

PAPER • OPEN ACCESS

Ambient-pressure high-temperature superconductivity in stoichiometric hydrogen-free covalent compound BSiC₂

To cite this article: Peng-Jen Chen and Horng-Tay Jeng 2020 *New J. Phys.* **22** 033046

View the [article online](#) for updates and enhancements.



PAPER

Ambient-pressure high-temperature superconductivity in stoichiometric hydrogen-free covalent compound BSiC₂

OPEN ACCESS

RECEIVED

19 September 2019

REVISED

6 February 2020

ACCEPTED FOR PUBLICATION

14 February 2020

PUBLISHED

25 March 2020

Original content from this work may be used under the terms of the [Creative Commons Attribution 4.0 licence](#).

Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Peng-Jen Chen^{1,2,3,4,7} and Horng-Tay Jeng^{1,5,6,7}¹ Institute of Physics, Academia Sinica, Taipei 11529, Taiwan² Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan³ Department of Physics, National Taiwan University, Taipei 10617, Taiwan⁴ Nano Science and Technology Program, Taiwan International Graduate Program, Academia Sinica, Taipei 11529, Taiwan and National Taiwan University, Taipei 10617, Taiwan⁵ Department of Physics, National Tsing Hua University, Hsinchu 30013, Taiwan⁶ Physics Division, National Center for Theoretical Sciences, Hsinchu 30013, Taiwan⁷ Authors to whom any correspondence should be addressed.E-mail: pjchen1015@gate.sinica.edu.tw and jeng@phys.nthu.edu.tw**Keywords:** superconducting materials, metallic covalent materials, first-principles calculationsSupplementary material for this article is available [online](#)**Abstract**

High superconducting critical temperature (T_c) of 73.6 K at ambient pressure is predicted in BSiC₂ by means of the first-principles electron–phonon calculations. Without the need for doping or pressurization, the stoichiometric BSiC₂ 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_{2g} mode is the main account for the strong EPC. In addition, we find that BC₃, derived from the replacement of Si in BSiC₂ by another C, is also superconducting with a high $T_c \sim 40$ 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 (~ 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 [2]. The highest $T_c \sim 55$ K is found in doped SmFeAsO [3, 4]. An even higher T_c is reported when depositing a single layer FeSe on SrTiO₃ [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 (LaH₁₀) exhibits superconductivity at temperatures close to 260 K under extremely high pressure [8]. At ambient pressure, MgB₂ exhibits the highest T_c (~ 39 K) [9] among all BCS-superconductors. MgB₂ consists of hexagonal B₂ layers intercalated with Mg²⁺ ions, making it isoelectronic to graphite with two-dimensional σ - and three-dimensional (3D) π -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 σ - and π - bands at the Fermi level. A phenomenological two-gap model has also been proposed to explain the observed specific heat of MgB₂ [18]. On the theoretical side, the two-gap nature is clearly demonstrated [19–23] and successfully explains many superconducting properties of MgB₂. It is also essential to mention that the metallization of the σ -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 σ -bands. For instance, CaB_2 , isostructural to MgB_2 , has been predicted to have a T_c of ~ 55 K [24]. However, it is metastable and may easily form CaB_6 and Ca clusters during the synthesis process [25]. Optimally hole-doped LiBC [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. Graphane [35] is theoretically claimed to exhibit superconductivity below ~ 100 K when hole-doped [36]. It is interesting to note that graphane has no π -bands due to the passivation of hydrogen atoms. Nevertheless, pure graphane, 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 σ -bands of sodalite NaC_6 are effectively electron-doped. Besides, the stability of this superconducting phase may need further confirmation⁸.

Recently, high T_c superconductivity in LaH_{10} (~ 260 K) and H_3S (~ 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 σ -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 σ -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 ($X = \text{Si}$ 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 σ -bands in MgB_2 are split by about 1.5 eV (with atomic displacements of boron being ~ 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.

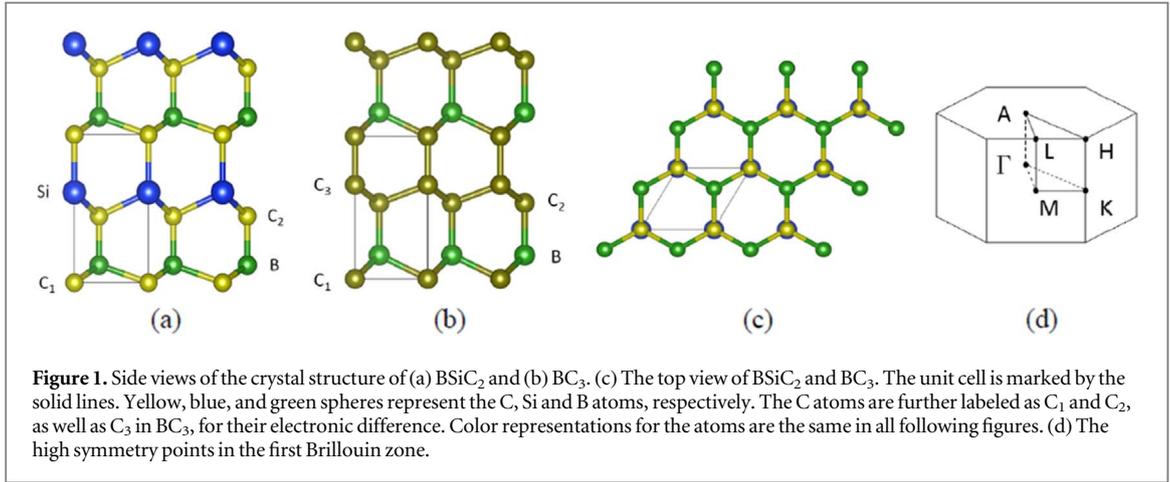
2. Computational methods

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 $28 \times 28 \times 24$ \mathbf{k} -mesh and a $14 \times 14 \times 8$ \mathbf{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, λ .

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

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

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].



or

$$T_c = \frac{f_1 f_2 \omega_{\ln}}{1.20} \exp \left[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right] \quad (2)$$

when $\lambda \geq 1.5$ where

$$\omega_{\ln} = \exp \left[\frac{2}{\lambda} \int d\omega \frac{\ln(\omega)}{\omega} \alpha^2 F(\omega) \right], \quad (3)$$

$$\alpha^2 F(\omega) = \frac{1}{2} \int_{\text{BZ}} d\omega \lambda_{q\nu} \omega_{q\nu} \delta(\omega - \omega_{q\nu}) \quad (4)$$

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

$$f_1 = \left[1 + \left(\frac{\lambda}{\Lambda_1} \right)^{\frac{3}{2}} \right]^{\frac{1}{3}}, \quad (5)$$

$$f_2 = 1 + \frac{\left(\frac{\langle \omega^2 \rangle^{\frac{1}{2}}}{\omega_{\ln}} - 1 \right) \lambda^2}{\lambda^2 + \Lambda^2} \quad (6)$$

with the parameters Λ_1 and Λ_2 being

$$\Lambda_1 = 2.46(1 + 3.8\mu^*), \quad (7)$$

$$\Lambda_2 = 1.82(1 + 6.3\mu^*) \times \frac{\langle \omega^2 \rangle^{\frac{1}{2}}}{\omega_{\ln}}. \quad (8)$$

The EPC constant can be computed as:

$$\lambda = \sum_{q\nu} \lambda_{q\nu} = \sum_{q\nu} \frac{\Pi''_{q\nu}}{\pi N_F \omega_{q\nu}^2} \quad (9)$$

with N_F being the density of states at the Fermi level and Π'' 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 BSiC₂ resembles that of the 2H-SiC, with the Si layers being alternatively replaced by the B layers. Further replacement of the Si layers in BSiC₂ by C layers leads to BC₃. The crystal structures of both materials are shown in figure 1. The C atoms are labeled as C₁ and C₂, as well as C₃ in BC₃, in figure 1 to distinguish from one another for they are electronically different. The relaxed lattice parameters are $a = 2.89 \text{ \AA}$, $c/a = 1.66$ for BSiC₂ and $a = 2.55 \text{ \AA}$, $c/a = 1.72$ for BC₃. Compared with $a = 3.08 \text{ \AA}$ and $c/a = 1.63$ in 2H-SiC [48], the crystals of both BSiC₂ and BC₃ shrink because Si that has a larger atomic radius is replaced. Owing to the common crystal structure and similar constituents, these two materials have similar band structure as shown in figure 2. In figure 2(b) for BC₃, there are three bands crossing

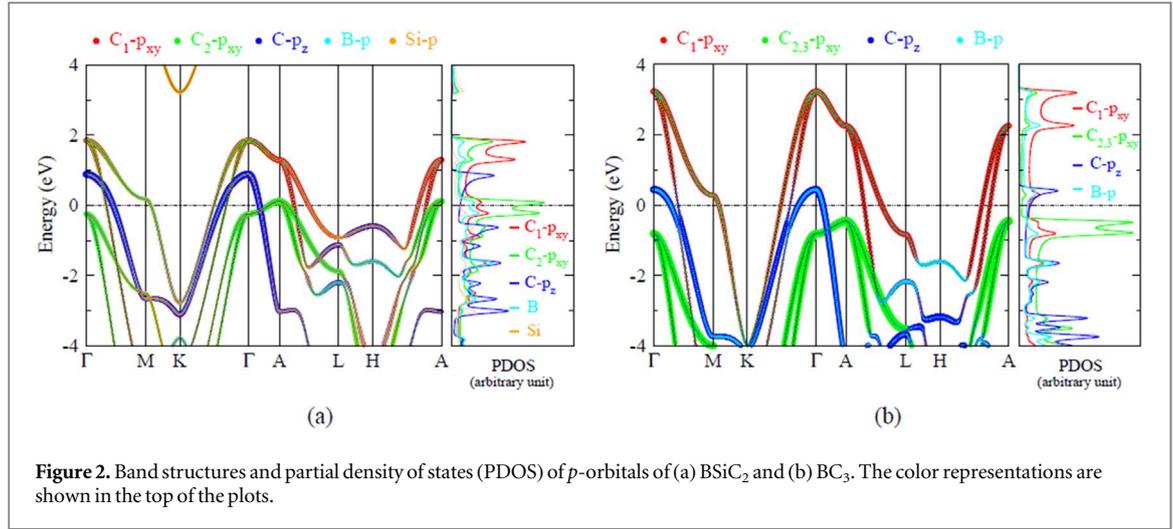


Figure 2. Band structures and partial density of states (PDOS) of p -orbitals of (a) BSiC₂ and (b) BC₃. The color representations are shown in the top of the plots.

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, $\rho_n = \sum_i f_i \langle \psi_i | \varphi_n \rangle$ where φ_n is the atomic orbital and ψ_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, C₁, C₂, and C₃ (the carbon that substitutes for the silicon in BSiC₂). These results support the covalent bonding nature in BC₃. While in BSiC₂ as figure 2(a) displays, there are five bands crossing the Fermi level. Four of them are composed of the C- $p_{x,y}$ 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 σ -bands crossing the Fermi level form two groups. The two σ -bands that are lower in energy come from C₂ and the other two mostly from C₁. The overall C- p_z components contribute to the pocket centering around Γ . The Löwdin charges of the C₁, C₂, 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–C 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 BC₃, the C- $p_{x,y}$ 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 BSiC₂ is the ground state of the hexagonal structures.

3.2. Phonons and superconductivity

The phonon spectra of BSiC₂ and BC₃, 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 BSiC₂, the E_{2g} mode shows an extremely strong EPC ($\lambda_{q_\pi} = 28.96$) at phonon wave vector $\mathbf{q}_\pi = \pi/c$ (A point). Similar to MgB₂, the E_{2g} mode shown in figure 3(c) couples strongly to the σ -bands that consist of C- $p_{x,y}$ 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 ~ 58.8 K). It is noted that the E_{2g} mode is significantly softened as compared to MgB₂ 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 BSiC₂ and will be discussed later in more detail. In BC₃, however, the E_{2g} mode remains in the high energy region (~ 80 meV). The resulting EPC of the E_{2g} mode is much weaker than that in BSiC₂. As figure 3(b) reveals, the acoustic phonons with in-plane momenta are responsible for the occurrence of superconductivity in BC₃. The calculated T_c for BC₃ is 39.3 K with $\lambda = 0.86$. We would like to mention that the values of T_c and λ 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 MgB₂, BC₃, and BSiC₂ for comparison. Some properties of the E_{2g} mode related to superconductivity in the three materials are listed in table 1. The EPC in MgB₂ originates mainly from the interactions between the E_{2g} mode and the B- $p_{x,y}$ electrons that form σ -bonds between the B atoms. These electrons are well confined within the two-dimensional boron sheets. Thus the EPC shows small q_z -dependence, namely, the relative vibration (or phase) of the E_{2g} mode between different boron

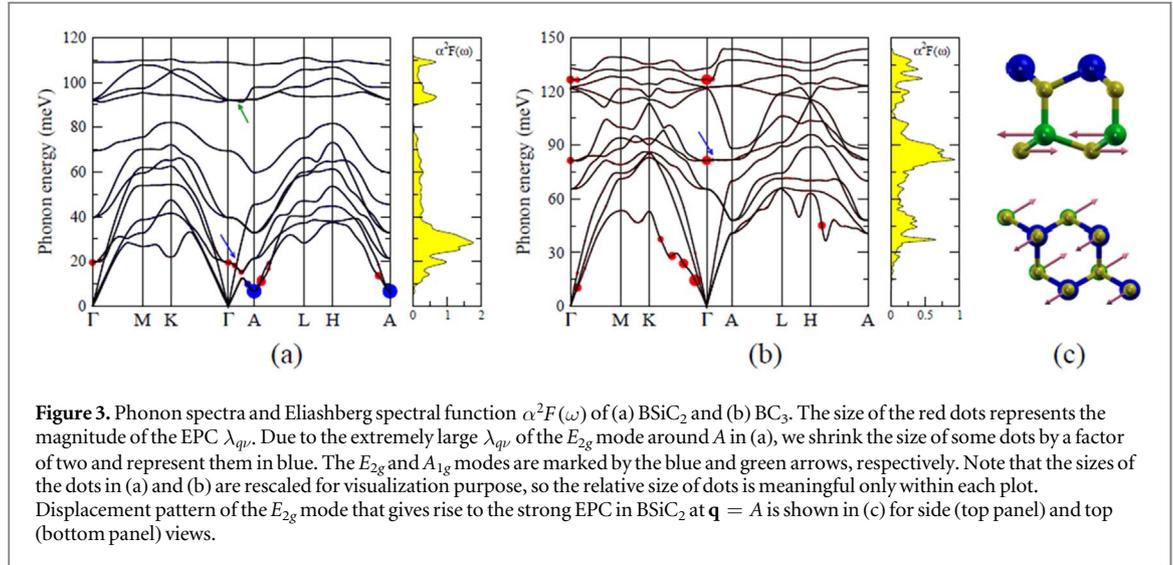


Figure 3. Phonon spectra and Eliashberg spectral function $\alpha^2F(\omega)$ of (a) BSiC₂ and (b) BC₃. The size of the red dots represents the magnitude of the EPC λ_{qv} . Due to the extremely large λ_{qv} of the E_{2g} mode around A in (a), we shrink the size of some dots by a factor of two and represent 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.

Table 1. Shown are the T_c (Kelvin) obtained from isotropic Eliashberg equation, total EPC constant, logarithmic average frequency ω_{ln} (Kelvin), the frequency ω (meV), the associated EPC constant λ and the PL (GHz) of the E_{2g} mode at Γ and A in the three superconductors.

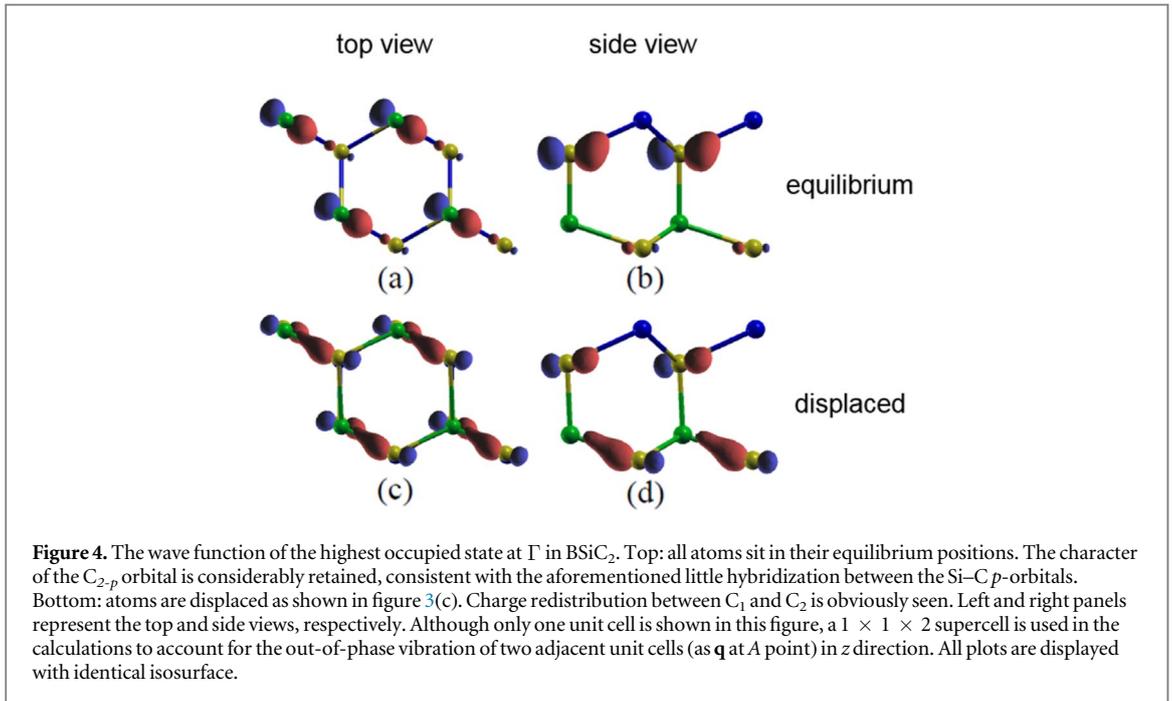
	T_c	Total λ	ω_{ln}	ω_{Γ}/ω_A	$\lambda_{\Gamma}/\lambda_A$	PL (Γ/A)
MgB ₂	25.2 ^a	0.70	728.5	66.88/60.10	2.79/2.08	2813/2107
BC ₃	39.3	0.86	728.1	81.57/81.17	0.91/0.18	1576/312
BSiC ₂	73.6	2.41	364.5	19.53/6.71	7.73/28.96	1323/584

^a 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].

sheets has negligible effect on the EPC. This is confirmed in our work (small variation of λ listed in table 1) and in a previous work by Kong *et al* [52]. As mentioned previously, the σ -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 σ -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 Γ . 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 and hybridizes with the B atoms, indicating *inter*-site orbital fluctuations. 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 Γ and along Γ –A (see supplementary information), although only the wave function at Γ 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



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 $C_{1-p_{x,y}}$ orbitals. The restoring force when vibrating in the E_{2g} mode is connected to the partial charge density ($|\psi(\mathbf{r})|^2$) of the $C_{1-p_{x,y}}$ states. As shown in figure 4(b), the partial charge density of $C_{1-p_{x,y}}$ 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 $10\text{--}10^2$ 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 10^3 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 \mathbf{k} -dependence in the EPC. If so, the use of Allen–Dynes–McMillan formula in this work that averages out the \mathbf{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

system BC₃ supports the peculiar behaviors of the EPC in BSiC₂. We would like to emphasize that such high- T_c superconductivity occurs without the need for doping or pressurization. Hydrogen-free crystal structure also alleviates the difficulties in sample growth.

Acknowledgments

The authors acknowledge National Center for High-Performance Computing (NCHC). H-T Jeng also thanks support from AS-iMATE-109-13 and CQT-NTHU-MOE, Taiwan. This work is supported by the Ministry of Science and Technology, Academia Sinica, National Taiwan University, and National Tsing-Hua University, Taiwan.

Notes

The authors declare no competing financial interest.

References

- [1] Schilling A, Cantoni M, Guo J D and Ott H R 1993 *Nature* **363** 56
- [2] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
- [3] Ren Z A *et al* 2008 *Europhys. Lett.* **83** 17002
- [4] Ren Z A *et al* 2008 *Chin. Phys. Lett.* **25** 2215
- [5] Tan S *et al* 2013 *Nat. Mater.* **12** 634
- [6] Ge J F, Liu Z L, Liu C, Gao C L, Qian D, Xue Q K, Liu Y and Jia J F 2015 *Nat. Mater.* **14** 285
- [7] Mazin I I, Singh D J, Johannes M D and Du M H 2008 *Phys. Rev. Lett.* **101** 057003
- [8] Somayazulu M, Ahart M, Mishra A K, Geballe Z M, Baldini M, Meng Y, Struzhkin V V and Hemley R J 2019 *Phys. Rev. Lett.* **122** 027001
- [9] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J S 2001 *Nature* **410** 63
- [10] Wang Y, Plackowski T and Junod A 2001 *Physica C* **355** 179
- [11] Bouquet F, Fisher R A, Phillips N E, Hinks D G and Jorgensen J D 2001 *Phys. Rev. Lett.* **87** 047001
- [12] Szabó P, Samuely P, Kačmarčík J, Klein T, Marcus J, Fruchart D, Miraglia S, Marcenat C and Jansen A G M 2001 *Phys. Rev. Lett.* **87** 137005
- [13] Yang H D, Lin J Y, Li H H, Hsu F H, Liu C J, Li S C, Yu R C and Jin C Q 2001 *Phys. Rev. Lett.* **87** 167003
- [14] Tsuda S, Yokoya T, Kiss T, Takano Y, Togano K, Kito H, Ihara H and Shin S 2001 *Phys. Rev. Lett.* **87** 177006
- [15] Giubileo F, Roditchev D, Sacks W, Lamy R, Thanh D X, Klein J, Miraglia S, Fruchart D, Marcus J and Monod P 2001 *Phys. Rev. Lett.* **87** 177008
- [16] Laube F, Goll G, Hagel J, Löhneysen H V, Ernst D and Wolf T 2001 *Europhys. Lett.* **56** 296
- [17] Bouquet F, Wang Y, Sheikin I, Plackowski T, Junod A, Lee S and Tajima S 2002 *Phys. Rev. Lett.* **89** 257001
- [18] Bouquet F, Wang Y, Fisher R A, Hinks D G, Jorgensen J D, Junod A and Phillips N E 2001 *Europhys. Lett.* **56** 856
- [19] An J M and Pickett W E 2011 *Phys. Rev. Lett.* **86** 4366
- [20] Kortus J, Mazin I I, Belashchenko K D, Antropov V P and Boyer L L 2001 *Phys. Rev. Lett.* **86** 4656
- [21] Bohnen K-P, Heid R and Renker B 2001 *Phys. Rev. Lett.* **86** 5771
- [22] Yildirim T *et al* 2002 *Phys. Rev. Lett.* **87** 037001
- [23] Liu A Y, Mazin I I and Kortus J 2001 *Phys. Rev. Lett.* **87** 087005
- [24] Choi H J, Louie S G and Cohen M L 2009 *Phys. Rev. B* **80** 064503
- [25] Oguchi T 2002 *J. Phys. Soc. Japan* **71** 1495
- [26] Rosner H, Kitaigorodsky A and Pickett W E 2002 *Phys. Rev. Lett.* **88** 127001
- [27] Dewhurst J K, Sharma S, Ambrosch-Draxl C and Johansson B 2003 *Phys. Rev. B* **68** 020504
- [28] Bharathi A, Jemima Balaselvi S, Premila M, Sairam T N, Reddy G L N, Sundar C S and Hariharan Y 2002 *Solid State Commun.* **124** 423
- [29] Souptel D, Hossain Z, Behr G, Löser W and Geibel C 2003 *Solid State Commun.* **125** 17
- [30] Fogg A M, Chalker P R, Claridge J B, Darling G R and Rosseinsky M J 2003 *Phys. Rev. B* **67** 245106
- [31] Fogg A M, Claridge J B, Darling G R and Rosseinsky M J 2003 *Chem. Commun.* **1348**
- [32] Fogg A M, Meldrum J, Darling G R, Claridge J B and Rosseinsky M J 2006 *J. Am. Chem. Soc.* **128** 10043
- [33] Gao M, Lu Z-Y and Xiang T 2015 *Phys. Rev. B* **91** 045132
- [34] Bazhironov T, Sakai Y, Saito S and Cohen M L 2014 *Phys. Rev. B* **89** 045136
- [35] Sofo J O, Chaudhari A S and Barber G D 2007 *Phys. Rev. B* **75** 153401
- [36] Savini G, Ferrari A C and Giustino F 2010 *Phys. Rev. Lett.* **105** 037002
- [37] Lu S, Liu H, Naumov I I, Meng S, Li Y, Tse J S, Yang B and Hemley R J 2016 *Phys. Rev. B* **93** 104509
- [38] Duan D, Liu Y, Tian F, Li D, Huang X, Zhao Z, Yu H, Liu B, Tian W and Cui T 2014 *Sci. Rep.* **4** 6968
- [39] Liu H, Naumov I I, Hoffmann R, Ashcroft N W and Hemley R J 2017 *Proc. Natl Acad. Sci. USA* **114** 6990
- [40] Drozdov A P, Erements M I, Troyan I A, Ksenofontov V and Shylin S I 2015 *Nature* **525** 73
- [41] Ma Y, Duan D, Li D, Liu Y, Tian F, Yu H, Xu C, Shao Z, Liu B and Cui T 2015 arXiv:1511.05291
- [42] Feng X, Zhang J, Gao G, Liu H and Wang H 2015 *RSC Adv.* **5** 59292
- [43] Zhong X, Wang H, Zhang J, Liu H, Zhang S, Song H-F, Yang G, Zhang L and Ma Y 2016 *Phys. Rev. Lett.* **116** 057002
- [44] Ribeiro F J and Cohen M L 2004 *Phys. Rev. B* **69** 212507
- [45] Giannozze P *et al* 2009 *J. Phys.: Condens. Matter* **21** 395502
- [46] Baroni S, de Gironcoli S and Dal Corso A 2001 *Rev. Mod. Phys.* **73** 515
- [47] Allen P B and Dynes R C 1975 *Phys. Rev. B* **12** 905
- [48] Denteneer P J H and van Haeringen W 1988 *Solid State Commun.* **65** 115
- [49] Oganov A R and Glass C W 2006 *J. Chem. Phys.* **124** 244704

- [50] Oganov A R, Lyakhov A O and Valle M 2011 *Acc. Chem. Res.* **44** 227
- [51] Lyakhov A O, Oganov A R, Stokes H T and Zhu Z 2013 *Comput. Phys. Commun.* **184** 1172
- [52] Kong Y, Dolgov O V, Jepsen O and Andersen O K 2001 *Phys. Rev. B* **64** 020501(R)
- [53] Choi H J, Roundy D, Sun H, Cohen M L and Louie S G 2002 *Nature* **418** 758
- [54] Choi H J, Cohen M L and Louie S G 2003 *Physica C* **385** 66