Abstract Muon spin rotation (μSR) experiments were performed on the intercalated graphite CaC₆ in the normal and superconducting state down to 20 mK. In addition, AC magnetization measurements were carried out resulting in an anisotropic upper critical field $H_{c2}$, from which the coherence lengths $\xi_{ab}(0) = 36.3(1.5)$ nm and $\xi_c(0) = 4.3(7)$ nm were estimated. The anisotropy parameter $\gamma^H = H_{c2}^{ab}/H_{c2}^{c}$ increases monotonically with decreasing temperature. A single isotropic $s$-wave description of superconductivity cannot account for this behavior. From magnetic field dependent μSR experiments, the absolute value of the in-plane magnetic penetration depth $\lambda_{ab}(0) = 78(3)$ nm was determined. The temperature dependence of the superfluid density $\rho_s(T)$ is slightly better described by a two-gap than a single-gap model.

Keywords Superconducting materials · Penetration depth · Muon spin rotation and relaxation

1 Introduction

The field of graphite intercalation compounds (GICs) gained attention after the discovery of the superconductor CaC₆ with a rather high value of the superconducting transition temperature $T_c \simeq 11.5$ K [1]. Superconductivity in GICs was first reported in the potassium-graphite compound KC₈ with $T_c \simeq 0.14$ K [2]. Until the discovery of the superconductor CaC₆, the highest $T_c$ was observed in KTi₅C₃ with $T_c \simeq 2.7$ K, synthesized under ambient pressure [3]. However, high pressure synthesis was found to increase $T_c$ up to 5 K in metastable compounds such as NaC₂ and KC₃ [4, 5]. According to experimental and theoretical work, CaC₆ can be described as a classical BCS superconductor with a single isotropic gap $\Delta_0 \simeq 1.7$ meV [6, 7]. The upper critical field $H_{c2}$ shows a remarkable anisotropy with zero temperature values $\mu_0 H_{c2}^{ab}(0) \simeq 0.3$ T and $\mu_0 H_{c2}^{c}(0) \simeq 1.9$ T, for the external field $H$ parallel to the $c$-axis or parallel to the $ab$-plane, respectively [8]. A recent ARPES study indicated the existence of a possible second superconducting gap [9] with a small zero temperature value $\Delta_{0,2} \simeq 0.2(2)$ meV. Tunneling experiments [10] gave strong indications for the existence of a superconducting anisotropic $s$-wave gap in CaC₆, providing different zero temperature gap values for changing current injection directions, $\Delta_0^c \simeq 1.7$ meV and $\Delta_0^{ab} \simeq 1.44$ meV. The muon-spin rotation (μSR) technique is a powerful method to characterize the superconducting gap symmetry in superconductors [11]. μSR measurements down to very low temperatures may allow to access a possible second small gap, which should manifest itself in the low temperature superfluid density in terms of an inflection point [11]. A recent μSR study [12] supports a single gap isotropic $s$-wave description of superconductivity in CaC₆, although the low temperature region was not studied. In this work, we present extended measurements down to 20 mK and investigate possible order parameter symmetries (single-gap isotropic $s$-wave, single-gap anisotropic $s$-wave, two-gap isotropic $s$-wave) by means of μSR experiments.
studies [1, 6, 7]. The temperature dependence of the upper critical field components \(H^c_{ab}(T)\) and \(H^a_{ab}(H||ab)\) are displayed in Fig. 1b. The values of the \(H^c_{ab}\) and \(H^a_{ab}\) were determined from AC magnetization using the procedure illustrated in Fig. 1a. The upper critical field is anisotropic and follows the temperature dependence as reported in [8] and [14]. In the framework of the anisotropic Ginzburg–Landau theory, the upper critical field for \(H||c\) and \(H||ab\) is given by

\[
\mu_0 H^c_{ab}(0) = \frac{\phi_0}{2\pi \xi_{ab}(0) \xi_c(0)},
\]

\[
\mu_0 H^a_{ab}(0) = \frac{\phi_0}{2\pi \xi_{ab}^2(0)},
\]

where \(\phi_0 = h/2e = 2.07 \times 10^{-15} \text{ T m}^2\) is the flux quantum, and \(\xi_{ab,c}\) are the corresponding coherence length components at zero temperature. With the linearly extrapolated values of the upper critical field at zero temperature, \(\mu_0 H^c_{ab}(0) = 2.1(3) \text{ T}\) and \(\mu_0 H^a_{ab}(0) = 0.25(2) \text{ T}\), and in the equation above we obtain \(\xi_{ab}(0) = 36.3(1.5) \text{ nm}\) and \(\xi_c(0) = 4.3(7) \text{ nm}\). These values are comparable to earlier reports such as resistivity measurements (\(\xi_{ab}(0) = 29.0 \text{ nm}\) and \(\xi_c(0) = 5.7 \text{ nm}\)) [8], or susceptibility studies (\(\xi_{ab}(0) = 35 \text{ nm}\) and \(\xi_c(0) = 13 \text{ nm}\)) [15]. Remarkably, the upper critical field \(H^c_{ab}\) shows a positive curvature in the studied temperature region which was not observed in previous investigations. A similar positive curvature was observed near \(T_c\) in MgB\(_2\) [16] where it was explained by a two-gap model. However, we should keep in mind that other explanations are also possible. Complementary experiments, such as studies of the superfluid density, as performed in this work, are necessary to draw definite conclusions. The temperature dependence of the upper critical field anisotropy \(\gamma_H = H^c_{ab}/H^c_{ab}\) is shown in the inset of Fig. 1b. We interpolated the measured upper critical field values with a third order polynomial and determined the ratio \(\gamma_H\). The anisotropy parameter \(\gamma_H\) increases monotonically with decreasing temperature, showing a similar temperature dependence as with MgB\(_2\) [17]. Note that a single gap isotropic s-wave description of superconductivity cannot account for this behavior of \(\gamma_H(T)\).

\(\mu\)SR experiments were carried out at the \(\pi\)M3 beamline using the GPS (General Purpose Spectrometer) and the LTF (Low Temperature Facility) spectrometers at the Paul Scherrer Institute PSI Villigen, Switzerland. Six pieces of CaC\(_6\) forming an area of \(\simeq 10 \times 14 \text{ mm}^2\) were used in the experiment. In the intercalation process, the Ca atoms penetrate from the side of the graphite sample and diffuse along the \(ab\)-plane. Reducing the sample size in the \(ab\)-direction favors Ca diffusion, and consequently leads to a higher sample
and after the $\mu$SR experiments, the same piece of CaC$_6$ was measured in the AC susceptometer, where no difference was observed by comparing the two measurements.

In the vortex state of a type II superconductor, the muons probe the inhomogeneous local magnetic field distribution $P(B)$ due to the vortex lattice [18]. From the second moment $\langle B^2 \rangle$ of $P(B)$, the in-plane magnetic penetration depth $\lambda_{ab}$ can be extracted according to the relation $\langle B^2 \rangle = C\lambda_{ab}^{-2}$ ($C$ is a field dependent quantity) from which the superfluid density $\rho_s \propto \lambda_{ab}^{-2}$ can be extracted [19]. Thus, $\mu$SR provides a direct method to measure the superfluid density in the mixed state of a type II superconductor. Figure 2a shows the $\mu$SR asymmetries $A(t)$ recorded in LTF in zero magnetic field above $T_c$ and at 20 mK. The two time spectra overlap, indicating the same magnetic ground state at both temperatures. The time dependence of the asymmetry can be described by the static Kubo–Toyabe formula, showing only the presence of randomly distributed nuclear magnetic moments, but no realization of magnetism. Figure 2b shows the $\mu$SR asymmetries taken at 15 K and at 20 mK in a field of $\mu_0 H = 80$ mT. A clear damping of the $\mu$SR signal at 20 mK is visible, which can be ascribed to the presence of the vortex lattice. For a detailed description of $\mu$SR studies of the vortex state in type II superconductors, see, e.g., [18]. The $\mu$SR time spectra were fitted to the following expression:

$$A^{TF}(t) = A_{SC}e^{(\sigma_{SC})^2/2} \cos(\gamma_\mu B_{SC}t + \phi) + A_{bg}e^{(\sigma_{bg})^2/2} \cos(\gamma_\mu B_{bg}t + \phi) + A_{Ag} \cos(\gamma_\mu B_{Ag}t + \phi)$$

(2)

Here, the indices SC, bg and Ag denote the sample (superconductor), the background arising from possible non-superconducting parts of the sample and the nonrelaxing silver background, respectively. $A$ denotes the initial asymmetry, $\sigma$ is the Gaussian relaxation rate, $\gamma_\mu = 2\pi \cdot 135.5342$ MHz/T is the muon gyromagnetic ratio, $B$ is the average magnetic field at the $\mu^+$ stopping site, and $\phi$ is the initial phase of the muon-spin ensemble. A set of $\mu$SR data were fitted simultaneously with $A_{SC}$, $A_{bg}$, $A_{Ag}$, $B_{bg}$, $B_{Ag}$, $\sigma_{bg}$, and $\phi$ as common parameters, and $B_{SC}$ and $\sigma_{SC}$ as free parameters for each temperature. The same expression was used to analyse the data recorded with the GPS spectrometer (here no silver background signal was present).

The analysis of the field dependence of the measured $\mu$SR relaxation rate $\sigma_{SC}$ allows to estimate the absolute value of the in-plane magnetic penetration depth $\lambda_{ab}$, assuming that CaC$_6$ can be described as a single isotropic $s$-wave gap superconductor. The measured values of $\sigma_{SC}$ are plotted in Fig. 3. To analyze our data, we used the formula

![Figure 2](image-url)
developed by Brandt [19]:

$$
\sigma_{\text{SC}} \simeq 0.172 \gamma_s \frac{\Phi_0}{2\pi} \left( 1 - \frac{B}{B_{c2}} \right) \times \left[ 1 + 1.21 \left( 1 - \frac{B}{B_{c2}} \right)^3 \right] \lambda_{ab}^{-2}, \quad (3)
$$

Although the formula was derived for high $\kappa$ type II superconductors ($\kappa \geq 5$), it was suggested to work also for low values of $\kappa$ at magnetic fields $\sqrt{B/B_{c2}} \geq 0.5$ [12]. From the measured $\mu$SR relaxation rates $\sigma_{\text{SC}}$ and (3), one obtains $\lambda_{ab}(0) = 78(3) \text{ nm}$ and $B_{c2}(0) = 170(5) \text{ mT}$. The solid line in Fig. 3 represents the corresponding fit (the point at 200 mT was not included in the fit). To estimate the Ginzburg–Landau parameter $\kappa$, we use our values of $\xi_{ab}(0) = 36.3(1.5) \text{ nm}$ and $\lambda_{ab}(0) = 78(3) \text{ nm}$ giving $\kappa \approx 2.1$. It is worth to mention that the value of $B_{c2}$ is smaller than that estimated from the AC magnetization measurements ($B_{c2}(0) \approx 250 \text{ mT}$).

It is generally assumed that the superfluid density $\rho_s$ is related to the in-plane magnetic penetration depth $\lambda_{ab}$ by the simple relation $\rho_s \propto \lambda_{ab}^{-2}$. However, for magnetic fields close to $B_{c2}$ this proportionality must be corrected because the order parameter $\psi(r)$ is reduced due to the overlapping vortices. In this case, the spatial average of the superfluid density is given by [12]:

$$
\rho_s(T) \simeq \langle |\psi(r)|^2 \rangle \lambda_{ab}^{-2}(T) \simeq \left( 1 - B/B_{c2}(T) \right) \lambda_{ab}^{-2}(T). \quad (4)
$$

where $\langle \ldots \rangle$ means the spatial average. Values of $\lambda_{ab}^{-2}$ were calculated using (3) and for the values of $B_{c2}$ we used the results of our AC magnetization measurements (see Fig. 1b). The temperature dependence of the superfluid density $\rho_s(T)$ determined at 80 mT is plotted in Fig. 4. We analyzed $\rho_s(T)$ using three different models: (i) single-gap isotropic s-wave (ii) single-gap anisotropic s-wave, and (iii) two-gap isotropic s-wave. To calculate the temperature dependence of the magnetic penetration depth within the local approximation ($\lambda \gg \xi$), we applied the following formula [20, 21]:

$$
\rho_s(T) = \rho_s(0) \times \sqrt{\frac{1}{\sin^2(\Delta(T/\Phi)^{1/2})}}, \quad (5)
$$

where $\rho_s(0)$ is the zero temperature value of the superfluid density, $\Delta = [1 + \exp((E - E_F)/k_B T)]^{-1}$ is the Fermi function, $\Phi$ is the angle along the Fermi surface, and $\Delta(T, \Phi) = \Delta(0) h(T/T_c) g(\Phi)$. The temperature dependence of the gap is expressed by $h(T/T_c) = \tanh(1.82[1.018(T_c/T - 1)]^{0.51})$ [22]. For the isotropic s-wave gap (i) $g^s(\Phi) = 1$ and for the anisotropic s-wave gap (ii) $g^a(\Phi) = (1 + a \cos 4\Phi)/(1 + a)$, where $a$ denotes the anisotropy of the gap. The two-gap fit was calculated using the so called $\alpha$-model and assuming that the total superfluid density is the sum of the two components [21, 22]:

$$
\rho_s(T) = \rho_s(0) \left( \frac{\rho(T, \Delta_{01})}{\rho(0, \Delta_{01})} + (1 - \omega) \frac{\rho(T, \Delta_{02})}{\rho(0, \Delta_{02})} \right). \quad (6)
$$

Here, $\Delta_{01}$ and $\Delta_{02}$ are the zero temperature values of the larger and the smaller gap, and $\omega$ ($0 \leq \omega \leq 1$) is a weighting factor representing the relative contribution of the larger gap to $\rho_s$. The results obtained for the different models are plotted in Fig. 4. The black line represents the result for...
the single $s$-wave gap model (i) with $\rho_s(0) = 96.5(5) \mu m^{-2}$, $\Delta_0 = 0.79(1) meV$, $T_c = 6.80(2) K$, and $2\Delta_0/k_BT_c = 2.70(5)$, describing CaC$_6$ as weak coupling BCS superconductor. The reduction of $T_c$ agrees well with our AC magnetization measurements for 80 mT. The blue, dotted line represents the anisotropic $s$-wave gap analysis (ii) with $\Delta_0 = 0.81(1) meV$ and $a \simeq 0.37$ for the gap anisotropy. These values do not agree with the reported ones from tunneling experiments ($\Delta_0^s \simeq 1.7 meV$ and $\Delta_0^{ab} \simeq 1.44 meV$) [10].

The two-gap analysis (iii) (red, dashed line) yields $\Delta_{0,1} = 0.85(2) meV$ for the larger gap and $\Delta_{0,2} = 0.23(1) meV$ for the smaller one. Only $\sim 9.4(3)\%$ of the superfluid density is associated with the smaller gap. The smaller gap agrees with $\Delta_{0,2} = 0.2(2) meV$ reported in [9]. Our larger gap value is significantly smaller ($\Delta_{0,1} = 1.9(2) meV$). Although the best agreement is found for the two-gap scenario, no final conclusion can be drawn from this analysis. All three scenarios describe the observed temperature dependence of the superfluid density. For a direct comparison with [12], we omitted the values of $\rho_s(T)$ below 2 K. In this case, the single $s$-wave gap fit yields $\rho_s(0) = 91.6(9) \mu m^{-2}$, $\Delta_0 = 0.84(1) meV$, $T_c = 6.75(2) K$, and $2\Delta_0/k_BT_c = 2.90(5)$. The values presented in [12] are: $\rho_s(0) = 85.1(3) \mu m^{-2}$, $\Delta_0 = 0.868(5) meV$, and $2\Delta_0/k_BT_c = 3.6(1)$. The higher applied magnetic field (120 mT in [12]) may account for the differences. Here, one should point out that our low temperature data are essential to determine the zero temperature values of $\rho_s$ and $\Delta$.

3 Conclusions

In conclusion, we carried out extensive AC magnetization measurements to map the temperature dependence of the upper critical field $H_{c2}^{ab}$ and $H_{c2}^{c}$ in CaC$_6$ and to evaluate the coherence length. The values of $\xi_{c}(0) = 36.3(1.5) nm$ and $\xi_{ab}(0) = 4.3(7) nm$ are in good agreement with those reported previously [8, 15]. We found that the upper critical field anisotropy $\gamma_H = H_{c2}^{ab}/H_{c2}^{c}$ increases with decreasing temperature. From magnetic field dependent $\mu$SR experiments, the absolute value of the in-plane magnetic penetration depth was determined to be $\lambda_{ab} \simeq 78(3) nm$, in agreement with previously reported values [7, 12]. Furthermore, low temperature $\mu$SR experiments were performed in order to map the whole temperature dependence of the superfluid density $\rho_s(T)$. We analyzed the temperature dependence of $\rho_s$ with three different models: (i) single-gap isotropic $s$-wave, (ii) single-gap anisotropic $s$-wave, and (iii) two-gap isotropic $s$-wave. All models describe the measured $\mu$SR data almost equally well, although a slightly better agreement was achieved using the two-gap model.

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