Possibility of superconductivity in graphite intercalated with alkaline earths investigated with density functional theory.

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Using density functional theory we investigate the occurrence of superconductivity in AC₆ with A=Mg,Ca,Sr,Ba. We predict that at zero pressure, Ba and Sr should be superconducting with critical temperatures (T_c) 0.2 K and 3.0 K, respectively. We study the pressure dependence of T_c assuming the same symmetry for the crystal structures at zero and finite pressures. We find that the SrC₆ and BaC₆ critical temperatures should be substantially enhanced by pressure. On the contrary, for CaC₆ we find that in the 0 to 5 GPa region, T_c weakly increases with pressure. The increase is much smaller than what shown in several recent experiments. Thus we suggest that in CaC₆ a continuous phase transformation, such as an increase in staging, occurs at finite pressure. Finally we argue that, although MgC₆ is unstable, the synthesis of intercalated systems of the kind MgₓCa₁₋ₓC₆ could lead to higher critical temperatures.

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I. INTRODUCTION

It has long been known that Graphite intercalated compounds (GICs) can display a superconducting behavior at low temperatures. However, until the discovery of ytterbium and calcium intercalated graphite \( (T_c(YbC_6)=6.5 \, \text{K} \) and \( T_c(CaC_6)=11.5 \, \text{K} \)), the critical temperatures achieved were typically inferior to 5 Kelvin. Very recently, it has been shown that even higher critical temperatures (up to 15.1 K) can be achieved in CaC₆ applying hydrostatic pressure (up to 8 GPa). This is presently the highest T_c reported in a GIC.

From a practical point of view GICs are appealing since carbon is a very versatile element. Beside the fact that the three most known carbon crystalline structures (Fullerene, Graphite and Diamond) display superconducting behavior upon intercalation or doping, carbon is also interesting for the possibility of making nanotubes which can display a superconducting behavior. Moreover the number of reagents which can be intercalated in graphite, by using chemical methods or high pressure synthesis, is very large. Consequently finding GICs with even higher critical temperatures is not a remote possibility. Therefore theoretical calculations can be a precious tool for the investigation of superconductivity in GICs.

The nature of superconductivity in intercalated GICs is still controversial. Due to their layered nature and to the presence of an intercalant band at the Fermi level (E_f), Csányi \textit{et al.} suggested a non-conventional exciton pairing mechanism. On the contrary Mazin \textit{et al.} proposed an electron-phonon mechanism mainly sustained by Ca vibrations. In a previous work we suggested that the pairing is mediated by the electron-phonon interaction. In particular the carriers are mostly electrons in the Ca Fermi surfaces coupled with Ca in-plane and C-out-of-plane vibrations. The calculation of the isotope effect coefficient showed that the contribution of Ca in-plane vibrations and C out-of-plane vibrations to superconductivity is comparable.

Experimental data seem to confirm that the pairing in CaC₆ and YbC₆ is indeed due to the electron-phonon interaction, but several open questions remain. From the exponential behavior of the penetration depth in CaC₆ Lamura \textit{et al.} deduced an isotropic gap of magnitude \( \Delta(0)=1.79\pm0.08 \) meV. A similar isotropic gap (\( \Delta(0)=1.6\pm0.2 \) meV) has been measured by scanning tunneling spectroscopy. The corresponding values of \( 2\Delta(0)/T_c \) are in agreement with the BCS theory. Similar conclusions have been obtained from the specific heat jump at superconducting transition. Thermal conductivity data in the presence of a magnetic field indicate that in YbC₆ the order parameter has s-wave symmetry too and exclude the occurrence of multiple gaps. Isotope effect measurements show a huge Ca isotope coefficient, \( \alpha(\text{Ca})=0.5 \), in disagreement with theoretical calculations. This is surprising, since the gap and specific heat data are correctly described by DFT calculations, meaning that the calculated electron-phonon coupling is probably correct. Even more interesting is that the total isotope effect would be probably larger than 0.5, although C-isotope effect measurements are necessary to confirm this and to judge the validity of the measurements of \( \alpha(\text{Ca}) \). In any case, the large Ca-isotope coefficient, the measured superconducting gap and the jump of the specific heat at the transition they all go in favor of a phonon mediated mechanism with, most likely, a single s-wave gap.

In this work we want to push a step forward the prediction that can be made by the electron-phonon theory. This is important since it may allow to identify GICs with higher critical temperatures and it also represents a significative benchmark for DFT simulations. It was noted that all the superconducting GICs possess an intercalant Fermi surfaces at E_f. This fact is relevant for both pairing mechanisms proposed. In the case of a con-
vential electron-phonon mechanism the electrons in the intercalant Fermi surface are the ones strongly coupled to the phonons. Thus we study the possible occurrence of superconductivity in graphite intercalated with alkaline earths (AC$_6$ with A=Ba,Sr,Mg). All these GICS have an intercalant Fermi surface at $E_F$ so they are good candidates for superconductivity. We predict the critical temperatures for BaC$_6$ and SrC$_6$ in the framework of the electron-phonon coupling theory.

As mentioned before, the critical temperature of CaC$_6$ and YbC$_6$ is enhanced with pressure. Resistivity measurements under pressure show that, at $\approx 8$ GPa, CaC$_6$ undergoes a structural phase transition to a new superconducting phase with a lower critical temperature. The new structure seems to be stable at least up to 16 GPa. In other successful works magnetic and resistive measurements were performed in a much smaller range of pressures (0-1.6GPa) and the behavior observed was confirmed. Pressure also increases the critical temperature of YbC$_6$ up to approximately 7.0 K at $\approx 2.0$ GPa.

In this case too a structural transition is seen towards a new superconducting phase with lower $T_c$. In both YbC$_6$ and CaC$_6$ the dependence of $T_c$ is linear with similar $\Delta T_c / \Delta P$ (0.4 for YbC$_6$ and 0.5 for CaC$_6$). The fact that $T_c$ can be enhanced with pressure suggests that this can be a general mechanism for superconducting in GICs. It is then important to study superconductivity as a function of pressure in BaC$_6$,SrC$_6$ and finally CaC$_6$.

After illustrating in section II and III the technical parameters and the lattice structures used in the simulations, we study the electronic structure (sec. IV), the phonon dispersions (sec. V) and the superconducting properties (sec. VI) of Alkaline-earth intercalated graphite at ambient pressure and at finite pressure. Particular emphasis is given to the case of CaC$_6$ under pressure (sec. VII).

### III. Crystal Structure

All the considered compounds are stage 1 at zero pressure. The atomic structure of CaC$_6$ involves a stacked arrangement of graphene sheets (stacking AAA) with Ca atoms occupying interlayer sites above the centers of the hexagons (stacking $\alpha\beta\gamma$). The crystallographic structure is R$\bar{3}$m where the Ca atoms occupy the 1a Wyckoff position (0,0,0) and the C atoms the 6g positions ($x$,x,1/2) with $x=1/6$. SrC$_6$ and BaC$_6$ have a slightly different crystal structure involving a stacked arrangement of graphene sheets (stacking AAA) with Sr and Ba atoms occupying interlayer sites above the centers of the hexagons with an $\alpha\beta$ stacking. The crystallographic structure is P6$_3$/mmc where the Sr,Ba atoms occupy the 2e Wyckoff position (1/3,2,3/4) and (1/3,2,3/4) and the C atoms the 12i positions (1/3,0,0). The experimental in plane lattice parameter a and the interlayer spacing c for the three structures are illustrated in table I.

| Material | Stacking | a,(Å) c,(Å) a,c (LDA) a,c (GGA) |
|----------|----------|-----------------------------|
| BaC$_6$  | $\alpha\beta\gamma$ | 4.302 5.25 4.280 5.00 4.350 5.20 |
| SrC$_6$  | $\alpha\beta\gamma$ | 4.315 4.95 4.285 4.80 4.325 5.00 |
| CaC$_6$  | $\alpha\beta\gamma$ | 4.333 4.524 4.29 4.36 4.333 4.51 |
| MgC$_6$  | $\alpha\beta\gamma$ | 4.317 3.75 4.35 3.95 |

### II. Technical Details

Density Functional Theory (DFT) calculations are performed using the espresso code and the generalized gradient approximation (GGA). We use ultrasoft pseudopotentials with valence configurations $3s^2 3p^6 4s^2$ for Ca, $4s^2 4p^6 4d^1 5s^1 5p^0$ for Sr, $5s^2 5p^6 5d^0 6s^2 6p^0$ for Ba, and $2s^2 2p^2$ for C. For Mg we use Troullier-Martins pseudopotentials with configuration $3s^1 3p^3 3d^0$. The wavefunctions and the charge density are expanded using a 35 Ry and a 600 Ry cutoff. The dynamical matrices and the electron-phonon coupling are calculated using Density Functional Perturbation Theory in the linear response. For the electronic integration in the phonon calculation (structure R$\bar{3}$m) we use a $N_k = 6 \times 6 \times 6$ and $N_q = 8 \times 8 \times 8$ uniform k-point meshes and Hermitian-Gaussian smearing ranging from 0.1 to 0.05 Ry. In order to obtain very accurate phonon-frequencies for the low energy modes (below 15 meV) it is crucial to use a large cutoff for the charge density (600 Ry at least) and a very high convergence threshold in the phonon calculations. For the evaluation of the electron-phonon coupling and of the electronic density of states we use $N_q = 25 \times 25 \times 25$ and $N_k = 20 \times 20 \times 20$ meshes respectively. For the $\lambda$ average over the phonon momentum $q$ we use a $N_q = 4 \times 4 \times 4$ $q$-points mesh. The phonon dispersion is obtained by Fourier interpolation of the dynamical matrices computed on the $N_q$ mesh.

Even if the structural symmetry of SrC$_6$ and BaC$_6$ are different from the one of CaC$_6$, in this work we consider the same rhombohedral symmetry group (namely R$\bar{3}$m with stacking $\alpha\beta\gamma$) for all the considered GICs. We do not expect this assumption to affect qualitatively the calculated electronic and phonon properties since the two structures differ only for large distance neighbors. Indeed the distances of the first and second nearest neighbors are the same. The differences between the metal lattice sites in the $\alpha\beta\gamma$ and in the $\alpha\beta\beta$ structures is equivalent to those existing in the fec and in the hcp structures.
The considered GICs are layered structures, but their band structure are clearly three-dimensional. This was understood in the case of CaC$_6$, since the rhombohedral angle (49.55°) is not too far from the one corresponding to the fcc structure (60°). The rhombohedral angles for BaC$_6$, SrC$_6$ and MgC$_6$ are 43.47°, 45.81°, 55.37°, respectively. Thus the rhombohedral angle is larger as c is reduced. This is even more evident comparing the behavior of the band-structure as a function of pressure in fig. 2 for SrC$_6$. Note in particular, that at 16.5 GPa (where the c parameter is the same as that of CaC$_6$ at zero pressure) the band structure is very similar to the one of CaC$_6$ at zero pressure. The larger bandwidths of the intercalant band as c is reduced reflects the higher three dimensional character of the structure.

The electronic density of states for the four considered compounds are very similar (see fig. 1) and also their values at the Fermi level are very close. No qualitative difference in the superconducting behavior of these systems can be attributed to the number of carriers at the Fermi energy (i.e. to the different value of N(0)).

The atomic-projected density of states is calculated using the Löwdin populations, $\rho_{\eta}(\epsilon) = \frac{1}{N_{\eta}}\sum_{k,n}\langle |\psi_{\eta n}(\mathbf{k})|^2 \delta(\epsilon_{kn} - \epsilon) \rangle$. In this expression $|\psi_{\eta n}(\mathbf{k})|^2$ are the orthonormalized Löwdin orbitals, $|\phi_{\eta n}(\mathbf{k})|^2$ the atomic wavefunctions and $S_{\eta,\eta'} = \langle \phi_{\eta n}(\mathbf{k}) | \phi_{\eta' n'}(\mathbf{k}) \rangle$. The density of states projected over the intercalant states has very similar value at $E_F$ for the three case and it is slightly reduced with decreasing Z. No particular differences respect to the case of CaC$_6$ are observed. In fig. 1(right) the size of the dots represents the projection over the intercalant atomic states.

The three Fermi surface sheets of BaC$_6$, SrC$_6$ and CaC$_6$ are shown in fig. 3. The sheets have been identified by the corresponding band index. As c is reduced passing from BaC$_6$ to SrC$_6$ the main difference is the change in the third sheet of the Fermi surface which is indeed a warped cylinder in BaC$_6$ and it becomes spherical in CaC$_6$. This is best seen analyzing the band structure in the $\Gamma L$ direction (namely the $e_z$ direction). In BaC$_6$ and SrC$_6$ there are no bands crossing $E_f$ along $\Gamma L$, while in CaC$_6$ the Ca-originated band crosses $E_f$.

### V. PHONON DISPERSION

The phonon dispersion of all the considered GICs can be divided in three regions. The high energy region is composed by in-plane Carbon-vibration (C$_{xy}$), the intermediate energy region by out-of-plane Carbon vibration (C$_z$), and the low energy region is mostly composed intercalant vibration (L$_1$, for in-plane and L$_2$ for out-of-plane, with I=Ba,Sr,Ca,Mg), as it was shown for CaC$_6$. Since the high energy branches ($\omega_{qz} > 100\text{meV}$) are weakly affected by the type of intercalant, for the sake of clarity, in some case we only plot branches in the low energy region of the spectra. These branches are those having the greatest contribution to the electron-phonon coupling.

The zero-pressure phonon dispersion of BaC$_6$, SrC$_6$ and CaC$_6$ are illustrated in figs. 4 and 5. As Z is reduced,
FIG. 1: (Color online) Band structure (left) and density of states projected over atomic orbitals (right) for several Alkali-earth GICs. The zero energy corresponds to the Fermi energy. The size of the dots represents the percentage of intercalant component. As a reference, in CaC₆ the dot at ≈0.6 eV at the L point represents 95%.

and consequently c is reduced, the lowest energy branch in the ΓX direction (which corresponds to in-plane momenta with k_z = 0) is softened. This is evident in CaC₆ where an incipient Kohn anomaly is found at X. While the reduction of c or Z softens the I_xy, the intercalant I_z out-of-plane vibrations are hardened.

This effect is also apparent from the analysis of the phonon dispersion of SrC₆ and CaC₆ under pressure. In SrC₆, the lowest branch at 16 GPa in the ΓX direction is almost imaginary, meaning that at this pressure the system is close to a structural instability. This instability is driven by the reduction in the c-lattice spacing. In MgC₆, at the theoretical lattice parameters, we find imaginary phonon frequencies at X, so that the system is probably unstable. As a consequence we did not calculate the full phonon dispersion.

VI. SUPERCONDUCTING PROPERTIES

The superconducting properties of Alkali-Earths GICs can be understood calculating the electron-phonon coupling $\lambda_{\nu}$ for a phonon mode $\nu$ with momentum $\mathbf{q}$:

$$\lambda_{\nu} = \frac{4}{\omega_{\nu}(0) N_k} \sum_{k,n,m} |g_{kn,k+qn}^\nu|^2 \delta(\epsilon_k) \delta(\epsilon_{k+qn})$$

where the sum is over the Brillouin Zone. The matrix element is $g_{kn,k+qn}^\nu = \langle kn | \delta V/\delta u_{\nu} | k + q m \rangle / \sqrt{2\omega_{\nu}}$, where $u_{\nu}$ is the amplitude of the displacement of the phonon and $V$ is the Kohn-Sham potential. The average electron-phonon coupling is $\lambda = \sum_{\nu} \lambda_{\nu}/N_\nu$ and its value for the different compounds and for different pressures is given in table IV.

The Eliashberg function

$$\alpha^2 F(\omega) = \frac{1}{2N_\nu} \sum_{\nu} \lambda_{\nu} \omega_{\nu} \delta(\omega - \omega_{\nu})$$

and the integral $\lambda(\omega) = 2 \int_0^\omega d\omega' \alpha^2 F(\omega')/\omega'$ are shown in fig. for BaC₆ and SrC₆. As for CaC₆, the largest contribution to $\lambda$ comes from modes below 75 meV.

An estimate of the different contributions of the in-plane and out-of-plane vibrations of the different atoms
to $\lambda$ can be obtained from the relation

$$
\lambda = \frac{1}{N_q} \sum_q \sum_{i\alpha,j\beta} [G_{q}]_{i\alpha,j\beta} [C_q^{-1}]_{j\beta,i\alpha}
$$

where $i, \alpha$ indexes indicate the displacement in the Cartesian direction $\alpha$ of the $i^{th}$ atom, $[G_{q}]_{i\alpha,j\beta} = \sum_{k,n,m} 4\tilde{g}_{i\alpha} \delta_{j\beta} \delta_\epsilon(kn)\delta_\epsilon(k+q,m)/[N(0)N_k]$, and $\tilde{g}_{i\alpha} = \langle \epsilon_i \rangle \delta \sum_{\text{V}} \delta_{q_{i\alpha}} |k+q|/\sqrt{2}$. The $C_q$ matrix is the Fourier transform of the force constant matrix (the derivative of the forces respect to the atomic displacements).

Using eq. 3 we decompose $\lambda$ restricting the summation over $i, \alpha$ and that over $i, \beta$ on two sets of atoms and Cartesian directions. The sets are $C_{xy}, C_z, I_{xy}$, and $I_z$, where $I=\{\text{Ba}, \text{Sr}, \text{Ca}\}$. The resulting $\lambda$ matrix for the different GICs and as a function of pressure are given in table III.

Except for of SrC$_6$ at 16.5 GPa, the off-diagonal matrix elements are negligible. In all the case the largest contributions to $\lambda$ comes from $C_z$ and $I_{xy}$ phonon modes. The coupling to these modes are enhanced as $Z$ and $c$ are reduced. A similar enhancement of $C_z$ and $I_{xy}$ occurs under pressure. When the pressure is too high, as in SrC$_6$ at $P=16.5$ GPa, the off-diagonal matrix elements increase and the attribution to $C_z$ or to $I_{xy}$ becomes ill-defined. Note also that the $C_{xy}$ and the $I_z$ modes are weakly affected by $Z$ or $c$-axis reduction.
FIG. 5: (Color online) Low energy region of the phonon dispersions of BaC$_6$, SrC$_6$ and CaC$_6$ at 0 GPa. The size of the blue dots (red squares) represents the amount of $I_{xy}$ ($I_z$), where $I =$ Ba, Sr, Ca vibrational.

The critical superconducting temperature is estimated using the McMillan formula:

$$T_c = \frac{\langle \omega \rangle}{1.2} e^{-\frac{1.04(1+\lambda)}{\lambda - \mu^* (1+0.62\lambda)}}$$

where $\mu^*$ is the screened Coulomb pseudopotential and 

$$\langle \omega \rangle = e^{\frac{1}{2}} \int_0^{+\infty} \alpha^2 F(\omega) \log(\omega)/\omega d\omega$$

the phonon frequencies logarithmic average. Results for $\langle \omega \rangle$ and for $T_c$ are shown in table IV using $\mu^* = 0.14$. For BaC$_6$ and SrC$_6$, $T_c$ increases as the interlayer spacing is decreased. For SrC$_6$ at 16.5 GPa the the result of McMillan formula is not correct. Indeed close to the transition the increase in $\lambda$ is only given by the softening of the Sr$_{xy}$ vibration close to X. In McMillan formula the limit $\omega_{q\nu} \rightarrow 0$ implies $T_c \rightarrow 0$ as $\langle \omega \rangle$ since $\lambda_{q\nu} \rightarrow \infty$ as $1/\omega_{q\nu}^2$. Unfortunately the use of McMillan formula in this limit is not correct since it deviates from the Migdal-Eliashberg results (ME), as known from the papers of McMillan and of Allen and Dynes (see fig. 1 in [26]). For this reason the calculation of $T_c$ for SrC$_6$ at P=16.5 GPa should be considered not reliable (and as a consequence it is not given in table IV).

VII. CaC$_6$ UNDER PRESSURE

The study of CaC$_6$ under pressure needs particular emphasis due to the interest motivated by the work of Gauzzi et al. showing a considerable increase of Tc which reaches its maximum of 15.1 K at 7-8 GPa. The increase of Tc has been confirmed by other two successive works measuring Tc in a much smaller range of pressure. At 8GPa the system seems to undergo a phase transition towards a different structure with a lower superconducting Tc.
To study the behavior of $T_c$ under pressure we calculate the phonon dispersion and the electron-phonon coupling at 5 GPa, for which a $T_c = 14K$ was detected in experiments. The comparison between the phonon dispersions at 0 GPa and 5 GPa is shown in fig. 8. As can be seen, while the lowest Ca phonon mode is slightly softened (mostly at X), the others Ca and C$_z$ phonon modes are hardened. However the overall change is fairly small and the Eliashberg functions $\alpha^2 F(\omega)$ at 0 and 5 GPa have no sizable differences (see fig. 9). At higher pressures the phonon frequencies become imaginary, similarly to what happens in SrC$_6$ at 16.5 GPa. In particular the largest softening occurs at X for the lowest Ca mode and it becomes negative in the range of 7-10 GPa. The lowest phonon frequency at X is extremely dependent on the Hermite-Gaussian smearing used in the calculation and as a consequence much larger k-point mesh must be used to correctly identify the phase transition (using a 10X10X10 mesh and smearing 0.04 still gives results which are not converged). However it is clear that at a sufficient high pressure the system will become unstable and the lowest Ca phonon frequency at X will approach zero.

More insight on the superconducting properties can be gained by computing $\omega_{\log}$ and $\lambda$ at 0 and 5 GPa. In this range of pressures these parameters have very similar values and consequently the critical temperature changes only slightly (see table IV), from 11.03 K at 0 GPa to 11.40 K at 5 GPa.

The calculation for $T_c$ under pressure are in stark disagreement with a recent theoretical calculation obtained using the same method (DFT) and the same code. The disagreement with the calculation in ref. 17 can be explained by the following. In ref. 17 the electron-phonon coupling is calculated close to the structural transition (at 10 GPa) where the Ca phonon frequency strongly softens. Just before the structural transition, $\omega_{Ca} \rightarrow 0$ and consequently $\lambda_{Ca} \rightarrow \infty$. In this limit (close to the transition), the behavior is highly non linear. On the contrary in ref. 12 the behavior is assumed linear between 0 GPa and 10 GPa. Our calculation at 5.0 GPa giving essentially the same $T_c$ as at 0 GPa shows that this is not the case.

We remark that in the calculation of the electron-phonon coupling at 0 and 5 GPa it is crucial to use at least a $4 \times 4 \times 4$ q-point mesh. If the smaller $2 \times 2 \times 2$ mesh is used, the electron-phonon coupling of the Ca modes is overestimated, since the point at X (which is included in the mesh and has a considerable electron-phonon coupling) has a too large weight. The consequent increase of $T_c$ under pressure is much larger than in the $4 \times 4 \times 4$ mesh.

From the preceding discussion it follows that DFT calculations give a non linear behavior of $T_c$ versus pressure, in stark disagreement with experiments. In particular the increase of $T_c$ as a function of pressure is too weak when compared with experiments. In the next section we discuss what can be the origin of such disagreement.

 VIII. CONCLUSIONS

In this work we theoretically investigated the occurrence of superconductivity in graphite intercalated with Alkaline earths (in particular Ba, Sr, Ca, Mg). Most of these systems have been already synthesized (BaC$_6$, SrC$_6$, and CaC$_6$), while MgC$_6$ has been proposed as a good candidate for superconductivity due to its light mass and small force constants, possibly leading to large electron-phonon coupling.

We predict the critical temperatures of BaC$_6$ and SrC$_6$ to be 0.23 K and 3.02 K respectively. Moreover we also

FIG. 8: Comparison between the phonon dispersion of CaC$_6$ at 0 GPa and at 5 GPa.
predict a substantial increase in the critical temperature under pressure for these two systems, namely at 8 GPa the critical estimated temperatures for BaC$_6$ and SrC$_6$ are 0.81 K and 5.16 K respectively. We hope that these predictions can stimulate additional experimental work so that the nature of the pairing in GICs can be further elucidated. Moreover it would be important to judge the reliability of DFT in calculating the superconducting properties of different GICs. Indeed, while superconducting gap and specific heat measurements are in very good agreement with DFT calculations the only available measure of the Ca isotope effect in CaC$_6$ is in stark disagreement with DFT predictions. The claim that the isotope effect coefficient of Ca is 0.5, if verified by the corresponding measurement of the C isotope effect, would open new perspectives.

We have also shown that MgC$_6$ is energetically unstable against phase separation in Mg and graphite. Moreover, even assuming that it can be synthesized using pressure methods, the minimized structure at zero pressure obtained using DFT has imaginary phonon frequencies at the point X. Nonetheless it is interesting to note that the softening at the point X occurs when the interlayer spacing is reduced in CaC$_6$ and is connected to a large electron-phonon coupling in this point. This information suggests that the T$_c$ of CaC$_6$ can probably be raised synthesizing Mg$_x$Ca$_{1-x}$C$_y$ alloys.

Concerning CaC$_6$, a puzzling problem is the dependence of the critical superconducting temperature upon pressure. Experimentally T$_c$ increases as a function of pressure, but as we have shown in this work, T$_c$ increases much faster than what DFT calculations predict. Further work is necessary to explain the origin of this disagreement, mainly on the experimental side. Indeed diffraction data as a function of pressure are absolutely necessary. If there is a phase transformation upon pressure, the structure minimized with DFT at finite pressure would not be correct. The fact that the T$_c$ versus pressure curves are very smooth seems to exclude an abrupt transition. A possibility is that a staging transition occurs in CaC$_6$ under pressure. This transition could be continuous, meaning that the staging occurs progressively in the sample. It is indeed well known that GICs are extremely sensitive to these kind of transitions occurring isothermally under very modest pressures. For example KC$_{24}$, which is a stage 2 GIC, starts a staging transition at 2.5 Kbar versus a stage 3 structure. The transition is continuous and completely achieved at $\approx$ 6.5 Kbar. Similar transitions have been reported in ref. for MC$_8$ and MC$_{12n}$ ($n=2,3,4$) with M=Rb, Cs. If such a transition occurs in CaC$_6$ then it would not necessarily show up in the T$_c$ versus pressures curves, but it would explain the disagreement between experiment and theory. Of course other more complicate explanations are possible, including unconventional superconductivity. In all the case, the origin of superconductivity in intercalated GICs is not yet completely understood.

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1. M. S. Dresselhaus and G. Dresselhaus, Adv. in Phys. 51, 1, 2002  
2. T. E. Weller, M. Ellerby, S. S. Saxena, R. P. Smith and N.T.
TABLE III: Decomposition of the electron-phonon coupling parameter into different vibrational components for several GICs

| C_0Ba | P=0 | C_0Sr | P=8 | C_0Ca | P=0 |
|-------|-----|-------|-----|-------|-----|
| C_{xy} | C_z | Ba_{xy} | Ba_z | C_{xy} | C_z | Sr_{xy} | Sr_z | C_{xy} | C_z | Ca_{xy} | Ca_z |
| 0.10  | 0.00 | -0.01  | 0.00 | 0.10  | 0.01 | -0.01  | 0.00 | 0.12  | 0.01 | -0.01  | 0.00 |
| 0.00  | 0.10 | 0.01  | -0.01 | 0.01  | 0.24 | 0.03  | -0.01 | 0.03  | 0.03 | 0.19  | -0.00 |
| 0.00  | 0.01 | 0.12  | -0.00 | 0.00  | 0.02 | 0.16  | -0.00 | 0.00  | 0.00 | 0.00  | -0.00 |
| 0.00  | 0.01 | 0.00  | 0.07 | 0.00  | 0.01 | 0.13  | 0.00 | 0.00  | 0.00 | 0.03  | 0.13 |

TABLE IV: Superconducting parameters of several GICs under pressure

| C_0Ba | P(GPa) | λ | \omega_{lq} (meV) | T_c (\mu^* = 0.14) K |
|-------|-------|---|----------------|-------------------|
| 0     | 0.38  | 22.44 | 0.23 |
| 8     | 0.45  | 20.63 | 0.81 |
| C_0Sr | P(GPa) | λ | \omega_{lq} (meV) | T_c (\mu^* = 0.14) K |
| 0     | 0.54  | 28.38 | 3.03 |
| 8     | 0.65  | 23.40 | 5.17 |
| 16.5  | 1.97  | 3.67  | nonsense |
| C_0Ca | P(GPa) | λ | \omega_{lq} (meV) | T_c (\mu^* = 0.14) K |
| 0     | 0.83  | 24.70 | 11.03 |
| 5     | 0.845 | 24.6  | 11.40 |

G. Csányi, P. B. Littlewood, A. H. Nevidomskyy, C. J. Pickard and B. D. Simons, Nature Physics 1, 42 (2005) and cond-mat/0503569

Skipper, Nature Phys. 1, 39 (2005) and cond-mat/0503570

3 N. Emery, C. Hérol, M. d’Astuto, V. García, Ch. Bellin, J. F. Maréché, P. Lagrange and G. Loupias, Phys. Rev. Lett. 95, 087003 (2005)

4 A. Gauzzi, S. Takashima, N. Takeshita, C. Terakura, H. Takagi, N. Emery, C. Hérol, P. Lagrange, G. Loupias, cond-mat/0603443

5 O. Gunnarsson, Rev. Mod. Phys. 69, 575-606 (1997)

6 E. A. Ekinov et al., Nature (London), 428, 542 (2004)

7 Z. K. Tang, L. Zhang, N. Wang, X.X. Zhang, G.H. Wen, G.D. Li, J. N. Wang, C. T. Chan, P. Sheng, Science 292, 2462 (2001)

8 G. Csányi, P. B. Littlewood, A. H. Nevidomskyy, C. J. Pickard and B. D. Simons, Nature Physics 1, 42 (2005) and cond-mat/0503569

9 D. Allender, J. Bray and J. Bardeen, PRB 7, 1020 (1973)

10 I. I. Mazin Phys. Rev. Lett. 95, 227001 (2005)

11 M. Calandra and F. Mauri, Phys. Rev. Lett. 95, 237002 (2005)

12 G. Lamara, M. Aurino, G. Cifariello, E. Di Gennaro, A. Andreone, N. Emery, C. Hérol, J. F. Maréché and P. Lagrange, cond-mat/0603539

13 N. Bergeal, V. Dubost, Y. Noat, W. Sacks, D. Roditchev, N. Emery, C. Hérol, J. F. Maréché P. Lagrange and G. Loupias, cond-mat/0604208

14 J. S. Kim, R. K. Kremer, L. Boeri, F. S. Razavi, cond-mat/0603539

15 M. Sutherland, N. Doiron-Leyraud, L. Taillefer, T. Weller, M. Ellerby, S. S. Saxena, cond-mat/0603664

16 D. G. Hinks, D. Rosenmann, H. Claus, M. S. Bailey, and J. D. Jorgensen, cond-mat/0604642

17 J. S. Kim, L. Boeri, R. K. Kremer, F.S. Razavi, cond-mat/0603539

18 R. P. Smith, A. Kusmartseva, Y. T. C. Ko, S. S. Saxena, A. Akrap, L. Forro, M. Laad, T. E. Weller, M. Ellerby, N. T. Skipper, cond-mat/0604204

19 http://www.pwscf.org

20 J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996)

21 D. Vanderbilt, PRB 41, 7892 (1990)

22 N. Troullier and J. L. Martins, Phys. Rev. B 43, 1993 (1991).

23 D. Guérard, M. Chaabouni, P. Lagrange, M. El Makrini et al., Phys. Rev. B 39, 1616 (1989)

24 The results for SrC_6(0.14) K

25 Even assuming a linear behavior, the theoretical Tc versus pressure slope is substantially smaller than the experimental one.

26 R. Clarke, N. Wada and S.A. Solin, Phys. Rev. Lett. 44, 1616 (1980)

27 N. Wada, Phys. Rev. B24 1065 (1981)