A Stable Binary BeB$_2$ phase

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Potential crystal structures of BeB$_2$ were explored using ab initio evolutionary simulations. A new phase with a Cmcm space group was uncovered. It was determined that the Cmcm phase is mechanically and dynamically stable and has a lower enthalpy, from ambient pressure up to 13 GPa, than any previously proposed phases, as measured using first-principles calculations. The crystal structure, phonon dispersion, phase transitions, and mechanical and electronic properties of this phase were investigated. It was determined that the Cmcm phase may transform into the F43m phase at pressures higher than 13 GPa. The band structures and density of states reveal that the Cmcm phase is metallic. In addition, the Vickers hardness was calculated using three empirical models. To explain the origin of the hardness, charge density difference maps and a Mulliken population analysis were carried out, which demonstrated that there are strong covalent interactions between B atoms. By analyzing the Crystal Orbital Hamilton Population diagrams, it was determined that the total interaction of the Be-B bonds is stronger than that of the B-B bonds, indicating a very complex bonding feature in the new phase. It was predicted that the new Cmcm phase is nearly absent of superconductivity.

Beryllium (Be) and boron (B) are elements that occupy adjacent positions in the periodic table, but they have quite different properties, as the former is a metal while the latter is a semiconductor under standard conditions. At ambient conditions, Be crystallizes in a hexagonal-close-packed (hcp) structure and transforms into a body centered cubic (bcc) crystal structure at 1523 K or approximately 400 GPa. It has gained considerable attention because of its simple atomic configuration and unusual behaviors. As it is highly transmissive to X-rays, Be is commonly used as a window material in X-ray equipment. It is also one of the most effective moderators and reflectors for neutrons used in nuclear reactors. In addition, its high weight, high melting point and high-strength performance result in it being widely used in aircraft, rockets, satellites and other aerospace applications, as well as in future fusion reactors. Although Be has several negative characteristics, such as potential toxicity that poses a manufacturing challenge, controlled handling procedures, such as the use of a glove box, can enable the success industrial synthesis of beryllium-containing compounds.

Boron is a semiconductor that becomes a metal, and even a superconductor, when placed under high pressure. Elemental boron has many allotropes that use the B$_{12}$ icosahedron as the basic unit, of which α-Boron is the most common. Boron-containing compounds have been investigated extensively due to their exotic physical properties, such as superconductivity, hardness and thermoelectric performance. For example, several transition metal diborides, such as OsB$_2$, IrB$_2$, ReB$_2$ and BC$_x$, possess high bulk and shear moduli and have been explored for use as potential super-hard materials.

When beryllium and boron combine, various Be-B phases ranging from beryllium-rich to boron-rich will form. Some Be-rich phases, such as the Be$_2$B phase, show a metallic character and are potential superconductors. Another beryllium-rich phase, Be$_3$B, is the only stable Be-rich phase at room temperature. Within the boron-rich compounds, BeB$_3$, found only in the MgIn$_3$ type (space group P6/mmc, one formula unit per cell), is found to be not stable. BeB$_5$, however, is highly stable at high pressures.

Although beryllium diboride has been known and studied for more than half century, there has still been no solid evidence that it exists with the stoichiometry BeB$_2$. The first announced synthesis of BeB$_{2.01}$ with $P6/mmm$ symmetry was later recognized to have a correct stoichiometry of BeB$_{2.75}$ with a surprisingly complex crystal structure. Very recently, Hermann, A. et al. systematically studied the binary Be-B phases at ambient and high-pressure conditions. In their work, they found that the most stable structure for BeB$_2$ at atmospheric pressure is cubic (space group $F43m$, NO.216), with a diamondoid boron network and beryllium atoms occupying interstitial tetrahedral sites. This structure is semiconducting and can be understood in terms of the Zintl-Klemm concept, making it unique among Be-B phases. Other proposed beryllium diboride phases can be classified into three crystal systems: (1) cubic, including the CaAl$_2$ structure (space group $Fd3m$, NO.227, eight units per cell, prototype MgCu$_2$) and “AlLiSi” structures (space group $F43m$, NO.216); (2) hexagonal,
including the MgB$_2$ crystal structure (space group $P6/mmm$, NO.191$^{26}$, one unit per cell, prototype AlB$_2$) and the CaIn$_2$ and MgGa$_2$ structures (space group $P63/mmc$, NO.194, two units per cell$^{25,26}$); and (3) orthorhombic, including the SrAl$_2$ structure (space group $Imma$, NO.74, four units per cell, prototype CeCu$_2$$^{7}$), another MgGa$_2$ structure (space group $Pbam$, NO.55, eight units per cell$^{26}$) and the “CaIn$_2$” structure (space group $Pnma$, NO.62$^{26}$). Many phases have already been found. At low pressure (under 160 GPa), the cubic phase (space group $F4 3m$, NO.216) is the most stable, while the $P63/mmc$ phase is dynamically unstable and can turn into low-symmetry $Pna2_1$. At pressures greater than 160 GPa, the $P63/mmc$ phase is more stable$^{3}$. There is still an open question regarding whether there exist other stable phases with low energy in the low pressure zone. Therefore, further theoretical studies, such as of the bonding between the atoms in $Cmcm$, electronic properties and mechanical properties, are important for this potential material.

In the present work, potential crystal structures of Be$_2$B$_2$ were extensively explored using $ab$ initio evolutionary simulations. A new phase with $Cmcm$ symmetry was uncovered. The crystal structures, phonon dispersions, mechanical properties, phase transitions, and electronic structures of this phase as well as other available phases were investigated. The band structures and density of states reveal that the new phase is metallic. Further study on the mechanical properties using three different methods was used to predict the Vickers hardness of the newly discovered $Cmcm$ phase. Charge density difference maps and Mulliken population analysis, as well as COHP diagrams, were also carried out to analyze the character of the bonding between the atoms in $Cmcm$ Be$_2$B$_2$. The superconductivity of the new $Cmcm$ phase was also investigated.

### Results

**Crystal Structure.** In a previous work, several phases were found both experimentally and theoretically. However, only four structures are stable according to the calculated phonon spectra in the present work. These are cubic (space group $F4 3m$, NO.216), orthorhombic (space group $Pnma$, NO.62), and hexagonal (space group $P63/mmc$, NO.194). In the present work, a new stable phase with space group NO.63 was uncovered by performing systematic structure searches for Be$_2$B$_2$. Its optimized equilibrium lattice parameters, axial ratio $c/a$ and unit cell volume are shown in Table 1. The crystal structure information of all other known dynamical stable phases are presented in Table 2$^{25,26}$. Table 1 reveals that the conventional unit cell of the new $Cmcm$ phase contains twelve atoms in total with two inequivalent Wyckoff positions 4$c$ and 8$f$ for Be and B atoms, respectively.

### Phonon Dispersion.

The phonon dispersion curves of the new phase as well as of other previously proposed crystalline structures were calculated to determine their dynamical stability, as shown in Figure 4. The new $Cmcm$ phase is dynamically stable, as there are no imaginary phonon frequencies detected in the whole Brillouin zone. For the previously proposed phases$^{25,26}$, the $Pbam$, $Pnma$, $F4 3m$ and $P63/mmc$ phases are dynamically stable according to the same rule. However, the appearance of imaginary frequencies indicates that the $P6/mmm$, $Fd 3 m$ and $Imma$ phases mentioned in previously published articles$^{25,26}$ are dynamically unstable.

### Phase Transition.

Figure 5 gives the calculated relative enthalpy as a function of pressure for all stable phases of Be$_2$B$_2$, relative to the $F4 3m$ phase. The inserted figures show the stable $Cmcm$ phase and the $F4 3m$ phase of Be$_2$B$_2$, before and after the phase transition at 13 GPa, respectively. As mentioned before, the latter has been considered in previous works to be the most stable phase at atmospheric pressure, having a structure with a diamondoid boron network and beryllium atoms occupying the interstitial tetrahedral sites. The polyhedron representation of the $F4 3m$ phase has also been marked, as shown in the bottom-right corner of Figure 5.

### Table 1: Optimized structural data for the new phase of Be$_2$B$_2$

| Space group | $a$  | $b$  | $c$  | $c/a$ | $x$ | $β$ | $γ$ | $ρ$  | $V$  |
|-------------|------|------|------|-------|-----|-----|-----|------|------|
| $Cmcm$      | 6.028| 5.120| 1.714| 90.0  | 90.0| 90.0| 2.206| 23.06|

### Table 2: Optimized structural data for other known phases of Be$_2$B$_2$

| Space group | $a$  | $b$  | $c$  | $c/a$ | $x$ | $β$ | $γ$ | $ρ$  | $V$  |
|-------------|------|------|------|-------|-----|-----|-----|------|------|
| $F4 3m$     | 4.311| 4.311| 4.311| 1.000 | 90.0| 90.0| 90.0| 2.539| 20.03|
| $Pnma$      | 5.064| 3.035| 5.285| 1.044 | 90.0| 90.0| 90.0| 2.505| 20.31|
| $Pbam$      | 4.656| 11.316| 2.997| 0.644 | 90.0| 90.0| 90.0| 2.577| 19.74|
| $P63/mmc$   | 3.004| 3.004| 5.014| 1.669 | 90.0| 90.0| 120.0| 2.597| 19.59|
As shown in Figure 5, the enthalpy of the newly uncovered phase increases with pressure within the studied pressure range up to 50 GPa, while the enthalpies of the other three stable phases (Pnma phase, Pbam phase, P63/mmc phase) have an inverse trend. It can be concluded that the Cmcm phase is more competitive than the previously known most stable F4\textit{3m} phase at pressures up to 13 GPa. When the pressure exceeds 40 GPa, the Pnma phase and P63/mmc phase have almost similar enthalpies, and both of them become more favorable than the new Cmcm phase. The cubic structure (F4\textit{3m} phase) continues to have the greatest stability in the pressure range from 13 GPa to 50 GPa. These results are consistent with the results previously found by Andreas Hermann et al.\textsuperscript{2}

First-principles methods were used to calculate the formation enthalpy of the new phase Cmcm (No.63) at different pressures.

As shown in Table 4, when the pressure is 1 atm, the formation enthalpy of the Cmcm phase is −256 meV/atom, which is within the range of formation enthalpies (−240 meV to −125 meV) of some proposed models for BeB\textsubscript{2.79} phases\textsuperscript{20}. This may explain why the BeB\textsubscript{2.79} phase with a very complex structure has been found experimentally, rather than the pure BeB\textsubscript{2} phase with the simple Cmcm structure. It also indicates that the proposed models of BeB\textsubscript{2.79} phases\textsuperscript{20} with enthalpies less than −56 meV/atom are more competitive. Upon comparing the formation enthalpy of the new phase (−0.056 eV/atom) with that of the most stable known phase F4\textit{3m} (−0.016 eV/atom), it may be observed that the former is more thermodynamically stable than any other known BeB\textsubscript{2} phase.

Using the same approach, the formation enthalpy of the Cmcm phase at 10 GPa and 15 GPa was calculated to be −39.7 meV/atom
Figure 4 | Phonon dispersion curves of available BeB۲ phases.
and $-32.2$ meV/atom, respectively. By comparing to the value at 1 atm ($-56.267$ meV/atom), it may be seen that the formation enthalpy value increases continuously with the pressure, indicating that increasing pressure is not beneficial for the synthesis of the \textit{Cmcm} phase. All of these conclusions agree well with those obtained from the pressure phase diagram\textsuperscript{2,20}, and the results will provide guidance for experimental work on BeB\textsubscript{2} synthesis.

In addition, to provide more “physics” of the phase transition, we have calculated the solid-solid structural phase transitions between the \textit{Cmcm} and \textit{F4 3m} phases at 13 GPa by using the VC-NEB method\textsuperscript{29}. Figure 6 illustrate the snapshots from a dynamical trajectory collected from transition path sampling connecting the \textit{Cmcm} phase and the \textit{F4 3m} phase. The energy barrier of the transition was calculated to be 0.25 eV/atom.

### Discussion

**Mechanical Properties.** Mechanical properties, including the elastic constants, bulk modulus, shear modulus, Young’s modulus, Poisson’s ratio, are the main bases for choosing and designing materials. Therefore, all these properties were calculated using the first-principles approach in this work. The elastic constants of all structures under the ambient pressure $C_{ij}$ were calculated with the strain-stress method combined with Hooke’s Law, as implemented in the CASTEP code\textsuperscript{30}. The results are listed in Table 5. In order to determine the mechanical stability of the new predictions, $C_{ij}$ has to satisfy the elastic stability criteria\textsuperscript{31}.

The mechanical stability condition and elastic constants of the orthogonal structure are positive. However, the following inequalities must also be satisfied to indicate stability:

\[
C_{11} + C_{22} - 2C_{12} > 0 \\
C_{11} + C_{33} - 2C_{13} > 0
\]

\[
C_{22} + C_{33} - 2C_{23} > 0 \\
C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0,
\]

As shown in Table 5, these values all meet the mechanical stability criteria, initially confirming that the \textit{Cmcm} phase is mechanically stable.

Based on the Voigt-Reuss-Hill approximation method\textsuperscript{32,33}, we can find the appropriate bulk modulus $B$ and shear modulus $G$ using the elastic constants. In addition, the values of Young’s modulus $E$ and Poisson’s ratio $\sigma$ can be calculated using the following formula:

\[
E = \frac{9BG}{3B+G} , \quad \sigma = \frac{3B-2G}{2(3B+G)}
\]

Usually, the bulk modulus $B$ is used to characterize a material’s resistance to volume deformation against external pressure, while the shear modulus $G$ measures a material’s ability to resist shear strain. Young’s modulus $E$ measures the resistance against longitudinal tensions. Among the 4 mechanical and dynamical stable BeB\textsubscript{2} phases, the \textit{Cmcm} phase has the lowest value of bulk modulus and the second lowest shear modulus, revealing that it has low resistance to compression and shear strain. In addition, the elastic constant $C_{22}$ (282 GPa) is significantly smaller than $C_{11}$ (492 GPa) and $C_{33}$ (690 GPa), revealing that resistance along the $b$ axis is much smaller than along the $a$ and $c$ axes.

In order to evaluate the ductility of the material, the $B/G$ values were calculated and are listed in Table 5. Higher $B/G$ values greater than 1.75 correspond to a ductile material, while values less than 1.75 correspond to a brittle material\textsuperscript{34}. As shown in Table 5, the $B/G$ value of the \textit{Cmcm} phase is approximately 1.01, suggesting that it is very brittle.

Poisson’s ratio reflects the strength of the covalent bond to some extent. A small Poisson’s ratio ($\sigma = 0.13$) indicates that the \textit{Cmcm} phase is more intensely covalently linked than the \textit{Pbam} phase ($\sigma = 0.29$) and \textit{P63/mmc} phase ($\sigma = 0.18$). These results show that the \textit{Cmcm} phase is likely to be a type of potential ultra-incompressible material, despite its bulk modulus and shear modulus not being very high.

Finally, the hardness of the \textit{Cmcm} phase was calculated in three different ways. Using a recently proposed simple empirical hardness formula $H = 2(G\sqrt{B})^{0.385} - 33$, the Vickers hardness of these phases was calculated. As the result shows, the \textit{Cmcm} phase has a hardness value of 36.8 GPa, approaching the critical value of a super-hard material, 40 GPa. It also reveals that the predicted hardnesses of the \textit{Pnma} phase and the \textit{F4 3m} phase are approximately 41.4 GPa and 42.3 GPa, respectively, implying that both of them are potential super-hard materials. The hardness value for the \textit{Cmcm} phase is also calculated to be 25.2 GPa using the formula of hardness given by Artem R. Oganov\textsuperscript{36} (details can be found in the computational methods section).

The hardness of the new phase was also calculated by the microscopic hardness model proposed by F.M. Gao et al.\textsuperscript{37,38} (details can be found in the computational methods section). The calculated parameters and hardness of the \textit{Cmcm} phase calculated by this model are listed in Table 6. It is found that the total hardness of the \textit{Cmcm} phase is only 13.8 GPa with this method.

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**Table 3: The parameters for structure used in the formation enthalpy calculation**

| phase | Space group | No. | $a$  | $b$  | $c$  | $\alpha$ | $\beta$ | $\gamma$ | $\rho$ |
|-------|-------------|-----|------|------|------|----------|---------|----------|-------|
| BeB\textsubscript{2} | \textit{Cmcm} | 63  | 2.996| 6.0428| 5.1017| 90       | 90      | 90       | 2.2029|
| Be    | \textit{P63/mmc} | 194 | 2.249| 2.249 | 3.569 | 90       | 90      | 120      | 1.9150|
| B     | \textit{R3 m} | 166 | 5.036| 5.036 | 5.036 | 58.076   | 58.076  | 58.076   | 2.496  |
Chen’s model gives the highest values (36.8 GPa) from these three models followed by Oganov’s model (25.2 GPa) while Gao’s model provides the lowest values (13.8 GPa), which may be caused by their applicability to the boron compounds and with metals. The scattered values of hardness predicted from these three different models reveal that although it has a simple crystal structure, the electronic structure and bonding characters of the newly uncovered Cmcm phase of BeB2 are quite complex, as will be analyzed below.

**Electronic Properties.** The electronic properties of the newly discovered phase, including energy band structures, total and partial density of states (DOS), and charge density maps, were calculated and are shown in Figure 7–9.

Figure 7 shows the calculated band structure along high symmetry directions, as well as the total and partial DOS of the optimized Cmcm structure from first-principles calculations within the GGA scheme. The overlapping of the valence bands and conduction bands around the Fermi level suggests that the new phase has a clear metallic character, which is confirmed by the finite value of total DOS at the Fermi level.

Figure 7 also plots the partial DOS of the novel Cmcm phase. It reveals that the total DOS of the upper part of the valence bands (from −9.5 eV to the Fermi level) is mainly contributed by the B-p state, while that of the conduction bands come from both the B-p and Be-p states. The Be-s state also contributes to the DOS of the conduction band (above 4 eV), while making a very slight contribution to that of the valence band. The B-s state contributes to the lower part of the valence band (less than −7.5 eV) and to the upper part of the conduction band, especially in the 4 eV to 8 eV region of the total DOS. As discussed above, there is significant hybridization of the s and p states from both Be and B in the region of 4 eV to 8 eV, implying the tendency to form covalent bonds between Be and B atoms.

Figure 8 plots the total DOS for all stable phases at ambient pressure, corresponding to the Cmcm, F4 3m, P63/mmc, Pnma and Pbam phases, from left to right. The dashed lines represent the position of the Fermi level. The first panel is the newly uncovered Cmcm phase, and the others are other known dynamically stable phases. Filling electrons at the Fermi level (approximately 1.18 states/eV/el.) shows that the new phase has an obvious metallic character, while the cubic F4 3m phase with a band gap of 0.95 eV indicates its semiconductor property at low and intermediate pressures. Except for the F4 3m phase, all other known phases are metallic, as shown in the last three panels of Figure 8.

Figure 9 shows electron density difference maps for the Cmcm phase on the selected slice (100) plane. It can be seen that electrons are gathered at the positions of the B atoms and especially between Boron-Boron bonds, as indicated by the region in red in the top left panel and its enlarged bottom left panel. After removing the atoms, it is clearly seen that electrons are transferred from the Be atoms to the B atoms, as shown in the right two panels. From the electron gathering region between Boron-Boron, one can speculate that there is a strong covalent interaction.

In order to give some insight into these bonding characters, an atomic and bond Mulliken population analysis, which can provide a

| Table 4 | Formation enthalpy for BeB2 phases at P = 1 atm |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Space group     | P6/mmm          | Pnma            | Pbam            | Fd3 m           | F4 3m           | P63/mmc         | Cmcm            |
| ΔHf (eV/atom)   | +0.404          | +0.138          | +0.238          | +0.853          | +0.019          | +0.166          | -0.056          |
| ΔHf’ (eV/atom)  | +0.120          | +0.099          | +0.179          | +0.687          | -0.016          | —               | —               |

Figure 6 | Snapshots from a dynamical trajectory collected from transition path sampling connecting (a) the Cmcm phase to (f) the F4 3m phase. Black dashed line means a bond disappears while purple solid line means a bond created compared to the previous snapshot. Boron (Beryllium) atoms are shown in green (gray) colors.
good way to quantitatively evaluate the charge transfer chemical bond strength of the studied system, was performed and analyzed by the CASTEP code, with the results listed in Tables 7 and 8. From Table 7, it can be clearly seen that electrons transfer from the Be atoms to the B atoms in the Cmcm phase, as the charges for Be and B are 0.69 and −0.34, respectively.

Now let us turn to the bond Mulliken population analysis results. A high nonzero value of overlap population indicates that there is a strong covalent character of the bond, while a small value close to zero shows that there is weak or no interaction between two related atoms and a negative value indicates that the atoms cannot form a bond. From Table 8, it may be seen that the bond population ranges from 0.20 to 1.63 for the Cmcm phase. The maximum number, 1.63, exists between Boron-Boron bonds, indicating their strong covalent character. However, the Be-B bond has very weak covalence, as its Mulliken population is only 0.20. The population of Be-Be is 0.34, respectively.

Table 5 | Calculated values of elastic constants Cijkl (in GPa), Bulk modulus B (in GPa), Shear modulus G (in GPa), Young’s modulus E (in GPa), Poisson’s Ratio σ, B/G ratio, and Vick’s Hardness (in GPa) calculated by Xing Qiu Chen’s formula for stable phases of BeB2 at 0 GPa and 0 K

| Cmcm | Pbam | Pnna | P63/mmc | F4 3m |
|------|------|------|---------|------|
| C11  | 492  | 477  | 458     | 515  | 482 |
| C22  | 282  | 555  | 519     | −    | −   |
| C33  | 690  | 530  | 482     | 389  | 220 |
| C44  | 96   | 22   | 228     | 160  | 220 |
| C55  | 263  | 25   | 146     | −    | −   |
| C66  | 109  | 224  | 116     | −    | −   |
| C12  | 35   | 83   | 0.4     | 128  | 81  |
| C13  | 34   | 36   | 0.5     | 80   | −   |
| C23  | 7    | 26   | 61      | −    | −   |
| B    | 169  | 205  | 175     | 218  | 215 |
| G    | 168  | 99   | 183     | 177  | 212 |
| E    | 379  | 256  | 407     | 418  | 479 |
| σ    | 0.13 | 0.29 | 0.11    | 0.18 | 0.13|
| B/G  | 1.01 | 2.07 | 0.96    | 1.23 | 1.01|
| Hc   | 36.8 | 9.5  | 41.4    | 29.4 | 42.3|

Superconductivity Properties. Encouraged by the relatively simple binary MgB2, having a superconductivity transition temperature of 39 K and the controversy regarding the reported superconductivity properties of BeB2 and BeB2.75, we also calculated the superconductivity properties of the Cmcm phase of BeB2. The Tc can be estimated from the Allen-Dynes modified McMillan equation,

\[
T_c = \frac{\omega_{ph} \exp \left\{ -\frac{1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right\}}{1.2},
\]

which has been found to be highly accurate for materials with an EPC constant $\lambda<1.5^{46}$, where $\omega_{ph}$ is the logarithmic average of the phonon frequency and $\mu^*$ is the effective Coulomb repulsion and was assumed to be constant at 0.1. The calculated spectral function $x^2F(\omega)$ and integrated $\lambda(\omega)$ of the Cmcm phase are plotted in Figure 11. Our results reveal that the Cmcm phase exhibits fairly low superconductivity properties, with a $T_c$ of only 0.1 K. These results shed light on the controversy regarding the reported superconductivity properties of BeB2 or BeB2.75. The synthesized sample may contain both BeB2 and BeB2.75 phases. When the BeB2 phase dominates, an absence of superconductivity would be observed, as shown in Ref. [21], while when the BeB2.75 phase dominates, superconductivity appears.

Table 6 | Parameters related to hardness and the value of Vickers hardness for Cmcm phase and the total hardness is 13.8 GPa

| bond | d (Å) | N | p | $N_v$ (Å$^{-3}$) | $p_v$ | fi | fm (10)$^{-3}$ | Hc (GPa) |
|------|------|---|---|----------------|------|----|--------------|---------|
| B-B  | 1.657| 6 | 0.84 | 0.998 | 0.57 | 0.387 | 0.953 | 30.9 |
| B-B' | 1.763| 12 | 1.63 | 0.828 | 0.581 | 0.953 | 18.5 |
| Be-B | 1.923| 12 | 0.24 | 0.505 | 0.807 | 0.889 | 8.4  |
| Be-B' | 2.021| 24 | 0.49 | 0.435 | 0.248 | 0.889 | 13.1 |
| Be-B" | 2.105| 12 | 0.20 | 0.385 | 0.882 | 0.889 | 12.4 |
Methods

*Ab initio* evolutionary simulations were run using the USPEX (Universal Structure Predictor: Evolutionary Xtallography) code. The USPEX code depends on VASP (Vienna *ab initio* simulation package) to achieve global optimization to calculate the enthalpy of crystal structures and explore the lowest enthalpy phase of a given elemental composition. Here, we used the USPEX code to search for stable compounds and structures with a fixed chemical composition of Be$_n$B$_{2n}$ ($n = 1$ to $5$); the Cmcm phase comes from the 25th structure with the stoichiometry of Be$_2$B$_4$. During the structure search, USPEX selects a whole range of $50$ generations to calculate, with each generation containing $50$ individuals. The settings used for the variation operators are as follows: $60\%$ of each generation was used to produce the next generation by heredity, $20\%$ comes from soft mutations, $10\%$ is produced randomly from space groups, and the rest is produced through lattice mutations. The minimum length of any lattice vector was defined as $2.0$ Å. The cutoff for USPEX relaxation and the $k$-points for resolution were $318$ eV and $2 \times 0.02$ Å$^{-1}$, respectively.

First-principles calculations were carried out using the density functional theory (DFT) approach by applying a generalized gradient approximation (GGA) for the exchange correlation functional. We applied the Ultrasoft pseudo-potential introduced by Vanderbilt, and the $k$-point samplings in the Brillouin zone were

![Figure 7](image) The electronic band structure and density of states for the Cmcm phase. The dashed transverse line denotes the Fermi level.

![Figure 8](image) Density of states for BeB$_2$ in various stable phases. From left to right: Cmcm, F43m, P63/mmc, Pnma and Pbam. The dashed lines represent the position of the Fermi level.

![Figure 9](image) Electron density difference plot (e Å$^{-3}$) for the Cmcm phase at a select slice of (100).
energy was performed using the Monkhorst-Pack Scheme. The convergence tests used a kinetic energy cutoff of 600 eV and a k-point of \(13 \times 7 \times 8\) for the predicted Cmcm phase in the geometry optimization calculations. The self-consistent convergence of the total energy was \(5 \times 10^{-7}\) eV/atom, the maximum force on each atom was below 0.01 eV/Å and the maximum atomic displacement was below \(5 \times 10^{-4}\) Å. The phonon dispersion curves were plotted using the super-cell calculation method applied in the Phonopy program. The calculation of the elastic constants and Mulliken overlap populations was carried out using the CASTEP code. From the calculated elastic constants \(C_{ij}\), the polycrystalline corresponding bulk modulus \(B_{1-B5}\) and shear modulus \(G\) [Table 8] for the predicted Cmcm phase can be expressed by:

\[
B_{1-B5} = 0.84, 1.657, 2.785, 2.915, 2.974
\]

For the complex crystal compounds, we considered three effects on hardness: the covalent component, the ionic component and the small metallic component. First, we defined a factor of metallicity \(f_m\) as \(n_n/n_u\) for a simple-structured compound, where \(n_n\) and \(n_u\) are the numbers of electrons that can be excited at the ambient temperature and the total number of valence electrons in the unit cell, respectively. According to the electronic Fermi liquid theory, the thermally excited electron number \(n_u\) can be described by the product of \(D_0\) and the energy width \(kT\), where \(k\) is the Boltzmann constant and \(T\) is the temperature. At the ambient temperature, \(kT\) is equal to 0.026 eV. Therefore, \(f_m\) can be written as:

\[
f_m = \frac{n_n}{n_u} = \frac{kT D_0}{n_e}. \tag{11}
\]

When the chemical bonds of a crystal are greater than or equal to two, we refer to it as a complex crystal. For the metallicity of complex crystals, the \(f_m\) can be calculated by:

\[
f_{m}^c = \frac{n_n^{c}}{n_u^{c}} = \frac{N_{Be}+N_{B}+N_{Be}+N_{B}}{N_{Be}+N_{B}}\tag{12}
\]

Because no d-orbital valence electrons are involved in the chemical bonds, the hardness of each bond for Cmcm phase can be expressed by:

\[
H_{B} = 350(N_{Be}^{e}E_{B}^{e}+N_{B}^{e}E_{B}^{e})^{-2.5}(E_{B}^{c}-E_{B}^{c}+E_{B}^{c}+E_{B}^{c})^{-2.5}, \tag{7}
\]

where \(E\) is the length of the bond, \(N_{Be}^{e}\) is the valence electron density (which can be calculated by)

\[
N_{Be}^{e} = \frac{Z_{Be}/N_{Be}+Z_{Be}/N_{Be}}{\sum (Z_{Be}/N_{Be})}; \tag{8}
\]

\[
N_{Be}^{e} = \frac{2Z_{Be}/N_{Be}}{\sum (Z_{Be}/N_{Be})}/[V(\frac{d_{e}^{Be}-B})], \tag{9}
\]

where \(Z_{Be}\) and \(Z_{B}\) are the valence electron numbers of the Be and B atoms constructing Be-B or B-B bonds, \(N_{Be}\) and \(N_{B}\) are the nearest coordination numbers of the Be and B atoms, \(N_{Be}\) is the number of bond in the unit cell, and \(V\) is the volume of the unit cell) and \(f_{B}\) is the Phillips ionicity of the bond. According to the generalized ionicity scale, the Phillips ionicity can be obtained from the following formula,

\[
f_{B} = \frac{f_{B}}{f_{B}^{735}} = 1 - \exp \left(-\left[P_{B}-P_{N}\right]^{0.735}\right), \tag{10}
\]

where \(f_{B}\) is the population ionicity scale of the chemical bond, \(P\) is the overlap population of the bonds, and \(P_{N}\) is the overlap population of the bonds in a specified pure covalent crystal (here 0.57 is adopted).

Details of Gao’s model are described below. The Vickers hardness of complex crystals can be calculated by a geometric average of all bonds as follows:

\[
H_{V} = \frac{H_{Be-B}^{1/6}}{6}\left(H_{B-B}^{1/12}\right), \tag{6}
\]

For the Cmcm phase, the total hardness is given by:

\[
H_{T} = \frac{\sum \left[N^{e} \right]}{\sum \left[N^{e} \right]/V}. \tag{5}
\]

Figure 10 | The crystal orbital Hamiltonian population (COHP) analysis of the bonding interactions in BeB$_2$ based on plane-wave calculations using the newly introduced pCOHP method. (a) for the Be-B bond. (b) for the B-B bond. All energies are shown relative to the Fermi level $E_F$. 

Table 7 | Atomic Mulliken populations for Cmcm phase

| Bond | Population | Charge | Total | Charge | Total | Charge |
|------|------------|--------|-------|--------|-------|--------|
| Be1-Be2 | 0.10 | 0.21 | 1.31 | 0.69 |
| B1-B2 | 0.84 | 2.50 | 3.34 | -0.34 |

Table 8 | Bond populations and bond lengths (Å) for Cmcm phase

| Phase | Bond | Population | Length | Bond | Population | Length |
|-------|------|------------|-------|------|------------|-------|
| Cmcm | Be1-Be2 | 0.84 | 1.657 | Be-Be | -0.24 | 2.785 |
|       | B1-B2 | 1.63 | 1.763 | B3-B5 | -0.01 | 2.915 |
|       | Be4-B1 | 0.24 | 1.923 | B2-B3 | -0.48 | 2.974 |
|       | Be2-B2 | 0.49 | 2.021 |  |
|       | Be3-B4 | 0.20 | 2.104 |  |
Figure 11 | The calculated spectral function $\alpha^2 F(\omega)$ and integrated $\delta(\omega)$ of the Cmcm phase.

Conclusions

In summary, a new stable phase of BeB$_2$ with the space group Cmcm was discovered by using ab initio evolutionary simulations. The Cmcm phase has a lower enthalpy than any previously proposed phase. The new structure is mechanically and dynamically stable, as determined by checking the calculated elastic constants and phonon dispersions, while several previously proposed phases (cubic: Fd $3$ m; hexagonal: Pb$m/mm$; orthorhombic: Imma) were found to be dynamically unstable. The Cmcm phase may transform to the cubic $F4 3m$ phase when the pressure exceeds 13 GPa. The calculated electronic band structure and density of state suggest that the uncovered new phase is metallic. Scattered hardness values calculated from three models suggest the complex electronic and bonding features of the Cmcm phase. The charge density difference maps and the Mulliken population analysis reveal that there are strong covalent interactions between the B atoms. The COHP diagrams show that the total interaction of Be-B bonds is stronger than that of B-B bonds. The Cmcm phase exhibits fairly low superconductivity properties, with a calculated $T_c$ of approximately 0.1 K. The current theoretical predictions will most likely promote further experimental and theoretical investigation on the Be-B system.

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Acknowledgments
This work was supported by the Research Foundation of Education Bureau of Hebei Province (J20131039), the Natural Science Foundation of Hebei Province (E201420243) and the NSFC (Grant No. 51121061), which is gratefully acknowledged.

Author contributions
C.Z.F. conceived the idea. Y.J. performed the ab initio evolutionary simulations and DFT calculations. Y.J. and J.L. carried out the hardness predictions. J.L. did the COHP analysis. X.D. performed the superconductivity properties calculations. C.Z.F and Y.J. wrote the manuscript with contributions from all.

Additional information
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Fan, C., Jin, Y., Li, J. & Dong, X. A Stable Binary BeB1 phase. Sci. Rep. 4, 6993; DOI:10.1038/srep06993 (2014).

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