Enhancing the superconducting transition temperature of BaSi$_2$ by structural tuning

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We present a joint experimental and theoretical study of the superconducting phase of the layered binary silicide BaSi$_2$. Compared with the layered AlB$_2$ structure of graphite or diboride-like superconductors, in the hexagonal structure of binary silicides the $sp^3$ arrangement of silicon atoms leads to corrugated sheets. Through a high-pressure synthesis procedure we are able to modify the buckling of these sheets, obtaining the enhancement of the superconducting transition temperature from 4 K to 8.7 K when the silicon planes flatten out. By performing $ab$ initio calculations based on density functional theory we explain how the electronic and phononic properties of the system are strongly affected by changes in the buckling. This mechanism is likely present in other intercalated layered superconductors, opening the way to the tuning of superconductivity through the control of internal structural parameters.

Nowadays, an important part of the activity research on superconductivity is focused on intercalated layered crystal structures. In these systems, where the relevant features for superconductivity are intrinsic to the layers, the bond buckling of the atoms forming the layers is a structural parameter known to damage the superconducting properties, regardless of the nature of the pairing mechanism [1]. The case of flat boron sheets in MgB$_2$ is well understood: superconductivity arises from a strong coupling between the $sp^2$ σ-bonding intralayer electrons of boron and the in-plane bond stretching phonons [2–4]. Besides, a buckling of the boron honeycomb structure, as observed in ReB$_2$ [5], was proved to decrease the superconducting transition temperature $T_c$. Nevertheless, recent studies on graphite intercalated superconductors, namely (Yb,Ca)C$_6$ [6] and the ternary silicide CaAlSi [7,8], characterized by large $T_c's$, point to the importance in these systems of the electron-phonon (EP) coupling between the interlayer electrons and the out-of-plane vibrational modes of the atoms composing the layer. In that case, the buckling phonon modes corresponding to the antiphase motion along the $c$-axis of the atoms in the sheets can lead to an enhancement of the EP coupling. Experimentally, the effect of buckling can either be explored by means of high-pressure or directly by chemistry. An excellent testbed for such studies is the trigonal phase of binary silicides, like CaSi$_2$ or BaSi$_2$, which constitutes a family of layered intercalated superconductors closely related to the graphite/diboride intercalated systems. Unlike the so-called AlB$_2$-like structure of graphite/diboride compounds, where the planes are flat, in the hexagonal structure of binary silicides the Si planes buckle.

In this Letter we investigate superconductivity in BaSi$_2$ and, in particular, we focus on its layered structure (EuGe$_2$-type structure, $P-3m1$ space group) [9,10]. As it is sketched in the inset of Fig. 2, trigonal BaSi$_2$ is made of planes of Ba arranged in a triangular lattice, interspersed with buckled hexagonal planes of Si. This phase is metallic and was found to be superconducting with a critical temperature of 6.8 K [11]. There are all the reasons to expect that BaSi$_2$ is a standard $s$-wave superconductor, where the mechanism of superconductivity can be obtained by studying the EP coupling. However, recent theoretical studies [12] of trigonal BaSi$_2$ yielded a value of $T_c$ almost an order of magnitude smaller than the early experimental finding of 6.8 K. These studies were based on state-of-the-art linear-response calculations within density-functional theory (DFT), that have proved to describe very accurately the superconducting properties of many other similar materials [13]. Analogous calculations for CaSi$_2$ in its trigonal high-pressure phase gave also a significant underestimation of $T_c$ [14]. Interestingly, the application of pressure on trigonal CaSi$_2$ was shown to increase the superconducting temperature up to 14 K [15]. This finding was discussed in terms of a structural phase transitions under pressure, which is expected to soften the phonon modes associated to the collapse of the corrugated Si planes [16].

In order to elucidate the origin of superconductivity in binary silicides, and at one time to shed light on the discrepant results found in literature, we performed a joint experimental and $ab$ initio study of the superconducting phase of BaSi$_2$. Our experimental data show that $T_c$ varies strongly with the degree of buckling of the Si planes. As in the case of CaSi$_2$ [13,16], by flattening the Si planes, we increase the superconducting transition temperature $T_c$ from 4 K up to 8.7 K. Our extensive DFT calculations allow us to determine how the buckling of the Si planes impacts the electronic and phonon band structures, and finally the EP coupling. Through the comparison of experimental and theoretical results
we infer that a soft phonon mode corresponding to the out-of-plane Si vibrations, and very sensitive to buckling, is responsible for the relatively high value of $T_c$ in BaSi$_2$ when Si planes get flatter. Moreover, our calculations put in evidence a correlation between the softening of this phonon mode and the Si-Si bond buckling. We expect that such a behavior is a general property of conventional superconductors presenting corrugated layers.

Polycrystalline metastable high pressure and high temperature trigonal samples of BaSi$_2$ were synthesized in a Belt-type apparatus from the commercial (Cerac incorporated) orthorhombic phase of BaSi$_2$ ($Pnnm$ space group) with a purity of 98%. Different trigonal structures were meta-stabilized by changing the temperature and the pressure conditions of synthesis according to the phase diagram of BaSi$_2$ [9, 17, 18, 26]. The structural characterizations were performed by X-ray diffraction $\theta$–2$\theta$ measurements done on a Bruker D8 Advance powder diffractometer (K$_\alpha$$_1$, Cu wavelengths). The Rietveld analysis (GSAS software) of the X-ray profiles confirms the trigonal phase with an average purity calculated to be more than 98%. The main phase impurity is the semi-conducting cubic BaSi$_2$ presenting the SrSi$_2$-type structure. The three adjustable cell parameters are the two lattice parameters $a$ and $c$ and the $z$ coordinate which represents the 2$d$-Wyckoff position of Si atoms ($z=0.5$ corresponds to completely flat Si planes). Among the different samples, the $z$ coordinate exhibits sizable variations depending on the pressure and on the temperature of synthesis. The two samples presenting the most pronounced structural difference were synthesized at (4.5 GPa, 500 $^\circ$C) and (4.5 GPa, 1000 $^\circ$C), and have, respectively, $[a=4.061(3)$ Å, $c=5.293(3)$ Å, and $z=0.565(1)]$ and $[a=4.065(3)$ Å, $c=5.347(4)$ Å, and $z=0.546(3)]$. The superconducting transition temperatures $T_c$ of those samples were measured in a SQUID (QD MPMS 5XL). In the left panel of Fig. 1 we can see that the temperature dependence of the zero-field-cooled (ZFC) magnetic susceptibility reveals a $T_c$ onset of 4 K for the phase with $z=0.565$ and 8.7 K for the one with $z=0.546$. For the second sample, with $T_c$ close to 9 K the $M$-$H$ loop was measured at 2 K ($z=0.546$), as shown in the right panel of Fig. 1. It evidences a type-II superconducting state with $H_{c1} \sim 75$ Oe and $H_{c2} \sim 7$ kOe. Using the Ginzburg-Landau equations [19], we estimate the penetration depth $\lambda \sim 3300$ Å and the coherence length $\xi = 104$ Å.

Our DFT calculations were performed with the ABINIT code [20]. The exchange-correlation functional was modeled by a Perdew, Burke, and Ernzerhof (PBE) generalized gradient approximation [21], while the electron-ion interaction was described by norm-conserving Troullier-Martins pseudopotentials [22] generated with the same functional. To obtain the phonon dispersion we employed density-functional perturbation theory. Proper convergence was ensured using a cut-off energy of 30 Ha and a $2^{3}$ $k$-mesh with the Monkhorst-Pack sampling of the Brillouin zone. A grid of $4^3$ $q$ phonon wave vectors and the tetrahedron technique was used for the integration over the Fermi surface. In the trigonal phase the lowest energy structure of BaSi$_2$ has lattice param-
Increasing the buckling of the Si-Si bond leads to a shift have mostly Si 3\textit{p} states. Also the pockets, formed by Ba and the 3\textit{p} states of Si. Also the pockets, formed by Ba 5\textit{d} and Si 3\textit{p}_{\textit{xy}} states, show a light decrease of area upon increase of \( z \), but on a smaller scale than the surface centered at \( A \). For larger values of \( z \) (up to 0.6) the Fermi surface does not change significantly from Fig. 3(c). For values of \( z \) smaller than 0.55 we can see the appearance of a third sheet of the Fermi surface composed purely of Si 3\textit{s} states. This effect can already be seen in Fig. 3(b) as a tiny yellow dot centered at the \( A \)-point. Note, however, that for \( z < 0.545 \) the system becomes structurally unstable, making therefore this region of limited practical importance. Looking at the density of states at the Fermi level [Fig. 3(d)] we see that it attains a maximum in the low-buckled region (\( z = 0.545 \)), then it decreases with increasing \( z \). These numbers already suggest that, from the electronic point of view, superconductivity is favored by smaller values of \( z \).

In order to verify this point, we calculated both the phonon modes and the EP coupling constants as a function of \( z \). At the equilibrium structure our calculated phonon frequencies are close to experimental values [26].

For \( z \) close to 0.5, i.e. for almost planar Si layers, the modes exhibit imaginary frequencies indicating a structural instability. In the stable region, most phonon frequencies show only a weak dependence on buckling. However, the \( A_{1g} \) optical phonons, which are mainly composed of vibrations of the Si atoms along the \( c \) axis (buckling modes), considerably soften upon decreasing \( z \), leading eventually to the structural instability. Moreover, the higher energy \( E_{g} \) mode, composed of Si vibrations in the \( xy \) planes, is slightly hardened with decreasing \( z \). In spite of these changes, the value of \( \Omega_{\text{log}} \), the weighted average

![FIG. 3: (Color online) Panel (a): Fermi surface of BaSi2 in the \( P - 3m1 \) structure [23]. Panels (b) and (c): two-dimensional cuts through the 3D Fermi surface perpendicular to the [001] direction for \( z = 0.55 \) and 0.58. The increase of the Fermi surface when the structure flattens out (smaller \( z \)) is evident. Panel (d): Electronic density of states as a function of \( z \).](attachment:image.png)

![FIG. 4: (Color online) Bottom panel: Eliashberg spectral function \( \alpha^2 F(\omega) \) (in the inset: EP coupling constant \( \lambda \)) as a function of \( z \). Top panel: \( T_{c} \) in K calculated with the McMillan formula. The shaded area shows the interval of \( T_{c} \) values when \( \mu^{*} \) varies from 0.06 to 0.125. For comparison the dashed line represent the experimental values of \( T_{c} \).](attachment:image.png)
of the phonon frequencies, remains basically unchanged in the optimal range 0.55 – 0.58, and therefore can not be responsible for the variations of $T_c$. At $z = 0.56$ we obtain the maximal value $\Omega_{\log} = 182\text{K}$; at $z = 0.55$ it is slightly smaller, $\Omega_{\log} = 170\text{K}$, for $z = 0.545$ it drops to 156 K and for $z = 0.57$ and $z = 0.58$ we found $\Omega_{\log} = 179\text{K}$ and 171 K, respectively.

To evaluate the superconducting transition temperature $T_c$ in the framework of the strong coupling theory of superconductivity $^227$$^228$ we need to calculate $\lambda$, which measures the average EP interaction (inset of the bottom panel of Fig. $^4$). As the calculation of $\lambda$ involves averaging over the Fermi surface, special care has to be taken to ensure the convergence of the results. In fact, an insufficient sampling can lead to a dramatic underestimation of $T_c$ $^12$. The screened coulomb interaction $\mu^*$ was set to 0.1, which is a standard choice for this kind of material. The Eliashberg spectral function $\alpha^2 F(\omega)$ is shown in the bottom panel of Fig. $^4$. There are two main peaks contributing to $\lambda$: the first, due to the acoustic modes, is fairly insensitive to changes in $z$; the second peak, due to the EP coupling of the $A_{1g}$ optical modes, moves to lower frequency, increasing its area and consequently its contribution to $\lambda$ with decreasing $z$. In the inset of the bottom panel of Fig. $^4$ one can see how this leads to a dramatic increase of the EP coupling constant $\lambda$ with $z$, and therefore to a maximum theoretical $T_c$ of around 6 K using the McMillian formulation $^22$ (top panel of Fig. $^4$).

Note that the experimental trend for the dependence of $T_c$ of BaSi$_2$ on the buckling is perfectly reproduced by our calculations, which explain also previous experimental findings for the similar compound CaSi$_2$. The slight underestimation of calculated $T_c$ is due to the neglect of multi-band effects that are known to enhance superconductivity in similar systems, like MgB$_2$ $^4$$^6$$^6$.

In conclusion, we presented an experimental and theoretical study of the layered binary silicide BaSi$_2$. We show that the buckling of the Si sheets can be modified experimentally by using different high-pressure and temperature conditions of synthesis. The reason for such a behavior can be found in our DFT calculations, which evidence a broad low-buckling interval where the total energy changes by less than 50 meV (580 K) per unit cell as a function of $z$. The electronic band structure calculations demonstrate that the density of states at the Fermi level significantly increases by reducing the buckling of the Si planes. However, the flattening of the Si layers is limited by a structural instability concomitant with the softening of the Si optical buckling phonon mode ($A_{1g}$). The coupling of this mode with electrons is also dramatically enhanced by flattening the Si planes, leading to the doubling (from 4 K up to 8.7 K) of the superconducting transition temperature. Such competition between superconductivity and structural distortion can be found in a wide variety of conventional superconductors, like the Chevrel-phases, the transition metal carbides, the cubic Ba$_{1-x}$K$_x$BiO$_3$, etc. This scenario is in full agreement with our experimental and theoretical findings of an increase of $T_c$ when Si planes flatten out, and it is compatible with previous measurements on the disilicide CaSi$_2$ $^{15}$$^{16}$. Moreover, the mechanism of tuning $T_c$ by controlling the buckling of the layers is likely to be present in many other layered superconductors, and therefore can provide a new path for optimizing $T_c$.

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