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Far-infrared signature of the superconducting gap in intercalated graphite CaC_6

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Terahertz reflectance spectra of the Ca-intercalated graphite CaC_6 reveal a superconducting gap below 11 K. The gap signature lacks a sharp onset to full reflectivity at $2\Delta_0$ but rather shows a distribution of gap values consistent with an anisotropic gap. The experimental data were successfully fitted to the gap distribution obtained from density-functional calculations of Sanna *et al.* [Phys. Rev. B **75**, 020511(R) (2007)]. The temperature dependence of the superconducting gap is characteristic for a BCS type superconductor.

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CaC_6 is exceptional in the series of intercalated graphite compounds because of its high superconducting transition temperature $T_c \approx 11.5$ K.[1,2] Several experiments indicate a conventional phonon-mediated superconductivity in CaC_6. The temperature dependence of the magnetic penetration depth $\lambda_{ab}(T)$ shows an exponential behavior at low temperatures, characteristic for a *s*-wave pairing mechanism.[3] The temperature and magnetic-field dependences of the electronic specific heat are consistent with a fully gapped superconducting order parameter.[4] Isotope effect studies show that superconductivity in CaC_6 is dominated by coupling of the electrons by Ca phonon modes.[5] It has been argued that coupling with low-energy Ca vibrations must be very strong to obtain the observed T_c, in disagreement with the specific-heat data that suggest a weak-coupling regime.[6] For an overview of theoretical and experimental studies, see Ref. 7. Despite of the recent efforts the origin of the superconducting mechanism in CaC_6 is still not fully understood.

One of the important parameters of a superconductor is the magnitude and the temperature dependence of the superconducting gap size. The gap Δ_0 of CaC_6 was measured[8] by scanning tunneling spectroscopy, $2\Delta_0 = 25.6 \pm 3.2$ cm^{-1}, yielding $2\Delta_0/k_BT_c = 3.35 \pm 0.42$, slightly less than the weak-coupling BCS value of 3.53. A subsequent scanning tunneling spectroscopy experiment[9] reported a much larger gap size $2\Delta_0 = 37.1 \pm 3.2$ cm^{-1} with $2\Delta_0/k_BT_c \approx 4.6$ in the strong-coupling regime. A recent point-contact spectroscopy measurement[10] gave an exceptionally small value for the *ab*-plane gap $2\Delta_0/k_BT_c = 2.83$, while in the *c* direction it was close to the BCS value $2\Delta_0/k_BT_c = 3.54$. These large discrepancies in the gap values deserve further clarification. The temperature dependence and the magnitude can be easily tested by infrared spectroscopy.[11] Infrared spectroscopy is a bulk method, while scanning tunneling spectroscopy probes the surface only; it is also a noninvasive method, as opposed to directional point-contact spectroscopy. Infrared photons with energy larger than $2\Delta_0$ break a Cooper pair in a process of scattering off impurities and create a pair of quasiparticles,[12,13] producing a steplike feature in infrared reflectance spectra. This characteristic signature of the superconducting gap increases along with increasing scattering rate of quasiparticles. Here we report the results of an infrared reflectance spectroscopy experiment on CaC_6 which reveal a distribution of superconducting gaps with the average value $2\Delta_0/k_BT_c$ consistent with the weak-coupling BCS value of 3.53. The experimental data are in very good agreement with the fit using the gap distribution obtained from *ab initio* density-functional calculations of Sanna *et al.*[14]

In our study we investigated the reflectance *R* of samples of CaC_6 between 3 and 15 K. We found typical signatures of the superconducting gap in the reflectance ratios R_{sc}/R_n of the superconducting and the normal state, respectively, and followed its temperature dependence. The appearance of the gap signature in R_{sc}/R_n indicates that CaC_6 is in the dirty limit with the quasiparticle scattering rate larger than $2\Delta_0$.

We measured the reflectivity of total of three samples, 27, 31, and 42, grown in Stuttgart[4] with dimensions in the *ab* plane of 3.7×3.5, 5.3×3, and 3.5×1.2 mm^2, respectively. The sample 31 was a mosaic composed of two pieces. Surfaces used for the reflectance measurements on samples 31 and 42 were obtained by cleaving the crystals while for 27 the outer surface of an as-grown sample was investigated. The superconducting properties of the samples were characterized by magnetic susceptibility[4] and dc resistivity measurements. The superconducting transition width ΔT_c determined as the temperature difference between 10% and 90% diamagnetic shielding on a typical sample was small, $\Delta T_c \approx 0.1$ K, and reaching 0.7 K on sample 42. The *ab*-plane resistivity measured in the normal state at 12 K on a number of samples was 0.8 $\mu\Omega$ cm. The *c*-axis resistivity measured just above T_c on sample from the same batch as sample 42 was 25 $\mu\Omega$ cm. Samples were loaded in a glovebox in a controlled argon atmosphere into the reflectance probe. After mounting into the cryostat Ar gas was replaced by He heat exchange gas. A polarizing Martin-Puplett interferometer SPS200 (Sciencetech, Inc.) equipped with a ^{3}He-cooled bolometer kept at 0.3 K was used to measure the spectra between 4 and 80 cm^{-1}. A mercury arc lamp was used as a light source. A small wire-grid polarizer was placed at the exit port of a light pipe inside the sample chamber in front of an aluminum-coated glass mirror which focused light on the sample. The **E** vector of light was perpendicular to the plane of incidence and parallel to the plane of carbon atoms, the *ab* plane. With this scattering geometry, the conductivity in the *ab* plane can be probed without contaminations from the *c*-axis conductivity. Light intensity reflected by the sample at $T < T_c$ was divided by the light intensity reflected by the sample in the normal state at 15 K.

The *T* dependence of relative reflectance is shown in

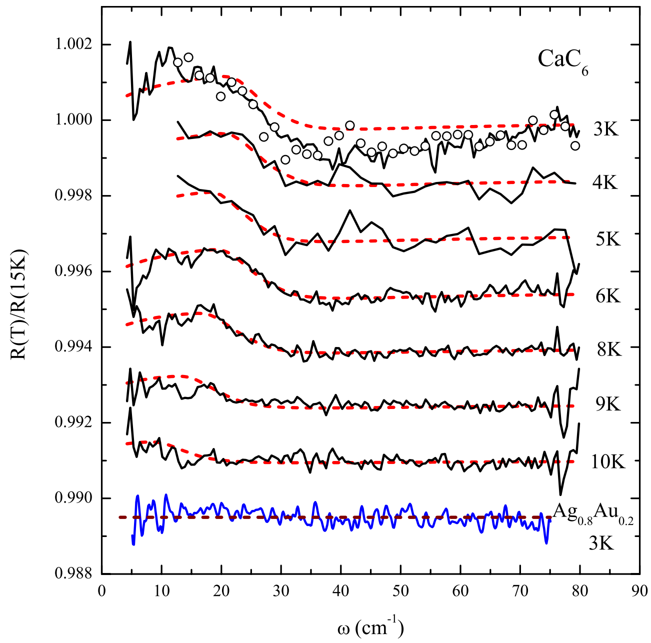

FIG. 1. (Color online) Reflectance spectra of CaC_6 (samples 31 and 42) in the superconducting state relative to the normal-conducting state at 15 K. Starting from 3 K the spectra are offset by −0.0015 in vertical direction. 4 and 5 K spectra were measured only on sample 42, the smaller size of which limited the spectral range and signal-to-noise ratio. The open circles represent the 3 K spectrum of sample 42. The dashed lines are fit results assuming a BCS superconductor below T_c with a scaled gap distribution (Ref. 14) and Drude-type conductivity at 15 K.

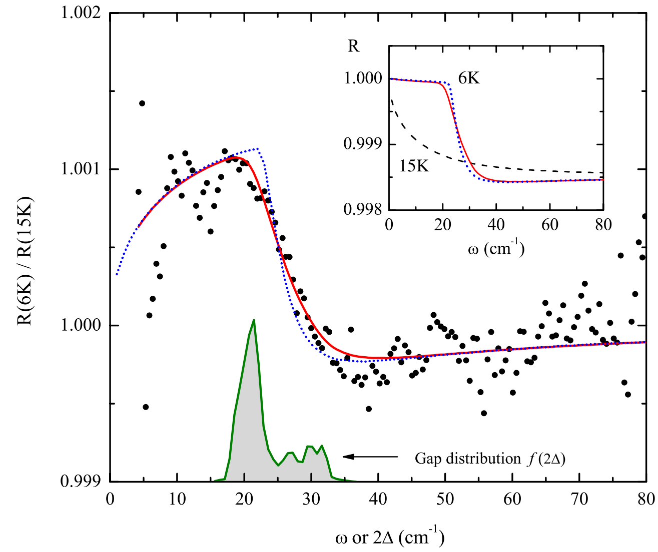

FIG. 2. (Color online) Reflectance of CaC_6 sample 31 at 6 K relative to 15 K (dots). The solid line is the best fit using the gap distribution (Ref. 14) scaled by a factor $s(6\text{K})=0.94$ (shaded area). The dotted line was obtained assuming an isotropic BCS superconductor with a gap $2\Delta(6\ \text{K})=22.6\ \text{cm}^{-1}$. Inset: the dashed line is calculated absolute reflectance in the normal-conducting state; the solid and dotted lines are the calculated absolute reflectances at 6 K for the gap distribution and single gap, respectively, as described in the text.

Fig. 1. A steplike feature observed below 30 cm^{-1} with its largest amplitude at 3 K decreases and shifts to lower frequency as T approaches T_c. To rule out the possibility of the steplike feature in the CaC_6 spectra being an artifact of the measurement method, a reference sample made of solid solution $Ag_{0.8}Au_{0.2}$ was measured simultaneously with the CaC_6 samples. Below 15 K, $Ag_{0.8}Au_{0.2}$ has a very small T dependence of the resistivity.[15] Between 4 and 80 cm^{-1} the reflectance ratio $R(3\ \text{K})/R(15\ \text{K})$ obtained from $Ag_{0.8}Au_{0.2}$ was a flat line with a noise to signal amplitude $\pm 2.5\times 10^{-4}$. The deviation from the flat line is an order of magnitude smaller than the size of step features observed in $R(T)/R(15\ \text{K})$ spectra of CaC_6 (Fig. 1).

To fit the data we calculated the zero angle reflectance using well-known relations between the complex dielectric constant $\epsilon(\omega)$ and the complex conductivity $\sigma(\omega)$ assuming a Drude-type conductivity for the normal state.[16] In the superconducting state the expression by Zimmermann *et al.*[17] for a BCS superconductor was used. The Zimmermann expression yields the complex conductivity normalized to the normal-state conductivity σ_{dc} and depends on parameters Δ_0, T_c, and T and the scattering rate γ. To calculate the (relative) reflectance, the dc conductivity σ_{dc} and the dielectric constant ϵ_∞ are needed. We used $\epsilon_\infty=4$, where contributions of all lattice and electronic oscillators above 80 cm^{-1} are included. σ_{dc} is related to the plasma frequency and the scattering rate according to $\omega_p^2=60\gamma\sigma_{dc}$, and one of them, γ or ω_p, is needed as an additional input parameter. The expression of Zimmermann *et al.*[17] can be extended to superconductors with a distribution of Δ by assuming that the conductivity in the superconducting state is given by the superposition of conductivities according to $\sigma_{sc}(\omega) = \Sigma_i f(2\Delta_i)\sigma_{sc}(\omega,2\Delta_i)/\Sigma_i f(2\Delta_i)$, where $f(2\Delta_i)$ is the distribution function of the gap. In the fitting procedure of $R(T)/R(15\ \text{K})$ the parameters ω_p, T_c, and T were fixed. In the first step a temperature-independent value for σ_{dc} was obtained for each sample and used in the second step to perform a complete fit with $\Delta(T)$ as a free parameter. In the case of gap distribution the fit result was a scaling factor $0 \leq s(T) \leq 1$, where $s(0)=1$. The scaling factor transforms the energy scale of the distribution. Assuming $f[2\Delta_i(T)] = f[2\Delta_i(0)]$ each gap value changes as $\Delta_i(T)=s(T)\Delta_i(0)$. To compensate for detector drifts, an additional fitting parameter k was introduced which multiplied the relative reflectance and ranged from 0.9982 to 0.9999.

The fits assuming two different gap models and corresponding absolute reflectances are shown in Fig. 2. The absolute reflectance in the superconducting state at frequencies below 2Δ is unity and drops at frequencies above the gap, $\omega > 2\Delta$ (see inset to Fig. 2). There are two different regimes in the normal-conducting state.[16] At low frequencies $\omega \ll \gamma$, the Hagen-Rubens square-root behavior is observed, $R \approx 1 - (2\omega/15\sigma_{dc})^{1/2}$. At higher frequencies $\omega \gg \gamma$, the reflectance flattens to $R \approx 1-(\gamma/15\sigma_{dc})^{1/2}$. First we fitted the 6 K spectrum using the single gap model and the plasma frequency $\omega_{ab}=6.6\ \text{eV} \approx 53\,000\ \text{cm}^{-1}$, as calculated by Mazin *et al.*[6] The fit obtained with $2\Delta(6\text{K})=22.6\ \text{cm}^{-1}$ is not perfect since the measured spectrum lacks a sharp onset of full reflectivity at 2Δ. The fit can be significantly improved (cf. Fig. 2) if the

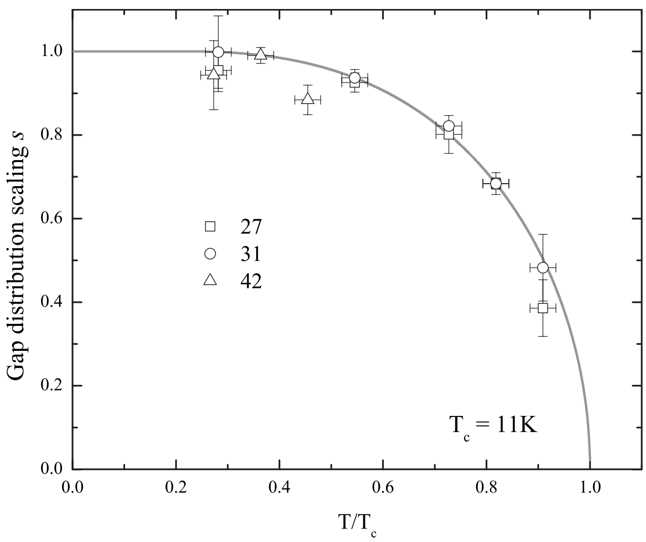

FIG. 3. Temperature dependence of the gap distribution scaling factor $s(T)$ from fitting relative reflectance spectra for samples 27, 31, and 42. The solid line is the temperature dependence of the gap of a BCS superconductor. The vertical error bars are three times the standard error as calculated from the fit covariance matrix. The temperature error is estimated to be about 2.5%.

gap distribution as obtained from the first-principles density-functional calculation of Sanna *et al.*[14] is used. The gap model of Sanna *et al.*[14] scaled by a factor of $s(T)<1$ was used to fit the whole temperature range of relative reflectances (cf. Fig. 1). The 6 K spectrum could also be fitted assuming a very broad Gaussian distribution of gap values, 8 cm^{-1} full width at half maximum and the peak at 24.7 cm^{-1}. This would be the justified for a low-quality sample with a smeared out superconducting transition but clearly not in the case for our samples that showed sharp transitions at T_c. The fit of relative reflectance spectra yielded normal-state conductivities $\sigma_{dc}=0.6(\mu\Omega\ \mathrm{cm})^{-1}$ for sample 27 and $1.2(\mu\Omega\ \mathrm{cm})^{-1}$ for samples 31 and 42, in good agreement with the measured dc resistivity (see above). Although the fit of relative reflectance gave a lower conductivity for sample 27, the quality of the fit (not shown) and the scaling factor $s(T)$ were similar to that of other two samples (cf. Fig. 3). Apparently there is a higher level of defects in the as-grown surface of sample 27, as opposed to cleaved surfaces on samples 31 and 42, which reduce the conductivity but do not affect the superconducting state.

In the following we discuss the results obtained for samples 31 and 42 which had the higher conductivity. The scattering rate obtained from our far-infrared reflectance spectra, $\gamma=\omega_{ab}^2/60\sigma_{dc}=39\ \mathrm{cm}^{-1}$, is larger than the maximum value of twice the gap at 0 K, $2\Delta_{0,\max}\approx 35\ \mathrm{cm}^{-1}$, putting CaC_6 in the dirty limit where $\gamma>2\Delta_0$. The dirty limit behavior is in accordance with magnetic penetration depth[3] and conduction-electron-spin-resonance measurements.[18] Assuming a Fermi velocity $v_F=5.3\times 10^7\ \mathrm{cm\ s}^{-1}$ (Ref. 6) the calculated mean free path amounts to $l_{\mathrm{mfp}}=v_F/\gamma=450$ nm. The coherence length determined by other experimental probes[2,4,8,19] is rather small, $\xi_{ab}=33$ nm, compared to the mean free path l_{mfp}. From $l_{mfp}\gg\xi_{ab}$ we should conclude that CaC_6 is in the clean limit. This contradiction, $l_{\mathrm{mfp}}\gg\xi_{ab}$ (clean limit) versus $2\Delta_{\max}<\gamma$ (dirty limit), could be caused by theoretical underestimation of ω_{ab} and overestimation of v_F and at least one of them should be measured in a separate experiment.[20]

The gap scaling factor $s(T)$ (Fig. 3) follows the temperature dependence of a s-wave superconductor.[21] The experimental errors are too large to obtain an independent determination of T_c from reflectance spectra or to make a statement whether strong-coupling effects are seen in the temperature dependence of the gap size. However, smaller than expected reflectance above the gap in 3 K spectra (Fig. 1) can be caused by strong-coupling effects that reduce the imaginary part of the complex conductivity.[22] It is not clear why such a deviation appears (for all measured samples) only at 3 K and not at 4 K, both temperatures substantially less than T_c. We saw no evidence of the expected low-frequency E_u phonon mode[23–26] around 115 cm^{-1} as it was outside the limits of optimal performance of our measurement setup.

To conclude, we have measured the temperature dependence of far-infrared reflectance spectra of CaC_6. The results confirm that CaC_6 is a s-wave superconductor with an anisotropic gap. The theoretically predicted gap distribution[14] is in accordance with our infrared data. The gap signature in the far-infrared spectra indicates that CaC_6 is in the dirty limit.

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