Theoretical prediction of phonon-mediated superconductivity with $T_c \approx 25$ K in Li-intercalated hexagonal boron nitride bilayer

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A superconducting transition temperature ($T_c$) up to 25 K in the Li-intercalated bilayer of hexagonal boron nitride (h-BN) is predicted according to ab-initio calculations. A $T_c$ higher than that of metal-intercalated graphene (MIG) is ascribed to the characteristic spatial distribution of electronic states near the Fermi level, which is distinctly different from that in MIG. In the Li-intercalated bilayer h-BN, the breaking of the symmetrical restriction and the increase in the overlap between the charge density and the Li in-plane motion enhance the electron–phonon coupling. Our results provide a new design guideline for two-dimensional superconductors based on intercalated layered materials.

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Two-dimensional (2D) materials have attracted attention as a new class of materials for applications in novel nanodevices. The varieties of chemical compositions among 2D materials enable us to realize almost every electronic property, such as metallic, semimetallic, semiconducting, insulating, and superconducting. Additionally, 2D superconductors will enable the manufacture of nano-superconducting quantum interference devices, which are important for realizing next-generation quantum information techniques. Therefore, researchers have performed extensive theoretical and experimental research to identify 2D superconductors.

The most well-known 2D superconductor is metal-decorated/intercalated graphene. Pristine graphene is not a superconductor, owing to its small density of states (DOS) around the Fermi level ($E_F$) and its symmetrical restriction in the electron–phonon coupling. The decoration or intercalation of alkali metal increases the DOS around $E_F$ via electron doping and gives rise to an additional interlayer band and vibrational modes, which enhance the electron–phonon coupling. The resulting superconducting transition temperature ($T_c$) reaches ~8.1 K.

The candidate materials for 2D superconductors are not limited to graphene-based materials. For example, silicene—the Si cousin of graphene—is also predicted to behave as a BCS-type superconductor after electronic doping. Recently, borophene (monolayer B compounds) and Li-intercalated phosphorene (bilayer of black phosphorus) were predicted to exhibit 2D superconducting properties with a $T_c$ higher than 15 K. These examples suggest the possibility of realizing a wide variety of novel superconductors based on 2D materials consisting of light elements.

In this study, hexagonal boron nitride (h-BN) is investigated as a new candidate for 2D superconductor materials. Both bulk and monolayer h-BN have wide energy bandgaps of approximately 5 eV, which makes them less suitable than other 2D materials as superconductors. Consequently, they have been less studied as candidates for superconductors. However, the metalization of h-BN via alkali-metal intercalation has been predicted theoretically. Additionally, Li-intercalated bulk h-BN materials were recently synthesized. The stronger interlayer interaction in h-BN compared with graphene might be advantageous for enhancing the electron–phonon coupling. Considering these factors, in the present study, ab-initio calculations were performed on the superconducting properties of systems comprising h-BN; specifically, Li-intercalated h-BN bilayer (hBN–Li–hBN). The obtained $T_c$ of 25 K is far higher than the previously reported values for metal-decorated/intercalated graphene. We also compared hBN–Li–hBN with Li-intercalated bilayer graphene (G–Li–G) to investigate the origin of the pronounced superconductivity in hBN–Li–hBN. We found that hBN–Li–hBN exhibits a higher $T_c$ than G–Li–G, which is because of the formation of characteristic bonds connecting two B atoms in the upper and lower h-BN layers, which results from the weak electronegativity of B. This finding provides a new guideline for designing 2D superconductors with a high $T_c$.

Ab-initio calculations were performed according to density functional theory and density functional perturbation theory using the QUANTUM ESPRESSO package. We adopted the local density approximation scheme for the exchange–correlation functional. The norm-conserving pseudopotentials created by the Martins–Troullier method were used for all the atoms in the models to describe the electron–ion interaction. Three-dimensional periodic boundary conditions and a slab model, where a vacuum layer over 12 A was introduced to avoid interaction between the neighboring unit cells along the z-axis, were adopted. The plane wave basis set was introduced, and the kinetic-energy cutoff and the charge cutoff were set as 60 and 240 Ry, respectively. The structures were fully relaxed until the forces acting on the atoms decreased below 1.0 × 10⁻² a.u. The Brillouin zone was sampled by 24 × 24 × 1 (12 × 12 × 6) k-mesh for 2D (bulk) structures. The dynamical matrices and phonon deformation potentials were calculated on a Γ-centered $6 \times 6 \times 1$ (6 × 6 × 3) q-mesh. The electron–phonon coupling constant and Eliashberg function were evaluated via interpolation using the maximally localized Wannier functions (MLWFs) through the Electron–Phonon Wannier package. MLWFs were determined on a 12 × 12 × 1 (12 × 12 × 6) k-mesh, and then the electron–phonon coupling quantities were interpolated on a fine electron (phonon) mesh of 120 × 120 × 1 (60 × 60 × 1) for 2D models, as well as 40 × 40 × 20 (20 × 20 × 10) for a bulk system.
First, we determine a stable structure of the hBN–Li–hBN system. In bulk h-BN, α–β layer stacking, where the B atoms of the upper layer are placed on top of the N atoms of the bottom layer and vice versa, is the stable configuration. However, the other stacking arrangement, where the B atoms of the upper layer are placed on top of the B atoms of the bottom layer (α–α stacking), may be stable when Li atoms are intercalated. We describe the unit cell of hBN–Li–hBN as a $\sqrt{3} \times \sqrt{3}R30^\circ$ h-BN supercell containing one Li atom and calculate the Li intercalation energy for α–β stacking and α–α stacking of the bilayer h-BN. We find that in the presence of intercalated Li atoms, the α–α stacking is stable and energetically more favorable than α–β stacking. A similar structural transformation is experimentally suggested for bulk Li-intercalated h-BN. Therefore, in the following analysis, we use the α–α stacking model (structural model and parameters are shown in Fig. 1 and Table I, respectively).

As shown in the electronic band dispersions and DOS in Fig. 2, hBN–Li–hBN becomes metallic because of the charge transfer from the Li atom. The interlayer band originating from the Li atom appears at approximately +1 eV from $E_F$. This is different from the case of Li-decorated graphene, where an interlayer band crosses $E_F$. The aforementioned stability and metallic states are obtained regardless of the exchange–correlation functional (for details, see Table S1 in the online supplementary data at http://stacks.iop.org/APEX/10/093101/mmedia). The phonon band dispersion, phonon DOS, isotropic Eliashberg function $\alpha^2F(\omega)$, and electron–phonon coupling constant $\lambda(\omega)$ of hBN–Li–hBN are shown in Fig. 3. $\alpha^2F(\omega)$ exhibits a high intensity over the entire energy region, which results in a large value of $\lambda$ (> 1.17).

$T_c$ is estimated as 25 K according to the McMillan–Allen–Dynes formula, and a Coulomb repulsion pseudopotential of $\mu^* = 0.14$ is employed, which was used in a previous calculation to reproduce experimental results. Compared with the other phonon-mediated 2D superconductors – Li-decorated graphene (5.7–8.1 K) and Ca-intercalated bilayer graphene (6.8–8.1 K) – this value is high and comparable to the highest reported values of $T_c$ induced by phonons in MgB$_2$ (39 K). To confirm this high $T_c$, we first checked the convergence of $T_c$ with respect to the calculation setup. Second, we estimated $T_c$ using the other two available methods: estimation via the McMillan–Allen–Dynes formula with the electron–phonon coupling on the coarse k- and q-mesh directly obtained by a density functional perturbation theory calculation and solving the anisotropic Eliashberg equations using Wannier interpolated electron–phonon coupling.

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**Table I.** Calculated parameters of hBN–Li–hBN and G–Li–G.

|           | $a$ (Å) | $c$ (Å) | $N(E_F)$ | $\lambda$ | $T_c$ (K) |
|-----------|---------|---------|----------|-----------|-----------|
| hBN–Li–hBN | 4.32    | 1.71    | 1.31     | 1.17      | 24.7      |
| G–Li–G     | 4.23    | 1.80    | 1.83     | 0.42      | 1.2       |

$a$ and $c$ are the crystal structural parameters indicated in Fig. 1. $N(E_F)$ is electronic density of states (eV/spin/unit cell) at the Fermi level. $\lambda$ is the total electron–phonon coupling, and $T_c$ is the superconducting critical temperature.
We found that their results are consistent with $T_c\approx 25\text{ K}$ (for details, see Figs. S1–S3 in the online supplementary data at http://stacks.iop.org/APEX/10/093101/mmedia). These results strongly support the observation that the $T_c$ in Li-intercalated bilayer h-BN is higher than that in metal-intercalated graphene.

These results raise a fundamental question: what is the origin of such a high $T_c$? To answer this, we calculated the same properties in Li-intercalated bilayer graphene (G–Li–G), for comparison. Similar to the case of hBN–Li–hBN (Fig. 1), the $\sqrt{3}\times\sqrt{3}\text{R}30^\circ$ unit cell was adopted, and the values of the structural parameters are listed in Table I. The calculated electronic band dispersion and DOS of G–Li–G are shown in Fig. 2. Both hBN–Li–hBN and G–Li–G have no interlayer (IL) band deriving from the Li s-orbital. The large number of bands originating from $\pi^*$ electrons in C atoms at $E_F$ leads to an increase in the DOS at $E_F$ [$N(E_F)$] in G–Li–G (see Table I). Although $N(E_F)$ is the main factor for increasing $\alpha^2 F(\omega)$ in phonon-mediated superconductors, the obtained $\alpha^2 F(\omega)$ for G–Li–G (in Fig. 3) exhibits smaller values in the low-energy region compared with that for hBN–Li–hBN. Consequently, as summarized in Table I, the total $\chi$ for G–Li–G are far smaller than those in hBN–Li–hBN.

On the basis of the previous studies on the superconductivity of metal-doped graphene, we can classify the phonon energy into the following three regions, according to the characteristics of $\alpha^2 F(\omega)$: the high-energy region where C in-plane vibrational modes (150–200 meV) mediate the transition between $\pi^*$–$\pi^*$ electronic states, the middle-energy region (50–100 meV) where C out-of-plane vibrational modes are the major cause of the scattering between $\pi^*$–IL electrons ($\pi^*$–$\pi^*$ scattering process is symmetrically forbidden by the selection rule), and the low-energy region (20–50 meV) where the in-plane vibration of adatoms gives rise to the coupling of $\pi^*$–$\pi^*$ electrons. In the case of G–Li–G, there is no IL electron, and a small $\alpha^2 F(\omega)$ is observed in the middle-energy region, as for Li-intercalated graphite. On the other hand, as for hBN–Li–hBN, $\alpha^2 F(\omega)$ exhibits a high intensity in the high-energy region, as well as the middle- and low-energy regions. According to the analogy drawn from the case of graphene, it is expected that the large $\alpha^2 F(\omega)$ in the middle- and low-energy regions originates from the $\pi^*$–$\pi^*$ electronic transition process via B/N out-of-plane and Li in-plane vibrational modes, respectively.

The reason for the improved electron–phonon interaction with B/N out-of-plane and Li in-plane vibrational modes in the case of hBN–Li–hBN is revealed by the distribution of the wavefunctions of several eigenstates around $E_F$. Figure 4 plots the charge-density distribution of the states indicated by the blue points on the electronic band dispersion in Fig. 2. The marked difference between hBN–Li–hBN and G–Li–G is the distribution of the charge density along the out-of-plane direction. The charge-density distributions connect the B atoms of the upper and bottom layers in hBN–Li–hBN. Such a spatial distribution of the wavefunction increases the electron–phonon scattering cross section via the Li in-plane vibrational modes and breaks the symmetrical restriction about $\pi^*$–$\pi^*$ scattering via B/N out-of-plane vibrational modes. The emergence of electron–phonon coupling due to the absence of the symmetrical constraint is also theoretically predicted in Li-intercalated bilayer phosphorene and has been experimentally confirmed in metal-intercalated black phosphorus. The symmetry breaking in the two aforementioned examples originated from the puckered structure in the phosphorene layer, which differs from what we propose in hBN–Li–hBN. Compared with hBN–Li–hBN, in G–Li–G, the charge density is localized on the respective graphene layers, and the intensity in the interlayer region is small. This striking difference of the charge-density distribution is universally observed in other eigenstates near $E_F$. Hence, this mechanism giving rise to electron–phonon coupling is retained even if the Fermi level shifts. The delocalized wavefunction in hBN–Li–hBN can be attributed to the nature of the B atom, i.e., its weak electronegativity. The bonds connecting the h-BN layers make the system more energetically stable, which explains the change of the stacking order from $\alpha$–$\beta$ to $\alpha$–$\alpha$ in hBN–Li–hBN.

The Li-intercalated bulk hBN (Li-hBN bulk) exhibits a lower $\chi$ (≈ 0.66) and $T_c$ (≈ 8.23 K) than hBN–Li–hBN, while the strong electron–phonon interaction is retained in bulk Li-hBN in the low-phonon energy region. The reason for the suppression of $\lambda$ is the blue shifts of the vibrational modes (Fig. 5). This result suggests the possibility to realize a higher $T_c$ in both the Li-intercalated h-BN bilayer and the bulk material by introducing strain or pressure that induces a redshift of the Li and B/N vibrational modes.
In summary, by using ab-initio calculation, we predicted that a Li-intercalated h-BN bilayer behaves as a novel 2D superconductor. Both $T_c$ estimation via the McMillan–Allen–Dynes formula and anisotropic Eliashberg equations yield $T_c \approx 25$ K, which is far higher than the values corresponding to all metal-doped graphene materials. The origin of such a high $T_c$ is the formation of an interlayer bond state between B atoms, which are strongly coupled to the Li in-plane and B/N out-of-plane vibrational modes. This is distinctly different from the electron–phonon coupling in other intercalated layer compounds. Our findings will provide a new guideline for designing 2D superconductors.

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