Ab initio superconducting temperature of BaSi$_2$ at ambient pressure

Bruno Rousseau$^{1,2}$ and Aitor Bergara$^{1,2,3}$

$^1$ Donostia International Physics Center (DIPC), Paseo de Manuel Lardizabal, 20018, Donostia, Basque Country, Spain
$^2$ Centro de Fisica de Materiales CSIC-UPV/EHU, 1072 Posta kutxatila, E-20080 Donostia, Basque Country, Spain
$^3$ Materia Kondentsatuaren Fisika Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea, 644 Postakutxatila, 48080 Bilbo, Basque Country, Spain
E-mail: a.bergara@ehu.es

Abstract. Barium silicide in the metastable trigonal phase is studied using ab initio methods. The band structure and the phonon spectrum are computed and analyzed. The electron-phonon coupling is found to have a substantial contribution coming from the $A_{1g}$ optical mode at $\Gamma$. The superconducting transition temperature is calculated using the Allen-Dynes formula, but is found to be an order of magnitude smaller than the experimental value; some tentative explanations for the disagreement are presented.

Hexagonal layered alloys have been the subject of intense study since the discovery of the exceptionally high superconducting transition temperature $T_c$ in MgB$_2$[1]. A high transition temperature has been found under pressure in CaSi$_2$[2], and Be$_2$Li has been predicted to become a superconductor at 80 GPa[3]. These layered alloys display a wide variety of phenomena, such as effective lowered dimensionality[4, 3], soft optical phonon modes enhancing superconductivity and phonon anharmonicity, some of which challenge current state-of-the-art computational methods.

Barium silicide (BaSi$_2$), has received relatively little attention despite having been found to superconduct at ambient pressure in an hexagonal layered structure. At ambient conditions, there are three known phases of BaSi$_2$: a stable orthorhombic phase (semiconductor), a metastable cubic phase (semiconductor), and a metastable trigonal phase (metallic) [5, 6]. This latter phase is obtained by submitting the stable phase to pressure and heat, and then quenching back to ambient conditions. This system, with space group symmetry $P\bar{3}m1$, was measured to have a superconducting transition at a critical temperature of $T_c = 6.8$ K[5].

The crystal structure of BaSi$_2$ in this phase is composed of planes of barium ions arranged in triangular lattices interspersed with planes of silicon ions forming hexagonal graphite-like lattices which are, however, buckled in the perpendicular direction to the planes. The barium ions are located such that they lie directly above (and below) the centers of the hexagons formed by the silicons (see Figure 1).

The electronic structure of the system was studied using density functional theory (DFT)[7, 8] and the phonons with density functional perturbation theory (DFPT)[9], as implemented in the QUANTUM-ESPRESSO (PWscf) computational package[10]. The electron-ion interactions were represented with ultrasoft pseudopotentials[11] and the Perdew-Wang[12] exchange correlation
functional (local density approximation, LDA): the states $5s$, $5p$, $5d$ and $6s$ of barium and $3s$, $3p$ of silicon were included in the valence. Energy cutoffs of 60 Rydbergs for the wave functions and 480 Rydbergs for the electronic density were found to be sufficient to insure convergence of the electronic properties. First Brillouin Zone (1BZ) integrations necessary to obtain the electronic structure were performed using a $12 \times 12 \times 8$ Monkhorst Pack mesh\[13\]. A $4 \times 4 \times 4$ mesh was used to compute the inter atomic force constants, from which the dynamical matrices could be interpolated to any desired point in the 1BZ. Electron-phonon calculations were performed on a finer $60 \times 60 \times 40$ electronic mesh.

The Wyckoff positions for the various ions in the unit cell for the space group $P\bar{3}m1$ are given, in crystalline units, by

$$
\begin{align*}
\text{Ba (1a)} & : 0 & 0 & 0 \\
\text{Si (2d)} & : 1/3 & 2/3 & z \\
\text{Si (2d)} & : 2/3 & 1/3 & -z
\end{align*}
$$

(1)

The cell parameters were relaxed to a pressure of 0 GPa such that the forces on the ions were less than $10^{-6}$ eV/a$_0$; the resulting parameters are compared to experiment in table 1; a schematic representation of the structure can be seen in figure 1.

The Fermi surface is presented in figure 2. The band structure, the density of states as well as some of its projections onto atomic orbitals are presented in figure 3; projections of states onto atomic orbitals are also presented in figure 4. The band structure exhibits shallow electron (about $M$) and hole (about $A$) pockets. The layered nature of the system is apparent in the projected bands. The bands with mostly Si $3(p_x + p_y)$ character disperse weakly along vertical directions, such as $\Gamma A$ or $ML$, but more strongly along in-plane direction, like $\Gamma K$; the orbitals

### Table 1. Various numerical values characterizing the structure of the system.

| Source           | $a$     | $c$     | $c/a$  | $z$  | $\angle \text{Si-Si-Si}$ | Si-Si distance |
|------------------|---------|---------|--------|------|--------------------------|----------------|
| $ab$ intio       | 4.05 Å  | 5.29 Å  | 1.31   | 0.43 | 111°                     | 2.45 Å         |
| Experiment[5, 14]| 4.06 Å  | 5.28 Å  | 1.30   | -    | 112°                     | 2.45 Å         |
Figure 2. Fermi surface of BaSi$_2$ and schematic first Brillouin zone (1BZ). The 1BZ is decorated in a symmetry-reducing manner, indicating that the point group ($\bar{3}m$) is not the point group which leaves the hexagonal prism invariant ($6/mmm$). Because of the periodicity in reciprocal space, however, opposite faces must be equivalent and there are no supplementary special points on the surface. The Fermi surface provides an example of this behavior: the surface inside the 1BZ does not have full $6/mmm$ symmetry, but the part which intersects the surface of the 1BZ does.

Figure 3. Bands and density of states near the Fermi energy, which is set at 0 eV. The projected density of states onto orthogonalized states corresponding to Ba 5$d$ and Si 3$p$ are also presented. The projected density of states for silicon is summed on the inequivalent sites, each yielding the same contribution (projections not shown are much smaller than the ones presented). Bands computed using the GGA approximation with the PBE functional[15, 16] with the LDA-relaxed structure were not significantly different from the bands presented above.

corresponding to these bands are surely mostly confined to the silicon layers. On the other hand, the bands with strong Si 3$p_z$ character are more dispersive along $\Gamma A$. The bands acquire a mostly Si 3$p_z$ and Ba 5$d$ character about the Fermi energy.

The phonon dispersion, as well as the phonon density of states and the partial electron-phonon coupling parameter are presented in figure 5. The dispersion neatly splits into three distinct
Figure 4. Projections of the states onto orthogonalized atomic orbitals. The thickness of the band lines indicates the amplitude of the projection onto the states (a) Si 3s, (b) Si 3(p_x + p_y), (c) Si 3p_z, and (d) Ba 5d. The projections for silicon are summed on the inequivalent sites.

Figure 5. (Left panel) Calculated phonon dispersion of BaSi_2. The radius of each circle is proportional to the partial electron-phonon coupling, \( \lambda_\nu(q) \). (Right panel) The phonon density of states, PDOS, compared to the Eliashberg spectral function, \( \alpha^2 F(\omega) \); both quantities are displayed using arbitrary scales to compare their features. The partial electron-phonon coupling \( \lambda(\omega) = \int_0^\infty d\omega' 2\alpha^2 F(\omega')/\omega' \) is also presented.

bands, from 0 to 3 THz (acoustic branches), from 4 to 6 THz, from 7 to 12 THz. The Eliashberg function follows closely the behavior of the phonon density of state, and two particularly narrow
frequency regions contribute heavily to the electron phonon coupling, at about 6 and 7 THz. The 7 THz mode at Γ, which has symmetry $A_{1g}$, couples quite strongly with the electrons. This mode corresponds to a motion along the $c$ axis of the silicon atoms. The value of $z$ is fairly close to 0.5, which would correspond to silicon atoms pinned onto their planes, leading to a different space group ($P6/mmm$).

The value of the superconducting transition temperature was computed using the well known Allen-Dynes modification of the McMillan formula, \[ T_c = \frac{\omega_{\log} \exp \left\{ -\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right\} }{1.2}, \] (2)

where $\lambda$ is the electron-phonon coupling constant and $\mu^*$ is the so called Coulomb pseudopotential which accounts in an approximate way for the electron-electron repulsion at the Fermi energy[19]. The computations yielded values of $\omega_{\log} \simeq 240$ K and $\lambda \simeq 0.33$. For $\mu^* = 0.1$ (a standard choice), $T_c \simeq 0.3$ K (larger values of $\mu^*$ yield smaller values of $T_c$), which is more than an order of magnitude smaller than the experimental result[5]. In fact, for the same values of $\mu^*$ and $\omega_{\log}$, the Allen-Dynes approximation to $T_c$ would require $\lambda \simeq 0.6$ in order to produce a result consistent with experiment: such a large difference most likely cannot be explained in terms of numerical errors in the computations.

The simplest approximations for $T_c$ thus fail to agree with the value obtained experimentally. The most likely source of error are the sweeping approximations wrapping up the entire electron-phonon interactions in terms of a single parameter, $\lambda$. Considering how non-spherical the Fermi surface is, it seems likely that the homogeneous approximations underlying the McMillan formula are seriously flawed in this system. Furthermore, the unavoidable use of a finite mesh for 1BZ integration imply that the very sharp contribution from the $A_{1g}$ phonon mode at Γ may not be well resolved (although it is not expected that this mode alone could improve the electron-phonon coupling by a factor of two). Finally, the substantial $d$ character of the bands at the Fermi energy suggest that electron correlations beyond the LDA or GGA approximation may be important. Solving the full Eliashberg equations may prove necessary in order to properly described superconductivity in BaSi$_2$; work is under way to address this issue. It is noteworthy that quite a similar situation occurs for the case of calcium silicide, CaSi$_2$. Under pressure, this compound was measured to acquire the same structure as the trigonal phase of BaSi$_2$ and to superconduct at temperatures up to 14 K[2, 20]; however, \textit{ab initio} calculations similar to those presented here yield a value of $T_c$ which is much too low[21]. Whatever insight may be acquired in studying BaSi$_2$ may well prove to be the key to understand $T_c$ in this other system.

Acknowledgments
The research herein presented was performed under project BFM2003-04428, funded by the Spanish Ministry of Education and Science.

References
[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Nature 410(6824) 63
[2] Sanfilippo S, Elsinger H, Nuñez Regueiro M, Laborde O, LeFloch S, Affronte M, Olcese G L and Palenzona A 2000 Phys. Rev. B 61 R3800–R3803
[3] Errea I, Martínez-Canales M and Bergara A 2008 Phys. Rev. B 78 172501
[4] Feng J, Hennig R G, Ashcroft N W and Hoffmann R 2008 Nature 451(7177) 445–448 ISSN 0028-0836 10.1038/nature06442
[5] Imai M, Hirata K and Hirano T 1995 Physica C: Superconductivity 245 12 – 14 ISSN 0921-4534
[6] Imai M, Hirano T, Kikegawa T and Shimomura O 1998 Phys. Rev. B 58 11922–11926
[7] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864–B871
[8] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133–A1138
[9] Baroni S, de Gironcoli S, Dal Corso A and Giannozzi P 2001 Rev. Mod. Phys. 73 515–562
[10] Giansozzi P http://www.quantum-espresso.org/
[11] Vanderbilt D 1990 Phys. Rev. B 41 7892–7895
[12] Perdew J P and Wang Y 1992 Phys. Rev. B 45 13244–13249
[13] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188–5192
[14] J Evers G O and Weiss A Angew. Chem. Int. Ed. Engl. 17 538
[15] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865–3868
[16] Perdew J P, Burke K and Ernzerhof M 1997 Phys. Rev. Lett. 78 1396
[17] Allen P B and Dynes R C 1975 Phys. Rev. B 12 905–922
[18] McMillan W L 1968 Phys. Rev. 167 331–344
[19] Morel P and Anderson P W 1962 Phys. Rev. 125 1263–1271
[20] Bordet P, Affronte M, Sanfilippo S, Núñez Regueiro M, Laborde O, Olcese G L, Palenzona A, LeFloch S, Levy D and Hanfland M 2000 Phys. Rev. B 62 11392–11397
[21] Nakanishi A, Ishikawa T, Nagara H and Kusakabe K 2008 Journal of the Physical Society of Japan 77 104712