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Superconductivity at ambient pressure in di[bis(ethylenedithio)tetrathiafulvalene]triiodide, $(BEDT\text{-}TTF)_2I_3$

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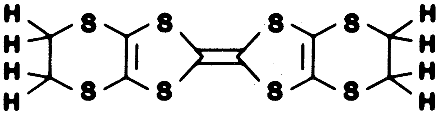
di[bis(ethylenedithio)tetrathiafulvalene]triiodide $[(BEDT\text{-}TTF)_2I_3]$ crystals in the form of distorted hexagon-shaped plates or blocks grown from 1,1,2-trichloroethane and in the form of needles grown from benzonitrile were found to be superconducting at ambient pressure below 1.40 ± 0.02 K. rf penetration depth measurements of the critical temperature and critical field are described. $(BEDT\text{-}TTF)_2I_3$ is the first known sulfur-based, ambient pressure organic superconductor.

INTRODUCTION

It has recently become clear[1-3] that charge-transfer salts of the type $(ET)_2X$ (X = univalent anion) derived from bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF or "ET" (see diagram below)



BEDT-TTF(ET)

comprise a new class of S-based organic conductors with promising new superconducting properties. Yagubskii *et al.*[4] and Kaminskii, Prokhorova, Shibaeva, and Yagubskii[5] have reported evidence that the salt $(ET)_2I_3$ is a member of this class and becomes superconducting at ambient pressure. This salt is, therefore, the *first* ambient pressure S-based organic superconductor and only the *second* presently known ambient pressure organic superconductor, the first being the Se-based superconductor $(TMTSF)_2ClO_4$.[6]

Yagubskii *et al.* reported the electrocrystallization of three forms of $(ET)_2I_3$ from benzonitrile solvent: two with the morphologies of thin flakes and one with the morphology of long needles. The needlelike crystals and one form of the flakes were found to be superconducting under ambient pressure at 1.4–1.5 K on the basis of four-probe resistivity measurements. In order to clarify the structure and stoichiometry, and to investigate the superconducting properties, we have electrocrystallized $(ET)_2I_3$ crystals from a different solvent as well as from benzonitrile. Details of an x-ray structural study of the crystals are described elsewhere.[7] In this Rapid Communication, we report on the superconducting transition temperature and critical magnetic field determined by rf penetration depth measurements.

EXPERIMENTAL PROCEDURES

$(ET)_2I_3$ crystals were grown by electrochemical oxidation of ET at a constant temperature of 23.4 °C in the presence of $(n\text{-}Bu_4N)I_3$ as the supporting electrolyte. With 1,1,2-trichloroethane (TCE) as the solvent, we obtained two types of $(ET)_2I_3$ crystals: large, flat, intergrown plates, and distorted hexagon-shaped crystals, typically more blocklike than flakelike with clearly discerned distorted-hexagon shapes. The structural studies showed that the intergrown plates had unit-cell parameters identical to those reported by Bender *et al.*[8] which exhibit a metal-insulator transition at about 140 K at ambient pressure. The hexagon-shaped crystals had unit-cell parameters identical to the flakelike and needlelike crystals reported by Yagubskii *et al.* to be superconducting. In benzonitrile solvent, we obtained only needlelike crystals of $(ET)_2I_3$ with unit-cell parameters identical to the superconducting crystals. In this respect, our results differ from the work of Yagubskii *et al.*, who obtained all their crystals (both needles and flakes) from benzonitrile. The x-ray data confirmed the 2:1 ($X = I_3^-$) stoichiometry with space group $P\bar{1}, Z = 1$.

rf penetration depth measurements[9,10] were carried out on crystals cooled in a pumped liquid-helium (He^4 or He^3) cryostat surrounded by a superconducting magnet. The samples were contained in epoxy cylinders which could be inserted in an rf coil consisting of approximately three hundred turns of copper wire wound on an epoxy coil form measuring 3.75 mm in length and 2.05 mm in diameter. The coil was operated at frequencies of ~ 513 kHz. The rf penetration depth was measured at temperatures down to 0.44 K and in fields up to approximately 15 kOe. Temperatures were determined from the vapor pressure above the liquid He^3 or He^4. Superconductivity was detected by the increase in the resonant frequency of the rf coil caused by the exclusion of the rf field from the sample by persistent shielding currents. Because changes in the rf frequency of 1 part in 10^5 can be detected easily in our system, this technique has a high sensitivity to superconductivity in the relatively small samples available for this experiment.

Small pieces of the intergrown plate crystals, the distorted hexagon-shaped crystals, and the needle crystals of $(ET)_2I_3$ were studied. The first two types had dimensions of $\sim 0.3 \times 0.4 \times 0.05$ mm^3, and the needles had dimensions of $\sim 2.0 \times 0.2 \times 0.05$ mm^3. About 20–40 crystals of each type were loosely packed into separate epoxy cylinders, each sample occupying a volume of $\sim 2 \times 10^{-4}$ cm^3 as determined from the total weights and theoretical (x-ray) densities. For comparison, crystals of $(TMTSF)_2ClO_4$, having the typical needle-shaped morphology, were packed into a container for similar rf studies. Microscopic examination of the packed containers showed predominant orientation of the needle axis of $(ET)_2I_3$ (for the needle-shaped crystals) and $(TMTSF)_2ClO_4$ along the cylinder axis parallel with the magnetic field direction. Because of their shape and dimensions, the two other crystal samples were probably randomly oriented in the field direction, but this could not be confirmed by visual inspection.

The epoxy containers of the different samples were attached together into a vertical stack along the axis of the cylinders, parallel to the direction of the magnetic field. The stack was attached to the base of a long rod of fiberglass-reinforced epoxy (G-10) which extended above the refrigeration volume. Vertical positioning of this rod moved the desired sample into the center of the rf coil without change in the temperature. The superconducting signal from a Nb sample attached to the stack was used to calibrate the position of the rod.

RESULTS

Using the above described technique, we detected superconductivity after slow cooling (~ 2 K/min) below 30 K in the $(TMTSF)_2ClO_4$ crystals and in the distorted-hexagon plates and needles of $(ET)_2I_3$ but *not* in the intergrown flakes. The superconductivity of the $(ET)_2I_3$ crystals was not suppressed by rapid cooling as it is in $(TMTSF)_2ClO_4$. The variation with temperature of the resonant frequency of the rf coil containing the distorted-hexagon plates of $(ET)_2I_3$ after a rapid cool down is illustrated in Fig. 1. This figure shows a broad transition which is not complete at the lowest temperature obtained, 0.44 K. The needles of $(ET)_2I_3$ and the slowly cooled $(TMTSF)_2ClO_4$ crystals gave similar broad transition curves.

Careful measurements with the samples immersed in superfluid He^4, with temperatures determined by vapor pressure thermometry, showed the onset of bulk superconductivity to occur at 1.40 ± 0.02 K for both the distorted hexagon-shaped crystals and the needles. This temperature is slightly lower than the 1.4–1.5 K transition determined by Yagubskii *et al.* using four-probe resistivity measurements. This difference is consistent with the broad transition width which allows a low resistance filament to be detected resistively before bulk conductivity in the sample can be detected inductively. In $(TMTSF)_2ClO_4$, for example, inductive measurements of T_c are as much as 0.3 K lower than resistive measurements.[11]

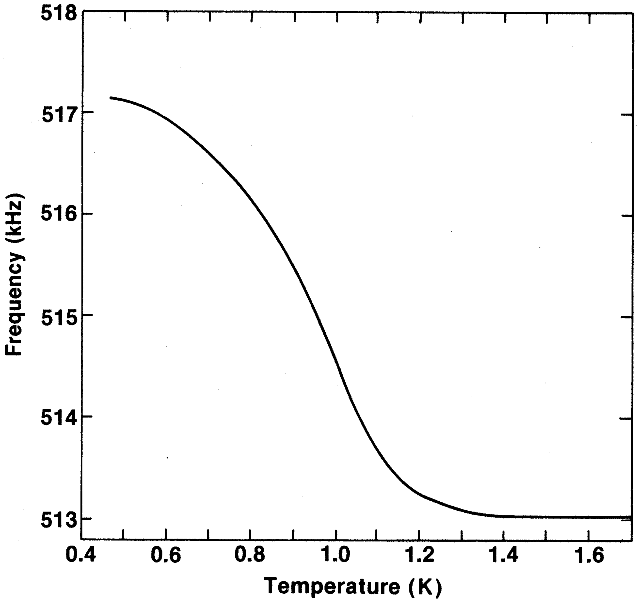


FIG. 1. Resonant frequency of the rf coil containing distorted-hexagon-shaped crystals of $(ET)_2I_3$ as a function of temperature in zero applied field after a fast cooldown.

The critical fields of the distorted hexagon-shaped crystals and needles of $(ET)_2I_3$ and of the reference material $(TMTSF)_2ClO_4$ were investigated by penetration depth measurements in an applied field. The change in oscillation frequency with field from the normal-state value for the distorted hexagon-shaped crystals at several temperatures and for the needlelike crystals of $(TMTSF)_2ClO_4$ are shown in Fig. 2. This figure shows an initial sharp drop in the rf fre-

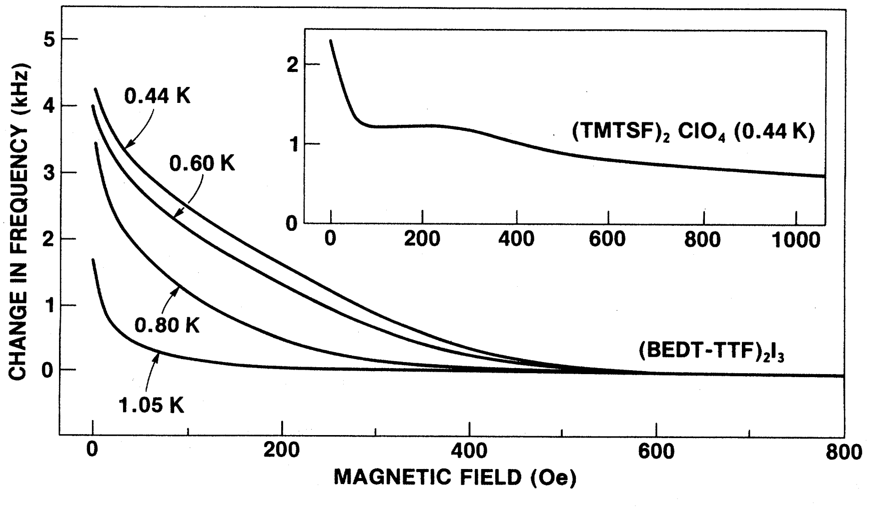


FIG. 2. Change in resonant frequency from the empty coil value for distorted-hexagon crystals of $(ET)_2I_3$ as a function of applied field at various temperatures. Inset shows the low-field region of a similar curve for needle-shaped crystals of slow cooled $(TMTSF)_2ClO_4$.

quency with increasing field for both $(ET)_2I_3$ and $(TMTSF)_2ClO_4$. This is consistent with the broad, incomplete transitions observed for these materials as a function of temperature. The initial penetration of the rf field occurs in those parts of the sample where superconductivity is not fully developed. The initial sharp drop in frequency is consistent with ac susceptibility measurements on $(TMTSF)_2ClO_4$ at 0.65 K.[11] For $(TMTSF)_2ClO_4$, anisotropy in the upper critical field appears as a long shoulder in the rf frequency versus field extending from about 200 to 800 Oe, where the field exceeds H_{c2} for a small percentage of the crystals oriented with the crystallographic *c* axis near the field direction. Beyond 1000 Oe, the rf frequency continues to decrease gradually, becoming equal to the empty coil frequency at 10 kOe, which is the critical field expected[12] for crystals oriented with the needle axis (crystallographic *a* axis) near, but slightly misaligned from, the field direction. Thus for our $(TMTSF)_2ClO_4$ crystals, full penetration of the rf field, which occurs when the rf frequency becomes equal to the empty coil value, coincides reasonably well with the transition to the normal state at H_{c2}.

For the distorted-hexagon crystals of $(ET)_2I_3$, detailed measurements near $H=0$ show that the sharp decrease in oscillation frequency occurs with the first application of the field. The smooth concave upward shape of the rf frequency versus field reveals no obvious features that can be associated with anisotropy in H_{c2}. Such anisotropy is expected from the roughly two-dimensional "corrugated sheet network" of S-S interactions observed[7] in this phase of $(ET)_2I_3$. The oscillation frequency becomes equal to the empty coil value at about 600 Oe, where full penetration of the sample by the rf field and, presumably, the transition at H_{c2} to the normal state occur. If there is no preferential orientation of the platelike crystals of $(ET)_2I_3$ in the magnetic field, this suggests that 600 Oe is the largest field at which bulk superconductivity occurs in $(ET)_2I_3$.

Penetration depth measurements for the needle shaped samples of $(ET)_2I_3$ aligned with the needle axis (crystallographic *a* axis) approximately along the field were very similar to those shown in Fig. 2. Full penetration for the needles was also achieved at about 600 Oe, suggesting that this is the upper critical field associated with directions near the crystallographic *a* direction.

Our estimates of the upper critical field are lower than those reported by Yagubskii *et al.*, who found zero resistance up to 2.0–2.5 kOe, and a slowly increasing magnetoresistance which had not reached the normal state value at 20 kOe, for the field along the crystallographic *b* axis. The difference may simply be due to strong anisotropy in H_{c2}, since none of our measurements put the field specifically along *b*. Alternatively, the difference may reflect the different sensitivities of the measuring techniques, with filamentary superconductivity dominating the resistive measurements and bulk superconductivity dominating the inductive measurements. Such effects are known to be quite important for $(TMTSF)_2ClO_4$, where critical fields measured inductively may be as much as an order of magnitude lower than those measured resistively.[11]

Finally, we note that the penetration depth in organic superconductors is typically rather large, so that full penetration of the magnetic field might be achieved below H_{c2} in samples whose physical dimensions are sufficiently small. A lower critical field H_{c1} of a few Oe implies a penetration depth of a few microns, and in $(TMTSF)_2ClO_4$ there is evidence for a highly anisotropic penetration depth as large as 0.04 mm in certain directions.[13] The smallest dimension of our $(ET)_2I_3$ crystals was ~0.05 mm, possibly of the same order as the penetration depth. If the penetration depth in $(ET)_2I_3$ is large enough, the differences between the resistive and inductive measurements of H_{c2} and T_c can be explained by the small crystal dimensions. Further work is underway to investigate these possibilities.

ACKNOWLEDGMENTS

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