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A novel two-dimensional MgB₆ crystal: metal-layer stabilized boron kagome lattice

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Based on first-principles calculations, we designed for the first time a boron-kagome-based twodimensional MgB₆ crystal, in which two boron kagome layers sandwich a triangular magnesium layer. The two-dimensional lattice is metallic with several bands across the Fermi level, and among them a Dirac point appears at the *K* point of the first Brillouin zone. This metal-stabilized boron kagome system displays electron-phonon coupling, with a superconductivity critical transition temperature of 4.7 K, and thus it is another possible superconducting Mg–B compound besides MgB₂. Furthermore, the proposed 2D MgB₆ can also be used for hydrogen storage after decoration with Ca. Up to five H₂ molecules can be attracted by one Ca with an average binding energy of 0.225 eV. The unique properties of 2D MgB₆ will spur broad interest in nanoscience and technology.

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Introduction

Two-dimensional (2D) materials have attracted intense interest since the discovery of graphene.¹ In addition to graphene, many other 2D materials have been predicted theoretically or successfully fabricated experimentally for application in nanotechnology and nanodevices,²⁻⁴ such as porous graphene,⁵ 2D BN,⁶ graphene oxide,^{7,8} silicene,^{9,10} MoS₂,¹¹ and metal carbides.¹² These 2D materials with special atomic configurations exhibit exotic electronic properties, such as Dirac cone band dispersion, direct band gap and so on. In order to meet the large need for materials for future nanotechnology,^{3,12,13} other new 2D materials are urgently demanded. With a liquid exfoliation method of layered materials, Coleman et al. successfully produced 2D BN, MoS₂ and WS₂ nanosheets.² Furthermore, Sun et al. synthesized non-layered 2D ZnSe and ZnS through a general lamellar hybrid intermediate strategy.¹⁴ Li et al. successfully fabricated 2D transition metal honeycomb on a metal substrate.¹⁵ Theoretically, group IV elements and group III-IV compounds were predicted to form stable 2D crystals.¹⁶ Moreover, several elemental boron 2D lattices were suggested to consist of a combination of hexagonal and triangular motifs.¹⁷⁻¹⁹



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In this work, based on first-principles calculation, we design a novel 2D MgB₆ crystal, in which two boron-kagome layers sandwich a Mg metal layer. The metal layer transfers electrons to the boron kagome layer to stabilize the whole structure. The dynamic stability is verified by the phonon modes without any imaginary frequency and by room temperature molecular dynamics. The designed structure is metallic with several bands across the Fermi level, two of which are linear-dispersion bands. This material may be used as a super-thin electrode in future nanoelectronics. Furthermore, electron–phonon coupling calculations predict that this 2D material can be a superconductor with a critical temperature of 4.7 K. Finally, this system after Ca decoration can also be used for hydrogen storage for nanoenergy applications.

Calculation method

In the present work, the geometry relaxations and molecular dynamics simulations were carried out with the Vienna Ab initio Simulation Package.²⁵ The Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation²⁶ was employed to describe the exchange correlation interactions, and the projector augmented

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wave (PAW) method²⁷ was used to describe the interactions between ion cores and valence electrons. A vacuum layer of 25 Å was used to decouple interactions of neighboring slabs. A planewave cutoff of 500 eV and a Monkhorst–Pack 13 \times 13 \times 1 K-mesh were used for geometry optimization until all the forces were smaller than 0.03 eV $Å^{-1}$. Ab initio molecular dynamics were taken on the canonical ensemble,²⁸ with a time step of 2 femtoseconds. During the simulation, a (4×4) supercell, which contained 96 B and 16 Mg atoms, was used to relieve the constraint of the (1×1) cell. To get precise vibrational information, phonon modes and electron-phonon coupling (EPC) were calculated using densityfunctional perturbation theory within the Quantum Espresso package.²⁹ The PBE Norm-conserving scheme (Troullier-Martinstype) was used to generate the pseudopotentials for B and Mg. The plane-wave cutoff was 120 Ry. A $(8 \times 8 \times 1)$ *q*-point mesh in the first Brillouin zone was used in the EPC calculation. A dense Monkhorst-Pack grid of $(16 \times 16 \times 1)$ was used to ensure k-point sampling convergence. To plot the phonon dispersion curve, 50 points were inserted between the neighboring high-symmetry points. The acoustic sum rule was applied to fit the phonon dispersion. To estimate the superconductivity critical temperature $(T_{\rm C})$, the Allen–Dynes formula³⁰ was used, which has been demonstrated in a metal-doped graphene system.^{31,32}

Results and discussion

B is a special element with variable valences. Compared to C, B lacks one electron and cannot form a stable honeycomb structure like that of graphene. Tang suggested a stable 2D B

structure with a hybridization of trianglular and hexagonal motifs.17 The triangular lattice, which has excess electrons, transfers electrons to the electron-deficient hexagonal lattice to stabilize the structure. A hexagon hole density η , the ratio of hexagon holes to the number of atoms in the perfect triangular lattice, is used to describe the amount of hexagonal motifs.¹⁷ Fig. 1 gives the unit cell of various boron 2D lattices. Fig. 1a1 and a2 show the pure triangular lattice, and its corresponding projected density of states (PDOS) for the in-plane (s, p_x , p_y) and out-of-plane (p_z) orbitals. At an energy of about -3.4 eV, there is a boundary (zero DOS) between the bonding and antibonding states of the in-plane orbitals. Obviously, the triangular lattice is not stable due to the occupation of the antibonding states. In fact, there is 0.5 electron (per boron) of over-occupation from the Fermi level to -3.4 eV. Here, the triangular lattice has the smallest $\eta = 0$ and thus the most excess electrons. In contrast, the boron hexagonal honeycomb lattice in Fig. 1d1 has the largest $\eta = 1/3$, and is the most electron-deficient of the four basic structures. The energy position (green line) at 3.5 eV in Fig. 1d2 can be taken as the electron balance position for the honeycomb lattice, because none of the antibonding states of the in-plane and out-of-plane orbitals are occupied while their bonding states are almost fully occupied. Therefore, the Fermi level in this case leads to a deficiency of one electron (per boron). In Fig. 1b2, another α sheet lattice¹⁷ with $\eta = 1/9$ has been reported with good stability and good electron balance. However, in Fig. 1c1, the kagome lattice, with $\eta = 1/4$ (between 1/9 and 1/3), should still lack the electrons needed to be stable. 0.8 eV in its DOS in Fig. 1c2 is the boundary between the bonding and antibonding states of the out-of-plane states, while 3.6 eV is the boundary of the



Fig. 1 The atomic structures and electronic structures of typical boron 2D lattices. (a1) Boron triangular, (b1) α sheet ref. 26, (c1) kagome lattice and (d1) honeycomb lattice. The hexagonal hole density η increases from (a1) to (d1). (a1) $\eta = 0$; (b1) $\eta = 1/9$; (c1) $\eta = 1/4$; (d1) $\eta = 1/3$. (a2)–(d2) Projected density of states (PDOS) for planar boron motifs. In-plane states (sum of s, p_x and p_y) and out-of-plane states (p_z) are marked by the solid blue line and the dashed red line, respectively. The Fermi level is set at the energy zero point, marked by the solid black line. The solid green line represents the possible energy-favorable position. (a3)–(d3) schematically illustrate their electron occupation levels and the blue dashed line indicates their electronic balance positions.

in-plane states. In other words, the antibonding out-of-plane states overlap with the bonding in-plane states between 0.8 and 3.6 eV in the kagome DOS. Therefore, the electron balance level must be selected in this energy window. We propose that the position at 1.2 eV (green line, the crossing of the two states) may be a suitable choice. The DOS from the Fermi level to the proposed position needs 0.4 electron per boron to be occupied. In summary, Fig 1a3–d3 schematically compares the electron occupation levels for the four kinds of boron 2D lattices above.

In bulk MgB₂,³³ which is constructed by sequential stacking of the B honeycomb and the Mg triangular lattice layers, each Mg atom transfers two electrons to the B honeycomb and thus B has a valence of -1 to form graphene-like honeycomb layers. Here, to stabilize the more complicated kagome lattice, we still employed an atomic Mg layer, which can be seen from the bulk Mg(0001) plane. The reasons are as follows. (1) The B kagome lattice, with optimized lattice parameters of a = b = 3.31 Å, matches well with the bulk Mg(0001) plane, which has lattice parameters of 3.21 Å. (2) In the MgB₆ form, 1/3 electron can transfer to one boron, close to the proposed electron deficiency of 0.4 per boron. The suggested structure is shown in Fig. 2. Two B kagome layers sandwich a Mg layer with relaxed lattice parameters of 3.40 Å. From the top view, the Mg atoms are located at the centers of the hexagonal holes of the B kagome layer to promote electron transfer. This is different from bulk MgB₂, in which the Mg atoms are located at the honeycomb centers from the top view. The detailed structure parameters for the 2D MgB_6 crystal are given in Table 1.



Fig. 2 The structure of MgB_{6} . (a) is the top view and (b) is the side view. The blue rhombic frame indicates the unit cell of MgB_{6} . The yellow and green balls represent B and Mg, respectively.

Table 1 $\,$ Optimized lattice constants and atomic positions for 2D MgB_6

Lattice constant	Atomic position
a = b = 3.404 Å c = 31.398 Å $\alpha = \beta = 90^{\circ}$ $\gamma = 120^{\circ}$	B (0.5, 0.5, 0.442) B (0, 0.5, 0.442) B (0.5, 0, 0.442) B (0.5, 0.5, 0.558) B (0, 0.5, 0.558) B (0.5, 0, 0.558) Mg (0, 0, 0.5)



Fig. 3 (a) Phonon dispersion of 2D MgB₆. (b) Bond length evolution at 300 K for an 8 ps molecular dynamics simulation. The black, red and blue lines represent the B–B bond, B–Mg bond and Mg–Mg bond, respectively.

Compared with bulk MgB_6 ,³⁴ this 2D MgB_6 crystal has a formation energy higher by 0.42 eV per atom due to the lack of bonding along the *z* axis. However, the dynamic stability of this 2D lattice is verified by its phonon dispersion without any imaginary frequency, as shown in Fig. 3a. Thus, the suggested 2D MgB₆ structure is a local minimum in the energy landscape. The largest frequency approaches 1200 cm⁻¹ at the Gamma point. The structure is also stable at room temperature, which can be inferred from the *ab initio* molecular dynamic simulations at 300 K in Fig. 3b. During an 8 ps simulation, the B–B, B–Mg, and Mg–Mg bond lengths all have very small fluctuations around their equilibrium bond lengths. Those results suggest that the present 2D structure is metastable and may at least possibly exist at room temperature.

To understand the stability, the local bonding between neighboring atoms was visualized. Here, the electron localization function (ELF) was used to analyze the bonding characteristics. Fig. 4a–c highlight sliced planes containing B–B, Mg–Mg, and B–Mg bonds. Fig. 4d–f display their corresponding ELFs. The ELF is about 0.8 between neighboring B atoms in Fig. 4d, which suggests a covalent B–B bond for the B kagome layer. Yet, the covalent character is not so obvious compared with the B–B bond in the B honeycomb layer of MoB₄ with an ELF of about 0.9.²⁴



Fig. 4 Electron localization function (ELF) of MgB_6 . (a–c) are slabs cut along the B–B bond, Mg–Mg bond and B–Mg bond planes. (d–f) are their corresponding ELFs. Color coding of atoms is the same as in Fig. 2.

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The ELF in the Mg–Mg layer, as shown in Fig. 4e, is about 0.3, suggesting low electronic density in this region. This is different from the bulk Mg metal with homogenous electron gas. The reason is that Mg transfers its electrons to the B kagome layer in 2D MgB₆, with little charge to form metallic bonds in its own plane. The ELF between the B atoms and Mg atoms has a significant contrast in Fig. 4f, indicating the formation of an ionic bond. Bader charge analysis also proves that Mg transfers electrons to its neighboring B atoms to form the ionic bond. Thus, the covalent bond of the B kagome layer and the ionic bond between B and Mg together stabilize this 2D structure.

Usually, 2D structures have higher formation enthalpies than the ground states of their bulk forms. For example, silicene has an energy cost 0.76 eV per atom greater than that of its bulk silicon.³⁵ Thus, silicene needs to be prepared on a metal substrate experimentally.¹⁰ Similarly to silicene, the proposed MgB₆ may be produced on a Mg(0001) substrate with consideration of the lattice match. With the molecular beam epitaxy (MBE) technique, the first B kagome layer might be obtained on the Mg substrate. Through the subsequent deposition of a Mg layer and the second B kagome layer, 2D MgB₆ may be possibly produced experimentally.

Next, the electronic band structure for this 2D MgB₆ structure is shown in Fig. 5a. Interestingly, at the *K* point of the first Brillouin zone, a Dirac point just crosses the Fermi level. Yet the band structure is different from that of graphene: several other bands also cross the Fermi level, making MgB₆ metallic. The states of the Dirac cone are mainly from the p_z orbital of the B kagome lattice, which can be inferred from its orbital spatial distribution in Fig. 5d. For graphene, the Dirac point states are derived from the p_z orbital of the honeycomb structure. So, in addition to the honeycomb structure, the kagome lattice may be another atomic conformation to form a Dirac point. From the atomic projected density of states (DOS) in Fig. 5b and c, the states are mainly derived from the p orbital of B whereas Mg has little contribution near the Fermi level.



Fig. 6 (a) Electron-phonon coupling parameter λ and (b) atomicallydecomposed phonon DOS of MgB₆.

This further proves that Mg donates electrons to the B kagome lattice. The metallic energy band of this structure suggests it to be a good choice of electrode material in future nanoelectronic devices.

As a compound which contains B and Mg, MgB₆ also has electron phonon coupling interactions. Fig. 6a and b give the phonon DOS and their Eliashberg function $[\alpha^2 F(\omega)]$. The strong EPC derives from the phonon modes around 360 cm⁻¹, which are mainly contributed by the vibration of the boron kagome lattice, along with a small contribution from the triangular Mg lattice. The frequency at about 360 cm⁻¹ is at the lower end of the frequency range of boron kagome layer and at the higher end of the frequency range for the Mg layer, so the coupling vibration for boron and Mg also contributes to the strong EPC around 360 cm⁻¹. These frequency modes are mainly contributed by the out-of-plane vibration of the boron kagome lattice, along with a small contribution from the B, Mg optical phonon



Fig. 5 Electronic structure of MgB₆. (a) Band structure of MgB₆. The dashed red ellipse marks the Dirac point. (b) and (c) are the projected DOS for B and Mg atoms. (d) Charge density plots of states at Dirac points of 2D MgB₆ with an isosurface value of $0.01 \text{ e } a_0^{-3}$. Here, a_0 is the Bohr radius. Up and down represent the two crossing states in the Dirac cone.

mode in the *z*-axis. This is similar to the case of a Li-doped graphene system in which the main contribution to the EPC originates from carbon vibration along the *z*-axis incorporated with Li modes.³² The EPC is quite different from that of bulk MgB₂.^{33,36,37} In MgB₂, the strong EPC derives from the phonon frequency at about 500 cm⁻¹, which arises from the E_{2g} phonon modes of the σ bond in the boron plane to distort the boron hexagon.³⁷ The total EPC parameter λ in bulk MgB₂ is 0.77 (ref. 37) and in the present 2D MgB₆ is 0.45. According to the Allen–Dynes formula,³⁰ if the Coulomb parameter μ^* is taken as 0.1, which has been previously applied to MgB₂,³⁸ the superconductivity critical temperature of 2D MgB₆ is lower than that of bulk MgB₂, it is another example of a Mg–B compound with superconductivity besides MgB₂.

The suggested 2D MgB₆ material also can be used as a hydrogen storage material when the metal atoms are decorated with Ca. Ca has a strong binding energy of about 3.0 eV with MgB₆, which is even 0.3 eV larger than that of Ca on graphyne.³⁹ The strong binding energy can be understood by its metastable lattice with an indication of a certain degree of chemical activity. Also, the binding energy is far larger than the cohesive energy of bulk Ca metal (1.84 eV per atom), which prevents the clustering of Ca atoms and thus hints at its dispersed distribution. Considering the van der Waals interactions,⁴⁰ this under-coordinated Ca can maximally bind five H₂, as shown in Fig. 7. The distances of Ca and H₂ are around 2.56–2.61 Å, slightly larger than that of Ca on graphyne.³⁹ The bond lengths of the H_2 molecules are 0.762–0.765 Å, as shown in Table 2. The additional binding energies upon adding another H₂ molecule are listed in Table 3, ranging from 0.14 eV to 0.30 eV per H₂ molecule, indicating that the



Fig. 7 H_2 chemical adsorption on Ca-decorated MgB₆. The blue and pink balls represent Ca and H, color-coding of other atoms is the same as in Fig. 2.

Table 2 Calculated $d_{\rm Ca-H}$ and $d_{\rm H-H}$ of five $\rm H_2$ adsorbed by Ca on 2D $\rm MgB_6$

H_2 (<i>n</i> th)	1	2	3	4	5			
$d_{\mathrm{H-H}}(\mathrm{\AA})$	0.764	0.765	0.762	0.765	0.764			
$d_{\text{Ca-H}}(A)$	2.561	2.603	2.612	2.578	2.580			

Table 3 The calculated additional (step-by-step) binding energy of H_2 molecules (eV per $H_2)$ on Ca decorated MgB_6 system

Ordinal number of H ₂	1	2	3	4	5
Additional binding energy	0.30	0.27	0.27	0.17	0.14

structure may be a suitable candidate for hydrogen storage at room temperature.⁴¹

Conclusion

In summary, we have successfully designed a 2D sandwich structure with two B kagome layers and an Mg layer. The structure is metallic with several bands crossing the Fermi level, two of which form the Dirac cone dispersing around the K point of the first Brillouin zone. The metallic electronic property suggests this structure may be a good electrode material in nanoelectronic devices. The 2D MgB₆ also has superconductivity, thus representing another superconductor besides MgB₂. This metastable structure with relatively high chemical reactivity can also be used in hydrogen energy storage. The present studies expand the field of 2D boron based materials for future nanoelectronics.

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