RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 35, NUMBER 5 15 FEBRUARY 1987-I

Pressure dependence of the conduction-electron-spin-resonance linewidth of the α and β phases of di-bis(ethylenediothiolo)tetrathiafulvalene triiodide

L. Forró
Institute of Physics of the University, Bijenička cesta 46,
Post Office Box 304, 41001 Zagreb, Yugoslavia

G. Sekretarczyk and M. Krupski
Institute of Molecular Physics of the Polish Academy of Sciences,
Smoluchowskiego 17/19, 60-179 Poznan, Poland

D. Schweitzer and H. Keller
Abteilung für Molekulare Physik, Max-Planck-Institut für Medizinische Forschung,
D-6900 Heidelberg, West Germany
and Anorganisch-Chemisches Institut der Universität Heidelberg, D-6900 Heidelberg, West Germany

(Received 1 December 1986)

We report conduction-electron-spin-resonance linewidth (ΔH) measurements of the α and β phases of the organic conductor di-bis(ethylenediothiolo)tetrathiafulvalene triiodide [(BEDT-TTF)$_2$I$_3$] in the 80–300-K temperature range under applied pressures of up to 5 kbar. ΔH increases under pressure in contrast to the predictions of the Elliot formula for the spin relaxation in metals. The pressure derivative $d(\ln\Delta H)/dP$ is -5.5 ± 1%/kbar and 9.8 ± 1%/kbar for the α and β phases of (BEDT-TTF)$_2$I$_3$, respectively.

The conduction-electron-spin-resonance (CESR) linewidth (ΔH) of metals is connected to the scattering rate (τ^{-1}) of electrons and to the spin-orbit coupling by the Elliot formula:[1] $\Delta H = (\Delta g)^2 \tau^{-1}/\gamma$, where $\Delta g = g - 2.0023$ measures the spin-orbit coupling, and γ is the electron gyromagnetic ratio. However, this relation fails to give the right magnitude and temperature dependence of the CESR linewidth of quasi-one-dimensional (Q1D) organic metals. For example, in the case of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)[2] ΔH is three orders of magnitude lower than expected from the known scattering time and spin-orbit interaction, and it increases on decreasing temperature although τ^{-1} is decreasing as measured in resistivity.

Several different interpretations of the CESR linewidth in Q1D conductors have been put forward in the last ten years. The common point of these theories is that symmetry restrictions due mainly to the 1D character of the electron band states limit the spin-orbit scattering in these materials. In order to reproduce the temperature dependence of ΔH 1D fluctuations,[3] interchain scatterings[4] or libronic modes[5] have been evoked.

The bis(ethylenediothiolo)tetrathiafulvalene (BEDT-TTF) molecule with monovalent anions or iodine complexes forms conducting salts which are less one dimensional than the compounds of the TTF-TCNQ or (TMTSF)$_2X$ families (where TMTSF represents tetramethyltetraselenafulvalene). For example, in the α and β modifications of (BEDT-TTF)$_2$I$_3$, abbreviated α-, β-(BEDT-TTF)$_2$I$_3$, the side-by-side interaction of the BEDT-TTF molecules is comparable to the face-to-face interaction.[6] The room-temperature conductivity (σ) is 20 $(\Omega\,\mathrm{cm})^{-1}$ and within a factor of 2 it is isotropic in the a-b plane for both compounds, while in the c^* direction σ is 0.02 $(\Omega\,\mathrm{cm})^{-1}$ for α-(BEDT-TTF)$_2$I$_3$ and 0.1 $(\Omega\,\mathrm{cm})^{-1}$ for β-(BEDT-TTF)$_2$I$_3$. The effect of this quasi-two-dimensional (Q2D) character of the electronic structure on the spin-relaxation rate initiated the present study. In this Communication we will discuss the pressure dependence of the ESR linewidth of the α- and β-(BEDT-TTF)$_2$I$_3$ since ambient pressure results have already been reported by several groups.[7–9]

We have performed our pressure- and temperature-dependent ESR measurements at the X band using a high-pressure apparatus, which works at pressures up to 5 kbar and at temperatures from 80 to 350 K.[10] The apparatus contains a cylindrical corundum resonator directly coupled to the waveguide by a matching corundum wedge. The pressure chamber in which the resonantor is placed is made of nonmagetic beryllium bronze. The temperature of the system was controlled by a nitrogen vapor flux pumped through a heat exchanger disposed outside the pressure chamber. In this work the pressure medium was petroleum ether.

The samples of α-,β-(BEDT-TTF)$_2$I$_3$ were prepared by electrocrystallization described previously.[6] One single crystal of typical dimensions $3\times2\times0.1$ mm^3 of β-(BEDT-TTF)$_2$I$_3$ was enough for the pressure-dependent ESR measurements, but ten aligned single crystals of α-(BEDT-TTF)$_2$I$_3$ of dimensions $3\times2\times0.2$ mm^3 were needed to have a satisfactory signal-to-noise ratio. The results reported here correspond to sample orientation in which the line shape was Lorentzian and did not change with pressure at 300 K. Below 150 K the line shape of the β-(BEDT-TTF)$_2$I$_3$ is Dysonian. Corrections in the linewidth due to the Dysonian line shape have not been done since even in the extreme skin depth case the correction is less than the experimental inaccuracy.

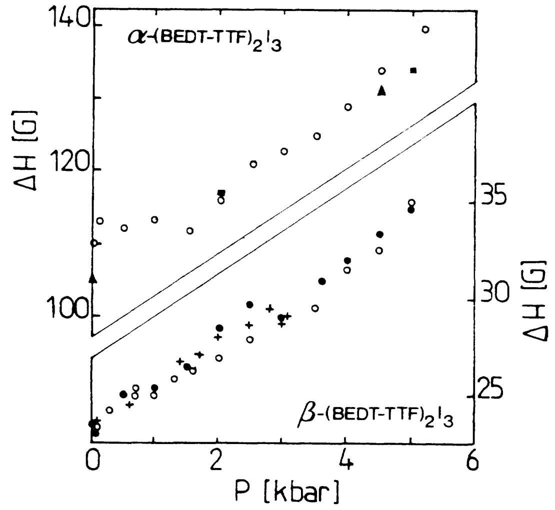

FIG. 1. Pressure dependence of the peak-to-peak linewidth ΔH at 300 K for α-(BEDT-TTF)$_2$I$_3$ and β-(BEDT-TTF)$_2$I$_3$. Different symbols mark different runs. The static (H_0) and microwave (H_1) field geometries are approximately $H_0 \| c^*$, $H_1 \| b$ for the α and $H_0 \| b$, $H_1 \| a$ for the β phase.

Figure 1 gives the pressure dependence of the CESR peak-to-peak linewidth at 300 K for α-(BEDT-TTF)$_2$I$_3$ and β-(BEDT-TTF)$_2$I$_3$. ΔH increases linearly for both compounds. The fractional pressure coefficient $[\Delta H(P) - \Delta H(1\text{ bar})]/\Delta H(1\text{ bar})\, P \equiv d\ln\Delta H/dP$ is 5.5 ± 1%/kbar of the α-(BEDT-TTF)$_2$I$_3$ and 9.8 ± 1%/kbar for the β-(BEDT-TTF)$_2$I$_3$.

The temperature dependence of ΔH for α-(BEDT-TTF)$_2$I$_3$ at three representative pressures, 1 bar, 2 kbar, and 5 kbar is shown in Fig. 2. The temperature dependence of the ambient pressure results agrees well with previous studies.[7-9] Increasing the pressure increases the linewidth by the same ratio at all temperatures in the metallic phase. The phase transition temperature $T_p = 135$ K at 1 bar marked with the abrupt fall of ΔH shifts down in temperature with pressure at the rate $dT_p/dP = -10$ K/kbar, in agreement with Refs. 11 and 12.

Figure 3 displays the temperature dependence of ΔH at 1 bar and 5 kbar for β-(BEDT-TTF)$_2$I$_3$. The increase of ΔH under pressure is temperature dependent, and tends to have a negative pressure coefficient below 100 K.

From the ESR signal the pressure dependence of the spin susceptibility (χ) of β-(BEDT-TTF)$_2$I$_3$ has been deduced at 300 K. χ decreases linearly with pressure by -4 ± 1%/kbar, in good agreement with the result of Ref. 8 obtained by the Faraday method.

In strictly 1D systems no spin relaxation can occur.[13] In order to account for the observed CESR linewidth of Q1D systems the first theoretical treatments[4,14] have introduced a partial 2D character of the electronic states. In Weger's approach[4] the measure of the 2D character was $\tau_\| / \tau_\perp$ ($\tau_\|$ on-chain scattering time, $\tau_\perp$ interchain tunneling time), which modifies the Elliot formula to

$$\Delta H \sim (\Delta g)^2 \tau_\|^{-1} \tau_\| / \tau_\perp = (\Delta g)^2 \tau_\perp^{-1} . \quad (1)$$

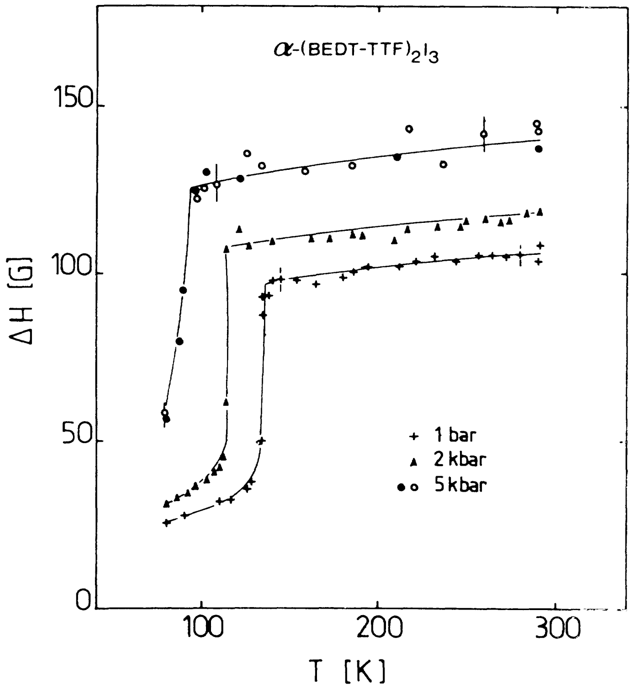

FIG. 2. Temperature dependence of the peak-to-peak linewidth ΔH for α-(BEDT-TTF)$_2$I$_3$ at 1 bar (+), 2 kbar (▲), and 5 kbar (●,○). The sample orientation in respect to H_0 and H_1 is the same as in Fig. 1.

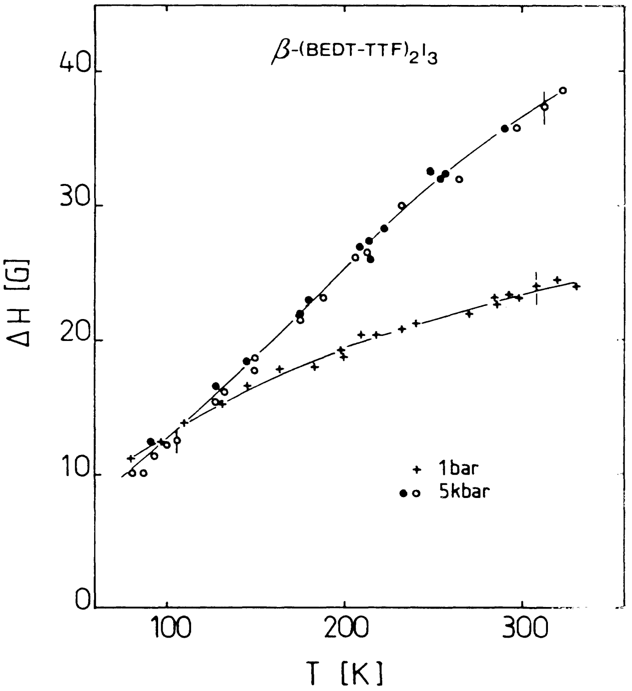

FIG. 3. Temperature dependence of the peak-to-peak linewidth ΔH for β-(BEDT-TTF)$_2$I$_3$ at 1 bar (+) and 5 kbar (●,○). The sample orientation in respect to H_0 and H_1 is the same as in Fig. 1.

This modification implies that as $\tau_{\parallel}/\tau_{\perp} \to 1$, that is in the 2D case, the Elliot formula for isotropic metals gives the right order of magnitude of ΔH. However, an isotropic metal with the same scattering rate ($\sim 10^{-15}$ sec) and $\Delta g (\sim 4\times 10^{-3})$ as α-, β-(BEDT-TTF)$_2$I$_3$ would have a linewidth three orders of magnitude larger. In spite of the 2D character of the electronic transport, the spin-orbit scattering is strongly reduced in α-, β-(BEDT-TTF)$_2$I$_3$. This reduction can be understood in a recent theoretical approach of Adrian[15] who has shown that a spin-orbit interaction cannot cause an electronic transition within a compound constituted of inversion-related identical molecules. To support his reasoning he has given an example: The linewidth of the (TMTSF)$_2X$ compounds where the molecules are identically oriented is always narrower than the linewidth of the fish-bone structured tetraselenafulvalene-tetracyanoquinodimethane (TSF-TCNQ). His argument can be applied in the case of α and β-(BEDT-TTF)$_2$I$_3$. ΔH of β-(BEDT-TTF)$_2$I$_3$ is narrow in spite of strong interchain interactions. The spin-orbit interaction is inactive in spin relaxation because of the almost identically oriented BEDT-TTF molecules (we neglect the slightly irregular stacking of donors), thus from the point of ESR β-(BEDT-TTF)$_2$I$_3$ is a Q1D compound. However, in the α phase there are two inequivalent BEDT-TTF stacks whose molecules are inclined approximately 70° to each other, so they are not inversion related any more, and interchain spin-orbit scattering is much more effective than in the β phase. This difference in structure is the reason why ΔH is 23 G in the β-(BEDT-TTF)$_2$I$_3$ and 110 G for α-(BEDT-TTF)$_2$I$_3$ at room temperature.

The decisive factor in treatment of ΔH by Adrian[5] is the torsional oscillation of the molecules which lifts the symmetry restrictions and enables on-chain and interchain spin relaxation. The temperature dependence of ΔH is mostly determined by the temperature dependence of these libronic modes. However, with increasing pressure the lattice becomes stiffer and the vibrational amplitudes decrease, which should result in a narrower linewidth opposite the experimental findings shown in Fig. 1. We remember that not only in α-, β-(BEDT-TTF)$_2$I$_3$, but also in all the cases studied up to now, the linewidth increases with pressure (see Table I). We note also that a formula which normalizes the Elliot expression to give the right magnitude of the linewidth but leaves the on-chain scattering rate $\tau_{\parallel}^{-1}$ to account for the decreasing linewidth with decreasing temperature in some cases,[14] cannot explain $d\Delta H/dP > 0$, since $\tau_{\parallel}^{-1}$ decreases strongly with pressure.

To describe the different temperature and pressure dependences of ΔH in Ref. 17 an empirical formula was proposed:

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

allowing on-chain and interchain spin relaxation, respectively. The a and b parameters should depend on temperature, intermolecular distances, relative molecular orientations, and also whether the electrons are hopping between the same type of molecule. In the second term in Eq. (2) the interchain tunneling rate given by the golden rule of the perturbation theory is

$$\tau_{\perp}^{-1} = (2\pi/\hbar) |t_{\perp}|^2 \tau_{\parallel}/h , \tag{3}$$

where $t_{\perp}$ is the interchain transfer integral. $\tau_{\perp}^{-1}$ gives the increase of ΔH with pressure since $\tau_{\parallel}$ increases strongly with pressure, by 20–30%/kbar for the majority of organic conductors. In TTF-TCNQ this term dominates not only the pressure dependence of ΔH ($d\ln\Delta H/dP = 33\%$/kbar) but also its temperature dependence, since ΔH increases with decreasing temperature. We note that experiments on progressively irradiated samples have also provided an evidence on the importance of the interchain spin relaxation in Q1D organic conductors.[18]

In single chain compounds like β-(BEDT-TTF)$_2$I$_3$ the temperature dependence of ΔH should be dominated by $\tau_{\parallel}^{-1}$, and its decreasing tendency under pressure compensates to some extent for the increase in $\tau_{\perp}^{-1}$. In TTF-TCNQ both the temperature and pressure dependences are dominated by $\tau_{\perp}^{-1}$ and $d\ln\Delta H/dP$ is three times larger than in β-(BEDT-TTF)$_2$I$_3$ although the compressibilities are quite similar.[19] Strictly speaking the $\tau_{\perp}^{-1}$ term should be introduced only if the transverse transport is diffusive. However, this is not too strong a condition for α-, β-(BEDT-TTF)$_2$I$_3$ since the magnitude of the dc conductivity of 20 $(\Omega\,\mathrm{cm})^{-1}$ in a tight-binding picture corresponds to a mean free path of 0.1 lattice spacing. It is less clear to what extent we can attribute $\tau_{\parallel}^{-1}$ to β-(BEDT-TTF)$_2$I$_3$ in Eq. (2) supposing coherent on-chain transport since the reported conductivity data are isotropic within a factor of 2 in the a-b plane. But if the transport is coherent along the stacks and diffusive between the stacks at high temperatures, and if on cooling down even the interstack transport becomes coherent one should observe decreasing linewidth with pressure. The crossover in the pressure dependence of ΔH around 100 K in the β-(BEDT-TTF)$_2$I$_3$ might be the consequence of such a change in the interchain transport.

In principle, increasing ΔH could be caused by increasing spin-orbit coupling that is by changes in Δg. This time we have not performed high-precision g-factor measurements, but in the case of TTF-TCNQ, (TMTTF)$_2$BF$_4$,[17] and NPQn(TCNQ)$_2$, Δg is pressure independent within

TABLE I. Pressure derivative $d\ln\Delta H/dP \equiv [\Delta H(P) - \Delta H(1\ \mathrm{bar})]/\Delta H(1\ \mathrm{bar})P$ at room temperature for different low-dimensional conductors.

	TTF-TCNQ	TMTTF-TCNQ	(TMTTF)$_2$BF$_4$	α-(BEDT-TTF)$_2$I$_3$	β-(BEDT-TTF)$_2$I$_3$
$d\ln\Delta H/dP$ (%/kbar)	+33[a] +28[a]	+18[a]	+9[b]	+5.5	+9.8

[a] Reference 16.

[b] Reference 17.

2% up to 5 kbar. This is comprehensible since g is a molecular property, and by contracting the lattice one does not expect to change molecular quantities.

In conclusion, the CESR linewidth of α and β-BEDT-TTF)$_2$I$_3$ increases under pressure in contrast to the predictions of the Elliot formula for spin relaxation in metals. We have proposed an empirical formula in which interchain transitions are responsible for the increasing linewidth under pressure.

Useful discussions with S. Bouffard, J. R. Cooper, A. Graja, and M. Weger are gratefully acknowledged.

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