Absence of superconductivity in the high-pressure polymorph of MgB$_2$

Yanning Ma,1,2,* Yanchao Wang,1 and Artem R. Oganov2,3

1National Lab of Superhard Materials, Jilin University, Changchun 130012, People’s Republic of China
2Laboratory of Crystallography, Department of Materials, ETH Zurich, Wolfgang-Pauli-Stress 10, CH-8093 Zurich, Switzerland
3Geology Department, Moscow State University, 119992 Moscow, Russia

(Received 22 October 2008; revised manuscript received 8 January 2009; published 2 February 2009)

We report a high-pressure orthorhombic KHg$_2$-type polymorph (space group Imma, 4 f.u./cell) of MgB$_2$ stable above 190 GPa predicted through ab-initio evolutionary simulations. The formation of this new phase results from the strong out-of-plane distortions of the two-dimensional honeycomb boron sublattice of the low-pressure AlB$_2$-type structure creating a peculiar tetrahedrally bonded three-dimensional boron network. This high-pressure phase is a weak metal and not superconducting, re-highlighting the key role of the planar boron sublattice in forming the superconducting state and clear structure-property relations that can enable design of new superconductors.

DOI: 10.1103/PhysRevB.79.054101

At ambient pressure, the superconducting MgB$_2$ (Ref. 1) crystallizes in the AlB$_2$-type hexagonal structure (space group $P6/mmm$), in which B atoms form two-dimensional (2D) honeycomb layers, and Mg atoms sit above the centers of the hexagons in between the B planes. Within the B layer, each B atom forms three $\sigma$ bonds ($sp^2$ hybridization), while a nonbonding $\pi$ ($p_z$) wave function is localized above and below the B plane. The superconductivity of MgB$_2$ in this hexagonal structure arises mainly from the strong coupling between the in-plane $E_{2g}$ phonon mode and the $\sigma$ bonding states,2–4 and the peculiar two-band superconducting nature5,7 has fundamentally raised the transition temperature to be $\sim$40 K.

Pressure could effectively shorten the interatomic distance of materials, and thus significantly alter their electronic bonding states to modify the physical properties and/or induce the formation of new physical states. Indeed, experiments demonstrated that the superconducting transition temperature ($T_c$) of MgB$_2$ decreases under pressure at a rate from $-0.8$ to $-2.0$ K/GPa (for example, see Refs. 8–12). This occurs continuously within the same structure and experimental measurements11,13–16 up to 57 GPa did not reveal any structural phase transitions. Later, Loa et al.17 and Shao et al.18 suggested that if the applied pressure is high enough, an isosymmetric transition to the UHg$_2$-type structure might be possible since AlB$_2$ and UHg$_2$ are isopointal structures, distinguished only by their $c/a$ ratios. However, our ab-initio calculations19 ruled out this transition after the optimized $c/a$ value of 1.15 at zero pressure decrease only slightly to 0.99 at 200 GPa, which is still well above the characteristic $c/a$ of 0.60–0.85 for UHg$_2$. Therefore, the high-pressure phase of MgB$_2$ remains unknown. The discovery of new stable crystal forms of MgB$_2$ is of great fundamental interest and, in particular, would help to unravel the key factors responsible for the formation of superconducting states—a knowledge that can even be used for design of new high-$T_c$ materials. In this paper, we have unraveled a high-pressure orthorhombic KHg$_2$-type structure of MgB$_2$ stable above 190 GPa and containing three-dimensional (3D) framework of B atoms, allowing us to re-highlight the major role of B-B $\pi$-bonded networks and charge transfer from metal atoms to B in the superconductivity.

Ab-initio evolutionary algorithm employed here was designed to search for the structure possessing the lowest free energy at given $P/T$ conditions. The significant feature of this methodology is the capability of predicting the stable structure with only the knowledge of the chemical composition. The details of the search algorithm have been described elsewhere.20–23 The evolutionary search was done with the USPEX code20–22 the underlying ab-initio structure relaxations were performed using density-functional theory (DFT) within the generalized gradient approximation (GGA) (Ref. 24) as implemented in the Vienna ab-initio simulation package (VASP) code.25 The all-electron projector-augmented wave (PAW) (Refs. 26 and 27) method was adopted with the choices of $1s^2$ cores both for Mg and B atoms. We used the plane-wave kinetic-energy cutoff of 400 eV which was shown to give excellent convergence of the total energies and structural parameters. Electron-phonon coupling (EPC) has been explored using the pseudopotential plane-wave method and density-functional perturbation theory28,29 as implemented in the QUANTUM-ESPRESSO package.30 A Troullier-Martins (TM) (Ref. 31) norm-conserving scheme was used to generate pseudopotentials for Mg and B with the choices of electronic configurations of $2p^53s^2$ and $2s^22p^1$, respectively. In these calculations we used a kinetic-energy cutoff of 60 Ry and a $8\times6\times6$ Monkhorst-Pack (MP) grid, for which tests showed excellent convergence of the computed properties. The technique for the calculation of EPC has been described in detail in our previous publication.32 Theoretical pressures are derived from the average of the diagonal components of the stress tensor in fine structural optimizations and confirmed by fitting the energy vs volume data to the Murnaghan equation of states. The use of TM or PAW method only affects slightly the theoretical pressures at the chosen volumes.

The variable-cell structure predictions were performed at 0, 100, 150, 200, 300, and 500 GPa with systems containing 3, 6, 9, 12, and 18 atoms in the simulation cell. At 0, 100, and 150 GPa, our simulations with the only input of chemical compositions of Mg:B = 1:2 predicted the most stable structure to be AlB$_2$ type [Fig. 1(c)], in complete agreement with experiment. This successful prediction encourages us to explore higher-pressure phases. Our evolutionary simulations...
At 200 GPa for KHg$_2$ phase, lattice parameters: $a = 4.795$ Å, $b = 2.855$ Å, and $c = 4.795$ Å; atomic positions: B at $8i$ (0.1817, 0.25, 0.5906) and Mg at $4e$ (0, 0.25, 0.1876).

at 200, 300, and 500 GPa identified a new stable orthorhombic $Imma$ structure (4 f.u./cell) [Fig. 1(d)]. This structure is analogous to that of intermetallic compound KHg$_2$.\textsuperscript{33} We have computed the full phonon-dispersion curves at 260 and 500 GPa and found no imaginary phonon frequencies, i.e., this structure is dynamically stable. The calculated enthalpies [Fig. 1(a)] show that the predicted new structure is thermodynamically stable above 190 GPa, where the current experimental techniques are readily accessible.

Our calculations suggest that the AlB$_2$ $\rightarrow$ KHg$_2$ structural transition is first order and is accompanied by a pronounced 4.5% volume drop [Fig. 1(b)] and an increase in connectivity in the B framework from 3 to 4 [Fig. 1(c) and 1(d)]. This transition is in many ways similar to the graphite-diamond transition: graphitelike B lattice of the AlB$_2$ structure [Fig. 1(c)] transforms into a 3D network [Fig. 1(d)] resembling diamond (or the hexagonal diamond). The formation of KHg$_2$ structure can be imaged to result from a strong out-of-plane distortion of the honeycomb B sublattice and concomitant displacements of the Mg atoms. As a result, B atoms form a strongly puckered network of tilted hexagons and the Mg atoms lie between opposite hexagons. At the transition, the number of nearest neighbors increases from 3 to 1+2+1, and the B-B distances increase from 1.561 Å in parent planar hexagons to 1.661 Å in the tilted hexagons of the child KHg$_2$ structure. The newly formed fourth covalent B-B bond between the hexagons (its length is 1.726 Å) is confirmed by the deformation electron-density plots.

Energy bands for KHg$_2$ structure at 200 GPa are shown in Fig. 2 to illustrate the electronic properties of the high-pressure polymorph. A weak band overlap implies this is a poor metal with a very small electronic density of states (DOS) at the Fermi level ($N_0$) [Fig. 3(c)]. 3D Fermi-surface pieces [Fig. 2(c)] are found to be mainly located along the

FIG. 1. (Color online) (a) Enthalpy of the KHg$_2$ structure (relative to AlB$_2$) with pressure. We used the $12 \times 12 \times 12$ and $8 \times 8 \times 8$ $k$ meshes for AlB$_2$ and KHg$_2$, respectively, for which total energies are converged to be better than $\sim$1 meV. (b) The calculated equations of state for the AlB$_2$ and KHg$_2$ phases, together with the experimental data from Ref. 16 for the AlB$_2$ phase. [(c) and (d)] Crystal structures of AlB$_2$ and KHg$_2$ phases, respectively. At 200 GPa for KHg$_2$ phase, lattice parameters: $a = 4.749$ Å, $b = 2.855$ Å, and $c = 4.795$ Å; atomic positions: B at $8i$ (0.1817, 0.25, 0.5906) and Mg at $4e$ (0, 0.25, 0.1876).

FIG. 2. (Color online) Band structures for the KHg$_2$ phase at (a) 200 GPa and (b) 500 GPa. Low-symmetry special $k$-points $V$ ($-0.49523, 0.49523, 0.49523$) and $H$ ($-0.33385, 0.33385, 0.6566$) had to be chosen to reveal band overlap. 3D Fermi-surface plots for the KHg$_2$ structure at (c) 200 GPa and (d) 500 GPa. Note that at 200 GPa, $\Gamma$ point is located in between two Fermi-surface pockets.
ABSENCE OF SUPERCONDUCTIVITY IN THE HIGH-

...experimental values provide an accurate description of band gaps, within 10% of the

...earliest in cubic/wurtzite BN, where each B atom contributes 0.75 electrons to the B-N bond. However, the formation of

...care was paid to the energy values of the eighth band

...Fermi surfaces, phonons, and EPC are not corrected.

...structure, as suggested by the continuous changes in lattice parameters with pressure. It is known that DFT usually underestimates the band gap. GW calculations (known to provide accurate description of band gaps, within 10% of the experimental values) were thus adopted to carefully confirm the metallicity of KHg$_2$ phase at 200 GPa. Particular care was paid to the energy values of the eighth band (highest valence band) and the ninth band (lowest conduction band) with respect to the Fermi energy. It turns out that with the GW correction, the ninth band moves above Fermi level, but the eighth band still crosses over the Fermi level. The metallic feature remains. Note that the GW calculation is only at an attempt to correct the band energies in assessment of the metallicity, but other results (e.g., electronic DOS, Fermi surfaces, phonons, and EPC) are not corrected.

...the electronic DOSs of the AlB$_2$ and KHg$_2$ phases suggest that p electrons of B atoms dominate the electronic behavior at the Fermi level. Therefore, it is essential to understand how the B framework is modified in order to uncover the physical origin of the $N_0$ drop at the transition [Fig. 3(c)]. In the AlB$_2$ phase, each B atom has three valence electrons that are used to form three coplanar $\sigma$ bonds ($sp^2$ hybridization). Under pressure, four B-B $\sigma$ bonds ($sp^3$ hybridization) are constructed for the KHg$_2$ phase. Note that four B-N covalent bonds are known earlier in cubic/wurtzite BN, where each B atom contributes 0.75 electrons to the B-N bond. However, the formation of four tetrahedral B-B covalent bonds is very unusual for any B-related materials. At the transition, the charge density localized at the three B-B bonds in the honeycomb lattice is depleted in order to allow the formation of the fourth bond between hexagons, consistent with the increase in the B-B distance. The resulting 3D framework lacks the system of $\pi$ bonds with mobile electrons and has more localized electrons, as a result of which the conductivity drops.

The projected phonon DOSs and the EPC spectral function $\alpha^2 F(\omega)$ for the KHg$_2$ structure at 200 GPa have been presented in Fig. 3(d). It is found that all the phonons contribute to the EPC, signifying an isotropic EPC feature originated from the 3D structural nature. This is in apparent contrast with the strongly anisotropic EPC behavior in AlB$_2$ structure. The obtained EPC $\lambda$ for KHg$_2$ phase at 200 GPa is 0.11, which is very small and has a zero $T_c$. To eliminate the pressure effect on the EPC of KHg$_2$ structure in view of the greatly depressed $T_c$ in AlB$_2$ structure, we optimized the KHg$_2$ structure to zero pressure and performed the EPC calculations. Again, the resulting $\lambda$ value is very small, 0.24 ($T_c \approx 0$ K). Therefore, we conclude that KHg$_2$-type MgB$_2$ is intrinsically not a good superconductor. The current calculations have confirmed that instead of materials compositions, the crystal structure is the dominant factor for superconductivity. Here, the B-layered structure is advantageous for high $T_c$.

The most fruitful and intuitive way to understand the electronic and structural properties of MgB$_2$ is to invoke its profound analogy with carbon. Graphite, in which carbon prefers the $sp^2$ hybridization, is an ambient pressure form of carbon with a zero band gap. Under sufficient compression, graphite transforms to diamond—a wide-gap insulator characterized by $sp^3$ hybridization. To be isoelectronic with carbon, B atom misses one electron. In MgB$_2$ this one missing
electron is donated by Mg atoms. If charge transfers were complete, the low-pressure hexagonal form would have (like graphite) a zero band gap, and the KHg₂ phase would be a wide-gap insulator (removing Mg from the KHg₂ structure and replacing B with C, after full structural optimization we see an insulating structure similar to hexagonal diamond). A consequence of incomplete charge transfer (as in MgB₂) is a finite DOS at the Fermi level (i.e., metallic character) and hole conductivity, as shown in Fig. 2. Mulliken population analysis suggests an increase in charge transfer from Mg to B at a rate of $4 \times 10^{-3}$ e/Γp; this naturally leads to a decrease in $N(0)$ (and $T_c$ for the AlB₂ phase) with increasing pressure [Fig. 3(c)]. These observations allow us to identify two key factors for superconductivity in MgB₂ and related brides. First, geometry and bonding in the B sublattice (graphite vs diamond, networks of delocalized $\sigma$ bonds vs frameworks of localized $\sigma$ bonds) are crucial. Second, as the amount of charge transfer (which determines the DOS at the Fermi level) depends on the electronegativity of the cation, we identify electronegativity of the donor atom as an important factor governing $T_c$. The first rule draws our attention to graphitelike (e.g., MgB₂ in the AlB₂ form) and fullerene-like (materials with B₁₂ icosahedra) structures with systems of delocalized $\sigma$ bonds (we note that for carbon, doped graphite and especially fullerenes are superconductors), while the second suggests a hole doping or replacing Mg with more electronegative cations (e.g., Be).37

Previously, Singh38 has proposed a pressure-induced B₁₂ mode softening in AlB₂ structure at 143 GPa by employing the semi-empirical lattice parameters. However, our calculations in use of the lattice data by ab-initio structural optimization do not support this.19 In fact, all phonon frequencies were found to increase with pressure up to the transition pressure of 190 GPa. We thus eliminate phonon softening as the driving force for the structural transition. Nevertheless, in view of the electronic DOS in KHg₂ structure [Fig. 3(b)], it is suggested that a well-defined electronic pseudogap might effectively lower the total energy and, together with its higher density, stabilize the new phase.

In summary, we have first reported a high-pressure KHg₂-type crystal form of MgB₂ found using the recently developed ab-initio evolutionary algorithm. This structure possesses an intriguing $sp^3$ B-B bonded network and displays a semimetallic behavior. The superconducting state is destroyed with the formation of this 3D B lattice. Our predictions re-highlight the major role of B-B $\pi$-bonded networks and charge transfer from metal atoms to boron. These ideas are useful for the design of novel superconductors.

Y.M. and Y.W. are thankful for the partial financial support from the China 973 Program under Grant No. 2005CB724400, the National Natural Science Foundation of China under Grant No. 10874054, the NSAF of China under Grant No. 10676011, and the 2007 Cheung Kong Scholars Programme of China. Y.M. and A.R.O. gratefully acknowledge financial support from the Swiss National Science Foundation under Grant No. 200021-111847/1.
mun. 175, 713 (2006).
37 In order to demonstrate our idea, we have performed EPC calculations for BeB2 within AlB2 structure. We use Be pseudopotential but adopt the atomic mass of Mg to better compare with MgB2. At zero pressure, the resulting $\lambda$ for BeB2 is 0.89, much larger than that (0.73) of MgB2. Note that the two EPC calculations for BeB2 and MgB2 are performed at nearly identical conditions to have a good comparison.