High-Temperature Superconductivity in Doped Boron Clathrates

Liang Ma(马良)[1,2,3], Lingrui Wang(王玲瑞)[1], Yifang Yuan(袁亦方)[1*], Haizhong Guo(郭海中)[1,2*], and Hongbo Wang(王洪波)[4]

[1]*Key Laboratory of Materials Physics (Ministry of Education), School of Physics and Microelectronics, Zhengzhou University, Zhengzhou 450052, China*
[2]*Institute of Quantum Materials and Physics, Henan Academy of Sciences, Zhengzhou 450046, China*
[3]*Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
[4]*State Key Laboratory of Superhard Materials & International Center for Computational Method and Software, College of Physics, Jilin University, Changchun 130012, China*

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The recent discoveries of near-room-temperature superconductivity in clathrate hydrides present compelling evidence for the reliability of theory-orientated conventional superconductivity. Nevertheless, the harsh pressure conditions required to maintain such high T_c limit their practical applications. To address this challenge, we conducted extensive first-principles calculations to investigate the doping effect of the recently synthesized LaB_8 clathrate, intending to design high-temperature superconductors at ambient pressure. Our results demonstrate that these clathrates are highly promising for high-temperature superconductivity owing to the coexistence of rigid boron covalent networks and the tunable density of states at the Fermi level. Remarkably, the predicted T_c of BaB_8 could reach 62 K at ambient pressure, suggesting a significant improvement over the calculated T_c of 14 K in LaB_8. Moreover, further calculations of the formation enthalpies suggest that BaB_8 could be potentially synthesized under high-temperature and high-pressure conditions. These findings highlight the potential of doped boron clathrates as promising superconductors and provide valuable insights into the design of light-element clathrate superconductors.

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Since the discovery of superconductivity by Onnes in 1911,[1] the pursuit of superconductors with higher superconducting transition temperatures (T_c) has been one of the central topics of scientific research activities. Recent breakthroughs in the clathrate hydrides family have shown T_c values exceeding 200 K under high pressures, raising the possibility of realizing room-temperature superconductivity.[2–10] The remarkable high-T_c superconductivity of clathrate hydrides is attributed to the formation of the peculiar H clathrate structure, resulting in large H-derived electronic density of states (DOS) at the Fermi level and exceptionally strong electron–phonon coupling (EPC) related to H–H vibrations.[11,12] However, the clathrate structures for hydrogen are highly atypical and can only be formed when hydrogen accepts enough additional electrons from metal atoms under extreme high-pressure conditions, which limit their practical applications.[13] Consequently, it is an urgent need to explore novel high-T_c superconductors under ambient pressure for both fundamental physics interest and practical application.

One promising strategy to achieve this goal is to explore other clathrate structures constructed by non-hydrogen elements such as boron (B), carbon (C), or silicon (Si), which have been suggested to realize the high-T_c superconductivity under moderate and even ambient pressures.[14] For instance, several metal silicide clathrates, largely based on Ba_8Si_{46}, are stable superconductors at ambient pressure with a maximum observed T_c of 8 K.[15–18] Furthermore, the clathrate SrB_3C_3 in sodalite-like structure, synthesized by Zhu *et al.* at 50 GPa,[19] is a hole conductor with a measured T_c of 20 K at 40 GPa, which can remain stable close to ambient pressure with an anticipated T_c around 31 K.[20] The successful synthesis of these light-element clathrate superconductors has inspired numerous theoretical investigations of related materials. A series of clathrate superconductors, proposed theoretically by substituting both host and guest atoms of SrB_3C_3 and clathrate hydride superconductors with other light elements, have been predicted with high-T_c superconductivity at ambient pressure, such as NaC_6 ($T_c \sim 116$ K), LaB_5N_5 ($T_c \sim 69$ K), $Al(BN)_6$ ($T_c \sim 47$ K), $Al_2(BN)_6$ ($T_c \sim 72$ K), CaB_3C_3 ($T_c \sim 48$ K), $Rb_{0.5}Sr_{0.5}B_3C_3$ ($T_c \sim 75$ K), and $K_{0.5}Pb_{0.5}B_3C_3$ ($T_c \sim 88$ K).[21–28] The wide range of possible substitution schemes for clathrate structures suggests that the doped light-element clathrates could offer a promising avenue for manipulating electronic properties and result in developing high-T_c superconductors at ambient pressure.

Recently, Ma *et al.*[29] reported the formation of a previously unknown boron-based clathrate structure, with chemical formula LaB_8, which possesses the boron-richest

*Corresponding authors. Email: yfyuan@zzu.edu.cn; hguo@zzu.edu.cn
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B_{26} cage that encapsulates a single La atom. In previous theoretical studies, we have established the potential of doped MB_8 clathrates as the substitutional structure for high-temperature superconductors, where Mg, Ca, Sr, and Y are substitutional elements in the MB_8 clathrates, resulting in the calculated highest T_c of 56 K in the SrB_8 clathrate.[29] This has motivated us to further investigate the possibility of achieving even higher T_c in MB_8 clathrates by selecting other guest atoms. To explore this possibility, we have investigated the electronic properties and electron–phonon interactions of the other doped MB_8 clathrates (M from groups IA, IIA, IIIA, and IIIB), where four dynamical stable MB_8 (M = Ba, Ga, In, and Tl) exhibit superconductivity at ambient pressure. Notably, the calculated T_c of BaB_8 reached 62 K at ambient pressure, surpassing the T_c of 39 K in MgB_2.[30] Furthermore, the investigation of the formation enthalpies as a function of pressure suggests that BaB_8 may be synthesized under high-pressure and high-temperature (HPHT) conditions, similar to the synthesis of LaB_8. Our results offer valuable insights for future experimental studies and provide guidance for the exploration of non-hydrogen clathrates as potential high-T_c superconductors.

Computational Method. Structural relaxations and electronic property calculations were performed using the Vienna *ab initio* simulation package (VASP)[31] with the exchange-correlation functional of generalized gradient approximation in versions of Perdew–Burke–Ernzerhof[32] and projector augmented wave pseudopotentials.[33] A plane-wave kinetic energy cutoff of 700 eV and Monkhorst–Pack k-meshes with grid spacing of $2\pi \times 0.03$ Å^{-1} were employed to ensure enthalpy calculations to converge to less than 1 meV/atom.[34] Phonon calculations were carried out using the finite displacement approach through the PHONOPY code.[35] The dynamical matrices and EPC were calculated using density functional perturbation theory[36] implemented in the Quantum-Espresso (QE) package with ultrasoft pseudopotentials and a kinetic energy cutoff of 60 Ry.[37] The Brillouin zones were all sampled on a $4 \times 4 \times 4$ q-grid (phonons), and the integration of the e–ph matrix elements was carried out on a $16 \times 16 \times 16$ k-grid (electrons). Since the Eliashberg equation can give a better description of strong EPC systems with constant $\lambda > 1.5$, the T_c values were calculated by solving both the Allen–Dynes modified McMillan equations[38] and the Eliashberg equations[39,40] with the Coulomb potential μ^* of 0.1 and 0.13. Structure prediction of BaB_x (x = 1–8) compounds was conducted using the CALYPSO code, which employs a swarm intelligence structure search method.[41,42] The simulations were performed with varying sizes of simulation cells containing 1, 2, and 4 formula units (f.u.) under a pressure of 150 GPa.

Results and Discussions. The covalent nature of all B–B bonds and the ionic characteristic of the La–B bond in LaB_8 allows for a wide range of possible substitution schemes for guest atoms.[29] Consequently, we employed more dopants from IA, IIA, IIIA, and IIIB groups, resulting in twelve MB_8 (M = Li, Na, K, Rb, Cs, Be, Ba, Sc, Al, Ga, In, and Tl) clathrates with the same basic $R\bar{3}m$ LaB_8 structure at ambient pressure. A full relaxation of the MB_8 at ambient pressure was first performed, followed by the examination of the dynamical stability of these compounds through phonon dispersion relations. The host-guest structure characteristic of MB_8 clathrate is depicted in Fig. 1, where the B atoms form an interconnected framework while the guest atoms occupy the central positions of the B-based cage. The results show that no imaginary phonon frequencies exist in the phonon spectrum of four doped MB_8 compounds (M = Ba, Ga, In, and Tl) at ambient pressure, indicating their dynamical stability (Fig. S1 in the Supplementary Material). Despite the distinct guest atoms, the crystal structures of the above four MB_8 clathrates exhibit the same space group and comparable lattice constants, suggesting that suitable guest atom substitution could preserve the stability of the structure. Detailed information on the structural characteristics of MB_8 compounds is provided in Table S1 in the Supplementary Material.

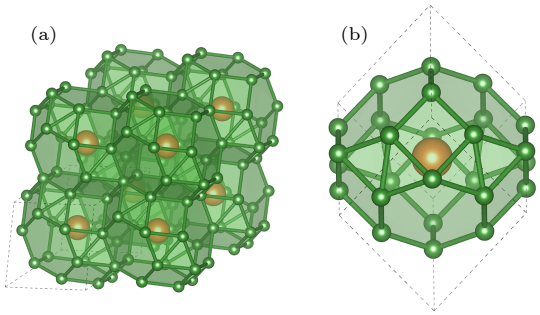

Fig. 1. (a) The crystal structure of clathrate MB_8 (M = Ba, Ga, In, and Tl). (b) The B_{26} cage consisting of twelve twisted rhombi and six twisted hexagons, with a single metal atom at the center.

Given the versatility of clathrate structures in terms of their tunable properties through guest atom substitution, we conducted band structure and density of states (DOS) calculations to elucidate the changes in the electronic properties of the doped MB_8 clathrates. Representative results for TlB_8 and BaB_8 are presented in Fig. 2 (with additional results shown in Fig. S2), revealing that all of the four doped MB_8 clathrates exhibit metallic phases with steep flat bands crossing the Fermi level. The orbital-resolved band structures demonstrate that the valence region close to the Fermi level is primarily composed of B-derived bands, while the guest M atoms are ionized and donate their charge to the B cages. This charge transfer nature is also evident from the evolution of the projected electronic density of states at the Fermi level for the doped MB_8 structures, where DOSs near the Fermi level are mainly contributed by the B atoms. Although the substitution of guest atoms has a relatively minor influence on the band structures, it effectively shifts the Fermi level due to the different valence electron counts of the guest atoms. For instance, in the case of alkaline earth element dopant Ba, the number of charge electrons is reduced by one electron compared to LaB_8, resulting in effective hole doping of the system and shifting the Fermi level towards the lower valence band. Consequently, the DOS value at the Fermi level (N_{Ef}) of BaB_8 is 3.50 states·eV^{-1}·f.u.$^{-1}$, significantly

higher than that of TlB_8 of 2.14 states·eV^{-1}·f.u.$^{-1}$ and 1.52 states·eV^{-1}·f.u.$^{-1}$ of LaB_8.[29]

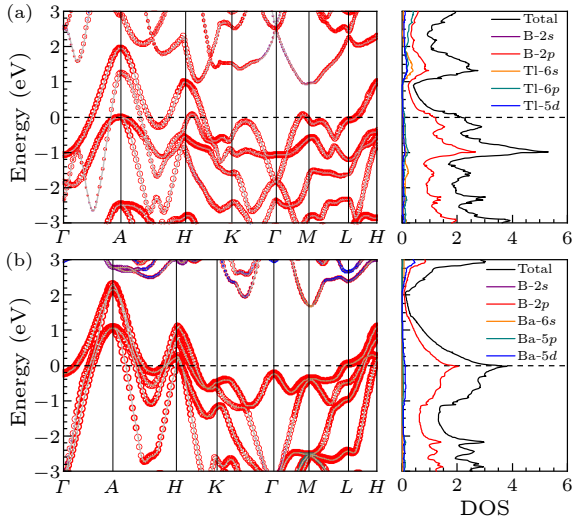

Fig. 2. Band structures and density of states (DOS, in units of states·eV^{-1}·f.u.$^{-1}$) for (a) TlB_8 and (b) BaB_8 at 0 GPa. The horizontal dashed lines indicate Fermi energy levels. The size of the circles represents the weights of the corresponding orbitals.

The presence of holes doped into the electronic band may result in a strong EPC to the bond-stretching phonons, similar to the mechanism observed in other notable covalent superconducting compounds such as MgB_2[30] and boron-doped diamond.[43] Previous work has shown the calculated T_c of 14 K in LaB_8 at ambient pressure.[29] Within similar structural characteristics, a high value of N_{Ef} is critical in enhancing the possibility of Cooper pair formation in MB_8, which is beneficial to boost the strength of the EPC and to promote superconductivity. Therefore, it is necessary to investigate the superconducting properties of these doped MB_8 structures, especially for BaB_8 clathrate.

We investigated the EPC interactions of the four dynamically stable doped MB_8 compounds (M = Ba, Ga, In, and Tl) at ambient pressure by solving both the Allen–Dynes modified McMillan equations[38] and the Eliashberg equations.[39,40] The phonon spectrum, projected phonon density of states (PhDOS), Eliashberg spectral function $\alpha^2F(\omega)$, and the integrated EPC strength λ of TlB_8 and BaB_8 are shown in Fig. 3 (results for other MB_8 compounds and the detailed information can be found in Fig. S3 and Table S2). The phonon spectra of all MB_8 clathrates exhibit two distinct parts, with the low-frequency range dominated by the vibrations of the M atoms due to their larger mass, and the high-frequency range driven by the vibrations of the B atoms. Furthermore, the EPC coupling predominantly originates from the vibrations of the B atoms, particularly the soft bond-stretching phonons in the mid-frequency range. In detail, the substitution of MB_8 clathrates with trivalent metal atoms from group ⅢA results in EPC coupling constants λ and calculated T_c similar to those of LaB_8,[29] due to the analogous electronic properties as mentioned above. For instance, the λ values for GaB_8, InB_8, and TlB_8 are 0.76, 0.65, and 0.67, leading to the calculated T_c values of 19.9 K, 19.3 K, and 20.3 K at ambient pressure, respectively. Notably, the substitution of divalent alkaline earth metal Ba significantly strengthens the EPC coupling compared to LaB_8. Among four doped MB_8 clathrates, BaB_8 stands out with the highest calculated EPC constant λ of 1.65, leading to the highest T_c value of 62 K when the screened Coulomb potential μ^* is set to 0.1. By comparing with the previous data, we found that BaB_8 exhibits the highest calculated T_c values among the alkaline earth metals, with calculated T_c values of 30 K, 52 K, and 56 K in MgB_8, CaB_8, and SrB_8, respectively.[29] It is noteworthy that the results contradict the initial expectation that BaB_8 would have a lower T_c compared to other alkaline earth metal dopants due to the heavier atomic mass of metal. The heavier atomic mass does decrease the phonon frequency, resulting in a lower value of ω_{log}, which is disadvantageous for superconductivity. However, the substitution of Ba effectively stabilizes the B_{26} cage and tunes the boron atomic density of states to peak at the Fermi level. Consequently, this modification significantly enhances the strength of EPC, as reflected in the higher value of λ, ultimately compensating for the deficiency and resulting in high-temperature superconductivity. In contrast, the smaller atomic radius of Mg induces a certain degree of lattice distortion, altering the interatomic distances of boron atoms and thereby reducing the boron atomic density of states at the Fermi level, resulting in a significant decrease in the strength of EPC strength λ (Table S2). Furthermore, the effects of pressure on the T_c were examined for BaB_8 (Table S4). The results show that T_c has a significant drop to 10 K at 150 GPa, driven by crystal lattice hardening and resulting reduction of λ from 1.65 at 0 GPa to 0.48 at 150 GPa.

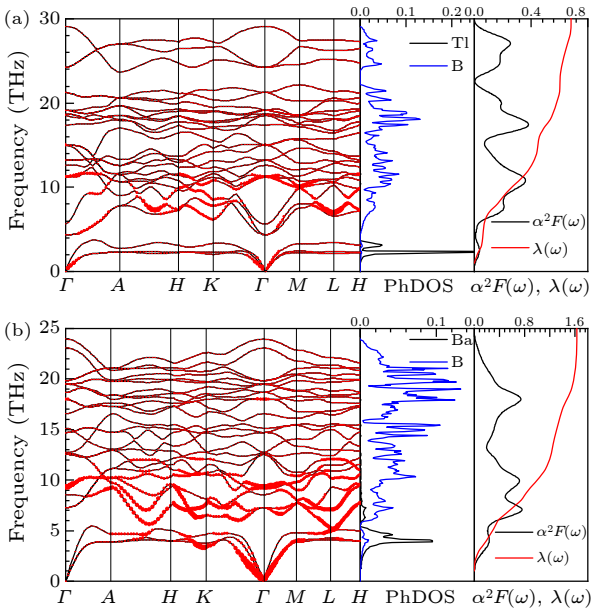

Fig. 3. Phonon dispersions, projected phonon density of states (PhDOS), Eliashberg spectral function $\alpha^2F(\omega)$, and integrated electron–phonon coupling (EPC) strength λ of (a) TlB_8 and (b) BaB_8 at 0 GPa. The size of the red dots represents the magnitude of the EPC.

To investigate the thermodynamic stability of doped $M\mathrm{B}_8$ compounds, we systematically examined the formation enthalpies as a function of pressure. Initially, we assessed the formation enthalpies using the formula $\Delta H = H(M\mathrm{B}_8) - H(M) - 8H(\mathrm{B})$, where $H(M)$ and $H(\mathrm{B})$ represent the enthalpies of the constituent elements in their respective ground-state structures at the same pressure, and $H(M\mathrm{B}_8)$ denotes the enthalpy of the optimized $M\mathrm{B}_8$ structure at corresponding pressures. A negative ΔH typically suggests the possibility of phase formation but not a rigorous metric.[44] As shown in Fig. 4(a), the formation of $M\mathrm{B}_8$ is only energetically favorable for LaB_8 at ambient pressure, while others possess positive formation enthalpies. As pressure increases, the formation enthalpies of BaB_8 continuously decrease, and finally become negative at pressures exceeding 30 GPa. However, the formation enthalpies of other $M\mathrm{B}_8$ clathrates remain positive up to 100 GPa.

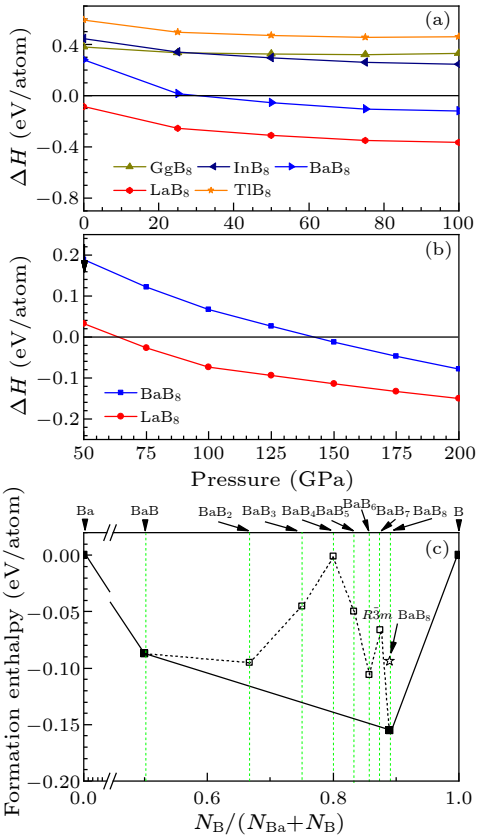

Fig. 4. Calculated enthalpy difference versus pressure for $M\mathrm{B}_8$, referenced to (a) the decomposition enthalpy into $M + 8\mathrm{B}$, (b) the decomposition enthalpy into $M\mathrm{B}_6 + 2\mathrm{B}$. (c) Thermodynamic stability of various Ba–B compounds with respect to elements Ba and B at 150 GPa. The energetically stable phases are shown using solid symbols connected by solid lines on the convex hull. The $R\bar{3}m$ BaB_8 structure is marked by a pentagram symbol.

We further calculated the more accurate formation enthalpies of BaB_8 with respect to BaB_6 and B under high pressures up to 200 GPa.[45,46] As shown in Fig. 4(b), the formation enthalpies of BaB_8 tend to become negative above 140 GPa. In support of this conclusion, we have plotted the convex hull data of BaB_8 at 150 GPa [Fig. 4(c)] by using the CALYPSO code.[41,42] The energetic stabilities of BaB_x compounds were evaluated from their formation enthalpies with respect to the dissociation products of Ba and B solids. Two new phases, $R\bar{3}m$ BaB and *Ibam* BaB_8, become stable under 150 GPa. Detailed structural information is provided in Table S5. It is noteworthy that the enthalpy of $R\bar{3}m$ BaB_8 is higher than that of *Ibam* BaB_8, suggesting its metastability. However, this does not entirely exclude the possibility of experimentally synthesizing the predicted clathrate structure. According to the previous investigation, approximately $50.5 \pm 4\%$ of the compounds in the Inorganic Crystal Structure Database (ICSD) exhibit metastability, and nearly 10% of synthesized metastable phases exhibit high formation enthalpies ($\Delta H > 67 \pm 2$ meV/atom),[44] while the enthalpy difference between $R\bar{3}m$ BaB_8 and *Ibam* BaB_8 is approximately 61 meV/atom at 150 GPa. Additionally, several clathrate structures with high-formation enthalpy have been successfully synthesized. For instance, the calculated formation enthalpy of clathrate $\mathrm{I}_{9.5}\mathrm{Si}_{44.5}$ is 130 meV/atom[47,48] and those of SiB_6 and C_{60} can reach 289 meV/atom[49,50] and 350 meV/atom,[51,52] respectively. Therefore, the possibility of experimentally synthesizing the doped clathrate BaB_8 cannot be completely ruled out. Given that LaB_8 has been successfully synthesized under HPHT conditions, BaB_8 exhibits similar trends in formation enthalpy changes and may be synthesized under HPHT experimental conditions as well. To validate this possibility theoretically, we investigated the reaction pathway for synthesizing BaB_8 using the harmonic approximation, as depicted in Fig. S4. The results indicated that the formation enthalpies of BaB_8 tend to become negative with temperature increases. Specifically, BaB_8 would be stable above $\sim$1800 K and 125 GPa along the reaction route of $\mathrm{BaB}_6 + 2\mathrm{B}$. We hope that our findings could provide theoretical guidance for development of superconducting clathrates composed of boron and other light-element atoms under ambient conditions and may stimulate future theoretical and experimental studies in this field.

In summary, we have conducted a comprehensive study of the stability and superconducting properties of doped $M\mathrm{B}_8$ clathrates. By performing a thorough scan of elements from groups IA, ⅡA, ⅢA, and ⅢB, we found four dynamical stable $M\mathrm{B}_8$ clathrates (M = Ba, Ga, In, and Tl) that exhibit promising conventional superconductivity under ambient pressure. Notably, BaB_8 exhibited a calculated T_c of 62 K, which is significantly higher than the calculated T_c value of 14 K of LaB_8. Moreover, the formation enthalpy calculations suggested that BaB_8 may be synthesized under high-temperature and high-pressure conditions and may act as a metastable high-T_c superconductor under ambient pressure. Overall, our findings contribute to the understanding of superconducting clathrates composed of light-element atoms under ambient conditions and lay the groundwork for future theoretical and experimental investigations in this field.

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