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THE EFFECT OF DISORDER ON THE METAL-INSULATOR AND SUPERCONDUCTOR PHASE TRANSITIONS IN THE α AND β PHASES OF (BEDT -TTF)$_2$I$_3$

*L. FORRO**, *S. BOUFFARD*

IRDI-DMECN-DTech/SESI, Centre d'Etudes Nucléaires,
92265 Fontenay aux Roses Cedex, France

D. SCHWEITZER

Abteilung für Molekulare Physik, Max-Planck-Institut für Medizinische
Forschung D-6100, Heidelberg, West Germany

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The effect of fast electron irradiation induced disorder on the high T_c (~ 8 K) superconducting transition in β - (BEDT-TTF)$_2$I$_3$, and on the metal -semiconductor transition at T_p = 137 K in α - (BEDT-TTF)$_2$I$_3$ was studied by resistivity measurements. Defects suppress both transitions at a rate of dT_c/dc ~ - 40 K/ %.

The BEDT-TTF molecules with monovalent anions or iodine complexes form conducting salts, which are less onedimensional (1D) than the compounds of the TTF-TCNQ or (TMTSF)2X families. For example in the α and β modifications of (BEDT-TTF)2I3, abreviated α, β - (ET)2I3, the side by side interaction of the ET molecules is comparable to the face to face interaction [1]. The room tempe-rature conductivity (σ) is 20-50 $(\Omega cm)^{-1}$ and, within a factor of two, isotropic in the a-b plane for both compounds while in the c* direction s is 0.02 $(\Omega\ cm)^{-1}$ for α-(ET)2I3 and 0.1 $(\Omega\ cm)^{-1}$ for β - (ET)2I3. From the point of view of transport properties, they can be considered as quasi-twodimensional (Q-2D) organic conductors.

The α-(ET)2I3 has a metal-insulator (M-I) transition at T_p = 135 K the nature of which has not been yet determined by structural studies [2]. In β - (ET)2I3 an incommensurate structural modulation builds up at 175 K but below this temperature the compound remains metallic and even becomes superconductor at T_c ~ 1.5 K . A pressure of 1.5 kbar suppresses the incommensurate long range order, and high T_c superconducting phase appears below 8 K [3,4].

The interest for the irradiation induced defect concentration dependence of the transport in α, β -(ET)2I3 salts is threefold. First it has been suggested by Schirber et al [5], that the high Tc phase can be induced also by applying strain on the sample. It is known that defects in organic compounds like TTF-TCNQ [6] dilate the lattice, creating strains in the crystal. So, for low defect concentrations, one should observe the appearance of the high Tc superconducting state in the β - phase. Furthermore we can extract the sensitivity of the phase transitions to irradiation, which is an important parameter for example for structural studies. Namely during the X-ray diffraction experiments one creates defects in the sample changing the characteristics of the transition temperature, correlation lengths, etc, of the sample.

Finally, the defect concentration dependence of the resistivity can show whether the interrupted strand model, which describes very well the transport in irradiated Q-1D conductors, is applicable in such a Q-2D matrix as α, β -(ET)2I3.

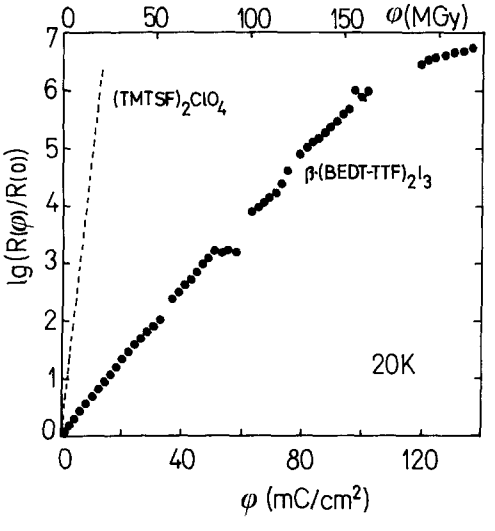
The samples of α, β -(ET)2I3 were prepared by electrocrystallization described previously [2]. Single crystals of typical dimensions of 3x1x0.1 mm^3 were mounted by platinum paste on 15 μm annealed gold wires for a four-probe conductivity measurement.

* Permanent address :
Institute of Physics of the University, Bijenicka 46, P.O.B.304, 41001 Zagreb, Yugoslavia

Defects in the samples were created by the 2.5 MeV electron beam of a Van de Graaff accelerator. The electron flux was typically 5 $\mu A/cm^2$ measured by a Faraday cup. The low dose irradiation of β -(ET)2I3 was carried out at 4.2 K in a liquid helium cryostat and measured, in situ, in 1.8-20K temperature range after each irradiation dose. The irradiation dose dependence of α -(ET)2I3 and β -(ET)2I3 at high doses were done in a closed cycle hydrogen cryostat.

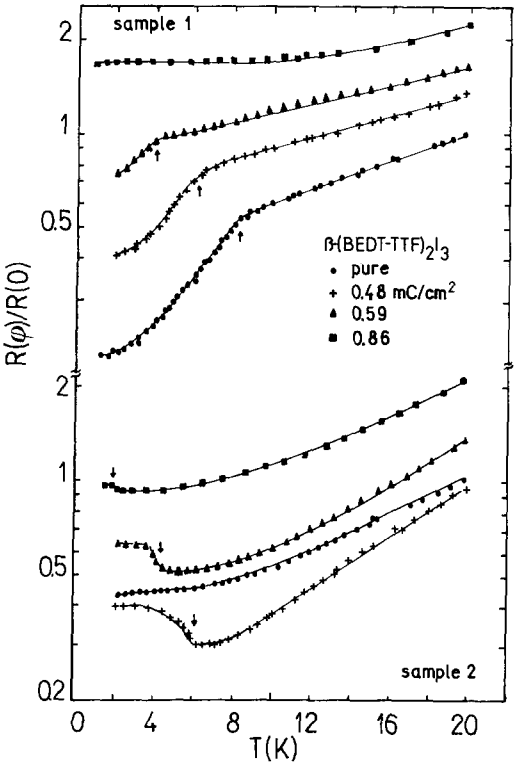
It has been proved previously that the defect concentration in Q1D organic metals scales with the total absorbed energy [7]. The electron fluence (mC/cm^2) can be transformed into absorbed dose according to the tables of electron stopping power by Page et al [8]. It has been determined in ESR study [9] of irradiated α, β -(ET)2I3 that 40MGy of absorbed energy (27mC/cm^2 of 2.5 MeV electrons) creates 1% of defected molecules.

Figure 1 shows the irradiation dose dependence of the normalized resistance of β - (ET)2I3 at 20K. After a linear increase at the very beginning of irradiation, the resistance increases exponentially over six orders of magnitude. Dotted line shows schematically the same quantity for (TMTSF)2ClO4 at 20K from the reference 10.

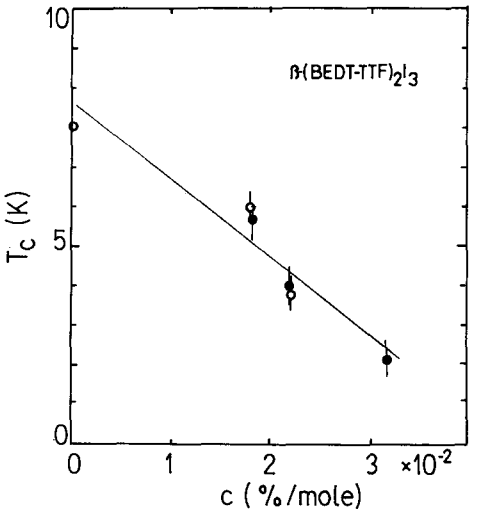


1 - Irradiation dose dependence (mC/cm^2) of the normalized resistance of β -(BEDT-TTF)2I3 at 20K. The upper scale shows the total absorbed energy (MGy). The behaviour of (TMTSF)2ClO4 is given by dotted lines (after ref. 10)

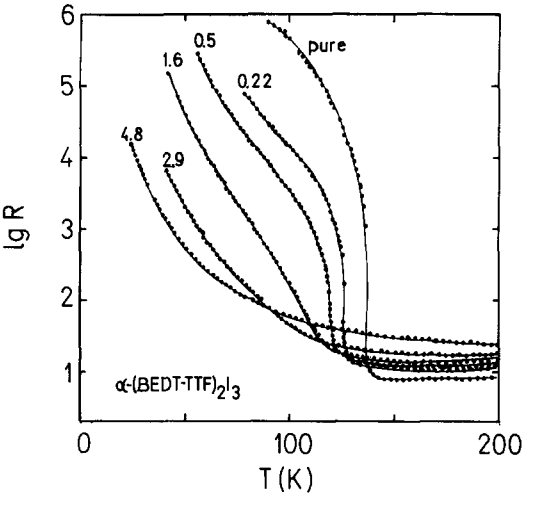
Figure 2 gives the resistance (R) normalized to 20K as a function of temperature for several irradiation doses. Sample 1 already shows a faster decrease of R below 8K which is the sign of the high Tc superconducting phase. For very low defect concen-trations this anomaly shifts down in temperature and for 0.032% / mole it disappears. In the pure state of sample 2, R increases monotonously with temperature, with a tendency to saturation below 10K. For .018 % / mole defect concentration the resistance unexpectedly decreases and changes slope in temperature (testifying the fragility of the low Tc (1.5K) phase) with a step-like increase of R at 6K. On further irradiation this increase of R decreases in amplitude and shifts down in temperature. We believe that this anomaly is due to the presence of high Tc superconducting phase in some parts of the sample, causing inhomogenous current flow and apparent increase of the voltage on the voltage leads. Its dose dependence is similar to that of the more usual uncomplete superconducting phase of sample 1. The defect concentration dependence of the



2 - Normalized resistance versus tempe-rature for two samples irradiated with different doses. Arrows mark the superconducting anomaly.



3 - Superconducting transition temperature versus defect concentration for β -(BEDT-TTF)2I3



4 - Resistance versus temperature for progressively disordered α -(BEDT-TTF)2I3. Num-bers on the curves give the defect concentration in percent of damaged molecules.

high Tc superconducting phase transition temperature is given in Figure 3, for both samples. It gives a value of -dTc/dc = 180-250 K/%, comparable to that of (TMTSF)2ClO4 [11]

Figure 4 displays the temperature dependence of resistivity of the pure and progressively irradiated α -(ET)2I3. The effect of disorder is to increase the resistance in the metallic phase and to shift the metal-insulator phase transition from 137K in the nominally pure sample downwards with an initial slope of dTp/dc : - 40K / %.

In an extensive study of irradiated Q1D organic metals it has been shown that the resistivity increases exponentially over several orders of magnitude with irradiation dose [6]. This behaviour has been interpreted within the interrupted strand model. In this model, irradiation induced defects break the conducting chain, forcing the electrons to jump to a neighbouring chain. The interchain jump is phonon assisted hopping so that the transverse ($\rho_{\perp}(c,T)$) and longitudinal ($\rho//(c,T)$) resistivities read as follows :

$$\rho_{\perp}(c,T) = \rho_{\perp}(0,T) \exp \Delta E\, c / kT \qquad (1)$$

$$\rho//(c,T) = \rho//(0,T) + \alpha c\, \rho_{\perp}(c,T) \qquad (2)$$

where ΔE is the activation energy for transverse jump, c is the defect concentration, and a is a geometrical factor close to 1. However in a bidimensional metal the blocking effect of the defects is not so effective, because there are many more possibilities for the electron to escape the defect potential, so the resistivity changes in agreement with Mathiessen-rule :

$$\rho(c,T) = \rho(0,T) + A\, c\rho(c) \qquad (3)$$

where $\rho(c)$ is temperature independent.

Optical measurements [12,13] on α, β -(ET)2I3 show that the ratio of the bandwidths along and perpendicular to the stacks is about 1.3 - 1.5. In such a 2D bandstructure one would expect the fulfillement of Mathiessen-rule. However, except of the linear dose dependence of the resistance at the very beginning of the irradiation (Figure 1 and sample 1 in Figure 2) the resistances increases exponentially with an activation energy of 7400K. This suggests that the same thing happens as in the Q1D case : defects produce the segmentation of chains, which modulates the energy levels on different segments. The difference in the energy levels of segments decouples the neighbouring chains, although originally the interchain transfer integral was strong. We note that similar effect of disorder was observed [10] in (TMTSF)2ClO4 at 20K where it is also a 2D metal. The faster increase of the resistivity of (TMTSF)2CLO4 in Figure 1 is partly due to the fact that less absorbed energy is needed for defect creation in this compound (10.5 MGy for 1% / mol of defects) than is β - (ET)2I3.

An unusual effect of disorder can be observed in Figure 2 for sample 2 : defects can induce the high Tc superconducting phase [14]. This result is coherent with the idea of Schirber et al [5] who have suggested that the high Tc phase can be induced by mechanical strains. It is known that molecules defected by irradiation dilate the lattice, make crosslinkings which introduce strain in the lattice. In the undamaged part of the sample, only just influenced by strains, high Tc superconducting phase could appear. However defects act as pairbreakers too, which decreases Tc (Figure 3). We note that structural studies of β -(ET)2I3 by Ravy et al [16] indicate the appearance of the high Tc phase in the sample irradiated during the structural study.

For the α -(ET)2I3 the resistance increase above Tp as predicted by formula (2), with an activation energy close to 7000K. Although the nature of the M-I transition at 167K is not known, it has similar sensitivity on defect concentration as the Peierls systems.

It is obvious from Figure 3 and 4 that which ever the nature of the phase transitions in the BEDT-TTF salts is they can be suppressed by a small amount of disorder. For exemple, in the (BEDT-TTF)2NO3, because of the disorder introduced by the unstability of the anions during the electrocrystallization, there is no sign of any phase transition [15], and the resistivity behaves very much like that of the most irradiated α -(ET)2I3 in Figure 4.

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