Novel high pressure structures and superconductivity of niobium disulfide

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We have investigated the pressure-induced phase transition and superconducting properties of niobium disulfide (NbS2) based on the density functional theory. The structures of NbS2 at pressures from 0 to 200 GPa were predicted using the multi-algorithm collaborative (MAC) structure prediction technique. The previously known 1T-, 2H-, and 3R-NbS2 were successfully reproduced. In addition, many metastable structures which are potential to be synthesized were also discovered. Based on the enthalpy calculations, we found that at 26 GPa NbS2 transits from the double-hexagonal (2H) structure to the tetragonal I4/mmm structure with a 10.6% volume reduction. The calculated elastic constants and phonon dispersion curves of I4/mmm-NbS2 confirm its mechanical and dynamical stability at high pressure. More interestingly, the coordination number of Nb in I4/mmm structure is eight which is larger than that in the traditional metal dichalcogenides, indicating a new type of bondings of Nb and S atoms. In the new Nb-S bondings, one Nb atom and neighboring eight S atoms form a [Nb8S8] hexahedron unit. Furthermore, I4/mmm-NbS2 exhibits a higher superconducting critical temperature than 2H-NbS2, as is resulted from the stronger electron-phonon coupling coefficients.

I. INTRODUCTION

Transition metal dichalcogenides (TMDs) MX2 (M = Nb, Ta, Mo, W, X = S, Se, Te) have intriguing properties, ranging from insulator to metal and superconductor, and thus always attract extensive interests of experimentalists and theorists. Thanks to their in-plane covalent bondings and weak interlayer van der Waals interactions, they could be easily exfoliated down to a monolayer which shows very exotic properties. For example, bulk MoS2 is an indirect-band-gap semiconductor11 while the monolayer MoS2 is a direct-band-gap semiconductor12. Consequently, the TMDs have shown exciting prospects for a variety of applications, such as catalysts and lubricants in the petroleum industry13, promising applications in nanoelectronics and optoelectronics14 and energy storage applications15.

The typical representative of TMDs is 2H-NbSe2, showing a large charge density wave (CDW) (at 33 K) that coexists with superconductivity (Tc = 7.2 K)16. Niobium disulfide (NbS2) also belongs to the family of TMD compounds. But the CDW order appeared in 2H-NbSe2 is absent in 2H-NbS23,10 and its occurrence is suppressed by the large anharmonic effects10. However, it also shows superconductivity at a similar transition temperature of Tc = 6 K11,13. More interestingly, the Tc of 2H-NbS2 increases smoothly from 6 K at zero pressure to ~8.9 K at 20 GPa13, also similar to the behavior of Tc in 2H-NbSe2 which increases to ~8.5 K at 10 GPa13. The upper critical field of 2H-NbS2 has an initial decrease as pressure increases, contrary to the increase of Tc, but above 8.7 GPa it increases again with pressure13.

NbS2 is a two-gap superconductor, similar to NbSe2. The heat capacity of a 2H-NbS2 has been measured down to 0.6 K and in magnetic fields up to 14 T by Kačmarčík et al17. The temperature dependence of the electronic specific heat can be attributed to either the existence of a strongly anisotropic single-energy gap or a two-gap scenario with the large gap about twice bigger than the small one. The field dependence of the Sommerfeld coefficient induces a magnetic field dependence of the superconducting anisotropy17. The two-gap scenario conclusions are supported by the absence of in-plane gap anisotropy in recent STM imaging of the vortex lattice in NbS215.

2H-NbS2 has a layered structure and therefore has large anisotropic electrical, optical, and magnetic properties. It has been applied as catalyst for the purification of petroleum14, cathode materials in secondary batteries15, humidity sensors16,17 and so on. In experiment, presently the one-layer trigonal 1T-NbS215, two-layer hexagonal 2H-NbS219 and three-layer rhombohedral 3R-NbS220,21 have been synthesized. Large-scale synthesis of 3R-NbS2 nanosheets has also been recently realized19. Different low dimensional structures of NbS2 have different physical and chemical properties. Low dimensional materials depend on and can be exfoliated from bulk materials. It is necessary to uncover as many crystal structures of NbS2 as possible. From some new crystals, it is expected to exfoliate some new-functional low dimensional materials.

It is known that pressure is able to modulate the properties of materials through changing their crystal structures. Furthermore, the structures of NbS2 under high pressure are fundamental to understand its su-
perconductive properties. The mechanism of pressure-induced superconductivity and the superconducting temperature in NbS$_2$ above 20 GPa still remain unknown to us. This motivates us to investigate the superconductivity of NbS$_2$ at higher pressures. In this work, we first predicted the high-pressure structures of NbS$_2$ and determined its phase transition sequence using the multi-algorithm collaborative (MAC) crystal structure prediction technique combined with the density functional theory (DFT). Then we calculated the superconducting critical temperature through electron-phonon coupling calculations.

The paper is organized as follows. Section II contains the computational details. The results and discussion are presented in Sec. III. Conclusions follow in Sec. IV.

II. COMPUTATIONAL DETAILS

In order to determine the high-pressure structures of NbS$_2$, we searched its low-energy structures from 0 to 200 GPa using our developed MAC crystal structure prediction technique.$^{22}$ The multi algorithms including the evolutionary, the simulated annealing, and the basin hopping algorithms are combined to collaboratively search the global energy minima of materials with the fixed stoichiometry. The MAC algorithm and all the relevant techniques are incorporated in the MUSE code.$^{22}$ The results were also carefully cross checked and confirmed by the CALYPSO code.$^{23–25}$ which is based on the particle swarm optimization algorithm.

The $ab$ initio optimizations for every structure generated by the MUSE code were performed with VASP package.$^{26–28}$ We tested the local density approximation (LDA) and the generalized gradient approximation (GGA) parametrized by Perdew, Burke and Ernzerhof (PBE)$^{26}$ for exchange correlation energy. The two approximations give the similar structures order in structure prediction. While the LDA calculated lattice constants are better than the GGA for NbS$_2$. So in the static calculations, we adopted the LDA exchange-correlation functional. The electron-ion interactions are described by the projector augmented wave (PAW) scheme.$^{29,30}$ The pseudopotentials for Nb and S have the valence electrons’ configurations of $4d^4s^14d^4$ and $3s^23p^4$, respectively. To achieve good convergences the kinetic energy cutoff and the $k$-point grids spacing were chosen to be 500 eV and 0.02 Å$^{-1}$, respectively. The accuracies of the target pressure and the energy convergence for all optimizations are better than 0.1 GPa and $10^{-5}$ eV, respectively. The searched systems contained 6, 9, 12, 15 and 18 atoms in the unit cell.

| Structure Method | Method | a (Å) | c (Å) | c/a | P (GPa) | Reference |
|------------------|--------|-------|-------|-----|--------|-----------|
| 1T'-NbS$_2$ VASP-LDA | 3.253 5.341 1.642 | 0 | This work |
| Experiment 3.420 5.938 1.736 | | | |
| 2H-NbS$_2$ VASP-LDA | 3.287 11.421 3.475 | 0 | This work |
| Experiment 3.418 11.860 3.470 | | | |
| 3R-NbS$_2$ VASP-LDA | 3.286 17.577 5.349 | 0 | This work |
| Experiment 3.335 17.834 5.336 | | | |

III. RESULTS AND DISCUSSION

A. Structure prediction for NbS$_2$ at high pressures

In our MAC structure searches$^{22}$ the structures were generated with symmetry constraints in the first generation and optimized with VASP package at fixed pressures. The pressures applied to crystal structures in optimizations go from 0 to 200 GPa with the interval of 20 GPa. At each fixed pressure, the enthalpies of these structures were calculated and compared to find the proper path towards the lowest-enthalpy structure. Results show that the previously known 2H-NbS$_2$ has the lowest enthalpy at lower pressures (below 20 GPa) and the I4/mmm structure has the lowest enthalpy at higher pressures (above 20 GPa). The previously known 1T' and 3R-NbS$_2$ structures were also easily reproduced. The large-scale 3R-NbS$_2$ nanosheets are synthesized very recently.$^{17}$ More interestingly, we found a new two-layer hexagonal structure whose energy is very close to 3R-NbS$_2$ at ambient pressure. We refer to it as 2H'-NbS$_2$. According to energy criterion, it is potential to be synthesized in experiment. Meanwhile, many other structures were found to be energetically competitive, including P3m1, P6$_4$22, P6$_2$22 structures, and so on. Among these structures, the trigonal P3m1 structure has lower energy with respective to the known 3R-NbS$_2$ in the whole pressure range of interest. So, it is also expected to be synthesized in experiment.

The calculated lattice constants of 1T', 2H', and 3R-NbS$_2$ are listed in Table I in comparison with experimental values.$^{16,17,19}$ We note that the lattice constants $a$ and $c$ of the three structures are all slightly underestimated in our LDA calculations. But the calculated $c/a$ values are all in good agreement with experiments. To further examine the three structures, we also simulated their X-ray diffraction (XRD) patterns and compare them with experimental data. The calculated XRD patterns of the three structures are all in excellent agreement with corresponding experiments (Fig. I), indicating that each structure is identical to the known one.
The new 2H’-NbS2 crystal has the 2H-MoS2 structure and can be formed by shifting one layer of atoms in 2H-NbS2. The shifting distance is 0.577 lattice constant a along typical direction. 2H’-NbS2 has six atoms in primitive cell with the lattice constants of 3.28, 3.28 and 11.65 Å at ambient pressure. The Nb and S atoms are at Wyckoff’s 2c positions (1/3, 2/3, 1/4) and 4f positions (1/3, 2/3, 0.62), respectively. We show the 2H’-NbS2 structure and the shifting direction in Fig. 2. The shifting direction is parallel to the layer plane (Fig. 2 f). That is to say that the structures of the two layers are the same. The unique difference between 2H’- and 2H-NbS2 is the relative positions of the two layers. The coordination numbers of Nb atoms in both 2H’- and 2H-NbS2 are six. One Nb atom and the neighboring six S atoms form a [NbS6] trigonal prism. Accordingly, the coordination numbers of S atoms in both 2H’- and 2H-NbS2 are three.

The new I4/mmm structure is plotted in Fig. 3. It has six atoms in conventional unit cell (three in primitive cell) with the lattice constants of 3.15, 3.15 and 7.91 Å at 26 GPa. The Nb and S atoms are at Wyckoff’s 2a positions (0.0, 0.0, 0.0) and 4e positions (0.0, 0.0, 0.34), respectively. More interestingly, the coordination number of Nb in I4/mmm is eight. In this new type of bondings, one Nb atom and neighboring eight S atoms form a [NbS8] hexahedron. The coordination number of S is four. To our knowledge, this type of covalent bondings has not been reported in TMD crystals. In general, in TMDs the metal atom has traditional six nearest neighbors. This new type of eight nearest neighbors in I4/mmm-NbS2 implies new potential chemical and physical properties, especially in two-dimensional crystals.

![FIG. 1: (color online). Simulated XRD patterns of 2H-NbS2, 3R-NbS2, and 1T-NbS2, in comparison with the corresponding experimental results (1T: [15] 2H: [16] 3R: [17].)](image)

B. Phase transition and structural stability of NbS2

In order to obtain the phase-transition sequence of NbS2 under compression, we calculated the energies for its different phases at 0 K and pressures from 0 to 200 GPa. The enthalpies vs pressure data of different structures with respect to 2H-NbS2 are plotted in Fig. 4 from which we note at 0 K the previously known hexagonal 2H-NbS2 is stable up to 26 GPa. Above 26 GPa, NbS2 transits to the tetragonal I4/mmm structure which remains stable up to a very high pressure, 200 GPa, the upper limit of our interest. Upon compression, NbS2 exhibits a volume reduction of 10.6% at 26 GPa (Fig. 5). This volume reduction directly results in the decrease of interlayer distance and the aggregation of S atoms around Nb atoms. Although at ambient conditions, 1T- and 3R-NbS2 have relatively higher energies than 2H-NbS2, they have been synthesized successfully. The energies of 2H’- and P3m1-NbS2 are close to that of 3R-NbS2, so we believe they are both potential to be synthesized in experiment. After all, the trigonal P3m1 structure has lower energy than the known 3R-NbS2 in the whole pressure range. The energies of P6222 and P6122 structures are
FIG. 3: (color online). Predicted $I4/mmm$ crystal structure. (a) The structure of $I4/mmm$-NbS$_2$. (b) Top view. (c) Front view. (d) Left view.

FIG. 4: (color online). Enthalpy differences of predicted structures relative to 2$H$-NbS$_2$ structure under high pressure.

The mechanical stability of 2$H$- and $I4/mmm$-NbS$_2$ are confirmed by their elastic constants (shown in Table II and Fig. 6) according to the elastic criteria of the hexagonal systems,

$$C_{11} > |C_{12}|, \quad (C_{11} + 2C_{12})C_{33} > 2C_{13}^2, \quad C_{44} > 0, \quad (1)$$

and tetragonal systems,

$$C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0,$$

$$C_{11} > C_{12}, \quad C_{11} + C_{33} > 2C_{13}, \quad 2(C_{11} + C_{12}) + C_{33} + 4C_{13} > 0,$$  

respectively. The increasing of the elastic constants of $I4/mmm$-NbS$_2$ with pressure reflect its enhanced stability as pressure increases (Fig. 6). The new 2$H'$ structure is also mechanically stable at ambient and high pressure according to the elastic criteria of the hexagonal crystals. While, the $P3m1$ structure is only stable at low pressures. It becomes mechanically unstable as pressure increases because of the appearance of negative shear modulus $C_{14}$. It is also worthy to note that the shear modulus $C_{44}$ of 2$H$-NbS$_2$ increases with pressure, but the $C_{44}$ values of 2$H'$-NbS$_2$ remain small as pressure increases. This implies 2$H$-NbS$_2$ is more stable than 2$H'$-NbS$_2$. So, it is easier to synthesize 2$H$-NbS$_2$ in experiment other than 2$H'$-NbS$_2$.

To further check the dynamical stability of the new structures, 2$H'$- and $I4/mmm$-NbS$_2$, we determined their vibrational frequencies using density functional perturbation theory (DFPT) as implemented in the QUANTUM-ESPRESSO package. For the exchange-correlation functional we used the Perdew-Zunger local-
TABLE II: The elastic constants of different NbS\textsubscript{2} structures under high pressure. The pressure (\(P\)) and elastic constants are all in GPa.

| Structure \(2H\) | \(C_{11}\) | \(C_{12}\) | \(C_{13}\) | \(C_{33}\) | \(C_{44}\) | \(C_{14}\) |
|-----------------|--------|--------|--------|--------|--------|--------|
| 0.00            | 174.16 | 77.34  | 9.70   | 58.80  | 65.26  | -       |
| 11.90           | 247.87 | 94.07  | 48.92  | 232.36 | 99.38  | -       |
| 21.69           | 314.77 | 127.03 | 70.09  | 324.01 | 139.63 | -       |
| 2\(H'\)        | 0.00   | 163.26 | 83.75  | 15.49  | 52.47  | 2.35   |
| 19.93           | 267.04 | 121.63 | 82.27  | 314.33 | 10.43  | -       |
| 47.17           | 336.47 | 186.91 | 134.25 | 593.40 | 15.98  | -       |
| \(P3m1\)       | 0.00   | 186.36 | 68.43  | 20.35  | 103.46 | 1.07   |
| 13.73           | 262.74 | 81.66  | 57.44  | 272.51 | 64.46  | -10.50 |
| 23.10           | 324.97 | 104.56 | 72.18  | 369.49 | 94.47  | -20.06 |

 density approximation (LDA)\textsuperscript{35} and ultrasoft pseudopotential\textsuperscript{36}. We applied the Vanderbilt ultrasoft pseudopotentials for Nb and S with the valence electrons configurations 4s\textsuperscript{2}4p\textsuperscript{6}4d\textsuperscript{2}5s\textsuperscript{2} and 3s\textsuperscript{2}3p\textsuperscript{4}, respectively. The ultrasoft pseudopotentials were generated with a scalar-relativistic calculation.

We carefully tested on \(k\) and \(q\) grids, the kinetic energy cutoff, and other technical parameters to ensure good convergence of phonon frequencies. The kinetic energy cutoff, the energy cutoff for the electron density, and the \(k\) grids were chosen to be 40 Ryd., 400 Ryd., and 16\(\times\)16\(\times\)16 Monkhorst-Pack (MP)\textsuperscript{35} meshes in both total energy and phonon dispersion calculations, respectively. We applied the Gaussian smearing method with the smearing width of 0.05 Ryd. For the dynamical matrices of the \(I4/mmm\) structure, we used a 2\(\times\)2\(\times\)2 \(q\) grid, giving 8 wave vectors \(q\) in the irreducible wedge of the first BZ. For the 2\(H\)- and 2\(H'\)-NbS\textsubscript{2}, the \(q\) grid meshes are 2\(\times\)4\(\times\)4, also giving 8 wave vectors.

Phonon dispersion curves (Figs. 7(b) and 8(a)) do not show any imaginary frequencies, indicating dynamical stability of \(I4/mmm\)- and 2\(H'\)-NbS\textsubscript{2}. So we believe \(I4/mmm\)- and 2\(H'\)-NbS\textsubscript{2} are both mechanically and dynamical stable. The phonon dispersion curve of 2\(H\)-NbS\textsubscript{2} are also presented in Fig. 8(b), compared to the experimental data\textsuperscript{39}. The agreement of our calculated phonon frequencies and the 300 K experimental data is quite good. By comparing the phonon dispersion curves of 2\(H\)- and 2\(H'\)-NbS\textsubscript{2}, we note the phonon frequencies of 2\(H'\)-NbS\textsubscript{2} exhibit softening near to A point (along the \(\Gamma\)-A, A-L and H-A directions), implying its metastability compared to 2\(H\) structure. This is consistent with the conclusions from the elastic constants calculations.

C. Electron-phonon coupling and superconductivity

We calculated the superconducting transition temperature \(T_c\) of NbS\textsubscript{2} using the Allen-Dynes\textsuperscript{35} form of the McMillan\textsuperscript{40} equation,

\[
T_c = \frac{\omega_{\text{ph}}}{1.2} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\mu)} \right],
\]
The Eliashberg spectral function, $\alpha^2 F(\omega)$, which measures the contribution of the phonons with frequency $\omega$ to the scattering of electrons, can be written as:

$$
\alpha^2 F(\omega) = \frac{1}{2\pi N(\epsilon_F)} \sum_{q\nu} \frac{\gamma_{q\nu}}{\omega_{q\nu}} \delta(\omega - \omega_{q\nu}),
$$

where $N(\epsilon_F)$ is the EDOS at the Fermi level. The linewidth of the phonon mode was calculated from:

$$
\gamma_{q\nu} = 2\pi \omega_{q\nu} \sum_{k,j} g_{k+q,j}^{q\nu} \epsilon_{k,j}^2 \delta(\epsilon_{k,j} - \epsilon_F) \delta(\epsilon_{k+q,j} - \epsilon_F),
$$

where $g_{k+q,j}^{q\nu}$ is the electron-phonon coupling matrix element. The Coulomb pseudopotential $\mu^*$ was taken the typical value $0.10$ in all the superconducting critical temperatures ($T_c$) calculations.

The calculated $T_c$ of $2H$- and $I4/mmm$-NbS$_2$ are plotted in Fig. 9 compared with recent experimental data. The resulting $T_c$s of $2H$-NbS$_2$ are in very good agreement with experiment and increase with pressure. It is interesting that the $T_c$ of $I4/mmm$ structure is higher than that of $2H$ structure and decreases with pressure. This is resulted from the stronger electron-phonon coupling coefficients $\lambda$ in $I4/mmm$-NbS$_2$ (Fig. 9). The phonon calculations indicate that $I4/mmm$ is unstable below 10 GPa. The highest $T_c$ of $I4/mmm$ (at 10 GPa) is $17.83$ K. From the electronic energy band structure of $I4/mmm$-NbS$_2$ (Figs. 7(a)), we note it is metallic. It is previously known that $2H$-NbS$_2$ is also metallic, so pressure does not change the metallic properties of NbS$_2$, but enhances the electron-phonon coupling effects and thus increases the superconducting critical temperature.

IV. CONCLUSIONS

In conclusion, we predicted three new $2H'$, $P3m1$, and $I4/mmm$-NbS$_2$ structures using the MAC crystal structure prediction technique. The new $2H'$-NbS$_2$ can be formed by shifting the layer of atoms along typical direction parallel to the layer plane. Based on enthalpy calculations, we found $2H$-NbS$_2$ transits to the tetragonal $I4/mmm$ structure at 26 GPa. The new bondings in $I4/mmm$ form a [NbS$_6$] hexahedron, which has not been reported in TMD crystals. More interestingly, the superconducting temperature of $I4/mmm$-NbS$_2$ is higher than that of $2H$-NbS$_2$ and decreases as pressure increases, resulted from the stronger electron-phonon coupling coefficients $\lambda$ in $I4/mmm$-NbS$_2$. In the stability region of $I4/mmm$ structure, the highest $T_c$ is $17.83$ K.

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