid Communication, 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 the 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 Rapid Communication 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 $\Gamma$, $\mathbf{K}$, and $\mathbf{K}'$, 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$_2$.

The structure of the monolayer NbSe$_2$ without CDW, isolated from the bulk phase $2\mathbf{H}_{\text{NbSe}_2}$, forms a two-dimensional hexagonal lattice in the two-dimensional space group $P6_3/m$, 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 close-packed 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 a pronounced soft phonon mode around $q = \frac{1}{2}a^*$ in our calculations, indicating a strong structural instability to the formation of a 3 × 3 supercell.

Density-functional theory (DFT) calculations were performed, within the generalized gradient approximation, parametrized by Perdew, Burke, and Ernzerhof to investigate the crystal structure, electronic structure, and lattice dynamics of monolayer NbSe$_2$ in the non-CDW and CDW phases [13,14]. The Kohn-Sham valence states were expanded in the plane-wave basis set with a kinetic energy truncation at 530 eV. An $18 \times 18 \times 1$ and a $6 \times 6 \times 1$ k grid centered at $\Gamma$ point were chosen for the sampling of the Brillouin zones of the non-CDW and CDW phase, respectively. The equilibrium crystal structure was determined by a conjugated-gradient relaxation.

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of ionic positions, until the Hellmann-Feynman force on each atom was less than 0.005 Å and a zero-stress tensor was obtained. Crystal structure of the NbSe$_2$ in the CDW state was obtained with multiple structural optimizations with a 3 × 3 supercell. Before each optimization, small random displacements were added to each atom to remove all discrete symmetries.

When the structure of monolayer NbSe$_2$ is relaxed in a 3 × 3 supercell, the CDW indeed forms, which can be characterized by a reconstruction of the Nb atomic layer, with concomitant displacements of Se atoms. In addition, 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 × 3 CDW reconstructions are found to be important, referred to herein as triangle and star phases (see Supplemental Material for details [11]). Figure 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 × 3 supercell. The star phase is characterized by overlapping star-shaped clusters, as displayed in Fig. 1(c), which is similar to bulk 2H-NbSe$_2$ in CDW state [15,16].

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

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

where $\psi_{\mu k}(r)$ is the Kohn-Sham wave function of the $\mu$th band at wave vector $k$, $\mu$ 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 according to the experiment [8]. 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 isodensity value $\rho = 1.49 \times 10^{-2} \text{ per meV per unit cell}$ is used to best match the experimental STM topography [1]. Since the tunneling current is proportional to the integration of local density of states within the energy window determined by Fermi energy and sample bias, $z(x,y)$ can be interpreted semiquantitatively as the topography revealed in a constant-current STM topographical scan.

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 Ref. [8], which shows an array of small triangles, we find that the simulated 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 nonmagnetic bulk counterpart. Previous first-principles investigations [9,10] indicate that the most stable state of monolayer NbSe2 without CDW order is antiferromagnetic in a 4 \times 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 analyze the spin susceptibility of monolayer NbSe2, 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]

\[
\chi_{\mu
u}^q(q,\omega) = -\frac{1}{N} \sum_{k,\mu,\nu} \{ f[E_s(k)] - f[E_\mu(k)] \}
\times \frac{\alpha^\alpha_s(k)\alpha_s^\nu(k+q)\alpha^\nu_s(k+q)}{\omega + E_s(k+q) - E_\mu(k) + i0^+},
\]  

(2)

where \( s, t, p, q \) denotes the orbital index, \( N \) is the number of lattice sites, and \( \alpha^\alpha_s(k) = \langle s|\mu k \rangle \) is the amplitude of the \( \mu \)th band at crystal momentum \( k \) on the \( \alpha \)th Wannier orbital, obtained by diagonalizing the tight-binding Hamiltonian. The static one-loop spin susceptibility is given by \( \chi_S(q) = \chi_{\mu\mu}^q(q,\omega = 0) \). In our non-spin-polarized DFT calculations of 3 \times 3 supercell of monolayer NbSe2, with and without (triangle or star) CDW and in-between, the manifold of nine 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 nine-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 are 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 states without and with CDW distortions, respectively. Figures 3(a) and 3(b) show the calculated \( \chi_S(q,\omega = 0) \) for different \( \alpha \) in 3 \times 3 supercells. When \( \alpha = 0 \), corresponding to the non-CDW phase, the spin susceptibility peaks at around \( M \) and \( K \), 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 the 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.

Our spin spiral calculations (see Supplemental Material for details [11]) suggest that the non-CDW phase of monolayer NbSe2 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 \times 3 supercell to include in both magnetic and CDW orders. We used the interpolation method described above to get a series of structures with different values of \( \alpha \) and carried out both non-spin-polarized and spin-polarized calculations for each kind of CDW.

Figures 4(a) and 4(b) show the calculated total energies, and Figs. 4(c) and 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 \( \alpha < 0.6 \), the magnetic phase, which has a collinear magnetic order as shown in Fig. 3(c), has lower energy than the nonmagnetic phase as displayed in Fig. 4(a). As \( \alpha \) increases, the difference of total energy between magnetic and nonmagnetic 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 nonmagnetic 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
FIG. 4. (a) Calculated total energy of $12 \times 3$ supercells in magnetic (blue) and nonmagnetic (red) calculations for triangle CDW (a) and star CDW (b), respectively. The energy of the triangle CDW phase is set to be zero. Computed magnetic moments of Nb atoms in $12 \times 3$ supercells at various values of $\alpha$ for triangle CDW (c) and star CDW (d), respectively.

with our previous spin susceptibilities 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 the 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 transformation of wave functions 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. Figure 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- and 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 consistent results. As displayed in Fig. 5(d), the density of states of the star phase at the Fermi level exhibits a 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 instability, 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 a 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 the 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 bulklike 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, as well as our computational fact that the energy of triangle CDW is always lower than the star CDW despite the functional we use, these results potentially favor the hypothesis that the triangle CDW might actually form.

This work was supported by National Natural Science Foundation of China (Grant No. 11725415), Ministry of
Science and Technology of the People’s Republic of China (Grant No. 2016YFA0301004), and the Key Research Program of the Chinese Academy of Sciences (Grant No. XPDPB08-4). Part of the calculations were performed on the Tianhe-I Supercomputer System.

F.Z. and Z.Z. contributed equally to this work.


