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Microwave-loss studies of organic superconductors

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We have conducted microwave-loss studies on organic superconductors. We report measurements on a series of crystals prepared from the bis(ethylenedithio)tetrathiafulvalene (ET) donor: α-$(ET)_2I_3$, β-$(ET)_2I_3$, κ-$(ET)_2Cu(NCS)_2$, κ-$(ET\text{-}d_8)_2Cu(NCS)_2$, and κ-$(ET)_2Cu[N(CN)_2]Br$. All compounds show clear evidence for superconductivity, although there is a marked difference in the quality of the crystals as reflected in the microwave signals. The latter three materials show sharp, well-defined transitions that are comparable to those observed in the high-T_c superconductors, and they exhibit highly anisotropic vortex motion. We confirm the T_c of 11.6 K for the organic superconductor κ-$(ET)_2Cu[N(CN)_2]Br$, which is 2–3 K higher than that of κ-$(ET)_2Cu(NCS)_2$. We also confirm the approximately 0.5-K isotopic enhancement in the T_c of κ-$(ET\text{-}d_8)_2Cu(NCS)_2$. The microwave-loss experiment is ideally suited for the search for superconductivity in organics and the experiment may be performed with the ease and quantity of material required for a melting-point determination—the measurement is nondestructive, contactless, and may be carried out on microgram samples.

INTRODUCTION

Magnetic-field-dependent or differential microwave absorption has become an indispensable technique for the study of high-T_c superconductors.[1,2] The method, which for practical purposes senses only superconductivity, can detect submicrogram quantities and distinguish multiple T_c phases, as well as telling something about the quality of the superconducting state achieved.

Surprisingly, to our knowledge, this technique has not been applied to the study of organic superconductors, in spite of the fact that the method is extremely sensitive and is a contactless technique. These latter considerations would appear to recommend the technique for organic materials, which are often available in very small quantities and are difficult to manipulate due to the fragile nature of the crystals.

In the present study we report measurements on a series of crystals prepared from the bis(ethylenedithio)tetrathiafulvalene (ET) donor: α-$(ET)_2I_3$,[3–6] β-$(ET)_2I_3$,[3–6] κ-$(ET)_2Cu(NCS)_2$,[7,8] κ-$(ET\text{-}d_8)_2Cu(NCS)_2$,[7,8] and κ-$(ET)_2Cu[N(CN)_2]Br$.[9] As prepared, α-$(ET)_2I_3$ undergoes a metal-insulator transition at 135 K,[5] but thermal annealing has been reported to convert the material into the α_t phase, which is an 8-K superconductor.[10–12] β-$(ET)_2I_3$ is a 1.5-K superconductor,[3,4] but the application of pressure (500 bar) below 120 K converts the material into the β^* phase which is also an 8-K superconductor.[13,14] It has also been reported that some of the β^* phase is produced by simply allowing the material to anneal at 120 K for a period of time.[15] κ-$(ET)_2Cu(NCS)_2$ is a 10.4-K superconductor, and the deutero-derivative κ-$(ET\text{-}d_8)_2Cu(NCS)_2$ has been reported to have slightly higher transition temperature.[7,8] κ-$(ET)_2Cu[N(CN)_2]Br$ is the most recently discovered organic superconductor and its T_c of 11.6 K is the highest yet to be reported.[9]

All of these materials are quasi-two-dimensional systems[16] and this is reflected in the platelike morphology of the crystals. The two largest dimensions of the crystals are associated with the conducting planes of ET molecules. The interactions between the organic planes are inhibited by the interposing layers of counterions. These alternating planes are perpendicular to the following axes: α-$(ET)_2I_3$ ($\boldsymbol{c}^*$), β-$(ET)_2I_3$ ($\boldsymbol{c}^*$), κ-$(ET)_2Cu(NCS)_2$ ($\boldsymbol{a}^*$), and κ-$(ET)_2Cu[N(CN)_2]Br$ ($\boldsymbol{b},\boldsymbol{b}^*$). Crystals were mounted for rotation about an axis lying parallel to the crystal face; that is, perpendicular to the axes given above. The axis of rotation was parallel to the microwave magnetic field and perpendicular to the static and modulation fields.

EXPERIMENT

Most of the samples were prepared by conventional methods reported in the literature[3–9] and our own variants of these syntheses have been reported in connection with other studies.[17,18] The iodide phases were distinguished by electron-spin-resonance (ESR) measurements as discussed below. κ-$(ET)_2Cu[N(CN)_2]Br$[9] was synthesized in a standard electrocrystallization cell from ET dissolved in an electrolyte prepared by stirring a solution of $PNP^+[N(CN)_2]^-$ [mp 217–9 °C, where PNP^+ is bis(triphenylphosphins)iminium] in 1,1,2-trichloroethane with excess cuprous bromide.

Microwave-loss measurements were made using computer-controlled electron-spin-resonance instrumentation with a Gunn-diode source. Standard operating conditions consisted of an applied static field of 100 G with 100 μW cavity power at 9.250 GHz and 3.2 G_{rms} field modulation at 100 kHz. Although there are H_{c1} and H_{c2} values reported in the literature for these materials,[16] measurements of microwave loss as a function of applied-field strength showed no obvious indication of either upper or lower critical fields for flux penetration. A stepping motor (1000 steps per revolution) was used for angular measurements, with data synchronously acquired as the sample was turned at 1 revolution per minute (rpm). Crystals were contained in 1-mm quartz capillaries terminated in a narrow slot to maintain their orientation.

RESULTS

κ-(ET)$_2$Cu(NCS)$_2$ and κ-(ET-d_8)$_2$Cu(NCS)$_2$

Figure 1 shows the differential microwave loss measured for a single crystal of this material cooled in a 100-G field parallel to the $\boldsymbol{a}^*$ axis. For this orientation, microwave currents drive vortices back and forth across the **b-c** plane. Above T_c, no field-dependent losses are detectable and the base line is truly a zero signal. There is a very abrupt rise at 8.5 K with a weak foot extending to 9 K. Good inorganic high-T_c samples do not show such a foot, and whether it reflects material inhomogeneities or variations in flux dynamics is uncertain. Conductivity experiments indicate a T_c of 10.2–10.4 K.[8] Other measurements in our laboratories (muon-spin rotation[17] and specific heat[18]) give values of about 9 K.

Below T_c, superconducting loss is quenched by increasing resistance to vortex motions. According to the Gittleman-Rosenblum model, dissipation per vortex varies as[19]

$$\omega^2\eta(\Delta x)^2=\omega^2\eta/(k^2+\omega^2\eta^2)\ , \tag{1}$$

with ω the microwave frequency, η the viscosity, Δx the amplitude of displacements excited by microwave currents, and k a pinning force constant. The viscosity may be estimated from the Bardeen-Stephen expression

$$\eta=\Phi_0 H_{c2}/\rho c^2\ , \tag{2}$$

with Φ_0 the flux quantum, H_{c2} the upper critical field, and ρ the normal-state resistivity. The rapid decrease of microwave loss with temperature indicates that viscous forces dominate at microwave frequencies.

At lower temperatures, the signal returns almost to the base line. Such behavior is only found with high-quality single crystals. Losses in polycrystalline superconductors are dominated by weak links and exhibit losses down to 4 K.

The high, normal-state resistivity of the organic superconductors, 10^{-2} to 10^{-3} Ω cm just above T_c in the case of κ-(ET)$_2$Cu(NCS)$_2$,[8] leads to appreciable microwave heating. The apparent onset of superconductivity is reduced 1 K with a 1-mW microwave power level, compared to the 100-μW level used for these characterizations. One notes in Fig. 1 a substantial "noise" increase in regions where loss is very temperature dependent. Often, at such temperatures, steady-state oscillations with periods of 1 sec were observed. We believe this is due to surface inhomogeneities and superconducting patches. Around such a patch the current density will be higher, as currents are drawn towards low-resistance regions, and local heating, proportional to the square of the current density, leads to a thermal runaway which eventually destroys the patch of superconductivity. We estimate a thermal diffusion coefficient of 10^{-4} cm^2/sec from the ratio of the thermal conductivity and the heat capacity, and the observed oscillation period then corresponds to distances of 100 μm.

A series of experiments were carried out in which crystals were annealed in various inert, oxidizing, and reducing atmospheres at temperatures up to 180 °C. No significant changes were found, apart from a gradual decrease in the superconducting response at the higher annealing temperatures and a greater tendency towards "oscillation." Microwave measurements are especially well suited for such studies as the changes in a particular crystal can be followed during an annealing sequence.[2]

Figure 1 also shows the variation of loss with the applied field parallel to the crystal's **b-c** planes. In this orientation, the flux motion induced by microwave currents is also parallel to these planes and does not require flux to cross these planes. The temperature dependence in this case is markedly different, increasing monotonically as the temperature drops. In terms of Eq. 1, the viscous resistance is much less and the loss now increases with viscosity. Similar behavior is found for polycrystalline copper-oxide-based superconductors of low quality with weak links dominating loss behavior. Angular alignment at this orientation is quite critical and, when the crystal is rotated but a few degrees, the low-temperature losses are quenched (*vide infra*). We infer that flux motion in this crystal is relatively uninhibited when this motion is not required to cross the **b-c** crystal planes.

The behavior of a deuterated single crystal, κ-(ET-d_8)$_2$Cu(NCS)$_2$, is shown in Fig. 2. Its response differs only in an upward shift of T_c of about 0.5 K.[8] Figure 3 shows the response of a thin film[20] grown on sapphire. The broader transition region and the persistent loss at lower temperatures indicate that this sample is of lower

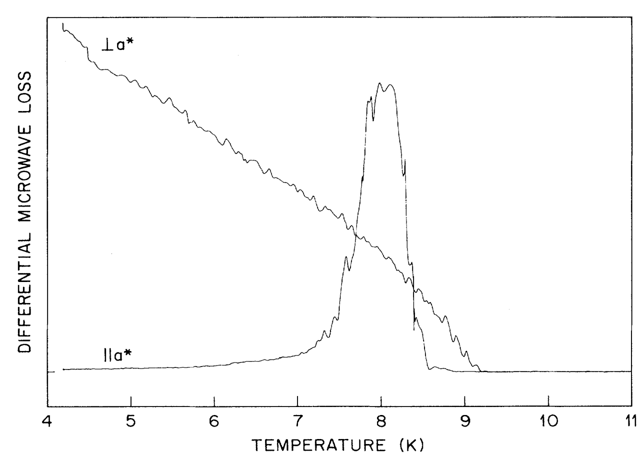

FIG. 1. Differential microwave loss for κ-(ET)$_2$Cu(NCS)$_2$ with the magnetic field parallel (∥) and perpendicular (⊥) to the $\boldsymbol{a}^*$ axis of the crystal.

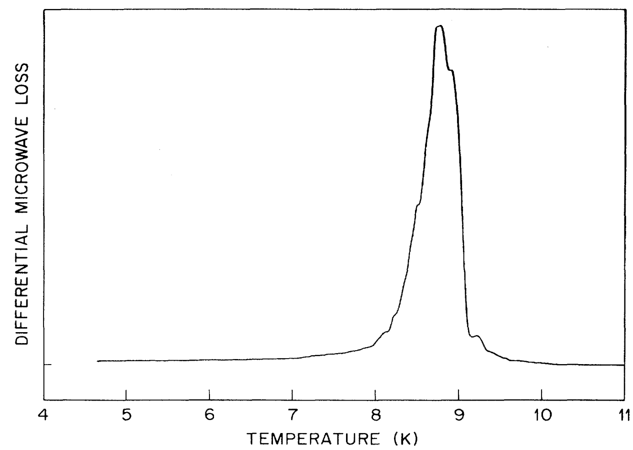

FIG. 2. Differential microwave loss for κ-(ET-d_8)$_2$Cu(NCS)$_2$ with the magnetic field parallel to the $\boldsymbol{a}^*$ axis of the crystal.

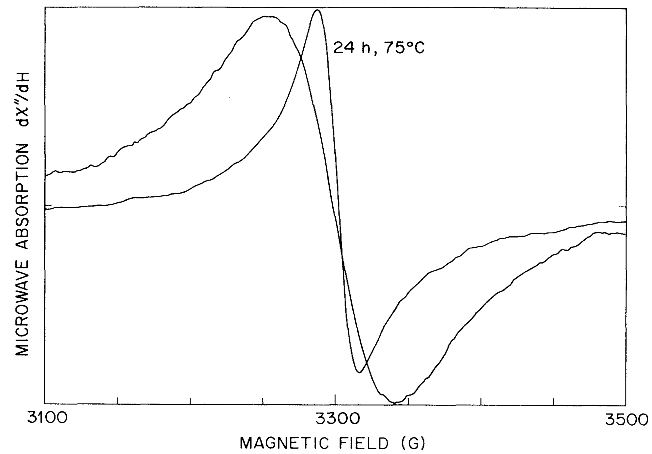

FIG. 4. ESR spectra of a single crystal of α-(ET)$_2$I$_3$, both before thermal treatment, and after heating at 75 °C for 24 h.

quality than those in Figs. 1 and 2, with weak links important at lower temperatures.

α-(ET)$_2$I$_3$

The ESR spectra of a single crystal of α-(ET)$_2$I$_3$ is shown in Fig. 4 both before thermal treatment and after heating at 75 °C for 24 h. It may be seen that the linewidth of the ESR line has changed from 87 to 28 G, which is characteristic of the conversion of α- to α_t-(ET)$_2$I$_3$.[10-12] Before thermal treatment the crystals of α-(ET)$_2$I$_3$ do not show microwave absorption down to 4.2 K. The lower trace in Fig. 5 shows the microwave differential loss as a function of temperature for this crystal, and it is apparent that the crystal shows an onset for superconductivity at about 8 K, which is enhanced on further heat treatment for a period of up to 3 or 4 days, beyond which the superconducting signal strength begins to decrease. Furthermore, by comparison with the materials discussed above, it is clear that the crystal quality does not support a well-developed superconducting state. This is in agreement with crystallographic studies of this phase transformation which have consistently shown that the resulting crystals of α_t-(ET)$_2$I$_3$ are of poor quality—to the point that the detailed crystal structure of this phase has not yet been obtained. The ac susceptibility measurements of superconductivity in α_t-(ET)$_2$I$_3$ show a broad transition,[11,12] which is still incomplete at a temperature of 1.3 K,[11] and ESR studies indicate that the crystals may remain a composite of both phases.[12] While the ESR linewidth narrows after a day of thermal treatment, the microwave experiments indicate that the crystal quality is relatively poor.

β-(ET)$_2$I$_3$

The magnetization of a single crystal of β-(ET)$_2$I$_3$ is shown in Fig. 6—this crystal had been allowed to stand for 24 h at 120 K in the magnetometer, before cooling to

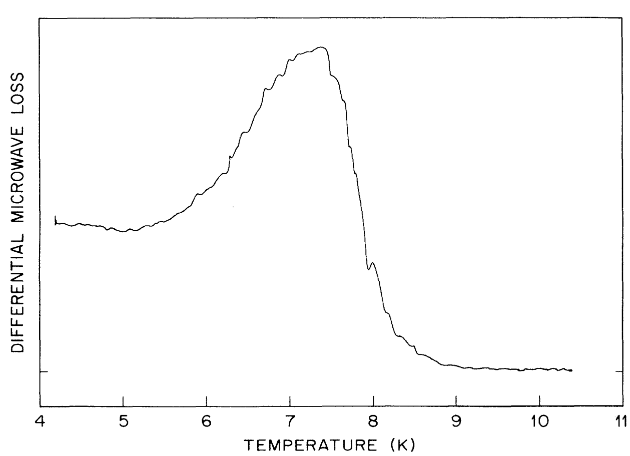

FIG. 3. Differential microwave loss for a thin film of κ-(ET)$_2$Cu(NCS)$_2$ grown on sapphire with the magnetic field parallel to the $\boldsymbol{a}^*$ axis of the crystal.

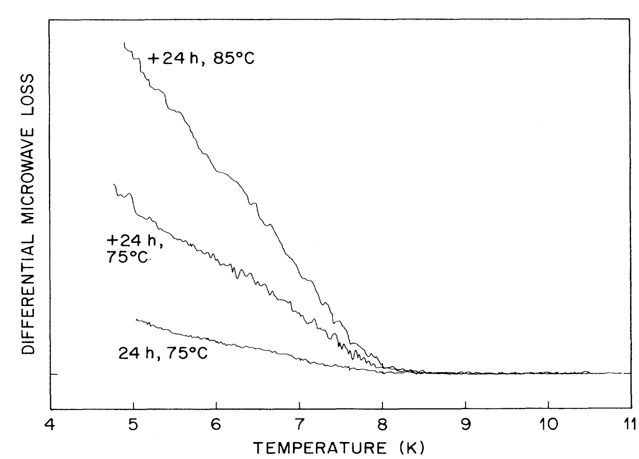

FIG. 5. Differential microwave loss for a single crystal of α-(ET)$_2$I$_3$, after heating at 75 °C for 24 h, and with additional thermal treatments of 24 h at 75 °C, and 24 h at 85 °C.

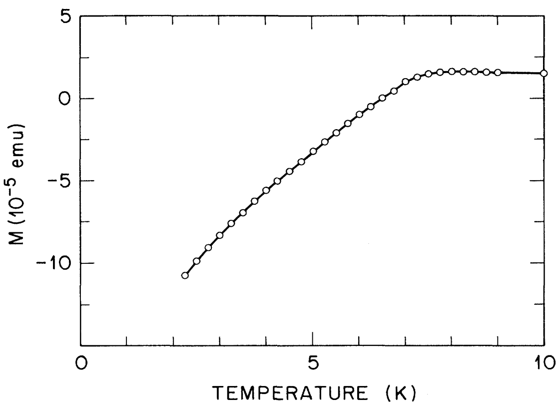

FIG. 6. Magnetization of a single crystal of β-$(ET)_2I_3$ in a field of 50 G. Data were taken upon cooling, after a 24-h anneal at 120 K in the magnetometer.

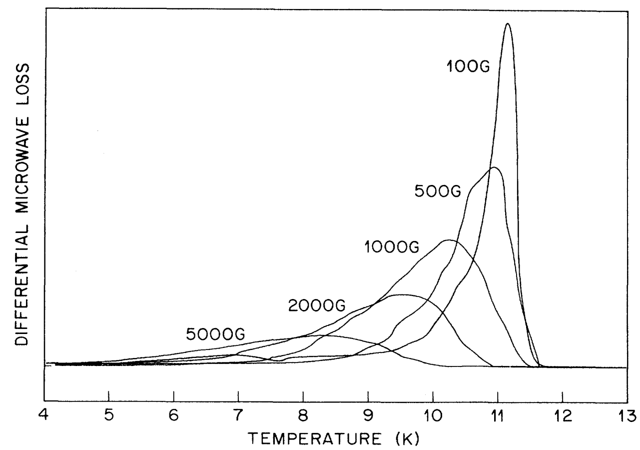

FIG. 8. Differential microwave loss for κ-$(ET)_2Cu[N(CN)_2]Br$ with the magnetic field parallel to the b^* axis of the crystal as a function of the applied-field strength.

low temperatures. Without the low-temperature anneal the crystals showed no evidence of superconductivity in magnetization or microwave measurements down to 4.2 K. The magnetization indicates that about 1% of the sample volume has become superconducting. The microwave experiment is able to detect superconductivity in a single crystal after 4 h at 120 K, which continues to increase (Fig. 7). Both measurements indicate a superconducting onset temperature between 7 and 8 K. Previous magnetization measurements of the ambient pressure conversion of the β to β^* phase at 108 K found $T_c \sim 4.5$ K (20-h anneal), $T_c \sim 6$ K (40 h), and $T_c \sim 7$ K (65 h).[15] With an applied field of 180 Oe, and without correction for demagnetization, the Meissner fraction amounted to 0.2% after 65 h.[15] Furthermore, the change in the wave vector of the superstructure which develops in β-$(ET)_2I_3$ below room temperature has been reported to require 30 h for completion and to be preceded by a 4-h induction period at ambient pressure.[21] This latter annealing period corresponds to about the time necessary for the detection of superconductivity with microwaves.

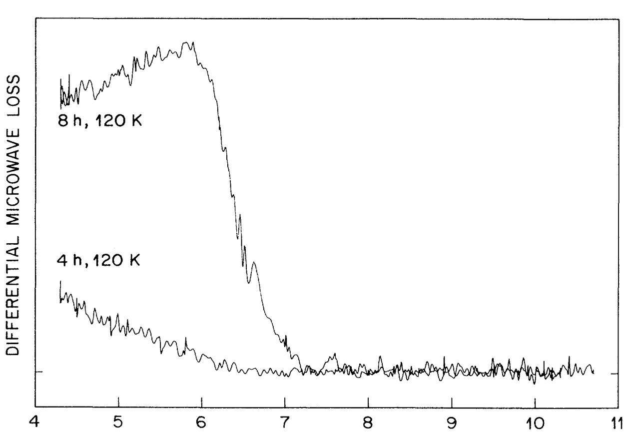

FIG. 7. Differential microwave loss for a single crystal of β-$(ET)_2I_3$ after standing at 120 K for 4 and 8 h in the spectrometer.

κ-$(ET)_2Cu[N(CN)_2]Br$

A T_c of 11.6 K has recently been reported for this material.[9] Microwave measurements, Fig. 8, confirm this value and show that single crystals of excellent quality can be obtained. The crystal used for the measurements

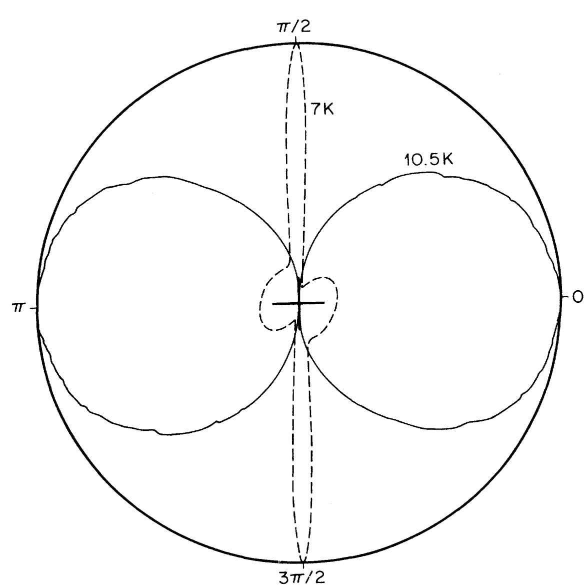

FIG. 9. Azimuthal plot of microwave loss for a crystal of κ-$(ET)_2Cu[N(CN)_2]Br$ at 7 and 10.5 K, where the length of the radius vector is proportional to the measured differential loss and the angle corresponds to that of the crystal's b^* axis with respect to the applied field.

reported in Figs. 8 and 9 was a parallelepiped-shaped plate with dimensions of $1.08 \times 1.08 \times 0.09$ mm^3 and a mass of 222 μg. Angular dependence of microwave loss for this crystal is shown in Fig. 9. In this polar plot, the length of the radius vector is proportional to the measured differential loss and the angle corresponds to that of the crystal's $\boldsymbol{b}^*$ axis with respect to the applied field. Just below T_c, this plot consists of two tangent circles with a node when the field lies in the $\boldsymbol{a}$-$\boldsymbol{c}$ plane. The circular shape is equivalent to a loss proportional to the magnitude of the component of the applied 100-G field normal to these planes, i.e., the number of vortices induced in these planes. At lower temperatures, however, a very sharp maximum occurs with the applied field perpendicular to the $\boldsymbol{b}^*$ axis. This behavior is identical to that of κ-(ET)$_2$Cu(NCS)$_2$, Fig. 1, and we conclude that these two materials have similar anisotropic motional behavior. Recent torque magnetometry studies have found evidence for extreme superconducting effective mass anisotropy in κ-(ET)$_2$Cu(NCS)$_2$ which is comparable to that found for some of the high-T_c cuprate superconductors, and indeed both classes of superconductors contain comparably spaced conducting planes.[22] One may also note the absence of any signs of a lower critical field, which might be expected to reduce flux penetration when the external field makes a shallow angle with the crystal's surface.

Figure 8 also reveals that, for fields > 100 G, the vortex density has a pronounced effect on differential loss, or loss per vortex. A maximum occurs well below T_c and its amplitude varies approximately inversely with field. If we presume that it is the viscosity which is primarily temperature-dependent through its relation to H_{c2}, then Eq. (1) indicates a loss maximum when $\omega\eta = k$, with a value inversely proportional to k or η. The field dependence then suggests $k \propto 1/H$, implying that "pinning" involves nearest-neighbor distances. To fully fit such an interpretation, however, requires the highly *ad hoc* presumption that field modulation affects only the number of vortices and not their density. While it is evident that vortex density has a profound effect on flux motion in this regime of field and temperature, a more quantitative description is called for.

The T_c of 11.6 K reported for this new material[9] indicates a superconducting transition temperature about 2 K higher than the closely related κ-(ET)$_2$Cu(NCS)$_2$. Reference to Figs. 1 and 8 shows that the microwave experiment finds T_c for κ-(ET)$_2$Cu[N(CN)$_2$]Br to be 2–3 K higher than for κ-(ET)$_2$Cu(NCS)$_2$.

SUMMARY

The microwave loss experiment is ideally suited for the search for superconductivity in the organics as it is nondestructive, contactless, and may be carried out on microgram samples. Measurements on κ-(ET)$_2$Cu(NCS)$_2$ and κ-(ET)$_2$Cu[N(CN)$_2$]Br show sharp well-defined transitions which are comparable to those observed in the high-T_c superconductors and they exhibit highly anisotopic vortex motion. The T_c of 11.5 K in the organic superconductor κ-(ET)$_2$cu[N(CN)$_2$]Br is confirmed by the microwave experiments, as is the isotropic enhancement of T_c in κ-(ET-d_8)$_2$Cu(NCS)$_2$.

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