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Enhanced superconductivity by strain and carrier-doping in borophene: A first principles prediction

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By first principles calculations, we predict that the recently prepared borophene is a pristine two-dimensional monolayer superconductor in which the superconductivity can be significantly enhanced by strain and charge carrier doping. The intrinsic metallic ground state with high density of states at Fermi energy and strong Fermi surface nesting lead to sizeable electron-phonon coupling, making the freestanding borophene superconduct with T_c close to 19.0 K. The tensile strain can increase the T_c to 27.4 K, while the hole doping can notably increase T_c to 34.8 K. The results indicate that the borophene grown on substrates with large lattice parameters or under photoexcitation can show enhanced superconductivity with T_c far above the liquid hydrogen temperature of 20.3 K, which will largely broaden the applications of such promising material.

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Since the discovery of graphene,^{1,2} two-dimensional (2D) monolayer materials have gained significant attention. Monolayer transition metal dichalcogenide MoS₂,^{3–5} *h*-BN,^{6–8} silicene,^{9–11} phosphorene,^{12,13} etc., were experimentally prepared. Interesting properties emerge in those monolayer materials, implying the promising applications in future electronic devices. However, among the reported remarkable properties of most of the prepared pristine monolayer materials, superconductivity was rarely found. It is due to the intrinsic semi-metal or semiconductor ground states of such materials. The vanishing density of states (DOS) at Fermi energy (E_F) prevents the emergence of superconductivity. A monolayer material showing superconductivity can be very useful in the nanoscale superconductor devices^{14–19} to achieve single-spin sensitivity for measuring and controlling. Lots of predictions suggested that such superconductivity can be introduced by the metallization of those monolayer materials, such as Li atom adsorption on graphene,^{20,21} hole doping in fully hydrogenated graphene,²² electron doping in graphene under strain,²³ monolayer MoS₂,^{24,25} silicene,²⁶ and phosphorene.^{27,28} However, in the experiment, there are only a few reports on monolayer superconductors. Superconductivity with T_c of 7.4 K was reported in the liquid gated MoS₂ thin flake.^{29,30} In such a system, the gate doped electrons are considered to be accumulated in the first layer, so the outermost layer can be seen as a free-standing monolayer superconductor. The monolayer FeSe grown on SrTiO₃ exhibits an interface enhanced superconductivity^{31–36} whose T_c is greater than 100 K.³⁶ In Li-adsorbed graphene, it seems that there is a potential superconducting gap found by angle resolved photoemission spectroscopy (ARPES) below 5.9 K.³⁷ However, more solid evidence of the intrinsic monolayer superconductors are still needed. The

reason why other predictions are still not verified might be the difficulty of the sample preparation. The pristine monolayer materials with intrinsic metallic states should be more promising to realize such superconductivity.

Very recently, borophene, the 2D monolayer boron, was experimentally prepared by different groups.^{38–40} Unlike the most reported monolayer materials mentioned above, borophene was not prepared by exfoliating the bulk layered materials, but was directly grown on some metal substrates. Different structures of borophene were reported by different groups (Ref. 38 reported the borophene with vacancy-free structure $x=0$; Ref. 40 reported two types of borophene with vacancy fraction $x=1/5$ and $1/6$), implying that the structures of borophene strongly depend on the preparation conditions. Remarkable properties such as anisotropic conductivity, negative Poisson's ratio, high Young's modulus in *a* direction potentially exceeding the value of graphene,³⁸ high sensibility of structure stability to the strain,⁴¹ and the potential anisotropic Dirac fermion in hydrogenated borophene⁴² were suggested in borophene, indicating the promising applications of the monolayer material. Considering the intrinsic metallic behavior with the high DOS at E_F ($N(E_F)$) verified by different reports,^{38,43,45} one can expect the possibility of superconductivity in this pristine monolayer material. Recently, Gao *et al.*⁴⁴ and Penev *et al.*⁴⁵ predicted the phonon-mediated superconductivity with T_c of 10–20 K for the experimentally reported structures. The borophene with vacancy-free structure was estimated to have the highest T_c compared with those with vacancy structures.⁴⁵

Here, we further demonstrate by first principles calculations that the superconductivity in the borophene with vacancy-free structure³⁸ could be significantly enhanced by strain and carrier doping. The tensile strain can increase the T_c to 27.4 K, while the hole doping can increase the T_c to 34.8 K, which are far above the liquid hydrogen temperature of 20.3 K. Our predictions suggest that the

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superconductivity in borophene grown on a substrate with large lattice parameters or under photoexcitation could be significantly enhanced, which will largely broaden the applications of such a promising material.

The calculations based on the density functional theory (DFT) were carried out using the QUANTUM-ESPRESSO package.⁴⁶ The ultrasoft pseudo-potentials⁴⁷ and the generalized gradient approximation (GGA) according to the Perdew-Wang 91 gradient-corrected functional⁴⁸ were used. To simulate the monolayer, a vacuum layer of 15 Å was used. The energy cutoff for the plane wave basis was set to 35 Ry. The Brillouin zone was sampled with a $32 \times 20 \times 1$ mesh of k -points. The Vanderbilt-Marzari Fermi smearing method with a smearing parameter of $\sigma = 0.02$ Ry was used for the calculations of the total energy and the electron charge density. The phonon dispersion and the electron-phonon coupling constants were calculated using the density functional perturbation theory (DFPT)⁴⁹ with a $16 \times 10 \times 1$ mesh of q -points. The double Fermi-surface averages of the electron-phonon matrix elements were calculated using $96 \times 96 \times 1$ k -points.

Our investigation starts from a hypothetical freestanding borophene. As shown in Fig. 1, borophene has a highly anisotropic crystal structure with a rectangular unit cell. There are corrugations along the b direction, while no pucker in the a direction is found. The fully optimized lattice parameters of freestanding borophene are $a = 1.611$ Å and $b = 2.872$ Å, which are smaller than the reported experimental values,³⁸ indicating the real lattice parameters are strongly dependent on the substrates.

Figure 2(a) shows the calculated band structure, which is in good agreement with the previous calculations.^{38,43,45} We denote the two bands crossing E_F as α and β bands, respectively. One can note that both these two bands do not cross E_F in the $\Gamma - Y$ and $S - X$ directions, which are parallel to the b direction, indicating the strong highly anisotropic electronic properties. Clearly, the out-of-plane corrugations along the b direction open a band gap along the $\Gamma - Y$ and $S - X$ directions. The two bands form the Fermi sheets symmetrical to $\Gamma - Y$ (Fig. 2(c)). The calculated DOS is shown in Fig. 2(b). The large $N(E_F)$ of 0.36 states/eV per unit cell indicates a good metallic behavior. A DOS peak locates at about 1 eV below E_F , indicating that hole doping should significantly increase $N(E_F)$.

Figure 3(a) shows the calculated phonon dispersion of borophene based on DFPT. We found the instability is very close to Γ , which was also reported by the previous

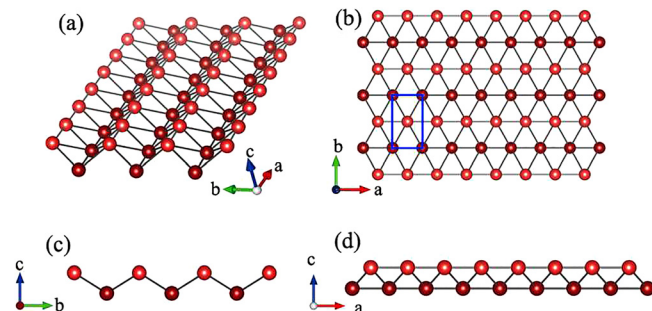


FIG. 1. Crystal structure of borophene. (a)–(d) The structure view from different directions. The unit cell is denoted with the blue rectangle in (b).

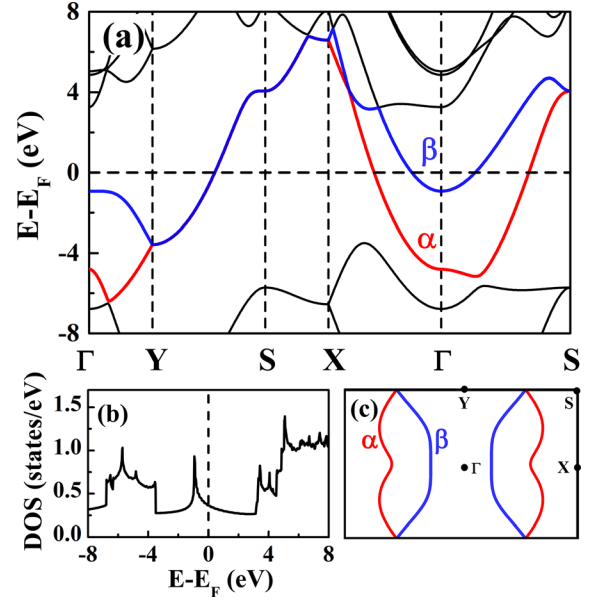


FIG. 2. Electronic properties of borophene: (a) band structure, (b) density of states, and (c) Fermi surfaces. The bands crossing E_F and their related Fermi surfaces are denoted as α (red color) and β (blue color).

calculations.^{38,41,43} Such instability is consistent with the instability against long-wavelength transversal waves, which is suggested to be fixed by defects, such as ripples or grain boundaries.³⁸ Besides, we found three notable softened acoustic modes (denoted with A, B, and C in Fig. 3(a)). The softened mode A close to X point was observed in the previous calculations.^{38,41,43,45} However, the mode B located at the approximate center of $\Gamma - X$ was absent in the previous calculations using the supercell method.^{38,41,43} The stability of the phonon modes we calculated permits us to estimate the electron-phonon coupling and the superconductivity in borophene accurately.

We decorate the calculated electron-phonon coupling strength at each mode (λ_{qv}) in phonon dispersion in Fig. 3(a), which is defined by

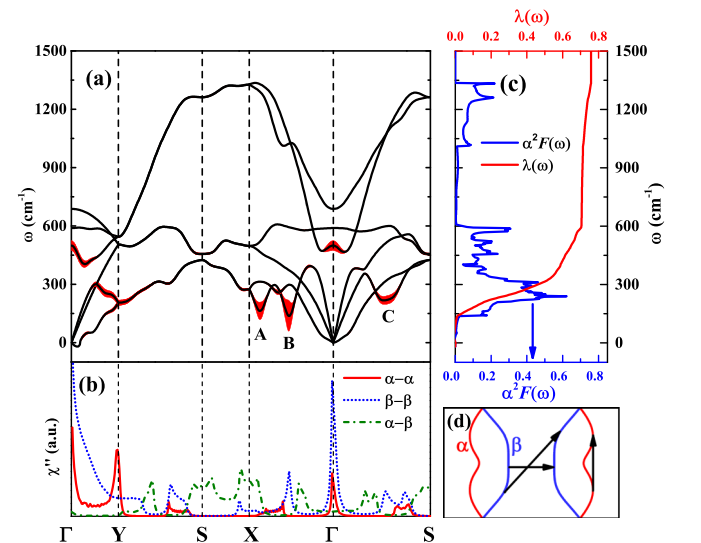


FIG. 3. (a) Phonon dispersion, (b) the imaginary part of the electron susceptibility χ'' , (c) Eliashberg function $\alpha^2 F(\omega)$ and integrated electron-phonon coupling strength λ , and (d) the possible nesting vectors of borophene. The phonon dispersion in (a) is decorated with red ribbons, proportional to the partial electron-phonon coupling strength λ_{qv} .

$$\lambda_{\mathbf{q}\nu} = \frac{\gamma_{\mathbf{q}\nu}}{\pi\hbar N(E_F)\omega_{\mathbf{q}\nu}^2}. \quad (1)$$

The phonon line width $\gamma_{\mathbf{q}\nu}$ is defined by

$$\gamma_{\mathbf{q}\nu} = 2\pi\omega_{\mathbf{q}\nu} \sum_{ij} \int \frac{d\mathbf{k}}{\Omega_{BZ}} |g_{\mathbf{q}\nu}(\mathbf{k}, i, j)|^2 \times \delta(\epsilon_{\mathbf{k},i} - E_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q},j} - E_F), \quad (2)$$

where $g_{\mathbf{q}\nu}(\mathbf{k}, i, j)$ is the electron-phonon coupling matrix element. Since Fermi surface nesting can be reflected by the imaginary part of electron susceptibility,

$$\chi''(\mathbf{q}) = \sum_{\mathbf{k}} \delta(\epsilon_{\mathbf{k}} - E_F) \delta(\epsilon_{\mathbf{k}+\mathbf{q}} - E_F). \quad (3)$$

According to such definitions (Eqs. (1)–(3)), the strong Fermi nesting will significantly enhance the electron-phonon coupling. As shown in Fig. 3(a), the softened modes A, B, and C predominately contribute to the electron-phonon coupling. At the locations of the modes B and C, there are sharp χ'' peaks of β - β band (Fig. 3(b)), indicating that the strong electron-phonon coupling is contributed by the nesting between the Fermi sheets formed by the band β - β , as shown in Fig. 3(d). On the other hand, at the location of the mode A, no substantial peak of χ'' can be found. Therefore, the electron-phonon coupling contributed by the mode A is mainly from the intrinsic large $g_{\mathbf{q}\nu}(\mathbf{k}, i, j)$. In addition, two acoustic modes around Y point also contribute to the sizeable electron-phonon coupling, which is due to the nesting formed by the band α - α (Figs. 3(b) and 3(d)). The contribution from the lowest optic mode around Γ is related to the intra-sheet nesting.

The total electron-phonon coupling constant λ can be obtained by

$$\lambda = \sum_{\mathbf{q}\nu} \lambda_{\mathbf{q}\nu} = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega, \quad (4)$$

where the Eliashberg spectral function is

$$\alpha^2 F(\omega) = \frac{1}{2\pi N(E_F)} \sum_{\mathbf{q}\nu} \delta(\omega - \omega_{\mathbf{q}\nu}) \frac{\gamma_{\mathbf{q}\nu}}{\hbar\omega_{\mathbf{q}\nu}}. \quad (5)$$

We plotted $\alpha^2 F(\omega)$ and integrated λ in Fig. 3(c). One can note that the large contribution of the electron-phonon coupling from modes A, B, C, and acoustic modes around Y point lead to a broaden peak from 100 cm^{-1} to 300 cm^{-1} . Such modes contribute about 70% of the total λ . The lowest optic mode around Γ leads to small peaks of $\alpha^2 F(\omega)$. We estimated the superconducting transition temperature T_c based on the Allen-Dynes-modified McMillan equation⁵⁰

$$T_c = \frac{\omega_{\log}}{1.2} \exp\left(-\frac{1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*}\right), \quad (6)$$

where the Coulomb pseudopotential μ^* is set to a typical value of 0.1.^{45,51} The logarithmically averaged characteristic phonon frequency $\omega_{\log}$ is defined as

$$\omega_{\log} = \exp\left(\frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \log \omega\right). \quad (7)$$

The calculated $\lambda = 0.79$ and $\omega_{\log} = 421.3$ K lead to $T_c = 19.0$ K. Such estimation indicates that borophene is a pristine monolayer superconductor, which coincides with the previous prediction.⁴⁵

Due to the Coulomb screening and strong bonding between FeSe and SrTiO_3 ,^{32,35} the monolayer FeSe grown on SrTiO_3 exhibits an interface enhanced superconductivity. However, if such bonding is weak, for example, in FeSe/graphene system, no enhanced superconductivity has been found.⁵² In the present system, the interaction between borophene and the substrate is very weak according to the experiments.^{38,40} Therefore, the substrate may have weak effects of Coulomb interaction and phonon coupling on borophene. Here, we considered only the strain effect on superconductivity introduced by the substrate. Therefore, we calculated the borophene under different strains to simulate the samples grown on the substrates with different lattice parameters. We found that borophene is stable under the strain range of $-2\% \leq \xi \leq 3\%$ (positive value means tensile strain, while negative value means compressive strain). Figure 4(a) shows the DOS of borophene under strain of -2% and $+3\%$. One can note that the tensile strain moves the DOS peak up toward E_F , while the compressive strain moves the DOS peak away from E_F . Figures 4(b) and 4(c) show the phonon dispersions of borophene under strain of -2% and $+3\%$, respectively. It can be found that the mode A is softened under compressive strain, while the modes B and C are hardened. On the other hand, the tensile strain hardens the mode A and significantly softens the modes B and C. We presented the variations of some superconductivity-related parameters in Figs. 4(d)–4(j). Generally speaking, the tensile strain enhances the electron-phonon coupling remarkably, and the compressive strain weakens electron-phonon coupling largely. The variation trend of λ coincides with that of $N(E_F)$, which is corresponding to the BCS theory.^{53–55} Moreover, according to Eq. (1), a mode with lower frequency will strongly contribute to the electron-phonon coupling. In the present case, the variation of electron-phonon coupling with strain is predominately contributed by the modes B and C, since the changes of the frequencies of such modes are more notable than those of mode A (Figs. 4(e)–4(g)). Figure 4(j) shows the estimations of T_c of borophene under different strains. According to the calculations, we can conclude that the substrates with larger lattice parameters will favor the superconductivity. For the sample under the tensile strain of 3%, for which the lattice parameters are very close to the reported experimental values,³⁸ T_c of 27.4 K is estimated, which is remarkably higher than the liquid hydrogen temperature of 20.3 K.

In the 2D monolayer systems, charge carrier doping is an easy way to control the electronic properties. Controls by using the gate-related methods to introduce electrons and using photoexcitation to dope holes are realized in many 2D systems.^{29,56–59} In the present case, since $N(E_F)$ is closely related to the electron-phonon coupling and can be easily tuned by the carrier-doping, which induces the change of E_F , we also investigated the carrier doping effects on borophene (Fig. 5). As expected, $N(E_F)$ decreases with the electron doping and increases with the hole doping (Figs. 5(a) and

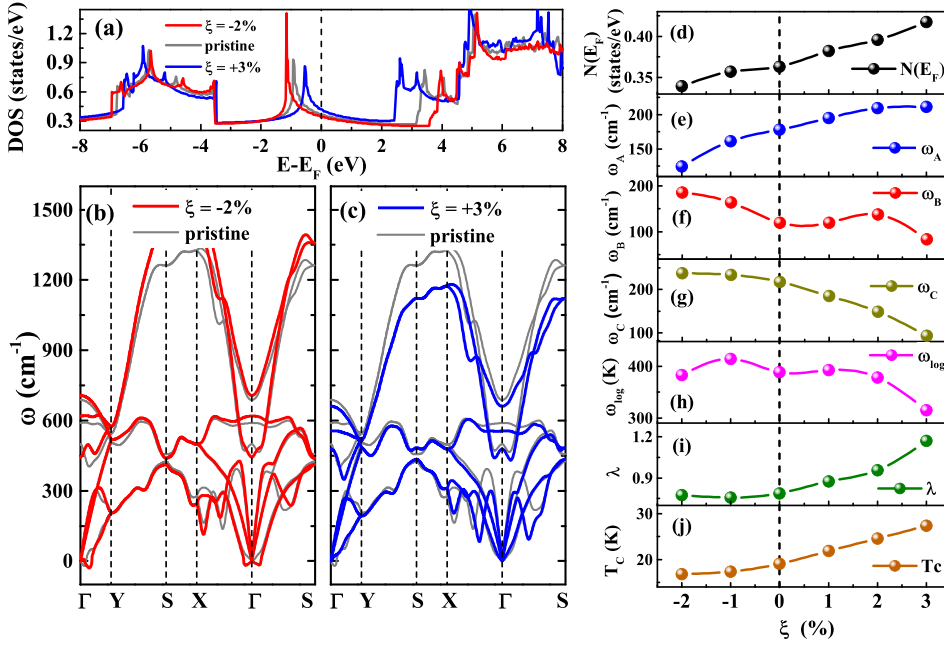


FIG. 4. (a) DOS of borophene under strain of -2% (red) and $+3\%$ (blue). DOS of the pristine freestanding borophene (grey) is presented for comparison. (b) and (c) are phonon dispersions of such samples, respectively. (d)–(j) show the strain effects on $N(E_F)$, ω_A , ω_B , ω_C , $\omega_{\log}$, λ , and T_c of borophene, respectively.

5(d)), since the carrier doping changes the distance between E_F and the DOS peak as mentioned above. However, unlike the strain effect, we found that the variation of λ is not the same as that of $N(E_F)$. As shown in Figs. 5(d) and 5(i), the hole doping increases $N(E_F)$ and λ . On the other hand, electron doping decreases $N(E_F)$ but increases λ , which can be understood from Figs. 5(e)–5(g): upon hole doping, the frequency of mode A changes slightly, while modes B and C are softened largely and mainly contribute to the increase of λ . On the contrary, upon electron doping, the frequencies of modes B and C slightly change, while mode A is significantly softened. Therefore, the electron doping increases λ and also decreases $\omega_{\log}$ remarkably (Figs. 5(h) and 5(i)). Therefore, from Fig. 5(j), we can conclude that the electron doping by an external gated electric field might be harmful for the superconductivity, while under photoexcitation, the

superconductivity of borophene can be significantly enhanced. With a low doping level of 0.1 hole/cell (equal to the doped hole density of $2.16 \times 10^{-14} \text{ cm}^{-2}$), the predicted T_c is as high as 34.8 K. Higher doping concentration will lead to phonon instability.

In conclusion, based on the first principles calculations, we demonstrate that the superconductivity in borophene with vacancy-free structure could be significantly enhanced by the tensile strain and hole doping. The intrinsic metallic ground state with high $N(E_F)$ and the strong Fermi surface nesting leads to the sizeable electron-phonon coupling, making the freestanding borophene superconduct with T_c of 19.0 K. The tensile strain can increase T_c to 27.4 K, while the hole doping can increase T_c to 34.8 K, which is far above the liquid hydrogen temperature of 20.3 K. Our predictions suggest that the superconductivity of borophene grown on a

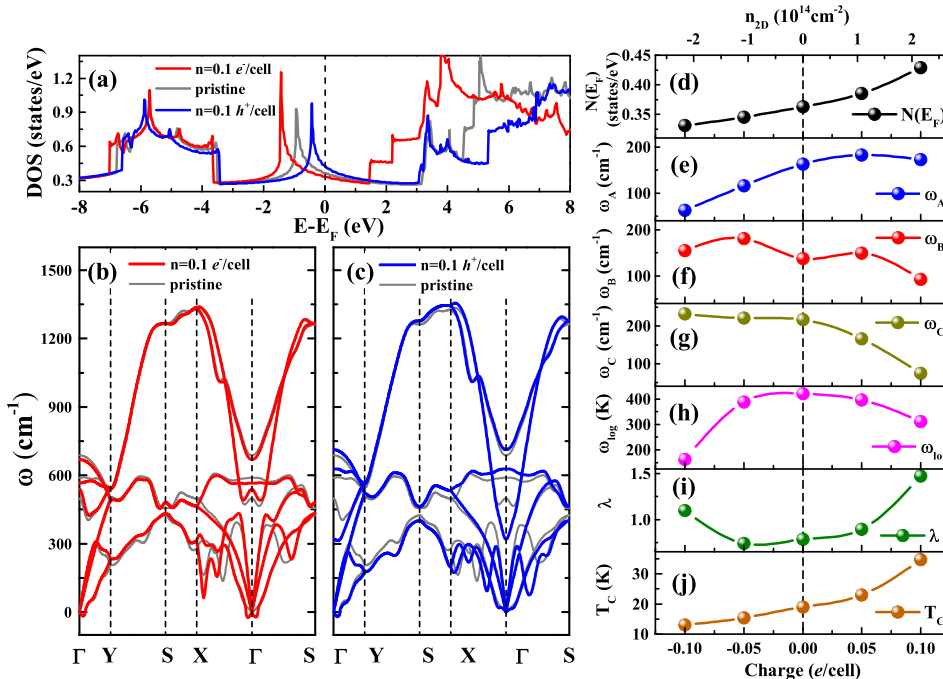


FIG. 5. (a) DOS of borophene doped by 0.1 electron (red) and 0.1 hole (blue). DOS of pristine freestanding borophene (grey) is presented for comparison. (b) and (c) are phonon dispersions of borophene of such samples, respectively. (d)–(j) show the carrier doping effects on $N(E_F)$, ω_A , ω_B , ω_C , $\omega_{\log}$, λ , and T_c of borophene, respectively.

substrate with large lattice parameters or under photoexcitation could be enhanced significantly, which will largely broaden the applications of such promising materials.

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- ¹K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666 (2004).
- ²K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature* **438**, 197 (2005).
- ³Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nat. Nanotechnol.* **7**, 699 (2012).
- ⁴A. Splendiani, L. Sun, Y. Zhang, T. Li, J. Kim, C.-Y. Chim, G. Galli, and F. Wang, *Nano Lett.* **10**, 1271 (2010).
- ⁵K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.* **105**, 136805 (2010).
- ⁶M. Corso, W. Auwärter, M. Muntwiler, A. Tamai, T. Greber, and J. Osterwalder, *Science* **303**, 217 (2004).
- ⁷D. Pacilé, J. C. Meyer, C. O. Girit, and A. Zettl, *Appl. Phys. Lett.* **92**, 133107 (2008).
- ⁸L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson *et al.*, *Nano Lett.* **10**, 3209 (2010).
- ⁹B. Aufray, A. Kara, S. Vizzini, H. Oughaddou, C. Léandri, B. Ealet, and G. Le Lay, *Appl. Phys. Lett.* **96**, 183102 (2010).
- ¹⁰B. Lalmi, H. Oughaddou, H. Enriquez, A. Kara, S. Vizzini, B. Ealet, and B. Aufray, *Appl. Phys. Lett.* **97**, 223109 (2010).
- ¹¹P. Vogt, P. De Padova, C. Quaresima, J. Avila, E. Frantzeskakis, M. C. Asensio, A. Resta, B. Ealet, and G. Le Lay, *Phys. Rev. Lett.* **108**, 155501 (2012).
- ¹²W. Lu, H. Nan, J. Hong, Y. Chen, C. Zhu, Z. Liang, X. Ma, Z. Ni, C. Jin, and Z. Zhang, *Nano Res.* **7**, 853 (2014).
- ¹³L. Li, Y. Yu, G. J. Ye, Q. Ge, X. Ou, H. Wu, D. Feng, X. H. Chen, and Y. Zhang, *Nat. Nanotechnol.* **9**, 372 (2014).
- ¹⁴S. De Franceschi, L. Kouwenhoven, C. Schönenberger, and W. Wernsdorfer, *Nat. Nanotechnol.* **5**, 703 (2010).
- ¹⁵J. Delahaye, J. Hassel, R. Lindell, M. Sillanpää, M. Paalanen, H. Seppä, and P. Hakonen, *Science* **299**, 1045 (2003).
- ¹⁶E. J. Romans, E. J. Osley, L. Young, P. A. Warburton, and W. Li, *Appl. Phys. Lett.* **97**, 222506 (2010).
- ¹⁷O. P. Saira, M. Meschke, F. Giazotto, A. M. Savin, M. Möttönen, and J. P. Pekola, *Phys. Rev. Lett.* **99**, 027203 (2007).
- ¹⁸M. Huefner, C. May, S. Kičín, K. Ensslin, T. Ihn, M. Hilke, K. Suter, N. F. de Rooij, and U. Staufer, *Phys. Rev. B* **79**, 134530 (2009).
- ¹⁹R. A. Klemm, *Layered Superconductors* (Oxford, U.K., 2012), Vol. 1.
- ²⁰G. Profeta, M. Calandra, and F. Mauri, *Nat. Phys.* **8**, 131 (2012).
- ²¹D. M. Guzman, H. M. Alyahyaci, and R. A. Jishi, *2D Mater.* **1**, 021005 (2014).
- ²²G. Savini, A. C. Ferrari, and F. Giustino, *Phys. Rev. Lett.* **105**, 037002 (2010).
- ²³C. Si, Z. Liu, W. Duan, and F. Liu, *Phys. Rev. Lett.* **111**, 196802 (2013).
- ²⁴Y. Ge and A. Y. Liu, *Phys. Rev. B* **87**, 241408 (2013).
- ²⁵M. Rösner, S. Haas, and T. O. Wehling, *Phys. Rev. B* **90**, 245105 (2014).
- ²⁶W. Wan, Y. Ge, F. Yang, and Y. Yao, *Europhys. Lett.* **104**, 36001 (2013).
- ²⁷D. F. Shao, W. J. Lu, H. Y. Lv, and Y. P. Sun, *Europhys. Lett.* **108**, 67004 (2014).
- ²⁸Y. Ge, W. Wan, F. Yang, and Y. Yao, *New J. Phys.* **17**, 035008 (2015).
- ²⁹J. T. Ye, Y. J. Zhang, R. Akashi, M. S. Bahramy, R. Arita, and Y. Iwasa, *Science* **338**, 1193 (2012).
- ³⁰J. M. Lu, O. Zheliuk, I. Leermakers, N. F. Q. Yuan, U. Zeitler, K. T. Law, and J. T. Ye, *Science* **350**, 1353 (2015).
- ³¹Q. Y. Wang, Z. Li, W. H. Zhang, Z. C. Zhang, J. S. Zhang, W. Li, H. Ding, Y. B. Ou, P. Deng, K. Chang *et al.*, *Chin. Phys. Lett.* **29**, 037402 (2012).
- ³²Y. Y. Xiang, F. Wang, D. Wang, Q. H. Wang, and D. H. Lee, *Phys. Rev. B* **86**, 134508 (2012).
- ³³S. He, J. He, W. Zhang, L. Zhao, D. Liu, X. Liu, D. Mou, Y. B. Ou, Q. Y. Wang, Z. Li *et al.*, *Nat. Mater.* **12**, 605 (2013).
- ³⁴W. H. Zhang, Y. Sun, J. S. Zhang, F. S. Li, M. H. Guo, Y. F. Zhao, H. M. Zhang, J. P. Peng, Y. Xing, H. C. Wang *et al.*, *Chin. Phys. Lett.* **31**, 017401 (2014).
- ³⁵J. J. Lee, F. T. Schmitt, R. G. Moore, S. Johnston, Y. T. Cui, W. Li, M. Yi, Z. K. Liu, M. Hashimoto, Y. Zhang *et al.*, *Nature* **515**, 245 (2014).
- ³⁶J. F. Ge, Z. L. Liu, C. Liu, C. L. Gao, D. Qian, Q. K. Xue, Y. Liu, and J. F. Jia, *Nat. Mater.* **14**, 285 (2015).
- ³⁷B. M. Ludbrook, G. Levy, P. Nigge, M. Zonno, M. Schneider, D. J. Dvorak, C. N. Veenstra, S. Zhdanovich, D. Wong, P. Dosanjh *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **112**, 11795 (2015).
- ³⁸A. J. Mannix, X. F. Zhou, B. Kiraly, J. D. Wood, D. Alducin, B. D. Myers, X. Liu, B. L. Fisher, U. Santiago, J. R. Guest *et al.*, *Science* **350**, 1513 (2015).
- ³⁹H. Sachdev, *Science* **350**, 1468 (2015).
- ⁴⁰B. Feng, J. Zhang, Q. Zhong, W. Li, S. Li, H. Li, P. Cheng, S. Meng, L. Chen, and K. Wu, *Nat. Chem.* **8**, 563 (2016).
- ⁴¹H. Wang, Q. Li, Y. Gao, F. Miao, X. F. Zhou, and X. G. Wan, *New J. Phys.* **18**, 073016 (2016).
- ⁴²L. C. Xu, A. Du, and L. Kou, e-print [arXiv:1602.03620](https://arxiv.org/abs/1602.03620).
- ⁴³B. Peng, H. Zhang, H. Shao, Y. Xu, R. Zhang, and H. Zhu, e-print [arXiv:1601.00140](https://arxiv.org/abs/1601.00140).
- ⁴⁴M. Gao, Q. Z. Li, X. W. Yan, and J. Wang, e-print [arXiv:1602.02930](https://arxiv.org/abs/1602.02930).
- ⁴⁵E. S. Penev, A. Kutana, and B. I. Yakobson, *Nano Lett.* **16**, 2522 (2016).
- ⁴⁶P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo *et al.*, *J. Phys.: Condens. Matter* **21**, 395502 (2009).
- ⁴⁷D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
- ⁴⁸J. P. Perdrew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiola, *Phys. Rev. B* **46**, 6671 (1992).
- ⁴⁹S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- ⁵⁰P. B. Allen and R. C. Dynes, *Phys. Rev. B* **12**, 905 (1975).
- ⁵¹M. Calandra and F. Mauri, *Phys. Rev. Lett.* **106**, 196406 (2011).
- ⁵²C. L. Song, Y. L. Wang, P. Cheng, Y. P. Jiang, W. Li, T. Zhang, Z. Li, K. He, L. Wang, J. F. Jia *et al.*, *Science* **332**, 1410 (2011).
- ⁵³J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **106**, 162 (1957).
- ⁵⁴J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
- ⁵⁵L. N. Cooper, *Phys. Rev.* **104**, 1189 (1956).
- ⁵⁶J. Biscaras, Z. Chen, A. Paradisi, and A. Shukla, *Nat. Commun.* **6**, 8826 (2015).
- ⁵⁷I. Vaskivskyi, J. Gospodarc, S. Brazovskii, D. Svetin, P. Sutar, E. Goreschnik, I. A. Mihailovic, T. Mertelj, and D. Mihailovic, *Sci. Adv.* **1**, e1500168 (2015).
- ⁵⁸D. F. Shao, R. C. Xiao, W. J. Lu, H. Y. Lv, J. Y. Li, X. B. Zhu, and Y. P. Sun, *Phys. Rev. B* **94**, 125126 (2016).
- ⁵⁹L. Stojchevska, I. Vaskivskyi, T. Mertelj, P. Kusar, D. Svetin, S. Brazovskii, and D. Mihailovic, *Science* **344**, 177 (2014).