Charge density wave instability and pressure-induced superconductivity in bulk 1T-NbS$_2$

Wei Wang, Bosen Wang, Zhibin Gao, Gang Tang, Wen Lei, Xiaojun Zheng, Huan Li, Mingxing, and Carmine Autieri

1College of Science, Guilin University of Technology, Guilin 541004, China
2Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
3Department of Physics, National University of Singapore, Singapore 117551, Republic of Singapore
4Theoretical Materials Physics, Q-MAT, CESAM, University of Liège, B-4000 Liège, Belgium
5International Research Centre MagTop, Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, PL-02668 Warsaw, Poland

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Charge density wave (CDW) instability and pressure-induced superconductivity in bulk 1T-NbS$_2$ are predicted theoretically by first-principles calculations. We reveal a CDW instability toward the formation of a stable commensurate CDW order, resulting in a $\sqrt{13} \times \sqrt{13}$ structural reconstruction featured with star-of-David clusters. The CDW phase exhibits one-dimensional metallic behavior with in-plane flatband characteristics and coexists with an orbital-density-wave order predominantly contributed by the $4d_{2z}^2$ orbital from the inner Nb atoms of the star-of-David cluster. By doubling the cell of the commensurate CDW phase along the layer stacking direction, a metal-insulator transition may be realized in the CDW phase in cases where the interlayer antiferromagnetic ordering and Coulomb correlation effect have been considered simultaneously. Bare electron susceptibility, phonon linewidth, and electron-phonon coupling calculations suggest that the CDW instability is driven by softened phonon modes due to the strong electron-phonon coupling interactions. CDW order can be suppressed by pressure, concomitant with the appearance of the superconductivity. Our theoretical predictions call for experimental investigations to further clarify the transport and magnetic properties of 1T-NbS$_2$. Furthermore, it would also be very interesting to explore the possibility to realize the CDW order coexisting with the superconductivity in bulk 1T-NbS$_2$.

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I. INTRODUCTION

Quasi-two-dimensional (2D) layered transition-metal dichalcogenides (TMDs) have attracted extensive attention in recent years. TMDC materials often crystallize in 1T or 2H polymorph with octahedral or trigonal prismatic coordination [1]. Many group-V TMDC materials MX$_2$ (M denotes the transition metals Nb or Ta, and X stands for the chalcogen elements Se or S) exhibit interesting phenomena and properties, such as charge density wave (CDW) order, superconductivity, metal-insulator transitions, magnetic ordering, and Mott physics [2–13]. However, even though possessing the same MX$_2$ chemical composition, different polytypes of MX$_2$ exhibit completely different physical properties. For example, 1T polymorphs of TaS$_2$ and TaSe$_2$ show complex CDW phase diagrams, including incommensurate, nearly commensurate, and commensurate CDW (CCDW) phases with prototypical $\sqrt{13} \times \sqrt{13}$ star-of-David structural reconstructions upon decreasing temperature [2,13,14]. Electronic structure transitions arising from the Mott-Hubbard physics is observed in the CCDW phase of 1T-TaS$_2$ [13], whereas the Mott insulating phase does not appear in bulk 1T-TaSe$_2$ even in the CCDW state [14]. In addition, the CDW instability in 1T polymorphs of TaS$_2$ and TaSe$_2$ can be suppressed under high pressure, and then the associated superconductivity emerges [13,15–19]. By contrast, the CDW order and superconductivity can coexist in the 2H-MX$_2$, exhibiting complicated competitive or cooperative relations [4,20–22]. Furthermore, the CDW phase transitions display a $3 \times 3$ periodicity in the bulk form of 2H-MX$_2$ [4,11,12]. However, previous research indicates that 2H-NbS$_2$ does not exhibit CDW order due to anharmonic suppression [23,24]. Recent experiments observe very weak superlattice peaks in 2H-NbS$_2$ corresponding to a commensurate $\sqrt{13} \times \sqrt{13}$ periodic lattice distortion, identical to the cases in 1T polymorphs of TaS$_2$ and TaSe$_2$, which may be stem from a local 1T-like environment in the 2H crystal arising from stacking faults [25].

In addition to the significant roles of the different polymorphs, the dimensionality also plays a profound impact on the transport properties, CDW order, and superconductivity of MX$_2$. The CDW phase of the monolayer 1T-TaSe$_2$ is identified to be a Mott insulator with an unusual orbital texture; however, the energy gap reduces significantly for the bilayer, while the trilayer and the bulk show a semimetallic and one-dimensional (1D) metallic behavior, respectively [14,26,27]. Contrary to the bulk phase, a $3 \times 3$ CDW order has been observed in the single-layer 2H-NbS$_2$; however, it is so fragile that it can be disturbed by small compressive strains [28–30]. Strain-induced phase separation between triangular and stripe

V. CONCLUSIONS

Further experiments and theoretical calculations are needed to test our model predictions and explanations. Our studies provide a strong theoretical foundation to guide the exploration of new CDW and superconducting materials, along with the potential for novel physical properties that may arise from the coexistence of these phenomena.
phases in charge-ordered \(1H-NbSe_2\) monolayer has been explored by *ab initio* calculations [31]. Compared to the bulk \(2H\) polymorph of NbSe\(_2\) and TaSe\(_2\), the CDW instability can be strongly enhanced in their monolayer [32,33]. By contrast, the CDW order of bulk \(2H\)-TaS\(_2\) vanishes in the 2D monolayer limit, accompanied with a substantial enhancement of the superconductivity, indicating a competition between CDW order and superconductivity [34,35]. Although it is difficult to synthesize bulk \(1T\) polymorph of NbSe\(_2\) and NbS\(_2\), few-layer thin films and monolayers have been prepared successfully [36–39]. Similar to other \(1T\) polytype CDW materials, the monolayer \(1T\)-NbSe\(_2\) is found to be a Mott insulator concomitant with the typical \(\sqrt{3}\times\sqrt{3}\) CDW order [38–41], and the monolayer \(1T\)-NbS\(_2\) is predicted theoretically to undergo a \(\sqrt{3}\times\sqrt{3}\) star-of-David structural reconstruction stabilized in a spin-1/2 magnetic insulating state [42].

The purpose of the present paper is to further explore the existence of CDW instability in bulk \(1T\)-NbS\(_2\) by first-principles calculations. We discover that the undistorted high-symmetry \(1T\)-NbS\(_2\) is unstable with softening phonon modes and undergoes a \(\sqrt{3}\times\sqrt{3}\) structural reconstruction to form a stable CCDW phase. Electronic structure calculations indicate that an orbital density wave (ODW) coexists with the CDW order in the CCDW phase featured with flat-band and 1D metallic characteristics. Once the interlayer antiferromagnetic (AFM) ordering and the on-site Coulomb repulsion interactions are taken into account simultaneously, a metal-insulator transition may be observed. By analyzing the Fermi-surface nesting function and calculating the electron-phonon coupling (EPC) constants, we propose that the CDW instability mainly arises from the strong electron-phonon interactions. The CDW order can be suppressed under high pressure, accompanied by the emergence of the superconductivity in the compressed phase. Further experimental and theoretical investigations on the structure and transport behavior of \(1T\)-NbS\(_2\) under pressure are necessary to better understand the intricate competitive or cooperative relations between CDW order and superconductivity in this material.

II. COMPUTATIONAL DETAILS

The density functional theory (DFT) calculations were performed using the QUANTUM ESPRESSO package [43] with a generalized gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof (PBE) functional [44]. The ultrasoft pseudopotentials were used to describe the interactions between electrons and ionic cores [45]. An energy cutoff of 45 Ry (540 Ry for the charge density) was chosen for our calculations. Considering the 2D layered structure of the bulk \(1T\)-NbS\(_2\), we performed geometrical optimization with van der Waals (vdW) corrections of DFT-D3 to obtain accurate lattice constants consistent with experiments [46]. The Brillouin zone (BZ) was segmented by a \(16 \times 16 \times 8\) Monkhorst and Pack (MP) grid for undistorted high-symmetry \(1T\)-NbS\(_2\), while a \(4 \times 4 \times 8\) MP grid was used for the CCDW structure [47]. The total energy and electron charge density calculations were performed by a Gaussian smearing method with a smearing parameter \(\sigma\) of 0.01 Ry. Using density functional perturbation theory, phonon dispersion curves and EPC were calculated on a \(8 \times 8 \times 4\) \(q\) grid, and a denser \(32 \times 32 \times 16\) \(k\) mesh was used for electron-phonon calculation for undistorted structures [48]. Electronic structures and density of states (DOS) are calculated by the Vienna *ab initio* simulation package (VASP) [49,50] within the GGA approach [44] and projector-augmented wave (PAW) potentials [51], where an energy cutoff of 520 eV was used. Because the electronic correlations and band gap are often underestimated in traditional DFT, the adding of a Coulomb correction in the energy functional produces an electronic structure scenario closer to the experimental observation. To more accurately describe the electronic correlations, we perform the first-principles electronic structure calculations also in GGA + \(U\), where an on-site Coulomb interaction \(U\) with a value of 2.95 eV was considered for the Nb 4d shell [40]. The Fermi surfaces are visualized using the FERMISURFER code [52].

III. RESULTS AND DISCUSSION

A. Undistorted high-symmetry structure of \(1T\)-NbS\(_2\)

As illustrated in Fig. 1(a), bulk \(1T\)-NbS\(_2\) displays a layered structure with space group \(P3m1\), and its corresponding BZ and high-symmetry points are illustrated in Fig. 1(b). Each Nb atom is surrounded by six nearest-neighbor S atoms with octahedral coordination, where the adjacent layers are held together by vdW forces. \(1T\)-NbS\(_2\) film has been synthesized successfully by atmospheric-pressure chemical vapor deposition at 600 °C with lattice parameters \(a = 3.4206\) Å and \(c = 5.9381\) Å [36]. Our optimized lattice parameters (\(a = 3.365\) Å and \(c = 5.954\) Å) are in good agreement with the experimental data.

To obtain fundamental features of the electronic structure of the high-symmetry phase, we calculate the band structure and the Fermi surface of the bulk \(1T\)-NbS\(_2\). As shown in Fig. 2, the electronic structure exhibits similar characteristics with other \(1T\) polymorph MX\(_2\) materials [53–55]. The bands around the Fermi energy (\(E_F\)) are dominantly contributed by Nb-4d orbitals, which are separated from the S-3p states by a gap of about 0.5 eV below the \(E_F\) [Fig. 2(a)]. Due to the quasi-2D nature of the layered structure, the two bands around the gap are nearly flat along the \(\Gamma\)-\(\Delta\) direction. Consistent with the octahedral crystal-field splitting, the five 4d orbitals are split into triply degenerate \(t_{2g}\) \((d_{x^2−y^2}, d_{z^2}−r_z, d_{xy})\) and doubly degenerate \(e_g\) \((d_{xz}, d_{yz})\) orbitals [40,42]. The bandwidths of the \(t_{2g}\) (\(\sim 3.5\) eV) and \(e_g\) (\(\sim 3\) eV) bands are rather large, which implies moderate electron-electron interactions [13]. Specifically, the \(t_{2g}\) bands crossing the \(E_F\) are occupied by one 4d electron, forming 2D electron pockets around the M point. Similar to other \(1T\)-MX\(_2\), the Fermi-surface features with sixfold petal structural sheets and weak dispersion along the \(k_z\) direction [Fig. 2(b)] clearly reflects the quasi-2D nature of the electronic states, which is consistent with the layered structure of \(1T\)-NbS\(_2\) [53–55].

Generally, it is an effective method to predict the CDW instability by first-principles phonon calculation [15,16,41,56,57]. The phonon spectra of the bulk \(1T\)-NbS\(_2\) are presented in Fig. 2(c). The phonon instability locating at a distinctive position is believed to be directly related to the CDW distortion, which exhibits softened phonon modes with imaginary frequency at the CDW vector \(q_{\text{cdw}}\).
imaginary phonon frequency at $q_{\text{cdw}}$ signifies structure reconstructions with a superlattice vector of $q_{\text{cdw}}$ [2]. Furthermore, the distributions of phonon frequencies at the plane of $q_z = 0$ in reciprocal space [Fig. 2(d)] confirms that the center of CDW instability is located definitely between $\Gamma$ and $M$ at $q_{\text{cdw}}$. The CDW instabilities of group-V dichalcogenides $MX_2$
are often characterized by $q_{cdw} \approx 0.25 - 0.33 \times \Gamma M$, depending on the different materials [2,41,58]. In bulk 1T-NbS$_2$, the maximally stable acoustic softened mode is located at $q_{cdw} \approx 0.267 \times \Gamma M$, which is very close to the ordering vector of $q_{cdw} = 1/\sqrt{3} \times \Gamma M$, the nearest vector along $\Gamma - M$ compatible with a $\sqrt{3} \times \sqrt{3}$ distortion [16]. This instability persists at all values of $q_z$, as shown in the inset of Fig. 2(c). Moreover, similar to the 1T polymorph of NbSe$_2$ and TaTe$_2$, there is a larger area of instability expanding to the $\Gamma - K$ line [41,57]. In the $\Gamma - A$ direction, the flatness of the optical branch implies the almost 2D dispersion, which is in line with the quasi-2D crystal structure of bulk 1T-NbS$_2$. We note that the CDW order is absent in 2H-NbS$_2$ due to anharmonic suppression, which has been demonstrated by the experimental phonon spectrum and fully anharmonic phonon dispersion curve calculation [23,24]. However, most of the first-principles investigations on the CDW order of TMDCs have not considered the anharmonic effects, but they are still in good agreement with experiments [40,53].

**B. Charge density wave phase and orbital density wave of 1T-NbS$_2$**

After observing the phonon instability for the undistorted high-symmetry phase, we recognize that the high-symmetry structure will undergo a $\sqrt{3} \times \sqrt{3} \times \Gamma$ structural reconstruction and transform to a stable CCDW phase with star-of-David clusters. Assuming a nonmagnetic ground state, we perform structural relaxation and obtain the CCDW structure depicted in Fig. 3(a). The $\sqrt{3} \times \sqrt{3} \times \Gamma$ superlattice consists of Nb clusters with two shells of six Nb atoms and a central 13th Nb atom coordinated by five kinds of S atoms (detailed atomic positions and the structural mode are presented in Table S1 and Fig. S1 of the Supplemental Material [59]). The lattice constants of the CCDW structure are $a' = 12.12 \text{ Å}$ and $c' = 5.97 \text{ Å}$ with space group $P\bar{3}$. As shown in Fig. 3(a), the central Nb atoms keep the same positions relative to the high-symmetry phase, while the peripheral Nb atoms slightly contract toward the central Nb atoms by 5.7% (inner one) and 4.3% (outer one), forming 13-atom star-of-David clusters in the Nb-atom plane, similar to the bulk 1T-TaS$_2$ [60]. As shown in Fig. S1 of the Supplemental Material [59], inside of the $\sqrt{3} \times \sqrt{3}$ star-of-David clusters, the distances between two nearest-neighbor Nb atoms are shorter than those in the undistorted 1T-NbS$_2$, leading to smaller Nb-S-Nb angles with respect to those of the undistorted phase. Conversely, on the boundary of two star-of-David clusters, the distances of two Nb atoms are longer and the Nb-S-Nb angles are larger. Furthermore, the S atoms outside the plane are affected by the in-plane displacements of Nb atoms, resulting in an out-of-plane buckling, which plays an important role in the orbital hybridization [53]. The in-plane Nb atoms’ distortion mode and the corresponding BZ reconstruction are presented in Fig. 3. Due to the lattice distortion, the lattice vectors of the CCDW phase rotate by $13.57^\circ$ with respect to the high-symmetry phase in real space. Accordingly, as shown in Fig. 3(b), the BZ of the CCDW phase also rotates by $13.57^\circ$, resulting in an in-plane $\sqrt{3} \times \sqrt{3}$ R = $13.57^\circ$ periodic lattice distortion [60]. As shown in Fig. S2 of the Supplemental Material [59], all frequencies of the phonon dispersion for the $\sqrt{3} \times \sqrt{3} \times \Gamma$ CCDW phase are positive, revealing that the CCDW phase is dynamically stable, and the nonmagnetic state of the CCDW phase is found to be more stable by 20 meV/NbS$_2$ with respect to the high-symmetry phase.

The structural distortion of the CCDW phase leads to modifications of the electronic structure. Compared with the band structures of the high-symmetry phase, we find significant changes around $E_F$ in the CCDW phase. As shown in Fig. 4(a), the band structure shows a remarkable in-plane gap of about 0.40 eV, which displays a very weak dispersion (flatband characteristic) along the in-plane $\Gamma - M - K - \Gamma$ direction but a strong out-of-plane dispersion along the $\Gamma - A$ direction. In contrast to the quasi-2D flower-shaped Fermi surface of the high-symmetry phase, the CCDW phase exhibits a pair of
FIG. 4. Electronic structures of the bulk $1T$-NbS$_2$ in the CCDW phase. (a) Band structure calculated within GGA, where the red balls represent orbital contributions with the $d_{z^2-r^2}$ character. (b) Fermi surface of the CCDW phase, where the color bar denotes the Fermi velocity. (c) The charge density distribution of the uppermost occupied states in real space; the isosurface value is 0.002 electrons/Å$^3$.

Furthermore, an interesting orbital texture within the $ab$ plane emerges which is intertwined with the CCDW [6,26,53]. The projected band structures and real-space charge density distributions illustrate that the highest occupied band arises dominantly from the Nb-$4d$ orbitals with $d_{z^2-r^2}$ character, as shown in Fig. S3 of the Supplemental Material [59] and Fig. 4(c). Such an orbital configuration is derived mainly from the inner Nb atoms in the star-of-David clusters. The contribution from the Nb atoms at the edge of the clusters is negligible. Therefore an orbital-density-wave order coexists with the CDW order, which is similar to the in-plane orbital texture of the $1T$ polymorph of TaS$_2$ and TaSe$_2$ [6,26,53]. The ODW and the CCDW coexist simultaneously with an identical spatial symmetry. The ODW indicates very little in-plane overlap between orbitals centered on neighboring clusters, while charge can only hop significantly along the layer stacking direction ($c$ axis), in agreement with the in-plane flatband characteristics and out-of-plane quasi-1D metallic nature of the electronic structure. The ODW discussed here is different from the orbital ordering studied extensively in strongly corre-
lateral electron systems [62]. The conventional orbital ordering stems mainly from the cooperative Jahn-Teller distortions or Kugel-Khomskii superexchange interactions [63,64], whereas the CCDW and the ODW in 1T polymorph of MX₂ are mainly attributed to electron-phonon coupling interactions [6,53].

C. Possibility of metal-insulator transition in the CCDW phase

The metal-insulator transition accompanied by the CCDW transition had been observed in the archetypical CDW system, 1T-TaS₂. However, the origins of the insulating phase and metal-insulator transition are still under extensive debate and have attracted huge interest [7,8,61]. It would be interesting to explore the possibility of realization metal-insulator transition by investigating the electronic correlation interactions and magnetic ordering in the CCDW phase of 1T-NbS₂. We calculate the electronic structure within spin-polarized GGA for the CCDW phase. Relative to the non-spin-polarized results, the energy is only lowered by a tiny value of 0.06 meV/NbS₂ within spin-polarized calculations. The small energy difference implies that the electronic correlation effect is not the essential reason for the distortion to the CCDW phase, which is consistent with the broad bandwidth of the Nb-4d bands in Fig. 2(a). Furthermore, the spin-up and spin-down subbands are identical to each other (Fig. S3 in the Supplemental Material [59]), and magnetic moment does not appear, implying the CCDW phase is still essentially a nonmagnetic state. Even though the Coulomb correlation effect and spin-orbit coupling (SOC) interactions are taken into account, the CCDW phase remains nonmagnetic. As shown in Fig. S3 of the Supplemental Material [59], although the in-plane gap has been enlarged by the on-site electron-electron interaction U, there is still no trace of magnetic behavior, indicating that it is hard to generate an energy splitting for the two spin channels and to realize a magnetic ordering state in the CCDW phase. In addition, SOC interactions have only minor impact on the electronic structures, so it is hard to change the out-of-plane metallic transport property and the nonmagnetic state [12,40,53].

In the CCDW phase of the 1T-NbS₂, each cluster is constituted by 13 Nb atoms and 26 S atoms, implying that there is one isolated 4d electron in every star-of-David cluster. Such an electronic configuration can create a half-filled band, and it results in a metallic behavior when the Coulomb correction is absent. In fact, no matter whether the spin-polarized, Coulomb correction or SOC interaction have been considered or not, the insulating property or magnetic behavior does not appear based on a 1 × 1 × 1 unit cell of the CCDW phase (Fig. S3 of the Supplemental Material [59]). The metallic behavior of the CCDW phase solely arises from the out-of-plane dispersion, where the interlayer coupling effect delocalizes the in-plane states and suppresses the spin polarization, finally leading to a nonmagnetic ground state [12,65].

However, if the stacking of layers doubles the cell of the CCDW phase, the insulating state can be expected by including an even number of orbitals. Therefore we construct a 1 × 1 × 2 supercell by doubling the cell of the CCDW phase along the stacking direction and artificially assign an interlayer AFM ordering by setting an antiparallel magnetic moments direction in near-neighbor layers. Unfortunately, without Coulomb corrections the system does not favor AFM order and still converges to the nonmagnetic metallic state. Only when AFM ordering and Coulomb corrections have been included simultaneously can a tiny band gap be opened up (Fig. 5 and Fig. S4 of the Supplemental Material [59]). Similar to the monolayer 1T-NbS₂ [42], the magnetic moments almost arise from the central Nb atoms of the cluster, whereas the contributions from the edge of the star-of-David cluster are negligible.

Previous theoretical investigations show that the monolayer 1T-TaS₂ is a ferromagnetic (FM) Mott insulator, and the bilayer is an interlayer AFM insulator in the CCDW phase, whereas the ground state of the bulk phase depends on U_{eff}/W (U_{eff} is the effective Coulomb correlation and W is the out-of-plane bandwidth) [12,53]. Coulomb interaction is indispensable to describe the ground state of the CCDW system. For the case of 1T-NbS₂, there is one isolated 4d electron in every star-of-David cluster of the CCDW phase. According to conventional band theory, an odd-number electron should form a half-filled band, resulting in a metallic behavior without the consideration of the on-site electronic correlation. As shown in Fig. S4 of the Supplemental Material [59], the metallic behavior of the CCDW phase preserves up to a moderate Coulomb correlation of 2 eV. Along with increasing electronic correlation, the Mott gap is opened up and the metal-insulator transition is observed. Nevertheless, we should aware that the energy difference between the insulating AFM state and the metallic nonmagnetic state is only about 0.5 meV/NbS₂ (U = 2.95 eV), indicating that the critical temperature for the out-of-plane AFM ordering is very low. Therefore it would be interesting to further clarify the existence of this insulating magnetic ordering state in bulk 1T-NbS₂ at low temperatures by magnetic property characterization and transport property measurement.

When the dimensionality reduces to the monolayer limit, a previous study has shown that the FM Mott insulating states can emerge in the CCDW phase of the 1T-MX₂, attributed to be a consequence of the 2D geometry [12,13,40–42,65].

FIG. 5. Electronic band structure of the AFM \( \sqrt{13} \times \sqrt{13} \) CCDW phase calculated using a \( 1 \times 1 \times 2 \) supercell within GGA+U.
Recent theoretical predictions pointed out that the CCDW phase of the single-layer 1T-NbS$_2$ exhibits a FM insulating nature [42]. However, we find a preset FM state converges to an interlayer AFM solution for the bulk 1T-NbS$_2$ with CCDW order, indicating that AFM ordering is a more reasonable ground state. We further inspect the role of the interlayer coupling interactions and the reduced dimensionality by enlarging the interlayer distance. As shown in Fig. 6, the FM state is unstable with higher energy relative to the AFM state, but the energy differences between them reduce rapidly along with increasing interlayer distance. Obviously, the energies almost become the same when the interlayer distances are enlarged by up to 60%. The interlayer coupling interactions become weaker and weaker. Finally, the system becomes essentially identical to the monolayer and a FM insulating state is realized in the monolayer limit [42]. The manipulations of transport properties and magnetic behavior by stacking manner of interlayer, interlayer distances, and intercalation deserve further study.

D. Mechanism of CDW transition and pressure-induced superconductivity

It has been thought that Fermi-surface nesting is one of the driving mechanisms of CDW order [2,3]. A quantitative evaluation of Fermi-surface nesting can be realized by calculating the electron susceptibility or the Fermi-surface nesting function [11]. The nesting function is the low-frequency limit of the imaginary part Im[\(\chi_0(q)\)] of the bare electronic susceptibility in the constant matrix element approximation, whereas the real part Re[\(\chi_0(q)\)] of the bare electronic susceptibility determines the stability of the electronic system. Therefore if the CDW order originates from the Fermi-surface nesting, peaks will appear simultaneously in both of Im[\(\chi_0(q)\)] and Re[\(\chi_0(q)\)] at the q$_{cdw}$ [10,11]. The real and imaginary parts of the electron susceptibility are defined as

\[
\text{Re}[\chi_0(q)] = \sum_k \frac{f(\varepsilon_k) - f(\varepsilon_{k+q})}{\varepsilon_k - \varepsilon_F},
\]

\[
\text{Im}[\chi_0(q)] = \sum_k \delta(\varepsilon_k - \varepsilon_F)\delta(\varepsilon_{k+q} - \varepsilon_F),
\]

where \(f(\varepsilon_k)\) is the Fermi-Dirac function, \(\varepsilon_k\) are the corresponding Kohn-Sham energies, and \(\varepsilon_F\) is the Fermi level.

For the undistorted bulk 1T-NbS$_2$, a grid of 18 K-points is used to calculate the DFT eigenvalues for further evaluation of the electron susceptibility. Then the DFT results are used to construct a tight-binding (TB) model Hamiltonian with the maximally localized Wannier functions (MLWF) method using the WANNIER90 code [66,67]. As shown in Fig. 2(a), the d-like bands split off from the p-like bands by an obvious gap around the Fermi level. Therefore the TB Hamiltonian is constructed with five Nb-4d orbitals. The bands derived from the five-orbital model perfectly match the DFT bands of the bulk 1T-NbS$_2$ in the high-symmetry phase (Fig. S5 of the Supplemental Material [59]). Subsequently, the resulting TB Hamiltonian is used to calculate the bare electron susceptibility [68–71]. Although the imaginary part of the electron susceptibility shows a maximum around the \(\Gamma\) point, which is owing to intraband contributions from a weakly dispersing band, this is irrelevant for the nesting [72,73]. Both of the real and imaginary parts of the susceptibility show no maxima at the positions of q$_{cdw}$ (Fig. 7). Consequently, the Fermi-surface nesting cannot account for the CDW instability in bulk 1T-NbS$_2$.

In addition to the Fermi-surface nesting mechanism, many researchers argue that the momentum-dependent electron-phonon interactions are required to explain the phonon mode softening and create CDW in quasi-2D TMDC systems [2,5,9–11]. The phonon linewidth reflects the strength of the EPC, which does not depend on the positive or imaginary nature of the phonon frequency [15,73]. The calculated phonon linewidth of the lowest phonon mode in the \(q_z = 0\) plane indicates that q$_{cdw}$ is in the area with the maximum (Fig. S6 of the Supplemental Material [59]), signifying the EPC may play an important role in CDW formation in 1T-NbS$_2$. Furthermore, even though it is problematic to calculate the quantitative EPC of the undistorted phase due to the imaginary frequencies around q$_{cdw}$, it is reasonable to eliminate the imaginary fre-
FIG. 8. Phonon dispersion curves and Eliashberg EPC spectral function $\alpha^2 F(\omega)$ with the integrated EPC constants $\lambda$ for the high-symmetry phase of 1T-NbS$_2$ calculated within a large smearing parameter $\sigma$ of 0.03 Ry.

FIG. 9. Evolution of (a) phonon dispersion and (b) $q_z$ dependence of the unstable acoustic branch of 1T-NbS$_2$ under high pressure. (c) Eliashberg spectral function $\alpha^2 F(\omega)$ and the EPC integral $\lambda(\omega)$ at pressure of 30 GPa. (d) The evolutions of EPC constants ($\lambda$) and superconducting temperatures ($T_c$) of compressed 1T-NbS$_2$.
Previous studies show that it is possible to suppress the CDW instability upon applying pressure and trigger superconductivity in $1T$-$MX_2$ [$13, 15-19, 57$]. As shown in Fig. 9(a), the unstable modes in the bulk of $1T$-$NbS_2$ gradually harden with increasing pressure. The unstable phonon modes of the high-symmetry structure will disappear completely, and a stable phase appears above the pressure of 30 GPa [Fig. 9(b)]. In order to inspect the relationship between the electron-lattice interaction and the CDW instability, we have calculated the EPC constants as a function of pressure in the high-symmetry phase. Along with increasing pressures, where the $1T$ structure becomes stable, $\alpha^2 F(\omega)$ shows an obvious change with a sharp decrease of its intensity, leading to a remarkable reduction of the EPC constant from 1.55 down to 0.82 as the CDW instability is suppressed [Fig. 9(c)]. Accompanied by the suppression of the CDW order, the superconductivity can emerge in the bulk of $1T$-$NbS_2$. The superconducting transition temperature $T_c$ is estimated by the Allen-Dynes–modified McMillan formula [77, 78]:

$$T_c = \frac{\omega_{log}}{1.2} \exp \left( -\frac{1.04(1+\lambda)}{\lambda - \mu^* - 0.62\lambda \mu^*} \right),$$

where the Coulomb pseudopotential $\mu^*$ is assumed to be 0.1, $\lambda$ is the EPC constant defined in Eq. (3), and $\omega_{log}$ is the logarithmic average frequency:

$$\omega_{log} = \exp \left( \frac{1}{\lambda} \int \frac{\log \omega}{\omega} \alpha^2 F(\omega) d\omega \right),$$

with the Eliashberg spectral function $\alpha^2 F(\omega)$ defined in Eq. (4).

At pressure of 30 GPa, the superconducting transition temperature $T_c$ is estimated to be 13.05 K, which is larger than those of the $1T$ polymorphs of TaS$_2$ and TaSe$_2$ as well as their doping compounds TaS$_{1-x}$Se$_x$ [17–19]. As the CDW instability is just suppressed and the system enters into the superconducting phase, the original imaginary frequency becomes positive, resulting in large $\lambda$ and high $T_c$. The EPC constants and superconducting transition temperatures of the compressed $1T$-$NbS_2$ decrease monotonously along with the increasing pressure [Fig. 9(d)]. The downward trend of the superconducting transition temperatures with increasing pressure is in qualitative agreement with previous theoretically predicted results of the $1T$ polymorph of TaS$_2$ and TaSe$_2$ [15, 16]. Generally, pressure-induced lattice deformation directly causes an enhancement of $N(E_F)$ at the Fermi level and the instability of phonon vibration modes. Electronic structure calculations indicate a tiny decrease of $N(E_F)$ along with the increasing pressure, whereas the phonons of the compressed superconducting phase display an overall blueshift compared to the ambient pressure phase $1T$-$NbS_2$ (Fig. S8 of the Supplemental Material [59]). Pressure compresses the lattice volume and the phonon spectra gradually harden, which leads to the reduction of $\lambda$ and a consequent decrease of the superconducting transition temperature.

It should be aware that superconductivity and CDW order are not absolutely exclusive with each other. Although CDW instability in pristine $1T$-TaS$_2$ has been predicted theoretically to be suppressed by high pressure [15], the coexistence of pressure-induced superconductivity with CDW order has been observed experimentally above 4 GPa [13, 17–19]. The superconductivity and its coexistence with CDW order under high pressure have been explained in terms of a microscopic phase separation in real space [13]. As shown in Fig. 9, the phonon spectrum gradually hardens with increasing pressure. The in-plane imaginary phonon modes have disappeared above 10 GPa, but the $q_x$ dependence of the unstable acoustic branch remains negative until the pressure increases up to 30 GPa. In addition, anomalies in the acoustic branches along the $\Gamma$-$M$ and $\Gamma$-$K$ directions persist, signaling the incipient CDW instability of the high-symmetry $1T$-$NbS_2$ even up to 30 GPa [15, 16]. We suspect that the CDW order may coexist with the superconducting state until the thorough suppression of the CDW instability by pressure, and the coexistence of CDW order with superconductivity could be a possible phase for this system. Further experimental studies on $1T$-$NbS_2$ under pressure can give us the details and address this issue.

**IV. CONCLUSIONS**

By employing first-principles calculation, we predict that bulk $1T$-$NbS_2$ is unstable due to a softened phonon mode and will transform to a stable CCDW phase with a $\sqrt{13} \times \sqrt{13}$ structural reconstruction. Electronic structure calculation suggests that the ODW can coexist with the CDW order in the CCDW phase. A metal-insulator transition can be realized in the CCDW phase, provided that the interlayer AFM ordering and the Coulomb correlation effect are taken into account simultaneously. Bare electron susceptibility, phonon linewidth, and EPC constant calculations suggest that the EPC interactions account for the CDW instability. Furthermore, the CDW order can be suppressed by high pressure, and superconductivity emerges in the compressed structure with moderate EPC interactions. Our theoretical predictions call for further experimental study of the electronic structure and magnetic properties of the $1T$-$NbS_2$. Moreover, it will be interesting to study the possibility of coexistence of CDW order and superconductivity in $1T$-$NbS_2$.

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