Coexistence of Superconductivity and Superhardness in Beryllium Hexaboride Driven by Inherent Multicenter Bonding

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ABSTRACT: Unique multicenter bonding in boron-rich materials leads to the formation of complex structures and intriguing properties. Here global structural searches are performed to unearth the structure of beryllium hexaboride (BeB₆) synthesized decades ago. Three BeB₆ phases (α, β, and γ) were predicted to be stable at ambient and high pressures. The ground state at ambient pressure, α-BeB₆, consists of a strong and uniformly distributed covalent B–B network, which results in exceptional elastic properties and a hardness of 46 GPa comparable to γ-B. Even more surprisingly, α-BeB₆ retains credible electron phonon coupling in the boron sublattice, and is predicted to be superconducting at 9 K. Above 4 GPa, β-BeB₆ is stabilized with alternating boron slabs and triangular beryllium layers analogous to the structure of MgB₂. The γ-BeB₆ is predicted to be superconducting at 24 K, similar to Nb₃(Al,Ge). The γ-BeB₆ is stable above 340 GPa. The understanding of intrinsic multicenter-bonding mechanism and related properties demonstrated in the very example of BeB₆ provides new insights for the design of tunable multifunctional materials.

B oron-rich materials are of great scientific interest for fundamental research and industrial applications. The versatility of boron bonding in solids has led to the realization of novel materials with intriguing properties. In many transition metal borides, e.g., OsB₂, ReB₂, and WB₂, strong B–B covalent network enhances the mechanical strength, resulting in superhardness. In MgB₂, strong electron–phonon interaction arises in a stiff sp² B–B network, driving this otherwise ordinary compound to superconductor at 40 K. Recent discoveries revealed, remarkably, that covalency, metallicity, and superconductivity may coexist in metal borides. Once combined with metal elements, B can form multicenter bonding with the “electron deficient” characteristics. A neighboring element, beryllium, is a light metal but well-known for its capability of forming covalent bonds. Combining B and Be, the Be–B systems are incredibly both covalent and metallic, and even possibly superhard. A number of beryllium borides were known. Beryllium tetraboride (BeB₄) was established experimentally at room temperature. High-temperature beryllium diboride (BeB₂) and hexaboride (BeB₆) phases have been reported more than half century ago, but their crystal structures are still unclear. BeB₂ was later proved to be in a complex BeB₂.75 stoichiometry with superconductivity (Tc = 0.72 K). Recent theoretical studies suggested a series of the stable structures from Be₅B to BeB₆, in which BeB₂ was predicted to be superhard.

Still, there is scant knowledge on beryllium hexaboride (BeB₆), although the hexaborides with other alkaline earth metals have been well studied. CaB₆ is a technologically important material with exceptional electrical conductivity. MgB₆ were predicted to be stable, and the synthesis is being actively attempted. Considering the promise of metal borides as tunable multifunctional materials, establishing the structure–property relationship of BeB₆ and the route for synthesis should be immediately pursued. This is accomplished in the present work via an ex nihilo exploration of the stable structures and properties of BeB₆ using a global structure search methodology. For the first time, the crystal structures of BeB₆ were identified at ambient and high pressures. Interestingly, BeB₂ was calculated to have both superconducting and superhard properties, which is very unusual but exciting. The BeB₆ is predicted to have a nontrivial Tc at 9 K.
comparable to that of MgB$_2$ and a very high hardness comparable to that of superhard $\gamma$-B. The importance of multicenter boron bonds is demonstrated in structural configurations and properties, which provide insights on the boride-based multifunctional materials.

Structural searches for BeB$_x$ ($x = 4, 6$ and $7$) were performed with 1–4 formula units (f.u.) per unit cell over a wide pressure range 0–450 GPa using the particle swarm optimization (PSO) algorithm implemented in the CALYPSO code,$^{24,25}$ combined with first-principles calculations. The method has been proven to be effective in predicting the structures of various compounds under pressure.$^{26-28}$ To test the credibility of this method, we have searched for the structures of BeB$_4$ and compared the results with ref $^{18}$. All structures reported in ref $^{18}$ have been successfully recovered by us with well reproduced phase transition pressures (Figure S1a in the Supporting Information). In addition, a new $P4_4/mmm$-type structure was predicted to be stable above 450 GPa (Figure S2a in the Supporting Information).

Enthalpies of the most stable structures of BeB$_6$ are compared in Figure 1 over the pressure range 0–400 GPa (see Table S1 for structural parameters in the Supporting Information). At ambient pressure, the most stable structure is a monoclinic $P2/m$ structure (denoted as $\alpha$-BeB$_6$). The $\alpha$-BeB$_6$ transforms to a trigonal P3 structure (denoted as $\beta$-BeB$_6$) near 4 GPa, which further transforms to another trigonal P3c1 phase (denoted as $\gamma$-BeB$_6$) at 340 GPa. The $\gamma$-BeB$_6$ is stable to at least 450 GPa. Relative stability of BeB$_6$ with respect to other Be–B phases was established by comparing the formation enthalpies ($\Delta H_f$) of known Be–B phases at different pressures (Figure S3 in the Supporting Information). At ambient pressure, BeB is the most stable stoichiometry. BeB$_6$ appears to be metastable at ambient but quickly becomes stable at high pressure. At 200 GPa, the $\Delta H_f$ of BeB$_6$ is $-135$ meV/atom, about 9 meV/atom above the convex hull, indicating good thermodynamic stability. In addition, the BeB$_6$ can be further stabilized at high temperature as revealed by previous experiment.$^{29,30}$ The dynamic stability of BeB$_6$ was established by phonon calculations. The absence of imaginary frequency confirms the stability of all three predicted phases (Figure S4 in the Supporting Information).

The $\alpha$-BeB$_6$ structure features rhomboid B$_4$ units, which are interconnected to extended B$_6$ ribbons and intercalated by beryllium (Figure 2a,b). This motif bears similarity to transition metal borides, but differs significantly from MgB$_6$ and CaB$_6$.$^{20,22}$ In both MgB$_6$ and CaB$_6$ metals act as electron donors, and B forms the B$_6$ octahedrons. It also differs from the bonding pattern in MgB$_2$, where the electronic octet is fulfilled by transferring the valence electrons of Mg to B, forming covalently bonded boron sheets that are isoelectronic to graphene. In BeB$_6$, the Be atom in fact participates in the (partially covalent) Be–B bonding rather than severing as an electron donor, which dictates that the structure of BeB$_6$ differs from other Zintl–Klemm compounds. The rhomboid B$_4$ in $\alpha$-BeB$_6$ has two distinct edge lengths, 1.776 and 1.893 Å, while neighboring units are connected by a shorter bond of 1.674 Å. This range of bond lengths is comparable to that of $\alpha$-B (1.669–2.020 Å)$^{30}$ and $\gamma$-B (1.661–1.903 Å)$^{31}$ The shortest bond (1.674 Å) is considerably shorter than those in FeB$_4$ (1.714 Å)$^{32}$ and WB$_4$ (1.698 Å)$^{33}$ suggesting a strong covalent network. The Be–B bond length in $\alpha$-BeB$_6$ is 1.873 Å, already within the sum of covalent radii of Be (1.02 Å) and B (0.85 Å)$^{34}$ The $\beta$-BeB$_6$ features cage-like boron slabs intercalated by beryllium (Figure 2c,d). The B–B bond lengths in the slab range from 1.740 to 1.977 Å, and within the interslabs, the B–B bonds are varied as well (1.800, 1.805, and 1.892 Å), while the Be–B bond lengths change from 1.952 to 2.023 Å, slightly greater than those in the $\alpha$-BeB$_6$. The $\gamma$-BeB$_6$ (Figure 2e,f) features buckled boron sheets similar to the 2D boron allotrope.$^{35}$ The formation of these sheets is a result of competition between two- and three-center bonding, which induces a Be$_2$ isoceles triangle (with bond lengths of 1.789 and 1.843 Å) connected by distorted B$_4$ rhomboids (with bond lengths of 1.745–2.023 Å). Remarkably, the shortest Be–B bond length in $\gamma$-BeB$_6$ is 1.790 Å, much shorter than those in $\alpha$-BeB$_6$ and $\beta$-BeB$_6$. This bond length is between typical single (1.87 Å) and double (1.68 Å) Be–B covalent length,$^{35}$ implying the relatively strong Be–B bonding in $\gamma$-BeB$_6$.

Intriguingly, the structure of $\beta$-BeB$_6$, e.g., slightly buckled B slabs alternated with triangular Be layers, closely resembles the structure of MgB$_2$ (hexagonal Mg layers alternated with graphitic B layers). The $c/a$ ratio of $\beta$-BeB$_6$ 1.12, is also very close to that in MgB$_2$ 1.14.$^{36}$ This structural similarity immediately called for the investigation of possible superconductivity in $\beta$-BeB$_6$. Assuming an isotropic superconducting gap, the calculated electron–phonon coupling parameter ($\lambda$) for the $\beta$-BeB$_6$ is 0.8, indeed similar to the value for MgB$_2$ (0.7) at the same level of theory. The average phonon frequency $\omega_{\text{ph}}$ in $\beta$-BeB$_6$ is 635 K. Using the Allen and Dynes extension of the McMillan equation,$^{36,37}$ and a nominal Coulomb pseudopotential ($\mu$*) of 0.13, the estimated superconducting critical temperature $T_c$ of $\beta$-BeB$_6$ is 24 K, close to the $T_c$ of Nb$_3$(Al,Ge) (23 K),$^{38}$ but lower than that of MgB$_2$ (39 K). The $\lambda$ and $\omega_{\text{ph}}$ of $\beta$-BeB$_6$ are much lower, e.g., 0.61 and 523 K, resulting in a lower estimated $T_c$ of 9 K. Finally, $\lambda$ for $\gamma$-BeB$_6$ is 0.57 with much lower $\omega_{\text{ph}}$ 248 K, using a $\mu^*$ = 0.13, and the evaluated $T_c$ is 3 K.

The elastic properties (Table S2 in the Supporting Information) suggest all three BeB$_6$ phases fulfilling the Born-Huang criterion.$^{39}$ Significantly, $\alpha$-BeB$_6$ exhibits an exceptionally high $C_{11}$ value of 827 GPa, even greater than that of cubic BN (820 GPa). This indicates an ultra-incompressibility of the short B–B bonds along the [001] direction. The bulk moduli for $\alpha$–B, $\beta$–B, and $\gamma$-BeB$_6$ are 222, 230, and 222 GPa, respectively, similar to $\alpha$-B, $\gamma$-B, B$_6$O, and B$_{13}$C$_2$ (211–228 GPa). Another intriguing finding is the high shear modulus of $\alpha$-BeB$_6$ (227 GPa) comparable to that of superhard $\gamma$-B (238 GPa). Furthermore, the Pugh’s ratio ($G/B$) of $\alpha$-BeB$_6$ is 1.02, again...
close to that of $\gamma$-B, 1.07. The Poisson’s ratio of $\alpha$-BeB$_6$ (0.12) is lower than that of $\beta$-BeB$_6$ (0.18), $\gamma$-BeB$_6$ (0.17), $\alpha$-B (0.14), and B$_6$O (0.15), but slightly higher than $\gamma$-B (0.11). The elastic similarity of $\alpha$-BeB$_6$ to $\gamma$-B indicates that the $\alpha$-BeB$_6$ may be a superhard material as well. Using an empirical model, we estimated the hardness of these materials. The estimated hardness for $\alpha$-B and $\gamma$-B are 39.8 and 50 GPa, respectively, in a very good agreement with the experimental values. The $\alpha$-BeB$_6$ was found as the hardest among the three BeB$_6$ phases, with the estimated hardness of 46.0 GPa, greater than those in $\beta$-BeB$_6$ (31.1 GPa) and $\gamma$-BeB$_6$ (31.9 GPa). It is significant that $\alpha$-BeB$_6$ may be a new superhard material with a low density.

The electronic band structures and density of states (DOS) for $\alpha$, $\beta$, and $\gamma$-BeB$_6$ are presented in Figure 3 and Figure S5 in the Supporting Information. All three structures have a metallic ground state, which, remarkably, is induced by covalent bonds. This is seen from the DOS at the Fermi level dominated by the B-$p$ bands, as well as the hybridization between B-$p$ and Be-$p$ bands in the valence region. Yet, the contribution of Be-$s$ states to the DOS is negligible, consistent with the characteristic of Be in which the $p$ orbitals usually participate in bonding. The DOS of $\alpha$-BeB$_6$ shows an impressive pseudogap, over 2.0 eV, around the Fermi level (Figure 3d). The DOS values within the pseudogap are almost constant, which results from the steep, nearly linear band (B-$p_x$ in $\Gamma$–Z, B-$p_y$ in D–E, and B-$p_z$ in B–D direction of Figure 3a). For $\beta$-BeB$_6$ and $\gamma$-BeB$_6$, the Fermi levels are outside the pseudogap.

The structural analogy between $\beta$-BeB$_6$ and MgB$_2$ results in similarities in their electronic structures. In $\beta$-BeB$_6$, all bands across the Fermi level are highly dispersive (Figure 3b). The B-$p_z$ states around the H point have 3D characteristics, while the $p_x$ and $p_y$ states along $\Gamma$–A are typically 2D. The 2D band along $\Gamma$–A indicates $\sigma$ bonding within the boron slabs, which induces strong electron–ion scattering and electron–phonon coupling and hence high $T_c$ (24 K). However, the boron slabs are slightly puckered, resulting in deformed $sp^2$ surface states (opposite to the planar honeycomb layer in MgB$_2$). Thus, the $\sigma$ bond in $\beta$-BeB$_6$ is weaker than that in MgB$_2$, responsible for a lower $T_c$. In
γ-BeB₆, on the other hand, the pₓ and pᵧ states are 3D, which mix with the pᶻ states forming nearly linear dispersion across the Fermi level. This corresponds to a 3D boron sublattice rather than 2D boron sheets. Calculated Bader charges indicate substantial charge transfer (∼1.65 e⁻) from Be atom to B₆ group, as found in the three BeB₆ phases, similar to that of MgB₂ (∼1.63 e⁻/Mg). As found in MgB₂, this electron transfer is critical for exotic electronic structures, as such graphite is isoelectronic to MgB₂ but only superconducting at 5 K when doped. The presence of Mg⁰²⁺ potential in the lattice strongly attracts the nonbonding π electrons causing σ to π transition. The deformed σ bands, as absent in graphite, contribute most of the electron–phonon coupling accounting for superconductivity. Such electronic deformation is also expected in BeB₆ in particular for the surface states of the B slabs. To provide insights into the predicted superhardness, the valence charge densities (VCD) for α-BeB₆, β-BeB₆, and γ-BeB₆ were calculated (Figure 4a–c). In α-BeB₆ the valence electrons are accumulated along B–B bonds and distributed uniformly in the lattice, forming a 3D isotropic covalent network (Figure 4a). This bonding situation is analogous to that of diamond, which results in high elastic moduli and superhardness. In β-BeB₆ and

Figure 3. Electronic band structure and density of states for α-BeB₆ (a,d), β-BeB₆ (b,e), and γ-BeB₆ (c,f). The horizontal dashed line in panels a, b, and c and the vertical solid line in panels d, e, and f represent Fermi level. Dominant B-p states at the Fermi level are responsible for the metallic feature.

Figure 4. Valence charge density of (a) α-BeB₆, (b) β-BeB₆, and (c,d) γ-BeB₆ in top and side views. The isovalue surfaces are plotted with the value of 0.75 e⁻/Å³. (e,f) Voronoi deformation density plotted on the (010) plane in α-BeB₆ showing rhomboid B₄ units and Be₂B₂ units. The valence charge density difference in the B₃ scalene in α-BeB₆ is shown in panel e.
\( γ \)-Be\( _{2}B_{6} \) on the other hand, the covalent bonds are distributed unevenly in the lattice. In \( β \)-Be\( _{2}B_{6} \), the valence electrons are primarily accumulated within the B slabs, leaving the interslab regions electron depleted (Figure 4b). Thus, the interslab regions are much weaker than the slabs themselves. In \( γ \)-Be\( _{2}B_{6} \) (Figure 4c,d), the valence electrons are also accumulated in preferred regions (areas surrounded by the \( B_{2} \)-\( I \) equilaterals), but depleted in others (areas surrounded by the \( B_{2} \)-\( II \) equilaterals). The weakly bonded regions in \( α \) and \( γ \)-Be\( _{2}B_{6} \) are responsible for their lower shear moduli and hardness. The bonding scenario in \( α \)-Be\( _{2}B_{6} \) is confirmed by the Voronoi deformation density, defined as the charge difference between a bonded crystal and superimposed noninteracting atoms (Figure 4e,f). In \( α \)-Be\( _{2}B_{6} \) the highest electron accumulations occur in the \( B_{2} \) rhomboids, \( B-B \) scalene, and \( B_{2} \) dumbbells. In particular, strong electronic accumulations in \( B-B-B \) scalene indicate polar \((3c, 2c)\) bonding, which is the primary bonding feature for \( α \)-B and \( γ \)-B.\(^{53,54} \) Thus, prominent 3D covalent network explains the superhard nature of \( α \)-Be\( _{2}B_{6} \). In addition, electron accumulations also occur between Be-B atoms in the \( B_{2}B_{2} \) units, revealing covalent interactions (Figure 4f). The strong \( B-B \) interactions in Be\( _{2}B_{6} \) phases were also supported by analyzing the Mulliken overlap populations (MOP). Great MOP values of B-B bonds, 0.55 (\( x \)), 0.61 (\( x \)), 0.62 (\( x \)), 0.70 (\( x \)) and 0.71 (\( x \)) per unit cell were found in \( α \)-Be\( _{2}B_{6} \) further confirming the highly covalent bonding nature. For \( β \)-Be\( _{2}B_{6} \) MOP values of B-B bonds vary between 0.32 and 0.80. Similar MOP values were also found in \( γ \)-Be\( _{2}B_{6} \), i.e., 0.32–0.77.

Before concluding, we note that Be\( _{2}B_{6} \) may also be a stable phase. Previous theoretical studies suggest that the 1:7 stoichiometry is dynamically stable for both Ca–B and Mg–B systems.\(^{5,7} \) To this end, we searched for the stable structures for Be\( _{2}B_{6} \) and found its formation enthalpy very close to that of Be\( _{2}B_{6} \), \( -7.43 \) eV.\(^{15} \) This study provides new insights on the bonding mechanism of superhard borides, which encourage experimental efforts in the synthesis.

### Computational Methods

Structural relaxations, mechanical properties and electronic structures calculations were carried out in the framework of density functional theory as implemented in the CASTEP code.\(^{40} \) The exchange and correlation of the electrons were treated by the generalized gradient approximation with the Perdew–Burke–Ernzerhof (GGA-PBE) functional.\(^{57} \) The \( 2s^2 \) and \( 2p^3 \) were treated as the valence electrons for Be and B, respectively. A kinetic cutoff energy of 400 eV and a dense \( k \)-point grid with the spacing of \( 2\pi \times 0.03 \) Å\(^{-1} \) was used for the Brillouin zone sampling, which yields an excellent convergence for the total energy. We have also calculated the band structure of Be\( _{2}B_{6} \) using the VASP code.\(^{38,49} \) A cutoff energy of 600 eV, dense Monkhorst–Pack \( k \) meshes, and appropriate \( N \)BANDS were used to ensure the accuracy of the band structure. The elastic constants were calculated from evaluation of stress tensor generated small strains; the elastic modulus and Poisson’s ratio were derived from Voigt-Reuss-Hill approximations.\(^{50} \) The Vickers hardness was estimated using an empirical model \( H_v = 20(k/G)^{0.585} - 3.0 \), where \( k = G/B.\(^{40} \) Phonon spectra of new proposed phases were calculated through finite displacement methods.\(^{51,52} \) Structure figures were obtained by using the VESTA package.\(^{53} \)

The calculation of phonon-mediated superconductivity was performed with the Quantum-ESPRESSO package\(^{3} \) with a kinetic energy cutoff of 80 Ry. This methodology is an extension of the BCS model to take into account the explicit form of the electron–phonon interactions in the Brillouin zone (BZ). Q-mesh of \( 3 \times 5 \times 4 \) and \( k \)-mesh of \( 12 \times 20 \times 16 \) for \( α \)-Be\( _{2}B_{6} \), \( q \)-mesh of \( 2 \times 2 \times 2 \) and \( k \)-mesh of \( 8 \times 8 \times 8 \) for \( β \)-Be\( _{2}B_{6} \) and \( q \)-mesh of \( 4 \times 4 \times 4 \) and \( k \)-mesh of \( 12 \times 12 \times 12 \) for \( γ \)-Be\( _{2}B_{6} \) were used in the first BZ for the electron–phonon matrix calculations. In the Allen–Dynes modified McMillan equation,\(^{54,57} \) the superconducting transition temperature \( T_c \) is estimated from the spectral function \( a^2F(\omega) \):

\[
T_c = \frac{\hbar \omega_{\text{log}}}{1.20} \exp \left( -\frac{1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\mu^*} \right)
\]

Here, the screened repulsive interactions are represented by the Coulomb pseudopotential \( \mu^* \), estimated by rescaling the Coulomb repulsion parameter \( \mu \) to include retardation effects. For typical metals, empirical values of \( \mu^* \) between 0.1 and 0.13 are usually considered reasonable. The average strength of the attractive interaction, \( \lambda \), is the first reciprocal moment of the spectral function, \( a^2F(\omega) \),

\[
\lambda = 2 \int_0^\infty \frac{\alpha^2 F(\omega)}{\omega} d\omega \approx \sum_{qj} \lambda_{qj} \omega(q)
\]

where \( \omega(q) \) is the weight (the weights account for the symmetries of the BZ) of a \( q \) point in the first BZ, and the EPC spectral function \( a^2F(\omega) \) is calculated by summing over the frequency-weighted phonon line width \( \gamma_{qj} \) for all participating modes \( qj \),

\[
a^2F(\omega) = \frac{1}{2\pi N_q} \sum_{qj} \frac{\gamma_{qj}}{\alpha_{qj}} \delta(\omega - \omega_{qj}) \omega(q)
\]

In this equation, \( N_q \) is the electronic density of electron states at the Fermi level. The line width \( \gamma_{qj} \) of a phonon mode \( j \) at wave vector \( q \), arising from EPC is given by

\[
\gamma_{qj} = 2\pi \alpha_{qj} \sum_{nm} \int \frac{d^3k}{\Omega_{BZ}^2} \left| \frac{\partial}{\partial \xi_n} \xi_{n,k+q} \right|^2 \delta(\xi_n - \xi_j)
\]

where the integral is taken over the first BZ, with \( \Omega_{BZ} \) as the volume of the BZ, and \( \xi_n \) are the Kohn–Sham eigenvalues with wave vector \( k \) in the \( n \)th band (measured with respect to the Fermi \( \xi_F \) level). Here, \( \xi_{n,k+q} \) is the electron–phonon
matrix element for scattering from an electron in the nth band at wave vector \( k \) state to the nth band at wave vector \( k + q \) via a phonon with wave vector \( q \).

**ASSOCIATED CONTENT**

\* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.6b02444.

Crystal parameters, Wyckoff positions, mechanical properties, formation enthalpy, crystal structure, phonon dispersion curves and phonon density of states, electronic properties, and XRD patterns for BeB\(_2\) for (x = 4, 6, and 7) (PDF)

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**Notes**

The authors declare no competing financial interest.

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