Electrodynamics of the Superconducting State of κ(BEDT-TTF)$_2$Cu(NCS)$_2$

O. Klein, K. Holczer,[a] and G. Grüner
Department of Physics and Solid State Science Center, University of California, Los Angeles, Los Angeles, California 90024

J. J. Chang
Department of Physics, Wayne State University, Detroit, Michigan 48202

F. Wudl
Department of Physics, University of California, Santa Barbara, Santa Barbara, California 93106
(Received 8 October 1990)

We have measured the surface impedance $Z_s = R_s + iX_s$ in the normal and superconducting states of κ(BEDT-TTF)$_2$Cu(NCS)$_2$, and have evaluated the conductivity σ_1. The temperature-independent X_s for $T \ll T_c$ and the weak maximum observed for σ_1 below T_c rule out unusual pairing. Our results are in good overall agreement with calculations based on a BCS ground state.

PACS numbers: 74.40.+k, 74.30.Ci

κ(BEDT-TTF)$_2$Cu(NCS)$_2$ [BEDT-TTF denotes bis(ethylenedithio)tetrathiafulvalene] is one member of the rapidly growing number of organic superconductors with strong two-dimensional characteristics. The question whether the superconducting state is of the conventional BCS type is controversial, some experiments[1-3] favoring unconventional pairing while others[4,5] showing good agreement with calculations based on a BCS ground state. Optical experiments[6] were not successful in determining the single-particle gap and are suggestive of states below the gap.

We have measured the surface impedance Z_s of κ(BEDT-TTF)$_2$Cu(NCS)$_2$ in the millimeter-wave spectral range at 35 and 60 GHz. In terms of the complex conductivity $\sigma = \sigma_1 - i\sigma_2$, the surface impedance is given by[7]

$$Z_s = \left(\frac{i\mu_0\omega}{\sigma_1 - i\sigma_2} \right)^{1/2} = R_s + iX_s \,, \tag{1}$$

where R_s and X_s are the surface resistance and surface reactance, and μ_0 is the permeability of the free space. In the normal state, where $\sigma_1 \gg \sigma_2$, $R_s = X_s = (\mu_0\omega/2\sigma_1)^{1/2}$. In the superconducting state, the surface reactance is proportional to the penetration depth λ (at temperatures where $\sigma_2 \gg \sigma_1$) and R_s is determined by losses due to thermally excited carriers within the penetration depth λ. Both R_s and X_s have been explored in detail, experimentally and theoretically for a wide range of conventional superconductors.[8]

Our experiments were conducted by employing resonant cavities operating at fixed frequencies. The specimens are placed inside the cavity at various positions (see below) and the signal is detected by a novel feedback configuration analogous to the one used in ESR.[9] The measured parameters are the resonance frequency f_0 and quality factor Q.[10] The changes due to the specimen normally represent a smal perturbation of the resonance, and are linearly related to the changes of the surface impedance of the specimen

$$\tfrac{1}{2}\Delta(1/Q) - i(\Delta\omega/\omega_0) = \gamma Z_s = \gamma(R_s + iX_s) \,, \tag{2}$$

where γ is a geometrical factor reflecting the dimensions of the sample and cavity. Γ can be calculated from the known sample dimensions.

For the specimens we have investigated, two different configurations have been applied to explore the anisotropy of the normal- and superconducting-state properties. In one configuration the sample is at the antinode of the ac magnetic field and the ac electric field is zero at the surface of the specimen (configuration I). In the other configuration $\mathbf{E}_{ac}$ is maximum and $\mathbf{H}_{ac}$ is zero at the surface (configuration II). In experiments where $\mathbf{E}_{ac}$ is parallel or $\mathbf{H}_{ac}$ perpendicular to the highly conducting *b-c* plane, the currents flow in the plane and we refer to the impedance as $Z_{s\parallel} = R_{s\parallel} + iX_{s\parallel}$.

In our experiments where the specimen is subjected to electromagnetic fields, demagnetization effects and misalignment of $\mathbf{H}_{ac}$ and $\mathbf{E}_{ac}$ with respect to the crystallographic axes may play a role. The former may lead to vortex contributions to the electrodynamic response, the latter to a mixture of in-plane and perpendicular-to-the-plane properties. We have obtained identical results for both configurations when the induced ac currents flow in the conducting planes, and we conclude that demagnetization effects (which could be relevant for configuration I, but not for configuration II) do not play a significant role.

Using the measured value for the quality factor, one can estimate the conductivity in the normal state just above T_c. Using cavity perturbation theory in the skin-depth regime[10] and approximating the sample shape with an oblate spheroid, we obtain a value for $\sigma_n(T=12\ \mathrm{K}) = 3.8\times10^3\ \Omega^{-1}\mathrm{cm}^{-1}$ in good agreement with dc[11] [$\sigma_n(T=12\ \mathrm{K}) = 5.0\times10^3\ \Omega^{-1}\mathrm{cm}^{-1}$] and far infrared[6]

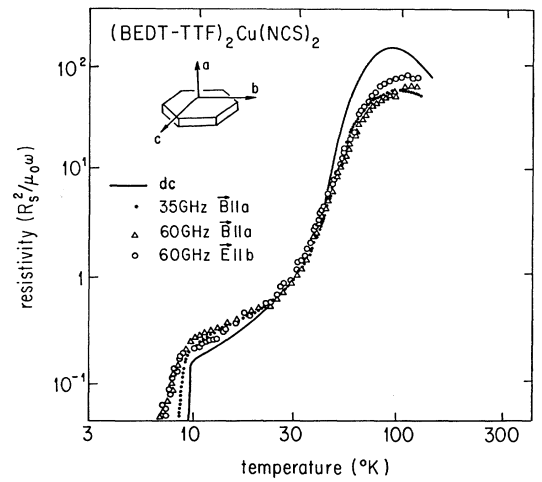

FIG. 1. Temperature dependence of ρ_{dc} and $2R_s^2/\mu_0\omega$ for κ(BEDT-TTF)$_2$Cu(NCS)$_2$. All quantities are normalized to the $T=30$ K dc resistivity value. (dc curve taken from Ref. 11.)

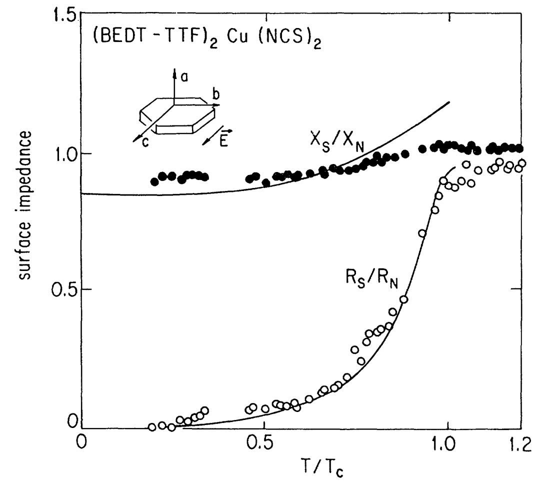

FIG. 2. Temperature dependence of the surface resistance $R_{s\parallel}$ and surface reactance $X_{s\parallel}$ for κ(BEDT-TTF)$_2$Cu(NCS)$_2$. The solid lines are the BCS prediction convoluted over 1 K for $l/\pi\xi_0=1.7$.

[$\sigma_n(T=12\text{ K})=2.0\times10^3\ \Omega^{-1}\text{cm}^{-1}$]. Thus, we conclude that misalignment effects are negligible.

The specimens were prepared by conventional electrochemical methods, and the superconducting transition temperatures were typically 9 K. Shielding diamagnetism measurements indicate a typical width of the transition temperature $\Delta T=1$ K. Such a significant width is evident from magnetization, dc resistivity, and specific-heat[5] studies conducted by other groups.

In Fig. 1 we display the dc resistivity together with $2R_s^2/\mu_0\omega$ measured along the conducting b-c plane. All quantities are normalized to their $T=30$ K value. For a metal $\rho_{ac}=2R_s^2/\mu_0\omega$, for $\omega\tau<1$ and, consequently, Fig. 1 suggests that in the normal state κ(BEDT-TTF)$_2$-Cu(NCS)$_2$ is a simple metal with a relaxation rate which exceeds $\omega/2\pi=2\text{ cm}^{-1}$ (60 GHz), in agreement with optical studies which lead to a relaxation time $1/\tau=1000\text{ cm}^{-1}$.[6] In this limit, from Eq. (1), $R_s=X_s=(\mu_0\omega/2\sigma_1)^{1/2}$, and both components of the impedance R_s and X_s have the same value. Just above T_c our high-frequency results are somewhat different from σ_{dc} available in the literature. Experiments on several specimen indicate that this is due to the difference in sample quality. We have also observed differences in the transition temperatures, as it is also evident from Fig. 1.

The temperature dependence of R_s and X_s, obtained for a configuration where the electric field is parallel to the c direction, is shown in Fig. 2. For data displayed in Fig. 2, the electric currents flow within the conducting plane, and consequently $R_{s\parallel}$ and $X_{s\parallel}$ are measured. Also, we have fitted $\sigma_N(T)$ the normal-state conductivity above T_c by a fourth-order polynomial, and used this to estimate σ_N, and consequently R_N and X_N [using Eq. (1)] in the temperature region below T_c. All data in Fig. 2 are normalized to R_N and X_N values obtained by this procedure.

Both the surface resistance and surface reactance depend on the parameters which determine the superconducting state. For a BCS superconductor, in the dirty limit the theory worked out by Mattis and Bardeen apply.[12] This limit, however, is not appropriate for κ(BEDT-TTF)$_2$Cu(NCS)$_2$. The normal-state dc conductivity and optical relaxation time leads to a mean free path $l\simeq100$ Å. The coherence length[13] $\xi=30$ Å, and the penetration depth $\lambda(T=0)=1\ \mu$m, all parameters referring to the in-plane quantities. We have calculat-

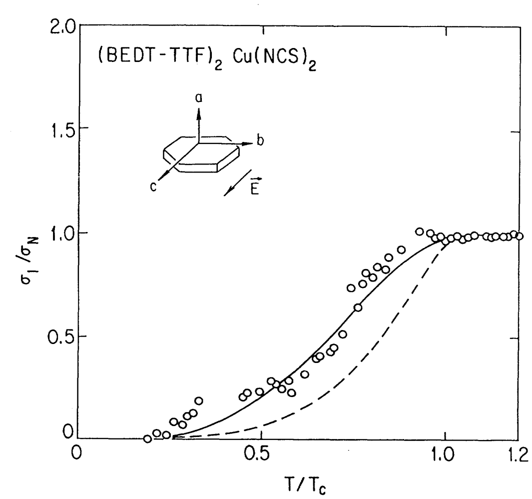

FIG. 3. Temperature dependence of the in-plane conductivity $\sigma_1(T)/\sigma_N(T)$. The solid line is σ_1 obtained using a BCS ground state; the dashed line is the result of the two-fluid model.

ed[14] R_s and X_s for various values of $l/\pi\xi_0$, assuming a two-dimensional BCS ground state, with a single-particle gap given by the weak-coupling limit $2\Delta = 3.5k_BT_c$. Calculations which take strong-coupling effects into account are currently pursued. The best fit to our data (Figs. 2 and 3) leads to a value of $l/\pi\xi_0 = 1.7$, and, consequently, to $\omega\tau = 0.27$ at $f = 60$ GHz, and this leads to a relaxation rate $1/\tau = 10$ cm^{-1}. This value is shorter than $1/\tau = 1000$ cm^{-1} obtained from optical studies and somewhat larger than $1/\tau = 2$ cm^{-1} which is evaluated using Shubnikov–de Haas measurements.[15] Some of these differences may reflect a frequency-dependent relaxation time and deviations from a single Drude response in the metallic state.

The relatively broad transition observed in κ(BEDT-TTF)$_2$Cu(NCS)$_2$ can crudely be modeled along the lines which have been done for interpreting the specific heat[5] by assuming a distribution of local transition temperatures in the specimen. Such a distribution is expected also to influence the temperature dependence of the electrodynamical response. We have modeled this by assuming that

$$X_s(T), R_s(T) = \int [X_s(T), R_s(T)] P(T-T')dT' , \quad (3)$$

where $R_s(T)$ and $X_s(T)$ are the calculated surface impedance parameters described before and $P(T)=1$ for $|T| < 0.5$ K and $P(T)=0$ outside this temperature range. The solid lines in Fig. 2 are $X_s(T)$ and $R_s(T)$ resulting from such a procedure. Although representing the broad transition with a simple distribution of independent local transition temperatures and calculating X_s and R_s using Eq. (3) is certainly an oversimplification, it is clear from Fig. 2 that one can account for the full in-plane electrodynamics with a BCS ground state and moderate sample quality. The normal-state skin depth $\delta = (2/\mu_0\omega\sigma)^{1/2} = 3.4$ μm at $f = 60$ GHz. With this value of δ, using the temperature dependence of X_s below T_c one can get the parallel penetration depth $\lambda_\parallel(T=0) = 1.4$ μm in excellent agreement with λ values evaluated from muon-spin-rotation (μSR) studies which lead to $\lambda_\parallel(T=0) = 0.70$ and 0.98 μm, respectively.[3,4] The agreement between our and the μSR results also demonstrates that misalignment effects do not play an important role.

We also note that within experimental error X_s displays only a weak temperature dependence at temperatures well below T_c. In this limit $X_s = \mu_0\omega\lambda_\parallel$, and, consequently, our results are in full agreement with $\lambda_\parallel(T)$ evaluated from μSR studies,[4] and in clear disagreement with the temperature dependence of $\lambda_\parallel$ evaluated from ac magnetization measurements.[1]

The behavior we obtained for the direction perpendicular to the b-c plane is qualitatively similar to that obtained for the in-plane quantities, however, the parameters are dramatically different. The normal-state resistivity is highly anisotropic,[16] with $\rho_\perp/\rho_\parallel = 10^3$, and this leads to the normal-state R_s and X_s which are a factor of $(10^3)^{1/2} \sim 30$ times larger than for the in-plane quantity. Using the skin depth $\delta_\perp = (2/\mu_0\omega\sigma_\perp)^{1/2}$ and a procedure analogous to that described above leads to $\lambda_\perp = 30$ μm.

Perpendicular to the planes, the coherence length $\xi_\perp < d$, where d is the interplanar separation. Under such circumstances, the situation is close to that of Josephson-coupled planes, with the resulting penetration depth[17]

$$\lambda_\perp = (hc^2\rho_\perp/8\pi^3\Delta)^{1/2} , \quad (4)$$

where $\rho_\perp$ is the conductivity perpendicular to the planes. Our surface resistance measurements give an approximate value $\rho_\perp = 1$ Ω cm just above the transition; this, together with $\Delta = 1.76k_BT_c$, leads to $\lambda_\perp = 32$ μm in excellent agreement with the experimentally obtained value.

We have also evaluated σ_1 and σ_2 in the superconducting state by using Eq. (1) and the measured R_s and X_s values. In Fig. 3 we display the conductivity σ_1 normalized to the (expected) normal-state conductivity σ_N which would be recovered at the same temperature. Also displayed in the figure are calculations based on the two-fluid and BCS model. While σ_1/σ_N calculated from the two-fluid model decreases as the temperature is decreased, the calculation based on the BCS ground state leads to a broad maximum, reflecting case-II coherence factor.[8] Although further experiments, including the measurement of $\sigma_N(T)$ below T_c by applying dc magnetic fields, are required to decide whether the observed rise of $\sigma_1(T)/\sigma_N(T)$ is due to case-II coherence effect, it is clear that our experimental results are in full agreement with a BCS ground state.[18]

We note that higher-momentum pairing leads to the rapid disappearance of the coherence peak[19] and is expected to give σ_1 values significantly below the solid line of Fig. 3. Our experiments, in contrast, lead to a conductivity which lies above the curve calculated for singlet pairing, and, consequently, we regard Fig. 3 as important evidence for a singlet ground state. A full analysis of our results will be reported later.[20]

In conclusion, the temperature-independent surface reactance for $T \ll T_c$ and the increase of σ_1 somewhat below T_c rule out a superconducting ground state which is significantly different from singlet pairing.

We believe that observations which suggest[1-3] an unconventional superconducting ground state are the consequence of nonideal sample quality, of the strongly anisotropic nature of the superconducting state and/or demagnetization effects. Spurious power-law temperature dependences of λ for $T \ll T_c$ are also often obtained in oxide superconductors[21] where it is believed that they may arise from the presence of inhomogeneous weak links regions. Although we have compared our experiments with weak-coupling theory, similar experiments on high-quality specimens and extension of our calculations for larger gap values may, in principle, establish whether strong-coupling effects are important and whether the gap exceeds the BCS value.

We thank D. Scalapino and D. Jerome for useful discussions. This research was supported by the National Science Foundation, Grant No. DMR89-13236.

[a]Permanent address: Central Research Institute for Physics, P.O. Box 49, H1525 Budapest, Hungary.

[1]K. Kanoda *et al.*, Phys. Rev. Lett. **65**, 1271 (1990); Physica (Amsterdam) **162C**, 405 (1989).

[2]T. Takahashi *et al.*, Synth. Met. **27**, A319 (1988).

[3]Y. J. Uemura *et al.*, in Proceedings of the Nato Advanced Research Workshop on Dynamics of Magnetic Fluctuations in High Temperature Superconductors, Crete, 1989 (to be published).

[4]D. R. Harshman *et al.*, Phys. Rev. Lett. **64**, 1293 (1990).

[5]J. E. Graebner *et al.*, Phys. Rev. B **41**, 4808 (1990).

[6]K. Kornelsen *et al.*, Solid State Commun. **72**, 475 (1989).

[7]See, for example, C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963).

[8]M. Tinkham, *Introduction to Superconductivity* (Kriegler, Melbourne, FL, 1975).

[9]K. Holczer and G. Grüner (to be published).

[10]M. Cohen *et al.*, Solid State Commun. **17**, 367 (1975).

[11]L. I. Buranov *et al.*, Zh. Eksp. Teor. Fiz. **95**, 322 (1989) [Sov. Phys. JETP **68**, 182 (1989)].

[12]D. C. Mattis and John Bardeen, Phys. Rev. **111**, 412 (1958).

[13]M. Tokumoto *et al.*, Synth. Met. **24**, A305 (1988).

[14]J. J. Chang and D. J. Scalapino, Phys. Rev. B **40**, 4299 (1989).

[15]N. Toyota *et al.*, J. Phys. Soc. Jpn. **57**, 2616 (1988).

[16]K. Oshima *et al.*, Synth. Met. **27**, A419 (1988).

[17]V. Ambegaokar and A. Baratoff, Phys. Rev. Lett. **10**, 486 (1963).

[18]Because of the expected temperature dependence of the relaxation time τ and mean free path l in the superconducting state, the calculations should be conducted by taking this effect into account. The theoretical curves shown in Fig. 2 are for one particular value $l = 1.7\pi\xi_0$, however, calculations of $R_s(T)$ and $X_s(T)$ for other l values indicate that $l(T)$ effects are small, and will not lead to a significant deviation from the solid line of Fig. 3.

[19]D. J. Scalapino (private communication).

[20]O. Klein, K. Holczer, and G. Grüner (to be published).

[21]J. R. Cooper *et al.*, Phys. Rev. B **37**, 638 (1988); L. Krusin-Elbaum *et al.*, Phys. Rev. Lett. **62**, 217 (1989).