

PULSED ESR INVESTIGATION OF SPIN TRANSPORT PROPERTIES
IN THE ORGANIC CONDUCTOR (PERYLENYL)₂ (AsF₆)_{0.75} (PF₆)_{0.35} · 0.85 CH₂Cl₂

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Spin transport properties in the organic conductor (perylene)₂⁺ X⁻ were studied in the temperature range of 4–300 K. Being constant in the “metallic” range ($D_{\parallel} = 1.8(2) \text{ cm}^2 \text{ s}^{-1}$), the diffusion constant D_{\parallel} exhibits a temperature activated behaviour in the low temperature range, at variance with the prediction invoking the model of an intrinsic semiconductor. A low-temperature divergence of the homogenous ESR line width, indicative of one-dimensional fluctuations, was also observed.

1. INTRODUCTION

LOW-DIMENSIONAL ORGANIC conductors have attracted much interest since the discovery of superconductivity in several different crystalline charge transfer (CT) complexes of the Bechgaard-type [1–3]. Up to date no system using pure hydrocarbons (HC) as donor molecules were found to exhibit superconductivity. Instead they are characterized by broad metal-to-insulator (MI) transitions in the temperature range of 120–200 K. In all systems studied so far the low temperature ground state was non-magnetic, thus rendering the HC charge transfer salts ideal candidates for magnetic resonance investigations. However, conventional cw ESR probing susceptibility and line width is of limited value for unravelling the microscopic behaviour of the charge transport.

A few systems, exhibiting extremely narrow ESR lines in the range of 10–30 mG, have been investigated by pulsed ESR. Especially the CT-complex (fluoranthene)₂X was utilized as a model compound [4]. In the high-temperature metallic phase the extreme one-dimensionality was proven from the analysis of the Hahn-echo decay function with [5] and without [6] the application of an external field gradient. The application of the well-established experimental method to other HC–CT complexes was impeded by electron-spin dephasing times T_{2e} in the sub- μs range.

We therefore developed a pulsed ESR apparatus with optimized time resolution, allowing the detection

of the echo signal within at least 200 ns referenced to the beginning of the first microwave pulse. With such a time resolution not only the spin diffusion constant in the metallic regime can be measured but also the relaxation rates in the low-temperature insulating phase can be investigated. In particular, we were interested, if remnants of SDW fluctuations could be detected via T_{2e} in the low-temperature regime, were susceptibility measurements showed a $T^{-0.75}$ behaviour, indicative of a random exchange Heisenberg antiferromagnetic chain (REHAC) [7].

2. EXPERIMENTAL

As has been shown recently [8], pure HC-charge transfer crystals with a high d.c. conductivity can be obtained when perylene (pe) is used as the basic building block. Crystals which were grown from a tetrahydrofuran (THF) solution had already been subject of magnetic resonance investigations and could be characterized as extremely one-dimensional [9]. The modification obtained from CH₂Cl₂ with PF₆ and AsF₆ as counterions crystallizes in the orthorhombic space group P_{nmn} in the composition (pe)₂ (AsF₆)_{0.75} (PF₆)_{0.35} · 0.85 CH₂Cl₂ [8]. It exhibits the largest reported room temperature dc conductivity (σ_{\parallel} (300 K) = 1200 (Ωcm)⁻¹) of a HC-salt in combination with a peak-to-peak ESR width of 0.5 G. Extensive experimental data about the magnetic and transport properties of the system were available [8, 10–12]. In particular the

susceptibility data indicated, that a pulsed ESR investigation should be feasible over the full temperature range from 4–300 K, so that the spin transport and details of the ESR relaxation in the low-temperature regime could be investigated.

Crystals were grown by the standard electrochemical procedure as has been reported elsewhere [8].

The spectrometer used was built around a bimodal ESR probe head using the design proposed by Biehl and Schmalbein [13]. Microwave pulses are formed using a fast low-power pin switch (ma 2662–0106) controlled by a Bruker pulse programmer (EP 385). The pulses are subsequently amplified with a pulsed 1 kW TWT amplifier (Appl. Systems Eng. 117X–1). The $\pi/2$ -excitation pulse was of 20 ns duration. Owing to the 60 dB decoupling of the excitation and detection channels, an undistorted Hahn-echo could be recorded at a delay of 150 ns with respect to the beginning of the first pulse. Details of the spectrometer will be given elsewhere [14].

3. RESULTS AND DISCUSSION

In the course of the investigations we noticed, that the relaxation properties of the sample could be changed irreversible if the sample was tempered at a temperature of approximately 90°C for several hours. In particular, the homogeneous ESR line width decreased by a factor of 2.5 at 300 K and the low temperature longitudinal relaxation time T_{1e} increased by the same factor. After thermal annealing, the T_1 and T_2 values were constant for at least several months and did not change under low temperature cycling. The crystal structure was not affected by this procedure [15]. This reproducible behaviour was also found for other (pe)₂X modifications and will be subject of further investigations. Apparently, the thermal annealing process affects only the microscopic properties of the crystal (viz. relaxation rates, diffusion constant) and does not show up in macroscopic properties like the d.c. conductivity.

T_{2e} and T_{1e} values for an as such grown and an annealed sample are shown as a function of temperature in Fig. 1. In the following only experiments are described that were performed on a sample which was kept for >12 h at 80°C and was found stable under further temperature treatment.

In the “metallic” range and down to 100 K, T_{1e} and T_{2e} were found equal within experimental error. The FID intensity (which is proportional to the $g = 2$ narrow resonance susceptibility) was nearly constant from room temperature to 50 K and then rose by approximately a factor of 6 to 4 K, following a $T^{-0.75}$ law in agreement with earlier results [10]. A similar behaviour was also observed for the fluoranthene radical salt [16].

As was demonstrated recently [6], diffusion of the electron spins can be measured by observing the Hahn

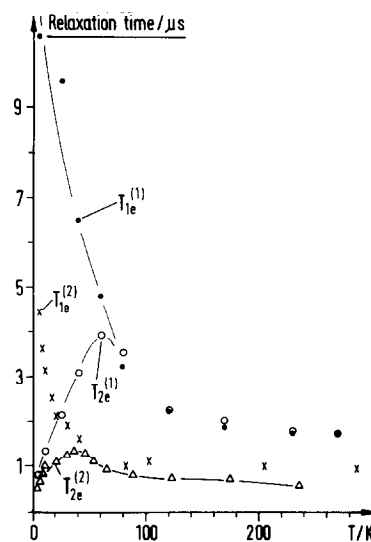


Fig. 1. Relaxation times T_{1e} and T_{2e} of an as such grown (2) and a thermally annealed sample of (perylene)₂ (AsF₆)_{0.75} (PF₆)_{0.35} · 0.85 CH₂Cl₂ as a function of temperature. The relaxation times were determined using a $\pi/2$ - π and a π - $\pi/2$ - π pulse sequence, except for T_{1e} (2), which was obtained from a π - $\pi/2$ sequence.

spin echo decay in an external magnetic field gradient. This technique can be used to study the temperature dependence of the spin diffusion constant. First results for the fluoranthene [17] and perylenyl [18] radical cation salts were presented recently. Figure 2 shows the echo intensity decay functions as a function of temperature. The experiment was performed using a constant field gradient of 90 G cm⁻¹, parallel to the crystallographic a axis, which is the high-conductivity direction. Measurements in the temperature interval from 270–130 K resulted in indistinguishable decays, leading to a temperature independent spin diffusion constant D_{\parallel} .

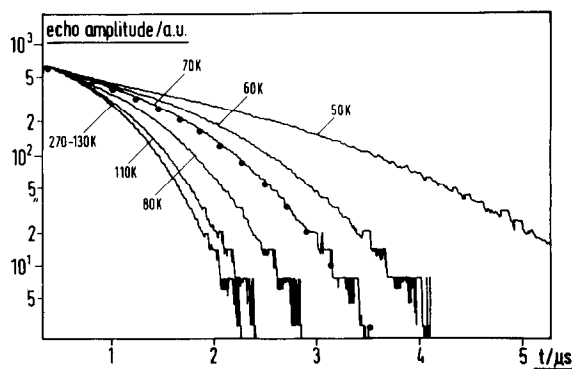


Fig. 2. Two-pulse echo decay function of (pe)₂ (AsF₆)_{0.75} (PF₆)_{0.35} · 30.85 CH₂Cl₂ (thermally annealed) in a field gradient of 90 G cm⁻¹ as a function of temperature. The echo amplitude was sampled with a boxcar integrator. Use of equation (1) leads to a perfect fit of the experimental data. A few calculated values are shown for the 70 K echo decay as an example.

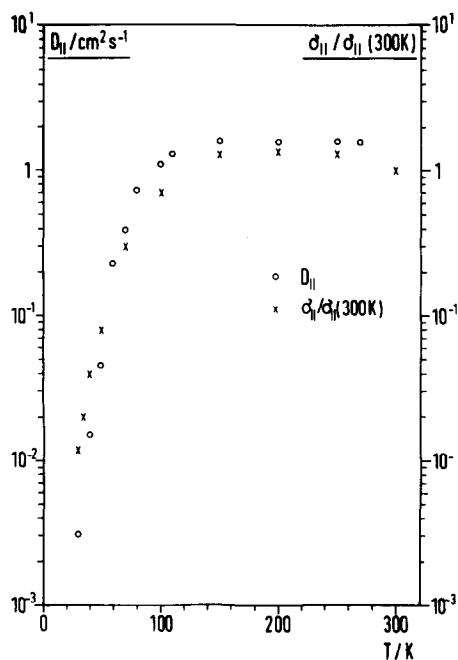


Fig. 3. Spin diffusion constant $D_{||}$ as obtained by fitting the data in Fig. 2 with equation (1). The d.c.-conductivity data had been measured by Bender *et al.* [8].

The decay functions could be fitted using the relation

$$M(t) = M_0 \exp(-t/T_{2e}) \exp\left(-\frac{1}{12} \gamma_e^2 G^2 D_{||} t^3\right) \quad (1)$$

in the usual notation [6]. The temperature dependence of $D_{||}$ is depicted in Fig. 3. Absolute values for $D_{||}$ were obtained by calibrating the field gradient with microscopic samples mounted in a measured distance in the cavity.

D.c.-conductivity data obtained earlier [10] show a strikingly similar temperature dependence. A detailed plot of the low-temperature regime reveals, that the diffusion constant and the d.c.-conductivity can well be described by a temperature-activated process, with activation energies differing by only 20% (see Fig. 4).

The conductivity data had been described by anticipating an intrinsic semiconductor with a band gap $E_g/2k_B = 210$ K. Within experimental error, the same band gap E_g was deduced from an analysis of the temperature dependence of the thermopower, also using the model of an intrinsic semiconductor [8]. In this model σ and the Seebeck coefficient are controlled by the thermally activated carrier concentration, the mobility of the carriers being a weak function of temperature, only. This is in apparent contradiction to the observed strong dependence of $D_{||}$ on T , which would rather indicate that the electric conductivity should be explained by invoking a thermally activated hopping process.

We have no explanation based on a microscopic

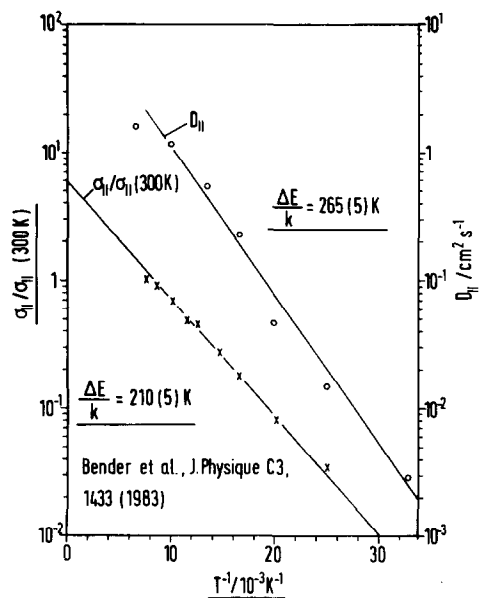


Fig. 4. Semi-log plot of $D_{||}$ and the normalized d.c.-conductivity in the "semiconducting" regime.

model for this discrepancy, but preliminary results obtained for other HC-charge transfer salts also indicate a strong dependence of $D_{||}$ on T in the "semiconducting" regime.

In the temperature range below 60 K, a divergence of the homogeneous ESR line width as measured by the 2-pulse echo is observed (see Fig. 1). In that range down to 4.2 K, the diffusion constant D was less than the detection limit of $10^{-3} \text{ cm}^2 \text{ s}^{-1}$, indicating localized spins within approximately $0.3 \mu \approx 10^3$ lattice constants.

Isolated, localized paramagnetic centers which could possibly arise from chain defects, would be subject to static hyperfine interaction (hfi) with magnetic nuclei in the crystal. Such an interaction could have been easily detected from a non-monotonous echo decay function ("echo envelope modulation") and would not result in a decrease of T_{2e} . Typical low concentration paramagnetic system show $T_{2e} \approx 5 \mu\text{s}$ in the Helium temperature range [19]. The complete absence of any echo envelope modulation and the independence of T_{2e} on a perdeuteration of the sample excludes hfi as a dominant relaxation source.

Time-independent magnetic dipolar interaction between highly concentrated paramagnetic localized centers could constitute a dipolar coupled spin system in which the 2-pulse dephasing time T_{2e} is governed by the second moment of the dipolar interaction. As is known from n.m.r., such a dipolar interaction can be probed by a solid echo or a Jeener echo sequence [20]. A signal can only be expected, if at least the two-spin correlations survive for the time of the echo sequence.

On the time scale of the experiment no solid echo

or Jeener-type echo could be detected, being indicative for the absence of a static electron spin dipolar system.

The most likely explanation for the low-temperature divergence of the electronic T_{2e}^{-1} therefore is the build-up of precursor effects of a one-dimensional phase transition. HC-charge transfer salts seem to be ideal candidates for the observation of such fluctuations, because the interchain interactions are exceptionally small. Microscopically, the system is expected to model its ground state with charge or spin periodicity with temperature-dependent fluctuations.

Tippie and Clarke have investigated the quasi-one-dimensional system (quinolinium)(TCNQ₂) and observed an empirical relation of the T_{2e}^{-1} dependence [7]. Figure 5 shows that T_{2e}^{-1} behaves according to the proposed relation

$$T_{2e}^{-1} \simeq \ln(T_0/T) \quad (2)$$

being indicative of a fluctuating spin density wave. Further experiments in the temperature range below 4 K are in progress to explore this model in more detail.

4. CONCLUSION

In contrast to the high-temperature range with its reasonably well understood "metallic" charge transport properties, spin transport and spin dynamics in the "insulating" state cannot be explained by invoking simple independent particle models. The extreme one-dimensionality of the system, as determined by the frequency dependence of the ¹H relaxation rate, is accounted for by defining a lower limit for the residing time of particular spin at one chain $\tau > 3.5 \times 10^{-10}$ s [21]. The resulting ratio for the intrachain and interchain transfer integrals amounts to $t_{\parallel}/t_{\perp} \simeq 10^5$, much larger than the TMTSF Bechgaard salts, thus leading to a nearly flat Fermi surface. The rather large intrachain interaction (band width 1.2 eV) in combination with the

transfer integral anisotropy apparently results in a convenient temperature range for the observation of one-dimensional fluctuations.

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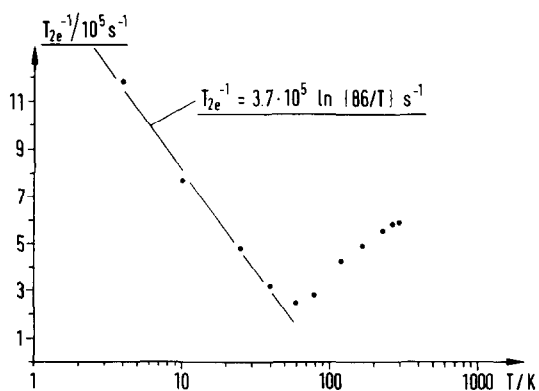


Fig. 5. Low-temperature spin dephasing rate T_{2e}^{-1} as a function of $\log T$, showing the low-temperature divergence of the homogeneous line width as proposed by Tippie and Clarke [7].