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Publisher: Taylor & Francis

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UK



Molecular Crystals and Liquid Crystals

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

Frequency Dependence of ESR in Pristine Trans-Polyacetylene: Line Width

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Version of record first published: 17 Oct 2011.

To cite this article: Kenji Mizoguchi, Kiyoshi Kume & Hideki Shirakawa (1985): Frequency Dependence of ESR in Pristine Trans-Polyacetylene: Line Width, Molecular Crystals and Liquid Crystals, 117:1, 459-462

To link to this article: http://dx.doi.org/10.1080/00268948508074665

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Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 459-462 0026-8941/85/1174-0459/\$10.00/0

985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd. Printed in the United States of America

FREQUENCY DEPENDENCE OF ESR IN PRISTINE TRANS-POLYACETYLENE: LINE WIDTH*#

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Abstract We measured a frequency dependence of ESR line width $\overline{\text{in (CH)}x}$ and (CD)x at frequencies $5 \sim 9,500$ MHz. From a detailed analysis we could independently deduce 1-D diffusion rate of electron spin (neutral soliton) D_{||}/c_{||}², and the trapped spin concentration C between 200 and 340 K.

ESR in pristine trans-polyacetylene has been intensively studied in order to clarify a nature of unpaired electron spin in it. However, it seems unclear what is an origin of ESR line width, because ESR experiment has been done only in the limited frequency range - X-band. In this report we show that a study of frequency dependence of ESR line width is a powerful tool to investigate the origin of ESR line width. We obtained the temperature dependence of electron spin diffusion rate $D_{//}/c_{/}$ and the width by trapping, independently, between 200 and 340 K. These results are completely consistent with the frequency dependence of electron spin-lattice relaxation by us 2 .

In Fig. 1 we showed ESR line width versus $f^{-1/2}$, where f is the frequency. This figure clearly shows $f^{-1/2}$ frequency dependence of the line width at higher frequencies than several tenth MHz. The solid line represents a theoretical fitting based on one-dimensional diffusive motion of the electron spin with slow three dimensional cutoff², where unique fitting parameter is the width by trapping. In this fitting we took into account electron-electron

dipolar and electron-nuclear hyperfine couplings². This analysis predicts a frequency independent secular width $T_2^{\prime-1}$, which is a motionally narrowed dipolar and hyperfine width, and a frequency dependent non-secular width $T_1^{\prime-1}$ - so called life time width. An upward deviation at X-band can be attributable to a g-shift anisotropy broadening. The residual width can be interpreted as the width by trapping, initially introduced by Nechtshein et al³.

Temperature dependence of this is shown in Fig. 2. From a

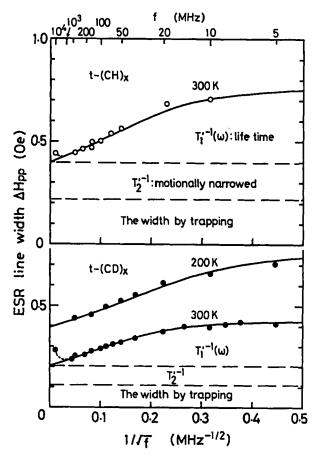


FIGURE 1 Frequency dependence of ESR line width.

requirement of homogeneous line width in the present temperature range 4 , trapped time should be shorter than that of local field. The trapped spin concentration in Fig. 2 must be interpreted as a

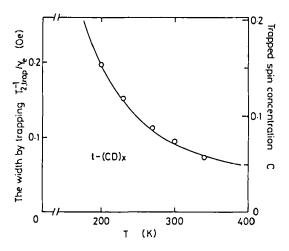


FIGURE 2 Temperature dependence of the width by trapping.

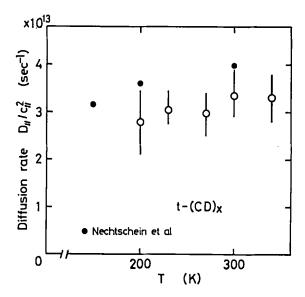


FIGURE 3 Temperature dependence of 1-D diffusion rate.

time ratio of the trapped time to the unit time. The solid line represents a predicted behavior from a trapping model by Nechtshein et al 3 with Eo/k $_{\rm B}$ =750 K and p=0.018, which can account the experimental data.

Further we can obtain $D_{//}/c_{//}^2$ from T_1^{-1} and T_2^{-1} with a correction of trapping and a similar process to T_1 of ESR^2 . Temperature dependence of I-D diffusion rate is shown in Fig. 3 together with that obtained from NMR T_1 by Nechtshein et al 3 . Both data agrees with each other very well, which suggests that NMR T_1 strongly reflects a relaxation to the I-D diffusing electron spins.

In the present ESR case there is no ambiguity and the analysis is simple, but in the NMR T₁ the analysis is very complicated and relaxation mechanism is not well defined, because of a presence of the relaxation to the fixed spins and a trapping problem 1 . Therefore, the analysis 2 of ESR T₁ and the present one is a strong and clear evidence of rapid 1-D diffusive motion of unpaired spin neutral soliton. NMR study by Holczer et al 5 in this conference partly solved one of questions in NMR T₁. Further, if 3-D cutoff by $f(\omega_1)$ term 3 was found at the same frequency as that in ESR T₁ case 2 , the ambiguity in NMR T₁ would be erased.

A detailed account of this work will appear elsewhere.

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