PHYSICAL REVIEW B **74**, 214513 (2006)

Effect of pressure on superconducting Ca-intercalated graphite CaC_6

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(Received 15 September 2006; published 20 December 2006)

The effect of pressure on the superconducting transition temperature (T_c) of the Ca-intercalated graphite compound CaC_6 has been investigated up to ~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 with in-plane vibrations of the Ca atoms. The implications of the present findings for the current debate about the superconducting mechanism in graphite intercalation compounds are discussed.

DOI: 10.1103/PhysRevB.74.214513 PACS number(s): 74.70.Ad, 74.25.Kc, 74.62.Fj

I. INTRODUCTION

The discovery of superconductivity in Yb- and Ca-intercalated graphites,[1,2] with significantly higher T_c's than found previously for alkali-metal graphite intercalation compounds (GICs), reinitiated the debate on the long-standing puzzle of the origin of superconductivity in GICs.[3] Possible pairing mechanisms under consideration range from unconventional exciton-or plasmon-mediated pairing[4] to the more conventional electron-phonon (*e*-ph) coupling mechanism.[5,6]

The core of the debate on the origin of superconductivity in the GICs lies in the so-called *interlayer* electronic bands which cross the Fermi level (E_F) in addition to the graphite π^* bands. Since the coupling of the π^* band electrons to the graphite phonons is not sufficient to yield the observed high T_c's,[6,7] the role of the interlayer bands and their degree of filling is considered to be essential for superconductivity with increased T_c's.[4] Csányi *et al.* proposed that the electrons in the interlayer bands can be considered as nearly free two-dimensional (2D) electrons propagating essentially between the graphene layers,[4] and pairing can be mediated by acoustic plasmons in these 2D metallic slabs.[8] 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.[5,6] This scenario gained some experimental support from recent penetration depth,[9] specific heat,[10] tunneling,[11] and Ca isotope effect[12] experiments in CaC_6.

Interestingly, the latter experiments showed a Ca isotope effect with $\alpha_{Ca}=0.5$, suggesting a dominant role of Ca-related modes in the superconducting pairing.[12] This finding, however, is at odds with the results of *ab initio* calculations[6] in which isotope exponents $\alpha_{Ca} \approx \alpha_C \approx 0.25$ 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).[13] 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.[4] 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.[14]

In this paper, we report the effect of pressure ($P \leqslant 16$ 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

CaC_6 samples were prepared as described in detail elsewhere.[2,10] 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 quasihydrostatic

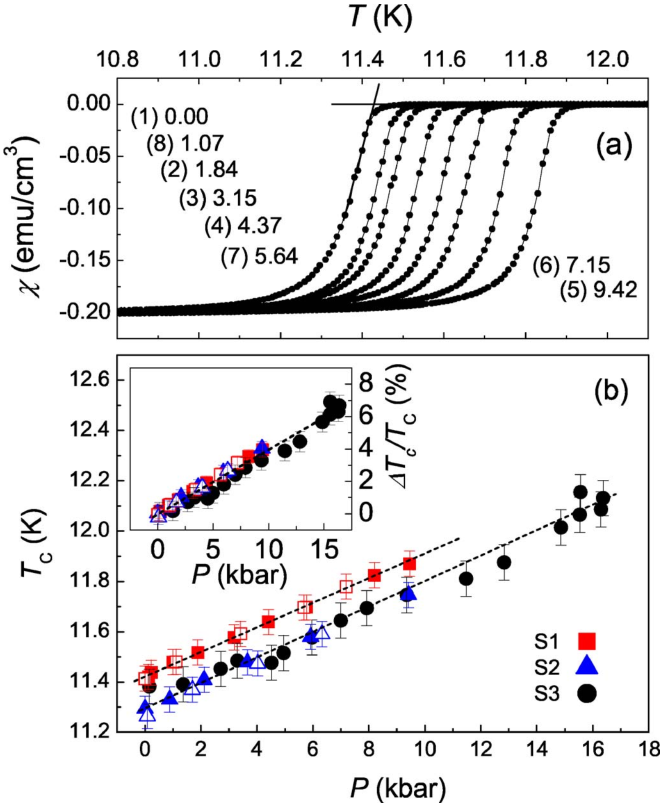

FIG. 1. (Color online) (a) Temperature dependence of the susceptibility for $\mathrm{CaC_6}$ (S1) at different pressures. The numbers next to the data and in the parentheses correspond to the applied pressure (kbar) and the sequential order of the measurement runs, respectively. T_c is determined as 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 $\mathrm{CaC_6}$ samples. The filled and open symbols are data taken at increasing and decreasing pressure, respectively. The dashed lines are guides to the eyes. The inset shows the relative change of T_c with pressure.

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. 1(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., $\mathrm{KHgC_4}$, $\mathrm{KC_8}$, $\mathrm{RbC_8}$, and ascribed to a pressure-induced change of the staging or of the intercalant sublattice.[15] No hysteresis in T_c or 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. 1(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 $\approx +0.4\%/\mathrm{kbar}$.[16] 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 $\mathrm{KHgC_8}$, $\mathrm{RbHgC_8}$, and $\mathrm{KTl_{1.5}C_4}$ whose T_c *decreases* under pressure with a rate of -2.2 to $-3.8\ \%/\mathrm{kbar}$.[15]

III. THEORY

To gain more insight into the possible coupling mechanism we performed a detailed density functional perturbation theory[17] (DFPT) study of the electronic and vibrational properties of $\mathrm{CaC_6}$ 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 cutoff energy of 30 and 300 Ry for the wavefunctions and the charge density, respectively. We used an $(8)^3$ Monkhorst-Pack grid and a 0.06 Ry Methfessel-Paxton smearing, which led to convergence of better than 0.1 mRy for the total and 5 $\mathrm{cm^{-1}}$ for the Γ-point frequencies. Phonon dispersion curves were obtained by a Fourier interpolation of the dynamical matrices calculated on a 4^3 grid in $\mathbf{q}$ space for $P=0$, 50, and 100 kbar, and a 2^3 grid elsewhere.

The electronic structure and phonon dispersion at ambient pressure are in excellent agreement with previous results.[6] The equation of state calculations yielded equilibrium lattice constants ($a_{rh}=5.16$ a.u., rhombohedral angle $\theta=49.90°$) in very good agreement with the experimental data ($a_{rh}=5.17$ a.u., $\theta=49.55°$), 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 nonintercalated 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 frequency for the relevant bosonic modes. Our calculations show that $N(E_F)$ *decreases* with increasing pressure because the interlayer band is emptied and the π^* bandwidth increases [see Fig. 2(c)]. In the following, we therefore investigate the alternative option to enhance λ (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.[21] The calculated phonon modes for $\mathrm{CaC_6}$ behave differently as a function of pressure depending on their eigenvector as seen, e.g., in the case of the Γ-point phonons [see Fig. 2(a)]: whereas the C in-plane modes ($\omega > 100$ meV) and the Ca out-of-plane modes ($\omega \sim 30$ meV) harden with pressure, the C out-of-plane modes ($50 < \omega$

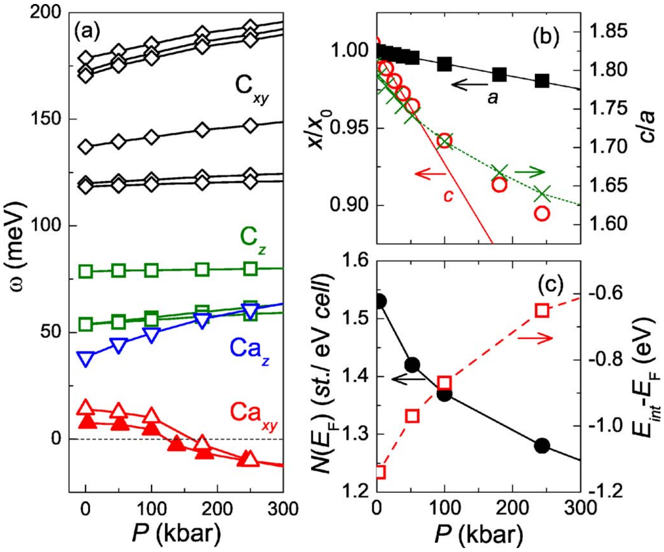

FIG. 2. (Color online) *Ab initio* pressure dependence of selected structural, electronic, and vibrational properties of CaC_6. (a) Frequencies of the Γ- (open symbols) and *X*- (solid symbols) point phonons. Imaginary frequencies are shown as negative. The labels indicate the atom giving the dominant contribution to the phonon eigenvector. (b) Variation of the in- and out-of-plane lattice constants and of the relative ratio. (c) $N(E_F)$ and position of the bottom of the interlayer bands with respect to E_F.

<100 meV) are almost unaffected. On the other hand, the lowest-lying optical mode at Γ, and an acoustical mode at *X* (Fig. 4), 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 π^* 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.[22]

To estimate the pressure dependence of the partial λ_{Ca} associated with the Ca in-plane vibrations, we employ a simple approximation based on the Hopfield formula: $\lambda_i = N(E_F)\langle I_i^2\rangle / M_i \langle \omega_i^2 \rangle$, where $\langle I_i^2\rangle$ is the *e*-ph matrix element, M_i is the phonon mass, and $\langle \omega_i^2\rangle$ is the square averaged phonon frequency. Assuming that $\langle I_{Ca}^2\rangle$ is constant and $\langle \omega_{Ca}^2\rangle$ can be approximated by the square of the lowest-lying optical phonon frequency at Γ, we find a significant increase of λ_{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 a dominant contribution to the coupling,[6] the increase of λ_{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,[4,23] 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 $\Omega_{pl}(\mathbf{q}) \sim q$, which can provide additional pairing routes for superconductivity.[8]

However, the electronic band structure (see Ref. 6) and the corresponding Fermi surface (FS) plot (see Fig. 3) reveal that the interlayer bands are 3D in character. Additionally, there is a substantial charge transfer to the graphite π^* 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 π^* bands, which display a warped cylindrical FS parallel to the *c* axis. With pressure, the dispersion of the π^* 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 acoustic plasmon dispersion is developed,[8] and the conventional plasmon dispersion, $\Omega_{pl}(\mathbf{q}) = \Omega_{pl} + \mathcal{O}(q^2)$ ($\Omega_{pl} \gg k_B T_c$) is fully recovered. Thus, even if any coupling due to acoustic plasmons is assumed, its strength will decrease with increasing pressure, adverse to our experimental observation.

Finally, we check whether the increase of λ due to the phonon softening is compatible with the observed increase of T_c under pressure by calculating the *e*-ph spectral function $\alpha^2F(\omega)$ and the frequency-dependent *e*-ph coupling parameter $\lambda(\omega) = 2\int_0^{\omega} \alpha^2 F(\Omega)\Omega^{-1} d\Omega$. Instead of the maximum experimental pressure ($P \approx 16$ 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 T_c up to

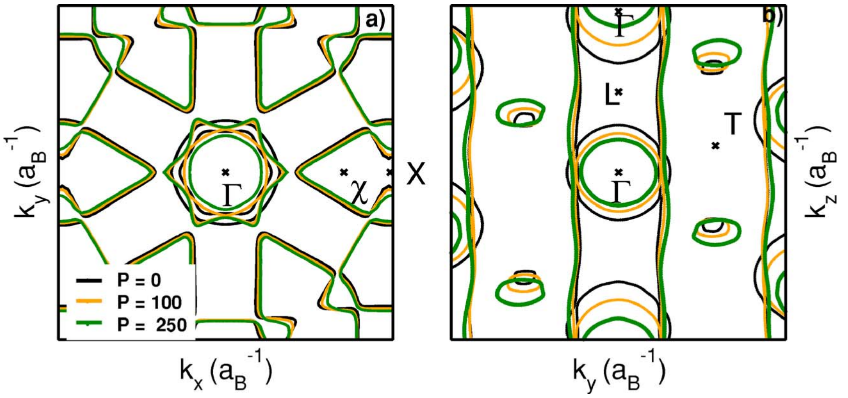

FIG. 3. (Color online) Cross section of the Fermi surface of CaC_6 at three different pressures ($P=0$, 100, and 250 kbar), in a plane orthogonal (a) and parallel (b) to the *c* axis. The spherical, 3D Fermi surface centered around Γ is due to the interlayer band, while the 2D π^* bands form a distorted cylinder along the *c* axis. The position of the special **k** points in this plot are relative to the $P=0$ lattice constants.

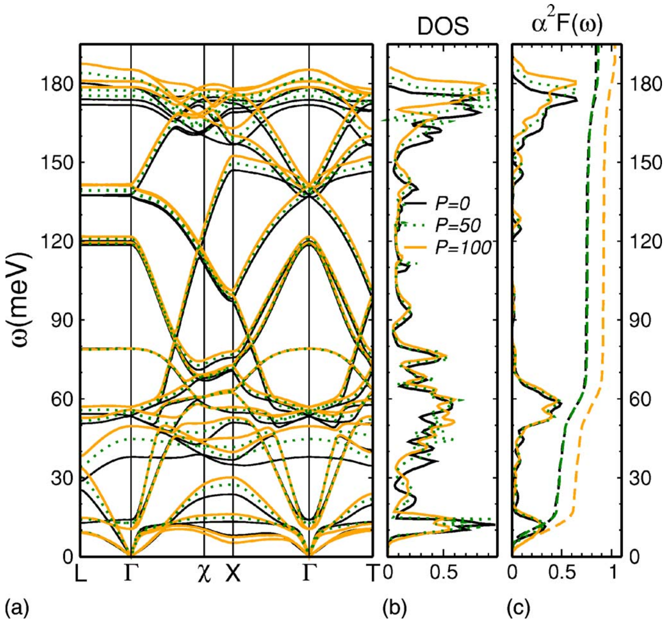

FIG. 4. (Color online) (a) Phonon frequencies and (b) density of states of CaC_6 for $P=0$, 50, and 100 kbar, along selected directions in the rhombohedral unit cell; the line $\Gamma-X$ is contained in the graphene planes, while $L-\Gamma$ is orthogonal to it. (c) Eliashberg function $\alpha^2F(\Omega)$ and frequency-dependent electron-phonon coupling $\lambda(\omega)=2\int_0^{\omega}\alpha^2F(\Omega)/\Omega d\Omega$.

$P\approx 16$ 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 close to the predicted structural transition, in order to get an estimate of the maximum attainable T_c in this system.

The *e*-ph spectral function $\alpha^2F(\omega)$ 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 $\lambda_{\text{Ca}}=0.42$ to $\lambda_{\text{Ca}}=0.62(0.44)$ 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 T_c using the McMillan formula[24]

$$T_c=\frac{\langle\omega_{ln}\rangle}{1.2}\exp\left(\frac{-1.04(1+\lambda)}{\lambda-(1+0.62\lambda)\mu^*}\right), \tag{1}$$

where $\langle\omega_{ln}\rangle$ is the logarithmic averaged phonon frequency and μ^* is the Coulomb pseudopotential. Inserting the calculated $\langle\omega_{ln}\rangle$ (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 T_c at zero pressure, we estimate that T_c 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 the density of states and $\langle\omega_{ln}\rangle$, and as a result, T_c 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 T_c.

IV. DISCUSSIONS

In Fig. 5, we plot the experimentally measured T_c from our work and also from Ref. 25, together with the calculated T_c as a function of pressure. Gauzzi *et al.*[25] recently observed a transition of T_c at ~80 kbar, accompanied by lattice softening, thus confirming our theoretical prediction of an upper bound on T_c due to lattice instability. However, 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 at ~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 first-stage KC_8 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 ~14 kbar,[27] but a sudden increase of T_c is observed already at ~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 *X*-point frequency with respect to **k**-point sampling, there

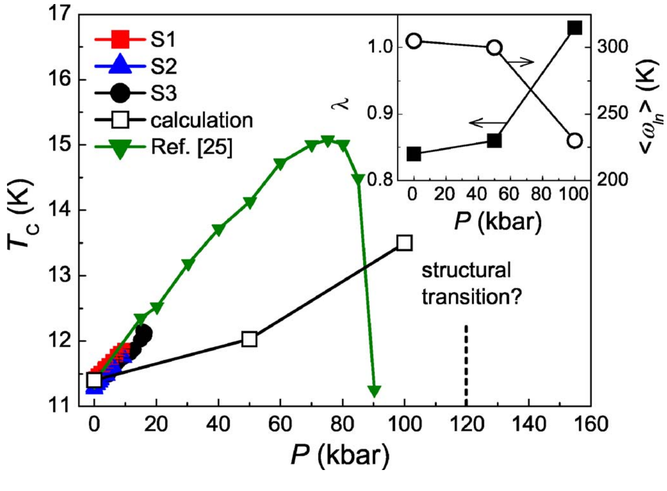

FIG. 5. (Color online) The calculated T_c (open squares) as a function of pressure together with the measured T_c in this work (as in Fig. 2) as well as that from Ref. 25. The dashed line indicates the point at which *ab initio* calculations predict a dynamical instability of the lowest *X*-point phonon. The inset shows a pressure dependence of the calculated *e*-ph coupling constant λ and the logarithmic averaged phonon frequency $\langle\omega_{ln}\rangle$. Both quantities have a strong nonlinear behavior.

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 ($\simeq 0.02$ K/kbar) than found in experiment, and a slightly nonlinear behavior, with a stronger increase in T_c at higher pressures.

Such discrepancies indicate that the harmonic, isotropic *e*-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 isotope effect,[12] which reported a surprisingly high isotope exponent for Ca, $\alpha(\mathrm{Ca}) \approx 0.5$, much higher than the value $\alpha(\mathrm{Ca}) = 0.24$ predicted by theory.[6] Assuming a nontrivial contribution from the C 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.[30] Further theoretical and experimental works are highly desirable in 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.[30] In graphite intercalation compounds, the vibrational modes associated with the intercalant are extremely soft, and transitions to different in-plane sublattices 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 origins (π^* 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 multigap superconductivity.[31]

Finally, we would like to compare our results with a very recent *ab initio* calculations.[29] 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 λ of only 0.015, and estimate an increase in T_c of ~ 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 λ are probably due to the use of different pseudopotentials and **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 *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 *e*-ph scenario due to softening of the in-plane Ca phonon modes, while it appears not to reconcile with the acoustic plasmon mechanism. In view of our 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.

ACKNOWLEDGMENTS

The authors acknowledge useful discussion with A. Simon, O. K. Andersen, G. B. Bachelet, and M. Giantomassi, and thank E. Brücher and S. Höhn for experimental assistance.

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