Superconductivity in intercalated group-IV honeycomb structures

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We present a theoretical investigation on electron-phonon superconductivity of honeycomb MX\textsubscript{2} layered structures. Where X is one element of the group-IV (C, Si or Ge) and M an alkali or an alkaline-earth metal. Among the studied composition we predict a T\textsubscript{c} of 7K in RbGe\textsubscript{2}, 9K in RbSi\textsubscript{2} and 11K in SrC\textsubscript{2}. All these compounds feature a strongly anisotropic superconducting gap. Our results show that despite the different doping and structural properties, the three families of materials fall into a similar description of its superconducting behavior. This allows us to estimate an upper critical temperature of about 20K for the class of intercalated group-IV structures, including intercalated graphite and doped graphene.

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A large research effort has been lately focused on atomic-thin layered materials and their properties\textsuperscript{1–3}. This was triggered by the creation of graphene from graphite\textsuperscript{4} and also motivated by the belief in many potential applications since thin systems can be significantly modified in their electronic properties simply by acting on parameters as stacking, chemical and physical doping\textsuperscript{5,6}. In fact this versatility is an extraordinary playground for searching for new superconductors (SC)\textsuperscript{7}. Many (low temperature) SC are already known in the class of graphite intercalated compounds GICs\textsuperscript{8–12}, graphene itself has been predicted to superconduct with a critical temperature (T\textsubscript{c}) of 18K upon Li doping\textsuperscript{13}.

Among all possible compounds, those chemically and structurally closer to graphite are the honeycomb lattices of Silicon\textsuperscript{14–17} and Germanium\textsuperscript{18,19}. Which also show superconductivity upon doping in the CaSi\textsubscript{2}, BaSi\textsubscript{2} and MGe\textsubscript{2} systems - M standing for a metallic element. Hence GICs and doped graphene are not unique systems, having a Si and Ge counterpart and can be seen as members of a generalized family of group-IV intercalated honeycomb lattices (gIV-ICs).

So far the highest T\textsubscript{c} reported on gIV-ICs is 11.5K in CaC\textsubscript{2}\textsuperscript{11,12}. This system is also the most studied among the family and its superconducting properties are rather well understood\textsuperscript{16,20–23}. In particular it is clear that an important role is played by the existence at the Fermi level of 2D electron like bands as well as anti-bonding C-\pi states. A sufficiently large intercalation is therefore a necessary condition to obtain high critical temperatures. But what is the highest conceivable T\textsubscript{c} in an intercalated graphite-like system? Could Si and Ge iso-morphs be better candidates than GICs? We will address these questions by restricting the investigation to the high doping limit of MX\textsubscript{2} structures. We will show by means of theoretical \textit{ab-initio} methods, that finding high temperature superconductivity in these families is a false hope. On the other hand breaking the record critical temperature of CaC\textsubscript{2} is likely to be possible.

Our work starts from the assumption of the EuGe\textsubscript{2} crystal (p – 3m1, 164) with trigonal symmetry. This structure can be easily intercalated\textsuperscript{24} and has high occurrence in phases of disilicides\textsuperscript{15,25,26} and germanides\textsuperscript{18,19,27}. Fig. 1 shows the structural prototype, this can be understood as a AlB\textsubscript{2} (P6/mmm, 191) structure with buckled honeycomb layer. The intercalated metal X occupy the 1a Wyckoff position (0,0,0) and the M atoms (honeycomb) occupy the 2d Wyckoff positions with coordinates (1/3, 2/3, z) and (2/3, 1/3, –z). All the systems were structurally relaxed within Kohn-Sham density-functional theory.\textsuperscript{28} We provide in the Supplemental Material all the optimized lattice parameters and atom coordinates (see Supplemental Material for details).

Fig. 1 shows the buckling (β) of the group-IV honeycomb layers and its variation on the intercalated X metal. We defined β = (|z – 1/2| · c), where c is the out-of-plane lattice parameter. Therefore β = 0 indicates that the AlB\textsubscript{2} symmetry was recovered after relaxation, with a completely flat honeycombs. Germanides and silicides show a full sp\textsuperscript{3} hybridization that induce a finite buckling in the structure. As clear from this figure, intercalating lighter ions induce a high buckling, while heavier ions tend to induce low-buckled plans. With the only exception of CaC\textsubscript{2}, in all intercalated graphites the AlB\textsubscript{2} structure was recovered after relaxation. A bond analysis shows that CaC\textsubscript{2} is in a mixture of sp\textsuperscript{2} – sp\textsuperscript{3} (75% – 25% respectively) and therefore at ambient pressure it shows a finite buckling. In this respect, it has been recently predicted by Li and coworkers\textsuperscript{29} that the flat-layered phase could be stabilized at high Pressures.

For all systems under investigation we compute phonons and electron-phonon coupling by means of density-functional perturbation theory.\textsuperscript{30} We found most of the intercalated carbon compounds dynamically unstable, except the Sr and Ca intercalation. Suggesting that the 1 to 2 intercalation is too large for this family. This is evidenced experimentally by the reported challenging synthesis of LiC\textsubscript{2}\textsuperscript{8}, that turns out to be metastable, partially loosing its Li content and converting in LiC\textsubscript{6}\textsuperscript{3,10}. On the other hand, with the exception of light-ion intercalants, most of the disilicides and digermanides are dynamically stable.

Eliashberg spectral functions\textsuperscript{31,32} \(\alpha^2F(\omega)\) for all dynamically stable systems are reported in Fig. 2. One can
Figure 1. (Color online) Buckling \( (\beta) \) of the honeycomb layer as a function of intercalated X element. Carbon (black dots), Silicon (red squares) and Germanium (blue triangles). Lines serve only as guide. The \( p - 3m1 \) crystal structure is also depicted in the plot. Intercalating Si and Ge honeycombs lead to a full \( sp^3 \) hybridization, contrary in C to a \( sp^2 \) flat-plans. Interested, CaC\(_6\) relax in a low buckled structure having a mixture of \( sp^2 - sp^3 \).

**clearly distinguish that the spectral functions are scaled in their frequency by the mass of the atom forming the honeycomb layer. And this extends not only, obviously, to the high energy modes that originate from strong in-layer bonds, but also to the low frequency modes that are dominated by the intercalant motion in the weak inter-layer potential. Indicating a chemical effect. We also observe that alkali metals (as compared with alkaline earths) lead to systematically lower phonon branches, therefore to an enhanced coupling strengths\(^{31}\)**

\[
\lambda = 2 \int \frac{\alpha^2 F(\omega)}{\omega} d\omega, 
\]

at the same time this lowers the average frequency, that we conventionally express as

\[
\omega_{\text{log}} = \exp \left[ \frac{2}{\lambda} \int \frac{\alpha^2 F(\omega) \ln(\omega)}{\omega} d\omega \right].
\]

From an electronic point of view, all the materials share a qualitative similar structure. As in the case of CaC\(_6\) or doped graphene, there are two type of electronic states located at the Fermi energy: anti-bonding \( \pi \) states provided by the honeycomb layer (C, Si, Ge) and 2D interlayer states with contributions from the M \( d \)-orbitals. These electronic states hybridize differently along the alkali or the alkaline-earth column and lead to different effective doping and band alignment. This affects the density of states at the Fermi energy (\( N(E_F) \)) and with it the occurrence of superconductivity, as we will show below.

\[
T_c = \frac{\omega_{\text{log}}}{1.2} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right].
\]

This formula depends on three parameters: the Coulomb pseudopotential \( \mu^* \) (here fixed to 0.1); the phonon frequency in the form of the logarithmic average \( \omega_{\text{log}} \); and the coupling constant \( \lambda \). The computed \( T_c \) and couplings \( \lambda \) are shown in Fig. 3.

In the limit of an homogeneous coupling in \( k \)-space, \( \lambda \) is proportional to \( N(E_F) \). Within BCS theory, this parameter splits as \( \lambda = VN(E_F) \), where \( V \) is the BCS coupling strength. In Fig. 3b) we observe a remarkable proportionality between \( \lambda \) and \( N(E_F) \). Leading to the conclusion that \( V \) is approximately the same on this MX\(_2\) class of systems, with the sole exception of few systems characterized by strong softening. Eventually this mode softening leads to a phononic instability and a structural phase transition. Although not belonging to this MX\(_2\) family we observe that CaC\(_6\) lies perfectly in this regime\(^{23,36}\).
Figure 3. (Color online) Bottom panel shows $\lambda$ (electron-phonon coupling) Eq. 1, as function of the density of state at the Fermi level, $N(E_F)$. Top panel shows the critical transition temperature calculated within Eq. 3 as function of $N(E_F)$ for the different compounds studied in this work. Gray-lines represent the phonon energy average $\omega_{\text{log}}$ (Eq. 2) ranging from 2 to 34 meV (dashed lines) as function of $N(E_F)$.

And similarly does MgB$_2$, however, this is accidental as we have ignored its multi-band nature$^{37-39}$.

These calculations predict several interesting superconductors in particular RbSi$_2$, RbGe$_2$ and SrC$_2$. RbGe$_2$ has the highest density of states and, as discussed above, this also leads to the highest $\lambda$, even though it shows a modest $T_C$ of 7K. In fact $T_C$ (see Eq. 3) depends also on the phonon energy, which is larger for systems of lower mass, SrC$_2$. Iso-mass lines are shown as a reference in Fig. 3a) to indicate how $T_C$ would increase with $\lambda$ (or $N(E_F)$). The analysis suggests the existence of an upper critical temperature for each family. This is imposed by the electronic structure, as $N(E_F)$ hardly would exceed the value of 0.7 states/eV/spin. Following the iso-mass lines in Fig. 3a this leads to the conclusion that an upper critical temperature of about 10K, 15K and 20K has to be expected respectively for the Ge, Si and Carbon families. We firmly believe that this conclusion can be extended beyond the MX$_2$ class, since different doping level will not plausibly affect the coupling strength. However, the coupling strength could be significantly affected only if $\sigma$ states were involved (as in MgB$_2$), but this would require an unphysical doping level.

We will now focus our investigation on three selected systems SrC$_2$, RbSi$_2$ and RbGe$_2$as they are the most interesting of each sub-family. Here we make use of density-functional theory for superconductors (SCDFT), as it is completely parameter free$^{40-42}$ and allows for a full k-resolved description$^{13}$.

It should be observed (see Fig. 4 a,b,c) that the electron phonon coupling in all these systems is rather anisotropic, meaning strongly k-dependent on the Fermi surface (FS). SrC$_2$ has a continuous distribution, while RbSi$_2$ and RbGe$_2$, have two disconnected FS with remarkably different coupling strength: stronger on the small FS around the $\Gamma$ point and weaker in the outer FS (at large $|k|$). The distribution of superconducting gaps on the Fermi energy (not shown) follows the anisotropy in $\lambda_k$, similarly to the behavior observed in bulk lead$^{44}$. The gap distribution function at $T = 0$ (i.e. the energy distribution of the SC gaps: $\Delta_{k_F}$), as well as the temperature dependence (in a two-band and single band model) are plotted in Fig. 4 d,e,f. Both RbSi$_2$ and RbGe$_2$ show two distinct gaps (like in MgB$_2$ or bulk lead$^{38,39,44}$), while SrC$_2$ has an anisotropic gap continuously distributed. This gap distribution reminds that of CaC$_6$$^{23,45,46}$. This anisotropy will affect the specific heat and the thermodynamical properties. However, unlike in MgB$_2$, the critical temperature is not much affected by it (less than 1K).

The role of coupling anisotropy on the superconducting behavior can be clearly understood within the qualitative model of Suhl, Mattias and Walker$^{47}$. The observed combination of a large anisotropy in the gap with a small enhancement in $T_C$ is a consequence of the strong interband coupling between $\pi$-states (having a smaller gap) and the interlayer states (that dominate on the larger gap). The gap distribution of SrC$_2$ is even broader and clearly cannot be completely captured within a two-band model. The system is in fact almost gapless, since the small $|k|$ part of the FS shows a negligible superconducting pairing as a consequence of the weak phononic coupling.

In order to assert on the possible synthesis of these new superconducting compounds, we have investigated their thermodynamic stability. The analysis on the energetics and dynamical stability shows that most silicides and germanides are energetically stable in this MX$_2$ phase. In particular RbSi$_6$ and RbGe$_6$ both stable with respect to elemental decomposition and also more stable than their RbSi$_6$ and RbGe$_6$ rhombohedral counterparts (see Supplemental Material for details). Therefore we can conclude that these two systems are likely to be accessible to the experimental synthesis.

The case of Carbon is less favorable since SrC$_2$ is less stable than its elemental counterpart, and also less stable than its SrC$_6$ counterpart. This is in complete analogy with the case of CaC$_6$ that is also more stable than CaC$_2$ and in agreement with the fact that both CaC$_6$ and SrC$_6$ have been synthesized$^{11,49}$. Nevertheless SrC$_2$ shows 4 stable polymorphs in the temperature range of 0 to 900 K$^{50,51}$. Since the system is dynamically stable, it may still be possible to find a way to its synthesis, perhaps by means of a non-equilibrium process or by high temperature and high pressure, as often used to synthesized clathrates$^{52}$, carbon borides$^{53}$ and layered disilicides$^{15,17,25,54}$ and germanides$^{18}$.

In summary, we have presented a theoretical study on honeycomb layered binary carbides, silicides and germanides intercalated by alkali or alkaline-earth metals. Our superconductivity analysis has shown that in this
Figure 4. (Color online) Fermi surface of SrC$_2$ (a) RbSi$_2$ (b) and RbGe$_2$ (c), shown in the Γ centered reciprocal unit cell (top view). The color scale (bottom left corner) gives the k-resolved electron phonon coupling $\lambda_k$. Superconducting gap as a function of temperature for SrC$_2$ (d) RbSi$_2$ (e) and RbGe$_2$ (f), computed within SCDFT$^{23}$. The red-dashed line is the isotropic behavior, blue-continuous lines are a minimal two-band approximation. The full gap distribution function$^{23,26}$ is given at $T = 0$ in as a filled area.

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We used the two plane-wave based code ABINIT \cite{28} and ESPRESSO \cite{29} within the Perdew-Burke-Ernzerhof (PBE) \cite{30} exchange correlation functional and the core states were accounted for by norm-conserving Troullier-Martins pseudopotentials \cite{31}. The pseudopotential accuracy has been checked against FP-LAPW method as implemented in the ELK code (http://elk.sourceforge.net/).

The phonon spectrum and the electron-phonon matrix elements were obtained employing density-functional perturbation theory. With the only exception of SrCr$_2$Si$_2$Ge$_2$, a cutoff energy of 60 Ry was used in the plane-wave expansion. A $8 \times 8 \times 8$ grid was used for all the materials under consideration. With the only exception of SrCr$_2$Si$_2$Ge$_2$ and SrSi$_2$, the Monkhorst-Pack \cite{32} $k$-grid was used for all the materials under consideration. A $4 \times 4 \times 4 q$-grid was used for all the materials under consideration. The $q$ sampling grid was increased to $8 \times 8 \times 6$ in order to achieve an accurate description of anisotropic properties.

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The phononic functional we use is an improved version with respect to Ref. 41 and 42 and is discussed in Ref. 48.