Superconductivity in layered binary silicides: A density functional theory study

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(Received 29 June 2011; revised manuscript received 12 October 2011; published 4 November 2011)

A class of metal disilicides (of the form XSi2, where X is a divalent metal) crystallizes in the EuGe2 structure, formed by hexagonal corrugated silicon planes intercalated with metal atoms. These compounds are superconducting like other layered superconductors, such as MgB2. Moreover, their properties can be easily tuned either by external pressure or by negative chemical pressure (i.e., by changing the metal), which makes disilicides an ideal testbed to study superconductivity in layered systems. In view of this, we present an extensive density functional theory study of the electronic and phonon band structures as well as the electron-phonon interaction of metal disilicides. Our results explain the variation of the superconducting transition temperature with pressure and the species of the intercalating atom, and allow us to predict superconductivity for compounds not yet synthesized belonging to this family.

DOI: 10.1103/PhysRevB.84.184503

PACS number(s): 74.70.Ad, 71.15.Mb, 74.20.–z, 74.25.Kc

I. INTRODUCTION

The surprising discovery of record-breaking superconductivity in MgB2 at 39 K (see Ref. 1) has been a guide for much of the experimental and theoretical research on conventional superconductivity for the past years. Many important results have appeared, and several structures (many of which hypothetical) with very high superconducting transition temperatures (Tc) have been proposed. Examples are Li2BC (Tc = 150 K),2 carbon clathrates (Tc = 77 K),3 silanes under high pressure (Tc = 17 K),5 or even metallic hydrogen, where Tc was predicted to reach as much as 242 K at extreme pressures of 450 GPa.6 Lately, we have also witnessed a revived interest in superconductivity of the so-called “covalent metals,” such as boron-doped diamond,7 intercalated graphite,11 doped silicon,12 doped silicon carbide,13 alkaline-earth silicon clathrates,14,15 binary silicides,6,17 ternary silicides,18 and many others. Note that superconductivity in all these systems is due to the electron-phonon mechanism, hence these materials can be classified as conventional Bardeen-Cooper-Schrieffer (BCS) superconductors.

One of the main characteristics of MgB2 (and also of other high-Tc superconductors like the cuprates or the iron pnictides) is the reduced dimensionality related to the layered nature. It is therefore not surprising that other layered materials composed of flat plans with sp2 bonding, such as CaC6 and YbC6,29,30 were extensively studied in the years following the discovery of MgB2. Another particularly interesting example of 2D-intercalated compounds are metal disilicides (of the form XSi2, where X is a divalent metal), which can possess either semiconducting or metallic phases.19,20 Superconductivity was found in such layered structures,16,19,21 with transition temperatures ranging from the mK to around 15 K.24 The EuGe2-type XSi2 disilicides crystallize in an hexagonal honeycomb structure with the metal atoms between the Si plans with an AA stacking. This forms an sp3 Si network that presents a natural buckling on the Si sheets.16,19,22 Experimentally, a large range of intercalating metals can be used, namely, alkaline-earth metals (Ca, Sr, Ba) and lanthanides (Eu, La, Ce, Pr, Th, Nd, Gd, Sm, Y, Dy, Yb, Er, Tm, Lu, etc.). More information about these compounds can be found in the excellent reviews on silicon polymorphous and 2D Si-puckered layers by Yamanaka,24 Imai,25 and Demchyna.26

Few experimental and theoretical works studied superconductivity in metal disilicides. For CaSi2, Tc was found experimentally to increase as a function of pressure, arriving at 14 K.16,17 This was interpreted as coming from a flattening of the Si planes, resulting from an sp3-sp2 phase transition above 16 GPa. The structure with flat Si planes (AlB2 phase) is not stable at ambient conditions, but can be in principle stabilized through hole doping, which leads to the filling of the π bands, increasing the sp2 character of silicon.26,27 More recently, superconductivity was found at 8.9 K in another disilicide, namely, BaSi2. This was achieved through the decrease of the buckling of the Si plane, affecting directly the electron-phonon coupling between the Si out-of-plane phonon and the heavy metal.28

It is clear from these two cases that there are two paths to reduce the bucking of the Si planes, and therefore to alter the superconducting transition temperature: (i) by applying positive mechanical pressure or (ii) by intercalation with larger ions (negative chemical pressure). Note that, however, these two paths have an opposite effect on the cell volume: it decreases in (i) but increases in (ii).

It is the aim of this work to give a better understanding of the mechanisms behind the variation of Tc in the disilicides and to provide hints on how superconductivity can be enhanced. For that, we perform density functional theory (DFT) calculations for different intercalating atoms, along the alkali earth column (Mg, Ca, Sr, Ba, Ra). After analyzing the electronic structure, phonon spectrum, and the electron-phonon coupling matrix elements, we correlate these properties to the transition temperatures obtained from McMillan’s formula.

The rest of this paper is organized as follows: in Sec. II, we give details on our numerical methodology. The discussion of the structural optimization is given in Sec. III, followed, in Sec. IV, by the results for the electronic structures and Fermi surfaces of disilicides. In Sec. V, we discuss the phonon properties, the electron-phonon coupling, and the
superconducting transition temperatures. Finally, we present our conclusions in Sec. VI.

II. METHODOLOGY

All calculations were performed within DFT using the ABINIT code,31 in the Perdew, Burke, and Erzernhof (PBE) generalized gradient approximation32 for the exchange-correlation functional. The electron-ion interaction was described by norm-conserving Troullier-Martins pseudopotentials33 generated with the same functional. Note that for the elements that compose our compounds and in the pressure range of interest the pseudopotential approximation is reliable. The phonon spectrum and the electron-phonon matrix elements were obtained employing density functional perturbation theory.34,35 The spectral function $\alpha^2 F(\omega)$ was calculated applying the tetrahedron technique for the integration over the Fermi surface. Proper convergence of these quantities was ensured by setting a cutoff energy of 30 Ha, a $16 \times 16 \times 16$ Monkhorst-Pack sampling,36 and a $4 \times 4 \times 4$ $q$ grid for the phonon wave vectors. Superconducting transition temperatures were calculated through the McMillan approximate solution40 of the Eliashberg equations.41

III. CRYSTAL STRUCTURES

For superconductivity, the most relevant phase of the disilicides compounds is the trigonal ($P\bar{3}m1,164$).20–22,28 This trigonal structure, depicted in Fig. 1, has metal atoms in the $1a$ Wyckoff position with reduced coordinates $(0,0,0)$ and Si in the $2d$ position with reduced coordinates $(1/3,2/3,z)$. The parameter $z$ is extremely important, as it measures the degree of buckling of the silicon planes: the value $z = 1/2$ means completely flat planes. In order to study the effect of chemical pressure, we mainly focused on intercalation with atoms of the column II-A (Mg, Ca, Sr, Ba, Ra). Moreover, the effect of mechanical pressure could be explored for CaSi$_2$ thanks to the availability of experimental data.16,17,22 Note that we incorporated the hypothetical trigonal structures for MgSi$_2$ and RaSi$_2$ in our set in order to have a better understanding on the variation of $T_c$ along the II-A column.

In Table I, we present the lattice parameters $a$, $c$, and $z_{opt}$ that resulted from the geometry optimization. As expected, going down the II-A column the unit cell expands (with the exception of Ra). Moreover, for heavy atoms, we obtain low buckled structures (close to the AlB$_2$ phase with a $z = 0.5$), while for light atoms the distortion increases leading to a highly buckled structure.

In Fig. 2, we plot the total energy as a function of the internal $z$ parameter at fixed volume. Besides the variation of value of $z$ corresponding to the minimum of the curves, we can also notice that the concavity of the curve increases with increasing atomic number. This concavity is related to the phonon mode that describes the off-plane deformation of the Si layers. One can deduce that, especially for heavy metal atoms, it costs very little energy to change significantly the corrugation of the layers. This was also verified experimentally, as it was possible to produce samples of BaSi$_2$ with different values of

![FIG. 1. (Color online) Crystal structure of the disilicides compounds in the trigonal phase ($P\bar{3}m1,164$). The metal atoms are the (green) dark gray larger balls, while the orange (light green) smaller balls represent Si atoms. (a) Projection of the crystal structure onto the $ab$ plane. (b) Layered structure where it is visible the buckling of the Si layer.](184503-2)
superconductivity. From Fig. 5, we can see that at the relaxed state for the metal disilicides studied in this work. The transition temperatures were obtained using McMillan’s formula\(^4\) with \(\mu^* = 0.1\). The underestimation of \(T_c\) can be related to the neglect of multiband effects in McMillan’s formula.\(^4\)

### IV. ELECTRONIC STRUCTURE AND FERMI SURFACE

The Fermi surfaces calculated for the different metal intercalations are illustrated in Fig. 4. For the elements of the column II-A, at the tuned \(z_{\text{tuned}}\) values (see Table II and empty squares in Fig. 3), the Fermi surface is composed of two parts: a large surface centered at the \(A\) points and smaller pockets around the \(M\) points. For these compounds, the bands around the \(A\) point have mostly Si \(3p_z\) character and disperse much more in the \(xy\) plane than along vertical directions. For the BaSi\(_2\) compound, we found that in the limit of structural stability (smallest \(z\)), a small third sheet of the Fermi surface composed purely of Si \(3s\) states appears in the Brillouin zone.\(^2\) This third sheet can already been seen at zero pressure in RaSi\(_2\), due to the negative chemical pressure exerted by this large atom. A surprising fact is the influence of the \(d\) states of the metal on the electronic properties, that probably leads to the stability of the trigonal phase. In fact, MgSi\(_2\) [see Fig. 4(a)] has a quite different Fermi surface from the other compounds, with small pockets around the \(H\) point. This is very likely one of the reasons why neither Mg nor Be form spontaneously a disilicide system.\(^2\)

Finally, in the panels (b) and (c) of Fig. 4 we see the Fermi surface of CaSi\(_2\) at zero and 16 GPa. (Our calculations agree with the electronic structure reported previously in Ref. 37.) The increase of the surface with pressure is evident, both around the \(A\) point, and in the pockets around the \(M\) points and that at 16 GPa cover the whole \(M-L\) region. Note that these latter states are composed predominantly by the hybridization of Si \(3p_z\) and Ca \(4d\) orbitals.

We now turn to the discussion of the electronic density of states at the Fermi level \(N(E_F)\), an important quantity for superconductivity. From Fig. 5, we can see that at the relaxed

\(z\) by changing the synthesis procedure.\(^2\) In the case of BaSi\(_2\), it turned out that the structures with values of \(z\) closer to 1/2 were more interesting as they exhibited larger values of \(T_c\).\(^2\)

In order to explore the superconducting properties of disilicides, we need to investigate a range of values of \(z\). To have a working definition for this range, we kept the structure fixed at its theoretical minimum, while allowing \(z\) to vary in a region that maximizes \(N(E_F)\), \(\lambda\), and \(T_c\), but at the same time assuring the stability of the structures by real phonon frequencies. In our opinion, this recipe generates a reasonable range of \(z\) that we can use to discuss the maximum possible transition temperature for each one of the elements of the XSi\(_2\) family studied in this work. We will refer as “tuned \(z\)” to the value of \(z = z_{\text{tuned}}\) that maximizes the density of states at the Fermi level and the superconducting transition temperature, while yielding real phonons. Those values are marked by empty squares in Fig. 3 and given in Table II. Figure 3 summarizes the ranges of \(z\) we used in this work (left panel), together with the corresponding variations in the Si-Si distances (right panel). We emphasize that these ranges correspond to variations of the total energy of only a few tens of meV per XSi\(_2\) unit, for example, for Ba it correspond to less than 50 meV. Small atomic numbers (Mg, Ca) favor highly buckled structures, while the SrSi\(_2\) system exhibits an intermediate behavior. Finally, the heavier and larger atoms Ba and Ra decrease the corrugation due to the increasing chemical pressure they exert on the Si planes. It is clear that by changing the intercalating atom, i.e., by applying chemical pressure, we can gain control on the corrugation of the hexagonal Si planes.

Another way to modify the buckling of the Si planes is applying an external pressure. As a function of the increasing external pressure, it is intuitive that the buckling of the Si-Si planes should decrease, while the Si–Si distance shortens (as the volume decreases). For the case of CaSi\(_2\), for example, \(z\) goes from 0.585 at zero pressure to \(z = 0.555\) at 16 GPa, while the Si–Si distance reduces from 2.40 Å at zero pressure to 2.21 Å at 16 GPa. It is important to remark that the typical bonding distance in a layered structure is around 2.3–2.7 Å,\(^4\) a range that is respected for all structures studied here at zero pressure. The shortening of the Si-Si distance can be explained from the experimental compressibility of the \(c\) axis, larger by a factor of two than the \(a\) or \(b\) axes.\(^2\) Note that under pressure, as the buckling decreases and the atoms approach, the hybridization of the states increases leading to strong modification of the electronic properties. In the case of the silicides, this leads to an enhancement of \(T_c\).
The behavior of $N(E_F)$ with respect to the intercalating atom is not monotonous across the II-A group (green dashed bars), decreasing from Mg to Ca, and then increasing again until Ra. The situation is different if one uses the tuned $z_{tuned}$ (gray solid bars), with $N(E_F)$ now increasing as a function of the atomic number of the metal. For light metals (like Mg), the out-of-plane Si phonon mode is stiff, and therefore there is not much freedom in flattening the planes. This leads to a small difference between $N(E_F)$ at the relaxed and tuned $z$. On the other hand, for Sr and Ca, one can increase the density of states by 40% and 60%, respectively, by tuning $z$. This effect is even larger under pressure. For example, at 16 GPa and low buckling, one can increase the density of states at the Fermi level of CaSi$_2$ relatively to its zero pressure and relaxed $z_{opt}$ by as much as 80%. This is explained by the large compressibility on the $c$ axis, which leads to an important decrease of volume, and by the softness of the off-plane Si phonon mode that easily allows for large variations of $z$.

V. PHONONS AND TRANSITION TEMPERATURE

Since there are three atoms per unit cell in the trigonal phase of metal disilicides, the phonon band structures are composed by three acoustic and six ($3 \times 3$) optical branches. The mechanical representation for the $1a$ and $2d$ positions in the space group $P-3m1$ is $M = A_{1g} + 2A_{2u} + 2E_u + E_g$, where $A_{1g}$ and $E_g$ (double degenerate) are Raman active modes, and $A_{2u}$ and $E_u$ (double degenerate) are infrared active modes. The three higher frequency optical modes involve vibrations of the Si atoms composing the hexagonal planes, while the other, lower-energy three optical modes are out-of-phase vibrations of the Si and metal atoms. These six optical modes, relative to the $P-3m1,164$ crystal symmetry of disilicides, are depicted in Fig. 6. The $E_g$ modes describe the in-plane oscillations of Si atoms, while the $E_u$ mode corresponds to the combined out-of-plane movement of the Si and metal atoms in the $xy$ plane. On the other hand, the $A_{1g}$ and $A_{2u}$ modes are characterized by the out-of-plane oscillations of, respectively, Si atoms, and out-of-phase Si and metal atoms.

![Figure 4](image_url)

**FIG. 4.** (Color online) Brillouin zone with high-symmetry points (a) and Fermi surfaces of MgSi$_2$ (b), CaSi$_2$ at the external pressure of 0 GPa (c), CaSi$_2$ at the external pressure of 16 GPa (d), SrSi$_2$ (e), and RaSi$_2$ (f). For RaSi$_2$, note the third sheet appearing at $\Gamma$ composed purely of Si 3$s$ states.

![Figure 5](image_url)

**FIG. 5.** (Color online) Electronic density of states at the Fermi level $N(E_F)$ for the systems studied in this work. The (green) light gray bars represent calculations at the relaxed geometry $z = z_{opt}$, while the dark gray bars are obtained for the tuned values $z = z_{tuned}$.

![Figure 6](image_url)

**FIG. 6.** (Color online) The six optical phonon modes present in the trigonal phase (space group $P-3m1,164$) of disilicides. The $E_g$ modes involve the movement of Si atoms in the $xy$ plane. The $A_{1g}$ mode represents the out-of-plane motion of the Si atoms. The double degenerate $E_u$ modes are the displacements of individual metal and Si ions in the $xy$ plane and the $A_{2u}$ mode is the corresponding out-of-plane displacement.
properties. We remind that, in conventional superconductivity, we should have high-frequency phonon modes strongly coupled to electrons in order to attain large transition temperatures. The related superconducting properties ($\omega_{\text{log}}$, $\lambda$, and $T_c$ calculated with McMillan's formula) are presented in Table II. There are two issues concerning to the use of McMillan's formula that should be noticed: (i) this formula requires a value for the parameter $\mu^*$ that describes the decrease of the transition temperature due to the breaking of the Cooper pairs interacting through the repulsive Coulomb interaction. In an overwhelming majority of the calculations of $T_c$ this value is semiempirical, or specified through a more or less educated guess. Typical values of $\mu^*$ are found between 0.1 and 0.2. For the values of $T_c$ in Table II, we used $\mu^* = 0.1$. (ii) McMillan's formula neglects multiband effects that are known to increase considerably $T_c$ for materials like MgB$_2$. As the structures studied here have several bands crossing the Fermi level, one can expect that our calculated values for $T_c$ are underestimated. This explains the differences between our calculated transition temperatures and experimental values for BaSi$_2$ and CaSi$_2$. In spite of these two limitations, trends should, however, be correctly described.

As expected, we find in general a softening of the phonon modes for structures with low buckling degree and this effect is enhanced when the mass of the intercalating metal atom increases. The acoustic modes are also found to disperse less for heavier metals. From the $\alpha^2 F(\omega)$ plots, we see that all phonon modes couple to electrons, but that the relative weights of each phonon vary with the intercalating metal. For Mg, the acoustic modes soften and are by far the most important, while for Ca, we also see a big peak coming from the high-energy $E_g$ phonon branch, and for Sr, Ba, and Ra, the mixed Si-metal lower-energy optical modes plays an important role.

For the lightest II-A metal studied, Mg, decreasing the buckling does not have a major influence on the $A_{1g}$ out-of-plane vibration that remains (at $\Gamma$) close to 340 cm$^{-1}$, while the $E_g$ frequency at $\Gamma$ remains at around 470 cm$^{-1}$. In this case, the phonon modes that cause the structural instability with decreasing $z$ are the acoustic modes that become imaginary at the points $M$ and $H$ of the Brillouin zone. Regarding the spectral function $\alpha^2 F(\omega)$ we see that the strongest electron-phonon coupling involves acoustic phonons. Consequently, $\omega_{\text{log}}$ is relatively low, which, combined with the moderate $\lambda = 0.79$, leads to a maximum $T_c$ for this structure of around 6 K.

Ca disilicide has been studied experimentally in Ref. 16 as a function of pressure, and it was found that it can achieve a superconducting transition temperature of 14 K. The samples with highest $T_c$ turned out to be close to the phase transition (at around 16 GPa) between the EuGe$_2$ phase and what was suggested to be the phase of CaSi$_2$ predicted by Kusakabe, which consists in completely flat Si planes ($z = 1/2$) in the AlB$_2$ structure, leading to a considerable reduction of the volume of the unit cell. However, linear-response calculations of the AlB$_2$ phase lead to imaginary phonons, and geometry optimization starting from the AlB$_2$ structure with a slightly broken symmetry yields again a highly buckled structure. These are clear indications that the AlB$_2$ structure is not stable in the relevant pressure range. On the
other hand, the EuGe\textsubscript{2} phase had been previously studied by Nakanishi\textsuperscript{38} and Loison.\textsuperscript{48} Both works, however, found a theoretical transition temperature much smaller than the maximum experimental value \( T_c = 14 \) K at 16 GPa.\textsuperscript{16} To resolve this issue, we note that, as we know from BaSi\textsubscript{2}, it is possible to modify \( z \) experimentally by applying external pressure, and consequently to enhance superconductivity in CaSi\textsubscript{2}.

In Fig. 7, we show the phonon dispersion for CaSi\textsubscript{2} calculated at the smallest \( z \) for which the lattice is theoretically stable. The highest phonon mode (that is strongly coupled to the electronic states) is the \( E_g \) in-plane vibration of the Si atoms at around 580 cm\textsuperscript{-1}. Then, at \( \Gamma \), we find the \( A_{2u} \) mode at 240 cm\textsuperscript{-1}, and the \( A_{1g} \) mode around 310 cm\textsuperscript{-1}. Note that these values are lower than the ones calculated by Nakanishi\textsuperscript{38} and Loison\textsuperscript{48} for the trigonal phase of CaSi\textsubscript{2}. This can be easily explained by the different \( z \) used in the calculations, as these previous works used the larger value obtained by geometry minimization within standard DFT.

It is interesting to see how the superconducting transition temperature increases with decreasing value of \( z \). At 16 GPa, and for the highly buckled sample, \( z = 0.5876, \lambda = 0.3, \) and \( T_c = 0.1 \) K in agreement with the previous calculations.\textsuperscript{38} Decreasing \( z \) to 0.57 leads to \( \omega_{\log} = 220 \) K and to a slight increase of \( \lambda = 0.44 \) and \( T_c = 1.5 \) K. As one reaches \( z = 0.56 \), there is a sudden increase of the electron-phonon coupling constant to \( \lambda = 0.90 \) with a \( T_c = 5.85 \) K. Finally, just before the structure instability indicated by the presence of imaginary phonon frequencies, we obtain for \( z = 0.557 \) the values of \( \lambda = 1.11, \omega_{\log} = 100 \) K, and \( T_c = 8 \) K. This number is of the same order of magnitude of the maximum experimental \( T_c = 14 \) K found for CaSi\textsubscript{2}. The slight underestimation can, moreover, be attributed to the neglect of multiband effects in the McMillan’s formula used.

We can now see that the large experimental values of \( T_c \) for CaSi\textsubscript{2} can be explained without resorting to exotic superconducting mechanisms. Furthermore, the presence of samples with different values of \( z \), can justify, in the same way as for BaSi\textsubscript{2},\textsuperscript{28} the dispersion of values of \( T_c \) found experimentally.

From panel (b) of Fig. 7, we can see that for CaSi\textsubscript{2} the phonon modes that contribute more to \( a^2 F(\omega) \) and therefore to \( \lambda \) are the two \( E_g \) modes and the acoustic modes. We should note that, in this case, the acoustic Ca modes become imaginary at low values of \( z \), and therefore are responsible for driving the system to instability.

For the case of heavier intercalated atoms (Sr, Ba, and Ra), we find that the phonon dispersions show very similar structures, the main difference being the energy of the eigenmodes. The Eliashberg spectral functions reveal two main peaks contributing to superconductivity: the first, due to the acoustic modes, less sensitive to changes in \( z \), and the second peak, due to the coupling of electrons with the \( A_{1g} \) mode, which moves to lower frequencies for smaller values of \( z \). Descending the II-A column we can also see how the decrease of \( z \) induced by the chemical pressure (i.e., by increasing the size of the intercalating atom) leads to an increase of the electron-phonon coupling constants and of the superconducting transition temperature. In fact, the Sr compound has the lowest value of \( \lambda \) with 0.50, leading to \( T_c = 2.2 \) K, followed by Ba with \( \lambda = 0.77 \) and \( T_c = 6.8 \) K. Finally, Ra leads to the highest values \( \lambda = 0.93 \) and \( T_c = 8.3 \) K. In conclusion, the order of \( T_c \) from the lowest to the highest is Sr, Mg, Ba, Ca, and Ra. Note that, recently, experimental x-ray diffraction measurements of BaSi\textsubscript{2} confirmed the variation of \( T_c \) as a function of buckling as predicted by \textit{ab initio} calculations.\textsuperscript{28}

For these heavy intercalating metals, the lattice instability related to the flattening of the hexagonal Si layers comes through the acoustic metal branch that becomes imaginary for small values of \( z \).

It is interesting to consider the relationship between superconductivity trends in the XSi\textsubscript{2} family and silicon clathrates having the same guest atoms (Ca, Sr, Ba). Both families are intercalated silicon structures, but they exhibit different structural constraints. In fact, there is no analogous to the buckling tuning parameter of XSi\textsubscript{2} in silicon clathrates, which, on the other hand possess various intercalation sites. If we consider the simplest and more studied case of the type-I clathrate structure X\textsubscript{4}Si\textsubscript{46} with only two intercalation sites, it has been found that the McMillan approximation holds, with \( T_c \) essentially controlled by the density of states at the Fermi level.\textsuperscript{49,51} This leads to a stronger dependence of \( T_c \) on the nature of the guest atom\textsuperscript{50} as there is no additional structural tuning parameter.

VI. CONCLUSIONS

In this paper, we studied several compounds belonging to the family of metal disilicides, namely, MgSi\textsubscript{2}, CaSi\textsubscript{2}, SrSi\textsubscript{2}, BaSi\textsubscript{2}, and RaSi\textsubscript{2}. We calculated using \textit{ab initio} density functional theory the electronic properties, phonon dispersions, electron-phonon coupling, and superconducting transition temperatures. All these quantities were obtained as a function of the internal coordinate \( z \), an important parameter that measures the buckling of the hexagonal Si planes in the structure. Our results show that it is possible to increase the density of electronic states at the Fermi surface in two different ways, either by reducing the buckling of the Si planes by means of external pressure or by intercalating heavier atoms between the Si sheets. The phonon modes show, as expected, a softening with increasing atomic number of the metal, and the largest electron-phonon coupling comes normally from the acoustic and lowest-lying optical modes. The calculated electron-phonon coupling constants allow to explain superconductivity in CaSi\textsubscript{2} and BaSi\textsubscript{2}, without the need of invoking exotic superconducting mechanisms. Furthermore, the experimental dispersion of values of \( T_c \) can be easily explained by the presence of samples with different values of \( z \).

ACKNOWLEDGMENTS

J.A.F.L. acknowledges the CONACyT, Mexico. S.B. acknowledges support from EU’s 7th Framework Programme (e-13 contract ETSF n.211956) and M.A.L.M. from the French ANR (ANR-08-CEXC8-008-01). Calculations were performed at GENCI (project x2011096017).
SUPERCONDUCTIVITY IN LAYERED BINARY ...