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Pressure-induced enhancement of superconductivity and superconducting-superconducting transition in CaC₆

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We measured the electrical resistivity, $\varrho(T)$, of superconducting CaC₆ at ambient and high pressure up to 16 GPa. For $P \leq 8$ GPa, we found a large increase of T_c with pressure from 11.5 up to 15.1 K. At 8 GPa, T_c drops and levels off at 5 K above 10 GPa. Correspondingly, the residual ϱ increases by ≈ 200 times and the $\varrho(T)$ behavior becomes flat. The recovery of the pristine behavior after depressurization is suggestive of a phase transition at 8 GPa between two superconducting phases with good and bad metallic properties, the latter with a lower T_c and more static disorder.

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The interest in Graphite Intercalated Compounds (GICs) has been recently renewed after the discovery of superconductivity with much higher T_c values than previously reported. The highest values hitherto reported are 6.5 and 11.5 K in YbC₆ and CaC₆, respectively [1, 2]. Magnetic penetration depth measurements [3] and *ab initio* calculations [4, 5] point at a conventional BCS *s*-wave scenario with a moderate electron-phonon coupling, $\lambda \approx 0.83$, and $2\Delta/T_c \approx 3.6$, where Δ is the superconducting gap. Contrary to a simple-minded picture of doped graphene layers, the above calculations indicate that the intercalant plays a non trivial role in the pairing. For example, the relevant electronic states in CaC₆ have a marked hybrid Ca-C character with a 40% Ca component [5].

These new results raise the questions of the maximum T_c that can be reached in GICs and of the role of the intercalant in enhancing T_c . In order to address these issues, in this letter we report on electrical resistivity, $\varrho(T)$, measurements in bulk superconducting CaC₆ at ambient and high pressure up to 16 GPa. To our knowledge this is the first study of the transport properties on CaC₆, for previously the superconducting transition was investigated only by means of magnetization measurements [1, 2].

Our results show that, for $P \leq 8$ GPa, pressure increases T_c in CaC₆ up to 15.1 K, the highest value hitherto observed for GICs. At 8 GPa, we find evidence of a structural phase transition that leads to a strong T_c reduction and to bad metal properties. Our

data analysis indicates that the T_c increase is caused by an enhancement of λ . The latter is found to increase anomalously near 8 GPa, which accounts for the observed structural instability. Thus, even higher T_c values might be obtained in CaC₆, provided the instability can be prevented.

For this work, we measured three bulk CaC₆ samples of size ≈ 1 mm \times 0.4 mm \times 0.2 mm prepared from platelets of *c*-axis oriented pyrolytic graphite, as described elsewhere [6]. The $\varrho(T)$ measurements were carried out in a conventional four-probe bar configuration using a dc method. Due to the high reactivity of CaC₆, the electrical contacts were made using silver paste in a glove box. The samples were subsequently protected by a layer of halogen-free cryogenic grease to enable handling in air. Owing to their platelet shape and *c*-axis orientation, the in-plane ϱ was measured.

The ambient pressure measurements prior and after pressurization were carried out in a commercial PPMS system. The high-pressure study was carried out using a cube-anvil press enabling the four-probe measurement of electrical resistivity under nearly hydrostatic conditions up to 16 GPa down to 2.5 K, as described in detail elsewhere [7]. The sample is mounted within teflon capsule filled with a fluorinert liquid used as pressure-transmitting medium. Each run of measurements was carried out at constant pressure on both cooling and heating by adjusting the load.

We first present and analyze the ambient pressure results. The $\varrho(T)$ curve is shown in Fig. 1.

One notes the low values of room temperature and residual resistivities, respectively $\rho_{300K}=46 \mu\Omega\text{cm}$ and $\rho_0=0.8 \mu\Omega\text{cm}$, the quite large residual resistivity ratio, $RRR \equiv \rho_{300K}/\rho_0=58$, and the pronounced linear T dependence in a wide temperature region above 150 K. For our superconducting samples, ρ_0 is defined as the ρ value at the onset of the transition. Taking into account the $\sim 10\%$ uncertainty in the geometry of the contacts, the ρ_{300K} value reported here agrees well with the value reported for single crystal whiskers of pure graphite [8]. Above T_c , the $\rho(T)$ curve was fitted by the generalized Bloch-Gruneisen formula [9], where the electron-phonon coupling function $\alpha^2F(\omega)$ was approximated by the following discrete decomposition into Einstein modes of energy ω_k [10]:

$$\alpha^2F(\omega) = \sum_k \alpha_k^2 F_k \delta(\omega - \omega_k) \quad (1)$$

The data of Fig. 1 are fitted using two modes of energies $\omega_1=136$ K and $\omega_2=600$ K and relative weights $\alpha_k^2 F_1=0.29$ and $\alpha_k^2 F_2=0.71$. The quality of the fit is so good that the fitting curve is indistinguishable from the experimental curve. Both energies and weights are in excellent agreement with the calculations of Calandra and Mauri [5]. Neither Eq. (1) with a single Einstein mode nor a restricted Bloch-Gruneisen formula with $\alpha^2F(\omega) \sim \omega^4$ account for the data. Thus, no definite power-law behavior, e.g. $\rho \sim T^5$, is seen at low temperatures. The low ρ_0 value and the absence of saturation of $\rho(T)$ at high temperatures suggest a small amount of static disorder and a large mean free path, well beyond the Ioffe-Regel limit.

The inset of Fig. 1 shows in detail the low-temperature region of the $\rho(T)$ curve. One notes a sharp superconducting transition with onset and zero-resistance values of 11.5 and 11.0 K respectively. The former value coincides with the onset value of previous magnetization data [2], so we conclude that the sample is homogeneous and the resistive transition is not of percolative type. The sharpness of the transition further supports the conclusion of sample homogeneity. In summary, the excellent agreement between the experimental electron-phonon coupling function within the Bloch-Gruneisen model and the theoretical calculations of Ref. [5] in addition to the above magnetic penetration depth study [3] give clear evidence of conventional BCS superconductivity for CaC_6 .

The results of the high pressure ρ measurements are shown in Figs. 2 and 3. Two distinct regimes below and above 8 GPa are found. In the former, the $\rho(T)$ curves preserve the features of the ambient pressure curve of Fig. 1. In particular, the behavior

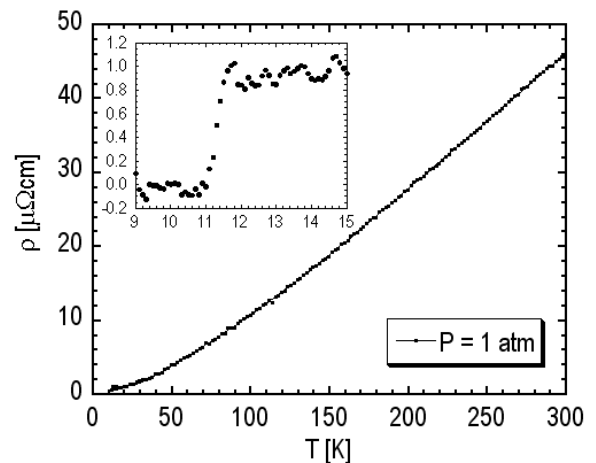


FIG. 1: In-plane resistivity of CaC_6 at ambient pressure. Note the linear behavior above 150 K, the low residual resistivity and the sharp superconducting transition at 11.5 K. The Bloch-Gruneisen fit described in the text is indistinguishable from the experimental curve.

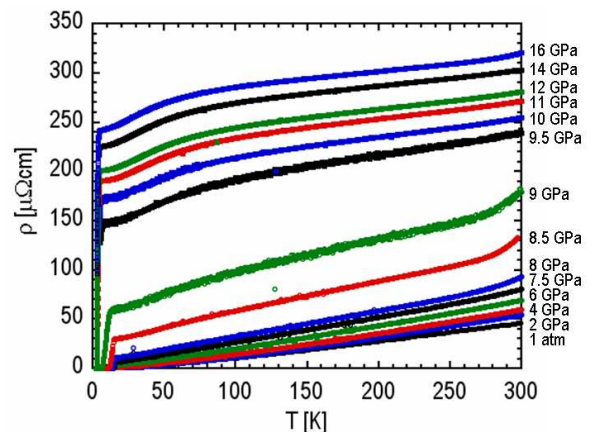


FIG. 2: (color online). Pressure-dependence of the in-plane resistivity of CaC_6 . Note the sudden increase of residual resistivity above 8 GPa accompanied by a drop of T_c down to 5 K (see Figure 3).

remains that of a conventional metal with a markedly linear T -dependence at sufficiently high temperature and low ρ_0 . By analyzing the data, the following variations with pressure are observed (see Fig. 4): 1. ρ_0 increases roughly quadratically with $\rho_0=0.8$ and $8 \mu\Omega\text{cm}$ at 1 atm and 8 GPa respectively; 2. the room temperature resistivity, ρ_{300K} , and the resistivity coefficient, $d\rho/dT$, increase linearly, with $\rho_{300K}=46$ and $94 \mu\Omega\text{cm}$ at 1 atm and 8 GPa respectively. 3. T_c increases linearly with a large rate ≈ 0.5 K/GPa and

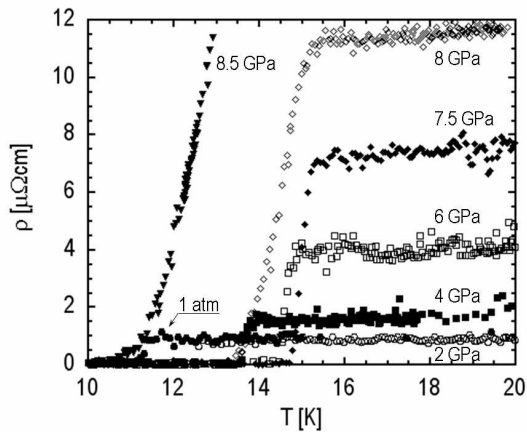


FIG. 3: Details of the superconducting transitions shown in Fig. 2. Note the transition broadening above 7.5 GPa.

reaches the maximum of 15.1 K at 7.5 GPa.

The correlation between T_c and $d\rho/dT$ suggests that the T_c increase is caused by a pressure-induced enhancement of the electron-phonon coupling. To verify this possibility, we applied the previous spectral analysis of electron-phonon coupling function to the pressure-dependent $\rho(T)$ curves. The result is summarized in Fig. 5. We indeed find a linear increase with pressure of the coupling constant for the 136 K mode, followed by an anomalous increase near 8 GPa. At 8.5 GPa, the coupling constant is 73% larger than at 1 atm. This increase is accompanied by a mode softening from 136 K at 1 atm down to 85 K at 8.5 GPa. No significant variations of coupling constant are observed for the 700 K mode. However, this mode exhibits a hardening up to ≈ 1100 K near 8 GPa.

The anomaly of both phonon modes near 8 GPa clearly indicates an incipient structural instability. In Fig. 3a one notes that ρ_0 suddenly increases up to nearly $200 \mu\Omega\text{cm}$, i.e. more than 200 times the ambient pressure value. This change corresponds to a pronounced flattening of the $\rho(T)$ curves accompanied by an incipient downward curvature at low temperatures followed by an indication of localization below 10 K. Indeed, the above Bloch-Gruneisen model does no longer account for the behavior of these curves and the previous spectral analysis of the electron-phonon coupling function is no longer applicable. This drastic change of regime in the normal state transport is concomitant to a sudden drop of T_c down to 5 K. The correlation between the ρ increase and the T_c drop is apparent by comparing Figs. 4a and 4b. In the 10-16 GPa region, no further significant changes are

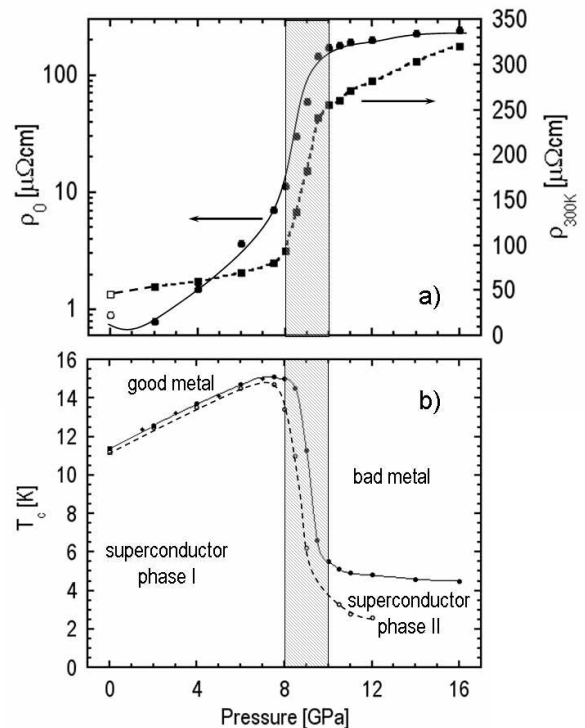


FIG. 4: Pressure dependence of ρ_0 and $\rho_{300\text{K}}$ (a) and of T_c (b). The dashed area denotes the pressure range where large variations are observed. Lines are a guide to the eye. In (a), open symbols refer to sample no. 2 measured only at 1 atm. In (b), full and open symbols and full and broken lines refer to respectively onset and offset values. Different symbols refer to three different samples.

observed. In particular, ρ_0 continues to increase, although slowly, and the flattening of the $\rho(T)$ curve becomes more pronounced. Interestingly, the T_c onset values levels off at 5 K, although the offset values continue to slowly decrease. At 14 GPa, the zero-resistance state is not yet achieved at 2.5 K. In Fig. 4b, it is noted that the transition width, calculated as the difference between onset and offset values, remains narrow (≤ 0.5 K) below 8 GPa. A large broadening is observed in the 8-10 GPa region, where T_c drops. The maximum broadening, as large as 6 K, is found at 9 GPa, i.e. exactly at the midpoint of the T_c drop. At larger pressure values, the transition sharpens back, although not completely, and the width is less than 2 K at 10.5 GPa.

The above results give evidence of a phase transition in the 8-10 GPa region. The transition broadening is an indication that fluctuations or a T_c distribution

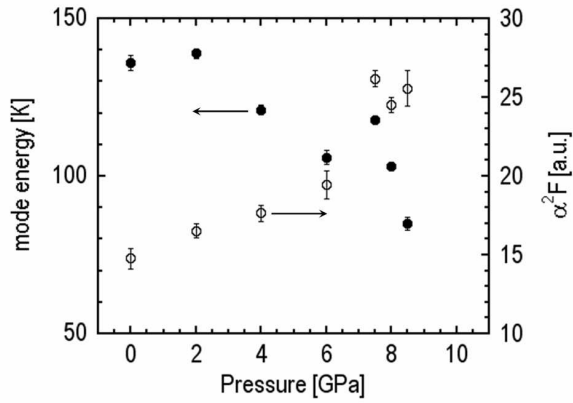


FIG. 5: Pressure-dependence of the energy and electron-phonon coupling constant for the 136 K phonon mode. Note the anomaly of the coupling near 8 GPa.

are present. A further evidence of phase transition is provided by the almost full recovery of the pristine $\varrho(T)$ behavior after depressurization (data not shown). Thus, extrinsic effects like pressure-induced micro-cracks can not be invoked to account for the large changes of resistivity and of superconducting properties observed. After depressurization, both ϱ_0 and ϱ_{300K} are higher than before pressurization. However, the difference is much smaller than the large change observed at 8-10 GPa. Specifically, we note the following. 1. After depressurization, ϱ_0 is larger by a factor of 8 only, to be compared with the factor of 200 of the 10 GPa data. 2. The overall behavior of $\varrho(T)$, is recovered after depressurization, although the RRR value is smaller (17 instead of 58) because of the larger ϱ_0 . 3. The superconducting transition of the pristine sample is fully recovered and both T_c and transition width are unchanged.

An *in situ* diffraction study under high pressure is required to unveil the phase transition at 8-10 GPa. At this point, we limit ourselves to note the following. 1. An incipient structural instability at ≈ 7 GPa, i.e. in good agreement with the experimental value, is predicted by *ab initio* calculations of phonon dynamics [11]. 2. One possible phase transition would be a modification of stacking sequence induced by pressure. Indeed, the different sequences found in the MC_6 family differ by a small amount of energy [6]. 3. The large increase of ϱ_0 gives evidence of a large amount of static disorder in the high pressure phase. This disorder may arise from a disordered rearrangement of the intercalant atoms or by a spatially incoherent buckling of graphene layers. This would strongly reduce the

mean free path of the charge carriers, thus accounting for the flattening of the $\varrho(T)$ curves observed experimentally. As a result, the transport regime would change from free electron-like into diffusive. Diffusive transport would be detrimental to superconductivity, in agreement with our experimental observation.

In summary, we reported the first $\varrho(T)$ measurements on bulk superconducting CaC_6 at ambient and high pressure up to 16 GPa. For $P \leq 8$ GPa, we found that T_c increases linearly with pressure up to 15.1 K with a large rate of 0.5 K/GPa. At 8-10 GPa, we gave evidence of a phase transition between a good and well ordered metal with relatively high T_c and a bad disordered metal with lower T_c . Our quantitative analysis of the pressure-dependent $\varrho(T)$ data accounts for the T_c increase in terms of a pressure-induced enhancement of the electron-phonon coupling. The anomaly of both relevant phonon modes near 8 GPa accounts for the structural instability leading to the bad metallic phase at high pressure. The present work suggests that still higher T_c values are possible in GICs, provided the structural instability at 8 GPa can be avoided. To examine this possibility, further studies are needed to unveil the structural properties and the role of disorder on the normal state and superconducting properties of the high-pressure phase.

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