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Manipulating superconductivity of 1T-TiTe₂ by high pressure

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Superconductivity of transition metal dichalcogenide 1T-TiTe₂ under high pressure was investigated by first-principles calculations. Our results show that the superconductivity of 1T-TiTe₂ exhibits very different behavior under hydrostatic and uniaxial pressure. The hydrostatic pressure is harmful to the superconductivity, while the uniaxial pressure is beneficial to the superconductivity. The superconducting transition temperature T_C at ambient pressure is 0.73 K, and it reduces monotonously under the hydrostatic pressure to 0.32 K at 30 GPa, while T_C increases dramatically under the uniaxial pressure along the *c* axis. The established T_C of 6.34 K under the uniaxial pressure of 17 GPa, below which the structural stability is maintained, is above the liquid helium temperature of 4.2 K. The increase of the density of states at the Fermi level, the red-shift of the phonon density of states/Eliashberg spectral function $F(\omega)/\omega^2 F(\omega)$, and the softening of the acoustic modes with pressure are considered as the main reasons that lead to the enhanced superconductivity under uniaxial pressure. In view of the previously predicted topological phase transitions of 1T-TiTe₂ under the uniaxial pressure (Q. Zhang *et al.*, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2013, **88**, 155317), we consider 1T-TiTe₂ as a possible candidate in transition metal chalcogenides for exploring topological superconductivity.

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1 Introduction

Transition metal dichalcogenides (TMDCs) MX₂, where M is a transition metal (*e.g.* M = Ti, Mo, Ta, W) and X is a chalcogen atom (S, Se, Te), are an emerging family of layered materials. The intra-layer is composed of an X–M–X sandwich structure, which is attracted by the van der Waals forces between the inter-layers. TMDC materials that can be a semiconductor, metal, charge density wave (CDW) system, or a superconductor have become a rich playground to discover new materials with diverse physical phenomena and properties. The broad application prospects of TMDCs, such as in transistors, photodetectors, electroluminescent devices,¹ van der Waals heterostructures with a high on/off current ratio,² and topological field-effect transistors based on the quantum spin Hall effect,³ have attracted great attention.

MTe₂ is a typical material with rich physical properties and exhibits unique properties compared to MS₂/MSe₂ due to the

strong p–d hybrid and spin–orbit coupling effect. For instance, competition between the charge/orbital density wave (CDW/ODW) and superconductivity was observed in IrTe₂,^{4,5} the topological Dirac point was found in the HfTe₂/AlN epitaxial system,⁶ large and non-saturating magnetoresistance,^{7–9} type-II Weyl points,^{10–13} and pressure-driven superconductivity^{14–16} were observed in WTe₂ and MoTe₂; a topologically non-trivial surface state with a Dirac cone was found in a PdTe₂ superconductor;¹⁷ and type-II Dirac fermions in PtTe₂^{18,19} were recently theoretically proposed and confirmed by experiment.

1T-TiTe₂ is a textbook Fermi-liquid system.^{20,21} Though it is a simple physical system, abundant physical phenomena can be realized *via* various kinds of manipulation. Anomalous electron transport was found in the back-gated field-effect transistors with 1T-TiTe₂ thin-film channels.²² A large negative magnetoresistance was reported in two-dimensional spin-frustrated 1T-TiTe_{2–x}I_x.²³ Bulk and monolayer 1T-TiS_{2–x}Te_x show topological phases under a certain concentration of S/Te.²⁴ 1T-TiTe₂ was recently predicted to undergo a series of topological phase transitions under high pressure.²⁵ 1T-TiTe₂ is a semi-metal with an overlap of valence and conduction bands of 0.6 eV,²⁶ however the superconductivity has not been experimentally found down to 1.1 K at ambient pressure.²⁷

Pressure, an important controllable parameter that can effectively tune the lattice structures and the corresponding band structure, has become an effective way to introduce

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superconductivity and study the relationship between the superconductivity and other physical phenomena in TMDCs. For instance, metallization and the highest onset T_C of 11.5 K were realized in MoS₂ under high pressure;^{28,29} the relationship between the CDW and superconductivity in 1T-TaS₂^{30,31} and 1T-TiSe₂^{32,33} was studied under high pressure; pressure-driven superconductivity and suppressed magnetoresistance were observed in WTe₂^{14,15} and MoTe₂.^{16,34}

In this work, we focus on the possibility of superconductivity of 1T-TiTe₂ under high pressure by first-principles calculations. Our results show that T_C at ambient pressure is 0.73 K, and it reduces under the hydrostatic pressure to 0.32 K at 30 GPa, while the uniaxial pressure along the c axis can increase T_C dramatically to 6.34 K maximally. We explain the different behavior of superconductivity under the hydrostatic/uniaxial pressure based on the varieties of electronic/phonon structures and the electron–phonon coupling effect.

2 Methods

The first-principles calculations based on density functional theory (DFT) were carried out using the QUANTUM-ESPRESSO package.³⁵ The ultrasoft pseudo-potentials and the local density approximation (LDA) according to the PZ functional were used. The energy cutoff for the plane wave (charge density) basis was set to 35 Ry (350 Ry). The Brillouin zone (BZ) was sampled with a $16 \times 16 \times 8$ mesh of k -points. The Vanderbilt–Marzari Fermi smearing method with a smearing parameter of $\sigma = 0.02$ Ry was used. The lattice constants and ions were optimized using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) quasi-Newton algorithm. Electronic properties are calculated including the spin–orbit coupling effect. Since the spin–orbit coupling effect is less important in describing the vibrational properties,^{36,37} the calculation of phonon dispersion is carried out neglecting this effect. The phonon dispersion and electron–phonon coupling constants were calculated using density functional perturbation theory (DFPT)³⁸ with an $8 \times 8 \times 4$ mesh of q -points. The double Fermi-surface averages of the electron–phonon matrix elements were calculated using a $32 \times 32 \times 16$ mesh of k -points.

3 Results and discussion

1T-TiTe₂ has a layered structure with the space group $P\bar{3}m1$ (1T-CdI₂ structure), with one Ti atom and two Te atoms located at the (0, 0, 0) and (1/3, 2/3, $\pm z$) sites, respectively. The crystal structure and BZ are displayed in Fig. 1. The optimized lattice parameters are 3.677 Å and 6.331 Å for a and c respectively. The lattice parameters are slightly underestimated by 2.4% compared with the experimentally obtained ones,^{21,39} and such underestimation exists normally in the LDA calculations. As expected, when the hydrostatic pressure is applied the lattice is suppressed, as shown in Fig. 2(a) and (b). Due to the weak van der Waals coupling between adjacent layers, the reduction of c is more substantial than that of a . By fitting the pressure–energy data to the Birch–Murnaghan equation of state, the bulk

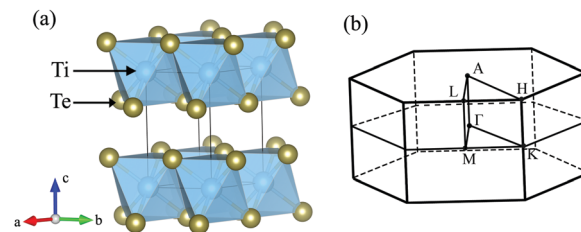


Fig. 1 (a) Crystal structure and (b) Brillouin zone of 1T-TiTe₂.

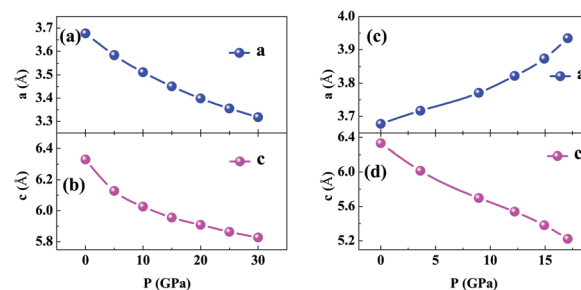


Fig. 2 Lattice parameters under the (a and b) hydrostatic pressure and (c and d) uniaxial pressure along the c axis.

modulus B_0 and its derivative B_0' for 1T-TiTe₂ were calculated to be 51.1 GPa and 4.54 respectively.

The calculated electronic structure of 1T-TiTe₂ at ambient pressure is shown in Fig. 3(c), which is in reasonable agreement with the previous experimental and theoretical reports.^{26,40} The density of states (DOS) near the Fermi level (E_F) is mostly contributed to by the Ti d and Te p orbitals. The electronic structure shows the semi-metal feature with the DOS at the Fermi level ($N(E_F)$) of 1.6 states per eV. The valence band maximum (VBM) and conduction band minimum (CBM) are located at the Γ and L points, respectively. The calculated phonon dispersion is shown in Fig. 3(d). The irreducible representations of the Γ point phonons are $\Gamma = E_g + A_{1g} + 2E_u + 2A_{2u}$, and the corresponding optical vibration modes are illustrated in Fig. 4(a). E_g and A_{1g} are Raman-active modes, and the calculated frequencies of 105/150 cm^{-1} for E_g/A_{1g} are very close to the 102/145 cm^{-1} observed in the experiment.⁴¹

Applying pressure reduces the lattice parameters and enhances the atom interaction, making the band structure more dispersive and increasing the overlap of the valence bands and conduction bands. The electronic structure and phonon dispersion under the hydrostatic pressure of 30 GPa are shown in Fig. 3(a) and (b), where the CBM of the electronic structure is changed from the L point to the M point. With the lattice parameters and Ti–Te bond length decreasing, the frequencies of the Γ phonons increase monotonously under the pressure as demonstrated in Fig. 4(b), and especially the variation of A_{2u} is more evident. Meanwhile, the phonons of the whole BZ also shift to higher frequency with the hydrostatic pressure, as illustrated for the phonon density of states $F(\omega)$ in Fig. 6(a).

Though the band structures are more dispersive, the $N(E_F)$ decreases with the hydrostatic pressure (Fig. 5(a)). To reveal the

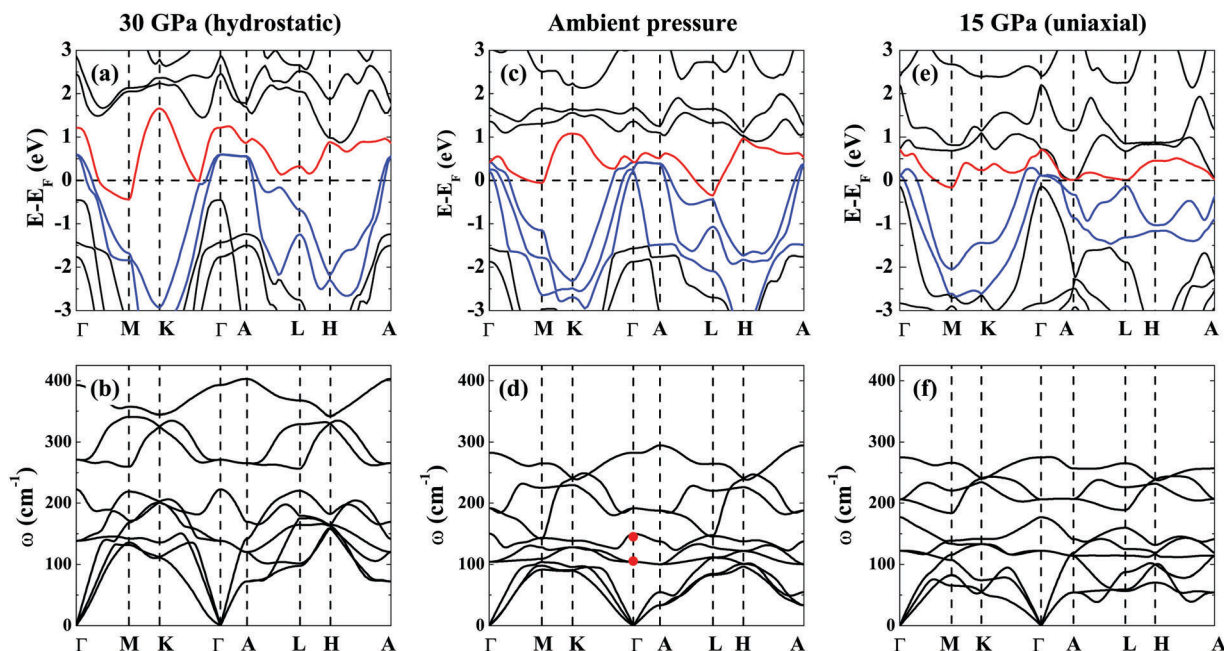


Fig. 3 Electronic structures and phonon dispersions of 1T-TiTe₂ under the (a and b) hydrostatic pressure of 30 GPa, (c and d) ambient pressure, and (e and f) uniaxial pressure of 15 GPa. The red dots in (d) denote the Raman frequencies observed in the experiment.⁴³ For the convenience of comparison, the valence and conduction bands crossing the E_F are shown in blue and red, respectively.

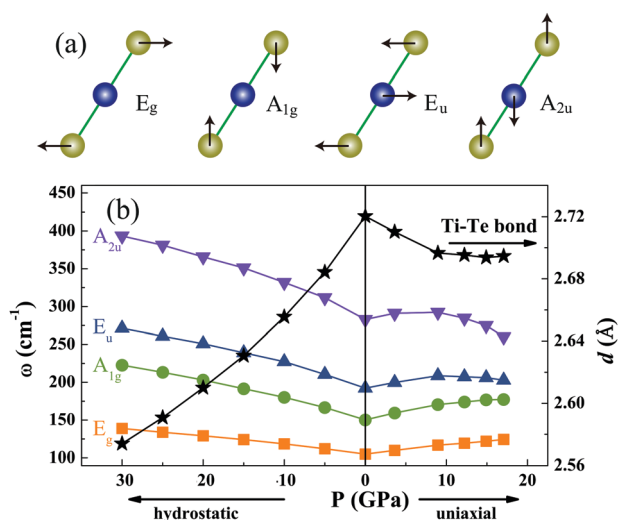


Fig. 4 (a) Schematic illustration of the optical vibration modes at the Γ point. Ti and Te are denoted by blue and dark yellow balls, respectively. (b) Phonon frequencies at the Γ point and Ti-Te bond length under the hydrostatic and uniaxial pressure.

pressure effect on the orbitals at the E_F , the partial DOS at the E_F ($N^P(E_F)$) is shown in Fig. 5(b) and (c). The $N^P(E_F)$ of Ti d decreases dramatically under the hydrostatic pressure (Fig. 5(b)), and the $N^P(E_F)$ of Te $p_x + p_y$ and p_z increases and decreases respectively under the hydrostatic pressure (Fig. 5(c)). The charge density at the E_F on the (110) plane under the hydrostatic pressure of 30 GPa and ambient pressure are also shown in Fig. 5(g) and (h).

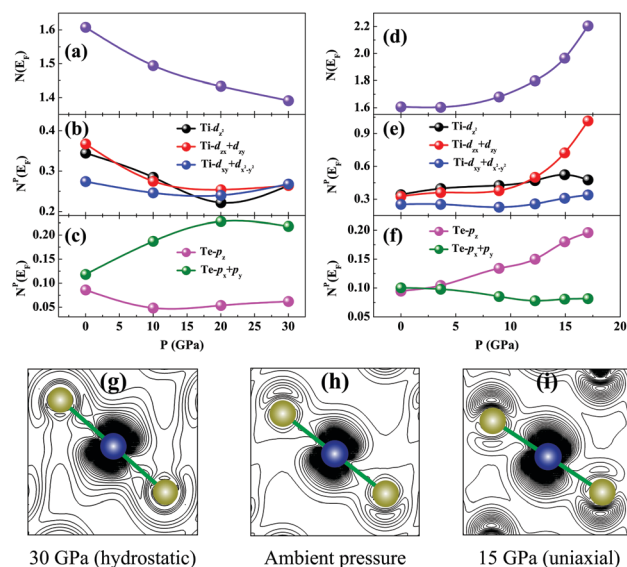


Fig. 5 $N(E_F)$ and $N^P(E_F)$ (in states per eV) under the (a-c) hydrostatic and (d-f) uniaxial pressure. The charge density at the E_F on the (110) plane under the (g) hydrostatic pressure of 30 GPa, (h) ambient pressure, and (i) uniaxial pressure of 15 GPa. The difference between two contour lines in (g-i) is set to the same value. Ti and Te are denoted by blue and dark yellow balls, respectively.

We estimated the superconducting transition temperature T_C based on the Allen-Dynes-modified McMillan equation:^{42,43}

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

where the Coulomb pseudopotential μ^* is set to a typical value of 0.1.^{33,44,45} The logarithmically averaged characteristic phonon frequency $\omega_{\log}$ is defined as:

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

The total electron–phonon coupling constant λ can be obtained by:

$$\begin{aligned} \lambda &= 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega \\ &= \sum_{\mathbf{q}\nu} \frac{2}{\hbar N(E_F) \omega_{\mathbf{q}\nu}} \\ &\quad \times \sum_{ij} \int \frac{d\mathbf{k}}{\Omega_{BZ}} |g_{\mathbf{q},\nu}(\mathbf{k}, i, j)|^2 \delta(\varepsilon_{\mathbf{k},i} - E_F) \delta(\varepsilon_{\mathbf{k}+\mathbf{q},j} - E_F), \end{aligned} \quad (3)$$

where $g_{\mathbf{q},\nu}$ is the electron–phonon coefficient, $\varepsilon_{\mathbf{k},i}$ and $\varepsilon_{\mathbf{k}+\mathbf{q},j}$ are the electron eigenvalues, and the Eliashberg spectral function is:

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu}) \frac{\gamma_{\mathbf{q}\nu}}{\hbar \omega_{\mathbf{q}\nu}}, \quad (4)$$

where α^2 stands for an average of the electron–phonon interaction, and $\gamma_{\mathbf{q}\nu}$ is the phonon linewidth.

T_C at ambient pressure is calculated to be 0.73 K, coinciding with the fact that superconductivity was not found above 1.1 K in the experiment.²⁷ As discussed above, applying hydrostatic pressure increases the phonon frequencies, therefore the Debye temperature rises, and so does $\omega_{\log}$ (Fig. 7(a)). Similar to $F(\omega)$, the Eliashberg function $\alpha^2 F(\omega)$ shifts to higher frequency with the increase of hydrostatic pressure (Fig. 6(b)). Therefore, according to eqn (3), λ decreases with the hydrostatic pressure (Fig. 7(b)). As a result, T_C decreases monotonously with pressure from 0.73 K at ambient pressure to 0.32 K at 30 GPa (Fig. 7(c)), indicating that the hydrostatic pressure does not benefit introduction of the experimentally detected superconductivity, which is unlike the cases of emerging superconductivity in semi-metal WTe_2 and MoTe_2 ^{14–16,34} under hydrostatic pressure.

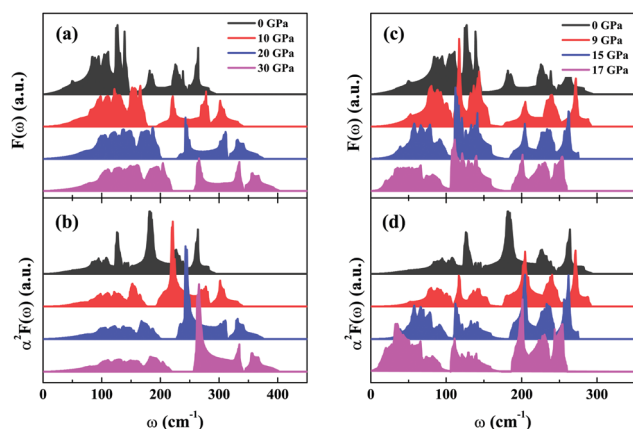


Fig. 6 (a and c) Phonon density of states $F(\omega)$ and (b and d) Eliashberg function $\alpha^2 F(\omega)$ under hydrostatic pressure (left) and uniaxial pressure (right).

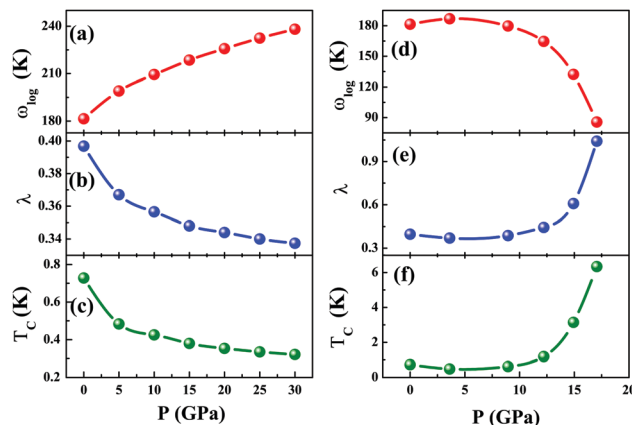


Fig. 7 Calculated λ , $\omega_{\log}$ and T_C of 1T-TiTe₂ under the (a–c) hydrostatic and (d–f) uniaxial pressure.

Due to the layered structure, uniaxial pressure along the c axis can be easily applied in the experiment. Therefore the superconductivity under the uniaxial pressure along the c axis is studied as well in our research. When the uniaxial pressure along the c axis is applied, the c axis reduces meanwhile the a axis expands (Fig. 2(c) and (d)). The variations of a and c are more evident under the uniaxial pressure than under the hydrostatic pressure. The average Poisson's ratio $\nu = -\Delta a/\Delta c$ in the range of our study is 0.23. The electronic structure is less dispersive and the overlap is reduced with the uniaxial pressure. The electronic structure under the uniaxial pressure of 15 GPa is shown in Fig. 3(e), where the CBM is changed from the L point to the M point. The phonon dispersion under the uniaxial pressure of 15 GPa is shown in Fig. 3(f), where the acoustic modes soften.

As demonstrated in Fig. 4(b), with the increase of uniaxial pressure, both the E_g and A_{1g} modes that only involve the vibrations of a Te atom increase monotonously, while the E_u and A_{2u} modes increase at first and then decrease as the pressure becomes larger than 8.9 GPa, which could be attributed to the combination of the expansion of the ab plane and the slow decrease of the Ti–Te length (Fig. 4(b)). Meanwhile, the variation of E_u and A_{2u} under the uniaxial pressure is less significant than that under the hydrostatic pressure due to the fact that the reduction of the Ti–Te length is much less than that under the hydrostatic pressure.

The uniaxial pressure raises the $N(E_F)$ very much (Fig. 5(d)). The $N^P(E_F)$ of Ti $d_{zx} + d_{zy}$ increases dramatically under the uniaxial pressure (Fig. 5(e)), and the trend of the $N^P(E_F)$ of Te $p_x + p_y$ and p_z under the uniaxial pressure (Fig. 5(f)) is opposite to that under the hydrostatic pressure. The increase of the $N^P(E_F)$ of Te p_z and Ti $d_{zx} + d_{zy}$ will increase the orbital overlap of Ti–Te atoms at the E_F as shown in Fig. 5(i), while the orbital overlap is not as such under the hydrostatic pressure (Fig. 5(g)). The strong σ band crossing the E_F due to the orbital overlap at the E_F is one of the main reasons of the high T_C of the superconductors MgB_2 ^{45–47} and H_3S .^{48,49}

As shown in Fig. 6(c), even though some optical phonon $F(\omega)$ peaks shift to a higher frequency in some cases, the overall $F(\omega)$

shifts to a lower frequency with the increase of uniaxial pressure, especially for the acoustic phonons, and the $\omega_{\log}$ decreases with uniaxial pressure as well (Fig. 7(d)). Similar to $F(\omega)$, $\alpha^2F(\omega)$ shifts to a lower frequency (Fig. 6(d)), and the proportion of its low frequency part increases with the uniaxial pressure due to the softening of the acoustic modes. According to eqn (3), the mode with a lower frequency and larger $\alpha^2F(\omega)$ will strongly contribute to the electron–phonon coupling. Therefore, as shown in Fig. 7(e), λ basically increases with the increase of uniaxial pressure. Considering the overall effects, T_C changes slowly at first while it increases dramatically as the uniaxial pressure becomes larger than 8.9 GPa (Fig. 7(f)). Superconductivity with a relatively high T_C often emerges in the vicinity of structural instability. Just beneath the structural instability, a T_C of 6.34 K under the uniaxial pressure of 17 GPa is estimated, above the liquid helium temperature of 4.2 K. Under higher uniaxial pressure, the structure is no longer stable, which is estimated from the calculated imaginary frequency in the acoustic modes. Our results show that the hydrostatic pressure is harmful to the superconductivity, while the uniaxial pressure is beneficial to the superconductivity of 1T-TiTe₂.

In order to show a clear relationship between $\alpha^2F(\omega)$, $N(E_F)$, λ and T_C , these physical parameters are discussed below. The δ functions in eqn (3) are approximately proportional to the $N(E_F)$. Noting the double δ functions about $\varepsilon_{\mathbf{k},i}$ and $\varepsilon_{\mathbf{k}+\mathbf{q},j}$ and the $N(E_F)$ in the denominator, we can conclude qualitatively that a larger $N(E_F)$ will contribute to a larger λ . From eqn (3), we can also conclude that the red-shift of $\alpha^2F(\omega)$ will contribute to a larger λ too. The relationship between the calculated λ and T_C is summarized in Fig. 8(a), where we can see that a larger λ will contribute to a larger T_C for both cases under the hydrostatic and uniaxial pressure. To demonstrate the above relationship qualitatively, we can refer to the Allen–Dynes–modified McMillan equation, *i.e.* eqn (1). The calculated results according to the above equation are shown in Fig. 8(a). Since $\omega_{\log}$ is also the function of λ , here we assume $\omega_{\log} = 75/\lambda$ K for simplicity. So qualitatively, a larger $N(E_F)$ and the red-shift of $F(\omega)/\alpha^2F(\omega)$ are in favor of a higher T_C .

The relationship between the calculated $N(E_F)$ and T_C is summarized in Fig. 8(b), where we can see that a larger $N(E_F)$ will contribute to a larger T_C for both cases under the hydrostatic and uniaxial pressure. To illustrate the relationship between the $N(E_F)$ and T_C more intuitively, one can refer to the original BCS function:^{50,51}

$$T_C = 1.14k_B^{-1}\hbar\omega_D e^{-1/N(E_F)V}, \quad (5)$$

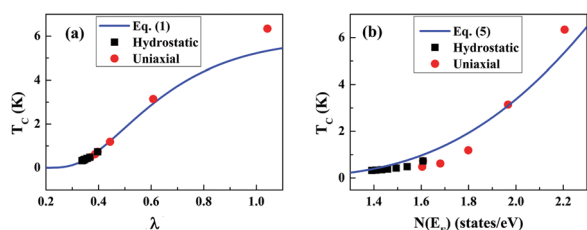


Fig. 8 Illustration of the relationship between (a) λ and T_C , and (b) $N(E_F)$ and T_C . Here, we assume that $\omega_{\log} = 75/\lambda$ K in eqn (1), and $1.14k_B^{-1}\hbar\omega_D = 500$ K and $V = 0.1$ eV in eqn (5).

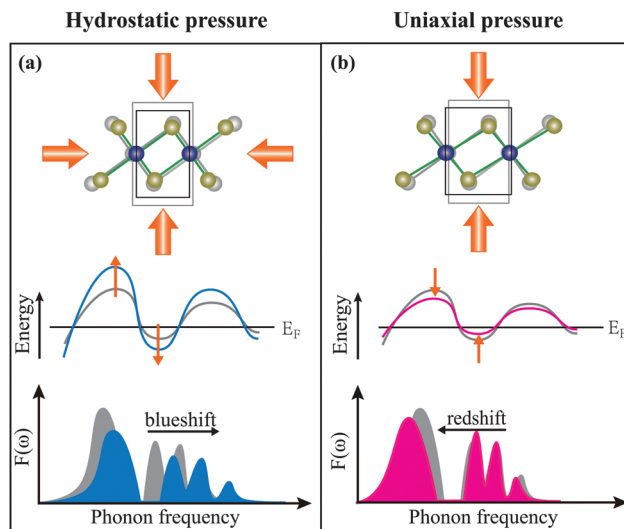


Fig. 9 Schematic diagram of the effects of (a) hydrostatic pressure and (b) uniaxial pressure on the crystal (top), electronic (middle), and phonon (bottom) structures. The gray symbols in each graph denote the corresponding states at ambient pressure. Ti and Te are denoted by blue and dark yellow balls, respectively.

where ω_D is the Debye cutoff frequency, and V is the electron–phonon coupling potential. The calculated results according to the above equation are also shown in Fig. 8(b). Here, we assume $1.14k_B^{-1}\hbar\omega_D = 500$ K and $V = 0.1$ eV for simplicity. So as a general rule of BCS, a larger $N(E_F)$ is in favor of a higher T_C .

We draw a schematic diagram to describe the effects of hydrostatic pressure and uniaxial pressure on the crystal, electronic and phonon structures (Fig. 9). Both a , c , and the Ti–Te bond are compressed under the hydrostatic pressure (Fig. 9(a)). The stronger band dispersion makes the $N(E_F)$ reduce. The phonon density of states $F(\omega)$ shifts to a higher frequency. The decrease of the $N(E_F)$ and the blue-shift of $F(\omega)$ are not in favor of superconductivity, as discussed above. While under the uniaxial pressure, c is suppressed and a is expanded accordingly (Fig. 9(b)). The band dispersion becomes weaker, therefore the $N(E_F)$ increases with the increase of uniaxial pressure. The acoustic phonon modes soften, and $F(\omega)$ shifts to a lower frequency. These two factors (the increase of the $N(E_F)$ and the red-shift of $F(\omega)$) are in favor of superconductivity, as discussed above. We think this physical scenario is not only applicable to 1T-TiTe₂, but also to other layered semi-metal TMDC materials. We propose that the uniaxial pressure can provide an alternative method for enhancing or finding superconductivity in TMDCs.

The previous investigation shows that 1T-TiTe₂ is topologically trivial at ambient pressure, but it was predicted to undergo a series of topological phase transitions under pressure, which are related to the band inversions at different points of the BZ.²⁵ Therefore applying the uniaxial pressure, one can expect to obtain the topological phase and the enhanced superconductivity in 1T-TiTe₂ at the same time. As suggested, introducing superconductivity into the topological material could make it become a topological superconductor,^{52,53} which has a full pairing gap in the bulk and a gap-less surface state consisting

of Majorana fermions. The possible topological superconductivity in 1T-TiTe₂ under pressure needs to be studied in the further experimental and theoretical studies.

4 Conclusions

Using first-principles calculations, we demonstrated that the superconductivity of 1T-TiTe₂ is suppressed under the hydrostatic pressure and enhanced under the uniaxial pressure. The increase of the $N(E_F)$, the red-shift of $F(\omega)/\alpha^2F(\omega)$, and the softening of the acoustic phonon modes with the uniaxial pressure contribute to the enhanced superconductivity. When the uniaxial pressure of 17 GPa is applied, the maximum T_C of 6.34 K in our research is obtained. The uniaxial pressure provides an alternative method to manipulate superconductivity in TMDCs. Under reasonable uniaxial pressure, the topological state and superconductivity may appear at the same time in 1T-TiTe₂. The superconductivity and topological property of 1T-TiTe₂ under pressure will expand its physics and applications.

Acknowledgements

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