Anisotropic superconductivity in bulk CaC_6

E. Jobiliong, H. D. Zhou, J. A. Janik, Y.-J. Jo, L. Balicas, J. S. Brooks, and C. R. Wiebe
Department of Physics and National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310, USA
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The intercalated graphite superconductor CaC_6 with $T_c \sim 11.5$ K has been characterized with angular dependent magnetoresistance measurements. Above T_c, the interplane resistivity can be fitted to the Bloch-Grüneisen model providing a Debye temperature of $\theta_D = 175$ K. From these parameters, the McMillan formula yields an electron-phonon coupling constant $\lambda \sim 1.1$, placing this material in the intermediate-to-strong coupling regime. For $1.4\ \mathrm{K} < T < T_c$, the upper critical field B_{c2} is found to be anisotropic and linear in temperature.

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Superconductivity in graphite intercalation compounds (GICs) has been known for decades, but progress to increase the transition temperature T_c (from 0.14 to 5 K) has been slow.[1–4] However, the recent discovery of relatively high T_c in materials such as YbC_6 and CaC_6 (8 and 11.5 K, respectively)[5,6] provides new impetus for the understanding of superconductivity in low-dimensional structures, and, recently, pressure has been used to raise the T_c of CaC_6 to 12.3 K at 16 kbar.[7] Current theory[8] supports a model in which T_c increases with increased charge transfer from the intercalant to the graphene layers. However, some members of this series seem to contradict this view. For example, in LiC_6, the charge transfer is larger than that of KC_8 ($T_c = 0.15$ K), but there is no evidence of superconductivity in LiC_6.[9] Superconductivity in GICs presents interesting questions since the constituent elements alone are not superconducting, and recent theoretical efforts have attacked this problem from the view of band structure.[10–12] The present consensus is that finely tuned electron-phonon interactions give rise to BCS-like superconductivity in GICs, limiting the maximum value of T_c.

In this Brief Report, systematic angular and temperature dependent upper critical field magnetoresistivity measurements on the new stage-I GIC superconductor CaC_6 are presented. A lithium-calcium alloy (of the ratio 3:1) was prepared in an argon glove box at 220 °C, and thin sheets of pristine highly oriented pyrolytic graphite were inserted. The entire sample mixture was sealed in a stainless-steel reaction container, and then placed on a hot plate at 350 °C for 10 days. The samples were extracted from the molten solution inside the glove box, and only very thin samples which exhibited shiny metallic surfaces were used. Air exposure was limited to about 1 h during mounting for magnetic or transport studies. Typical sample sizes were $1.5 \times 1\ \mathrm{mm}^2$ in area and thickness of 0.2 mm. Resistivity was measured using a conventional four-probe method with a current of 1 mA applied along the c axis.[13] Measurements were carried out with a rotation probe in a He-flow cryostat with an 8 T superconducting magnet.

The interplane (c-axis) resistivity and the dc susceptibility vs temperature are shown in Fig. 1. dc susceptibility measurements (lower inset of Fig. 1) yield a superconducting transition temperature $T_c = 11.5$ K in a field of 50 G applied parallel to the ab plane. From the saturation of the diamagnetic signal, the samples used were estimated to have a superconducting volume fraction of about 90%.

We first consider the temperature dependence of the interplane (c-axis) resistance in CaC_6 shown in Fig. 1. Below about 250 K, the resistance decreases monotonically and exhibits an approximate T^2 dependence between about 50 K and T_c. A similar behavior for the temperature dependent resistivity is seen in the compound YbC_6, where the crossover to T^2 occurs below 30 K.[5] (As will be discussed below, there is a constant nonzero background resistance below T_c.) Several models have been used to describe c-axis transport in acceptor-type GICs. These include variable-range hopping in parallel with band conduction[14] and impurity and phonon-assisted hopping.[15,16] However, in donor compounds where the conductivity is considerably higher, band conduction should become important,[15] and in the CaC_6 sample studied here, we estimate the interplane conductivity at room temperature to be $8.7 \times 10^3\ \Omega^{-1}\,\mathrm{cm}^{-1}$, which is a typical value for donor GICs.[17] In light of the above, we have considered both a low temperature Fermi liquid dependence

$$\rho = \rho_0 + AT^2 \tag{1}$$

(where A is the T^2 Fermi liquid prefactor) and, at higher temperatures, a phonon-assisted conduction model[18]

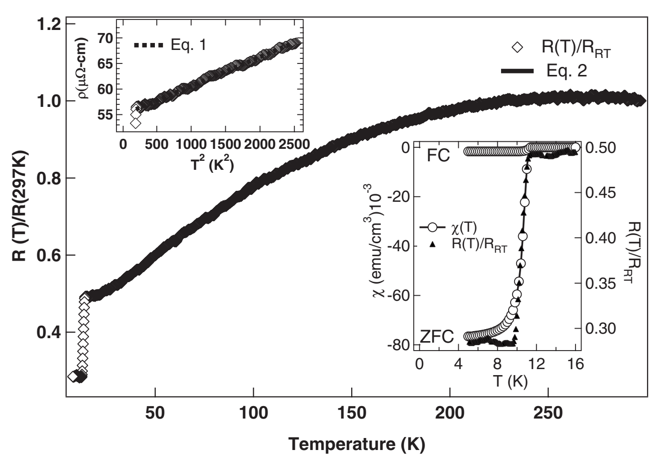

FIG. 1. Interplane resistivity of CaC_6 vs temperature normalized to 297 K (RT). Above 50 K, the data are fitted to Eq. (2). Upper inset: resistivity vs T^2 fitted to Eq. (1) below 50 K. Lower inset: dc susceptibility for field-cooled (FC) and zero-field-cooled (ZFC) conditions for a 50 Oe field applied in the ab plane. Details of the resistive transition near T_c are also shown for comparison.

$$\rho(T) = \rho_0 + aT^2 + BT^5 \int_0^{\theta_D/T} \frac{x^5}{(e^x - 1)(1 - e^{-x})} dx \qquad (2)$$

to describe the data. [In Eqs. (1) and (2), ρ_0 is temperature independent.] In Eq. (2), the second term aT^2 is related to phonon-assisted hopping,[15,16] and the last term is related to the electron-phonon scattering, also known as the Bloch-Grüneisen formula. (Here, we note that $x=\hbar\Omega/kT$, where Ω is the phonon frequency and θ_D is the Debye temperature.) Referring first to the upper inset of Fig. 1, between T_c and 50 K, Eq. (1) fits the data very well, with $\chi^2=0.001$, yielding $A=7.4(0.02)\times10^{-9}\ \Omega\,\mathrm{cm}/\mathrm{K}^2$. For the temperature range[19] of 50 to 250 K, the fit for Eq. (2) [in terms of $R(T)/R(297\ \mathrm{K})$] shown in Fig. 1 yields $\theta_D=175(26)$ K, $a=-7.96(0.14)\times10^{-7}\ \mathrm{K}^{-2}$, and $B=1.70(0.3)\times10^{-11}\ \mathrm{K}^{-5}$, with $\chi^2=0.011$. θ_D is slightly lower than that for other GICs fitted with this model (which range from 200 to 300 K).[20,21]

Using $\theta_D=175$ K as obtained above, the electron-phonon coupling parameter λ can be estimated from the McMillan equation[22]

$$\lambda = \frac{\mu \ln\left(\frac{1.45T_c}{\theta_D}\right) - 1.04}{1.04 + \ln\left(\frac{1.45T_c}{\theta_D}\right)(1 - 0.62\mu)}, \qquad (3)$$

where μ is the screened potential. For $\mu=0.1$, $\lambda=1.1$. This is larger than the theoretical prediction using density functional theory ($\lambda=0.83$).[23] The high value of λ indicates that this material is in the intermediate-to strong-coupling regime. Other superconducting GICs typically have lower values for λ (between 0.2 and 0.5) and, correspondingly, lower T_c's.[3,24,25] This suggests that the value of λ in CaC_6 is correlated with the high value of T_c.

The interplane resistivity and critical fields as a function of applied field for $B_{\perp layer}$ and $B_{\parallel layer}$ are shown in Figs. 2(a) and 2(b). To obtain the critical field values, several criteria were considered:[26] B_{zero} refers to the field where the resistance first rises from zero (with the offset taken into account). $B_{inflection}$ is the inflection point of the resistance vs field (determined from the peaks in dR/dB). B_{edge}, depicted by the dashed lines, corresponds to a change of slope in the magnetoresistance. B_{normal} is the estimated field where the resistance reaches the full normal state. The critical field values thus obtained are plotted in the main panels of Fig. 2. Also plotted is the T_c value (at 50 Oe $\perp c$) from the susceptibility data (from Fig. 1) and the susceptibility measurements for CaC_6 reported previously for $B\parallel c$.[6] As seen in other GIC compounds,[25,27,28] a linear dependence of B_{c2} on temperature is observed, which is insensitive to the criteria used to determine B_{c2}. This linear dependence, most clearly exhibited by $B_{inflection}$, indicates that the anisotropy is temperature independent, and there is no evidence of dimensional crossover in the range of temperature investigated.

The critical field in the anisotropic Ginzburg-Landau theory can be written as[29]

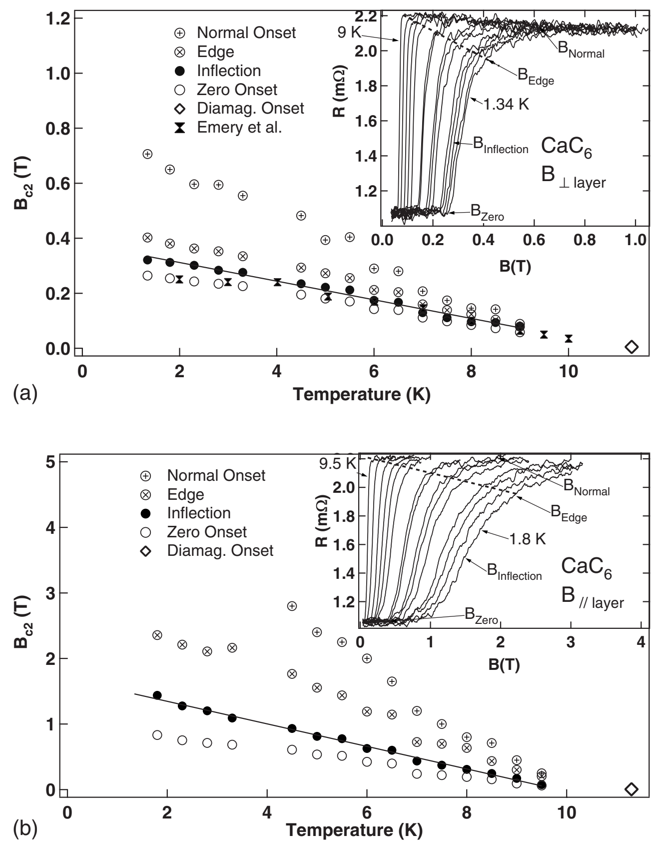

FIG. 2. Critical field measurements for CaC_6. (a) $B_{\perp layer}$ and (b) $B_{\parallel layer}$. The interplane resistance is shown vs $B_{\perp layer}$ (upper inset) and $B_{\parallel layer}$ (lower inset) at different temperatures. $B_{c2}(T)$ was obtained from the criteria indicated in the insets (see text and Ref. 26). The diamagnetic onset point is from the susceptibility data in Fig. 1. dc susceptibility data from Ref. 6 are also shown in (a). Solid lines: fits of Eq. (4) to $B_{inflection}$.

$$B_{c2}^i = \frac{\Phi_0}{2\pi\xi_j(T)\xi_k(T)} = \frac{\Phi_0}{2\pi\xi_j(0)\xi_k(0)}\left(1 - \frac{T}{T_c}\right), \qquad (4)$$

where $\Phi_0=h/2e=2.07\times10^{-15}\ \mathrm{T\,m}^2$ is the flux quantum and ξ is the coherence length. The indices i, j, and k represent the cyclic permutation of the directions a, b, and c. By applying Eq. (4) to the data in Figs. 2(a) and 2(b), we obtain, for instance, from the inflection point criteria, the correlation lengths $\xi_\perp(0)=5.7$ nm and $\xi_\parallel(0)=29.0$ nm. This can be compared to dc susceptibility measurements[6] of 13.0 and 35.0 nm, respectively. Here, we note in Fig. 2(a) that the B_{zero} criteria yields the lowest B_{c2} values, corresponding to previous susceptibility measurements.[6] Clearly, criteria which yield higher B_{c2} values will also give smaller coherence lengths.

The anisotropy of the critical field in CaC_6 is shown in Fig. 3. (Here, 90° corresponds to $B_{\parallel layer}$.) Due to the significant changes in the shape of the magnetoresistance vs angle near both the onset and normal state fields, only B_{zero}, $B_{inflection}$, and a new criterion, $B_{intercept}$, were used to determine the angular dependent critical field. The latter criterion, $B_{intercept}$, derived by extrapolation as shown in the inset of

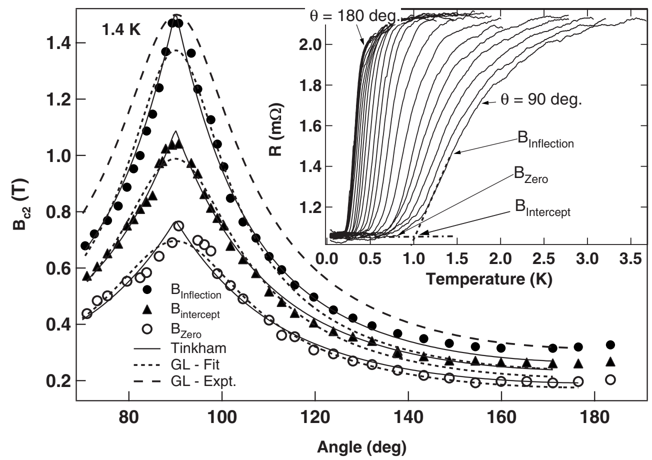

FIG. 3. Angular dependence of B_{c2} for CaC_6 at 1.4 K derived from the magnetoresistance data (inset). B_{c2} was determined for three different criteria (see text and Ref. 26). The dashed and solid lines are fits to Eqs. (5) and (6), respectively; the dotted line is for Eq. (5) with $B_{c2\parallel}$ and $B_{c2\perp}$ fixed.

Fig. 3, was used to account for the small change of slope that occurs above B_{zero} near $B_{\parallel layer}$.

A comparison of the data in Fig. 3 can be made with two models to determine the dimensionality. The first is the anisotropic Ginzburg-Landau (GL) theory, which is valid when the interlayer spacing is much smaller than the c-direction coherence length. In this case, the upper critical field depends on the angle between the normal to the layers and the applied field through[31]

$$\left[\frac{B_{c2}(\theta)\cos(\theta)}{B_{c2\perp}}\right]^2+\left[\frac{B_{c2}(\theta)\sin(\theta)}{B_{c2\parallel}}\right]^2=1, \qquad (5)$$

where the upper critical fields for directions parallel and perpendicular to the ab plane are $B_{c2\parallel}$ and $B_{c2\perp}$. The second is based on the Tinkham model, which describes noncoupled superconducting films thinner than the coherence length. In this case, the angular dependence of the layers is found to be[32]

$$\left|\frac{B_{c2}(\theta)\cos(\theta)}{B_{c2\perp}}\right|+\left[\frac{B_{c2}(\theta)\sin(\theta)}{B_{c2\parallel}}\right]^2=1. \qquad (6)$$

This model describes the angular dependence of the magnetoresistivity for thin films and for two-dimensional superconductors in general.[33] The applicability of the models can be determined near 90°, where the GL model and the Tinkham model produce a rounded and a cusplike feature, respectively. This comparison is shown in Fig. 3 for the B_{c2} data for different criteria. (The GL model with fixed experimental values of $B_{c2\parallel}=1.5$ T and $B_{c2\perp}=0.3$ T is also shown for the $B_{inflection}$ data.) Here, the Tinkham model appears to best describe the data.

We now summarize our experimental findings for CaC_6 by discussing the B_{c2} anisotropy, the linear B_{c2} temperature dependence, and the Fermi liquid character, in turn.

The estimated c-axis coherence length $\xi_\perp(0)$, from Fig. 2, is in the range 4.7–13 nm (using the B_{normal} and B_{zero} criteria). Even with the smallest estimate for $\xi_\perp(0)$, the unit cell spacing is still about 3.5 times smaller (even ten times smaller for the graphene layer spacing),[30] and it is surprising that the Tinkham model describes so well the cusp-like behavior for B_{c2} in Fig. 3. (Compare, for instance, with the clear GL behavior seen in $NbSe_2$.[31]) It is possible that the nonzero background resistance in the superconducting state may play a role since it indicates that some layers are not stoichiometrically intercalated and that these normal layers, in series with the superconducting layers, contribute to the resistance. However, all other indications are that the samples are bulk superconductors with optimum T_c and B_{c2} values, so it is not clear that a small number of nonsuperconducting layers would induce the Tinkham-like behavior near $B_{c2\parallel}$.

The critical fields follow a linear dependence on temperature. A theory to understand the mechanism of superconductivity in GICs has been proposed by Al-Jishi,[10] where superconductivity arises from a coupling between the graphene π bands and the intercalant layer s band. This model predicts a linear dependence of the critical field on temperature,[8] but is valid only in the weak-coupling regime ($\lambda < 0.4$). However, our results indicate that CaC_6 is in the intermediate coupling regime. Although other models have recently been proposed to explain the origin of superconductivity in CaC_6,[12,23,34] there is no quantitative explanation [other than the simple GL expression in Eq. (4)] for the linear dependence of the upper critical field. The linear H_{c2} behavior to very low temperatures is not expected from the standard BCS theory.[35] However, this behavior has been seen in other compounds such as K_3C_{60},[36] which has a very anisotropic Fermi surface. Fermiology experiments in CaC_6 can clarify this possibility.

The low temperature T^2 Fermi-liquid-type dependence of the resistivity is consistent with the description of CaC_6 as a BCS-like superconductor. Penetration depth measurements[37] and heat capacity experiments[7] have shown that the superconductivity is s wave and BCS-like, respectively. It is surprising that such a large T_c of 11.5 K is observed, but given the large coupling parameter deduced from our measurements (and, recently, through specific heat experiments[7]), it is likely that the origin of the superconductivity is through finely tuned electron-phonon interactions. We have calculated the Kadowaki-Woods ratio for CaC_6 based on the T^2 coefficient ($A=7.4\times10^{-9}\ \Omega\,\text{cm}/\text{K}^2$ from the inset of Fig. 1) divided by the square of the linear heat capacity coefficient from recent measurements ($\gamma=5.91\ \text{mJ}^2/\text{mol}^2\,\text{K}^2$)[7] to yield $r_{KW}=1.6\times10^{-4}\ \mu\Omega\,\text{cm}(\text{mol K}/\text{mJ})^2$. r_{KW}, which is a measure of the electron-electron scattering, is over ten times the value found in heavy fermion compounds [$a_0=10^{-5}\ \mu\Omega\,\text{cm}(\text{mol K}/\text{mJ})^2$].[38] The only other value which is larger than this in the literature is for $Na_{0.7}CoO_2$, where $r_{KW}=50a_0$.[39] Since heat capacity is isotropic, in-plane and interplane conduction measurements are needed in CaC_6 for a complete comparison.[39]

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