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Microwave surface impedance of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene: Evidence for unconventional superconductivity

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High-sensitivity microwave-impedance measurements performed on the quasi-two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ give sound evidence for an unconventional type of superconductivity. The penetration depth $\lambda(T)$ is in excellent agreement with recent muon-spin-relaxation measurements which are consistent with anisotropic pairings with lines of nodes in the energy gap. The real part of the conductivity σ_1 shows a peaked structure which is free of coherence factor effects and results from a competition between two temperature dependences, the penetration depth and the inelastic relaxation time of the normal fluid.

The synthesis of new superconductors raises fundamental questions concerning the nature of the mechanism responsible for quasiparticle attraction and the symmetry properties of the superconducting ground state. Among these new materials, the organic superconductors are theoretically and experimentally very attractive because of possible new pairing schemes related to their low dimensionality and the occurrence of various magnetic phenomena. The family of organic conductors (BEDT-TTF)$_2X$, based on the BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene] molecule, has been extensively studied;[1] among the various possible phases ($\alpha,\beta,\theta,\kappa,\ldots$) synthesized, many have shown a superconducting ground state at low temperatures under pressure. In their normal states these superconducting compounds present a pronounced quasi-two-dimensional character: an isotropic conductivity in a highly conducting plane and a parallel to perpendicular (to the plane) conductivity ratio larger than 100;[2] a flat variation of the magnetic susceptibility as a function of temperature;[3] poor nesting properties;[4(a)] well-defined two-dimensional (2D) Fermi surface (Shubnikov–De Haas).[4(b)] Such regular normal-state properties would indicate favorable conditions for a conventional pairing in these organic superconductors as compared to more correlated 1D systems. This is, however, a question that has not yet been settled by the different experimental data gathered on many compounds.

It is our intention to address this question by studying the compound κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ which is an ambient pressure superconductor showing a two-dimensional character and for which the superconducting state has been investigated by various techniques. The muon-spin-relaxation (μSR) measurements of Harshman *et al.*,[5] and the surface impedance studies of Klein *et al.*[6] and Holczer *et al.*[7] have all been interpreted as signatures of conventional S-wave-type pairing; this is also supported, though indirectly, by the measurement of the isotope effect in the β phase of the iodine compound.[8] In contrast, magnetic-susceptibility studies of Kanoda *et al.*[9] and recent μSR measurements of Le *et al.*[10] have shown a linear variation of the penetration depth at low temperatures which is rather consistent with anisotropic pairing with lines of nodes in the energy gap; the absence of a coherence peak in the NMR (nuclear magnetic resonance) relaxation rate[11] could be explained by such a mechanism. The controversy about the nature of the pairing mechanism is thus well alive in this compound.

Among the various properties of superconductivity, the magnetic penetration length $\lambda(T)$ is certainly one of the most fundamental: from the low-temperature limit the ratio of the superconducting carrier density n_s to the carrier effective mass m^* is deduced while its temperature dependence provides information regarding the ground-state symmetry. Another essential feature of the BCS theory is the presence of coherence factors. We know that in conventional superconductors these factors have a pronounced effect on ultrasonic attenuation and electromagnetic absorption;[12] they also give rise to the Hebel-Slichter anomaly in the nuclear relaxation rate. A similar anomaly is also expected in the real part of the microwave conductivity σ_1 due to the same coherence factors. Such a peak has only been observed recently in lead[13(a)] and niobium.[13(b)] This coherence peak is suppressed by magnetic scattering while significant gap anisotropies and strong electron-phonon coupling may act to broaden the peak; the anomaly is also strongly affected for higher angular momentum pairing. Finally, it has been shown recently that inelastic electron scattering can introduce a peaked temperature dependence on the microwave conductivity in Y-Ba-Cu-O crystals,[14] a feature that is not a manifestation of coherence but the result of two competing temperature dependences, namely, those of the normal-fluid density and the scattering time.

We present in this paper high-precision microwave-surface-impedance data which corroborate unconventional-type superconductivity for this 2D superconductor. An important peak well below T_c is clearly observed on σ_1 but it is shown to be not associated to coherence effects. The temperature dependence of the penetration depth deduced from the surface reactance is in perfect agreement with the recent μSR study of Le *et al.*;[10] moreover this dependence which is free from any vortex line motion effect is obtained in zero magnetic field for a larger temperature range.

The single crystals were grown by the electrocrystallization method in a 1,1,2-trichloroethane–acetylacetonate mixture using BEDT-TTF prepared by Larsen-Lenoir[15] synthesis and $[P(C_6H_5)_4]Cu(NCS)_2$ as electrolyte. Under these conditions the best superconducting properties were consistently obtained for crystals grown at 50 °C in a large electrochemical cell. Crystal structure was confirmed by x-ray analysis. Single crystals of the same batch yield similar microwave properties; to get the highest sensitivity, we choose a thin crystal having the largest surface, a shiny platelet of typical size $1.5 \times 0.8 \times 0.05$ mm^3. The crystal showed no surface texture or defects; the crystal seemed also free of internal subgrain structure. The superconducting critical temperature was 9.05 K.

The microwave experiment was conducted according to a standard cavity perturbation technique which consists of measuring the frequency shift $\Delta\omega/\omega_0$ and the variation of the quality factor $\Delta(1/2Q)$ of a rectangular copper resonator after insertion of a conducting sample. The cavity is operated at 17 GHz in a TE_{102} transmission mode. The disk-shaped sample (platelet) is located at the antinode of the ac magnetic field $\mathbf{H}_{ac}$. This field being perpendicular to the highly conducting *b-c* plane, the currents are then flowing across this plane and the parallel surface impedance may be obtained. Frequency changes can be measured with a precision of one part in 10^8 and the precision on the temperature is 5 mK. A static magnetic field up to 10 T can be applied perpendicular or parallel to the *b-c* plane.

In the skin-depth approximation, the surface impedance Z_S is related to the complex conductivity $\sigma^* = \sigma_1 - i\sigma_2$ by the equation

$$Z_S = [i\omega\mu_0/(\sigma_1 - i\sigma_2)]^{1/2} = R_S + iX_S \ , \quad (1)$$

where ω is the angular frequency and μ_0 the free space permeability. The surface resistance R_S and reactance X_S are then related to the experimental parameters by

$$\Delta(1/2Q) + i[\alpha/(1-N) - \delta\omega/\omega] = \beta(R_S + iX_S) \ . \quad (2)$$

The constants N and α are, respectively, the depolarization and filling factors; the constant β reflects the geometries of the sample and the cavity. The ratio $\alpha/(1-N)$ is the limiting value of the frequency shift when infinite conductivity is considered. The determination of σ_1 and σ_2 from Eq. (1) is straightforward if high-precision data are available; this requires the simultaneous measurement of R_S and X_S. This last difficulty explains why such kinds of data have not been obtained in the past on conventional superconductors.

In the normal state ($T > T_c$) the real part of the conductivity σ_1 is much larger than the imaginary part σ_2 and following Eq. (1) $R_S = X_S = (\mu_0\omega/2\sigma_n)^{1/2} = R_n$. The index n refers here to the normal-state conductivity and resistance. In order to be completely independent of geometrical factors, we will be discussing only relative values R_S/R_n and X_S/R_n. The inversion of Eq. (1) will then yield relative conductivities σ_1/σ_n and σ_2/σ_n. In the superconducting state ($T < T_c$), the surface reactance X_S is directly related to the in-plane penetration depth λ by the relation

$$X_S(T) = \omega\mu_0\lambda(T) \ . \quad (3)$$

As we apply a time varying magnetic field to the sample, an electric field is induced within the superconductor; this electric field produces then a normal current which gives rise to a power loss from which the surface resistance R_S in the two-fluid model[16] is found to be proportional to

$$R_S \sim \omega^2\sigma_1\lambda^3(T) \ , \quad (4)$$

where σ_1 is the conductivity of the normal fluid.

In Fig. 1(a) we display the temperature dependence of the surface resistance R_S and reactance X_S for $T < 20$ K. In the normal state ($T > T_c$) both sets of data are identical, an observation which is clearly indicative of the skin-depth regime. The dc resistivity has also been measured over the same temperature range by a four-probe technique on a crystal of the same batch: these data have been transformed to R_{dc} in the same figure. There is perfect agreement with the microwave data in the normal state, another indication that the surface-impedance approximation is valid. On both R_S and X_S the width of the transition is much larger than the one observed on conventional superconductors.[13] This is not believed to be due to crystal inhomogeneities or critical-temperature distribution but an intrinsic property of the organic superconductor. In Fig. 1(a) the normal-state resistance R_n' has been obtained with a 10 T magnetic field applied perpendicular to the *b-c* plane. For this orientation the crys-

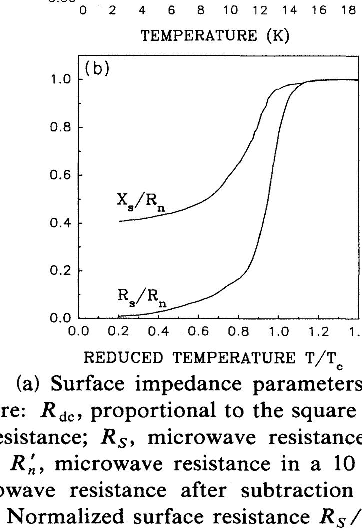

FIG. 1. (a) Surface impedance parameters as a function of temperature: R_{dc}, proportional to the square root of the direct current resistance; R_S, microwave resistance; X_S, microwave reactance; R_n', microwave resistance in a 10 T magnetic field; R_n, microwave resistance after subtraction of magnetoresistance. (b) Normalized surface resistance R_S/R_n and reactance X_S/R_n as a function of the reduced temperature T/T_c.

tal is brought easily to its normal state since the perpendicular critical field H_{c2} is only ~6 T at 1.8 K.[1,2] We can also observe that R_n' is not coincident with R_S for $T > T_c$: this is due to a sizable magnetoresistance contribution for this field orientation. This magnetoresistance can be extracted from R_S vs H^2 plots obtained at fixed temperatures; for field values $H > H_{c2}(T)$, a linear variation is observed and then the zero-field extrapolated value of R_S yielded R_n. The curve R_n [Fig. 1(a)] has been obtained from such field scans at every 1 K over the temperature range 2–18 K; this curve will now be considered to be the normal-state resistance for the overall temperature range. This precise determination of R_n at all temperatures allows us to display in Fig. 1(b) the normalized surface resistance R_S/R_n and reactance X_S/R_n as a function of reduced temperature $t = T/T_c$ in zero magnetic field [$T_c = 9.05$ K; this is identified as a clear departure from linearity on curve X_S of Fig. 1(a)].

These normalized data for κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ are more precise and somewhat different from the data of Klein *et al.*[6] obtained at higher frequency (60 GHz). This could be due partly to an improved sensitivity and partly to the fact that, here, the measured R_n is available to calculate the ratios. The variation of X_S/R_n below T_c is larger in our microwave data and no saturation is observed down to $t = 0.2$. The normalized resistance reaches its $T = 0$ value very slowly around 2 K. This is in clear contrast with the behavior observed on conventional superconductors: a rapid saturation of X_S/R_n and an exponential decrease of R_S/R_n.[13] These normalized data have been used to calculate the normalized complex conductivity according to Eq. (1). The real part of the conductivity σ_1/σ_n is shown in Fig. 2(a) as a function of the reduced temperature. Below T_c a broad maximum centered around $t = 0.6$ is observed. At low temperatures the decrease is not exponential and, at $t = 0.2$, we have still 50% of the normal-state value. As it is well established in conventional superconductors, coherence effects lead to a Hebel-Slichter anomaly in the T_1^{-1} nuclear relaxation rate below T_c. A similar anomaly is also expected in σ_1/σ_n as a function of temperature[12] and, indeed, it has been recently observed in Pb [Ref. 13(a)] and Nb.[13(b)] We show in Fig. 2(a) two curves for σ_1/σ_n representing ways to effectively soften the singularity. Curve I was obtained by the introduction of a uniform smearing of the BCS energy gap which can be related to a small anisotropy; the smearing is chosen (10^{-6}) to adjust the maximum value of σ_1/σ_n to the experimental value. Obviously this procedure fails to reproduce the experimental curve: the maximum is located always very near T_c and the decrease at low temperatures is exponential. Curve II was obtained by using a complex gap $\Delta^*(T)$ to take account of inelastic phonon scattering below T_c following a procedure of Fibich[17] to fit the T_1^{-1} peak in aluminum; the parameters used for the fit are the effective mass $m^* = 3.5 m_e$ (Ref. 1) and the Debye frequency $\omega_D \approx 100$ K (Ref. 18) with a BCS gap for the real part. Although this procedure worked perfectly for niobium,[13(b)] it fails to reproduce the experiment on κ-(BEDT-TTF)$_2$Cu(NCS)$_2$: the peak is wider than in curve I but it still occurs at a higher temperature with an exponential decrease. In contrast to previous results and interpretation,[6] coherence effects thus seem inefficient to explain the observed peak in σ_1/σ_n.

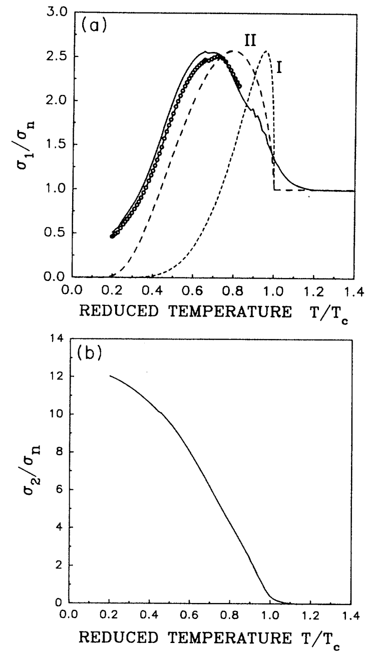

FIG. 2. Normalized microwave conductivity as a function of temperature. (a) Real part σ_1/σ_n: (——), from Eq. (1); (- - -), curve I; (— — —) curve II, (o-o-o), from Eq. (5). (b) Imaginary part σ_2/σ_n (dirty limit calculation).

This then raises the question of the physical conditions which are favorable for this observation. The losses due to the normal fluid calculated in Eq. (4) *without coherence factors* can be normalized to yield the following equation:

$$\sigma_1/\sigma_n = (R_S/R_n)(\delta/\lambda)^3 , \qquad (5)$$

where $\delta(T)$ is the normal-state skin-depth and $\lambda(T)$ the penetration depth. For the latter, it is possible to use Eq. (3) to deduce the penetration length $\lambda(T)$ from the surface reactance; the absolute value of X_S is dependent upon the geometrical factor β and we must then use the measured dc resistivity to get an order of magnitude. By extrapolating the data to zero temperatures we get $\lambda(0) \sim 20\,000$ Å, a value approximately two times larger than the value found in the literature[5] probably because of a larger imprecision on the absolute value of the dc resistivity. In order to be independent of geometrical factors, we will consider only the ratio $\lambda(T)/\lambda(0)$ which is shown in Fig. 3. These data are in excellent agreement with the recent μSR measurements[10] obtained for $t < 0.6$; in the microwave experiment no magnetic field is present and the data extend to T_c. These data clearly confirm that the in-plane penetration depth cannot be explained by an *S*-wave state as in conventional isotropic superconductors (dashed curve); one should expect a nearly constant value at low temperatures contrary to what is shown here. Our data are instead consistent with the predicted curvatures[10] for anisotropic pairings with lines of nodes in the energy gap.

So by using $\lambda(T)$ determined from X_S and the normal-

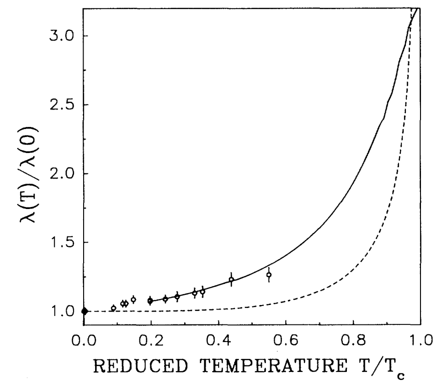

FIG. 3. Normalized penetration depth $\lambda(T)/\lambda(0)$ as a function of the reduced temperature: microwave data (full line), μSR data from Le *et al.* (symbols), conventional isotropic superconductivity (dashed curve).

state resistance for $\delta(T)$ we obtain the data shown as circles in Fig. 2(a) for σ_1/σ_n. A maximum is indeed appearing as a function of temperature around $t=0.6$; it is identical to the one shown in Fig. 2(a) by inverting directly Eq. (1) without specifying any model. As suggested by the measurement of R_n shown in Fig. 1 for $T<T_c$, the scattering rate can be written as $1/\tau=1/\tau_0+1/\tau_{\rm ine}$ where an inelastic scattering time is introduced. As the temperature is decreased, the observed maximum is the result of a competition between two temperature dependences, an increasing inelastic scattering time $\tau_{\rm ine}(T)$ and a decreasing penetration depth $\lambda(T)$. Such a temperature competition has also been used to explain the microwave resistance of a high-quality Y-Ba-Cu-O single crystal;[14] in this high-T_c superconductor however, R_n cannot be measured directly by applying a magnetic field since H_{c2} is too large and moreover the penetration depth used was obtained from the literature since it could not be measured directly during the microwave experiment. This is why the organic superconductor is so interesting experimentally: excellent crystal quality, laboratory critical fields, and simultaneous measurement of the conductivity σ_1 and the penetration depth $\lambda(T)$. The absence of a similar anomaly in T_1^{-1} is nevertheless consistent with the σ_1 presented here since no scattering time appears in the NMR relaxation rate; the huge peak observed on T_1^{-1} (Ref. 11) is magnetic field dependent and it has been tentatively explained by flux melting,[19] not by coherence effects.

Finally let us look now at the temperature dependence of σ_2/σ_n in Fig. 2(b). When decreasing the temperature below T_c, it increases rapidly in a familiar way from zero at T_c up to a value around 13; no saturation is seen down to $t=0.2$. In the dirty limit at low frequencies, the imaginary part of the conductivity is related to the gap $\Delta(T)$ by the simple analytical expression $\sigma_2/\sigma_n=\pi\Delta/\hbar\omega\tanh[\Delta(T)/2k_BT]$.[12] For niobium[13(b)] this expression yields the value $2\Delta(0)/k_BT_C\approx3.8$ in agreement with a strongly coupled BCS superconductor; the ratio obtained here is only 0.48. If the use of the preceding limit is adequate, this result again shows strong deviations with respect to a conventional superconductor.

In summary we have presented high-precision microwave-surface-impedance results on κ-(BEDT-TTF$)_2$Cu(NCS$)_2$ which bring additional evidence for unconventional pairing in this compound. The magnetic penetration depth has been measured in zero magnetic field for reduced temperatures $0.2<t<1.0$: excellent agreement with recent μSR results which concluded that a S-wave pairing cannot explain the observed temperature dependence is obtained. As for the broad anomaly obtained in σ_1/σ_n, it was shown to be free from any coherence factor effects and it can be reproduced by taking into account the increasing inelastic-scattering time for quasiparticles of the normal fluid and the decreasing penetration depth below T_c. Unconventional superconductivity seems thus to characterize κ-(BEDT-TTF$)_2$Cu(NCS$)_2$ and this occurs despite the recently measured isotope effect originating from intramolecular phonons on the similar compound β-(BEDT-TTF$)_2$I$_3$ which is likely to favor isotropic-type pairing.

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[1]See, for example, T. Ishiguro and K. Yamaji, *Organic Superconductors,* Springer Series in Solid State Sciences Vol. 88 (Springer-Verlag, Berlin, 1990); Proceedings of the International Conference on the Science and Technology of Synthetic Metals: ICSM'88, Santa Fe, New Mexico, 1988 [Synth. Met. **27**, (1988)]; Proceedings of the International Conference on the Science and Technology of Synthetic Metals, Tubingen, Federal Republic of Germany, 1990 [Synth. Met. **42**, (1991)].

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