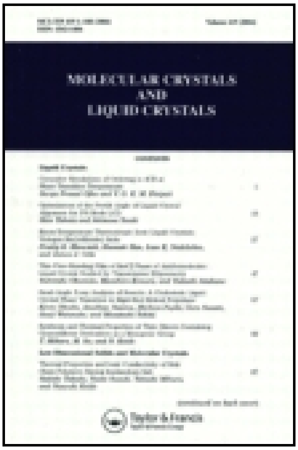

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Superconductivity above 2 K At Ambient Pressure in Iododibromide (IBr_2^-) Charge-Transfer Salts of Bis (ETHYLENEDITHIO) TETRATHIAFULVALENE, BEDT-TTF

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To cite this article: K. Douglas Carlson , G. W. Crabtree , L. N. Hall , F. Behroozi , P. Thomas Copps , L. M. Sowa , L. Nunez , M. A. Firestone , Hau H. Wang , Mark A. Beno , Thomas J. Emge & Jack M. Williams (1985): Superconductivity above 2 K At Ambient Pressure in Iododibromide (IBr_2^-) Charge-Transfer Salts of Bis (ETHYLENEDITHIO) TETRATHIAFULVALENE, BEDT-TTF, Molecular Crystals and Liquid Crystals, 125:1, 159-168

To link to this article: http://dx.doi.org/10.1080/00268948508080096

Mol. Cryst. Liq. Cryst. 1985, Vol. 125, pp. 159-168
0026-8941/85/1254-0159/$15.00/0

Printed in the United States of America

SUPERCONDUCTIVITY ABOVE 2 K AT AMBIENT PRESSURE IN IODODIBROMIDE (IBr_2^-) CHARGE-TRANSFER SALTS OF BIS(ETHYLENEDITHIO)TETRATHIAFULVALENE, BEDT-TTF

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Abstract Crystals of the charge-transfer salt $(BEDT\text{-}TTF)_2IBr_2$, derived from the sulfur-based organic donor bis(ethylenedithio)tetrathiafulvalene [BEDT-TTF], have been synthesized by electrocrystallization and studied by rf penetration depth measurements at ambient pressure and temperatures down to 0.45 K. One of two phases was found to be superconducting with T_c = 2.3-2.8 K. This phase, denoted as β-$(BEDT\text{-}TTF)_2IBr_2$, is isostructural with the superconducting triiodide salt, β-$(BEDT\text{-}TTF)_2I_3$. Evidence for the existence of a metastable superconducting phase of the BEDT-TTF/IBr_2 system with T_c near 4.2 K is given.

INTRODUCTION

There is considerable interest in the new family of sulfur-based organic conductors derived from bis(ethylenedithio)tetrathiafulvalene [BEDT-TTF] because of their potentially rich variety of metallic and superconducting properties.[1-5] Parkin et al.[1] discovered superconductivity in this family in the salt (BEDT-

TTF)$_2$ReO$_4$, which showed a superconducting transition near 2 K at pressures above 4 kbar. Yagubskii et al.[2] recently discovered that the salt β-(BEDT-TTF)$_2$I$_3$ is the first ambient pressure superconductor in this family, a result which has since been confirmed by others.[3-5] The bulk superconducting transition temperature (T_c) of this I_3^- derivative has been determined to be 1.4-1.6 K, which is slightly higher than the maximum value of 1.2 K measured for the previously known Se-based ambient pressure organic superconductor (TMTSF)$_2$ClO$_4$.[6] An orthorhombic phase derived from the BEDT-TTF/I$_3$ system, but with unknown composition, has also been reported to be an ambient pressure superconductor with T_c = 2.5 K.[7] This indicates that the radical-cation donor salts of BEDT-TTF are promising materials for the design of organic superconductors with ambient pressure superconducting transition temperatures in the region of 2 K and higher. In a recent communication,[8] we reported that a second BEDT-TTF salt, β-(BEDT-TTF)$_2$IBr$_2$, is an ambient pressure superconductor with T_c ~2.7 K. In the present article, we describe the experiments which confirm the existence of a superconducting state in this IBr$_2^-$ anionic derivative.

EXPERIMENTAL METHODS

The crystal specimens of the ET/IBr$_2$ (ET denotes BEDT-TTF) system used in this study were grown by electrochemical oxidation of ET in the presence of (n-Bu$_4$N)IBr$_2$ with THF as the solvent. The electrocrystallization produced numerous lustrous black crystals consisting of a mixture of two or more different crystallographic phases. We have thus far identified only two distinct phases, which we have denoted as the α and β phases. Both phases are triclinic crystals with space group P$\bar{1}$, Z = 1, and stoichiometry 2:1, thus being expressible by the formula $(ET)_2IBr_2$. We found the β phase to be superconducting and isostructural with the superconducting β phase of $(ET)_2I_3$.[9] The $(BrIBr)^-$ anion is linear and centrosymmetric with a Br-I distance of 2.702(1) Å, which is about 7% shorter than the I-I distance [2.912(1) Å] in I_3^-. The α phase is not superconducting and is similar to, but not isostructural with, the nonsuperconducting triclinic α phase of $(ET)_2I_3$.[3] Detailed structural and synthesis information on these two phases is presented elsewhere.[8] We used x-ray diffraction methods and ESR measurements[10] to select a few crystals of each pure phase to establish the existence or absence of a superconducting state.

The rf penetration depth measurements were carried out on crystals cooled in a pumped liquid-helium (He^3 or He^4) cryostat surrounded by a superconducting magnet. The equipment and procedures were the same as those employed in our previously reported rf inductive studies of $(ET)_2I_3$.[3] Superconductivity was detected by an increase in the rf resonant frequency in an LC circuit due to the exclusion of the rf field from the sample by the Meissner currents. With frequencies measured to 1 part in 10^5 Hz, this technique enabled us to detect superconductivity in less than 5 μg of sample.

RESULTS

A 13 μg sample consisting of two small β-phase crystals showed an increase in the resonant frequency of 44 Hz at temperatures near ~1 K. This signal increased with decreasing temperatures and vanished at temperatures near 3 K. Several samples of pure α-$(ET)_2IBr_2$, one weighing as much as 330 μg, gave no detectable frequency increase down to the lowest temperature obtained with pumped liquid He^3, ~ 0.45 K. These results demonstrate that β-$(ET)_2IBr_2$, but not α-$(ET)_2IBr_2$, has a superconducting state. Because the signal from individual β-phase crystals was too small for precise determinations of critical temperatures and fields, larger quantities of the natural mixtures and pure β-phase crystals were used to characterize the superconducting properties.

Measurements of the critical temperatures and fields were carried out on several natural mixtures, each with different crystallization parameters. The results for these samples varied slightly, with values of T_c occurring in the range of 2.3–2.7 K. Figure 1 compares the change in resonant frequency as a function of temperature in zero applied magnetic field for two of the samples of a natural mixture of β-$(ET)_2IBr_2$ with that for a sample of β-$(ET)_2I_3$ reported previously.[3] The onset of superconductivity occurred at 2.32 ± 0.04 K and 2.73 ± 0.04K in the IBr_2^- samples and at 1.40 ± 0.02 K in the I_3^- sample. All three curves have similar shapes with superconducting transitions extending over a range of 1 K or more. The transition for the sample with T_c = 2.32 K was incomplete down to the temperature of pumped liquid He^4, ~ 1 K. Further measurements with pumped liquid He^3 showed saturation (constant frequency) in the rf signal beginning near 0.8 K, indicating a completed transition at this temperature. The transition for the sample with T_c = 2.73 K was

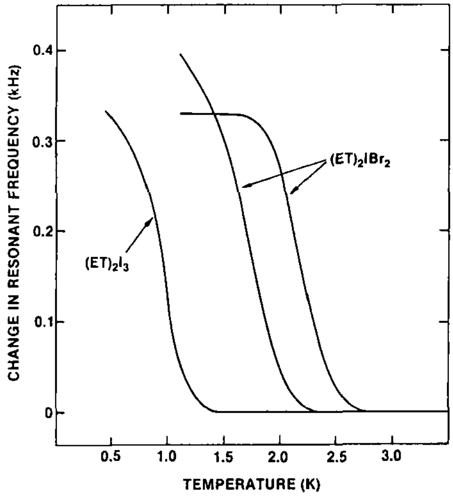

FIGURE 1. Change in resonant frequency from the empty coil value for samples of β-$(ET)_2IBr_2$ and β-$(ET)_2I_3$ as a function of temperature in zero applied magnetic field. Two different samples with T_c = 2.32 K and T_c = 2.73 K are shown for β-$(ET)_2IBr_2$. The sample with T_c = 2.32 K gave saturation in the rf signal near 0.8 K. The changes in resonant frequency for β-$(ET)_2I_3$ were scaled by a factor of 0.08 to account for its larger volume.

complete near 1.7 K. A polycrystalline sample of pure β-$(ET)_2IBr_2$ weighing ~500 μg gave T_c = 2.81 ± 0.03 K. The superconducting transition curve for this sample was similar to those illustrated in Figure 1, except that the transition was somewhat sharper near the onset temperature, possibly due to a more homogeneous collection of crystals, and the increase in resonant frequency amounted to ~2.3 kHz near 2 K due to the increased volume of superconducting material.

The origin of the variation in measured values of T_c (2.3 - 2.8 K) is unclear at this time. This variation likely represents differences in crystal quality and chemical purity. Alternatively, this variation may be due to particle-size effects in which the London penetration depths are comparable to the dimensions of the crystals, as has been noted in earlier studies of $(TMTSF)_2ClO_4$.[12] Different samples of β-$(ET)_2I_3$, however, exhibit similar variations in T_c (1.2 - 1.6 K), and this has been shown to be independent of particle sizes.[11]

Critical fields were studied by measurements of the change in rf resonant frequency at constant temperature as a function of applied magnetic field. Two such field sweeps are shown in Figure 2 for the sample with T_c = 2.32 K. One observes an initial sharp drop in resonant frequency with increasing magnetic field followed by a gradual decrease to the normal-state resonant frequency at higher field, qualitatively similar to field sweeps previously reported[3] for a polycrystalline sample of β-$(ET)_2I_3$. For $(ET)_2IBr_2$ the values of H_{c2}, defined as the field where the resonant frequency deviates from its normal state value, were appreciably higher: ~ 900 and 1800 Oe at temperatures near 1 K and 0.45 K, respectively, compared to ~ 425 and 650 Oe at similar temperatures for polycrystalline β-$(ET)_2I_3$. These measurements of an average H_{c2} for randomly oriented crystals give a qualitative confirmation of the superconducting state but no quantitative data on the anisotropy of the upper critical magnetic fields. We have recently found[11] for β-

$(ET)_2I_3$ that H_{c2} for fields parallel to the crystallographic c* axis is comparable to the average H_{c2} of polycrystalline samples whereas H_{c2} for fields parallel to the crystallographic ab plane are larger by more than an order-of-magnitude. Similar strong anisotropy is expected for β-$(ET)_2IBr_2$ on the basis of its isostructural character. In these initial studies the crystal sizes were too small and the morphologies too irregular to perform detailed critical field measurements as a function of orientation.

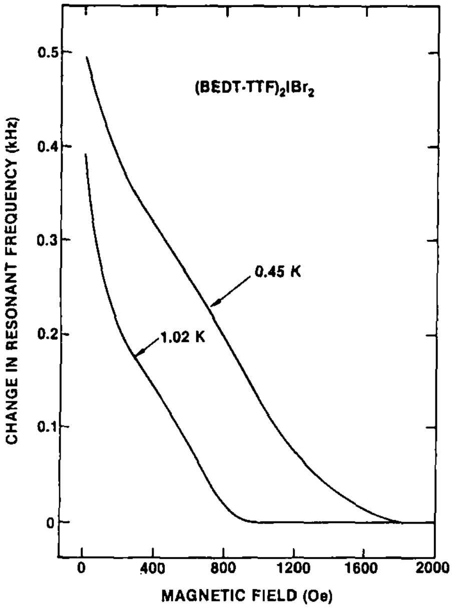

FIGURE 2. Change in resonant frequency from the empty coil value for the β-$(ET)_2IBr_2$ sample with T_c = 2.32 K as a function of applied magnetic field.

The rf measurements on one natural mixture gave unusual results. This sample initially exhibited superconductivity with $T_c = 4.22 \pm 0.04$ K. This value was unaltered by very slow cooling or rapid quenching below 40 K. In attempts to measure the critical fields, however, we found that the rf signal indicative of superconductivity suddenly vanished at temperatures near 4 K after application of a weak magnetic field. Immediately after this loss, remeasurement of the superconducting transition curve gave $T_c = 2.40 \pm 0.04$ K with an rf signal at saturation comparable to that obtained for the curve with $T_c = 4.2$ K. The comparable rf signals suggest the occurrence of a transition from a phase with $T_c = 4.2$ K to a more stable phase with $T_c = 2.4$ K instead of an initial mixture of two different superconducting materials. Measurements of H_{c2} for the phase with $T_c = 2.4$ K gave ~ 1000 Oe at 0.43 K and 724 Oe at 1.05 K. After aging one week in air at room temperature, undisturbed in its container, this sample gave $T_c = 2.71 \pm 0.02$ K and values of H_{c2} consistently larger by ~ 200 Oe at each temperature. These values of T_c and H_{c2} are quite comparable with those obtained in the other samples of $(ET)_2IBr_2$. X-ray analysis confirmed the existence of β-phase crystals in this sample, suggesting that the increase in T_c after aging represents some annealing of strains and/or defects in the β crystals. We were unable to recover the 4.2 K superconducting state after aging the sample for seven weeks, nor was it observed in any other sample. Although the origin of our observations of superconductivity near 4 K is unclear, the work of Yagubskii et al.[7] suggests a comparably high T_c for the orthorhombic phase of the ET/I_3 system. While these authors report $T_c = 2.5$ K for this phase, their resistivity data indicate that the onset of superconductivity occurs near 4 K.

It is remarkable that β-$(ET)_2IBr_2$ with T_c = 2.8 K exhibits superconductivity at ambient pressure higher by a factor of two than does isostructural β-$(ET)_2I_3$. There are two differences between the anions which might produce such a large change in T_c. The important structural difference is the 7% decrease in the length of the centrosymmetric $(BrIBr)^-$ anion relative to $(I{-}I{-}I)^-$. This shorter length leads to a smaller unit cell volume, shorter S-S distances and increased S-orbital overlap in the electronically conducting sulfur atom network. This increased overlap should lower T_c because it broadens the conduction band and reduces the density of states at the Fermi level. The important electronic difference between the anions is the larger electronegativity of Br relative to I. The effect of this larger electronegativity on the band structure and electron-phonon interaction is difficult to predict by use of elementary arguments, but this electronic property must be important since T_c is much higher for the IBr_2^- derivative. In any case, the large changes in T_c between I_3^- and IBr_2^- suggest that the ET family will allow for the first time an experimental correlation of the structural and electronic properties of the anions with much more substantial changes in the superconducting properties than are exhibited by the family of TMTSF derivatives.

ACKNOWLEDGMENT This research was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, under contract W-31-109-ENG-38. L. N. H., P. T. C., L. M. S., L. N., and M. A. F. are research participants sponsored by the Argonne Division of Educational programs. F. B. is on leave from the University of Wisconsin-Parkside, Kenosha, Wisconsin. We thank S. A. Bogacz of this laboratory for translations of the original Russian articles on $(ET)_2I_3$.

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