Effect of Pressure on Superconducting Ca-Intercalated Graphite CaC$_6$

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The effect of pressure on the superconducting transition temperature ($T_c$) of the Ca-intercalated graphite compound CaC$_6$ has been investigated up to $\sim 16$ kbar. $T_c$ is found to increase under pressure with a large relative ratio $\Delta T_c / T_c$ of $\approx +0.4\%/\text{kbar}$. Using first-principles calculations, we show that the positive effect of pressure on $T_c$ can be explained within the scope of electron-phonon theory due to the presence of a soft phonon branch associated to in-plane vibrations of the Ca atoms. Implications of the present findings on the current debate about the superconducting mechanism in graphite intercalation compounds are discussed.

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I. INTRODUCTION

The discovery of superconductivity in Yb- and Ca-intercalated graphites, with significantly higher $T_c$'s than found previously for alkali-metal graphite intercalation compounds (GICs) re-initiated the debate on the long-standing puzzle of the origin of superconductivity in GICs. Possible pairing mechanisms under consideration range from unconventional exciton- or plasmon-mediated couplings to the more conventional electron-phonon ($e$-$ph$) coupling mechanism.

The core of the debate on the origin of superconductivity in the GICs are the so-called interlayer electronic bands which cross the Fermi level ($E_F$) besides the graphite $\pi^*$ bands. Since the coupling of the $\pi^*$ band electrons to the graphite phonons is not sufficient to yield the observed high $T_c$'s, the role of the interlayer bands and their degree of filling is considered to be essential for superconductivity with increased $T_c$. Csányi et al. proposed that the electrons in the interlayer bands can be considered as nearly-free 2-dimensional (2D) electrons propagating essentially between the graphene layers, and pairing can be mediated by acoustic plasmons in these 2D metallic slabs. However, there is a growing body of evidence that the interlayer bands have sufficiently strong coupling with both in-plane intercalant and out-of-plane graphite phonon modes to allow for the relatively high $T_c$'s within the scope of a standard $e$-$ph$ coupling mechanism. This scenario gained some experimental support from recent penetration depth, specific heat, tunneling, and Ca isotope effect experiments in CaC$_6$.

Interestingly, the latter experiments showed a Ca isotope effect with $\alpha_C \approx 0.5$, suggesting a dominant role of Ca-related modes in the superconducting pairing. This finding, however, is at odds with the results of ab-initio calculations in which isotope exponents $\alpha_C \approx \alpha_E \approx 0.25$ have been concluded. The fact that the out-of-plane phonon modes of the host layers cannot be ignored gains substantial support from recent investigations on other layered compounds, e.g. CaAlSi ($T_c \sim 8$ K), where Ca atoms are located in between Al-Si honeycomb sheets (AlB$_2$ structure type). Hence, a deeper understanding of the superconducting pairing, and of the nature and role of the electronic and vibrational states involved, will provide useful insight into superconductivity in the GICs as well as other recently discovered "high-$T_c$" superconductors.

The investigation of the pressure dependence of $T_c$ is a key experiment to test and compare these theoretical predictions. The degree of filling of the interlayer bands, crucial for the acoustic plasmon pairing mechanism, depends not only on the charge transfer from the intercalant, but also on the separation of the graphene sheets. By applying hydrostatic pressure the graphite layer spacing, and hence the energy of the interlayer bands, can be continuously tuned without affecting the chemical composition. On the other hand, a comparison of the pressure dependence of $T_c$ with the results of first-principles calculations of the electronic and vibrational properties of the GICs could support or rule out the hypothesis of an $e$-$ph$ mediated coupling mechanism.

In this paper, we report the effect of pressure ($P \leq 16$ kbar) on $T_c$ of CaC$_6$ and compare our results with ab-initio calculations of the electronic and vibrational properties carried out as a function of pressure. Based on our calculations, we argue that the increase of $T_c$ with pressure can be understood within the scope of $e$-$ph$ coupling as a consequence of a softening of phonon modes involving Ca in-plane vibrations, while it is at odds with an acoustic plasmon mechanism. We also show that there is some discrepancy between the $T_c$ measured from experiment and that predicted by isotropic, harmonic Migdal-Eliashberg theory, and discuss possible ways to improve the agreement between experiments and theory.
II. EXPERIMENT

CaC₆ samples were prepared as described in detail elsewhere[10]. The $T_c$’s of three samples were determined from the temperature dependence of the $dc$ (samples S1 and S2) and of the $ac$ magnetic susceptibility (sample S3). The variation of $T_c$ between our samples is less than ~ 0.1 K. All samples show a sharp superconducting transition with a width $\Delta T_c \sim 0.15$ K between 10% and 90% of the diamagnetic signal, indicating good sample quality. Cu-Be piston-anvil-type pressure cells were used to apply quasi-hydrostatic pressures with silicon oil as the pressure transmitting medium. To monitor the pressure, $T_c$ of Pb (99.9999%) was determined simultaneously.

At ambient pressure, the onset of the superconducting transition of our samples is ~ 11.4 K, consistent with previous reports[2]. The superconducting transition is clearly shifted to higher temperatures as the pressure is raised (see Fig. I(a)). Up to 16 kbar there is no indication of an abrupt change of $T_c$ or a narrowing or broadening of the transition, as frequently observed in other superconducting GICs, such as e.g. KHgC₄, KC₆, RbC₈, and ascribed to a pressure-induced change of the staging or of the intercalant sublattice[18]. No hysteresis in $T_c$ as well as in the shape of $\chi(T)$ was observed between the data taken with increasing and decreasing pressure. Thus the possible shear stresses due to solidification of pressure medium do not affect significantly the superconducting properties of the samples.

The pressure dependence of $T_c$ for three samples is shown up to 16 kbar in Fig. II(b). For all samples, $T_c$ increases under pressure almost linearly with a slope of 0.042 - 0.048 K/kbar. Depending on the sample, $T_c$ and the ratio $dT_c/dP$ vary slightly, but the relative change $(1/T_c)dT_c/dP$ is the same within error bars for all samples and amounts to $\approx +0.4 \%/\text{kbar}^{10}$. Such a pressure dependence of $T_c$ is adverse to the behavior of many $sp$ superconductors in which often a negative pressure dependence of $T_c$ is found. Also it is in contrast to other intercalated graphites, such as KHgC₄, RbHgC₈ and KTI₃C₄ whose $T_c$ decreases under pressure with a rate of -2.2 ~ -3.8 %/kbar[15].

III. THEORY

To gain more insight into the possible coupling mechanism we performed a detailed Density Functional Perturbation Theory (DFPT)[17] study of the electronic and vibrational properties of CaC₆ and explored the pressure range up to 500 kbar to investigate whether lattice instabilities occur. In our calculations we employed ultrasoft pseudopotentials[18] with a generalized Gradient Approximation[19] for the exchange-correlation functional. The eigenfunctions were expanded on a plane-wave basis set[20] with a cut-off energy of 30 Ryd and 300 Ryd for the wavefunctions and the charge density, respectively. We used a (8)³ Monkhorst-Pack grid and a 0.06 Ryd Methfessel-Paxton smearing, which led to convergence of better than 0.1 mRyd for the total and 5 cm⁻¹ for the Γ-point frequencies. Phonon dispersion curves were obtained by a Fourier interpolation of the dynamical matrices calculated on a 4³ grid in q-space for P=0, 50 and 100 kbar and a 2³ grid elsewhere.

The electronic structure and phonon dispersion at ambient pressure are in excellent agreement with previous results[4]. The Equation of State calculations yielded equilibrium lattice constants ($a_{ch} = 5.16$ a.u., rhombohedral angle $\theta = 49.90^0$) in very good agreement with the experimental data ($a_{ch} = 5.17$ a.u., $\theta = 49.55^0$), and a bulk modulus ($B_0 \approx 103$ GPa) larger than that of pure graphite, but close to that of other GICs[15]. The compressibility remains anisotropic ($k_{c}/k_{a} \approx 9$) but is significantly reduced as compared to non-intercalated graphite [see Fig. 2(b)].

First of all, we notice that, in general, the coupling strength between electrons and any bosonic modes can be approximated by $\lambda \propto N(E_F)\langle I^2 \rangle /\langle \omega^2 \rangle$, where $N(E_F)$ is the electronic density of states at $E_F$, $\langle I^2 \rangle$ is the electron-boson matrix element, and $\langle \omega^2 \rangle$ is the square averaged

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1}
\caption{(Color online) (a) Temperature dependence of the susceptibility for CaC₆ (S1) at different pressures. The numbers next to the data and in the bracket corresponds to the applied pressure (kbar) and the sequential order of the measurement runs. $T_c$ is determined as the temperature where the extrapolation of the steepest slope of $\chi(T)$ intersects the extrapolation of the normal state $\chi(T)$ to lower temperatures. (b) Pressure dependence of $T_c$ for three CaC₆ samples. The filled and open symbols are data taken at increasing and decreasing pressure, respectively. The dashed lines are guide-to-eyes. The inset shows the relative change of $T_c$ with pressure.}
\end{figure}
frequency for the relevant bosonic modes. Our calculations show that $N(E_F)$ decreases with pressure because and the interlayer band is emptied and the $\pi^*$ bandwidth increases. (cfr. Fig. 2(c)). In the following, we therefore investigate the alternative option to enhance $\lambda$ (and $T_c$) by a reduction of the frequency of the relevant bosonic modes.

First, we consider electron-phonon coupling. Although unusual, the softening of a particular phonon mode, usually an indication of an incipient lattice instability, can induce a pressure increase in $T_c$. The calculated phonon modes for CaC$_6$ behave differently as a function of pressure depending on their eigenvector as seen, e.g., in the case of the $\Gamma$-point phonons (see Fig. 2(a)): whereas the C in-plane modes ($\omega > 100$ meV) and the Ca out-of-plane mode ($\omega \sim 30$ meV) harden with pressure, the C out-of-plane mode ($50 < \omega < 100$ meV) are almost unaffected. On the other hand, the lowest-lying optical mode at $\Gamma$, and an acoustical mode at $X$ (Fig. 2), both mainly involving in-plane Ca vibrations, are considerably softened with pressure. At higher pressures ($P \gtrsim 120$ kbar), these modes drive the system unstable. Frozen-phonon calculations reveal that this mode couples to both the interlayer and the $\pi^*$ bands, and that the mechanism which causes its instability is similar to that giving rise to the anharmonicity of the $E_{2g}$ mode in MgB$_2$.

To estimate the pressure dependence of the partial $\lambda_{\text{Ca}}$ associated with the Ca in-plane vibrations, we employ a simple approximation based on the Hopfield formula: $\lambda_i = N(E_f)\langle I^2_i \rangle / M_i \langle \omega_i^2 \rangle$, where $\langle I^2_i \rangle$ is the $i$-ph matrix element, $M_i$ is the phonon mass, and $\langle \omega_i^2 \rangle$ is square averaged phonon frequency. Assuming that $\langle I^2_{\text{Ca}} \rangle$ is constant and $\langle \omega_{\text{Ca}}^2 \rangle$ can be approximated by the square of the lowest-lying optical phonon frequency at $\Gamma$, we find a significant increase of $\lambda_{\text{Ca}}$ by 20% at $P = 50$ kbar, and 60% at $P = 100$ kbar with respect to its zero-pressure value. Since the low energy phonon modes give dominant contribution to the coupling, the increase of $\lambda_{\text{Ca}}$ can be strong enough to overcome the reduction of $N(E_F)$ and as a result, increase $T_c$.

In contrast, it appears that the other proposed pairing mechanism, namely acoustic plasmon-mediated pairing in the interlayer bands, can hardly be reconciled with the observed pressure dependence of $T_c$. The basic assumption of this model is the existence of 2D metallic layers sandwiched by dielectric layers. If this is the case, due to the significant anisotropy of the Fermi velocity and incomplete screening, the plasmon dispersion develops a low-energy acoustic branch, $\Omega_{\text{pl}}(q) \sim q$, which can provide additional pairing routes for superconductivity.

However, the electronic band structure (cfr. Ref. 6) and the corresponding Fermi surface (FS) plot (see Fig. 4) reveal that the interlayer bands are 3D in character. Additionally, there is a substantial charge transfer to the graphite $\pi^*$ states. Both findings question the basic assumptions of this model already at ambient pressure. The anisotropy of the Fermi velocity emerges almost exclusively from the graphite $\pi^*$ bands, which display a warped cylindrical FS parallel to the $c$ axis. With pressure, the dispersion of the $\pi^*$ bands along the $c$ axis increases and the 3D character of the electronic structure grows. When the system becomes more 3D, a gap in the conventional plasmon dispersion is developed, and the conventional plasmon dispersion, $\Omega_{\text{pl}}(q) = \Omega_{\text{pl}} + O(q^2)$ ($\Omega_{\text{pl}} \gg k_B T_c$) is fully recovered. Thus, even if any coupling due to acoustic plasmons is assumed, its strength will decrease with pressure, adverse to our experimental observation.

Finally, we check whether the increase of $\lambda$ due to the phonon softening is compatible with the observed in-
total phonon eigenvectors. The largest contribution to the peaks well separated in energy, corresponding to differ-
ence the modes at 100 (50) kbar. The second largest contribution from the ω
crease of Tc under pressure by calculating the e-ph spectral function α2F(ω) and the frequency-dependent e-ph coupling parameter λ(ω) = 2∫ω α2F(Ω)Ω−1dΩ. Instead of the maximum experimental pressure (P ≈ 16 kbar), we choose to run these calculations at two higher pressures, P = 50 and 100 kbar. We notice, in fact, that the experimental variation of Tc up to P ≈ 16 kbar is too small to be resolved by the accuracy of DFT calculations. Therefore, we choose two pressures where the calculated frequencies are all real (i.e. the system is structurally stable), and where our approximated Hopfield equation predicts a sizable increase in λ; the second point (P = 100 kbar) is chosen closed to the predicted structural transition, in order to get an estimate of the maximum attainable Tc in this system.

The e-ph spectral function α2F(ω) displays three peaks well separated in energy, corresponding to different phonon eigenvectors. The largest contribution to the total e-ph coupling comes from the in-plane Ca phonons, which increases λCa = 0.42 to λCa = 0.62 (0.44) at P = 100 (50) kbar. The second largest contribution from the C out-of-plane vibrations remains essentially unchanged, since the modes at ~70 meV are insensitive to the pressure. The total λ increases from 0.84 at P = 0 to 0.86 at P = 50 kbar and 1.03 at P = 100 kbar, which results entirely from the soft Ca in-plane modes.

We estimate the effect of pressure on Tc using the McMillan formula24,

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

where \( \langle \omega_{\text{in}} \rangle \) is the logarithmic averaged phonon frequency and \( \mu^* \) is the Coulomb pseudopotential. Inserting the calculated \( \langle \omega_{\text{in}} \rangle \), (305 K at P = 0, 300 K at P = 50 kbar, and 230 K at P = 100 kbar), and setting \( \mu^* = 0.145 \), which reproduces the experimental Tc at zero pressure, we estimate that Tc should increase from 11.4 K to 13.5 (12) K from P = 0 to P = 100(50) kbar. Therefore the effect of the phonon softening for the in-plane Ca vibration is strong enough to overcome those of the decrease of DOS and \( \langle \omega_{\text{in}} \rangle \), and as a result, Tc increases with pressure. We also predict that the phonon softening will drive the system unstable for \( P \gtrsim 120 \) kbar, thus imposing a theoretical limit to the maximum attainable Tc.

IV. DISCUSSIONS

After finishing the present work, an experimental study up to \( P \approx 160 \) kbar was posted on the cond-mat archive25. Here a transition of Tc at ~80 kbar was observed, accompanied by lattice softening, thus confirming our theoretical prediction of an upper bound on Tc due to lattice instability. In Fig. 5 we plot the experimentally measured Tc, from our work and Ref. 25, together with the calculated Tc as a function of pressure. We notice that, even though the positive pressure dependence is well reproduced by our ab-initio calculations, there are still some discrepancies between experiment and theory, which we shall now discuss in detail.

First of all, while experimentally the (structural) transition is found at 80 kbar, we predicted it to take place

![FIG. 4: (Color online) (a) Phonon frequencies and (b) density of states of CaC6 for P = 0 (black), P=50 (green), P = 100 kbar (orange), along selected directions in the rhombohedral unit cell; the line Γ – X is contained in the graphene planes, while L−Γ is orthogonal to it. (c) Eliashberg function \( \lambda(\omega) = 2 \int_0^\omega \alpha^2F(\Omega)\Omega^{-1}d\Omega \).](image1)

![FIG. 5: (Color online) The calculated Tc (open squares) as a function of pressure together with the measured Tc in this work (same as Fig. 3 as well as Ref. 25 (green triangles). The dashed line indicates the point at which ab-initio calculations predict a dynamical instability of the lowest X-point phonon. The inset shows a pressure dependence of the calculated e-ph coupling constant, λ and the logarithmic averaged phonon frequency, \( \langle \omega_{\text{in}} \rangle \). Both quantities have a strong non-linear behavior.](image2)
at \( \sim \) 120 kbar. It is well known that the structural transition pressure for the GICs is very sensitive to several experimental details. For example, the previous pressure experiments on 1st-stage KC\(_6\) showed large hysteresis of the transition pressure as well as significant time dependence of the order of days or weeks\(^{26}\). In particular, we note that in the GICs \( T_c \) can show a strong anomaly even before a structural transition takes place. For example, in KC\(_8\), an intercalant structural transition occurs at \( \sim 14 \) kbar\(^{27}\), but a sudden increase of \( T_c \) is observed already at \( \sim 4 \) kbar\(^{28}\). On the other hand, this kind of error is also within the accuracy of DFT. While it could possibly be reduced by a more careful convergence of the \( \mathbf{k} \) point frequency with respect to \( \mathbf{k} \) points sampling, there would always be an uncertainty of 10 - 20 kbar related to the choice of the exchange and correlation functional or of the basis set\(^{29}\). However, even if DFT can fail to predict the exact transition pressure, it is usually much more accurate in describing structural trends as a function of pressure. Therefore, it is quite surprising to notice that the behavior of \( T_c \) with pressure predicted by theory deviates from that measured experimentally: in particular, theory predicts a much slower increase in \( T_c \) \((\sim 0.02 \text{ K/kbar})\) than experiment, and a slightly non-linear behavior, with a stronger increase in \( T_c \) at higher pressures.

Such discrepancies indicate that the harmonic, isotropic \( c\)-\( ph \) coupling theory may not be sufficient to describe quantitatively the behavior of CaC\(_6\) and other GICs. This confirms what was shown by a very recent, puzzling experiments on the \( \pi \) phonon\(^{32}\), which reported surprisingly high isotope exponent for Ca, \( \alpha(\text{Ca}) \approx 0.5 \), much higher than the value \( \alpha(\text{Ca}) = 0.24 \) predicted by theory\(^{33}\). Assuming a nontrivial contribution from the \( \pi \) phonon modes, the total isotope exponent will exceed the BCS value of 0.5. Also, discrepancies between the isotropic, harmonic Migdal-Eliashberg theory and experiment are found in the specific heat and the upper critical fields\(^{34}\). Further theoretical and experimental works are highly desirable along this direction.

The first possibility to improve the agreement between theory and experiment would be taking into account anharmonic effects or nonlinear coupling of the in-plane Ca phonon modes\(^{35}\). In graphite intercalation compounds, the vibrational modes associated to the intercalant are extremely soft, and transitions to different in-plane sublattice as well as staging are frequently observed\(^{15,27}\), which indicates that these modes are strongly anharmonic.

The second approximation which may not be justified, in the present case, is that of an isotropic electron-phonon coupling. As we have previously discussed, the Fermi surface of CaC\(_6\) is highly anisotropic and is formed by two bands, which have very different electronic origin \((\pi^* \text{ and interlayer})\), and are hence coupled to different phonon modes. Therefore, different sheets of the Fermi surface would give very different contributions to the total electron-phonon coupling, possibly giving rise to a "smeared" multi-gap superconductivity\(^{31}\).

Finally, we would like to compare our results with a very recent \textit{ab-initio} calculations\(^{39}\). Here the authors study, using the same code\(^{20}\), but different pseudopotentials, the behavior of CaC\(_6\) as a function of pressure. Similarly to us, they find a structural transition driven from the softening of the \( X \) point phonon, at some pressure between 70 and 100 kbar, thus lower than ours and close to the experimental value. Between 0 and 50 kbar, they find an increase in \( \lambda \) of only 0.015, and estimate an increase in \( T_c \) of \( \sim 0.3 \) K; they do not calculate the \( T_c \) at any other pressure besides 0 and 50 kbar, so it is not possible to compare directly the pressure behavior of the two sets of calculations, but the overall qualitative picture seems to be the same; the numerical differences in the transition pressure and \( \lambda \) are probably due to the use of different pseudopotentials and \( \mathbf{k} \)-point sampling. To explain the difference between theory and experiment, the authors of this paper propose still another possibility, that a continuous staging transition takes place under pressure. This is of course a possibility which should be taken into account, but a definitive answer in this sense could come only from X-ray or neutron diffraction measurements under pressure.

In conclusion, we presented measurements and \textit{ab-initio} calculations of the pressure dependence of \( T_c \) in CaC\(_6\). We demonstrated that the positive pressure dependence of \( T_c \) can be understood within an \( c\)-\( ph \) scenario due to softening of the in-plane Ca phonon modes, while it appears not to reconcile with the acoustic plasmaon mechanism. In view of new experimental findings, we also discuss which effects beyond the isotropic, harmonic Migdal-Eliashberg theory would have to be taken into account to obtain a full quantitative and qualitative agreement between theory and experiments in CaC\(_6\), and possibly other graphite intercalation compounds.

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