Evidence for gap anisotropy in CaC_6 from far-infrared and point-contact spectroscopy

J.S. Kim and R.K. Kremer;
U. Nagel, D. Hüvonen, E. Joon and T. Rõõm (NICPB, Tallinn, Estonia); R.S. Gonnelli, D. Daghero, D. Delaude, M. Tortello and G.A. Ummarino (Politecnico di Torino, Italy);
V.A. Stepanov (P.N. Lebedev Physical Institute, Moscow, Russia);
A. Sanna (Università degli Studi dell'Aquila, Italy and Freie Universität Berlin);
G. Profeta (Università degli Studi dell'Aquila, Italy);
S. Massidda (Università degli Studi di Cagliari, Italy)

About three years ago Weller *et al.* reported superconductivity in alkaline earth intercalated graphite AEC_6 (AE = divalent alkaline earth) with T_c's up to 11.5 K for CaC_6, significantly higher than that of of the alkali metal intercalated graphite phases studied before. This discovery stimulated much research on the investigation of their properties as well as the search for new superconducting graphite intercalated compounds (GICs). In this effort our group has successfully prepared samples of these new AE GICs and investigated experimentally and theoretically (in close collaboration with Abt. Andersen of our Institute) their superconducting properties. Also we discovered SrC_6 as a new superconductor ($T_c = 1.65$ K) in this series [1,2].

One of the most important parameters of a superconductor is the superconducting gap $\Delta(T)$, especially its magnitude and temperature dependence. Several early experiments on CaC_6 evidenced a single, isotropic, *s*-wave gap with a ratio $2\Delta/k_BT_c$ close to that expected from weak-coupling BCS theory. Tunneling spectroscopy investigations, on the other hand, pointed to an isotropic gap with a magnitude more than 40% higher than that found before, establishing an unsatisfying rather large uncertainty for the superconducting gap $\Delta(0)$ ranging from $2\Delta(0) = 3.2$ to 4.6 meV. However, all techniques employed to measure the gap so far, were either bulk techniques and could not distinguish between in-plane and out-of-plane gap or probed the gap along the *c*-axis direction.

On the other hand, recent first-principles density functional calculations of the superconducting properties of CaC_6 have predicted the presence of a moderately anisotropic gap which varies between $2\Delta(0) = 2.2$ meV and 4.6 meV, depending on the position in the Brillouin zone and which part of the Fermi surface (π or interlayer sheets) mediate the Cooper pairing. Another aspect of the gap properties of CaC_6 which was also widely debated and never conclusively ruled out was the possibility of two or multi-band superconductivity.

To investigate the superconducting gap in CaC_6, especially with respect to a non-isotropic and multi-band character, we have carried out detailed far-infrared terahertz spectroscopy as well as point-contact Andreev reflection spectroscopy parallel and perpendicular to the *c*-axis direction on high-quality samples of CaC_6.

In superconductors infrared photons with energy larger than 2Δ break Cooper pairs in a process of scattering off impurities and create pairs of quasiparticles. This scattering leads to a step-like feature in the reflectance spectra. This step as the characteristic signature of the opening of the superconducting gap increases along with increasing scattering rate of the quasiparticles.

In the superconducting state the infrared zero-angle reflectance spectra of CaC_6 show such step-like features below ≈ 4 meV. The amplitude of the step is largest at ≈ 3 K. The onset shifts to lower energies and the amplitude decreases as the temperature approaches T_c. Figure 1 shows the reflectance at 6 K normalized to the reflectance in the normal state at 15 K. In order to obtain information about the superconducting gap and its temperature dependence, the zero-angle reflectance spectra were fitted by using well-known relations between the complex dielectric constant $\varepsilon(\omega)$ and the

complex conductivity $\sigma(\omega)$ assuming a Drude-type conductivity in the normal state and results for a BCS (Bardeen-Cooper-Schrieffer) superconductor using $\Delta(0)$, T_c and the scattering rate γ as fitting parameters. As additional input parameters for the fit a dc-conductivity $\sigma_{dc} \approx 1\,\mu$S/cm, consistent with the dc-resistivity measurements and a dielectric constant ε_∞, were used. The resulting fit with a single BCS gap with $2\Delta(0) = 2.8$ meV shown as a dotted line in Fig. 1 reveals some deviations which can be markedly reduced if an anisotropic gap is used.

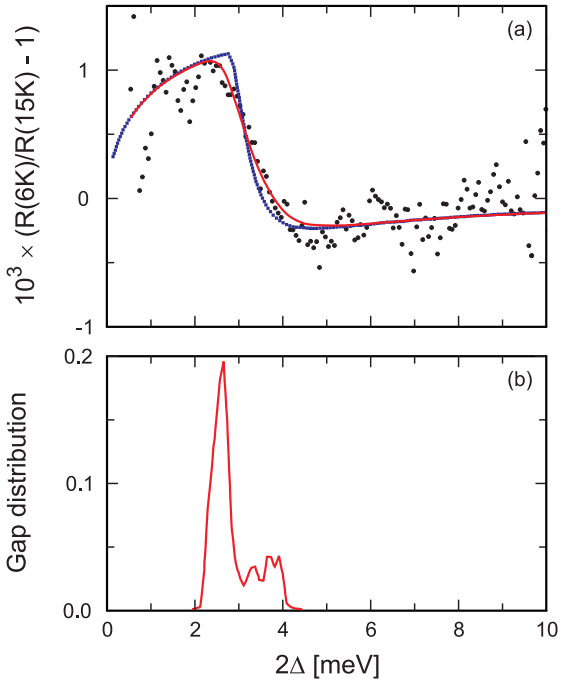

Figure 1: (a) Reflectance of CaC_6 at 6 K relative to its reflectance at 15 K. The solid line represents he best fit using a normalized gap distribution according to Sanna *et al.* [3] with the energy scaled by a factor of 0.94 (panel (b)) (details see [4]). The dotted line is the reflectance calculated by assuming an isotropic BCS gap of $2\Delta = 2.8$ meV.

For this the formalism was extended by assuming that the conductivity in the superconducting state results from a superposition of conductivities according to

$$\sigma_{sc}(\omega) = \sum_i f(2\Delta_i)\sigma_{sc}(\omega, 2\Delta_i) / \sum_i f(2\Delta_i),$$

where $f(2\Delta_i)$ is the distribution function of the gaps according to Sanna *et al.* [3] scaled by a factor $0 \le s(T) \le 1$ which transforms each gap value according to $\Delta(T) = s(T)\,\Delta(0)$ (see Fig. 1(b)) and details in [4]). Using the gap distribution suggested by Sanna *et al.* the fits improved significantly (solid line in Fig. 1(a)). A similarly, good fit, however, can also be achieved if a Gaussian distribution of gaps with peak value $2\Delta(0) = 3.1$ meV and 1 meV FWHM (full width at half maximum) is used. The fitted temperature dependence of the IR spectra resulted in gaps which are in good agreement with the BCS temperature dependence confirming that CaC_6 is an *s*-wave superconductor. The occurrence of the gap signature in the far-infrared spectra indicates that CaC_6 is a superconductor in the dirty limit. The infrared data are in accordance with the predicted gap distribution based on a moderately anisotropic gap.

Final confirmation of the anisotropic superconducting order parameter in CaC_6 came from point-contact Andreev reflection spectroscopy (PCAR) [5]. In order to measure the PCAR, instead of the standard metal tip, point contacts in our experiments were made by using a very small drop of Ag conductive paint (diameter $\approx 50\,\mu$m), attached on an etched or freshly cleaved surfaces of the sample. Such 'soft' point contacts were found particularly stable both in time and towards temperature variation and they provide current injection mainly perpendicular to the contact plane [6]. The size of the samples allowed us to apply contacts either on the flat surface ($\| c$) or on the edges ($\| ab$).

Figure 2 shows the temperature dependence of a typical set of normalized conductances versus bias voltage measured with current injection either $\| c$ or $\| ab$. A total of 35 contacts with resistances ranging between 0.5 Ω and 6.4 Ω were investigated. The conductance traces show typical Andreev-reflection characteristics with an almost flat conductance at $|V| \ge 8$ meV and no dips indicating a violation of pure ballistic conduction in the contacts. The conductances were fitted to a modified single-band 3-dim Blonder-Tinkham-Klapwijk (BTK) model using the order parameter $\Delta(T)$, the barrier-height parameter Z and a broadening parameter Γ to account for finite quasiparticle lifetime and extrinsic broadening effects.

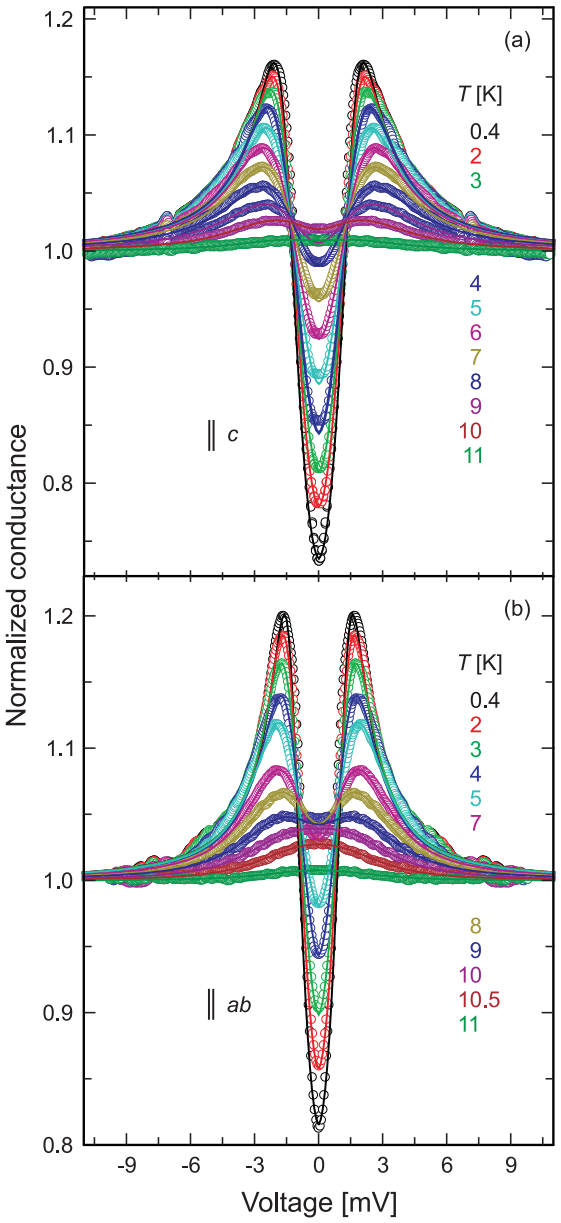

Figure 2: Normalized point contact conductance $\mathrm{d}I/\mathrm{d}V$ versus applied voltage V at various temperatures for current injection direction $\| c$ (a) and $\| ab$ (b). The solid lines represent fits with the Blonder-Tinkham-Klawijk model. At 0.4 K, the values of the fitting parameters are:
$2\Delta = 2.88$ meV, $\Gamma = 0.61$ meV, and $Z = 0.75$ and $2\Delta = 3.4$ meV, $\Gamma = 0.84$ meV and $Z = 0.97$ for injection $\| ab$ and $\| c$, respectively.

Figure 3 displays a fit of the temperature dependence of the order parameter $\Delta(T)$ with the BCS-type temperature dependence. A difference of $\Delta(0)$ between the gaps measured $\| c$ and $\| ab$ is clearly revealed. The critical temperatures T_c (Andreev critical temperatures of the junctions) averaged over the investigated set of different samples amounted to 11.3(1) K, in very good agreement with the bulk critical temperature of the samples. The fitted gaps showed a Gaussian distribution with values of $2\Delta_{ab}(0) = 2.70(28)$ meV and $2\Delta_c(0) = 3.42(16)$ meV. A fit of a two-band BTK model did not show any improvement of the fits.

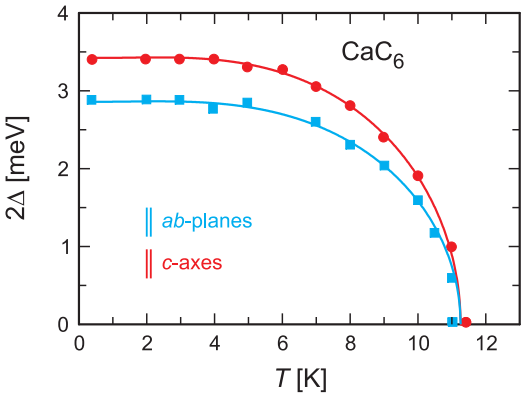

Figure 3: Temperature dependence of the superconducting gap as obtained from the fits of the Blonder-Tinkham-Klapwijk model to the normalized conductances. The solid lines are fits assuming a BCS-type temperature dependence of the order parameter $\Delta(T)$.

Using recent results of the electronic structure for CaC_6 [3] detailed *ab initio* model calculations of the Andreev conductance for the two injection directions were performed. Especially Z and Γ were varied to cover the relevant parameter range found from the fits to the experiment.

These calculations showed excellent agreement of the theoretical with the experimental conductance curves. Even though characteristic dips or shoulders in the Andreev conductance curves were smeared out by the finite quasiparticle lifetime $\Gamma \neq 0$, the conductance traces still contain the anisotropy information which can be revealed by the fitting procedures.

In conclusion, the first directional point-contact Andreev reflection measurements in CaC_6 carried out down to ≈ 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 PCAR curves give further support for our findings and indicate that the actual gap anisotropy in CaC_6 could be even slightly larger.

[1] *Kim, J.S., R.K. Kremer L. Boeri and F.S. Razavi.* Physical Review Letters **96**, 217002 (2006).

[2] *Kim, J.S., L. Boeri, J.R. O'Brien, F.S. Razavi and R.K. Kremer.* Physical Review Letters **99**, 027001 (2007).

[3] *Sanna, A., G. Profeta, A. Floris, A. Marini, E.K.U. Gross and S. Massidda.* Physical Review B **75**, 020511(R) (2007).

[4] *Nagel, U., D. Hüvonen, E. Joon, J.S. Kim, R.K. Kremer and T. Rõõm.* Physical Review B **78**, 041404(R) (2008).

[5] *Gonnelli, R.S., D. Daghero, D. Delaude, M. Tortello, G.A. Ummarino, V.A. Stepanov, J.S. Kim, R.K. Kremer, A. Sanna, G. Profeta and S. Massidda.* Physical Review Letters **100**, 207004 (2008).

[6] *Gonnelli, R.S., D. Daghero, G.A. Ummarino, V.A. Stepanov, J. Jun, S.M. Kazakov and J. Karpinski.* Physical Review Letters **89**, 247004 (2002); *Gonnelli, R.S., D. Daghero, G.A. Ummarino, A. Calzolari, M. Tortello, V.A. Stepanov, N.D. Zhigadlo, K. Rogacki, J. Karpinski, F. Bernardini and S. Massidda.* Physical Review Letters **97**, 037001 (2006).