Evidence for gap anisotropy in CaC$_6$ from directional point-contact spectroscopy

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We present the first results of directional point-contact spectroscopy in high quality CaC$_6$ samples both along the $ab$ plane and in the $c$-axis direction. The superconducting order parameter $\Delta(0)$, obtained by fitting the Andreev-reflection (AR) conductance curves at temperatures down to 400 mK with the single-band 3D Blonder-Tinkham-Klapwijk model, presents two different distributions in the two directions of the main current injection, peaked at 1.35 and 1.71 meV, respectively. By ab-initio calculations of the AR conductance spectra, we show that the experimental results are in good agreement with the recent predictions of gap anisotropy in CaC$_6$.

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The discovery of a relatively “high-$T_c$” superconductivity in graphite intercalated with Ca$^1,2$, Yb$^1$, and, very recently, Sr$^3,4$ has strongly revived the interest in the Graphite Intercalated Compounds (GICs) and their physics. The Ca-intercalated graphite, CaC$_6$, with its “record” $T_c$ of about 11.5 K, in particular, has been the subject of various theoretical and experimental investigations in the past two years (for a short review of the initial results see$^5$). One of the most important questions, however, is still not clear: what is the magnitude and anisotropy of its superconducting gap? The first experiments (STM, penetration depth, specific heat) on CaC$_6$ have evidenced a single, apparently isotropic, s-wave gap with a ratio $2\Delta/k_BT_c$ of the order of the BCS value$^6,7,8$. Recent tunnel spectroscopy results, on the other hand, claimed the presence of an isotropic gap with a magnitude more than 40% higher than that reported earlier$^8$. The spread of gap values measured up to now range between 1.6 meV$^6$ and 2.3 meV$^9$. The important point is that all these experiments have either probed a bulk property$^8$ or a directional one along the $c$-axis direction$^3,7,9$. As pointed out in Ref.$^8$ the presence of anisotropic or two-gap superconductivity in CaC$_6$ cannot be ruled out until tunneling or point-contact measurements are performed also along the $ab$ direction.

On the other hand, recent first-principles density functional calculations of the superconducting properties of CaC$_6$ have supported the presence of a moderately anisotropic gap which varies between 1.1 and 2.3 meV, depending on the $k$-point and the $\pi$ or interlayer (IL) sheet of the Fermi surface (FS) involved$^{11}$. Such an anisotropy can be revealed by directional spectroscopy measurements performed along both $c$ and $ab$ direction.

In this paper we present the results of point-contact Andreev-reflection (PCAR) spectroscopy performed on high-quality bulk samples of CaC$_6$$^8$. By using a special technique to realize the contacts, that proved very successful and effective in the case of MgB$_2$$^{11,12}$, we were able to perform directional PCAR spectroscopy at very low temperature both along the $ab$ plane and the $c$-axis direction. Two different gap distributions in the two directions can reproducibly be extracted from the experimental data. When compared to the results of new first-principles calculations these findings unequivocally prove the anisotropy of the superconducting gap in CaC$_6$.

The high-quality CaC$_6$ bulk samples used for our measurements were synthesized by reacting highly oriented pyrolytic graphite (with a spread of the $c$ axis orientation $\leq 0.4^\circ$) for several weeks at 350°C with a molten alloy of Li and Ca$^8$. The resulting CaC$_6$ samples have a shiny golden surface. They are very sensitive to air and moisture which rapidly damage the sample surfaces. X-ray analysis has shown mainly the CaC$_6$ reflections with a small (<5%) contribution from impurity phases. Further details on the characterization of the samples may be found in Ref.$^8$. All samples used for PCAR spectroscopy (size $\approx 1\times1\times0.2$ mm$^3$) were selected to have a very sharp superconducting transition ($\Delta T_c(100\%-90\%) = 0.1$ K) with the onset at $T_c = 11.4$ K.

The point contacts were made by using a non-conventional technique we called “soft” PCAR spectroscopy$^{11,12}$. Instead of using the standard metallic tip, a very small ($\varnothing \approx 50$ μm) drop of Ag conductive paint, put on the etched or freshly cleaved surfaces of the sample is used as a counter electrode. Such contacts are particularly stable both in time and towards temperature variations and they allow to inject the current mainly perpendicular to the contact plane. A fine tuning of the junction characteristics at low temperature can be done by applying short voltage or current pulses. Further details on the technique can be found in Refs.$^{11,13}$

Due to the mentioned high sensitivity of CaC$_6$ samples’
surface to air, the room-temperature preparation of the contact was done inside a sealed glove bag filled with pure He gas or in a glove box with Ar atmosphere. After the contact was made the junction was very rapidly transferred to the cryostat in a sealed container. Contacts were made either on the flat ab-plane surface or on the narrow lateral side of the samples. Referring to the main direction of current injection, we call them c-axis and ab-plane contacts, respectively (see insets of Fig. 1).

The conductance curves, \(dI/dV\) vs. \(V\), were obtained by numerical differentiation of the measured \(I-V\) curves and subsequently normalized by dividing them by the normal-state conductance measured at \(T \geq T_c\). For this reason, in all the contacts, we therefore carefully studied the temperature dependence of the conductance in order to determine the critical temperature of the junction, i.e. the ‘Andreev critical temperature’, \(T^A_c\). In an overall of 35 different contacts, \(T^A_c\) was found to be 11.3±0.1 K, in best agreement with the bulk \(T_c\)’s of the samples and in contrast with a previous report [6]. This fact proves the high quality of samples and surfaces in the contact region. For simplicity, we will therefore refer to the critical temperatures of the contacts as \(T_c\) in the following.

Fig. 1 shows several raw conductance curves as function of bias voltage measured both in ab-plane contacts (a) and in c-axis ones (b) at 4.2 K. The curves show clear Andreev-reflection (AR) features, an almost flat conductance (at \(V > 8 - 10\) meV) and no dips that usually are a sign of the failure in reaching the conditions for pure ballistic conduction in the contact [14, 15]. The normal resistance \(R_N\) of all the good contacts is between 0.75 and 6.4 Ω. By knowing the mean free paths and the residual resistivities of CaC\(_6\) along the ab plane and in the c-axis direction, i.e. \(\ell_{ab} = 74\) nm, \(\ell_c = 4.7\) nm, \(\rho_{ab} = 0.8\) μΩ cm and \(\rho_{c} = 24\) μΩ cm [16, 17], we can apply the Sharvin formula for the contact resistance in the ballistic regime in order to determine the contact radius \(a = (A\rho_0\ell/3\pi R_N)^{0.5}\) [18]. The condition for full ballistic transport (\(a \ll \ell\)) is totally verified in ab-plane contacts, where \(a_{ab} \approx 6 - 18\) nm. In c-axis junctions, where \(a_c \approx 14 - 24\) nm but the conductance curves do not show any sign of heating [13], the presence of at least 30 parallel contacts in the junction area is expected.

After normalization, the conductance curves were fitted to the modified 3D Blonder-Tinkham-Klapwijk (BTK) model [18, 19, 20]. In the single-band form it contains three fitting parameters: The gap \(\Delta\), the barrier-height parameter \(Z\) and the broadening \(\Gamma\) which accounts for both intrinsic (quasiparticle lifetime) and extrinsic phenomena that broaden the AR conductance [14].

In order to increase the experimental resolution of our measurements we decided to perform part of the PCAR experiments at very low temperature in a Quantum Design measurement system (PPMS) with \(^4\)He insert.

Fig. 2 (a) shows the normalized conductance curves (circles) of a typical ab-plane contact at various temperatures from 400 mK up to \(T_c\). At any temperature the single-band 3D BTK model fits the data very well (solid lines). At the lowest \(T\), the values of the fitting parameters are: \(\Delta = 1.44\) meV, \(\Gamma = 0.61\) meV and \(Z = 0.75\). In panel (c) we display the order parameter \(\Delta\) obtained from the data given in (a). Its temperature dependence almost perfectly follows the BCS-like expression (solid line) with \(2\Delta(0)/k_BT_c = 2.98\) which is sensibly smaller than expected from BCS theory.

In Fig. 2 (b) and (d) we report the same data for a c-axis contact. As for the ab-plane case, the curves are well fitted by the single-band 3D BTK model which gives at 400 mK: \(\Delta = 1.7\) meV, \(\Gamma = 0.84\) meV and \(Z = 0.97\). The temperature dependence of \(\Delta\) is very close to the expected BCS one with a ratio \(2\Delta(0)/k_BT_c = 3.48\), in best agreement with the weak-coupling BCS value.

It is worth noticing that the \(Z\) values observed in c-axis contacts (between 0.74 and 1.01) are systematically greater than those of ab-plane contacts (between 0.48 and 0.75). According to the 3D BTK model [20], this difference can be explained by the different Fermi velocities of CaC\(_6\) in the ab plane (\(v_{ab} = 0.54 \times 10^5\) m/s) and along c axis (\(v_c = 0.29 \times 10^5\) m/s), thus confirming the directionality of our point contacts.

The AR curves shown in Fig. 1 and 2 are rather small in amplitude, as already observed in all the “soft” PCAR measurements on MgB\(_2\) and related compounds [11, 12, 13], resulting in \(\Gamma\) values substantially greater than those expected for the quasiparticle lifetime. As recently observed in lithographically fabricated Cu-Pt-Pb nanocontacts [21], this additional broadening can be explained by the presence of pair-breaking effects induced by the scattering in a thin disordered layer present at the NS interface. This is the case of our point contacts, due to a disordered layer on the surface of Ag grains that also makes the residual resistivity of the paint be five orders of magnitude greater than in pure Ag.

The reproducibility of the PCAR data was very good. Most of the contacts, obtained both in \(^4\)He and in \(^3\)He
cryostat, show $dI/dV$ curves and temperature dependencies of quality similar to that presented in Fig. 2. In 15 $ab$-plane contacts the order parameter $\Delta(0)$ ranged between 1.1 meV and 1.7 meV with the distribution shown in Fig. 3 (a). In 14 $c$-axis contacts $\Delta(0)$ ranged between 1.3 meV and 1.94 meV with the distribution shown in Fig. 3 (b). The figure also shows the Gaussian curves that best fit the distributions. They are peaked at $1.3 \text{meV}$ and $1.94 \text{meV}$ with the distribution respectively, as determined from the BTK fits shown in (a) and (b). Solid lines are the BCS-like fits.

However, the clear difference observed between the most probable $\Delta(0)$ values in $ab$-plane and $c$-axis contacts provides strong evidence for a gap anisotropy in CaC$_6$.

In order to compare our results with the theoretical predictions of gap anisotropy in CaC$_6$ we calculated the Andreev-reflection conductance curves by first-principles methods. We have a SN junction where $S = \text{CaC}_6$ and $N = \text{Ag}$. Let’s label with the suffix $i = 1, 2, 3$ the three sheets of the CaC$_6$ Fermi surface (FS) ($\pi$ and interlayer (IL) bands). If $\mathbf{n}$ is the unitary vector in the direction of the injected current, $v_{ik,n} = v_{ik} \cdot \mathbf{n}$ are the corresponding components of the Fermi velocities in the superconductor at wave vector $\mathbf{k}$ for band $i$-th. Taking into account that Ag has a quasi-spherical FS and an almost constant Fermi velocity $v_F \neq v_{ik}$, the corresponding quantity in the normal metal will be $v_{N,n} = v_N$. Following Refs. 22, 23 we finally obtain the total AR conductance as:

$$\sigma(E,n) = \frac{\sum_i \langle \sigma_{ikn} \rangle \langle \frac{v_{ik,n}^2}{v_{ik}[v_{ik,n}+v_N]^2} \rangle_{FS_i}}{\sum_i \langle \frac{v_{ik,n}^2}{v_{ik}[v_{ik,n}+v_N]^2} \rangle_{FS_i}}$$

where: $\langle \cdot \rangle_{FS_i}$ is the integral over the $i$-th FS, i.e.

$$\langle \frac{v_{ik,n}^2}{v_{ik}[v_{ik,n}+v_N]^2} \rangle_{FS_i} = \int_{v_{ik,n}>0} \frac{v_{ik,n}^2}{v_{ik,n}^2+v_N^2} S(E_{ik}) d^3 k.$$

$\sigma_{ikn}(E)$ is the BTK conductance of the $i$-th band expressed in terms of the quantities $N_{ik}^p(E) = E/\sqrt{E^2 - \Delta_{ik}^2}$ and $N_{ik}^}\Delta(E) = \Delta_{ik}/\sqrt{E^2 - \Delta_{ik}^2}$ (whose real parts are the quasiparticle and the pair density of states in the same band, respectively) and of $Z_n$ values. $\Delta_{ik}$ is the gap value for band $i$-th at point $\mathbf{k}$ over the FS, recently calculated from first principles [10]. The values of $Z_n$ used in the calculation are taken similar to those of the curves shown.
However, for Γ(Ca) gap becomes more important and the conductance as expected from the shape of the FS, the role of the IL gap at about 1.38 meV and a broad shoulder (mainly associated with Ca FS) in the theoretical calculations. This fact appears reasonable if one considers that the first-principle calculations of Ref. [10] led to an underestimation of Tc of about 17%.

In conclusion, the first directional PCAR measurements in CaC6 carried out also at T = 400 mK both along the ab-plane and the c-axis direction give strong and reproducible evidence of the predicted anisotropic nature of the superconducting gap in this GIC. New first-principles calculations of the expected anisotropy in the AR conductance curves fully support this conclusion and indicate that the actual gap anisotropy in CaC6 could be even slightly greater than theoretically predicted.

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