Ambient-pressure high-temperature superconductivity in stoichiometric hydrogen-free covalent compound BSiC$_2$

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Abstract

High superconducting critical temperature ($T_c$) of 73.6 K at ambient pressure is predicted in BSiC$_2$ by means of the first-principles electron–phonon calculations. Without the need for doping or pressurization, the stoichiometric BSiC$_2$ exhibits strong electron–phonon coupling (EPC) and highest $T_c$ among BCS-superconductors at ambient pressure. Also, it is hydrogen-free that makes easier the sample growth. The dramatic softening of the $E_g$ mode is the main account for the strong EPC. In addition, we find that BC$_3$, derived from the replacement of Si in BSiC$_2$ by another C, is also superconducting with a high $T_c \approx 40$ K. Our work indicates that these materials form a new family of high-$T_c$ BCS-superconductors at ambient pressure.

1. Introduction

Superconductivity is one of the most intriguing phenomena in materials science. Searching for new superconductors that exhibit high $T_c$ is of equal importance. Superconductors can be classified into various types according to the pairing mechanism, and the ones that exhibit highest $T_c$ within each class are the following. For cuprates, the highest $T_c$ at ambient pressure is observed in HgBaCaCuO ($\sim 135$ K) [1], which is also the one that exhibits highest $T_c$ among all types of superconductors at ambient pressure. Many other cuprates also exhibit $T_c > 100$ K. Recently, iron-based superconductors are found to show high $T_c$. The highest $T_c \approx 55$ K is found in doped SmFeAsO [3, 4]. An even higher $T_c$ is reported when depositing a single layer FeSe on SrTiO$_3$ [5, 6]. Although the pairing mechanism is not yet fully understood, it is believed that the antiferromagnetic spin-fluctuations might be responsible for the pairing in iron-based superconductors [7]. For BCS-superconductors, it is experimentally demonstrated very recently that the lanthanum hydride (LaH$_{1.8}$) exhibits superconductivity at temperatures close to 260 K under extremely high pressure [8]. At ambient pressure, MgB$_2$ exhibits the highest $T_c$ ($\sim 39$ K) [9] among all BCS-superconductors. MgB$_2$ consists of hexagonal B$_2$ layers intercalated with Mg$^{2+}$ ions, making it isoelectronic to graphite with two-dimensional $\sigma$- and three-dimensional (3D) $\pi$-bands formed by the $sp^2$ and $p_z$ orbitals, respectively. It has been shown by means of various techniques [10–17] that there are two distinct superconducting gaps resulted from the $\sigma$- and $\pi$-bands at the Fermi level. A phenomenological two-gap model has also been proposed to explain the observed specific heat of MgB$_2$ [18]. On the theoretical side, the two-gap nature is clearly demonstrated [19–23] and successfully explains many superconducting properties of MgB$_2$. It is also essential to mention that the metallization of the $\sigma$-bands, via the effective hole-doping, is the main account for the superconductivity.
Since the discovery of the high $T_c$ in MgB$_2$, there have been several works that theoretically propose possible BCS-superconductors with high $T_c$ due to the hole-doped $\sigma$-bands. For instance, CaB$_6$, isostuctural to MgB$_2$, has been predicted to have a $T_c$ of $\sim 55$ K [24]. However, it is metastable and may easily form CaB$_{12}$ and Ca clusters during the synthesis process [25]. Optimally hole-doped LiBC$_3$ [26, 27] could be superconducting with $T_c \sim 100$ K. Unfortunately, it is reported that heavily hole-doped LiBC causes severe shrinkage of the crystal [28–32], making the calculations based on the rigid shift of the Fermi level (virtual crystal approximation, VCA) invalid. Some Li-intercalated layered borocarbides are reported to become superconductors at 17–54 K, depending on the effective hole-doping level from Li intercalation [33, 34]. These numerical results of Li-intercalated borocarbides do not suffer from the VCA problem and hence the predicted $T_c$ might be reliable once successfully synthesized. Graphene [35] is theoretically claimed to exhibit superconductivity below $\sim 100$ K when hole-doped [36]. It is interesting to note that graphene has no $\sigma$-bands due to the passivation of hydrogen atoms. Nevertheless, pure graphene, i.e. the fully hydrogenated graphene, has not been successfully synthesized up to now. Similarly, to what extent will the dopants distort the structure and then disrupt the electron–phonon coupling (EPC) calculated with VCA using the pristine crystal remains a question. Noteworthy to mention, high $T_c$ has also been predicted in dense carbon–based material: sodalite NaC$_6$ [37]. Different from the above-mentioned materials, the $\sigma$-bands of sodalite NaC$_6$ are effectively electron-doped. Besides, the stability of this superconducting phase may need further confirmation$^8$.

Recently, high $T_c$ superconductivity in LaH$_{10}$ ($\sim 260$ K) and H$_3$S ($\sim 200$ K) under extremely high pressure has been theoretically predicted [38, 39] and then experimentally realized [8, 40]. Soon after, several hydrides are also predicted to reveal superconductivity under high pressure [41–43]. These findings indicate the BCS-type superconductors can achieve quite high $T_c$. Nonetheless, despite the excitement in the near realization of room temperature superconductivity, the required extremely high pressure prohibits further applications. Furthermore, the control of hydrogen during the sample growth is always an issue that needs careful treatment. Therefore, it is desirable to find a stoichiometric hydrogen-free material that shows high $T_c$ at ambient pressure.

Except for NaC$_6$, the aforementioned predicted superconductors, not yet realized though, have some common features. First, they crystallize in honeycomb structure. Second, the $\sigma$-bands that consist of the orbitals of the honeycomb constituents cross the Fermi level due to (effective) hole-doping; in other words, they are metallic covalent compounds. Third, light atoms are involved in the $E_{2g}$ or $E_{2g}$-like (referred to as $E_{2g}$ hereafter for brevity) mode that couples strongly to the $\sigma$-bands. Following this direction, we start from a semiconductor, 2H–SiC, and effectively hole-dope it by replacing half of Si by B. We find by first-principles scheme that the pristine BXC$_2$ (X = Si and C) are superconductors with $T_c$’s being about 74 K and 40 K for BSiC$_2$ and BC$_3$, respectively, based on the (Allen–Dynes–)McMillan formula. It is noted that our predicted $T_c$ in BC$_3$ is close to that of its cubic isomer at optimal doping [44]. Further investigation reveals unusual effect of the strong EPC in BSiC$_2$. Generally, strong EPC is accompanied by dramatic band splitting owing to the corresponding large deformation potential. For example, the $\sigma$-bands in MgB$_2$ are split by about 1.5 eV (with atomic displacements of boron being $\sim 0.06$ Å [20]) under the influence of the $E_{2g}$ mode [19, 22]. Interestingly, the even stronger EPC in BSiC$_2$ is not associated with severe splitting of the energy bands. This is because the main reason for the strong EPC in BSiC$_2$ is the considerably softened $E_{2g}$ mode and the moderate-to-strong phonon linewidth (PL). In BC$_3$, on the contrary, softening of the $E_{2g}$ mode is absent. The acoustic phonons, instead of the optical $E_{2g}$ phonons as in BSiC$_2$, play a more important role in making BC$_3$ superconducting.

2. Computational methods

The electronic and electron–phonon calculations are performed using QUANTUM ESPRESSO (QE) code [45]. Ultrasoft pseudopotentials with PBE functionals are used in all calculations. A $28 \times 28 \times 24$ $k$-mesh and a $14 \times 14 \times 8$ $q$-mesh are used in the electronic and phonon calculations. The energy cutoff of the plane wave expansion is 50 Ry. The (electron-)phonon calculations are carried out within the framework of density functional perturbation theory [46] implemented in QE. A smearing energy of 0.015 Ry is used to deal with the discrete electronic states around the Fermi level in the calculations of PLs, and hence the EPC constant, $\lambda$.

Having obtained the EPC strength, the $T_c$ can be estimated by using the McMillan formula, with corrections by Allen and Dynes [47]:

$$T_c = \frac{\omega_{\text{in}}}{1.20} \exp \left[ -\frac{1.04(1 + \lambda)}{\lambda - \mu^2(1 + 0.62\lambda)} \right] \quad \text{(1)}$$

$^8$While having obtained consistent crystal and band structures of the sodalite NaC$_6$, our phonon calculation indicates dynamical instability that disagrees with the results shown in [37].
where

\[
\omega_{ln} = \exp \left[ \frac{2}{\lambda} \int_{BZ} \frac{d\omega}{\omega} \alpha^2 F(\omega) \right],
\]

are the logarithmic average frequency and the isotropic Eliashberg spectral function, respectively, and

\[
\begin{align*}
    f_1 &= 1 + \left( \frac{\lambda}{\Lambda_1} \right) \frac{1}{\lambda^2 + \Lambda^2}, \\
    f_2 &= 1 + \left( \frac{\omega_{ln}^2}{\omega_{ln}} - 1 \right) \frac{1}{\lambda^2 + \Lambda^2}
\end{align*}
\]

with the parameters \( \Lambda_1 \) and \( \Lambda_2 \) being

\[
\begin{align*}
    \Lambda_1 &= 2.46(1 + 3.8\mu^s), \\
    \Lambda_2 &= 1.82(1 + 6.3\mu^s) \times \frac{1}{\omega_{ln}}
\end{align*}
\]

The EPC constant can be computed as:

\[
\lambda = \sum_{\mathbf{q} \mathbf{v}} \lambda_{\mathbf{q} \mathbf{v}} = \sum_{\mathbf{q} \mathbf{v}} \frac{\Pi''_{\mathbf{v} \mathbf{v}}}{N_F \omega_{ln}^2}
\]

with \( N_F \) being the density of states at the Fermi level and \( \Pi'' \) the PL. The screened Coulomb potential \( \mu^* = 0.1 \) is used in the estimation of \( T_c \).

3. Results and discussion

3.1. Crystal and electronic structures

Inherited from 2H–SiC, the crystal structure of BSiC\(_2\) resembles that of the 2H–SiC, with the Si layers being alternatively replaced by the B layers. Further replacement of the Si layers in BSiC\(_2\) by C layers leads to BC\(_3\). The crystal structures of both materials are shown in figure 1. The C atoms are labeled as C\(_1\) and C\(_2\), as well as C\(_3\) in BC\(_3\), for their electronic difference. Color representations for the atoms are the same in all following figures. (d) The high symmetry points in the first Brillouin zone.
the Fermi level and the B-p orbitals contribute to the Fermi surfaces as well. Rather than the formation of the expected sp\(^3\) orbitals, the p\(_{xy}\) and p\(_{z}\) orbitals of C and B are almost decoupled; the hybridization happens between C\(_{p_{xy}}\) and B\(_{p_{xy}}\) orbitals and between C\(_{p_z}\) and B\(_{p_z}\) orbitals. The decoupling of in-plane and out-of-plane components of orbitals, which may take place in layered materials where the crystal structure creates the anisotropy, is quietly rare in a 3D material. The Löwdin charges, \(P_n = \sum_i \langle \psi_i | \phi_i \rangle\) where \(\phi_i\) is the atomic orbital and \(\psi_i\) is the Kohn–Sham wave function whose occupancy is denoted by \(f_i\), are 2.89, 3.93, 4.04, and 4.08 for B, C\(_1\), C\(_2\), and C\(_3\) (the carbon that substitutes for the silicon in BSiC\(_2\)). These results support the covalent bonding nature in BSiC\(_2\). While in BSiC\(_2\) as figure 2(a) displays, there are five bands crossing the Fermi level. Four of them are composed of the C\(_{p_{xy}}\) orbitals (red and green bands) and the remaining one is from the C\(_{p_z}\) orbital (blue band). The distinction between the two C atoms can be seen by noting that the four \(\sigma\)-bands crossing the Fermi level form two groups. The two \(\sigma\)-bands that are lower in energy come from C\(_2\) and the other two mostly from C\(_1\). The overall C\(_{p_z}\)-components contribute to the pocket centering around \(\Gamma\). The Löwdin charges of the C\(_1\), C\(_2\), B, and Si atoms are 4.75, 4.39, 2.90, and 2.86. While boron retains most of its valence electrons, silicon seems to donate one valence electron to carbon, acting electronically as a dopant; the covalency of the Si-bonds is reduced since one valence electron of silicon is donated to, rather than shared with, the neighboring carbon. This is also evidenced by the partial density of states in figure 2(a) that the Si-p orbitals (orange line) contribute less to the valence bands than carbon. Similar with BC\(_3\), the C\(_{p_{xy}}\), and C\(_{p_z}\) orbitals barely hybridize. The presence of such decoupling in a 3D covalent material is bizarre and may have profound meaning; it implies that there exist two kinds of Fermi surface that are different and decoupled from each other, which can possibly lead to two-gap superconductivity. This interesting property will be discussed later. We have also performed structural search using universal structural predictor: evolutionary xtallography [49–51] and found that our predicted BSiC\(_2\) is the ground state of the hexagonal structures.

### 3.2. Phonons and superconductivity

The phonon spectra of BSiC\(_2\) and BC\(_3\), as well as the EPC strengths, are shown in figures 3(a) and (b). The E\(_{2g}\) and A\(_{1g}\) modes are marked by the blue and green arrows, respectively. In BSiC\(_2\), the E\(_{2g}\) mode shows an extremely strong EPC (\(\lambda_{\mathbf{q}} = 28.96\)) at phonon wave vector \(\mathbf{q}_e = \pi / \sqrt{3} \mathbf{A}\) point. Similar to MgB\(_2\), the E\(_{2g}\) mode shown in figure 3(c) couples strongly to the \(\sigma\)-bands that consist of C\(_{p_{xy}}\) orbitals. The total EPC constant \(\lambda = 2.41\) yields a \(T_c = 73.6\) K. (The commonly used Allen–Dynes–McMillan formula (equation (1)) yields \(\sim 58.8\) K.) It is noted that the E\(_{2g}\) mode is significantly softened as compared to MgB\(_2\) and other materials with similar honeycomb structure [24, 26, 27, 33, 34, 36]. The softening of the E\(_{2g}\) mode plays a critical role in the strong EPC in BSiC\(_2\) and will be discussed later in more detail. In BC\(_3\), however, the E\(_{2g}\) mode remains in the high energy region (\(\sim 80\) meV). The resulting EPC of the E\(_{2g}\) mode is much weaker than that in BSiC\(_2\). As figure 3(b) reveals, the acoustic phonons with in-plane momenta are responsible for the occurrence of superconductivity in BC\(_3\). The calculated \(T_c\) for BC\(_3\) is 39.3 K with \(\lambda = 0.86\). We would like to mention that the values of \(T_c\) and \(\lambda\) of both materials have little dependence on the smearing energy used to deal with the density of states around the Fermi level, which indicates the numerical reliability of our results.

It is worthwhile to discuss the superconductivity in MgB\(_2\), BC\(_3\), and BSiC\(_2\) for comparison. Some properties of the E\(_{2g}\) mode related to superconductivity in the three materials are listed in table 1. The EPC in MgB\(_2\) originates mainly from the interactions between the E\(_{2g}\) mode and the B–p\(_{xy}\)-electrons that form \(\sigma\)-bonds between the B atoms. These electrons are well confined within the two-dimensional boron sheets. Thus the EPC shows small \(q_e\)-dependence, namely, the relative vibration (or phase) of the E\(_{2g}\) mode between different boron

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**Figure 2.** Band structures and partial density of states (PDOS) of \(p\)-orbitals of (a) BSiC\(_2\) and (b) BC\(_3\). The color representations are shown in the top of the plots.
sheets has negligible effect on the EPC. This is confirmed in our work (small variation of $\lambda$ listed in table 1) and in a previous work by Kong et al [32]. As mentioned previously, the $\sigma$-bands are split by 1.5 eV due to the strong EPC resulting from the vibration of the $E_{2g}$ mode [19, 22]. The stretch (compression) of the $\sigma$-bonds induces depletion (aggregation) of charges. We refer to this as the intra-site orbital fluctuations under which the electrons remain spatially confined between (or shared by) the bonded atoms. Intra-site orbital fluctuations due to EPC commonly take place in most materials, including BC3.

The influence of the $E_{2g}$ mode on the orbitals of BSiC2 shows distinct behaviors, however. Figure 4 displays the wave function of the highest occupied state at $\Gamma$. For the equilibrium structure as shown in figures 4(a) and (b), the charges center around the site of C2 atoms. This is consistent with the aforementioned little hybridization between the Si–C $p$-orbitals. The out-of-phase frozen phonon ($\mathbf{q} = \pi/c$, i.e. A point, with largest displacement being 0.03 Å and increment in total energy per formula unit being 0.26 meV) induces strong spatial redistribution as depicted in figures 4(c) and (d). Notably, the band splitting is only ~0.2 eV with this distortion (see supplementary information is available online at stacks.iop.org/NJP/22/033046/mmedia) despite its strong EPC ($\lambda = 23.91$). It is apparent that a substantial weight of the wave function transfers to C1 atoms. This is consistent with the aforementioned little hybridization between the bonded atoms. The inter-site orbital fluctuations bring about the charge transfer from C2 to C1 atoms. We would like to emphasize that the inter-site orbital fluctuations take place in the highest occupied state at $\Gamma$ and along $\Gamma$–A (see supplementary information), although only the wave function at $\Gamma$ is shown in figure 4 for demonstration. For the Si–C2 bonds, however, there does not exist any phonon mode that can give rise to hybridization. As a result, the charge densities around the Si atoms remain low. This finding paves a new way of searching for new BCS-superconductors of high $T_c$ if the inter-site orbital fluctuations are found to exist.

In comparison with the recently found or proposed high-$T_c$ BCS superconductors at high pressure, BSiC2 is advantageous in two aspects. First, BSiC2 exhibits high $T_c$ at ambient pressure. Although interesting from scientific point of view and pioneering in science advances, superconductivity existing at high pressure can hardly be used for further applications. Second, all these recently found or proposed high-$T_c$ BCS superconductors contain hydrogen, which is difficult to control during the growth of crystals, especially under the condition of high pressure. Because hydrogen is highly responsible for the strong EPC, superconductivity may be suppressed if hydrogen atoms do not

| Material | $T_c$ (K) | $\lambda$ | $\omega_{in}$ (GHz) | $\omega_T/\omega_n$ | $\lambda_T/\lambda_A$ | PL ($\Gamma/A$) |
|----------|----------|----------|---------------------|--------------------|---------------------|---------------|
| MgB2     | 25.2     | 0.70     | 728.5              | 66.88/60.10        | 2.79/2.08           | 2813/2107     |
| BC3      | 39.3     | 0.86     | 728.1              | 81.57/81.17        | 0.91/0.18           | 1576/312      |
| BSiC2    | 73.6     | 2.41     | 364.5              | 19.53/6.71         | 7.73/28.96          | 1323/584      |

$^1$ The experimental value of 39 K can be reproduced by taking into account the anisotropy in the EPC and anharmonicity of the $E_{2g}$ mode [23, 53, 54].

Figure 3. Phonon spectra and Eliashberg spectral function $\sigma^2 F(\omega)$ of (a) BSiC2 and (b) BC3. The size of the red dots represents the magnitude of the EPC $\lambda_{EPC}$. Due to the extremely large $\lambda_{EPC}$ of the $E_{2g}$ mode around $\Gamma$ in (a), we shrink the size of some dots by a factor of two and represent them in blue. The $E_{2g}$ and $A_{1g}$ modes are marked by the blue and green arrows, respectively. Note that the sizes of the dots in (a) and (b) are rescaled for visualization purpose, so the relative size of dots is meaningful only within each plot. Displacement pattern of the $E_{2g}$ mode that gives rise to the strong EPC in BSiC2 at $\mathbf{q} = A$ is shown in (c) for side (top panel) and top (bottom panel) views.
occupy the proper sites. The hydrogen-free crystal structure prevents BSiC₂ from this problem. As a result, we propose that BSiC₂ is a promising high-\( T_c \) BCS superconductor in both fundamental studies and applications.

Now we are left with a question as to why the \( E_{2g} \) mode in BSiC₂ is significantly softened. Recall that the \( E_{2g} \) mode involves the compression of the B–C₁ bonds and couples mostly to the C₁-\( p_{x,y} \) orbitals. The restoring force when vibrating in the \( E_{2g} \) mode is connected to the partial charge density \( \langle \psi^2(r) \rangle \) of the C₁-\( p_{x,y} \) states. As shown in figure 4(b), the partial charge density of C₁-\( p_{x,y} \) states around the Fermi level is low and therefore the restoring force of the \( E_{2g} \) vibration is expected to be small. This in turn puts the \( E_{2g} \) mode of BSiC₂ in the low energy region. The softening of the \( E_{2g} \) mode is an essential account for the high \( T_c \) in BSiC₂. The PL, nonetheless, plays an equally important role. Deduced from equation (9), the required PL for nontrivial contributions to superconductivity is of the order of 10–10⁵ GHz, depending on the phonon energies. As shown in table 1, the PL of the \( E_{2g} \) mode in MgB₂ is of the order of 10¹⁵ GHz while the corresponding high phonon energy pulls down the strength of the EPC to lie in the moderate-to-strong regime. In BC₃, the high energy of the \( E_{2g} \) mode results in a weaker coupling strength. The special characteristic that BSiC₂ bears is that it possesses the merits of having a low-energy \( E_{2g} \) mode while retaining a relatively large PL. Therefore, the EPC in BSiC₂ is much stronger than that in MgB₂, despite a smaller PL. This is also the reason why the strong EPC does not cause severe band splitting in BSiC₂.

The two-gap nature, as is observed in MgB₂, is an interesting phenomenon in superconductors. In MgB₂, the broken symmetry of the \( p_{x,y} \) and \( p_z \) orbitals of boron leads to two kinds of Fermi surfaces that are significantly different in their band components. These two different kinds of Fermi surfaces couple distinctly to phonons, resulting in two superconducting gaps. Similar with MgB₂ electronically, the coexistence of Fermi surfaces with \( p_{x,y} \) and \( p_z \) components in BSiC₂ seems to imply the possibility of two distinct superconducting gaps and the anisotropic \( k \)-dependence in the EPC. If so, the use of Allen–Dynes–McMillan formula in this work that averages out the \( k \)-dependence of the EPC would incur an underestimated EPC, which means the \( T_c \) so obtained would be lower than its real value. Taking MgB₂ as an example, the calculated \( T_c \) with the isotropic picture is about 25 K. The anisotropy of the EPC and anharmonicity of phonons have to be taken into account to reproduce the experimental value of 39 K [23, 53, 54]. Thus, if BSiC₂ really shows the two-gap feature and the conclusion drawn from MgB₂ is also applicable to BSiC₂, its real \( T_c \) would be even higher than the calculated value of 73.6 K and possibly comparable to those of the cuprates. Further investigation on this issue is called for.

**4. Conclusion**

In summary, we predict a new BCS-superconductor, BSiC₂, whose \( T_c \) at ambient pressure may be comparable with those of cuprates when the possible two-gap nature is taken into account. Its isostructural material, BC₃, is also predicted to have a \( T_c \sim 40 \) K. Similarly, the possible two-gap nature may further increase its real \( T_c \). BSiC₂ is distinct from other BCS-superconductors in that its strong EPC stems from the significantly softened \( E_{2g} \) mode and the inter-site orbital fluctuations. The comparison of the resulting EPC and \( T_c \) with MgB₂ and the related
The authors declare no competing financial interest.

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**Notes**

The authors declare no competing financial interest.
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