ELECTRON SPIN ECHO DETERMINATION OF SPIN DIFFUSION IN THE ONE-DIMENSIONAL CONDUCTOR (FLUORANTHENYL)$_2^+(PF_6)_x(SbF_6)_{1-x}$

J. Sigg, Th. Prisner, K.P. Dinse, H. Brunner, D. Schweitzer and K.H. Hausser

Max-Planck-Institut, Abteilung Molekulare Physik, 6900 Heidelberg, F.R.G.

Résumé - Une relation de $5 \times 10^6 \leq D_\parallel / D_\perp \leq 5 \times 10^8$ pour la constante de diffusion en chaîne en proportion de celle entre-châines a été déterminée sur la base de la fonction de désintégration des échos de spin de $(Fa_2)_X^-$. La valeur résultante de $2 \times 10^{13} \leq D_\parallel \leq 2 \times 10^{16}$ rad s$^{-1}$ est conforme à la conductibilité à courant continu de $\sigma = 10 - 100 \, (\mu\text{cm})^{-1}$.

Abstract - From the electron spin echo decay function of $(Fa_2)_X^-$ a ratio of $5 \times 10^6 \leq D_\parallel / D_\perp \leq 5 \times 10^8$ for the inner stack to out-of-stack diffusion rates was determined. The deduced value of $2 \times 10^{13} \leq D_\parallel \leq 2 \times 10^{16}$ rad s$^{-1}$ is consistent with the bulk dc-conductivity of $\sigma = 10 - 100 \, (\mu\text{cm})^{-1}$.

It is well-known that in a one-dimensional conductor the particular spin dynamics of the one-dimensional electron spin diffusion should be detectable from the ESR absorption line-shape. In such a case the long persistence of the spin correlation functions $<S_1^2(t)S_2^2(0)> t^{-1/2}$ results in a characteristic exp($-\gamma t^3/2$) time dependence of the relaxation function [1-3] and therefore the ESR absorption line-shape is distinctly non-Lorentzian. However, such a line-shape analysis can be cumbersome especially because deviations from a Lorentzian line are noticeable only in the far wings of the absorption signal [1,4].

In the case of the quasi one-dimensional radical cation salts $(Fa)_X^- (Fa = Fluoranthene, X = PF_6, AsF_6, SbF_6$ etc.) however, because of the rather long electronic relaxation time $T_{2e}$ [5] the relaxation function can be probed directly via an electron spin echo (ESE) experiment [6]. In contrast to the line-shape analysis the direct measurement of the decay of the transverse magnetization in a one-dimensional system $\varnothing(t) = c \cdot \exp(-\gamma t^3/2)$ [1] by a free induction decay (FID) or an ESE experiment displays the critical $t^{3/2}$ dependence most clearly at short times. However, systems studied so far were characterized by rather broad ESR lines impeding the necessary short time recording because of spectrometer dead-time problems. In addition, time-independent contributions to the ESR line-width could easily mask the time dependence of $\varnothing(t)$ due to the diffusion process.

A Hahn spin-echo experiment, on the other hand, discriminates against static contributions to $\varnothing(t)$, and provided the spectrometer dead-time $t_d < \gamma^{-1}$, the echo decay function $\varnothing(e)(t)$ can give conclusive evidence for low dimensional diffusion and possibly interchain diffusion [6]. By introducing an intrachain diffusion rate $D_\parallel$ and an interchain rate $D_\perp$ with $D_\parallel >> D_\perp$ a characteristic time $t_o [1]$ can be derived defining the time region $t < t_o$ with $\varnothing(e) (2t) \cdot \exp(-2(yt)^{3/2})$ and $t > t_o$ with the slower "conventional" time decay $\varnothing(e) (2t) \cdot \exp(-2y't)$. Thereby the characteristic rate $t_o^{-1}$ is completely defined by the intra and interchain diffusion rates [1]:
On the other hand, the decay parameter $\gamma$ which can be obtained experimentally from an ESE experiment is related to the intrachain diffusion rate $D_\parallel$ by [3]:

$$\gamma = \frac{1}{8}(a^2 + 4/5 \, d^2 + n \, R^2) \cdot (\omega_c D_\parallel)^{-1/2}$$

Here $a$ and $d$ are the isotropic and anisotropic dipolar electron nuclear interactions, $n$ is the spin concentration per site and the quantity $\gamma n R/\omega_c$ can be considered as an effective electronic spin dipolar field originating from spins on neighbouring chains. The cut-off frequency $\omega_c$ limits the divergence of the $\omega^{-1/2}$ dependence of the spectral density function as measured, for instance, by nuclear spin lattice relaxation rates. It has to be mentioned that in the derivation of Eq. (2) [3] several simplifying assumptions were made which are also applicable for $(Fa_2)^+X^- [6]$. ESE decay functions of a polycrystalline sample of $(Fa_2)(PF_6)_x(SbF_6)_{1-x}(x \approx 0.5)$ were measured over the temperature range 140 K to 300 K thus covering the highly conducting regime ($\sigma(300 K) \approx 10^{-100} \, (\Omega \, cm)^{-1}$) and the semi-conductor range below the phase transition at 183 K [7]. Typical decay functions in the highly conducting range at 192 K and in the semi-conducting range at 145 K are depicted in Figs. 1 and 2. In order to show the characteristic behaviour of $\varphi(e)(2\tau)$ at 192 K, the function was plotted using a $\tau$ and $\tau^{3/2}$ scale. The signal obeys an $\exp(-2(\gamma \tau)^{3/2})$ dependence up to times $2\tau \approx 20 \mu s \approx t_0$. Experimental artefacts which might impose a deviation from a simple exponential decay $\exp(-2 \gamma' \tau)$ were excluded by lowering the sample temperature below the transition temperature of 183 K and recording ESE decays under identical experimental conditions at 145 K (see Fig. 2). The observed echo decay then follows an $\exp(-2 \gamma' \tau)$ dependence.

![Fig. 1: ESE decay function $\varphi^e(2\tau)$ plotted vs. $\tau$ a) and vs. $\tau^{3/2}$ b.](image)
For an estimate of $D_\parallel$ from Eq. (2) values for $a$, $d$, $\sqrt{n R}$ must be adopted. In a recent experiment [8] the spin concentration per Fluoranthen molecule $n = 2.1 \cdot 10^{-2}$ was determined at 285 K. Using an interchain distance $b_\mu = 9.7$ Å and an intrachain distance $c = 3.3$ Å [7] one obtains $\sqrt{n R} = 2 \cdot 10^8$ rad s$^{-1}$. This value can be interpreted as an average dipolar field of $\sqrt{n R}/\gamma = 11.5$ G. The isotropic electron-nuclear hf couplings have been determined for the Fluoranthen anion radical only. Taking these values as representative for the cation also, a second moment $\langle a^2 \rangle^{1/2} \approx 1.6 \cdot 10^6$ rad s$^{-1}$ is obtained. From the observed positive Overhauser enhancement of the proton NMR signal when applying a saturating microwave field at the electronic Larmor frequency it was concluded that $a^2 > d^2$ [6]. On the other hand, in an aromatic C-H fragment $d$ is not much smaller than $a$ and $d^2 \approx 0.3 \ldots 0.5$ $a^2$ can be assumed. Since the cut-off frequency is limited by $\omega_c \Gamma = (2)^{-2/3}$ (4 µs)$^{-1}$ and since $\omega_c \approx \omega_D$ (min) = $22 \times 2 \pi \times 10^6$ rad s$^{-1}$ [8], where $\omega_D$ is the lowest Larmor frequency for which an ($\omega$)$^{-1/2}$ dependence could be detected, an interchain diffusion rate of $2 \cdot 10^{13}$ rad/s $\leq D_\parallel \leq 2 \cdot 10^{16}$ rad/s is obtained. The deduced range for $D_\parallel$ could be confirmed [6] by analysing the proton spin lattice rates $T_1^{-1}$ obtained recently for (Fa)$_2$PF$_6$ [8].

From Eq. (1) an upper limit for the interchain diffusion rate $D_\parallel$ can be deduced. When taking $t_D = 20$ µs a value $D_\parallel \lesssim 4 \cdot 10^7$ rad/s is obtained. If the spin diffusion also reflects the charge diffusion, an estimate of the mean free path $\lambda$ and the intrinsic one-dimensional conductivity $\sigma_\parallel$ can be obtained. Using [9] $1 = 2 \pi \hbar X_m N^{-1} (\mu_0)^{-1}$ and $\sigma_\parallel = 2 e^2/\hbar d_\mu^2$ with a Pauli susceptibility

\[
X_m = 3.1 \times 10^{-5} \text{ cm}^3/\text{mol} \quad \text{[8]}
\]

leads to values $10^{-2} \lesssim 1 \lesssim 10$ cm and $6 \lesssim \sigma_\parallel \lesssim 6 \cdot 10^3$ $(\Omega \text{cm})^{-1}$. The latter value has to be compared with the bulk 1D conductivity at room temperature of $\sigma_b = 10 - 100$ $(\Omega \text{cm})^{-1}$.
which gives a lower limit to the intrinsic conductivity $\sigma_{\parallel}$. This suggests that the actual value of $D_{\parallel}$ is close to the upper limit given above.

The ratio $5 \times 10^6 \lesssim D_{\parallel}/D_{\perp} \lesssim 5 \times 10^8$ for the intra and inter-stack diffusion rates which emerges from the characteristic time $t_0 \approx 20 \mu s$ is consistent with the picture of a highly anisotropic electric conductor based on the several order-of-magnitude difference between the $\pi$-electron transfer integrals parallel and perpendicular to the aromatic stacks.

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Note: We have just learnt that Fluoranthene is about equipotent as mutagen for human lymphoblasts as Benzo[α]pyrene [10].