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Low-temperature microwave surface impedance of the conventional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

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We have performed measurements of the microwave surface impedance $Z_S = R_S + iX_S$ of the organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ down to $T = 0.8$ K. The reactance X_S, and therefore the penetration depth λ, exhibits no temperature dependence for $T \ll T_c$. This result is in full agreement with calculations of the BCS ground state and gives no indication of unconventional pairing. Furthermore, we have evaluated the complex conductivity $\hat{\sigma} = \sigma_1 + i\sigma_2$ and find a pronounced peak in σ_1 below T_c which can be identified as a coherence peak.

The κ phase of the two-dimensional organic conductor Di-(bisethylenedithio-tetrathiafulvalene)dithiocyanocuprate [i.e., (BEDT-TTF)$_2$Cu(NCS)$_2$] is the most prominent representative of the more than twenty superconducting salts of the BEDT-TTF family.[1] Even five years after its discovery,[2] the question of whether the superconducting state is of the conventional BCS type remains controversial. Various experiments examining the superconducting state of the BEDT-TTF materials indicate deviations from what is expected for singlet pairing. The critical field shows an unexpected behavior at low temperatures[3] and the ^{1}H nuclear spin-lattice relaxation rate was found[4] to have an anomalous temperature dependence. Some measurements of the specific heat exhibit a strange T^3 law,[5] but others[6] find the specific heat in agreement with the BCS predictions. These experiments have been interpreted in terms of triplet pairing, spin density wave transitions below T_c, and vortex glass transitions as expected for a ground state with higher momentum pairing. While both NMR and specific heat measurements are sensitive also to quasiparticle excitations, the parameters which characterize the electrodynamics, the penetration depth λ, and surface resistance R_S, are free from such complications. Consequently, the magnitude and temperature dependence of these parameters may, in principle, distinguish between the various possible symmetries of superconducting states. Low frequency magnetization measurements[7] with $H_{\rm ac}$ parallel to the layers led to an unusually large penetration depth along the (bc) plane, and a T^2 dependence suggesting higher momentum pairing. Studies of the reversible magnatization,[8] however, show evidence of conventional Cooper pairing. From the scaling behavior of the radio-frequency penetration depth, Sridhar *et al.*[9] recently argued for a nonconventional Meissner state where the penetration depth cannot be defined in the common way. Direct experiments of the penetration depth employing muon spin rotation (μSR) techniques are also highly controversial, one[10] suggests s-wave pairing, the other[11] shows important deviations from the BCS behavior below 1.5 K. A similar situation has arisen for measurements of the microwave surface impedance. The surface reactance X_S, which is proportional to λ, was found to be temperature independent for $T \ll T_c$ in both configurations parallel and perpendicular to the layers.[12–14] Recently, however, microwave surface impedance experiments were reported,[15] which show a slight temperature dependence of the penetration depth down to $0.2T_c$. In order to clarify the situation we have performed studies of the microwave surface impedance of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at 35 GHz down to temperatures as low as 0.8 K. Besides the temperature dependence of the penetration depth, we have evaluated the real and imaginary parts of the conductivity in the superconducting state.

The κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has been prepared by the standard electrochemical crystal growth procedure.[1] ac susceptibility measurements on crystals of the same batch as that used for the microwave experiments show a superconducting transition at $T_c = 8.6$ K (i.e., 10% change in the ac-susceptibility signal) with a width of approximately 1 K. The surface resistance R_S and the surface reactance X_S were measured as functions of temperature. For this purpose, we employed a cylindrical 35 GHz copper cavity which could be cooled down to ^{3}He temperatures.[16] The specimen was placed in the maximum of the magnetic field with $\mathbf{H} \perp (bc)$ plane so that the eddy currents would run within the highly conducting planes. By measuring the frequency and the quality factor of the empty and loaded cavity we were able to evaluate both components of the complex surface impedance.[17] In terms of the complex conductivity $\hat{\sigma} = \sigma_1 + i\sigma_2$, the surface impedance Z_S normalized to its free space value is defined as

$$Z_S = R_S + iX_S = \left(\frac{i\mu_0\omega}{\sigma_1 - i\sigma_2}\right)^{1/2} . \qquad (1)$$

In the normal state, at frequencies $\omega\tau \ll 1$, $\sigma_1 \gg \sigma_2$, and consequently

$$R_S = X_S = \left(\frac{\mu_0\omega}{2\sigma_{\rm dc}}\right)^{1/2} , \qquad (2)$$

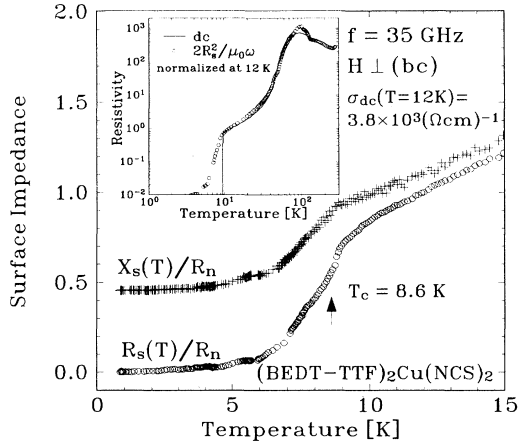

FIG. 1. Temperature dependence of the surface resistance R_S and the surface reactance X_S for κ-(BEDT-TTF)$_2$-Cu(NCS)$_2$ along the (bc) plane. The inset shows the dc resistivity and $2R_S^2/\mu_0\omega$; all quantities are normalized to their $T = 12$ K resistivity value.

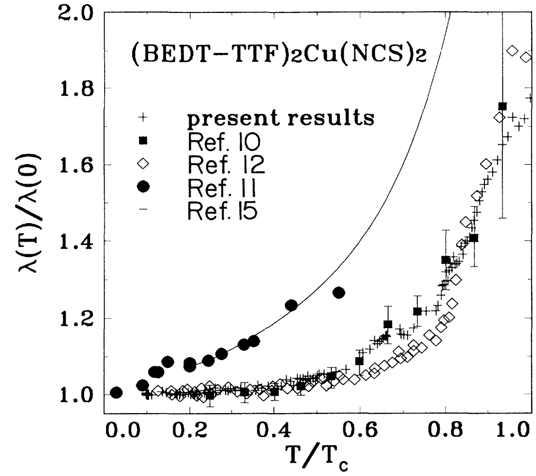

FIG. 2. Temperature dependence of the penetration depth of (BEDT-TTF)$_2$Cu(NCS)$_2$ in the superconducting state (T_c = 8.6 K) in comparison with previous millimeter wave results of Holczer *et al.* (Ref. 12) and Achkir *et al.* (Ref. 15), and μSR experiments of Harshman *et al.* (Ref. 10) and Le *et al.* (Ref. 11). The experiments probe $\lambda_{\|}$, except for the data of Ref. 12 where $\lambda_\perp/40$ is shown.

i.e., the surface resistance is equal to the surface reactance in the so-called Hagen Rubens limit, and $\sigma_1(\omega \ll 1/\tau) \approx \sigma_{\rm dc}$. At low frequencies, the resistivity is therefore given by $\rho(T) = 2R_S^2/\mu_0\omega$. In the inset of Fig. 1 we display the resistivity along the (bc) plane evaluated in this way from microwave measurements at 35 GHz together with $\rho_{\rm dc}$; the data are normalized and $\sigma_{\rm dc}(T = 12\text{ K}) = 3.8 \times 10^3$ $(\Omega\text{ cm})^{-1}$. The temperature dependences of R_S and X_S are displayed in Fig. 1. We calibrated the surface resistance by the normal state surface resistance $R_n = (\mu_0\omega/2\sigma_{dc})^{1/2}$.

Previous millimeter wave experiments[13] indicate that at 60 GHz, the assumptions of Eq. (2) may not be satisfied, in particular $1/\tau$ may become comparable to ω. In agreement with optical reflectance measurements,[18] the scattering rate $1/2\pi\tau$ seems to be frequency dependent and varies from 1000 cm^{-1} in the midinfrared, to over 50 cm^{-1} in the far infrared, to about 20 cm^{-1} at 60 GHz. From Shubnikov–de Haas measurements, a value of $1/2\pi\tau = 2$ cm^{-1} has been obtained.[19] As shown below, we can fit our experimental data at 35 GHz best with a scattering rate of $1/2\pi\tau = 16$ cm^{-1}, i.e., $\omega\tau \approx 0.1$. Due to the proximity of the measurement frequency of 1 cm^{-1} to the scattering rate, X_S is about 10% above the R_S value just above T_c.

In the superconducting state, well below T_c, the surface reactance is given by

$$X_S(T) = \mu_0\omega\lambda(T), \tag{3}$$

where $X_S(T)$, which is proportional to the measured frequency shift, is proportional to the penetration depth λ and therefore can be directly compared with various models of the superconducting state. Since we oriented the sample's (bc) plane normal to the microwave magnetic field, we probed the penetration depth within the highly conducting planes. The relevant surface is the sum of the small sides around the sample, i.e., parallel to the a axis. Since the evaluation of the resonator constant and sample geometry is difficult, the absolute value was obtained by using the skin depth $\delta = (2/\mu_0\omega\sigma)^{1/2}$ of the normal state which is related to the surface reactance: $X_S = \mu_0\omega\delta/2$. The measured penetration depth of (BEDT-TTF)$_2$Cu(NCS)$_2$ is displayed in Fig. 2 in comparison with published results. The absolute value of the zero temperature penetration depth was found in agreement with the literature value of $\lambda_0 = 0.8$ μm as obtained by μSR (Refs. 10 and 11) and surface impedance measurements.[13] The earlier experiments of Holczer *et al.*[12] probed the penetration depth normal to the planes; in this case $\lambda_\perp/40$ is plotted in order to compare it with the in-plane results. With the exception of Refs. 11 and 15, there is a good agreement between all the measurements. Even with the extended temperature range down to 0.8 K and the increased precision of $\delta\lambda/\lambda = \pm\, 0.007$, no conclusive indication of a temperature dependence of the penetration depth can be found below $0.3T_c$. The theoretical predictions[20] are plotted in Fig. 3 where the dotted line is the London limit, the full line is the two fluid expression $\lambda_T(T) = \lambda_0[1 - (T/T_c)^4]^{-1/2}$ [close to $\lambda(T)$ as would be observed for strong coupling], and the dashed line represents the local regime. The experimental data are well described by assuming a singlet ground state. While triplet pairing results in a linear temperature dependence, s-wave pairing leads to a flat behavior with $\lim_{T\to 0} d\lambda(T)/dT = 0$.

The complex conductivity $\hat\sigma(\omega)$ in the superconducting state can be evaluated from Eq. (1) using the experimentally accessible R_S and X_S as input parameters:

$$\sigma_1 = \frac{2\mu_0\omega R_S X_S}{(R_S^2 + X_S^2)^2} \text{ and } \sigma_2 = \frac{\mu_0\omega(X_S^2 - R_S^2)}{(R_S^2 + X_S^2)^2}. \tag{4}$$

In order to normalize the conductivity to the normal

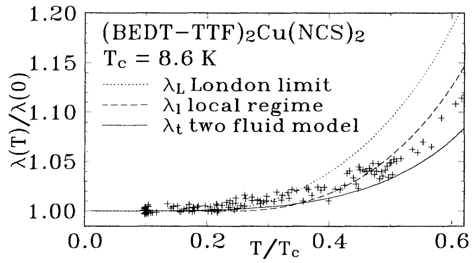

FIG. 3. The penetration depth in (BEDT-TTF)$_2$Cu(NCS)$_2$ as a function of temperature compared with theoretical predictions. The dotted line is the BCS weak-coupling limit, the dashed line represents the local regime, and the full line is the two fluid model. In agreement with the calculations there is no appreciable temperature dependence below $0.3T_c$.

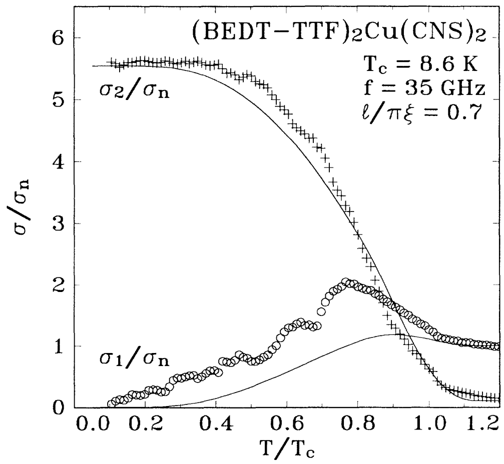

FIG. 4. Temperature dependence of the normalized components σ_1 and σ_2 of the optical conductivity of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ at 35 GHz. The solid lines represent the results of the BCS theory with $\ell/\pi\xi_0 = 0.7$.

state value, we assume a temperature dependent scattering rate yielded by a quadratic fit of the normal state resistivity above T_c, and extrapolate this behavior below the transition. The resulting σ_n has a temperature dependence not far from the result obtained by microwave measurement[15] of the normal state down to 1.8 K in the presence of a magnetic field well above H_{c2}. In Fig. 4 we display both components of the complex conductivity $\sigma_1(T)$ and $\sigma_2(T)$ in the highly conducting (bc) plane, normalized to the normal state value at $T = 12$ K. For a BCS superconductor in the dirty limit (i.e., $\ell/\pi\xi_0 \ll 1$), the equations worked out by Mattis and Bardeen[21] give the electrodynamic response. This limit may not be appropriate for (BEDT-TTF)$_2$Cu(NCS)$_2$, since the mean free path $\ell = 150$ Å, and the coherence length $\xi_0 = 70$ Å.[22] The null result in the search for the superconducting gap 2Δ, which is expected at approximately 25 cm^{-1} but does not show up in optical measurements,[23] points in the same direction. We have calculated R_S and X_S, or σ_1 and σ_2, for various values of $\ell/\pi\xi_0$, assuming a two-dimensional BCS ground state, with a single particle gap given by the weak-coupling limit $2\Delta(T = 0\text{K}) = 3.5k_BT_c = 21$ cm^{-1}. Since the accuracy of the measured frequency shift (i.e., determining X_S and strongly related to σ_2) exceeds the precision of the amplitude change in our measurement, we gave priority to the fit of the σ_2 data (Fig. 4). This leads to a value of $\ell/\pi\xi_0 = 0.7$, and with $v_F = 4.7 \times 10^6$ cm/s, consequently to $1/2\pi\tau = 16$ cm^{-1} for the scattering rate or $\omega\tau = 0.07$. In order to describe the smooth onset of the superconducting transition we employed a Gaussian distribution of T_c with a standard deviation of 0.25 K. In the dirty limit the imaginary part of the conductivity σ_2 is related to the superconducting energy gap.[20] However, σ_2/σ_n tends to the ratio $1/\omega\tau$ in the clean limit at low temperatures, and therefore we can extract very little information from σ_2.

The dominant feature of the σ_1 curve is the peak below the superconducting transition temperature (Fig. 4), which can be explained by the BCS model: a broad maximum is expected as a manifestation of the case-II coherence factor.[20] The size of the coherence peak depends on the coherence factor in addition to the divergency of the excitation density of states at the gap edge. The maximum is broadened by a distribution of the transition temperature T_c. Its height depends on scattering effects and on the coupling. The peak is enhanced compared to previous 60 GHz experiments,[13,14] where it was almost smeared out because the photon energy was comparable to the single particle gap Δ (the size of the peak goes as $\ln \frac{\hbar\omega}{2\Delta}$). In our calculations we restricted ourselves to the weak-coupling limit, i.e., $\Delta(T{=}0\text{ K})/k_BT_c = 1.76$, but note that the analysis of the strong-coupling limit[24] would improve the fit of both σ_1 and σ_2 as discussed for Pb.[25] We note that higher-momentum pairing leads to the rapid disappearance of the coherence peak and is expected to give σ_1 values significantly below the solid line in Fig. 4. A similar temperature dependence for $\sigma_1(T)$ was observed in both orientations normal and parallel to the planes,[14] which indicates that the divergency in the optical response of the system is identical at various orientations.

Recent microwave experiments at 17 GHz by Achkir et al.[15] produce similar results for σ_1. Their interpretation, however, is contrary, since the authors oppose the application of the BCS theory to (BEDT-TTF)$_2$Cu(NCS)$_2$ and apply an inelastic scattering term $1/\tau_{\text{ine}}$, with $1/\tau = 1/\tau_0 + 1/\tau_{\text{ine}}$, in order to explain the observed peak. From this point of view, the maximum of $\sigma_1(T)$ is the result of the increasing inelastic scattering time τ_{ine} and the decreasing penetration depth λ as the temperature decreases. The low-temperature resistance of the normal state, measured in a large magnetic field of 10 Tesla,[15] lends no support to this assumption. In fact, our results as well as Achkir's may be explained within the BCS theory, by assuming a smearing of the transition, deviation from the Hagen-Rubens limit $\omega\tau \ll 1$, and incorporation of strong-coupling effects.[24]

We conclude that the temperature dependence of

$\sigma_1(T)$, as shown in Fig. 4, does not conclusively contradict the BCS predictions, while the temperature dependence of the penetration depth $\lambda(T)$ strongly supports the assertion that the pairing is s wave in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Further studies of the conductivity peak in high quality samples have to be conducted over a wide range of frequencies in order to investigate the influence of scattering effects.

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