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Linear and nonlinear electrodynamic responses of bulk CaC_6 in the microwave regime

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The linear and nonlinear responses to a microwave electromagnetic field of two *c*-axis oriented polycrystalline samples of the recently discovered superconductor CaC_6 ($T_C \approx 11.5$ K) is studied in the superconducting state down to 2 K. The surface resistance R_S and the third order intermodulation distortion, arising from a two-tone excitation, have been measured as a function of temperature and microwave circulating power. Experiments are carried out using a dielectrically loaded copper cavity operating at 7 GHz in a "hot finger" configuration. The results confirm recent experimental findings that CaC_6 behaves as a weakly coupled, fully gapped, superconductor. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2769763]

One of the main priorities following the discovery of a superconductor, outside of a full comprehension of the microscopic mechanisms involved in the condensate state, is the study of its electrodynamic properties, in order to understand whether the material can be useful for practical applications. Amongst other parameters, the response of the superconductor to an electromagnetic field at high frequencies is an important test to determine its possible use in resonant cavities for particle accelerators or in passive devices for mobile and satellite communications. CaC_6, setting a record T_C of 11.5 K in the family of graphite intercalated compounds (GICs),[1,2] is potentially able to replace niobium for the internal coating of accelerating cavities or in other niche applications (such as extremely stable oscillators or highly selective filters), where performance requirements are more stringent than cryogenic issues.

We report here a study of the linear and nonlinear microwave properties of bulk samples of this superconductor, synthesized from highly oriented pyrolytic graphite.[3] The results are then compared with measurements performed on Nb. Data have been taken on two platelike *c*-axis oriented polycrystals, having a roughly squared shape of maximum size $2.5 \times 2.5\ \text{mm}^2$ and thickness of 0.1 mm. Because CaC_6 is highly reactive when exposed to oxygen, the samples were accurately cleaved in an inert atmosphere before each run.

For measuring the electrodynamic response of the samples under test, we used an open-ended dielectric single-crystal sapphire puck resonator operating at the resonant frequency of 7 GHz in a "hot finger" configuration. The resonator enclosure is made of oxygen-free high conductivity copper, whereas the sample holder is a low loss sapphire rod, placed at the center of the cavity in close proximity to the puck dielectric crystal. The cavity is excited with a transverse electric TE_{011} mode, which produces a magnetic field oriented normally to the sample surface, therefore inducing *a-b* plane screening currents in the material under test. By using a micrometer screw, the position of the sample placed on the sapphire rod, and therefore the puck-to-sample distance, can be changed in order to get the maximum sensitivity. A schematic view of the experimental apparatus is shown as an inset in Fig. 1.

The experimental data are taken using two different circuital configurations. The first one is in a single-tone mode, where the cavity is excited at its resonance, sweeping the frequency of the microwave applied field, and the surface resistance R_S of the sample under test is extracted as a function of temperature T and microwave surface field H_{rf}, using a standard perturbation method. Measurements are performed via a vectorial network analyzer. Of course, in order to ensure that the (virtually) zero field surface resistance is

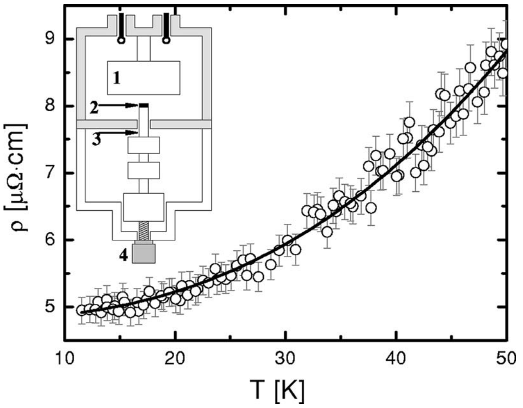

FIG. 1. Microwave resistivity in the normal state for $T \ll \Theta_D$ (CaC_6 sample 1) at 7 GHz. The dotted line is a numerical fit for the expression $\rho = a + bT^n$. In this graph, $n = 2.5$. inset: a schematic drawing of the experimental setup, consisting of a copper cavity loaded by a single crystal sapphire (1), with the sample (2) placed in close proximity on the top of a dielectric "hot finger" (3), movable by using a micrometer screw (4).

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being extracted, care must be taken to keep power at a suitably low level. To study the behavior of $R_S(H_{\mathrm{rf}})$, a linear amplifier is used, allowing us to raise the power circulating in the cavity up to some kilowatts. The second configuration we used is in a two-tone mode, to study the third order intermodulation distortion (IMD) generated in the CaC_6 samples, similar to the one reported in Ref. 4. Briefly, two pure frequencies f_1 and f_2 ($>f_1$) with equal amplitudes are generated by two phase-locked synthesizers. The frequencies are separated symmetrically around the center frequency and spaced by 10 kHz, so that both f_1 and f_2 are well within the 3 dB bandwidth of the resonator. The two signals are combined and applied to the resonant cavity where the sample under test has been inserted, and the output signals (the two main tones and the two third order IMDs at $2f_1$-f_2 and $2f_2$-f_1) are then monitored as a function of the input power by using a spectrum analyzer. Further details can be found in Refs. 5 and 6.

Supposing that the electrodynamic response of CaC_6 in the normal state is local—consistently with the experimental observation that the screening response in the superconducting state lies in the dirty limit[7]—from the surface resistance measurement, we can calculate the microwave resistivity ρ_n using the formula for the classical skin depth: $[R_S=(\pi\mu_0 f\rho_n)^{0.5}]$, where μ_0 is the vacuum permeability and f is the resonance frequency. The residual term ρ_{n0}, defined as the onset of the superconducting transition, is close to 5 $\mu\Omega$ cm, consistent with values reported in literature for the dc resistivity measured on samples from the same source.[8] The low temperature ($T \ll \Theta_D \approx 600$ K,[9] where Θ_D is the Debye temperature) dependence of ρ_n is shown in Fig. 1 to follow a power law T^n (continuous line), with the exponent n ranging between 2 and 3 (in the graph $n=2.5$). Assuming that electron-phonon scattering is the dominant contribution determining the resistivity of CaC_6, the observed power law behavior shows some deviation as to the universal (ρ_{n0}, λ) graph of all metals,[10] λ being the coupling constant. According to this phenomenological plot, there are two reasonably well separated regions of $\rho_{\mathrm{eph}}(T)$ behavior at low temperatures T^{3-5} and T^2, respectively, depending on the values of ρ_{n0} and λ. The $n=3$ to $n=2$ transition usually takes place, increasing both the electron-phonon coupling λ and the disorder ρ_{n0}. Metals with $\lambda \leqslant 0.9$ should never enter nor be close to the T^2 region, independent of the amount of disorder. The observed discrepancy can be an indication that the strong coupling constant of CaC_6 might be a bit larger than previously calculated ($\lambda \approx 0.85$).[9,11]

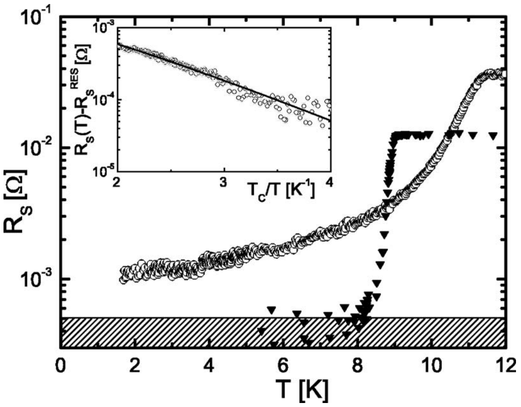

FIG. 2. R_S vs T for CaC_6 sample 1 (○) at 7 GHz. Data obtained for a Nb bulk sample at the same frequency are shown for comparison(▼). The hatched region indicates the sensitivity limit of the experimental setup. In the inset, $(R_S - R_{\mathrm{res}})$ vs T_C/T is plotted below $T_C/2$ on a semilog scale for the same sample. The continuous line represents the exponential behavior predicted by the BCS theory with a strong coupling ratio $2\Delta(0)/k_BT_C=3.1$.

The microwave surface resistance $R_S(T)$ of bulk CaC_6 in the superconducting state is plotted in Fig. 2, showing the expected sharp transition at T_C and a rapid drop as T decreases. At temperature well below T_C, R_S tends to saturate, reaching a high residual value more or less below 3 K. In spite of the good quality of the sample, the data cannot be consistently fitted in the overall temperature range within a BCS framework, since extrinsic surface effects are dominant at the lowest temperatures. These residual losses come very likely from the presence of calcium oxides and hydroxides on the CaC_6 surface, in spite of the care taken in keeping the sample in a controlled environment during each run. For comparison, in the same figure, we show data taken on a high quality Nb commercial sample (Goodfellow) having a similar size as CaC_6. In this last case, R_S values are well below the limit of sensitivity (evidenced by the hatched region in the graph) already at 6 K. For T less than $T_C/2$, in conventional superconductors the surface resistance behavior can be phenomenologically described using the standard BCS exponential dependence, after subtracting from the data a residual term R_{res} related to the extrinsic losses. This is done in the inset of Fig. 2, where the quantity $R_S - R_{\mathrm{res}}$ is displayed as a function of T_C/T at low temperatures, and $R_{\mathrm{res}}=1.1$ mΩ is chosen. Once this residual value is subtracted, the low temperature data do show an exponential temperature dependence, according to $R_S \propto \exp-(\Delta(0)/k_BT)$. A linear dependence on the semilog scale is clearly seen at low T, that is, an unambiguous and direct signature of the superconducting gap. The behavior does not change if slightly different values for R_{res} are taken. A number of best fits has been also performed, allowing R_{res} to vary within 10% (range imposed by the experimental uncertainty), and for T_C/T ranging between 2 and 4 only (that is, approximately from 6 to 3 K), because of the large scattering of data at the lowest temperatures. The critical temperature T_C $=11.5$ K has been independently determined using an inductive technique[7] and well agrees with the value obtained from the $R_S(T)$ measurement. From the fit procedure, we yield a strong coupling ratio $2\Delta(0)/k_BT_C=(3.1\pm0.6)$. The resulting gap $\Delta(0)=1.5\pm0.3$ meV is compatible with the results obtained from penetration depth (1.8 meV) (Ref. 7) and scanning tunneling microscopy (1.6 meV) measurements.[12] The slightly depressed values are possibly related to the fact that microwave impedance measurements are more sensitive to the surface properties than other spectroscopic techniques.

In Fig. 3, the behavior of R_S as a function of the microwave surface field H_{rf} is reported at six different temperatures. H_{rf} refers to the peak value on the sample surface, evaluated using the CST MWS electromagnetic simulation code. The $R_S(H_{\mathrm{rf}})$ dependence is extremely flat for temperatures as high as 8 K, which is quite encouraging, taking into account the polycrystalline nature of the samples. Above 8 K, the dependence of R_S on the field is more pronounced, with a steeper slope but with no evidence of a sharp transition related to some threshold field.[5] One must note, however, that measurements carried out at 4 K on the Nb bulk sample of similar size used for comparison show no dependence at all up to the maximum available circulating power

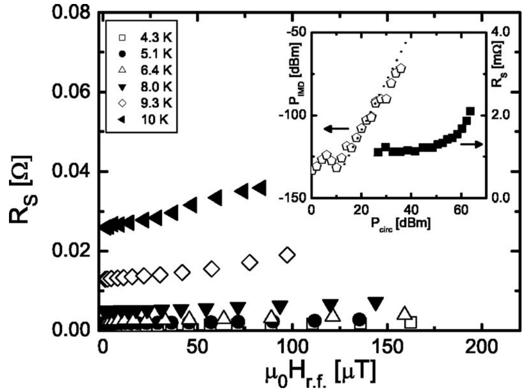

FIG. 3. $R_S(H_{rf})$ is shown at various temperatures for CaC_6 sample 1 at 7 GHz. In the inset, the IMD power P_{IMD} and the surface resistance at 4 K as a function of the power circulating in the cavity are plotted for comparison.

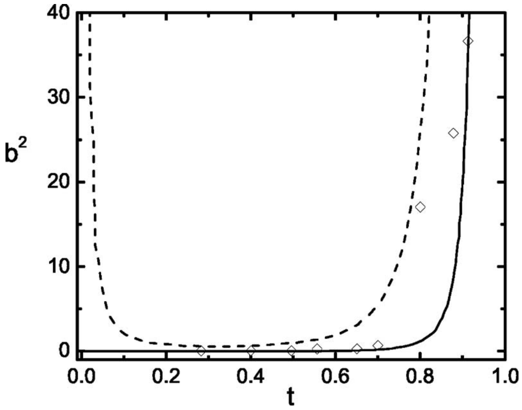

FIG. 4. Nonlinear parameter b^2 (proportional to the IMD power) vs the reduced temperature $t=T/T_C$ for CaC_6 sample 2. Continuous and dashed line represents the temperature behavior for the nonlinear coefficient expected in the case of the standard *s*-wave and *d*-wave models respectively.

P_{circ} (above 1 kW). In the extremely low power region—where the surface resistance of CaC_6 shows no detectable variation with the microwave field at all—the IMD response follows the theoretical cubic dependence on P_{circ}.[4] This can be observed in the inset of Fig. 3, where the output power due to the third order IMD P_{IMD} is plotted as a function of P_{circ}. The dotted line represents the expected slope of 3. The surface resistance R_S dependence is also shown for comparison. This graph clearly shows that we are looking at very tiny effects arising well below any change can be detected in the first order response, likely due to intrinsic mechanisms of nonlinearity. According to the theory first set by Dahm and Scalapino,[13,14] the nonlinear response of a superconductor measured by P_{IMD} can be used as a very sensitive probe of the superconducting gap function symmetry by means of a nonlinear parameter $b(T)$. This is done explicitly deriving the relation between P_{IMD} and b^2 for the case of a microstrip resonator. After this original work, the validity of the expression has been extended[15] to other resonant structures, including dielectrically loaded cavities, the only difference being the introduction of an additional factor Λ, strong function of the cavity parameters. In particular, Λ depends on the resonant mode and on the effective area covered by the superconducting surface. Since these quantities do not change with T, we can extend the procedure used for measurements in microstrips and striplines[16,17] to the case of our dielectric resonator.

The next step is to extract the nonlinear parameter b^2 as a function of temperature for a fixed value of the circulating power P_{circ}. Since the proportionality term between P_{IMD} and b^2 has never been derived explicitly, we have to use an empirical procedure to compare the experimental points with the expected theoretical behaviors. The results are shown in Fig. 4. In the case of CaC_6, the dependence that best accounts for our data is the one expected for a superconductor with *s*-wave symmetry,[18] since most of the data lie on that theoretical curve (solid line). To better clarify this point, we plotted in Fig. 4 the temperature dependence for a *d*-wave case (dashed line) too.[13]

In summary, we have presented a study of the electrodynamic response of bulk CaC_6 samples at 7 GHz as a function of temperature and microwave power. In spite of the fact that the surface properties of this GIC in the microwave region are far from being optimized, the temperature dependence of its surface resistance, cleared of extrinsic effects, can be well explained within the conventional BCS theory. A single-valued and finite gap can be extracted from the data, consistent with recent measurements of the superfluid density performed on samples from the same source. In a similar way, data from IMD measurements indicate that the observed nonlinearity follows the temperature dependence expected for an *s*-wave superconductor. Finally, the power dependence of R_S is encouraging, in spite of the polycrystalline nature of the samples under test.

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