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New Be-intercalated Hexagonal Boron Layers Structure of BeB₂

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Abstract

Using genetic algorithm method and first-principle calculations, we performed searches for low-energy crystal structures of BeB₂. We found a new family of structures, where the B atoms form hexagonal layers intercalated by Be atoms. The lowest-energy structure has formation energy of -99.47 meV/atom with 4 formula units in the unit cell, which is much more stable than the models proposed before. The formation energies of structures in the new structure family can be well described by an Ising-like model with “anti-ferromagnetic” coupling between the displacements of Be atoms from the mid-plane between two B layers. We also performed phonon calculation as well as electronic band structure calculation to verify the stability and investigate the electronic properties of the newly found structure.

After the discovery of superconducting MgB_2 [1], many efforts have been made to find new superconducting materials with structures similar to MgB_2 [2, 3, 4, 5, 6]. Most of the works have been done by simply substituting Mg or doping with other light alkali or alkaline earth elements in MgB_2 [2, 3, 4, 5, 6] because light elements were believed to be able to increase the T_c by increasing the phonon frequencies according to the BCS theory [7]. Beryllium got much of attention because it sits right above Mg in the periodic table of the elements. Many theoretical works have been done to investigate the stability and electronic properties of BeB_2 , where its atomic structure was adopted from the existing structure prototypes such as AlB_2 -, RuB_2 -, or OsB_2 -prototype. On the other hand, there were some experiments studies on the atomic structures of BeB system long time ago [8, 9], and the BeB_2 phase was identified as $P6/mmm$ structure with $a = 9.79 \text{ \AA}$ and $c = 9.55 \text{ \AA}$. However, the atomic positions of the BeB_2 structure have not been resolved. Afterward, a number of other phases of BeB system (BeB_3 [10] or $\text{Be}_{1.09}\text{B}_3$ (or the equivalent $\text{BeB}_{2.75}$) [11, 12] phases) were also identified with exactly the same crystal symmetry and lattice parameters as those proposed for BeB_2 . It has been argued that the older measurements would have detected the $\text{Be}_{1.09}\text{B}_3$ phase rather than the BeB_2 phase [13].

There were also attempts to find the low-energy structures of BeB_2 recently by modifying the known structural prototypes [13, 14] or by evolutionary algorithm search [13]. Although BeB_2 in AlB_2 structure type is the most commonly used structure for BeB_2 in electronic structure calculations [2, 3, 4, 5, 6], this structure is unfavorable energetically with positive formation energy of 120.0 meV/atom and unstable dynamically with soft phonon modes [13, 14]. On the other hand, a AlLiSi -type structure was also proposed for BeB_2 which has formation energy of -16.0 meV/atom [13,14].

In this study, we performed a “from scratch” search for low-energy crystal structures of BeB_2 by genetic algorithm method and first-principle calculations. We found a new family of intercalated low energy structures of BeB_2 , whose formation energies can be well described by Ising-like model with the “anti-ferromagnetic” coupling interaction between the displacements of Be atoms. The lowest-energy structure has formation energy of -99.47 meV/atom, which is -83.27 meV/atom lower than the formation energy of the “best-structure” proposed in the literature so far. We also analyze the electronic band structure and the possibility of being

superconducting of the newly found lowest-energy structure. The stabilities of the newly found structure for other alkali or alkaline earth elements are also discussed.

The crystal structure search for BeB_2 was performed “from scratch” by real space cut-and-paste genetic algorithm method [15, 16, 17] with $Z = 4, 6$ and 8 formula units (f. u.). The only given information was the composition; Initial unit cells and atomic positions were generated randomly without symmetry constrains. The structure relaxations were done by density functional theory [DFT] [18] calculations within generalized-gradient approximation [19] with the projector-augmented wave method [20, 21] using VASP code [22]. The kinetic energy cutoff of the calculations was 420 eV and the Monkhorst-Pack's scheme [23] was used for Brillouin zone sampling. A high-quality k-point grid, which is corresponding to a k-point mesh of $14 \times 7 \times 8$ for the below proposed lowest-energy structure, was used in all calculations. All structures were fully relaxed until the forces on each atom smaller than $0.01 \text{ eV}/\text{\AA}$. The references for the formation energy calculations were the ground-state structures of Be and B, which are the hexagonal close-packed Be and the α -hR12 B structures, respectively. The phonon spectrums were calculated by finite-difference method [24] with a supercell of $2 \times 2 \times 2$ using Phonopy code [25] in combination with VASP code. The electron-phonon coupling was calculated by Quantum-Espresso code [26] within local density approximation [27] with kinetic energy cutoff of 408 eV, k-point mesh of $32 \times 16 \times 16$ and phonon q-point mesh of $4 \times 2 \times 2$. The atomic structure was re-optimized within Quantum-Espresso code to make the calculation consistent.

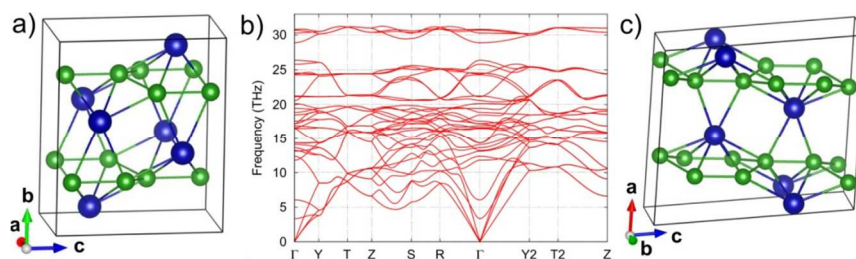


Figure 1. (a) The atomic structure of Cmcm BeB_2 structure and (b) its phonon band structure and (c) the atomic structure of C2/m BeB_3 structure. The solid lines in the (a) and (c) figures show the unit cell. The big (blue) and small (green) spheres are Be and B atoms, respectively.

The lowest-energy structure from our search is an orthorhombic intercalated structure with the symmetry of space group $Cmcm$ (#63) (Fig. 1a) and the formation energy of -99.47 meV/atom, which is -83.27 meV/atom lower than that of the most stable structure proposed in the literature so far [13]. The $Cmcm$ structure consists of 4 f. u. in the unit cell with the lattice parameters and the atomic positions given in Table I. The B atoms form rippled hexagonal layers shifted from each other laterally half of lattice vector \mathbf{a} . Each Be atom is at the hollow site (above the center of B hexagon) of one B hexagonal layer, while it is at the bridge site (above the center of bond between 2 B atoms) of the other B hexagonal layer, making the Be atoms coordinated by 8 B atoms. This $Cmcm$ structure can be built directly from the well-known $P6/mmm$ AlB_2 -family structure by doubling the unit cell in the lattice vector \mathbf{c} direction, then shifting the lower half of the new unit cell laterally by half of lattice vector \mathbf{a} . We note that the BeB_2 $P6/mmm$ structure is both energetically and dynamically unstable since it has a positive formation energy of 120.5 meV/atom and some soft phonon modes in our calculations as well as other works [13, 14]. The shifting of the lower half of the doubled unit cell stabilizes the new $Cmcm$ BeB_2 structure by gaining 219.92 meV/atom in the total energy. In addition, our phonon calculation (Fig. 1b) also confirms that the $Cmcm$ BeB_2 structure is dynamically stable without any soft phonon modes. The shifting of the lower half of the doubled cell also shortens the Be-B bond-length from 2.22 Å in BeB_2 $P6/mmm$ structure to 3 different Be-B bond-lengths in the $Cmcm$ structure: 2.08 Å between the Be atom and the 2 bridging B atoms, 2.03 Å between the Be atom and another 2 B atoms sharing the same vertical plane with bridging B atoms, and 1.93 Å with the rest 4 B atoms of the B hexagon, respectively. It is interesting that this intercalated B hexagonal layers motif is also a profound motif in BeB_3 system. Such a motif is also clearly seen in the lowest-energy structure of BeB_3 (Fig. 1.c) from our search for $Z = 2$ and 4 f. u., where the same parameters setting as used for BeB_2 case were used. The structure shown in Fig. 1.c is a $C2/m$ structure with 4 f. u. in the unit cell, which is identical to the one found in previous study [13]. The lattice parameters and the atomic positions of this structure are also given in Table I. As can be seen clearly in Fig. 1, the local environment of Be atoms in the $C2/m$ BeB_3 structure is exactly the same as that in the $Cmcm$ BeB_2 structure, where the Be atoms are at the hollow site of one B hexagon while they are at the bridge site of another B hexagon, making the Be atoms coordinated by 8 B atoms. The extra B atoms in the BeB_3 structure aggregate at the boundary of the unit cell and break the B hexagonal layers in to rippled B hexagonal ribbons.

In the Be-B phase diagram, the only stable alloy phase is $\text{Be}_{29}\text{B}_{81}$ with primitive cell containing 110 atoms [13]. Although the Cmc BeB_2 structure is the lowest energy structure from our search with unit cell up to 8 formula units, the formation energy of the Cmc BeB_2 structure is 14.8 meV/atom above the tie-line connecting the formation energies of the $\text{Be}_{29}\text{B}_{81}$ and the pure Be structures. We also calculated the free energies of the three phases as the function of temperature by taking into account the contribution from the vibration entropy. We found that the free energy of the Cmc BeB_2 structure is always above the tie-line in the temperature range from 0 K to 1000 K. This means that the Cmc BeB_2 structure is a thermodynamically metastable structure for a wide range of temperature. More crystal structure searches with larger unit cells could be interesting and are our future studies.

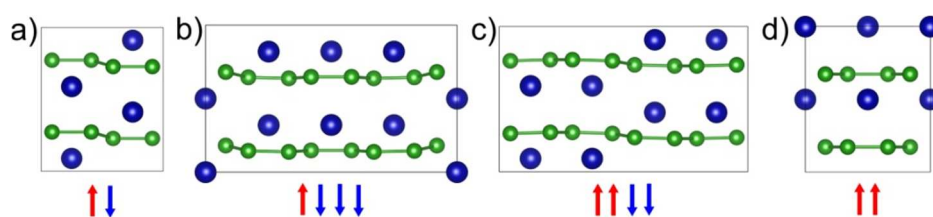


Figure 2. The atomic structures of (a) Cmc, (b) Amm2, (c) Cmca and (d) Fmm2 BeB_2 structures looking along the lattice vector **a**, **b**, **a** and **a**, respectively, and their corresponding “spin configurations” shown below. The Be atoms are at the hollow site of the closer B layer and at the bridge site and the other B layer.

Structure	Parameters	E_{form}	Atom	x	y	Z
Cmc	a = 2.9708	-99.47	Be (4c)	0.00000	0.58868	0.25000
BeB_2	b = 6.0499		B (8f)	0.00000	0.72768	0.58908
Z = 4	c = 5.1324		Be(2a)	0.00000	0.00000	-0.00003
			Be(2b)	0.50000	0.00000	0.67898
Amm2	a = 10.265	-59.90	Be (4c)	0.25092	0.00000	0.18020
BeB_2	b = 2.9791		B (4c)	0.58050	0.00000	0.35196
Z = 8	c = 6.0157		B (4c)	0.66902	0.00000	0.86192
			B (4c)	0.83012	0.00000	0.85514
			B (4c)	0.08023	0.00000	0.31879
Cmca	a = 2.9823	-55.20	Be (8f)	0.00000	-0.09134	0.37403
BeB_2	b = 6.0128		B (8f)	0.00000	0.76380	0.54475
8 f.u.	c = 10.268		B (8f)	0.00000	0.72856	0.20546
Fmm2	a = 2.9801	-28.29	Be (4a)	0.00000	0.00000	-0.00128
BeB_2	b = 5.1329		B (8c)	0.00000	0.16102	0.67253

Z = 4	c = 5.9932					
	a = 5.9890					
C2/m	b = 2.9250		Be (4i)	0.06190	0.00000	0.69550
BeB ₃	c = 6.7620	-17.74	B (4i)	0.84250	0.00000	0.03660
Z = 4	α = 90.00		B(4i)	0.26270	0.00000	0.18890
	β = 83.28		B(4i)	0.76190	0.00000	0.56840
	γ = 90.00					

Table I. The lattice parameters in Å, the formation energies E_{form} in meV/atom and the atomic positions of low-energy structures of BeB₂ and BeB₃ systems.

In our search with $Z = 4$ we also obtained several other very low energy structures, which are Amm2 and Cmca structures with 8 f. u. in the unit cells and Fmm2 structure with 4 f. u. in the unit cell (Fig. 2). The detail lattice parameters, the formation energies and the atomic positions of these structures are given in Table I. Although our phonon calculations show that these structures are dynamically unstable, it is interesting that all these structures have the same structural motif seen in the Cmcm structure: Be intercalated structures with 2 adjacent hexagonal B layers shifted laterally from each other along the **a** axis such that each Be atom at the hollow site of one B layer is simultaneously at the bridge site of the other B layer as shown in Fig. 2. We can see clearly from Fig. 2 that the only difference between these 4 structures is the sequence of Be atoms at hollow sites or bridge sites of one of the B layers. If we use the displacement of Be atom (moved up or down) from the mid-plane between 2 B layers to describe the sequence of Be atoms in these structures, we can describe the Cmcm structure as up-down configuration, the Amm2 structure as up-up-up-down configuration and so on, as indicated by arrows in Fig. 2. In this way we can exactly map the structure description into a one dimensional Ising spin model with the displacements of the Be atoms playing the role of spin eigenvalues. With interaction truncated at the next nearest-neighbor and assuming the interaction strengths J_0 , J_1 , and J_2 are constants, we can write the Ising-like model Hamiltonian for the structures of BeB₂ as:

$$H = -\frac{1}{2}J_1 \sum_{NN} S_i \cdot S_j - \frac{1}{2}J_2 \sum_{NNN} S_i \cdot S_j - J_0 \sum_i S_i$$

where S_i is the displacement of Be atom, which has the value of 1 or -1 for the “up” or “down” displacement. NN stands for nearest-neighbor and NNN for next nearest-neighbor. By a least square fitting to the energies of the four BeB₂ structures above, we obtained $J_0 = 59.64$ meV, $J_1 = -35.59$ meV, and $J_2 = 4.31$ meV with a surprisingly small residual $\sigma = 0.31$ meV. This result suggests that the energies of the low-energy structures of BeB₂ can be well described by the

Ising-like model. Ising-like models have been successfully applied to describe metallic alloy systems in cluster expansion approaches [28], where the chemical occupancies of the alloy constituents play the role of spin eigenvalues. Here we show an interesting case of using Ising-like model to describe a system with the displacement of atoms as the spin eigenvalues. In order to further validate of the Ising-like model for BeB_2 , we construct several new BeB_2 structures with the Be-displacement sequences as up-up-up-down-down-down (3-3), up-up-down-down-down-down (2-4), up-down-down-up-down-down (1-2-1-2) or up-down-up-down-up-up-down-down (1-1-1-1-2-2). We calculate the energies of these structures by DFT and compare the energies with the results from the Ising-like model using the interaction parameters determined above. It turns out that the formation energies predicted by the Ising-like model are in very good agreement with those values obtained by DFT calculations with the energy differences in the DFT error range of 1 ~ 2 meV/atom. For example, the formation energies predicted from the Ising-like model and from the DFT calculation are -46.80 and -47.97 meV/atom for the 3-3 configuration, -46.80 and -46.81 meV/atom for the 2-2 configuration, and -68.00 and -67.10 meV/atom for the 1-2-1-2 configuration, respectively. This result shows that there is a whole family of low-energy Be intercalated structures of BeB_2 , which can be well described by the Ising-like model with “anti-ferromagnetic coupling” between Be displacements. Thus, the Cmcm structure is the lowest-energy structure of the structure family, while the Fmm2 structure with ferromagnetic configuration is the highest energy structure of the structure family.

In order to compare the stability of the Cmcm structure with the P6/mmm AlB_2 -family structure for other alkali or alkaline earth diborides (MB_2), we calculated the formation energies of the MB_2 in P6/mmm and Cmcm structures for $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{Mg}, \text{Ca}, \text{Sr},$ and Ba . The results show that the Cmcm structure is more stable than P6/mmm structure for $\text{RbB}_2, \text{CsB}_2, \text{SrB}_2$ and BaBe_2 , but the formation energies of Cmcm RbB_2 and CsB_2 are positive, indicating that these two compounds are energetically unstable. For CaB_2 , the Cmcm structure was transformed to Cmmm structure, which is the same structure as the ground-state structure of CaB_2 recently proposed [29]. The P6/mmm structure is more stable than Cmcm structure for all other MB_2 compounds, among them only P6/mmm LiB_2 and MgB_2 have negative formation energies.

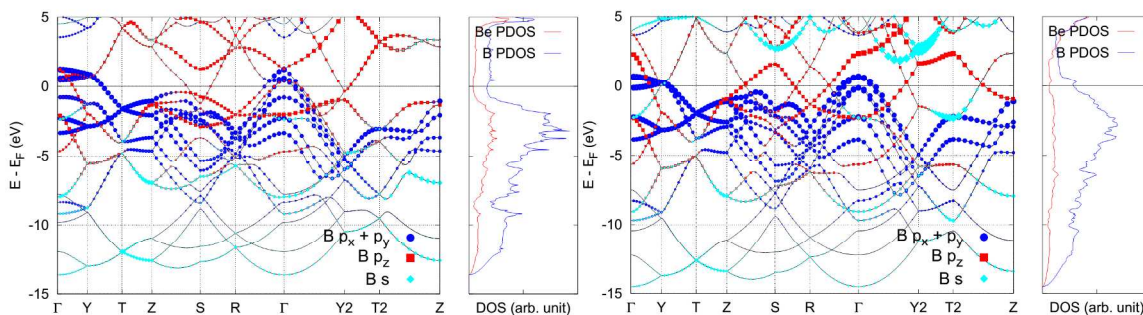


Figure 3. The electronic band structures of (left) Cmcm and (right) P6/mmm BeB₂ structures and their corresponding projected density of states. The blue circles and red squares and cyan diamonds show the $p_x + p_y$ -, p_z - and s -characters of B.

We also performed electronic band structure calculation for the Cmcm BeB₂ structure as shown in Fig. 3, where the band characters of B are also shown. For comparison, we also show the electronic band structure of the P6/mmm BeB₂ calculated using an orthorhombic unit cell with $a = 2.931 \text{ \AA}$, $b = 5.725 \text{ \AA}$ and $c = 5.071 \text{ \AA}$, which is the doubled cell we mentioned above. Due to the similarity between the Cmcm and P6/mmm BeB₂ structures, their band structures are very similar as can be seen in Fig. 3. The flat bands with strong B p -character near the Fermi level from Γ to Y point in the Cmcm structure were shifted up above the Fermi level from the P6/mmm structure, making the density of states at the Fermi level in the Cmcm structure substantially smaller than of that of the P6/mmm structure. This shifting can be attributed the B's band broadening resulting from the shortening of bonding between Be and B atoms. The density of states near the Fermi level of Cmcm structure is contributed mainly from B layers and the bands near the Fermi level have strong B p -character, while the deep laying bands have very strong B s character, which are similar to the band structure of MgB₂. Thus, we also investigate the possibility of Cmcm BeB₂ structure for superconductor through electron-phonon coupling via the BCS mechanism. The results from our calculation using Quantum-Espresso code showed that the effective phonon frequency is high ($\omega_{\text{log}} = 797 \text{ K}$), but the density of state at Fermi level is not so large (1.01 states/eV/unit cell). The electron-phonon coupling coefficient is also quite small, which is 0.25 in our calculation. Thus, the critical temperature for possible superconducting in Cmcm BeB₂ is very small, $\sim 45 \text{ mK}$ according to the Allen-Dynes modified formula [30] if the Coulomb coefficient $\mu^* = 0.10$ is used. There are several experimental efforts in measuring the superconducting critical temperature of BeB₂ [31, 32]. Both Felner [31] and

Mori [32] showed that the superconducting critical temperature of BeB₂ should be very small when they could not observe superconductivity with temperature as low as 1.8 K and they attributed the low superconducting critical temperature or the absence of superconductivity to the low density of state at the Fermi level. Our results are consistent with these experimental observations. Doping BeB₂ by other less electron alkali metals may help increase density of states at the Fermi level and hence the critical temperature.

In summary, we performed “from scratch” genetic algorithm search for low energy structures of BeB₂ with $Z = 4, 6$ and 8 f. u. We found a new family of low-energy Be-intercalated structures, whose energies obey a Ising-like model with “anti-ferromagnetic” coupling between Be atoms’ displacements. The lowest energy structure in our search is a Cmc₂m BeB₂ structure with 4 f. u. in the unit cell and formation energy of -99.47 meV/atom, which is -83.27 meV/atom lower than the literature proposed structure so far. The bands near the Fermi level of the Cmc₂m BeB₂ structure have strong B p character as that in the superconducting MgB₂. However, the critical temperature of Cmc₂m BeB₂ structure for superconducting is very small because of the small electron density of states at the Fermi level as well as the small electron-phonon coupling although the typical phonon frequency is high.

Note added: During the revision of the manuscript, we became aware of the work by S. Shah and A. N. Kolmogorov [33], where they incorrectly indexed the Cmc₂m BeB₂ structure as Pnnm.

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