Phonon-mediated superconductivity in Mg intercalated bilayer borophenes

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Using first-principles calculations, we investigate the structural, electronic and superconducting properties of Mg intercalated bilayer borophenes $B_xMgB_y$ ($x = 2-5$). Remarkably, $B_2MgB_2$ and $B_3MgB_3$ are predicted to exhibit good phonon-mediated superconductivity with a high transition temperature ($T_c$) of 23.2 K and 13.3 K, respectively, while $B_4MgB_4$ is confirmed to be more practical based on the analyses of its stability. The densities of states at in-plane orbitals at the Fermi level are found to be dominant at the superconducting transition temperature in Mg intercalated bilayer borophenes, providing an effective avenue to explore Mg–B systems with high $T_c$.

Introduction

Two-dimensional (2D) materials including graphene,1 silicene,2–4 phosphorene,5,6 and h-BN7–9 have attracted tremendous interest due to their novel properties. Theoretical studies have suggested a set of freestanding borophenes by introducing hexagonal vacancies in the triangular lattice,10–15 where the hexagonal vacancy density ($\eta$) and the coordination number (CN) of boron atoms are used for the description and classification of borophenes.11 Experimentally, borophenes of a striped phase ($\delta_{1,2}$ and $\beta_{1,2}$) and a homogeneous phase ($\chi_3$) have been successfully synthesized on a Ag(111) surface using a B atomic source, as confirmed by first-principles simulations.18,19 During the nucleation and growth on the Ag(111) surface,20 the $\beta_{1,2}$ sheet with 1/6 vacancies is energetically preferable, whose computed band structures agree with the observed angle-resolved photoelectron spectrum,21 with simulated STM images in better agreement with the experimental observation.22 Due to their structural diversity, borophenes have been supposed to possess potential applications in catalysis,23 Li-ion batteries,24–26 electronic devices,27–32 and superconductors.33–38

Due to the vanished density of states at the Fermi level, metal adatom doping is necessary to induce superconductivity in a graphene sheet.39,40 The superconducting transition temperatures ($T_c$) were estimated to be 8.1 K and 1.4 K for monolayer LiC$_6$ and CaC$_6$, respectively, while they were 0.9 K and 11.5 K for graphite intercalated compounds LiC$_6$ and CaC$_6$.41,42 In a recent experiment, Li-intercalated bilayer graphene (C$_6$LiC$_6$) showed no sign of superconductivity down to 0.8 K, while superconductivity was observed at 2 K in Ca-intercalated bilayer graphene (C$_6$CaC$_6$).43 Different from graphene, borophenes are mostly metallic, and the conventional BCS superconductivity in borophenes33–36 and 2D boron allotropes45–49 is ubiquitous. In the bulk MgB$_2$ with a high $T_c$ of 39 K, phonon-mediated superconductivity stems from the boron layers, owing to the in-plane stretching vibrational modes of boron.45–49 The $T_c$s in other bulk Mg–B systems, e.g. MgB$_2$, Mg$_x$B$_{10}$, and Mg$_2$B$_4$, were estimated to be below 3 K,50 and the $T_c$ in Mg intercalated bilayer kagome borophene (B$_x$MgB$_x$-kagome) was predicted to be 4.7 K.51

In this paper, we have investigated Mg intercalated bilayer borophenes with $\eta = 1/3$, 1/4, 1/5, and 1/6, focusing on their structural stabilities, electron–phonon coupling (EPC) properties and possible superconductivity. The projected electronic density of states (EDOS) and Eliashberg function are calculated to demonstrate the superconducting mechanism in these structures, as well as the orbital-resolved and phonon-perturbed band structures and the corresponding vibrational patterns. We predict that a metastable sandwich structure of B$_2$MgB$_2$ exhibits superconductivity with the highest $T_c$, where the B atoms form a hexagonal lattice with a triangular Mg sheet. To balance the structural stability and superconducting properties, B$_4$MgB$_4$ will be more practical according to the formation enthalpy versus $T_c$ characteristics.

Methods

Our calculations were performed based on density functional theory (DFT) implemented in the QUANTUM-ESPRESSO package.52
The LDA norm-conserving scheme (von-Barth–Car type) was used to generate pseudopotentials for B and Mg. The plane-wave cutoff energy was set to 100 Ry. A vacuum region of 15 Å was adopted to avoid the interaction of the periodic images. All the structures were fully relaxed until the Hellmann–Feynman force on each atom was less than $10^{-5}$ Ry per Bohr. A Methfessel–Paxton\textsuperscript{51} smearing width of 0.02 Ry was used for the corresponding electronic self-consistent cycles. For calculations of electronic properties, $16 \times 16 \times 1$ (16 $\times$ 12 $\times$ 1) Monkhorst–Pack\textsuperscript{54} $k$ meshes were used for $B_xMgB_2$, $B_yMgB_3$, and $B_zMgB_4$ ($B_xMgB_3$).

The phonon frequencies and EPC parameter $\lambda$ were calculated with $8 \times 8 \times 1$ and $8 \times 6 \times 1$ phonon wave-vector meshes and $64 \times 64 \times 1$ and $64 \times 48 \times 1$ denser $k$ meshes, respectively. To estimate $T_c$, the McMillan–Allen–Dynes formula\textsuperscript{55} was used with a retarded Coulomb pseudopotential $\mu^*$ of 0.1.

**Results and discussion**

The structures of Mg intercalated bilayer borophenes considered in this paper are schematically shown in Fig. 1(a). 2D $B_xMgB_2$ is constructed from layered bulk $MgB_2$, and the $B_1$ ($\delta_1$) sheet with $\eta = 1/3$ is a hexagonal lattice. There are two typical configurations for borophenes with $\eta = 1/4$, named $\delta_1$ and kagome (see the inset of Fig. 1(b)).\textsuperscript{51} The Mg intercalated bilayer kagome borophene ($B_xMgB_3$-kagome) was predicted to be a superconductor with $T_c = 4.7$ K.\textsuperscript{51} Energetically, the Mg intercalated bilayer $\delta_4$ borophene ($B_xMgB_4$) shown in Fig. 1(a) with a calculated $T_c$ of 6.0 K (see Fig. 1(b)) is more stable than the $B_yMgB_3$-kagome by 0.075 Ry per cell (1.02 eV per cell). The Mg intercalated bilayer $\chi_3$ borophene ($B_xMgB_3$), whose $\lambda$ is estimated to be 0.64 (see Table 1), has a little higher $T_c$ than the monolayer $\chi_3$ sheet. Surprisingly, the superconductivity vanishes in the Mg intercalated bilayer $\beta_{12}$ borophene ($B_xMgB_3$), while the $\beta_{12}$ borophene's $T_c$ was estimated to be 13.8 K.\textsuperscript{54}

In order to study the relative structural stability of the Mg intercalated bilayer borophenes ($B_xMgB_3$), we have calculated the formation enthalpy $\Delta H(x)$ as\textsuperscript{56}

$$\Delta H(x) = E_x - yE_1 - (1 - y)E_0,$$

where $E_x$, $E_1$, and $E_0$ are the normalized total energies of $B_xMgB_3$, bulk Mg, and the $x$ sheet, respectively, and $y = 1/(1 + 2x)$. As shown in Fig. 1(b), the formation enthalpies of $B_xMgB_3$, $B_yMgB_3$, and $B_zMgB_3$ are all negative, indicating the relative stability of these 2D structures. $B_xMgB_2$ and $B_xMgB_3$-kagome\textsuperscript{51} should be less stable because of the positive formation enthalpy.

Experimentally, the layered bulk MgB$_2$ is found to be superconducting with a $T_c$ of 39 K. Our calculated $T_c$ for MgB$_2$ is 24.8 K, which is in agreement with previous computational results.\textsuperscript{50,57} Note that the calculated $T_c$ is 23.2 K for 2D $B_xMgB_2$ from the layered bulk MgB$_2$, which is the highest $T_c$ in the low-dimensional Mg–B system. For comparison, we consider the artificial layered bulk MgB$_2$ based on the sandwich structure $B_xMgB_2$, including the layered bulk MgB$_4$, MgB$_3$, and MgB$_2$. Our calculations indicate that MgB$_3$ and MgB$_4$ are dynamically stable, while the dynamical stability of the layered bulk MgB$_2$ is poor due to the presence of imaginary phonon frequencies in the Brillouin zone. Among these bulk structures, the densities of states of the in-plane orbitals at the Fermi level are dominant at the superconducting $T_c$, as shown in Table 1. Interestingly, for the Mg intercalated bilayer borophenes, it is also found that

![Fig. 1](image-url)
$T_c$ decreases with decreasing in-plane EDOS at the Fermi level, rather than the total EDOS. This finding provides an effective avenue to explore Mg–B systems with high $T_c$s.

In a previous theoretical study, the $T_c$ of pristine borophenes decreases as the stabilities increases, where the B$_2$ ($\delta_3$), B$_3$ ($\delta_4$), B$_4$ ($\gamma_3$), and B$_5$ ($\beta_{12}$) sheets with higher $T_c$s are less stable than the $\alpha$ sheet. The strain from the substrate and carrier doping also modulates $T_c$.[34] Note that the negative formation enthalpies of B$_3$MgB$_3$, B$_4$MgB$_4$, and B$_5$MgB$_5$ show that the structural stabilities of the Mg intercalated bilayer borophenes can be greatly enhanced. Moreover, the Mg intercalated borophenes also show the possible low-dimensional boron–magnesium configurations and their changed superconducting properties due to their reduced dimensions compared with their bulk counterparts.

To balance the structural stability and superconducting properties, we show the calculated $T_c$s of these Mg–B structures as a function of formation enthalpy in Fig. 1(b). The formation enthalpies of bulk MgB$_2$ are all lower than those of sandwich structures. Among magnesium borides, except for bulk MgB$_2$, the other superconducting ones in previous theoretical studies had $T_c$s below 3 K.[30] Herein, the layered MgB$_4$ has a calculated

![Fig. 2](image-url) The projected EDOS of (a) B$_2$MgB$_2$, (b) B$_3$MgB$_3$, (c) B$_4$MgB$_4$, and (d) B$_5$MgB$_5$ and the Fermi surfaces of (e) B$_2$MgB$_2$, (f) B$_3$MgB$_3$, (g) B$_4$MgB$_4$, and (h) B$_5$MgB$_5$. The Fermi level is set to zero, marked by the solid black line.
\( T_c \) of 5.2 K. MgB\(_2\) is the most stable with the highest \( T_c \). Of the sandwich structures, B\(_2\)MgB\(_2\) possesses the highest \( T_c \) but with the poorest structural stability, B\(_3\)MgB\(_3\) and B\(_5\)MgB\(_5\) are more stable compared with B\(_2\)MgB\(_2\), while the corresponding \( T_c \)s are much lower. Split the difference, B\(_4\)MgB\(_4\) has a high calculated \( T_c \) of 13.3 K combined with a relatively good structural stability, which will be more practical in superconducting applications.

According to conventional BCS theory,\(^{58}\) the phonon-mediated superconductivity depends on the characteristic phonon frequency \( \omega_0 \) and the EPC parameter \( \lambda \),

\[
\lambda = N_F V_{cp},
\]

where \( N_F \) is the EDOS at the Fermi level and \( V_{cp} \) is the effective pairing attractive potential.\(^{44}\) Compared with the \( \chi_3 \) (B\(_3\)) sheet, the \( N_F \) of B\(_2\)MgB\(_4\) is increased by \( \sim 60\% \), which comes from the in-plane orbitals \( (s + p_x + p_y) \). However, the \( N_F \) of B\(_5\)MgB\(_5\) is reduced by \( \sim 15\% \) than that of the \( \chi_{12} \) (B\(_2\)) sheet, and the contribution of the in-plane orbitals is decreased by \( \sim 80\% \).

For the Mg intercalated bilayer borophenes, we show the projected EDOS and Fermi surface in Fig. 2. From B\(_2\)MgB\(_2\) to B\(_5\)MgB\(_5\), the amplitude of the \( p_z \) orbitals is fairly small, while there are great changes in the amplitude of the in-plane orbitals in the \( -4 \) to \( 4 \) eV energy range. The in-plane part of the \( N_F \) of B\(_2\)MgB\(_3\), which changes a little near the Fermi level, accounts for only 12% of total \( N_F \). Therefore, the Fermi contour of B\(_3\)MgB\(_3\) almost all consists of \( p_z \)-derived pockets. The Fermi contour of B\(_2\)MgB\(_2\) consists of a double ring pocket and a double star pocket centered at the \( \Gamma \) point derived from the in-plane orbitals, and the six arms of the double star extended along the six \( \Gamma \)–\( M \) directions. The Fermi contour of B\(_5\)MgB\(_5\) also includes a big ring pocket centered at the \( \Gamma \) point and a small ring pocket centered at the \( K \) point derived from the \( p_z \) orbitals. For B\(_3\)MgB\(_3\), the Fermi contour consists of a rectangular pocket centered at \( Y \) (0, 0.5) derived from the in-plane orbitals, and three \( p_z \)-derived ellipsoidal pockets centered at \( X \) (0.5, 0), \( S \) (0.5, 0.5), and \( Y \), respectively. The Fermi contour of B\(_5\)MgB\(_5\) shows two \( p_z \)-derived dumbbell-shaped pockets centered at \( \Gamma \) with some borders paralleled to the \( H-H' \) line, whose midpoint is \( Y \) (0, 0.5).

The phonon dispersions with phonon linewidth \( \gamma_{q\omega} \) and Eliashberg function \( \sigma^2F(o) \) and \( \lambda(o) \) are shown in Fig. 3. Our calculations with LDA norm-conserving pseudopotentials show the dynamical stability of these sandwich structures without imaginary phonon frequencies in the Brillouin zone. The B\(_4\)MgB\(_4\)-kagome shows the dynamical stability with PBE norm-conserving pseudopotentials, which is consistent with the result of ref. 51. The imaginary phonon frequency of the transverse branch near the \( \Gamma \) point was found in the simulations of borophenes,\(^{33,35}\) germanene\(^2\) and other 2D materials,\(^{59,60}\) where the emergence of imaginary frequencies is due to the numerical difficulties in accurate calculation rather than a sign of structural transition.\(^{59}\) Imaginary phonon frequencies of the acoustical branch also occur near the \( \Gamma \) point in all these sandwich structures shown in Fig. 1(a) with PBE norm-conserving pseudopotentials. Fortunately, these imaginary frequencies have almost no influence on our EPC results. The \( \lambda \) and \( T_c \) are found to be almost the same under both PBE and LDA functionals.

As shown in Fig. 3, the vibration modes in the \( 400-800 \) cm\(^{-1}\) frequency range induce the main EPC in B\(_3\)MgB\(_2\), while those of \( 100-400 \) cm\(^{-1}\) induce the main EPC in B\(_2\)MgB\(_3\) and B\(_5\)MgB\(_5\). For B\(_3\)MgB\(_3\), the phonon linewidths of the vibration modes in the \( 100-800 \) cm\(^{-1}\) frequency range are fairly small, leading to a small \( \lambda \) and the disappearance of superconductivity. Fig. 4 shows the EPC distribution in the Brillouin zones of these Mg intercalated borophenes. For B\(_3\)MgB\(_3\) and B\(_5\)MgB\(_5\), the region with the largest EPC is around \( \Gamma \) and \( Y \), respectively, which is consistent with the phonon linewidth shown in Fig. 3. For B\(_4\)MgB\(_4\), the point with the
largest EPC is Y, and the region with large EPC is along the H–H′ line, in which the phonon linewidth is fairly great in the 200–400 cm$^{-1}$ low frequency range and the 1000–1100 cm$^{-1}$ high frequency range. For B$_3$MgB$_3$, the region around the Γ point contributes to the major EPC, whose strength is far less than those of B$_2$MgB$_2$, B$_3$MgB$_3$, and B$_4$MgB$_4$.

The EPC in B$_3$MgB$_3$ is induced by the multiple vibration modes. Fig. 5(a) shows the orbital-resolved band structures of B$_3$MgB$_3$ and the band structure perturbed by the A$_1$ vibrational pattern at Γ (see Fig. 3(b) and 5(c)). This A$_1$ mode, in which the B atoms vibrate vertically and the Mg atoms remain silent, greatly affects the p$_z$ orbitals near the Fermi level. Fig. 5(b)
shows the orbital-resolved band structures of $B_4$MgB$_4$ and the band structure perturbed by the $B_4$ vibrational pattern at Y (see Fig. 3(c) and 5(d)). This $B_4$ mode, in which half of the B atoms vibrate vertically and the Mg atoms vibrate horizontally, greatly affects the $p_z$ orbitals along the H–H′ line and the in-plane orbitals along the Γ–S line at the Fermi level.

**Conclusion**

In summary, we have studied the electronic structure and EPC in Mg intercalated bilayer borophenes, and their corresponding bulk structures. We predict that $B_2$MgB$_2$ and $B_4$MgB$_4$ should exhibit phonon-mediated superconductivity with a relatively high $T_c$ and $B_4$MgB$_4$ would be more practical due to its better stability, indicating the possible superconductivity in the low-dimensional Mg–B system. The Mg intercalation will modulate the EDOS of the in-plane orbitals at the Fermi level, which is dominant at the superconducting $T_c$ in Mg intercalated bilayer borophenes. These findings pave the way for the superconducting applications of two-dimensional Mg–B materials.

**Conflicts of interest**

There are no conflicts to declare.

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**References**