

ELECTRON SPIN ECHO EXPERIMENTS ON THE QUASI ONE DIMENSIONAL ORGANIC METAL: (Perylene)₂X₁·2/3 THF (X = AsF₆⁻, PF₆⁻)

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Abstract The analysis of the electron spin echo decay function shows an exceptionally good quasi one dimensional behaviour for the electron spin diffusion.

It has been demonstrated recently¹⁻⁵ that time resolved ESR can be used advantageously to study details of spin transport processes in a variety of organic conductors. Extremely narrow ESR linewidths in the order of 0.1 to 1 μ T are found in the case of radical cation salts, being composed of pure hydrocarbons as constituents for the aromatic stacks and of suitable anions like PF₆⁻, AsF₆⁻, SbF₆⁻.

The analysis of detailed ESR linewidth and relaxation data resulted in a microscopic picture of the electron spin transport in these systems, especially in the diffusion constant $D_{||}$ parallel to the aromatic stacks.

Maresch et al.⁵ have determined $D_{||}$ directly by analysing the electron spin echo decay function in a field gradient for the system (fluoranthenyl)₂⁺ AsF₆⁻ and found $D_{||} = 1.3 \text{ cm}^2 \cdot \text{s}^{-1}$, in agreement with our earlier estimate⁴.

From the crystal structure of this compound a large anisotropy of the charge transport can be inferred. It was expected from analogy to the similar trans-poly-acetylene systems that the off-

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stack hopping rate would be so slow that the characteristic $\exp(-\gamma t)^{3/2}$ time dependence of the relaxation function of a highly one dimensional electron spin diffusion might be directly observable.

Owing to the dead time of the ESE spectrometer, echoes could be observed with an effective dead time of $2\mu\text{s}$ only, thus asking for a characteristic time t_0 , defining the cut-off of the one dimensional diffusion of at least $10\mu\text{s}$. This is three orders of magnitude longer than the value observed for $\text{trans}-(\text{CH})_x$ from line shape analysis⁷ and from proton relaxation data⁸.

It is obvious that only excellent crystals with a minimum of lattice defects and/or paramagnetic impurities can be expected to lead to an observable $\exp(t^{3/2})$ effect, because only the extreme long time behaviour of the one dimensional correlation function is tested.

It was the purpose of our study to demonstrate that the $\exp(t^{3/2})$ decay characteristic can reproducibly be observed for selected crystals grown under controlled conditions and with a specific composition of anions. For the study we have chosen the donor perylene and have grown crystals of the type $(\text{Pe})_2(\text{AsF}_6)^{0.45}(\text{PF}_6)^{0.55} \cdot 2/3 \text{ THF}$ (1); $(\text{Pe})_2\text{PF}_6 \cdot 2/3 \text{ THF}$ (2); and $(\text{Pe})_2\text{AsF}_6 \cdot 2/3 \text{ THF}$ (3), (Pe = perylene, THF = tetrahydrofurane).

Figure 1 shows the ESE decay function of a single crystal of (1) at 205 K, which is in the "metallic" range of the dc conductivity and at 92 K, well below the transition temperature to the non-metallic range.

The deviation of the short time values from an attempted exponential fit by more than a factor 2 is much larger than the experimental error. Possible non-linearities of the detection channel were excluded by attenuating the signal by 20 dB directly after the microwave circulator. The linearity of the detection channel is also demonstrated by the pure exponential decay function observed for the same sample, just lowering the temperature to 92 K.

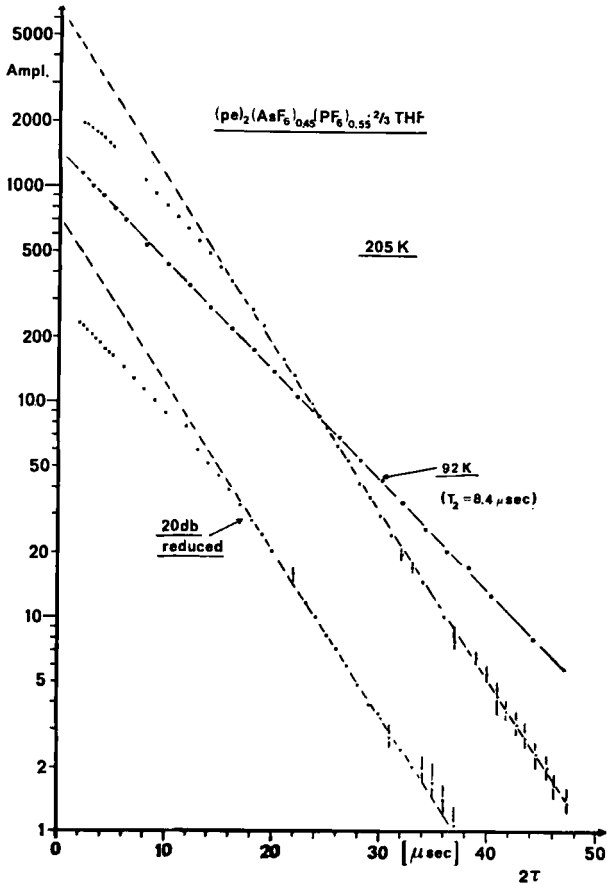


Fig. 1) ESE decay function of a single crystal of (1).

ESE decay functions of single crystals of the "single anion" type (2,3) always could be fitted with a single exponential. It should be noted, that we had several samples of the "mixed anion" type (1), which also showed a single exponential decay.

Apparently minor modifications in crystal growth can result in effects masking the $\exp(-t^{3/2})$ behaviour. In order to verify our analysis which predicts an extremely small cut-off frequency $\omega_e \approx 10^5 \cdot s^{-1}$, the proton nuclear relaxation rate T_{1N} has been measured

as a function of the proton larmor frequency ω_N ⁹. This method has the advantage that T_{1N} is only sensitive to the diffusive spins. Contributions from spin interactions between various mobile and localized electronic spins are not seen.

The relaxation rate $T_{1N}^{-1}(\omega_N)$ shows a definite $\omega^{-1/2}$ dependence for the range 270 to 20 MHz measured for (1)⁹. An additional value has been determined in the rotating frame for $\omega_{Nr}/2\pi = 200$ kHz, which extrapolates from the T_{1N}^{-1} values within experimental error⁹, showing that the analysis of the ESE decay function in terms of an extremely one dimensional diffusion process is basically correct. The analysis of the ratio of the in-stack to out-of-stack diffusion rates⁴ results in the case of (1) in a value of $D_{||}/D_{\perp} > 10^7$ with $D_{||} = 1 \text{ cm}^2 \cdot \text{s}^{-1}$.

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