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THE EFFECT OF DISORDER ON THE CONDUCTION ELECTRON SPIN RESONANCE LINEWIDTH OF THE α AND β PHASES OF $(BEDT\text{-}TTF)_2I_3$

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We present the electron spin resonance linewidth of α and β phases of the organic conductor di-*bis* (ethylenedithiolo) tetrathiafulvalene driiodide $[(BEDT\text{-}TTF)_2I_3]$ disordered by fast electron irradiation. In the high temperature metallic phase the linewidth decreases in both phases with defect concentration in contrast to the predictions of the Elliott mechanism for spin relaxation in metals.

THE CONDUCTION ELECTRON SPIN resonance (CESR) linewidth (ΔH) is one of the less understood properties of quasi one-dimensional (Q1D) organic conductors. The difficulty in the interpretation of the experimental results comes from the variety in magnitude and temperature dependence of ΔH even within the same family of conductors. For example in the TSF-TCNQ family the linewidth ranges from an unobservably braod value (HMTSF-TCNQ) to 60 G (TMTSF-DMTCNQ), and from decreasing ΔH with temperature (TSF-TCNQ) to an increasing one (TMTSF-TCNQ, TMTSF-DMTCNQ). One can say that only HMTSF-TCNQ behaves consistently with the normal expectation for the spin relaxation in metals, because for the scattering rate (τ^{-1}) of 10^{-15} sec (which is the right order of magnitude for the majority of organic conductors), ΔH should be too braoad to be observable.

It has been suggested that the narrow linewidth is due to the 1D nature of the electronic band, and with increasing dimensionality of the organic conductors the Elliott-theory of the spin relaxation of isotropic metals could be applicable [2].

In the recently synthesized anion radical salts of the *bis* (ethylenediothiolo) tetrathiafulvalene (BEDT-TTF) molecule, the side-by-side interction is comparable to the face-to-face interaction [3] and they have thus a far more two-dimensional (2D) band structure than HMTSF-TCNQ. However the CESR linewidth is still very narrow. For example ΔH of the α and β modifications of $(BEDT\text{-}TTF)_2I_3$, abbreviated α-, β-$(BEDT\text{-}TTF)_2I_3$, is 125 G and 23 G respectively at room temperature [4–6].

It has been demonstrated previously on numerous organic conductors, that in the Q1D case the linewidth decreases with defect concentration [7] which is opposite to the case of isotropic metals. The question of the response of the ESR linewidth for a system with 2D band structure to disorder through radiation induced defects has provoked the present study.

The samples of α-, β-$(BEDT\text{-}TTF)_2I_3$ were prepared by an electrocrystallization technique described previously [3]. From a large single crystal of α-$(BEDT\text{-}TTF)_2I_3$ samples of typical dimensions $3 \times 1 \times 0.05\,mm^3$ were cut out. The hexagonal shaped β-$(BEDT\text{-}TTF)_2I_3$ single crystals had an approximate dimension of $2 \times 1 \times 0.1\,mm^3$. The samples were irradiated at 21 K with 2.5 MeV electrons from the Van de Graaff accelerator of Fontenay-aux-Roses. In organic metals defects are created mainly by electronic excitations or ionisation and the defect concentration scales with the average absorbed energy [8]. From the low temperature Curie tail one can extract the spin concentration created by irradiation.

It has been shown by Zuppiroli *et al.* [9] that the number of localized spins and the number of defects agree within a factor of two. In α-, β-$(BEDT\text{-}TTF)_2I_3$

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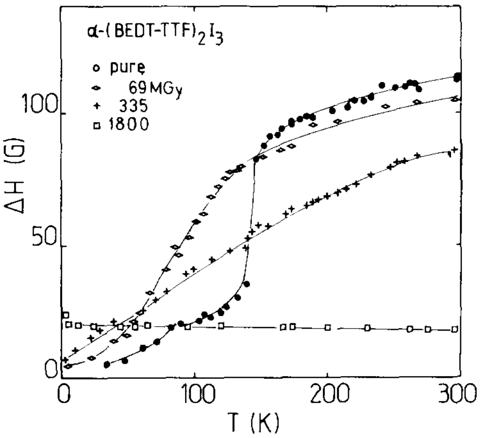

Fig. 1. Temperature dependence of the peak-to-peak linewidth for α-(BEDT-TTF)$_2$I$_3$ at several irradiation doses in orientation $H_0 \parallel c^*$, $H_1 \parallel b'$.

40 MGy of absorbed energy is necessary to create 1 % of defects per mole (1 Gray = 1 Gy = 100 rads = 1 joule kg^{-1}).

The temperature dependent ESR spectra were recorded by a conventional X-band spectrometer equipped with a continuous flow helium cryostat. Fig. 1 gives the temperature dependence of the peak-to-peak linewidth of α-(BEDT-TTF)$_2$I$_3$ for several irradiation doses. In the metallic phase the linewidth decreases with increasing irradiation dose. The phase transition which is marked by the abrupt fall of ΔH in the pure sample, shifts down in temperature and smears out for the irradiated samples.

Figure 2 displays the temperature dependence of the peak-to-peak linewidth of β-(BEDT-TTF)$_2$I$_3$ for the pure sample and two representative irradiation doses. For 300 MGy the linewidth slightly decreases at high temperatures and slightly increases below 50 K in respect to the pure sample. With a dose of 1800 MGy ΔH becomes temperature independent apart from the weak upturn below 40 K.

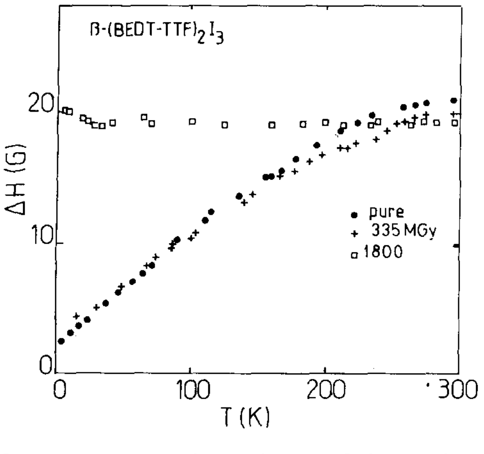

Fig. 2. Temperature dependence of the peak-to-peak linewidth for β-(BEDT-TTF)$_2$I$_3$ at different irradiation doses in orientation $H_0 \parallel c^*$, $H \parallel$ a.

The variation of the linewidth and g-factor with irradiation dose at 300 K is presented in Fig. 3 for both α and β-(BEDT-TTF)$_2$I$_3$. For the α-phase ΔH decreases monotonously from 115 G of the pure sample to 18 G for the highest dose. The linewidth for the β-phase is rather constant in the irradiation range where the g-factor is constant and decreases to 18 above 900 MGy absorbed energy. Note that in isotropic metals ΔH increases withdefect concentration [10]. In the upper part of Fig. 3 the g-factor shows a step-like irradiation dose dependence. This behaviour correlates with the irradiation dose dependence of the Pauli susceptibility which starts to fall in the same range where the g-value does. This should mean the breakdown of the band description for α-, β-(BEDT-TTF)$_2$I$_3$ above 900 MGy of irradiation dose. In the following, we deal mostly with the discussion of results below this dose.

Integrating the ESR signal one can obtain the spin susceptibility χ. In the pure α-(BEDT-TTF)$_2$I$_3$, χ has a similar temperature dependence like ΔH with no detectable Curie tail. For low irradiation doses (φ < 335 MGy) χ does not change in the metallic

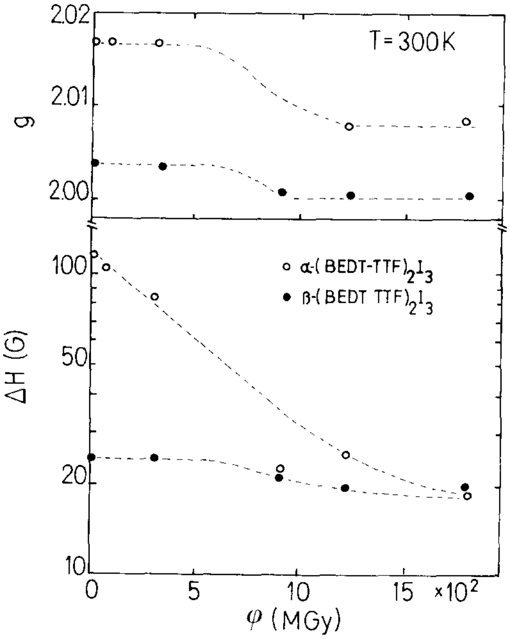

Fig. 3. Irradiation dose dependence of the peak-to-peak linewidth and g-factor for α- and β-(BEDT-TTF)$_2$I$_3$ at room temperature. The orientations are the following: $H_0 \parallel c^*$(○), and $H_1 \parallel b'$ for α-(BEDT-TTF)$_2$I$_3$ and $H_0 \parallel$ a, $H_1 \parallel c^*$ for β-(BEDT-TTF)$_2$I$_3$(●). The accuracy in orientation is ~ 10 degree.

phase, but the abrupt fall in the pure sample below 135 K is smeared out and a Curie tail proportional with the irradiation dose shows up. In the studied temperature range (down to 3.8 K) the Curie tail was well fitted by AT^{-1}, where A is a constant proportional with the number of localized spins. The analysis of the dose dependence of the Curie tail gives that 40 MGy of absorbed energy creates 1 %/mole of localized spins. For higher doses ($\varphi \gtrsim 500$ MGy) A has a tendency towards saturation which can be connected with the probability of having paired spins on the same defected molecule which does not give a paramagnetic signal.

In the β-(BEDT-TTF)$_2$I$_3$ below 200 K the ESR lineshape is strongly Dysonian, due to the skin-effect. It means that the volume giving the ESR signal changes with temperature and defect concentration because of the temperature and defect concentration dependence of the microwave conductivity of the sample. In such a case the integration of the ESR signal gives an uncertain magnitude for χ; the reliable value can be obtained by static susceptibility measurements. The qualitative information on χ given by the ESR study of β-(BEDT-TTF)$_2$I$_3$ is that in irradiated sample a Curie tail shows up in low temperatures like in the α-(BEDT-TTF)$_2$I$_3$.

Before the interpretation of the defect concentration dependence of the spin relaxation rate one should first understand the characteristics of ΔH of the pure samples. It has been suggested in a previous publication [11] on the pressure dependence of the ESR linewidth of α-, β-(BEDT-TTF)$_2$I$_3$ that the narrow ΔH results from the crystal structure of these compounds.

This suggestion is based on the work of Adrian [12] who has shown that the spin-orbit interaction is inactive in spin relaxation within a compound constituted of inversion-related identical molecules. In β-(BEDT-TTF)$_2$I$_3$ the BEDT-TTF molecules are almost identically oriented [3, 13] and in consequence ΔH is very narrow, 23–25 G at room temperature. In the (BEDT-TTF)$_2$I$_3$ there are two inequivalent BEDT-TTF stacks whose molecules are inclined approximately 70° to each other. The loss of the inversion symmetry results in a five times broader linewidth with respect to the α-phase.

The temperature dependence of the linewidth suggests that ΔH is governed by $\tau_\parallel^{-1}$, the electron-phonon scattering rate measured in the resistivity. However ΔH increases under pressure [11], while $\tau_\parallel^{-1}$ strongly decreases with it. In [11] a general formula was proposed for the conduction electron spin resonance linewidth:

$$H = (\Delta g)^2(a\tau_\parallel^{-1} + b\tau_\perp^{-1}), \tag{1}$$

where $\tau_\parallel^{-1}$ is on chain scattering frequency, $\tau_\perp^{-1}$ is an interchain tunneling rate and a and b are parameters. $\tau_\perp^{-1}$ decreases with temperature and defect concentration while it increases under pressure. $\tau_\parallel^{-1}$ reacts in the opposite way to all these changes. The relative balance of the two terms determines the temperature, pressure and defect concentration (c) dependence of ΔH. The decreasing linewidth with defect concentration can be interpreted as follows. Defects produce segmentation of the "infinite" chains, which results in mismatch in the energy levels of the neighbouring chains. In consequence the transition rate between the segments becomes activated:

$$\tau_\perp^{-1}(c) = \tau_\perp^{-1}(0)\exp(-\Delta E/kT), \tag{2}$$

where the activation energy is linearly proportional to the defect concentration. This term describes very well the initial decrease of ΔH for TTF-TCNQ, TMTSF-DMTCNQ, (TMTSF)$_2$ClO$_4$ [7] etc., that is in Q1D compounds where one has incoherent transverse and coherent on chain electronic motion. It is not evident to what extent can one attribute $\tau_\parallel^{-1}$ relaxation rate in α-, β-(BEDT-TTF)$_2$I$_3$ since the in plane conductivity of 20 $(\Omega\,\mathrm{cm})^{-1}$ gives a mean free path of the order of 0.1 intermolecular spacing. The linebroadening coming from the spinflop rate between the two nonequivalent chains decreases strongly by segmentation in the α phase, reaching 18 G for the highest defect concentration. In the β phase the participation of the interchain spin-flop rate is much smaller due to the difference in crystal structure; its decrease on defect concentration could be compensated to some extent by the opposite tendency of $\tau_\parallel^{-1}$. At low temperatures, where the system behaves like a really good metal, ΔH increases with defect concentration (Fig. 2).

At the highest defect concentration ΔH of both α- and β-(BEDT-TTF)$_2$I$_3$ is 18 G which should mean that the spin relaxation is determined by a local on-molecular process, e.g. by the dipolar interaction of the electrons with the surrounding nuclei.

A second model which could qualitatively explain the decreasing linewidth with defect concentration is where the linewidth is attributed to a libronic motion of molecules lifting the symmetry restrictions [12]. Cross-linkings between the molecules due to irradiation result stiffer lattice [14], decreasing amplitude of the torsional oscillations and in consequence narrower linewidth. However, in this model one would expect a linear concentration dependence of ΔH while in the majority of organic conductors ΔH decreases exponentially with c and even for a few percent of defect molecules ΔH falls off by a factor of 2–3.

In conclusion, we have determined an anomalous behaviour of the conduction electron spin resonance linewidth on disorder introduced by electron irradiation in α-, β-(BEDT-TTF)$_2$I$_3$. In the α phase ΔH decreases exponentially with irradiation dose, while in the β-phase it decreases very little at room temperatures. For comparison in an isotropic metal ΔH increases with defect concentration.

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