Prediction of superconducting properties of CaB$_2$ using anisotropic Eliashberg theory

Hyoung Joon Choi, Steven G. Louie, and Marvin L. Cohen

1Department of Physics and IPAP, Yonsei University, Seoul 120-749, Korea
2Department of Physics, University of California, Berkeley, California 94720, USA
3Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

(Dated: June 15, 2009)

Superconducting properties of hypothetical simple hexagonal CaB$_2$ are studied using the fully anisotropic Eliashberg formalism based on electronic and phononic structures and electron-phonon interactions which are obtained from ab initio pseudopotential density functional calculations. The superconducting transition temperature $T_c$, the superconducting energy gap $\Delta(k)$ on the Fermi surface, and the specific heat are obtained and compared with corresponding properties of MgB$_2$. Our results suggest that CaB$_2$ will have a higher $T_c$ and a stronger two-gap nature, with a larger $\Delta(k)$ in the $\sigma$ bands but a smaller $\Delta(k)$ in the $\pi$ bands than MgB$_2$.

PACS numbers: 71.15.Mb, 74.20.Fg, 74.70.Ad, 61.50.Ah

The discovery of superconductivity in MgB$_2$ with its remarkable superconducting transition temperature $T_c$ as high as 39 K has triggered many investigations of related materials including various binaries: BeB$_2$, CaB$_2$, NaB$_2$, SrB$_2$, CuB$_2$, ZrB$_2$, TaB$_2$, OsB$_2$, YB$_2$, MgBe$_2$, MgB$_2$, and LiB$_2$, and ternaries: CaBeSi$_2$, LiBC$_2$, NaBC$_2$, Mg$_2$-$x$Na$_x$B$_2$, Mg$_{2-x}$Cu$_x$B$_2$, Mg$_{2-x}$Cu$_x$B$_2$, Mg$_{2-x}$Cu$_x$B$_2$, LiBC$_2$, and Be$_2$C$_2$. For these compounds, their structural, electronic, and superconducting properties are studied extensively as well. Even with these efforts, however, the highest $T_c$ observed experimentally in these compounds is still that of MgB$_2$. There have been theoretical predictions of higher $T_c$’s than 39 K, for example, $T_c \sim 50$ K in CuB$_{2-x}$C$_x$ and $T_c \sim 100$ K in hole-doped LiBC.

One of the interesting candidates for a higher $T_c$ is the hypothetical simple hexagonal CaB$_2$, with the same crystal symmetry as MgB$_2$, with all Mg atoms being replaced by Ca atoms. First-principles calculations predict that the simple hexagonal CaB$_2$ should have a greater unit cell (both $a$ and $c$ lattice constants are longer) and a much larger value for the density of states (DOS) at the Fermi energy ($E_F$) than MgB$_2$. Both features are favorable for a higher $T_c$, since MgB$_2$ is found to have a positive dependence of $T_c$ on the unit-cell volume and more generally, a larger DOS at $E_F$ can result in a greater electron-phonon coupling constant. Although CaB$_2$ is an attractive candidate for superconductivity, it has not been synthesized as yet, nor has it been extensively studied theoretically for superconductivity. Since the Fermi surface of CaB$_2$ is predicted to consist of multiple sheets similar to those in MgB$_2$, it will be necessary to use the anisotropic Eliashberg theory to deal with the effects of possible variations of the superconducting energy gap on the Fermi surface as in the case of MgB$_2$.

In this work, we perform density-functional ab-initio pseudopotential calculations to determine the lattice constants of the hypothetical simple hexagonal phase of CaB$_2$, and we calculate its electronic structure, phonon spectrum, and electron-phonon properties. From these material properties, we construct the fully anisotropic Eliashberg equations to obtain the superconducting properties such as $T_c$, the momentum-dependent superconducting energy gap $\Delta(k, T)$, and the specific heat as functions of temperature $T$. These results predict that CaB$_2$ has a higher $T_c$ than MgB$_2$ and a larger difference between the superconducting energy gap in the $\sigma$ and $\pi$ bands when compared with MgB$_2$.

We consider the hypothetical simple hexagonal CaB$_2$ shown in Fig. 1. The atomic structure has exactly the same symmetry as MgB$_2$, having one Ca and two B atoms in a unit cell. We determine the lattice constants $a$ and $c$ by minimizing the total energy of the system obtained from first-principles pseudopotential density-functional calculations. In the calculations, plane waves of energy up to 60 Ry are used to expand the electronic wavefunctions, norm-conserving pseudopotentials are used to describe the electron-ion interaction, and the local density approximation is employed to deal with the electron-electron interactions effectively. In more detail, we use the partial-
core correction\textsuperscript{27} for the Ca pseudopotential, Ceperley-Alder exchange-correlation energy\textsuperscript{28} of the Perdew-Zunger parameterization,\textsuperscript{29} a 12 \times 12 \times 12 k-point grid to evaluate the self-consistent electron density, and a 18 \times 18 \times 12 k-point grid for Fermi-surface properties.

For simple hexagonal CaB\textsubscript{2}, the calculated lattice constants at ambient pressure are $a = 3.185$ Å and $c = 4.060$ Å. Thus the $c/a$ ratio is 1.27. Compared with theoretical values for MgB\textsubscript{2} (which are $a = 3.07$ Å and $c = 3.57$ Å, with $c/a = 1.16$), $a$ in CaB\textsubscript{2} is 4\% greater and $c$ is 14\% greater. To check the ratio $c/a$ at high pressure, we obtain the lattice constants at 30 GPa, which are $a = 3.014$ Å and $c = 3.842$ Å. Thus, the $c/a$ ratio is still 1.27 at this pressure. The obtained $c/a = 1.27$ is larger than 1.165 known as the maximal $c/a$ ratio of existing diborides,\textsuperscript{30} and this is in agreement with previous calculations.\textsuperscript{3,4,5,6,7} Since the hexagonal CaB\textsubscript{2} has not been synthesized successfully, its formation energy and stability have been studied theoretically.\textsuperscript{17,20} Hexagonal CaB\textsubscript{2} is predicted to be stable with respect to hcp Ca and rhombohedral B ($\alpha$-B\textsubscript{12})\textsuperscript{22}, but unstable to a phase separation into fcc Ca and CaB\textsubscript{6} and less stable than $\delta$-CaB\textsubscript{2} phase.\textsuperscript{20} As reported theoretically, hexagonal CaB\textsubscript{2} may not be the lowest phase energetically, but our frozen-phonon calculations at high symmetry points, which will be presented below, do not show any structural instability from the simple hexagonal phase.

With the optimized lattice constants, we perform first-principles electronic structure calculations. Figure 2 shows the obtained band structure along the high symmetry lines and the Fermi surface. Overall, the band structure of CaB\textsubscript{2} is similar to MgB\textsubscript{2}. In Fig. 2(a), the $\sigma$ and the $\pi$ bands are from the boron $sp^2$ and $p_z$ orbitals, respectively. The full bandwidth of the $\sigma$ bands is reduced substantially, compared with MgB\textsubscript{2}, because of the larger B–B bond length. As in the case of MgB\textsubscript{2}, the Fermi energy in CaB\textsubscript{2} is lower than the top of the $\sigma$ bands, producing two cylindrical hole-type sheets along the Γ–A line [red and orange regions in Fig. 2(b)]. While the hole-type sheets are close to those in MgB\textsubscript{2} qualitatively, the electron-type sheet from the $\pi$ bands in CaB\textsubscript{2} is quite different from the one in MgB\textsubscript{2}. In MgB\textsubscript{2}, the $\pi$ bands are above $E_F$ at the $M$ and $K$ points; however, in CaB\textsubscript{2}, they are below $E_F$. Thus, CaB\textsubscript{2} has only one electron-type Fermi surface from the $\pi$ bands [the blue sheet in Fig. 2(b)], missing the Fermi surface along the $K$–$L$ line that is present in MgB\textsubscript{2}. Hence, as shown in Fig. 2(b), the Fermi surface in CaB\textsubscript{2} consists of three sheets: two hole-type cylindrical ones along $\Gamma$–$A$ lines and one electron-type along $H$–$L$ lines. The density of states at the Fermi level in CaB\textsubscript{2} is 0.96 states/eV per formula unit, which is much larger than 0.69 states/eV for MgB\textsubscript{2}. The contributions of the three sheets of the Fermi surface to the DOS at $E_F$ are 12\%, 32\%, and 56\% from the inner and outer hole-type sheets and the electron-type sheet, respectively. Our results for the band structures are in good agreement with the results using the full-potential linear muffin-tin orbital (FP-LMTO) method.\textsuperscript{23}

To consider electron-phonon interactions, we calculate the phonon structures in CaB\textsubscript{2} based on the frozen-phonon method. In the first step, phonon frequencies and polarizations are obtained at high symmetry points of the Brillouin zone by frozen-phonon methods, and then in-
terpolated to the full Brillouin zone by interpolating the dynamical matrix. In the frozen-phonon calculations, we extract quadratic and higher-order dependences of the total energy on atomic displacements, and calculate harmonic and anharmonic phonon frequencies with and without using the harmonic approximation.

Figure 3(a) shows the calculated phonon dispersions along the high symmetry lines, with and without anharmonicity. The phonon frequencies are calculated by constructing the dynamical matrices at the high-symmetry points and interpolating them along the high-symmetry lines. In our frozen-phonon calculations, the increase of the total energy with boron displacements are highly anharmonic for $E_{2g}$ modes (the $\Sigma - \Sigma$ bond stretching modes) at the $\Gamma$ and $A$ points. This is consistent with the reported large anharmonicity in $\Gamma$ in CaB$_2$. We find that the $E_{2g}$ frequency is 45.2 meV in the harmonic case and 55.8 meV in the anharmonic case, both of which are substantially lower than those in MgB$_2$. All the phonon frequencies at the high symmetry points are positive, and therefore do not indicate structural instabilities.

The upper panel in Fig. 3(b) shows the phonon density of states obtained by interpolating the dynamical matrix throughout the Brillouin zone with anharmonicity included. Compared with MgB$_2$, the phonons in CaB$_2$ have lower frequencies. Phonon modes associated with Ca atoms should have lower frequencies because of heavier atomic mass of Ca relative to Mg. In addition, phonon modes associated with B atoms also have lower frequencies because of the elongation of B–B bonds.

We calculate the momentum-dependent Eliashberg function $\alpha^2 F(k, k', \omega)$ from the difference in the self-consistent potential with and without frozen phonons, using the anharmonic phonon frequencies, and then take the average on the Fermi surface to obtain the isotropic Eliashberg function $\alpha^2 F(\omega)$, as shown in the lower panel in Fig. 3(b). From $\alpha^2 F(\omega)$, we can evaluate the average electron-phonon coupling constant $\lambda = 2 \int d\omega \alpha^2 F(\omega)/\omega$ and the logarithmically averaged phonon frequency $\omega_{\alpha}(n) = \exp[(2/\lambda) \int d\omega \alpha^2 F(\omega) \ln \omega/\omega]$. This gives $\lambda = 0.69$ and $\omega_{\alpha}(n) = 50$ meV, respectively. The value of $\lambda$ is 13% larger and $\omega_{\alpha}(n)$ is 34% smaller than those for MgB$_2$.

We obtain the superconducting properties in CaB$_2$ using the fully anisotropic Eliashberg formalism. The anisotropic Eliashberg equations at imaginary frequencies are given as

$$Z(k, i\omega_n) = 1 + \sum_{k' n'} W_{k k'} \lambda(k, k', n - n')$$

$$\times \frac{\omega_{n'}}{\sqrt{\omega_{n'}^2 + (\Delta(k', i\omega_n))^2}}.$$  \hspace{1cm} (1)

$$Z(k, i\omega_0) \Delta(k, i\omega_0) = \pi T \sum_{k' n'} W_{k k'} [\lambda(k, k', n - n') - \mu^*(\omega_c)]$$

$$\times \frac{\Delta(k', i\omega_n)}{\sqrt{\omega_{n'}^2 + (\Delta(k', i\omega_n))^2}}.$$  \hspace{1cm} (2)

where $\omega_n = (2n + 1)\pi T$ is the fermionic Matsubara frequency at temperature $T$, $Z(k, i\omega_n)$ and $\Delta(k, i\omega_n)$ are the momentum-dependent renormalization function and the gap function, respectively, and $\lambda(k, k', n)$ represents the momentum-dependent electron-phonon interaction. Definitions of symbols and details of the numerical method are described in Refs. 22, 33, and 34. Here, we assume that the Coulomb pseudopotential $\mu^*$ is isotropic, since its momentum dependence is not as strong as that of the electron-phonon interaction, and assume $\mu^*(\omega_c) = 0.12$ for the cut-off frequency $\omega_c = 0.5$ eV, as assumed for MgB$_2$.

We obtain $T_c$ by finding the highest $T$ at which the anisotropic Eliashberg equations [Eqs. (1) and (2)] have a non-trivial solution for $\Delta(k)$. With the assumed value of $\mu^*(\omega_c) = 0.12$, we obtain $T_c = 48$ K, which is about 10 K higher than that of MgB$_2$. To check the sensitivity of $T_c$ to $\mu^*$, we also consider $\mu^*(\omega_c) = 0.10$ and 0.14, obtaining $T_c = 50$ and 46 K, respectively. Thus, we can expect a higher $T_c$ in CaB$_2$ than in MgB$_2$ even in the case of relative large $\mu^*$.

With Eqs. (1) and (2), and their analytic continuations to the real-frequency axis, we calculate the superconduct-
ing properties below $T_c$. Figure 4(a) shows the calculated superconducting energy gap on the Fermi surface at $T = 4$ K, where the average values of $\Delta(k)$ on the three sheets of the Fermi surface are well separated from one another and they are 9.1, 8.2, and 1.5 meV, respectively, with the average on the two hole-type sheets being 8.4 meV. As shown in Fig. 4(b), when compared with MgB$_2$, the average value $\Delta_\sigma$ of $\Delta(k)$ on the $\sigma$ bands (the hole-type sheets) is substantially larger but $\Delta_{\pi}$ for the $\pi$ bands is slightly smaller at low $T$, indicating an enhanced two-gap nature for CaB$_2$. Figure 4(c) shows the calculated electronic specific heat as a function of temperature. Because of the higher DOS at $E_F$ and the larger $\lambda$, the normal-state specific heat $C_N$ above $T_c$ is expected to be larger in CaB$_2$ ($C_N = \gamma T$ with $\gamma = 3.82$ mJmol$^{-1}$K$^{-2}$) than in MgB$_2$ ($\gamma = 2.62$ mJmol$^{-1}$K$^{-2}$). In addition, since $\Delta_\sigma$ in CaB$_2$ is smaller in magnitude than in MgB$_2$, the specific heat at $T < 10$ K has a bigger hump in CaB$_2$.

To summarize, we obtained the lattice constants, the electronic and phononic structures, and electron-phonon interactions in hypothetical simple hexagonal CaB$_2$ using first-principles calculations. We then calculated the superconducting transition temperature $T_c$, the superconducting energy gap $\Delta(k,T)$, and the specific heat using the fully anisotropic Eliashberg formalism. The obtained Fermi surface in CaB$_2$ consists of three sheets rather than four as in MgB$_2$, and the phonon frequencies are lower than in MgB$_2$. A substantially higher $T_c$ is predicted for hexagonal CaB$_2$, and furthermore the multiple superconducting energy-gap feature is expected to be enhanced in CaB$_2$, with larger $\Delta_\sigma$ and smaller $\Delta_{\pi}$ than in MgB$_2$.

This work was supported by the KRF (Grant No. KRF-2007-314-C00075), by the KOSEF under Grant No. R01-2007-000-20922-0, by NSF under Grant No. DMR07-05941, and by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, U.S. Department of Energy under Contract No. DE-AC02-05CH11231. Computational resources have been provided by KISTI Supercomputing Center (Project No. KSC-2008-S02-0004), NSF through TeraGrid resources at SDSC, and DOE at Lawrence Berkeley National Laboratory’s NERSC facility.

* Email: h.j.choi@yonsei.ac.kr

1. J. Nagamatsu, N. Nakagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, Nature (London) 410, 63 (2001).
2. G. Satta, G. Profeta, F. Bernardini, A. Coniemenia, and S. Massidda, Phys. Rev. B 64, 104507 (2001).
3. N. I. Medvedeva, A. L. Ivanovskii, J. E. Medvedeva, and A. J. Freeman, Phys. Rev. B 64, 020502(R) (2001).
4. P. Ravindran, P. Vajeeston, R. Vidya, A. Kjekshus, and H. Fjellvåg, Phys. Rev. B 64, 224509 (2001).
5. N. I. Medvedeva, J. E. Medvedeva, A. L. Ivanovskii, V. G. Zubkov, and A. J. Freeman, Pis’ma Zh. Eksp. Teor. Fiz. 73, 378 (2001) [JETP Lett. 73, 336 (2001)].
6. S. V. Okatov, A. L. Ivanovskii, Y. E. Medvedeva, and N. I. Medvedeva, Phys. Status Solidi B 225, R3 (2001).
7. T. Oguchi, J. Phys. Soc. Jpn. 71, 1495 (2002).
8. M. M. Mehl, D. A. Papaconstantopoulos, and D. J. Singh, Phys. Rev. B 64, 140509(R) (2001).
9. V. A. Gasparov, N. S. Sidorkov, I. Z. Zver’kova, and M. P. Kulakov, JETP Lett. 73, 532 (2001).
10. H. Rosner, W. E. Pickett, S.-L. Drechsler, A. Handstein, G. Behr, G. Fuchs, K. Kenkov, K.-H. Müller, and H. Eschrig, Phys. Rev. B 64, 144516 (2001).
11. Y. Singh, A. Niazi, M. D. Vannette, R. Prozorov, and D. C. Johnston, Phys. Rev. B 76, 214510 (2007).
12. M. Calandra, A. N. Kolmogorov, and S. Curtarolo, Phys. Rev. B 75, 144506 (2007).
13. H. Rosner, A. Kitaigorodsky, and W. E. Pickett, Phys. Rev. Lett. 88, 127001 (2002).
14. J. K. Dewhurst, S. Sharma, C. Ambrosch-Draxl, and B. Johansson, Phys. Rev. B 68, 020504(R) (2003).
15. A. Lazicki, C.-S. Yoo, H. Cynn, W. J. Evans, W. E. Pickett, J. Olamit, Kai Liu, and Y. Ohishi, Phys. Rev. B 75, 054507 (2007).
16. S. Lebègue, B. Arnaud, P. Rabiller, M. Alouani, and W. E. Pickett, Europhys. Lett. 68, 846 (2004).
17. Y. Sun, D. Yu, Z. Liu, T. Wang, J. He, J. Xiang, D. Zheng, and Y. Tian, Supercond. Sci. Technol. 20, 261 (2007).
18. Y. Sun, D. Yu, Z. Liu, J. He, X. Zhang, Y. Tian, J. Xiang, and D. Zheng, Appl. Phys. Lett. 90, 052507 (2007).
19. J. E. Mousa, J. Noffsinger, and M. L. Cohen, Phys. Rev. B 78, 104506 (2008).
20. A. N. Kolmogorov and S. Curtarolo, Phys. Rev. B 74, 224507 (2006).
21. C. Buzea and T. Yamashita, Supercond. Sci. Technol. 14, R115 (2001), and references therein.
22. H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, Nature (London) 418, 758 (2002).
23. H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, Phys. Rev. B 66, 020513(R) (2002).
24. J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C 12, 4409 (1979).
25. M. L. Cohen, Phys. Scr. T1, 5 (1982).
26. N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).
27. S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B 26, 1738 (1982).
28. D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).
29. J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
30. B. Aronsson, T. Lundstrom, and S. Rundqvist, Refractory Borides, Silicides and Phosphides (Methuen, London, 1965).
31. T. Yildirim, O. Gulseren, J.W. Lynn, C.M. Brown, T. J. Udovic, Q. Huang, N. Rogado, K. A. Regan, M. A. Hayward, J. S. Slusky, T. He, M. K. Haas, P. Khalifah, K. Inumaru, and R. J. Cava, Phys. Rev. Lett. 87, 037001 (2001).
32. P. B. Allen and B. Mitrovic, in Solid State Physics, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1982), Vol. 37, p. 1, and references therein.
33. H. J. Choi, M. L. Cohen, and S. G. Louie, Physica C 385, 66 (2003).
34. H. J. Choi, M. L. Cohen, and S. G. Louie, Phys. Rev. B 73, 104520 (2006).
35 C.-Y. Moon, Y.-H. Kim, and K. J. Chang, Phys. Rev. B 70, 104522 (2004).

36 I. I. Mazin, O. K. Andersen, O. Jepsen, A. A. Golubov, O. V. Dolgov, and J. Kortus, Phys. Rev. B 69, 056501 (2004).

37 H. J. Choi, D. Roundy, H. Sun, M. L. Cohen, and S. G. Louie, Phys. Rev. B 69, 056502 (2004).