

Multigap anisotropic superconductivity in borophenes

Yinchang Zhao,^{1,*} Shuming Zeng,² Chao Lian,³ Zhenhong Dai,^{1,†} Sheng Meng,^{3,4,‡} and Jun Ni^{2,4,§}

¹*Department of Physics, Yantai University, Yantai 264005, People's Republic of China*

²*State Key Laboratory of Low-Dimensional Quantum Physics, Department of Physics, Tsinghua University, Beijing 100084, People's Republic of China*

³*Beijing National Laboratory for Condensed Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*

⁴*Collaborative Innovation Center of Quantum Matter, Beijing 100084, People's Republic of China*



(Received 29 July 2018; revised manuscript received 10 October 2018; published 26 October 2018)

We use *ab initio* anisotropic Migdal-Eliashberg formalism to examine the pairing mechanism and the nature of the superconducting gaps in experimentally fabricated borophenes. Our results indicate that the superconducting transition is dominated by a standard phonon-mediated mechanism, and multiple anisotropic superconducting gaps with critical temperatures T_c even approaching 33 K are present in the freestanding form of the fabricated borophenes. These findings provide a different perspective for superconductivity in borophenes.

DOI: [10.1103/PhysRevB.98.134514](https://doi.org/10.1103/PhysRevB.98.134514)

I. INTRODUCTION

With the fabrication of borophenes (boron monolayers) on the Ag(111) surfaces [1,2], many interesting features such as a negative Poisson's ratio [3], high lithium-storage capacity [4], antiferromagnetism [5], Dirac-cone and double-Dirac-cone dispersions [6,7], anisotropic electronic and thermal conductivities [8,9], etc., have been extensively studied in borophenes. At the same time, the phonon-mediated superconductivity in borophenes and borophene-based monolayers has also attracted great interest due to the presence of strong electron-phonon interaction (EPI) [10–16]. For instance, the freestanding forms of the experimentally observed δ_6 , χ_3 , and β_{12} borophenes have been predicted based on the Allen-Dynes theory to hold the superconducting critical temperature T_c close to the liquid-hydrogen temperature [10–13]. Moreover, the EPI and T_c in the freestanding δ_6 and β_{12} borophenes can be further enhanced by the modulation of external strain and/or carrier doping [14,15]. The Fermi surfaces (FSs) in δ_6 , χ_3 , and β_{12} borophenes are mainly formed by the $s + p_{x,y}$ orbitals (σ bond) and p_z orbitals (π bond), and thus, the strong EPI results from the coupling between phonons and the σ and π electrons around the Fermi level [10–15], resembling the coupling characteristics in MgB_2 [17,18]. Besides the formation of FSs from multiple bonds, the electronic behavior in δ_6 , χ_3 , and β_{12} borophenes also exhibits an apparent anisotropy [1,2,8–15] which is comparable to the electronic structure of MgB_2 [17,18]. Enlightened by the strong anisotropy of EPI and multiple superconducting gaps in MgB_2 , the similarity of the electronic structures and coupling characteristics in borophenes to those in MgB_2 hints

that the isotropic EPI used for the Allen-Dynes formula in previous works may not be enough to reveal the superconducting properties in borophenes, especially the nature of the superconducting gaps. Furthermore, to date, the study of the nature of the superconducting gaps in borophenes has not yet been addressed.

In this paper, we investigate from first principles the pairing mechanism and the nature of the superconducting gaps in the freestanding forms of the experimentally observed δ_6 , χ_3 , and β_{12} borophenes. To this end, the fully anisotropic Migdal-Eliashberg equations [19] are solved to obtain the critical temperatures T_c and the variations of the EPI and superconducting gaps on the Fermi surfaces. Strong anisotropy of the EPI and multiple anisotropic superconducting gaps with T_c even approaching 33 K are captured, while previous *ab initio* results have shown that the isotropic EPI produces a T_c in the range of 12.0–25.6 K through the Allen-Dynes formula [10–15]. Our findings give a different perspective on superconductivity in borophenes.

II. METHODS

The calculations are carried out within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [20] to the density-functional theory using plane waves and norm-conserving pseudopotentials [21,22], as coded in the QUANTUM ESPRESSO package [23]. The plane-wave kinetic energy cutoff and charge density cutoff are chosen to be 90 and 360 Ry, respectively, and the structures are fully optimized until the force on each atom is less than 10^{-6} Ry/bohr. For simulations of the Brillouin-zone (BZ) integrations, the $40 \times 72 \times 1$, $48 \times 48 \times 1$, and $60 \times 40 \times 1$ $\mathbf{k}$ -point meshes with Marzari-Vanderbilt smearing [24] of 0.02 Ry are used to calculate the self-consistent electron densities of δ_6 , χ_3 , and β_{12} borophenes. The subsequent phonon modes are computed based on density-functional perturbation theory [25] within the $20 \times 36 \times 1$, $12 \times 12 \times 1$, and $12 \times 8 \times 1$

*y.zhao@ytu.edu.cn

†zh dai@ytu.edu.cn

‡smeng@iphy.ac.cn

§junni@mail.tsinghua.edu.cn

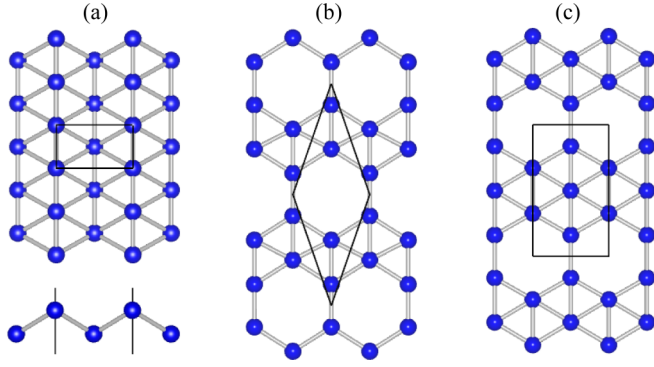


FIG. 1. Atomic structures of (a) δ_6 , (b) χ_3 , and (c) β_{12} borophenes. The lateral view of the δ_6 borophene is also shown in the lower image in (a).

$\mathbf{q}$ meshes, respectively. We employ the EPW code [26–29] to calculate the superconducting gaps and critical temperatures T_c . To obtain the electronic wave functions required for the Wannier-Fourier interpolations [30] in EPW, non-self-consistent calculations are performed within the same meshes of the BZ as those used in the above phonon calculations. For the anisotropic Migdal-Eliashberg equations, the $200 \times 360 \times 1$, $240 \times 240 \times 1$, and $240 \times 160 \times 1$ interpolated $\mathbf{k}$ - and $\mathbf{q}$ -point grids are utilized in δ_6 , χ_3 , and β_{12} borophenes, respectively. These grids are much denser than those used in the calculations for superconducting gaps in MgB_2 and Li-decorated graphene [19,31] and thus ensure the convergence of the superconducting gaps in δ_6 , χ_3 , and β_{12} borophenes (see Fig. S1 in Ref. [32]). In addition, the same value of Coulomb pseudopotential $\mu_c^* = 0.10$ as that used in the previous works [11–14] is selected to estimate the superconducting gaps and T_c for comparison.

III. RESULTS AND DISCUSSION

The atomic structures of the freestanding forms of the three borophenes observed in experiment are shown in Fig. 1. The structure of δ_6 borophene is formed by triangular motifs with an out-of-plane buckling of 0.88 Å, while χ_3 and β_{12} borophenes are planar structures without buckling. The vacancy concentration η , which represents the ratio between the number of vacancy sites and number of total sites (including vacancy) in each unit cell, is zero for δ_6 borophene, 1/5 for χ_3 borophene, and 1/6 for β_{12} borophene. The optimized lattice constants along the a and b axes for δ_6 (β_{12}) borophene are 2.86 (2.92) and 1.61 (5.05) Å, respectively, and the cell parameter of χ_3 borophene is 4.43 Å, with an acute angle of 38.18° in the rhombic primitive cell. These results are consistent with those in previous works [1,2,12–14].

The band structures and FSs for δ_6 , χ_3 , and β_{12} borophenes are plotted in Fig. 2, in which the projection of the electron linewidth Σ'' on the bands is also shown. The band structures manifest metallicity clearly for these borophenes, in good agreement with the results in the literature [2,10–14]. There are two bands for δ_6 and χ_3 borophenes and three bands for β_{12} borophene crossing the Fermi level. The electronic states on the red and blue sections of the FSs, as indicated in Fig. 2, are mainly composed of $s + p_{x,y}$ orbitals (σ bond) and

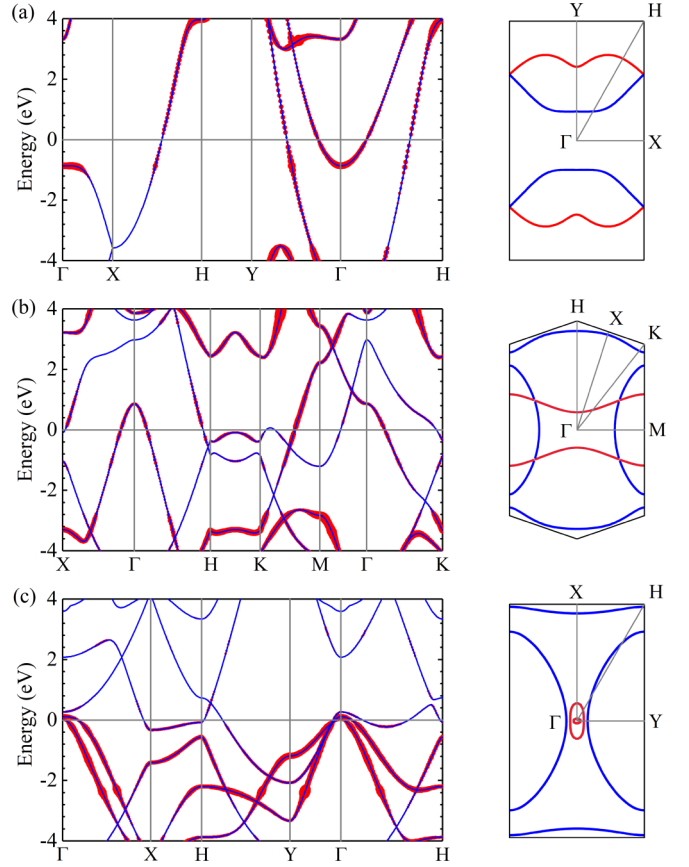


FIG. 2. Band structures with the projection of electron linewidth Σ'' (left) and Fermi surfaces (right) of (a) δ_6 , (b) χ_3 , and (c) β_{12} borophenes.

p_z orbitals (π bond), respectively, according to the previous calculations [10,13]. The electron linewidth Σ'' [26], which is inversely proportional to the electron lifetime and can be taken as an indicator of the EPI strength [29,33], has a large projection on the bands around the Fermi level, as shown in Fig. 2, signifying a strong EPI in these borophenes.

We now focus on the phonon frequency dispersions and EPI strengths in δ_6 , χ_3 , and β_{12} borophenes. The isotropic Eliashberg spectral function

$$\alpha^2 F(\omega) = \frac{1}{N_F N_{\mathbf{k}} N_{\mathbf{q}}} \sum_{n\mathbf{k}, m\mathbf{k}', \nu} |g_{n\mathbf{k}, m\mathbf{k}'}^{\nu}|^2 \times \delta(\epsilon_{n\mathbf{k}}) \delta(\epsilon_{m\mathbf{k}'}) \delta(\omega - \omega_{\mathbf{q}\nu}) \quad (1)$$

and the cumulative EPI strength

$$\lambda(\omega) = 2 \int_0^{\omega} d\omega' \frac{\alpha^2 F(\omega')}{\omega'} \quad (2)$$

are used to investigate the frequency-dependent and total EPI strengths, where N_F is the density of states per spin at the Fermi level, $N_{\mathbf{k}}$ ($N_{\mathbf{q}}$) is the total number of $\mathbf{k}$ ($\mathbf{q}$) points, $\epsilon_{n\mathbf{k}}$ is the energy eigenvalue of the Kohn-Sham state $|n\mathbf{k}\rangle$ relative to the Fermi level, and $g_{n\mathbf{k}, m\mathbf{k}'}^{\nu}$ represents the electron-phonon matrix element for the scattering between the electronic states $|n\mathbf{k}\rangle$ and $|m\mathbf{k}'\rangle$ through the phonon mode $|\mathbf{q}\nu\rangle$ with the wave vector $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ and frequency $\omega_{\mathbf{q}\nu}$. The phonon dispersion

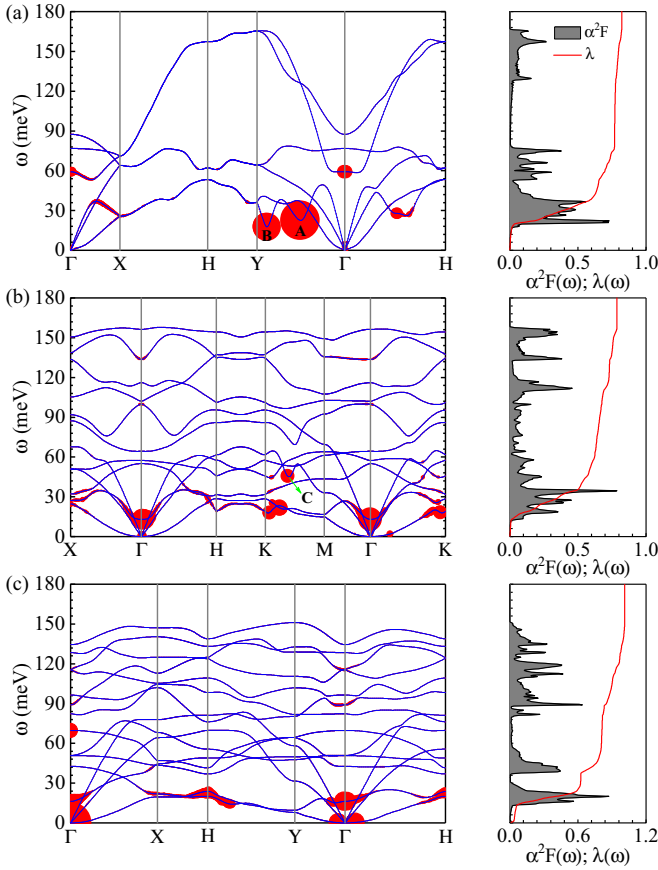


FIG. 3. Phonon dispersions with the projections of the EPI matrix element $\lambda_{\mathbf{q}\nu}$ (left) and Eliashberg spectral functions $\alpha^2 F(\omega)$ with the cumulative EPI strength $\lambda(\omega)$ (right) of (a) δ_6 , (b) χ_3 , and (c) β_{12} borophenes.

with the projections of the EPI matrix element $\lambda_{\mathbf{q}\nu}$ and the Eliashberg spectral function $\alpha^2 F(\omega)$ with the cumulative EPI strength $\lambda(\omega)$ are shown in Fig. 3. We find that the low-energy phonon modes are key to achieving a high EPI in these borophenes. For δ_6 borophene, the phonon modes with energy below 50 meV provide the main EPI, which accounts for about 80% of the total EPI. The EPI projection on the phonon spectrum indicates that the softest modes around the A and B points labeled in Fig. 3(a) cause the strongest EPI, giving rise to the maximum peak of the Eliashberg spectral function. For χ_3 and β_{12} borophenes, about 78% of the total EPI is induced by the phonons with energy lower than 60 meV. The low-energy modes close to the HK and KM lines for χ_3 borophene and the XH and HY lines for β_{12} borophene and the softest optical modes around the Γ points for both of them have conspicuously large EPI projection, resulting in the maximum peaks of the Eliashberg spectral function in χ_3 and β_{12} borophenes. Overall, our calculated total EPI strengths $\lambda = 0.82, 0.79$, and 1.01 for δ_6 , χ_3 , and β_{12} borophenes, respectively, are comparable to previous results [10–15].

Noticeably, our calculations show that the softest phonon modes around the A and B points for δ_6 borophene have no imaginary frequency captured, as shown in Fig. 3(a), which agrees well with the computational results in the literature [1,3,8,10,13,14,34,35]. However, conspicuous imaginary

frequencies were detected at the two points for δ_6 borophene based on the calculations in Ref. [11], which means a possible structural instability. Because the strongest EPI occurred around these points, the appearance of negative frequencies indicates that the δ_6 phase may be unstable against a charge density wave (CDW) transition. If the system somehow manages to stabilize via a transition to a CDW phase, it is unclear whether superconductivity survives or not due to the competition with the CDW. Thus, to clarify this issue, we recalculate the phonon dispersion of δ_6 borophene by using the same parameters as in Ref. [11] and find that no imaginary frequency appears around the A and B points and the phonon dispersions along the ΓY line are very consistent with those in the literature [1,3,8,10,13,14,34,35], as shown in Fig. S2 in Ref. [32]. Similar to the results in Refs. [8,12,13], our calculation also shows a phonon softening but without imaginary frequency near the C point for χ_3 borophene, as shown in Fig. 3(b), in contrast to the negative frequency claimed at this point in Ref. [11].

In addition, there is also no imaginary frequency around the Γ points in δ_6 , χ_3 , and β_{12} borophenes based on our calculations, as shown in Fig. 3, while Refs. [11,12,14] exhibit small imaginary frequencies around the Γ points, which are attributed to the numerical difficulties in accurate calculation of the rapidly decaying interatomic forces and can be eliminated by a small tensile strain according to the analyses therein. Although the small imaginary frequencies around the Γ points have no influence on the calculated superconducting properties [11,12], we find after a detailed test that the small imaginary frequencies around the Γ point for χ_3 and β_{12} borophenes can be removed by using the exchange-correlation functional of the GGA-PBE combined with a large kinetic energy cutoff (e.g., 90 Ry in the present work) if a norm-conserving pseudopotential is chosen, in contrast to the local-density approximation (GGA-PBE) exchange-correlation functional with a kinetic energy cutoff of 70 Ry used in Ref. [11] (Ref. [12]). For δ_6 borophene, our present parameters are also enough to produce a convergent phonon dispersion without imaginary frequency around the Γ point, different from the result in Ref. [14], where a kinetic energy cutoff of 35 Ry together with the ultrasoft pseudopotential was used. In fact, it has been checked that a kinetic energy cutoff of 55 Ry is required to obtain a convergent phonon dispersion if one uses the ultrasoft pseudopotential, as shown in Fig. 1 in the Supplemental Material in Ref. [10].

To observe the anisotropy in the EPI, we study the momentum-resolved EPI parameter $\lambda_{\mathbf{n}\mathbf{k}}$, which is written as

$$\lambda_{\mathbf{n}\mathbf{k}} = \sum_{\mathbf{m}\mathbf{k}',\nu} \frac{1}{\omega_{\mathbf{q}\nu}} \delta(\epsilon_{\mathbf{m}\mathbf{k}'}) |g_{\mathbf{n}\mathbf{k},\mathbf{m}\mathbf{k}'}^{\nu}|^2. \quad (3)$$

The variation of the EPI parameter $\lambda_{\mathbf{n}\mathbf{k}}$ on the FS is shown in Figs. 4(a)–4(c). Compared with the FS plotted in Fig. 2, one can see that the electronic states on the blue section of the FS (π bond) in δ_6 borophene and the states on the red section of the FS (σ bond) in χ_3 and β_{12} borophenes remain relatively strong EPI. Obviously, due to the additive effect, the crossing points between different bands on FS have the largest $\lambda_{\mathbf{n}\mathbf{k}}$. In addition, it is noteworthy that the $\lambda_{\mathbf{n}\mathbf{k}}$ data points used in the plots correspond to electrons within ± 0.2 eV from the Fermi

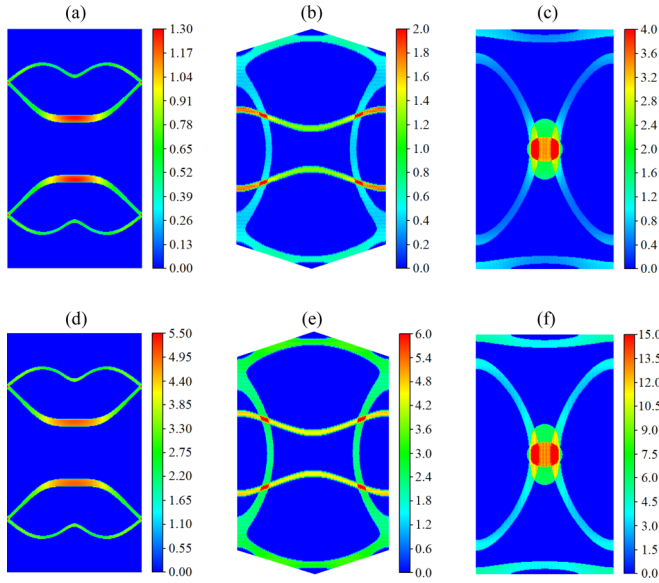


FIG. 4. (a)–(c) Momentum-resolved EPI parameters $\lambda_{n\mathbf{k}}$ on the FS for δ_6 , χ_3 , and β_{12} borophenes, respectively. (d)–(f) Momentum-resolved superconducting gaps $\Delta_{n\mathbf{k}}(\omega=0)$ (in meV) at 6 K on the FS for δ_6 , χ_3 , and β_{12} borophenes, respectively. The $\lambda_{n\mathbf{k}}$ and $\Delta_{n\mathbf{k}}(\omega=0)$ data points correspond to the states within ± 0.2 eV from the Fermi level.

level, which makes $\lambda_{n\mathbf{k}}$ of different bands near the Γ point in β_{12} borophene overlap, and thus, the additive effect is also found in this borophene, although there is no band crossing on the FS.

The superconducting properties of δ_6 , χ_3 , and β_{12} borophenes are obtained from the self-consistent solution of the fully anisotropic Migdal-Eliashberg equations on the imaginary axis at the fermion Matsubara frequencies $\omega_j = (2j+1)\pi T$ (with j being an integer) for each temperature T according to [19,29]

$$Z_{n\mathbf{k}}(i\omega_j) = 1 + \frac{\pi T}{N_F \omega_j} \sum_{m\mathbf{k}'j'} \frac{\omega_{j'}}{\sqrt{\omega_{j'}^2 + \Delta_{m\mathbf{k}'}^2(i\omega_{j'})}} \times \delta(\epsilon_{m\mathbf{k}'})\lambda(n\mathbf{k}, m\mathbf{k}', \omega_j - \omega_{j'}), \quad (4)$$

$$Z_{n\mathbf{k}}(i\omega_j)\Delta_{n\mathbf{k}}(i\omega_j) = \frac{\pi T}{N_F} \sum_{m\mathbf{k}'j'} \frac{\Delta_{m\mathbf{k}'}(i\omega_{j'})}{\sqrt{\omega_{j'}^2 + \Delta_{m\mathbf{k}'}^2(i\omega_{j'})}} \times \delta(\epsilon_{m\mathbf{k}'})[\lambda(n\mathbf{k}, m\mathbf{k}', \omega_j - \omega_{j'}) - \mu_c^*], \quad (5)$$

where $Z_{n\mathbf{k}}(i\omega_j)$ is the mass renormalization function, $\Delta_{n\mathbf{k}}(i\omega_j)$ is the superconducting gap function, and

$$\lambda(n\mathbf{k}, m\mathbf{k}', \omega_j - \omega_{j'}) = N_F \sum_v \frac{2\omega_{qv}}{(\omega_j - \omega_{j'})^2 + \omega_{qv}^2} \times |g_{n\mathbf{k}, m\mathbf{k}'}^v|^2 \quad (6)$$

represents the anisotropic EPI parameter dependent on momentum and energy. The calculated superconducting gaps $\Delta_{n\mathbf{k}}(i\omega_j)$ at 6, 16, and 22 K along the imaginary axis using the anisotropic Migdal-Eliashberg equations (4) and (5)

and a Coulomb pseudopotential of $\mu_c^* = 0.10$ are shown in Figs. 5(a)–5(c). As temperature T rises, the solutions along the imaginary axis become more spaced out, which is a consequence of the fact that the Matsubara frequencies are given by $\omega_j = (2j+1)\pi T$, where a high T means a large frequency space of $2\pi T$. The Matsubara frequency cutoff in the Migdal-Eliashberg equations is set to be 1.0 eV, and thus, different numbers of frequency points are used for different temperatures. Obviously, the superconducting gap function along the imaginary axis is purely real and displays a downtrend with increasing frequency. The distributions of the superconducting gaps $\Delta_{n\mathbf{k}}(\omega=0)$ as a function of temperature T with $\mu_c^* = 0.10$ are shown in Figs. 5(d)–5(f). A two-gap superconducting nature of χ_3 and β_{12} borophenes can be found, while a single gap is obtained in δ_6 borophene. Meanwhile, the anisotropy of the gaps is clearly distinguished in these borophenes. The variation of the gaps $\Delta_{n\mathbf{k}}(\omega=0)$ at 6 K on the FS is shown in Figs. 4(d)–4(f), which is similar to the distribution of $\lambda_{n\mathbf{k}}$ on FSs and further verifies the anisotropy of the superconducting gaps.

For δ_6 borophene, the blue bands on the FS (π bond) have a relatively high superconducting gap that lies in the range of 2.6–5.3 meV with an average value of about 4.8 meV at 6 K, while the gap on the red FS bands (σ bond) is 2.6–3.6 meV, with 3.4 meV being the average value at the same temperature. This finding is in sharp contrast to the gap nature in MgB_2 , where the σ bond of the boron layers dominates the EPI and superconductivity [18]. This can be explained by the fact that the π bond has strong coupling with both in-plane and out-of-plane phonon vibrations in δ_6 borophene due to the out-of-plane buckling structure. Because of the hybridization between the σ - and π -bond-induced gaps, an anisotropic single gap with an average value of about 4.0 meV at 6 K is finally present in δ_6 borophene, as shown in Figs. 5(a) and 5(d). The highest temperature at which the gap vanishes is the critical temperature T_c . In δ_6 borophene, we find a significantly enhanced $T_c \approx 27.0$ K compared with the values of 19.7 and 14.0 K in Refs. [12,13] and a ratio $2\Delta_0/k_B T_c = 3.52$, with $\Delta_0 = 4.1$ meV as the average gap at 0 K, nearly identical to the ideal BCS value of 3.53 [36], supporting the theory that a standard phonon-mediated mechanism is the superconducting origin.

Different from the case for δ_6 borophene, the red bands on the FS (σ bond) in χ_3 borophene possess a higher superconducting gap, which is in the range of 4.8–5.2 meV, with an average value of about 5.0 meV at 6 K. Meanwhile, the gap arising from the blue FS states (π bond) lies between 2.4 and 3.7 meV, with an average value of about 3.3 meV at the same temperature. As a result, a two-gap anisotropic superconducting nature is clearly distinguished in χ_3 borophene, as shown in Figs. 5(b) and 5(e), which is very analogous to that in MgB_2 , where the electron states on the FS arising from the σ bonds of the honeycomb boron layers gave a much higher superconducting gap than the gap induced by the π electrons of the boron layers [18]. As shown in Fig. 5(e), the calculated critical temperature T_c in χ_3 borophene is about 26.2 K, higher than the values of 12.0, 12.1, and 24.7 K in Refs. [11–13].

Similarly, the red FS state (σ bond) in β_{12} borophene has a higher superconducting gap within a range of 6.0–6.5 meV at 6 K. However, the gap originating from the blue FS states

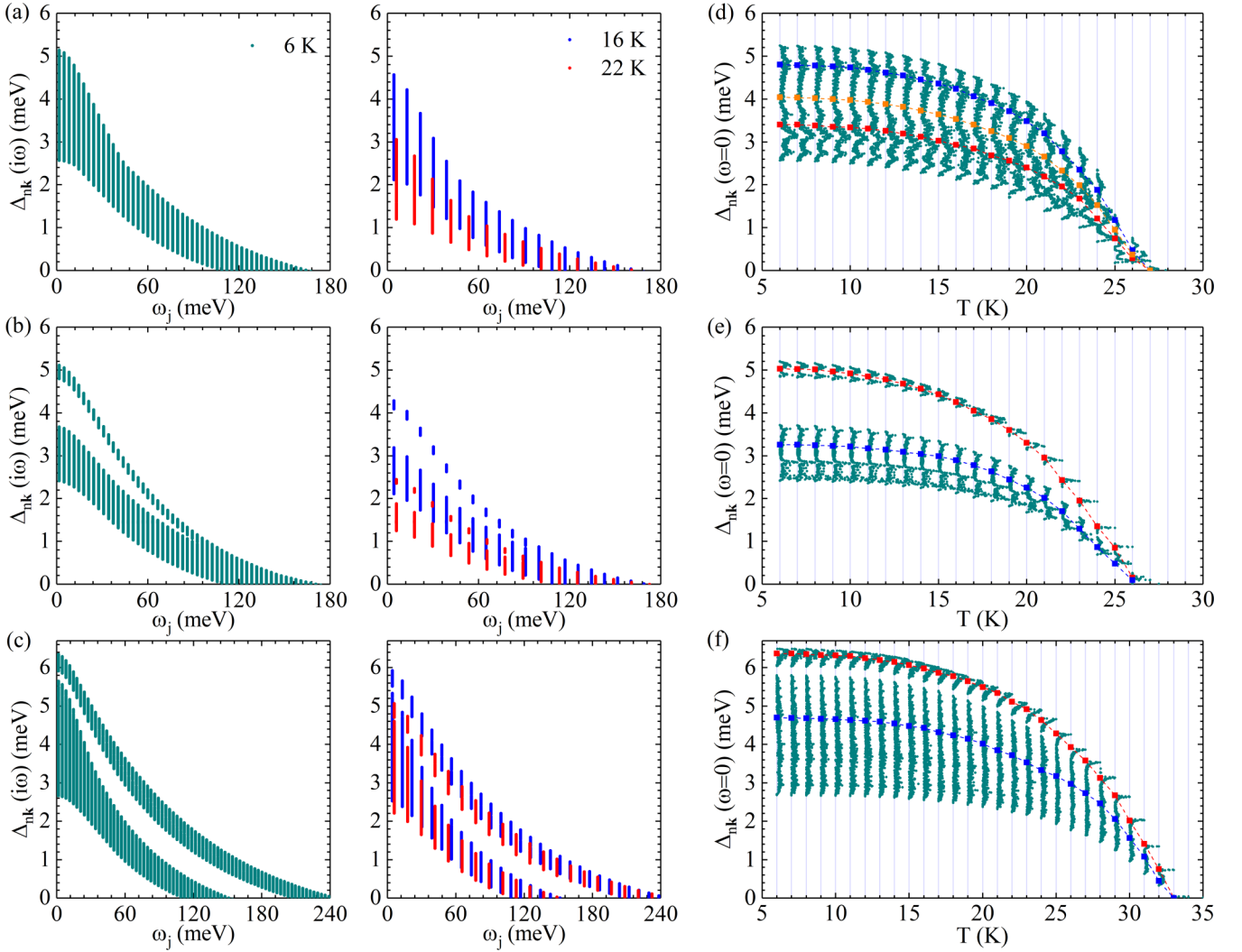


FIG. 5. (a)–(c) Superconducting gap $\Delta_{nk}(i\omega_j)$ at 6 K (left) and 16 and 22 K (right) along the imaginary axis for δ_6 , χ_3 , and β_{12} borophenes, respectively. (d)–(f) Distribution of the superconducting gap $\Delta_{nk}(\omega=0)$ as a function of temperature T for δ_6 , χ_3 , and β_{12} borophenes, respectively. The lines with red and blue squares represent the average gaps arising from the red (σ bond) and blue (π bond) bands on the FS, respectively. The line with orange squares in (d) represents the average value of the entire anisotropic single gap.

(π bond) in β_{12} borophene possesses very strong anisotropy within a large range of 2.7–5.8 meV at the same temperature. According to the distribution range of the gaps induced by the σ and π electrons on the FS, a very small interval between the two gaps is obtained, e.g., 0.2 meV at 6 K, and thus, a two-gap-like nature can be found below about 25 K, as shown in Figs. 5(c) and 5(f). Nevertheless, due to the involved Wannier interpolation procedure, such a small interval is not sufficient to support β_{12} borophene being a two-gap superconductor. Moreover, the interval between the two gaps becomes zero at $T \geq 25$ K, and the two gaps hybridize. It has been reported that because of the gap hybridization a very anisotropic two-gap superconductivity appears as a three-gap nature in MgB_2 monolayers [37,38]. The hybridization of the σ - and π -bond-induced gaps in β_{12} borophene signifies that an anisotropic single-gap superconductivity appears in this monolayer. As shown in Fig. 5(f), our calculated T_c in β_{12} borophene achieves 33.0 K, which is about twice the values of 13.8, 16.0, and 18.7 K obtained in previous works [11–13].

From the isotropic gap $\Delta(\omega)$ on the real axis [19,29], one can obtain the normalized quasiparticle density of states (DOS) in the superconducting state $N_S(\omega)$:

$$\frac{N_S(\omega)}{N(E_F)} = \text{Re} \left[\frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}} \right], \quad (7)$$

where $N(E_F)$ is the normal DOS at the Fermi level. The quasiparticle DOSs at 6, 16, and 22 K for δ_6 , χ_3 , and β_{12} borophenes are plotted with respect to the normal DOS in Fig. 6. Since the superconducting gap $\Delta(\omega)$ on the real axis in Eq. (7) is calculated in EPW from the imaginary-axis Eliashberg equations by the analytic continuation method of Padé approximations [39,40], the relatively smooth quasiparticle DOSs are obtained in Fig. 6. The solid and dashed blue horizontal arrows represent the average values of the σ and π electron-induced superconducting gaps at 6 K, respectively, which coincide with the peaks of the quasiparticle DOSs at the same temperature. In addition, the gaps in the

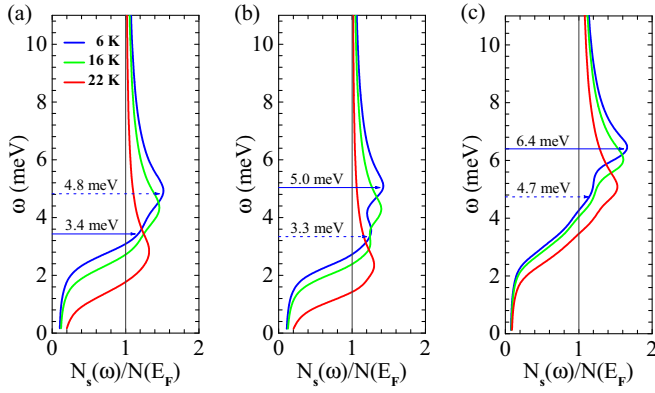


FIG. 6. Quasiparticle superconducting DOS at 6, 16, and 22 K for (a) δ_6 , (b) χ_3 , and (c) β_{12} borophenes. The vertical dark gray line represents the DOS in the normal state. The superconducting DOS $N_s(\omega)$ has been scaled so that its high-energy tail coincides with the normal-state DOS.

superconducting DOSs tend to close with the increase of temperature, consistent with the results shown in Fig. 5.

In addition, owing to the electron doping, lattice mismatch, and phonon vibration suppression arising from the Ag(111) substrate [1,2], the superconductivity of δ_6 , χ_3 , and β_{12} borophenes on the Ag(111) surfaces would be severely

influenced by the evident reduction of T_c [12,13]. To investigate the effect of the Ag(111) substrate on the superconductivity in δ_6 borophene, we carry out the anisotropic Migdal-Eliashberg equation calculations in a slab structure. In this structure, the (1×3) δ_6 borophene lies on the rectangular unit cell of the Ag(111) surface [1]. Considering the computational cost, we use three layers of silver atoms to mimic the Ag(111) substrate. Thus, there are six boron atoms and six silver atoms in each unit cell of this slab structure. The ground-state structure is obtained by relaxation of inner coordinates for silver and boron atoms, as shown in Figs. 7(a) and 7(b). The calculated band structure and phonon dispersion for this slab structure are plotted in Figs. 7(c) and 7(d), in which the electronic states of silver atoms are about 3 eV below the Fermi level and the phonons of silver atoms are distributed in the range of 0–20 meV. The calculated T_c is about 6.5 K, as shown in Fig. 7(e), while a T_c of 5.3 K is predicted based on the Allen-Dynes formula with an isotropic EPI in the same slab structure [13].

For χ_3 and β_{12} borophenes, the unit cells of the corresponding slab structures are fairly large [2], and thus, a tremendous workload would be required for the anisotropic Migdal-Eliashberg equation calculations. To mimic the effect of the Ag(111) substrate on superconductivity in these two borophenes, we take only the effect of electron doping and lattice mismatch induced by the Ag(111) surface into account, which has a certain reliability according to the results in

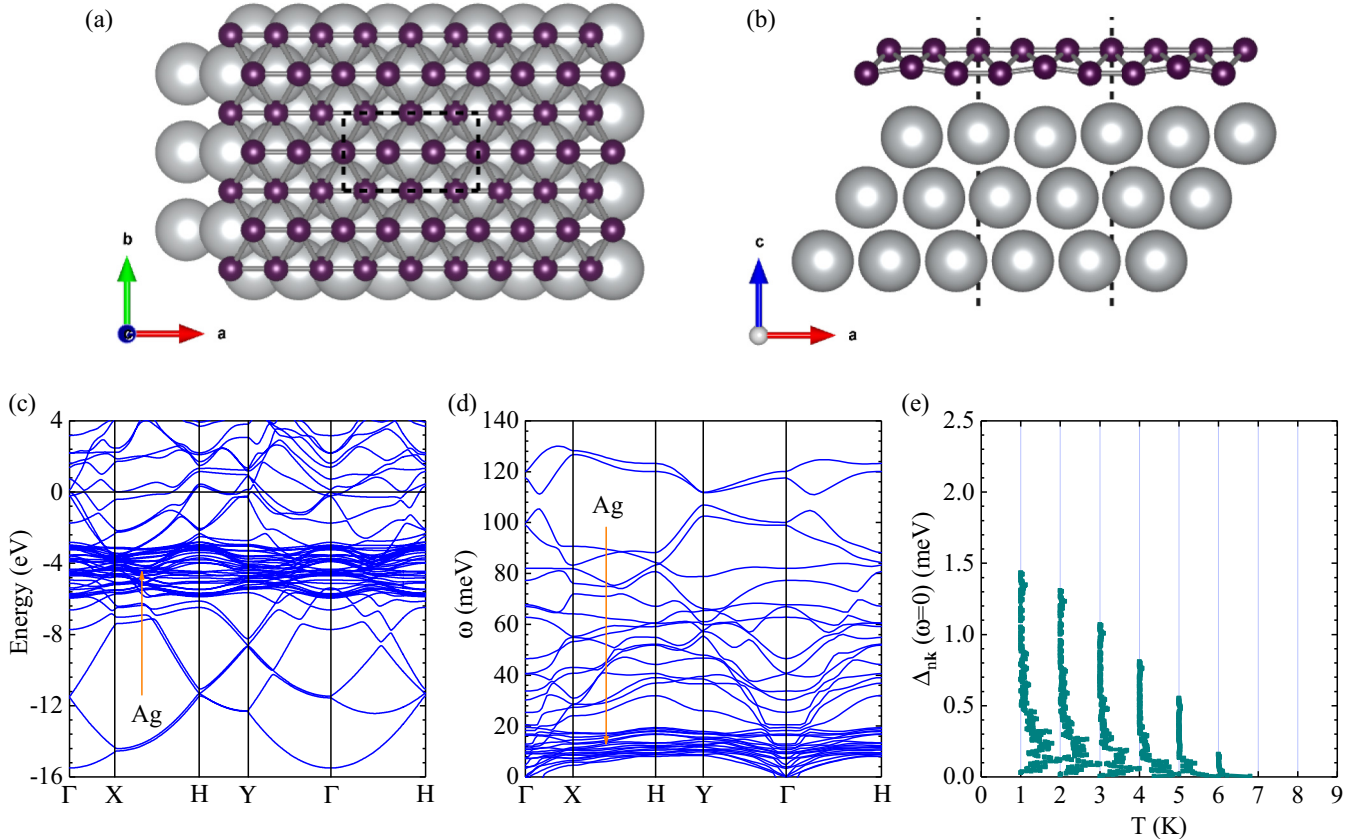


FIG. 7. (a) Top and (b) lateral views for the δ_6 borophene on three layers of the Ag(111) substrate. The large gray and small purple balls represent the Ag and B atoms, respectively. (c) and (d) The corresponding band structure and phonon dispersion. (e) The calculated superconducting gap $\Delta_{nk}(\omega = 0)$ versus temperature T .

Ref. [12]. The slab simulation in Ref. [2] shows a charge transfer of $0.03e$ per boron atom from the Ag substrate to borophene. After deposition, the periodicity of borophene along the $[\bar{1}\bar{1}2]$ direction of the Ag(111) surface is confirmed in experiment to be $15.0688 \text{ \AA}$ [2], and uniaxial tensile strains of 3.3% and 2.7% are generated in χ_3 and β_{12} borophenes, respectively, due to the lattice mismatch [2,12]. With the influence of the electron doping and tensile strains mentioned above, our calculations give a T_c of about 19.3 and 11.0 K in χ_3 and β_{12} borophenes, respectively (see Fig. S3 in Ref. [32]), while values of 14.5 and 8.0 K were claimed for these two borophenes with the same electron doping and tensile strains in a previous study [12].

Obviously, both previous works [12,13] and our present calculations indicate that the Ag(111) substrate has an adverse effect on superconductivity of δ_6 , χ_3 , and β_{12} borophenes. Thus, it is interesting to enhance T_c in some ways. In view of the strong dependence of the crystal structures of borophenes on the noble-metal substrate used [41], it is possible to grow a novel borophene with T_c higher than those of the present studied systems by adopting a different substrate. In addition, it has been demonstrated that for six monolayers of MgB_2 the influence of the Mg substrate on superconductivity is minimized, and consequently, the freestanding calculation within *ab initio* Eliashberg theory becomes fairly accurate [38]. Similarly, multilayer boron sheets on a suitable substrate are also proposed to obtain a possible freestandinglike borophene to increase T_c . For instance, a bilayer boron sheet, which can be deemed to be two layers of δ_6 borophenes, has also been predicted to be stable on the Ag(111) substrate based on the *ab initio* evolutionary algorithm, as shown in Fig. S8 in Ref. [1]. In this bilayer structure on the Ag(111) surface, the top boron layer holds a distinctly weak effect from the Ag substrate, and thus, a higher T_c than that in δ_6 borophene on the Ag(111) surface is expected. With different experimental conditions, the bilayer boron structure would probably be grown on the Ag(111) surface, although the experimental measurement up to now has supported a monolayer model [1].

Finally, we emphasize that a multigap superconductor is characterized by separate superconducting gaps opening on evidently different parts of the FS [42]. In δ_6 , χ_3 , and β_{12} borophenes, the FSs are formed by multiple bands with distinctly different orbital projections (σ or π orbitals) and thus possess evidently different parts, promising separate superconducting gaps. Another typical example is MgB_2 , in which the FS comprises two bands formed by the σ and π electrons

of boron and thus gives rise to a two-gap superconducting nature [18]. Therefore, for the system with a complicated FS composed of bands with different orbital features, the application of the anisotropic Migdal-Eliashberg equations is more appropriate to obtain an anisotropic EPI, a multigap anisotropic superconducting nature, and a pertinent T_c , in contrast to the isotropic superconductivity calculated from the Allen-Dynes formula by using an isotropic EPI.

IV. CONCLUSION

In summary, we have systematically investigated the pairing mechanism and the nature of the superconducting gaps in δ_6 , χ_3 , and β_{12} borophenes. We found a very anisotropic single-gap superconductivity with $T_c \approx 27.0 \text{ K}$ in δ_6 borophene and revealed that the π electrons on the FS give rise to the stronger EPI and higher gap due to the out-of-plane buckling structure. For χ_3 borophene, our results showed a two-gap anisotropic superconductivity with T_c of about 26.2 K. The σ states on the FS play a crucial role in the EPI and superconducting behavior in this planar borophene, which is analogous to the superconducting nature in MgB_2 . For β_{12} borophene, because of the gap hybridization, a very anisotropic single-gap nature is concluded, although a very small interval between the σ and π electron-induced gaps is detected below about 25 K. Strikingly, the calculated T_c in β_{12} borophene approaches 33.0 K, which is about twice the values obtained from the Allen-Dynes formula using the isotropic EPI. These results provide a conventional phonon-mediated mechanism for superconductivity in δ_6 , χ_3 , and β_{12} borophenes. In addition, we have also estimated the effect of the Ag(111) substrate on the superconductivity in δ_6 , χ_3 , and β_{12} borophenes and found that the Ag substrate plays an adverse role in the superconductivity in these borophenes, consistent with the prediction in previous works. Thus, employing different substrates or growing multilayer boron sheets on a suitable substrate is proposed to enhance T_c .

ACKNOWLEDGMENTS

This research was supported by the Natural Science Foundation of Shandong Province for Doctoral Program under Grant No. ZR2017BA017; the National Natural Science Foundation of China under Grants No. 11704322, No. 11774396, and No. 11774195; and the National Key Research and Development Program of China under Grants No. 2016YFA0300902 and No. 2016YFB0700102.

- [1] A. 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, M. J. Yacaman, A. Ponce, A. R. Oganov, M. C. Hersam, and N. P. Guisinger, *Science* **350**, 1513 (2015).
- [2] B. 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).
- [3] H. Wang, Q. Li, Y. Gao, F. Miao, X.-F. Zhou, and X. G. Wan, *New J. Phys.* **18**, 073016 (2016).

- [4] H. Jiang, Z. Lu, M. Wu, F. Ciucci, and T. Zhao, *Nano Energy* **23**, 97 (2016).
- [5] X.-F. Zhou, A. R. Oganov, Z. Wang, I. A. Popov, A. I. Boldyrev, and H.-T. Wang, *Phys. Rev. B* **93**, 085406 (2016).
- [6] A. Lopez-Bezanilla and P. B. Littlewood, *Phys. Rev. B* **93**, 241405 (2016).
- [7] F. Ma, Y. Jiao, G. Gao, Y. Gu, A. Bilic, Z. Chen, and A. Du, *Nano Lett.* **16**, 3022 (2016).
- [8] T. Tsafack and B. I. Yakobson, *Phys. Rev. B* **93**, 165434 (2016).

- [9] G. Liu, H. Wang, Y. Gao, J. Zhou, and H. Wang, *Phys. Chem. Chem. Phys.* **19**, 2843 (2017).
- [10] Y. Zhao, S. Zeng, and J. Ni, *Phys. Rev. B* **93**, 014502 (2016).
- [11] E. S. Penev, A. Kutana, and B. I. Yakobson, *Nano Lett.* **16**, 2522 (2016).
- [12] M. Gao, Q.-Z. Li, X.-W. Yan, and J. Wang, *Phys. Rev. B* **95**, 024505 (2017).
- [13] Y. Zhao, S. Zeng, and J. Ni, *Appl. Phys. Lett.* **108**, 242601 (2016).
- [14] R. C. Xiao, D. F. Shao, W. J. Lu, H. Y. Lv, J. Y. Li, and Y. P. Sun, *Appl. Phys. Lett.* **109**, 122604 (2016).
- [15] G. Li, Y. Zhao, S. Zeng, M. Zulfiqar, and J. Ni, *J. Phys. Chem. C* **122**, 16916 (2018).
- [16] J.-H. Liao, Y.-C. Zhao, Y.-J. Zhao, H. Xu, and X.-B. Yang, *Phys. Chem. Chem. Phys.* **19**, 29237 (2017).
- [17] J. M. An and W. E. Pickett, *Phys. Rev. Lett.* **86**, 4366 (2001).
- [18] H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, *Nature (London)* **418**, 758 (2002).
- [19] E. R. Margine and F. Giustino, *Phys. Rev. B* **87**, 024505 (2013).
- [20] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
- [21] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
- [22] M. Fuchs and M. Scheffler, *Comput. Phys. Commun.* **119**, 67 (1999).
- [23] P. 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).
- [24] N. Marzari, D. Vanderbilt, A. De Vita, and M. C. Payne, *Phys. Rev. Lett.* **82**, 3296 (1999).
- [25] S. Baroni, S. de Gironcoli, A. Dal Corso, and P. Giannozzi, *Rev. Mod. Phys.* **73**, 515 (2001).
- [26] F. Giustino, M. L. Cohen, and S. G. Louie, *Phys. Rev. B* **76**, 165108 (2007).
- [27] F. Giustino, *Rev. Mod. Phys.* **89**, 015003 (2017).
- [28] J. Noffsinger, F. Giustino, B. D. Malone, C.-H. Park, S. G. Louie, and M. L. Cohen, *Comput. Phys. Commun.* **181**, 2140 (2010).
- [29] S. Ponc , E. Margine, C. R. Verdi, and F. Giustino, *Comput. Phys. Commun.* **209**, 116 (2016).
- [30] A. A. Mostofi, J. R. Yates, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, *Comput. Phys. Commun.* **178**, 685 (2008).
- [31] J.-J. Zheng and E. R. Margine, *Phys. Rev. B* **94**, 064509 (2016).
- [32] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.98.134514> for the additional vibrational and superconducting properties in borophenes.
- [33] Y. Zhao, Z. Dai, C. Zhang, C. Lian, S. Zeng, G. Li, S. Meng, and J. Ni, *New J. Phys.* **20**, 043009 (2018).
- [34] H. Sun, Q. Li, and X. Wan, *Phys. Chem. Chem. Phys.* **18**, 14927 (2016).
- [35] B. Peng, H. Zhang, H. Shao, Y. Xu, R. Zhang, and H. Zhu, *J. Mater. Chem. C* **4**, 3592 (2016).
- [36] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
- [37] J. Bekaert, A. Aperis, B. Partoens, P. M. Oppeneer, and M. V. Milo ević, *Phys. Rev. B* **96**, 094510 (2017).
- [38] J. Bekaert, L. Bignardi, A. Aperis, P. van Abswoude, C. Mattevi, S. Gorovikov, L. Petaccia, A. Goldoni, B. Partoens, P. M. Oppeneer, F. M. Peeters, M. V. Milo ević, P. Rudolf, and C. Cepek, *Sci. Rep.* **7**, 14458 (2017).
- [39] H. J. Vidberg and J. W. Serene, *J. Low Temp. Phys.* **29**, 179 (1977).
- [40] C. Leavens and D. Ritchie, *Solid State Commun.* **53**, 137 (1985).
- [41] Z. Zhang, Y. Yang, G. Gao, and B. I. Yakobson, *Angew. Chem.* **127**, 13214 (2015).
- [42] H. Suhl, B. T. Matthias, and L. R. Walker, *Phys. Rev. Lett.* **3**, 552 (1959).