Specific Heat of the Ca-Intercalated Graphite Superconductor CaC₆

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The superconducting state of Ca-intercalated graphite CaC₆ has been investigated by specific heat measurements. The characteristic anomaly at the superconducting transition (Tₖ = 11.4 K) indicates clearly the bulk nature of the superconductivity. The temperature and magnetic field dependence of the electronic specific heat are consistent with a fully-gapped superconducting order parameter. The estimated electron-phonon coupling constant is \( \lambda = 0.60 \) - 0.74 suggesting that the relatively high \( T_c \) of CaC₆ can be explained within the weak-coupling BCS approach.

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The recent discovery of superconductivity in Ca- and Yb-intercalated graphite has refocused considerable interest onto graphite intercalated compounds (GICs) [1, 2]. The superconducting transition temperature for Ca- and Yb-intercalated graphite is \( T_c \approx 11.5 \) K and 6.5 K, respectively, significantly higher than the alkali-metal intercalated graphite phases studied in the 1980’s [3]. Similar to MgB₂ where the hexagonal B sheets are intercalated with Mg, in the GICs the Ca or Yb atoms are sandwiched by the honeycomb graphene layers. The intercalated metal ions act as donors and transfer charge into the interlayer bands. In contrast to MgB₂ with a strong electron-phonon coupling of the B \( \sigma \)-bands, the coupling strength of the graphite \( \pi \)-bands to in-plane phonon modes is expected to be small. Also out-of-plane phonon modes will not couple to the \( \pi \)-band because of the antisymmetric character of the \( \pi \)-orbitals. Thus the superconducting mechanism for the GICs could be rather different than that of MgB₂.

The superconducting mechanism, now under debate, relies on the other partially filled bands: the so-called interlayer bands. From the detailed comparison between the superconducting and non-superconducting GICs, Csányi et al. found that the filling of the interlayer state is essential for stabilizing the superconductivity in GICs [4]. Based on this result and the consideration about the layered structure of the GICs, they proposed an unconventional electronic paring mechanism involving excitons [5] or low-energy acoustic plasmons [6]. The latter has been discussed as a possible mechanism for the high \( T_c \) of the intercalated metal halide nitrides [7]. Soon after, however, Mazin [8] and Calandra et al. [9] suggested that the interlayer band originates from the \( s \)-band of the intercalant, and an ordinary electron-phonon coupling mechanism involving the intercalant phonon and the out-of-plane C phonon modes would be sufficient to explain the relatively high \( T_c \) in the GICs. In order to shed light on this controversy, further experimental studies on the superconducting properties of the GICs are required.

Specific heat (\( C_P \)) measurements are known to be a powerful tool to investigate the superconducting states. Since \( C_P \) probes the quasi-particle excitation across the superconducting gap, its temperature and magnetic field dependence reflect the nature of the superconducting state such as gap symmetry, presence of multi-gaps, and coupling strength between electrons and phonons (or other bosonic excitations). So far, there has been no \( C_P \) study on the superconducting state of the GICs, mostly because the low \( T_c \) was experimentally difficult to reach, and the sample homogeneity was not sufficient for reliable studies. In this Letter, we report the temperature and magnetic field dependence of \( C_P \) for high-quality bulk CaC₆ samples. In zero-field measurements we observe a sharp \( C_P \) anomaly at \( T_c \approx 11.4 \) K. The detailed temperature and magnetic field dependence of \( C_P \) clearly show a fully gapped superconducting order parameter, and fit very well to the weak coupling BCS prediction.

The Ca-intercalated graphite samples were synthesized by reacting highly oriented pyrolytic graphite (HOPG, Alfa Aesar, spread of the c-axis orientation 0.4(1)°) with a molten lithium-calcium alloy at 350°C for several weeks (cf. Ref. [2]). Since the metal alloy and the intercalated sample are air sensitive all handling was done in purified argon atmospheres. X-ray diffraction patterns (not shown) dominantly show reflections of CaC₆ (the distance between graphene layers, \( d = 4.50 \) Å), and contained no reflections related to non-intercalated graphite. Weak additional reflections [10] possibly due to Li/Ca-intercalated graphite phases [11] were observed. The contribution of the impurity phase is estimated to be less than 5% to the total heat capacity. The magnetic susceptibilities were determined in a MPMS SQUID magnetometer (Quantum Design). The superconducting transition temperature of our samples is \( T_c = 11.40(5) \) K (see the inset of Fig. 1), consistent with previous reports [2]. The transition width determined as the temperature...
difference between 10% and 90% diamagnetic shielding is only 0.1 K, smaller than found in previous reports [2]. After demagnetization correction, the volume fraction was estimated to be \( \approx 100\% \). The heat capacity for a sample of \( \approx 5 \) mg was measured using a PPMS calorimeter (Quantum Design) employing the relaxation method. To thermally anchor the crystals to the sapphire sample platform and to orient the samples with respect to the magnetic field \( (H \parallel c) \), a minute amount of Apiezon N grease was used. The heat capacity of the platform and the grease, which amounted to \( \approx 40-60\% \) over the whole temperature range, was determined in a separate run and subtracted from the measurements for the samples.

Figure 1 shows the temperature dependence of \( C_P \) at \( H = 0 \) and \( H = 10 \) kOe applied along the \( c \)-axis. A sharp anomaly at \( T_c \) is resolved indicating the bulk nature of the superconductivity in our sample. The onset of 11.40 K determined from the specific heat jump is consistent with the \( T_c \) obtained from the susceptibility measurements. A small offset of \( C_P/T \) at \( H = 0 \) \( (\gamma_{ns} = 0.65 \pm 0.13 \text{ mJ/mol K}^2 \) and a slight hump of \( C_P/T \) at \( H = 10 \) kOe were observed below 3 K (see the right inset of Fig. 1), which probably originate from paramagnetic impurities or a non-superconducting fraction in our sample. \( \gamma_{ns} \) is only \( \approx 10\% \) of the Sommerfeld coefficient \( \gamma_N \) extracted from the normal state \( C_P(T) \) as discussed below. If we assume that \( \gamma_{ns} \) corresponds to the non-superconducting part of our sample, the volume fraction of the superconducting portion can be estimated as \( 1 - (\gamma_{ns}/\gamma_N) \approx 90\% \) proving a good quality of our GIC sample. The upper critical field \( H^*_c \) along the \( c \)-axis has been reported to be \( \approx 2.5 \) kOe [2], thus the normal state \( C_P(T) \) can be obtained when the superconductivity is completely suppressed by a magnetic field \( H = 10 \) kOe. A clear deviation from Debye \( T^3 \) law seen in the normal state \( C_P \) can be attributed to a contribution from the low-lying optical phonon modes. Recent ab-initio calculations also show the presence of low frequency modes mainly involving vibration of the intercalated Ca [3]. The normal state \( C_P \) can be described by \( C_P = \gamma_N T + C_{lattice}(T) \) where \( \gamma_N T \) is the electronic contribution, and \( C_{lattice}(T) = \beta T^3 + \delta T^5 \) is the lattice contribution. The solid line in Fig. 1 is the best fit to the \( H = 10 \) kOe data below \( T < 12 \) K, yielding the parameters, \( \gamma_N = 6.66(1) \text{ mJ/mol K}^2, \beta = 65.1(3) \text{ mJ/mol K}^4 \) and \( \delta = 0.256(3) \text{ mJ/mol K}^6 \). Considering the offset of \( C_P/T(H = 0), \gamma_{ns}, \) the Sommerfeld coefficient for the superconducting part of the sample is \( \gamma_N \approx \gamma_N - \gamma_{ns} = 6.01 \pm 0.14 \text{ mJ/mol K}^2 \). The corresponding Debye temperature \( \Theta_D(0) = 598(3) \) K, which is much higher than that of pure graphite (\( \Theta_D(0) = 413 \) K) and the alkali metal GICs (e.g. 235 K for \( \text{KC}_8 \) [12], but comparable with \( \Theta_D(0) = 590 - 710 \) K for \( \text{LiC}_6 \) [13]).

The specific heat difference \( \Delta C_P \) between the normal and superconducting state is shown in Fig. 2. The solid line is the theoretical fit based on the ‘\( \alpha \)-model’ assuming an isotropic \( s \)-wave BCS gap \( \Delta(T) \) scaled by the adjustable parameter, \( \alpha = \Delta(0)/k_B T_c \) [14]. For the weak coupling limit \( \alpha \) is 1.76. The detailed temperature dependence of \( \Delta C_P(T) \) was fitted by three adjustable pa-

**FIG. 1:** (Color online) Temperature dependence of the specific heat at \( H = 0 \) and \( 10 \) kOe. The solid (black) line through the data points at \( H = 10 \) kOe (also in the right inset) is a fit described in the text. (Left inset) The temperature dependence of the susceptibility with \( H = 6 \) Oe under zero-field cooled(ZFC) and field-cooled(FC) modes. (Right inset) The low temperature behavior of \( C_P(T) \). The (red) solid line for \( C_P(T) \) at \( H = 0 \) is a linear fit for \( 2 \text{ K} < T < 3 \text{ K} \).

**FIG. 2:** (Color online) Temperature dependence of \( \Delta C_P(T) = C_P(H = 0)/T - C_P(H = 10 \text{ kOe})/T \). The (red) solid line is the best fit according to the \( \alpha \)-model assuming an isotropic \( s \)-wave BCS gap as described in the text. The electronic contribution of the specific heat \( C_{es} \) is plotted on a logarithmic scale against \( T_c/T \) in the inset. The (red) straight line in the inset is the exponential fit for \( 2.5 < T_c/T < 5.5 \).
parameters: $\alpha$, Sommerfeld coefficient $\gamma$, and $T_c$. The data are very well reproduced by $\alpha = 1.776$, $\gamma = 5.91$ mJ/mol K$^2$ and $T_c = 11.30$ K. The normalized specific heat jump, $\Delta C_P/\gamma T_c$ is 1.432, which is close to the weak limit BCS value, 1.426. The normalized electronic specific heat, $C_{es}/\gamma T_c$ in the superconducting state is shown in the inset. The solid line is an exponential fit to the data for $2.5 \leq T_c/T \leq 5.6$ using the form $C_{es}/\gamma T_c \propto \exp(-0.82\alpha T_c/T)$ with $\alpha = 1.65(1)$. $C_{es}$ exponentially vanishes for $T \to 0$ K, clearly manifesting the absence of gap nodes in the superconducting state. The $\alpha$ value is somewhat lower than that from the $\alpha$-model fit in which the ratio $\Delta(0)/k_B T_c$ is mostly determined by the shape of the $C_P$ jump near $T_c$. However the discrepancy is less than 10%, in contrast to MgB$_2$ where the discrepancy is more than 60% due to the presence of two gaps.

Figure 3 shows the temperature dependence of $C_P/T$ measured with different magnetic fields. Superconductivity is gradually suppressed, and the quasiparticle contribution increases with magnetic field. $T_c(H)$ determined by the mid-point over the $C_P$ anomaly is plotted in the inset with the error bar corresponding to the transition width. The $T_c(H)$ obtained from the susceptibility measurements (not shown) are in good agreement with those found from $C_P(T)$. For comparison, we also plot the predicted curve based on the Werthamer-Helfand-Hohenberg (WHH) theory. $H_{c2}(T)$ shows a linear dependence down to $T/T_c \approx 0.2$ and a clear deviation to the WHH prediction, which deserves further investigation. The best fit for low fields results in $(dH_{c2}/dT)_{T_c} = 219.1(8)$ Oe/K and the linear extrapolation of $H_{c2}(T)$ to $T = 0$ K yields $H_{c2}^{ab}(0) = 2.48$ kOe, which corresponds to an $ab$-plane coherence length, $\xi_{ab}(0) \approx 360$ Å. From $H_{c2}^{ab}(0) \approx 7$ kOe along the $ab$-plane [2], the $c$-axis coherence length, $\xi_c(0) \sim 130$ Å ($\gg d = 4.50$ Å) is obtained. This result indicates the 3-dimensional nature of superconductivity in CaC$_6$.

The magnetic field dependence of the Sommerfeld coefficient $\gamma(H)$ provides information about the superconducting gap symmetry. For a gapped superconductor, the quasiparticle excitations are expected to be confined in the vortex cores, and $\gamma(H)$ is proportional to the density of vortices resulting in $\gamma(H) \propto H$. In contrast, when the superconducting gap is highly anisotropic or has a gap node, the delocalized quasiparticles near the gap minima cause a nonlinear magnetic field dependence such as $\gamma(H) \propto H^{1/2}$. The normalized $\gamma(H)$ for CaC$_6$ is displayed in Fig. 4. $\gamma(H)$ for $T \to 0$ K is determined from the linear fit for $2$ K $\leq T \leq 4$ K (see the inset of Fig. 4) after subtracting the offset of $\gamma_N(H = 0)$. As a consistency check, we also plot $C_P(T,H)/T \propto C_{es}(T,0)/T + C_{lattice}/T$ at the lowest temperature in the present measurements ($T = 2$ K) after subtraction of $C_P(H = 0)/T \propto C_{es}(T,0)/T + C_{lattice}/T$. Both curves are normalized with $\gamma(H = 10$ kOe).

As shown in Fig. 4, $\gamma(H)$ increases linearly with $H$ for low fields up to $H \approx 0.3 H_{c2}$. This behavior is strongly
adverse to $\gamma(H) \propto H^{1/2}$ expected for nodal superconductivity and also in contrast to two-band superconductivity [13]. Recent calculations found that even for an isotropic-gapped type-II superconductor, $\gamma(B) \propto B$ behavior persists only up to a certain crossover field, $B^* [19]$. For the isotropic superconducting gap, $B^*$ is expected to be $\approx 0.32 B_{c2}$ which is reduced as the degree of the anisotropy for the superconducting gap increases. Since $C_P(H)$ measurements were done in the field-cooled mode, we can approximately estimate the ratio between the crossover field and the upper critical field $B^*/B_{c2} \approx H^*/H_{c2} = 0.60 - 0.74$, in a good agreement with recent calculations [8].

The estimated electron-phonon coupling constant $\lambda$ for CaC$_6$. At first, $\lambda$ can be estimated from a comparison between $\gamma_N$ and the density of states at the Fermi level $E_F$, $N(0)$ using the equation $\gamma_N = (2\pi^2 k_B^2 \rho_0^3)/3N(0)(1+\lambda)$. If we take $N(0) = 1.50$ states/eV-cell from recent calculations [2], we obtain $\lambda \approx 0.60 - 0.74$ using our $\gamma_N = 6.01 \pm 0.14$ mJ/mol K$^2$. Alternatively, we can also estimate $\lambda$ based on the McMillan formula [20].

$$T_c = \frac{\Theta_D}{1.45} \exp \left[ \frac{-1.04(1+\lambda)}{\lambda - (1+0.62\lambda)^{\mu^*}} \right]. \quad (1)$$

Here, $\mu^*$ is the Coulomb pseudopotential. Taking $T_c = 11.4$ K and $\Theta_D = 598(3)$ K from the normal state $C_P$, we obtain $\lambda = 0.60 - 0.71$ with $\mu^*$ ranging from 0.10 to 0.15. All these results are in good agreement with each other, and imply that CaC$_6$ obviously belongs to the weak coupling regime. Recent calculations [2] also predicted $\lambda$ to be $\approx 0.83$, in accordance with the measured $\lambda$. Consistently, the superconducting gap ratio, $2\Delta(0)/k_B T_C = 3.3 - 3.6$ is also close to the BCS value 3.52.

In conclusion, we have reported the first specific heat measurements for the superconducting and normal state of high-quality bulk CaC$_6$ samples. The specific heat anomaly at $T_c$ is clearly resolved indicating the bulk nature of the superconductivity. Both the temperature and magnetic field dependence of $C_P$ strongly suggests a fully-gapped superconducting order parameter. The estimated electron-phonon coupling constant $\lambda$ is 0.60 - 0.74, in a good agreement with recent calculations. These results suggest that CaC$_6$ is a fully-gapped, weakly-coupled, phonon-mediated superconductor without essential contributions from alternative paring mechanisms. We cannot rule out the possibility of a superconducting gap anisotropy or a multi-gap scenario in this system [21], however, if any, the difference between the largest and smallest gaps will be rather small. Very recently, Lamura et al. [22] reported the in-plan penetration depth, $\lambda_{ab}$ for the bulk CaC$_6$ sample. A clear exponential temperature dependence of $\lambda_{ab}$ indicates a fully-gapped superconductivity in CaC$_6$, which is consistent with our $C_P$ study.

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