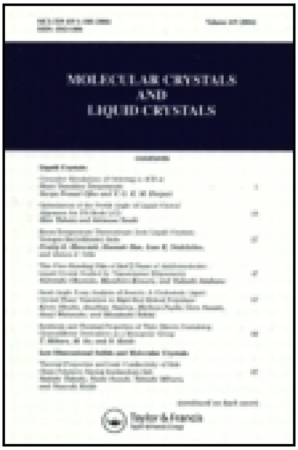
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Frequency Dependence of ESR in Pristine Trans-Polyacetylene: Spin Lattice Relaxation Time T_1

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FREQUENCY DEPENDENCE OF ESR IN PRISTINE TRANS-POLYACETYLENE: SPIN LATTICE RELAXATION TIME T_1*#

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Abstract We have measured ESR T_1 in pristine trans-polyacetylene at frequencies 5∿450 MHz and at temperatures 4.2∿300 K. This experiment provided a new evidence of one dimensionally moving neutral solitons.

On the nature of neutral solitons in trans-polyacetylene, intensive discussions were recently made based upon many theoretical[1] and experimental[2] studies. Among them, NMR and ESR work played an essentially important role because the neutral soliton carries a magnetic moment. In this report we wish to present an experiment which provides a new evidence of one dimensionally moving neutral solitons[3]. We measured a frequency dependence of ESR T_1 over a wide range of 5∿450 MHz.

Cis films were prepared by a Ziegler-Natta catalyst[7]. Trans-isomerization was made at 150∿180 °C from several minutes to several hours to change the spin densities. For ESR spectrometer between 5∿450 MHz a hybrid junction and a double balanced mixer were used. T_1 was measured by a CW saturation method at $T > 150$ K where ESR lines are homogeneous, and a saturation recovery method at $T < 150$ K. The spin echo method was inapplicable at several tenth MHz because of the dead time problem.

Room Temperature[3]

The frequency dependence of measured T_1^{-1} in trans (CH)x and (CD)x was presented in Fig. 1. The characteristic feature of these

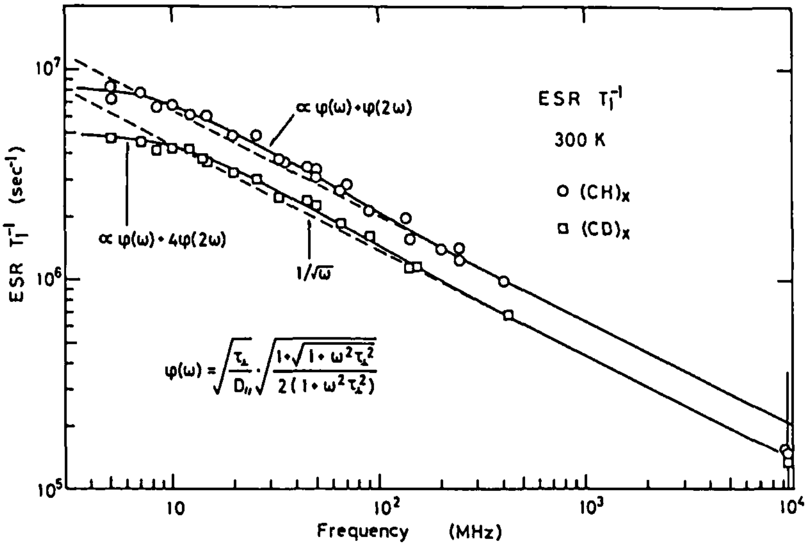

FIGURE 1 Frequency dependence of ESR T_1. See also ref.3.

results is that at lower frequencies $f < 10^7$ Hz, the T_1^{-1} is nearly constant and at $f > 10^7$ Hz, it approaches a $\omega^{-1/2}$ variation. This behavior is interpreted by one-dimensional diffusive motion of electron spins with a low frequency cutoff. The fitted solid lines express the case of TTF.TCNQ[8], where $1/\tau_\perp$ is the cutoff frequency.

The obtained behavior can not be interpreted without the model of one-dimensionally diffusing electron spins. If the electron spins were fixed, the frequency dependence would be ω^{2n}, where n is an integer between 0 and 2 for direct, Raman and Orbach-Aminov relaxation processes. A relaxation mechanism involving a spin diffusion process as was pointed out for the ^{1}H NMR case[5-6], should not be effective for this ESR case. Further, the presence of hyperfine part, that is, the observed T_1^{-1} is different in (CH)x and (CD)x, requires the movement of electron spins. According to our detailed numerical analysis on relaxation process[3], the diffusion rate $D_{//}/c_{//}^2$ with $c_{//}$=2.46 A, was found to be 3.7 ± 1.6 and 1.1 ± 0.5 x 10^{13} s^{-1} from the dipolar and hyperfine parts, respectively.

Temperature Dependence at T > 150 K (Fig. 2)

A pronounced temperature variation in this region was found in the cutoff frequency f_c. With lowering temperature the f_c decreased proportionally to T^2 (the insert of Fig.2). A possible explanation of this phenomena will be a mechanism proposed by Kivelson[9]. However, the temperature variation due to this mechanism is much steeper. A similar cutoff phenomena has been found by Clark et al[6] for a corresponding NMR case. The cutoff was around 20 Oe at room temperature, which is similar to our ESR result. This may suggest

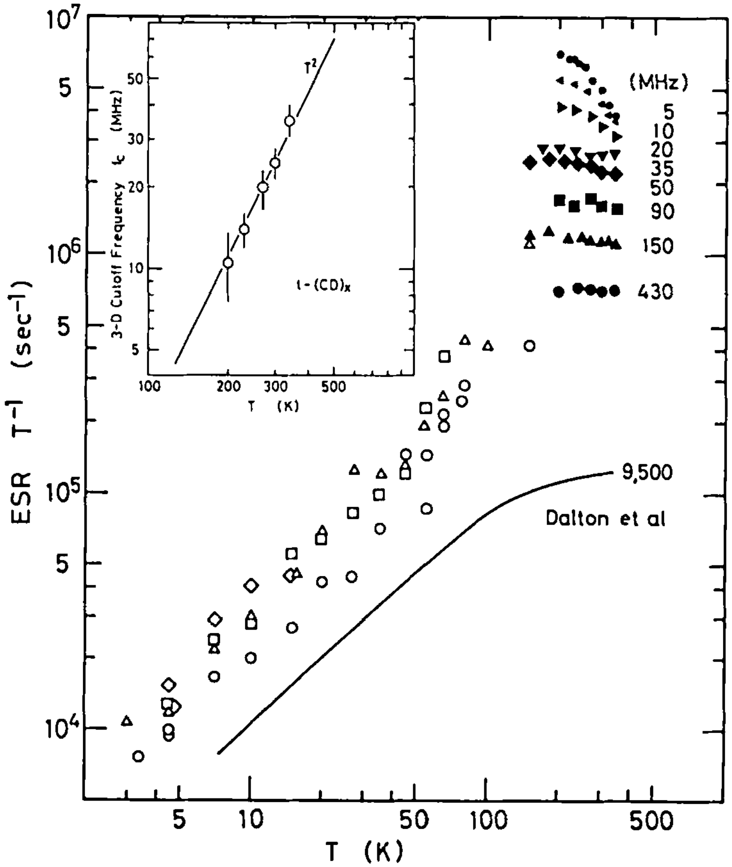

FIGURE 2 Temperature dependence of ESR T_1 and f_c (the insert).

that the NMR cutoff is due to ω_e instead of ω_n. However, that interpretation is in conflict with the fact that another cutoff field due to ω_n, which should be higher than that due to ω_e by about one thousand times, was not found experimentally[4-5]. Further their temperature dependence completely differs from ours.

We can extract a temperature variation of $D_{//}$ from that of T_1^{-1}, if we know the temperature variation of the number of fixed neutral solitons[10]. The discussion will be given in our separate paper in this proceeding[11].

Temperature Dependence at T < 150 K (Fig. 2)

When the temperature crossed 150 K, a qualitative change appeared. This qualitative change across 150 K is believed to be caused by the trapping of neutral solitons. A similar rather abrupt change around 150 K has been found in a nuclear enhancement experiment by Clark et al[6].

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*See also ref.11 for ESR line width presented in these Proceedings.

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