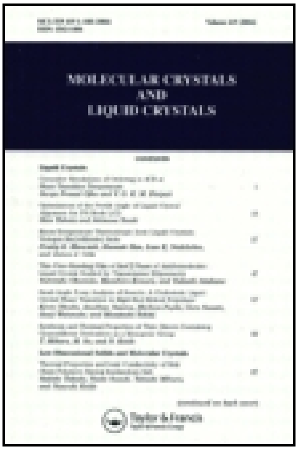

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Nuclear Relaxation and Exciton Dynamics in $(\oslash_3AsCH_3)(TCNQ)_2$

F. Devreux [a] & M. Nechtschein [a]

[a] Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, Section de Résonance Magnétique, B.P 85 Centre de Tri, 38041, Grenoble Cedex, France

Version of record first published: 28 Mar 2007.

To cite this article: F. Devreux & M. Nechtschein (1976): Nuclear Relaxation and Exciton Dynamics in $(\oslash_3AsCH_3)(TCNQ)_2$, Molecular Crystals and Liquid Crystals, 32:1, 251-254

To link to this article: http://dx.doi.org/10.1080/15421407608083664

Mol. Cryst. Liq. Cryst., 1976, Vol. 32, pp. 251–254

Printed in Holland

Nuclear Relaxation and Exciton Dynamics in ($\varnothing_3$AsCH$_3$) (TCNQ)$_2$

F. DEVREUX and M. NECHTSCHEIN

Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, Section de Résonance Magnétique, B.P 85 Centre de Tri, 38041 Grenoble Cedex, France

The spin dynamics in one-dimensional (1-d) systems displays typical properties, which can be studied from the frequency dependence of the nuclear relaxation time (T_1). In this manner, evidence for 1-d spin diffusion processes has been given in Heisenberg systems such as Tanol,[1] TMMC,[2,3] CsMnCl$_3$.2H$_2$O.[2,4] Similar studies can be performed in 1-d itinerant spin systems such as TCNQ salts.[5] The present work is devoted to the exciton motion in the radical salt ($\varnothing_3$AsCH$_3$)$^+$(TCNQ)$_2^-$. This compound exhibits thermally accessible magnetic states, which can be described in terms of localized (Frenkel) triplet excitons, as shown by the EPR fine structure observed at low temperature ($T < 180$ K).[6] The activation energy for the population of the triplet states (exciton concentration: $c(T)$) is $J/k \simeq 720$ K.[6] The absence of hyperfine structure shows that the excitons are moving. An order of magnitude of the jumping frequency has been given from the width of the motional narrowed EPR line[7] and from the observation of an Overhauser effect,[8] i.e. $\nu_j \sim 10^{10}\ \mathrm{s}^{-1}$.

We have recently reported measurements of the proton T_1 performed in polycrystalline ($\varnothing_3$AsCH$_3$) (TCNQ)$_2$ as a function of the frequency at $T = 145$ K.[5] The results have been interpreted in terms of a 1-d random walk of the excitons along the TCNQ chains. In the present study we have extended the measurements over the temperature range 100–300 K, in order to investigate the temperature dependence of ν_j.

The proton nuclear relaxation rate $(T_1)^{-1}$ has been plotted in Figure 1 as a function of the inverse square root of the nuclear Larmor frequency $(\nu_N)^{-1/2}$ for different temperatures. In this plot, straight lines ($T_1^{-1} \propto \nu_N^{-1/2}$ + const.) give evidence of 1-d diffusive processes.[1–5] The relaxation rate is given by

$$1/T_1 = c[\Omega_+ \phi^+(\nu_e) + \Omega_z \phi^z(\nu_N)] \qquad (1)$$

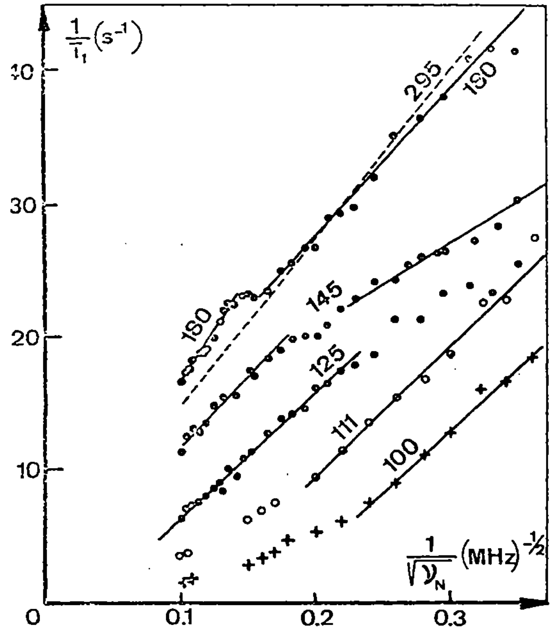

FIGURE 1 Proton spin-lattice relaxation rate as a function of the inverse square root of the nuclear Larmor frequency ($\nu_N^{-1/2}$). The experimental points at room temperature have not been represented.

where c is the exciton concentration, $\Omega_\alpha(\alpha = z, +)$ are geometrical factors associated with the hyperfine couplings, ν_e is the electronic Larmor frequency ($\nu_e = 660\ \nu_N$), and $\phi^\alpha(\nu)$ is the frequency correlation function of the electronic spins: $\phi^\alpha(\nu) = \langle S_n^\alpha(t) S_n^{\alpha *}(0)\rangle_\nu$; where S_n is the spin of the triplet exciton located at site n. The time modulation of $S_n^\alpha(t)$ involves the complete exciton Hamiltonian, including terms of transfer, collision (or exchange), creation—annihilation, and exciton-phonon coupling.[9] It is reasonable to assume—as in Ref. 5—that the exciton transfer along the TCNQ chains is the leading process at low temperature/weak exciton concentration. On the other hand, at high temperature/large exciton concentration, the exchange term must play an important role.

We interpret the experimental results (Figure 1) as follows:

1) First, consider the lowest temperatures. It clearly appears that $(T_1)^{-1}$ becomes very small for $\nu_N^{-1/2} < 0.1\ \text{MHz}^{-1/2}$; hence there is very few components of the exciton motion spectrum at frequency $\nu > 10^8\ s^{-1}$. It is thus inferred that the contribution to $(T_1)^{-1}$ comes from the nuclear frequency

part: $\phi(\nu_N)$. The straight lines at 100, 111, and 125 K result from diffusive behaviour in the ν_N region.

2) At 145 and 180 K, two straight lines can be distinguished, that we attribute to diffusive behaviours in the ν_N, and in the ν_e regions, in agreement with our previous study.[5]

3) By continuity we attribute the straight line obtained at room temperature to diffusive behaviour in the ν_e region.

Expressing the diffusive part of $\phi(\nu)$ as the frequency correlation function of a simple 1-d random walk motion, i.e. $(4\pi\sqrt{\nu_j\nu})^{-1}$, the slopes of the straight lines in the ν_N, and in ν_e region, are given by

$$p_N = \frac{c\Omega_z}{4\pi\sqrt{\nu_j}} \qquad p_e = \frac{c\Omega_+}{4\pi\sqrt{660\,\nu_j}} \tag{2}$$

The geometrical factors Ω_z and Ω_+ are explicitly given by:[9,10]

$$\Omega_z = \frac{4\pi}{5}\gamma_e^2\overline{d^2} \qquad \Omega_+ = \frac{4\pi}{15}\gamma_e^2(7\overline{d^2} + 5\overline{a^2}) \tag{3}$$

where $\overline{d^2}$ and $\overline{a^2}$ represent the mean square of the dipolar and scalar contributions of the hyperfine coupling, respectively. The ratio of the slopes, which is actually not temperature dependent within the experimental error, yields $\Omega_+/\Omega_z = 16 \pm 2$. If the scalar coupling a is known we can determine the value of ν_j. In Ref. 5 we have presented a self-consistent model for evaluating $\overline{a^2}$. Here we assume a priori that only the protons of the TCNQ molecules—namely 8 over 26—have a scalar contribution, and for the value of the scalar coupling we take half the value given for the TCNQ$^-$ radical in solution, i.e.: (1/2) 1.4 = 0.7 Gauss.

We have determined ν_j at the different temperatures, considering the diffusive behaviour of $\phi(\nu)$ either in the ν_N region, or in the ν_e region (or in both regions). The results are represented in Figure 2, where we have plotted log ν_j as a function of $1000/T$. It appears that ν_j is temperature dependent according to an activated process whose activation energy is $E \simeq 0.12 \pm 0.01$ eV. This result is to be compared to the activated processes observed for the spin-exchange broadened—or narrowed—EPR line[11] and for the electronic spin-lattice relaxation time.[12] These processes were shown to present activation energies which exceed the activation energy for the exciton concentration. It was suggested that the "excess" was due to the activation energy for the self-diffusion of the excitons, the values of which was found to be essentially one half the "self energy" of the triplet exciton due to exciton-photon interaction.[13] We thus confirm by this study that the diffusive motion of the excitons is activated and we give a value for the activation energy.

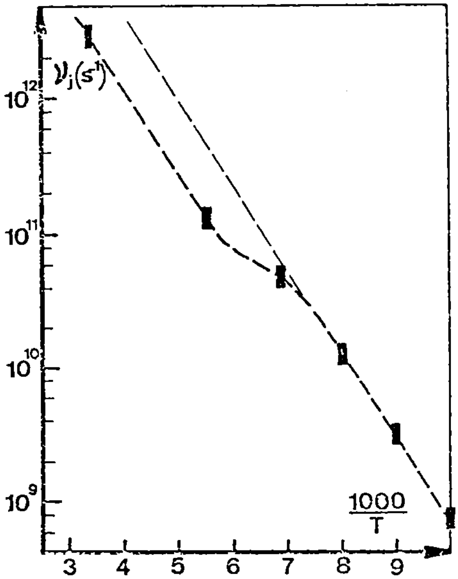

FIGURE 2 Semi-log plot of the jumping frequency ν_j versus $1000/T$.

Finally, we note that it seems there are two parts in the plot log ν versus $1000/T$ (Figure 2), corresponding probably to two different regimes of the 1-d spin diffusion. In the two regimes the activation energy for ν_j is about the same, but in the high temperature regime there is a decrease of the effective diffusion coefficient by a factor of ~4.

References

1. J-P. Boucher, F. Ferrieu, and M. Nechtschein, *Phys. Rev. B*, **9**, 3871 (1974).
2. F. Borsa and M. Mali, *Phys. Rev. B*, **9**, 2215 (1974).
3. M. Ahmed-Bakheit, Y. Barjhoux, F. Ferrieu, M. Nechtschein, and J-P. Boucher, *Solid State Com.*, **15**, 1, 25 (1974).
4. F. Ferrieu, *Physics Letters*, **49A**, 3, 253 (1974).
5. F. Devreux and M. Nechtschein, *Solid State Com.*, **16**, 3, 275 (1975).
6. D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1061).
7. Z. G. Soos, *J. Chem. Phys.*, **44**, 1729 (1966).
8. B. Marticorena and M. Nechtschein, 17th Colloque AMPERE, North-Holland, p. 505.
9. F. Devreux, Thèse de 3ème Cycle, Université de Grenoble, 1972.
10. F. Devreux, J-P. Boucher, and M. Nechtschein, *J. Physique*, **35**, 271 (1974).
11. M. T. Jones and D. B. Chesnut, *J. Chem. Phys.*, **38**, 1311 (1963).
12. M. T. Jones, *J. Chem. Phys.*, **40**, 1837 (1964).
13. Z. G. Soos and M. McConnell, *J. Chem. Phys.*, **43**, 3780 (1965).