

## Electron-spin-echo experiments on the one-dimensional conductor $[(\text{fluoranthene})_2]^+[(\text{PF}_6)_x(\text{SbF}_6)_{1-x}]^-$ ( $x \approx 0.5$ )

J. Sigg, Th. Prisner, K. P. Dinse, H. Brunner, D. Schweitzer, and K. H. Hausser  
*Abteilung für Molekulare Physik, Max-Planck-Institut für Medizinische Forschung,  
 D-6900 Heidelberg 1, West Germany*

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The electron-spin-echo decay function was determined for the conducting phase of  $[(\text{C}_{16}\text{H}_{10})_2]^+X^-$  in the temperature range 183–300 K. The decay function exhibited an  $\exp[-(\gamma t)^{3/2}]$  dependence, characteristic of one-dimensional spin diffusion. The ratio  $5 \times 10^6 \leq D_{\parallel}/D_{\perp} \leq 5 \times 10^8$  for the inner-stack-to-out-of-stack diffusion rates was determined from the characteristic time  $t_0$ , at which the electron-spin-echo decay function changed to the “conventional”  $\exp(-2\gamma\tau)$  form. The deduced value  $2 \times 10^{13} \leq D_{\parallel} \leq 2 \times 10^{16}$  rad/s is consistent with the bulk dc conductivity and with recently determined nuclear spin-lattice relaxation rates. The overall assumption of highly mobile electronic spins was confirmed by an Overhauser-type experiment.

### I. INTRODUCTION

During the last few years the discovery of highly conducting hydrocarbon radical cation salts<sup>1–4</sup> has stimulated several investigations concerning the basic principles of this new class of conductors. Apart from conductivity measurements,<sup>1,3</sup> optical reflectance studies<sup>3,5</sup> and electron-spin-resonance (ESR) experiments<sup>3,6,7</sup> gave conclusive evidence of a low-dimensional electronic conductor. In particular in a recent paper the influence of the mobile electronic spins on relaxation of the proton spins in the cations and of the fluorine spins in the anions were studied by pulse nuclear-magnetic-resonance (NMR) methods in some detail.<sup>8</sup> In the temperature range above the phase transition in  $[(\text{fluoranthene})_2]^+X^-$  ( $X = \text{PF}_6, \text{AsF}_6$ ) at 183(3) K, the temperature dependence of the proton relaxation time  $T_{1n}$  was dominated by mobile spins, being interpreted in the model of a Fermi gas. By a Schumacher-Slichter-type experiment<sup>9</sup> the electronic spin density was determined and the deduced Fermi energy was in good agreement with the value determined from optical experiments.<sup>3,5</sup>

Taking the model of a one-dimensional conductor as rather well established, the particular spin dynamics of one-dimensional spin diffusion should be detectable from the ESR line shape. As is well known,<sup>10–12</sup> the long persistence of the spin correlation functions  $\langle S_i^z(t)S_j^z(0) \rangle \sim t^{-1/2}$  results in a characteristic  $\exp[-(\gamma t)^{3/2}]$  time dependence of the relaxation function. The resulting absorption line shape is distinctly non-Lorentzian, and therefore

careful line-shape analysis could be used to provide evidence for a dominantly one-dimensional spin-diffusion mechanism. However, such line-shape analysis can be cumbersome, especially because deviations sometimes got noticeable only far in the wings of the absorption signal.<sup>10,13</sup>

In case of the fluoranthenyl radical cation salts  $(\text{Fa}_2)^+X^-$  ( $X = \text{PF}_6, \text{AsF}_6$ ), however, because of the rather long electronic relaxation time  $T_{2e}$ ,<sup>7</sup> the relaxation function can be probed directly quite conveniently via an electron-spin-echo (ESE) experiment.

In this paper we report the first ESE results on mixed single crystals  $(\text{Fa}_2)^+[(\text{PF}_6)_x(\text{SbF}_6)_{1-x}]^-$  ( $x \approx 0.5$ ) as a function of the temperature. As is shown below, the echo-decay function closely follows the postulated  $\exp[-(\gamma t)^{3/2}]$  dependence for temperatures above the phase transition at 183 K, characteristic for a highly one-dimensional conductor. Independently, the high mobility of the electronic spins, consistent with a metallic conduction mechanism,<sup>14</sup> was proven with an Overhauser experiment for the proton spins on the aromatic subunits.<sup>15</sup>

### II. EXPERIMENT

X-band ESE experiments were performed with a home-built spectrometer, consisting of a slotted-tube resonator,<sup>16</sup> a Hewlett-Packard 8672a microwave synthesizer, and a Hughes 1277H traveling-wave tube (TWT) amplifier. Microwave pulses of  $\sim 5$  W and  $t_p \geq 50$  ns could be applied to the cavity. The signal was decoupled from the excitation line by a

three-port circulator. It was first amplified by a low-noise TWT amplifier (WJ 424 STD) and subsequently homodyne-detected with a double balanced mixer (RHG Electronics Lab DM 8-12 AB). With an additional amplification (dc–5 MHz) by 20 dB, the signal could be optimized on a scope and/or recorded with a Tektronix 7612 D fast digitizer linked to a microprocessor data-accumulation system. Spurious signals caused by cavity ringing or due to pin-diode transients were subtracted off resonance, thus leading to undistorted free-induction-decay (FID) or echo signals. The dead time of the spectrometer was  $\leq 200$  ns.

With the maximum microwave power used, a  $\frac{1}{2}\pi$  pulse time  $t_{\pi/2} = 90$  ns was obtained, corresponding to  $B_1 = 1$  G in the rotating frame. Hahn echoes were measured using a  $\frac{1}{2}\pi\text{-}\tau\text{-}\pi$  pulse sequence, whereas  $T_{1e}$  was measured by a  $\pi\text{-}\tau\text{-}\frac{1}{2}\pi$  sequence.

The cavity was inserted in a He cryostat and the temperature was measured with a calibrated Ge resistor (Lake Shore Cryogenics DRC-70). The temperature could be varied between 140 and 300 K by filling the radiation shield of the cryostat with liquid  $N_2$ .

Overhauser experiments were performed using a cylindrical cavity with a coaxial NMR coil. The proton NMR signal was determined by using a high-power pulse spectrometer. The apparatus, which is otherwise used for optical-nuclear-polarization (ONP) experiments, is described in detail elsewhere.<sup>17</sup>

The  $(\text{Fa}_2)^+X^-$  radical cation salts were obtained by anodic oxydation<sup>1,2</sup> in an electrochemical cell of three compartments separated from each other by glass filters. 1 g fluoranthene, 1 g  $(\text{C}_4\text{H}_6)_4\text{NPF}_6$ , and 1 g  $(\text{C}_4\text{H}_6)_4\text{NSbF}_6$  were dissolved in 100 ml  $\text{CH}_2\text{Cl}_2$  and saturated with dry nitrogen. The crystals were grown at  $-25^\circ\text{C}$  using a constant current of 50  $\mu\text{A}$  and a potential of about 2.5 V.

### III. THEORY

Following the derivation of ESR line shapes in nearly one-dimensional systems given by Hennessy *et al.*,<sup>10</sup> the decay of the transverse magnetization may be approximated by

$$\phi(t) = C \exp[-(\gamma t)^{3/2}]. \quad (1)$$

Here it was assumed that the spin correlation function  $\langle S_i^z(t)S_j^z(0) \rangle$  obeys a one-dimensional diffusion equation, resulting in

$$\langle S_i^z(t)S_j^z(0) \rangle \sim \left[ \frac{\tau_c}{t} \right]^{1/2} \quad (2)$$

for  $t \rightarrow \infty$ . The line shape of the absorption line

$f(\omega)$  at frequency  $\omega$  is related to  $\phi(t)$  by its Fourier transform. Three-dimensional exchange, in contrast, leads to an exponential dependence of  $\phi(t)$ , resulting in a Lorentzian line-shape function. In a conventional cw absorption experiment, deviations between Lorentzian and one-dimensional line shapes are most pronounced in the wings. A careful analysis of interchain hopping rates which destroy the one-dimensional character of the diffusion process therefore requires a line-shape analysis with values  $(H_0 - H)/\Delta H_{1/2} \geq 10$ .

In contrast, the direct measurement of  $\phi(t)$  by a FID would display the critical  $t^{3/2}$  dependence most clearly at short times. However, systems studied so far were characterized by rather broad ( $\Delta H_{1/2} \geq 0.5$  G) lines, impeding the necessary short-time recording because of spectrometer dead-time problems. In addition, time-independent contributions to the ESR linewidth (*viz.*, crystal imperfections) could easily mask the time dependence of  $\phi(t)$  due to the diffusion process.

A Hahn spin-echo experiment, however, discriminates against static contributions to  $\phi(t)$ , and provided the spectrometer dead time  $t_d < \gamma^{-1}$ , the echo-decay function  $\phi^{(e)}(t)$  can give conclusive evidence for low-dimensional diffusion and possibly interchain diffusion. Although the elimination of *static* inhomogeneities to the echo-decay function is obvious, the correlation of the echo-decay function  $\phi^{(e)}(t)$  with the homogeneous line shape is less evident. In a recent publication<sup>18</sup> the conditions for a direct proportionality between  $\phi^{(e)}(t)$  and the Fourier transform of the line-shape function  $f(\omega)$  have been restated in terms of a correlation-function analysis. If the system under investigation consists of a two-level system being coupled to a bath, and assuming that the transition dipole matrix can be factorized into a constant overall dipole strength and an  $N$ -by- $N$  unitary matrix ( $N$  denoting the number of bath states), the echo-decay function  $\phi^{(e)}(t)$  is proportional to a four- $\hat{\mu}$  correlation function,

$$\phi^{(e)}(2\tau) \sim \langle \hat{\mu}(-\tau)\hat{\mu}(0)\hat{\mu}(\tau)\hat{\mu}(0) \rangle. \quad (3)$$

Here  $\hat{\mu}$  denotes one component of the transition dipole operator and  $\tau$  is the  $\frac{1}{2}\pi\text{-}\pi$  pulse distance. For times long compared to the correlation time of both operators, the four- $\hat{\mu}$  correlation function can be factorized into the product of two  $\hat{\mu}$  functions,

$$\langle \hat{\mu}(-\tau)\hat{\mu}(0)\hat{\mu}(\tau)\hat{\mu}(0) \rangle = \langle \hat{\mu}(-\tau)\hat{\mu}(0) \rangle \langle \hat{\mu}(\tau)\hat{\mu}(0) \rangle, \quad (4)$$

thus implying that

$$\phi^{(e)}(2\tau) \sim \left| \int_{-\infty}^{\infty} d\omega \exp(-i\omega\tau)f(\omega) \right|^2. \quad (5)$$

In this model the echo-decay function  $\phi^{(e)}(t)$  is connected to the line-shape function  $f(\omega)$  in the way usually assumed, and by using

$$\int_{-\infty}^{\infty} d\omega \exp(-i\omega\tau) f(\omega) \sim \phi(\tau), \quad (6)$$

we find

$$\phi^{(e)}(2\tau) \sim |\phi(\tau)|^2. \quad (7)$$

Anticipating a transverse magnetization decay function  $\phi(t) \sim \exp[-(\gamma t)^{3/2}]$ , we finally have

$$\phi^{(e)}(2\tau) \sim \exp[-2(\gamma\tau)^{3/2}]. \quad (8)$$

Defining  $\tau_{1/e}$  by the pulse delay leading to an echo decay to the value  $1/e$ , the decay parameter  $\gamma$  is obtained as

$$\gamma^{-1} = 2^{2/3} \tau_{1/e}. \quad (9)$$

Introducing an *intrachain* diffusion rate  $D_{||}$  and an *interchain* rate  $D_{\perp}$  with  $D_{||} \gg D_{\perp}$ , a characteristic time  $t_0$  can be derived, defining the time region  $\tau < t_0$  with

$$\phi^{(e)}(2\tau) \sim \exp[-2(\gamma\tau)^{3/2}]$$

and  $\tau > t_0$  with the slower "conventional" time decay  $\phi^{(e)}(2\tau) \sim \exp(-2\gamma\tau)$ . The characteristic time  $t_0$  is defined by<sup>10</sup>

$$t_0 = \left(\frac{3}{8}\right)^{2/3} \left[\frac{2\pi\tilde{D}}{c^2}\right]^{1/3} (D_{\perp})^{-4/3}, \quad (10)$$

with the diffusion coefficient  $\tilde{D}$  given by

$$\tilde{D} = \pi^{1/2} D_{||} c^2 \quad (11)$$

and  $c$  denoting the intrachain distance. This leads to

$$t_0^{-1} \approx D_{\perp} \left[\frac{D_{\perp}}{D_{||}}\right]^{1/3}, \quad (12)$$

$t_0$  being completely defined by the intrachain and interchain diffusion rates.

The decay parameter  $\gamma$ , which can be obtained experimentally from an ESE experiment, can be related

to electron-nuclear and electron-electron dipole-dipole interactions using a memory-function approach as shown by Holczer *et al.*<sup>12</sup> Defining the halfwidth at half maximum (HWHM) by  $\Delta\omega$ , the following relations are obtained:

$$\gamma \approx \Delta\omega, \quad (13)$$

$$\Delta\omega = \frac{1}{8} (a^2 + \frac{4}{5} d^2 + nR^2) (\omega_c D_{||})^{-1/2}. \quad (14)$$

Here a cutoff frequency  $\omega_c$  is introduced which limits the divergence of the  $\omega^{-1/2}$  dependence of the spectral-density function as measured, for instance, by nuclear-spin-lattice relaxation rates. Isotropic and anisotropic dipolar electron-nuclear interactions are denoted by  $a$  and  $d$ , respectively, and  $n$  is the spin concentration per site, and the quantity  $\sqrt{n}R/\gamma_e$  can be considered as an effective electronic spin-dipolar field originating from spins on neighboring chains.

In the derivation of Eq. (14) several simplifying assumptions were made, being justifiable for *trans*-polyacetylene. In particular, because of the rather low spin concentration per site, only *interchain* couplings have been taken into account. In addition spacial averages had been performed to account for the polycrystalline nature of the samples. Both assumptions are applicable also for  $(\text{Fa}_2)^+X^-$  (*vide infra*).

With the use of the spacial average expression for  $R$ , one gets

$$R^2 = \frac{9}{10\sqrt{2}} \sum_{\mu} \left[ \frac{2\hbar\gamma_e^2}{\sqrt{3}cb_{\mu}^2} \right]^2, \quad (15)$$

where the summation runs over the neighboring chains,  $c$  is the intersite distance in the chain, and  $b_{\mu}$  denotes the interchain distance.

The product  $(\omega_c D_{||})^{1/2}$  can be evaluated from Eq. (14) by inserting experimental values for  $\Delta\omega$  and  $n$ , and by using average hyperfine (hf) couplings for the aromatic unit. Moreover, a range for  $D_{||}$  can be derived by using  $\omega_c \geq \Delta\omega$  and  $\omega_c \leq \omega_p$ , where  $\omega_p$  is the lowest Larmor frequency for which a  $(\omega)^{-1/2}$  dependence could be detected. This leads to

$$\frac{1}{64} (a^2 + \frac{4}{5} d^2 + nR^2)^2 (\Delta\omega)^{-2} \omega_p^{-1} \leq D_{||} \leq \frac{1}{64} (a^2 + \frac{4}{5} d^2 + nR^2)^2 (\Delta\omega)^{-3}. \quad (16)$$

In the derivation of Eq. (14) it was assumed that electronic spin-lattice relaxation does not contribute significantly to the ESR line shape, or, in our case, to the ESE decay function  $\phi^{(e)}(t)$ . For the system investigated here, this is only approximately true, however, because we found  $\gamma^{-1} \approx 0.5-0.3T_{1e}$ . The order-of-magnitude approximations obtained for  $D_{||}$

by applying Eq. (14), however, are not affected.

In an independent way  $D_{||}$  can be obtained from the analysis of the proton spin-lattice relaxation rate  $T_{1n}^{-1}$  as a function of the nuclear Zeeman frequency  $\omega_n$ . If  $T_{1n}^{-1}$  is shown to follow a  $(\omega_n)^{-1/2}$  dependence, characteristic for one-dimensional electron spin diffusion,  $D_{||}$  can be obtained from the slope of

$T_{1n}^{-1}$  vs  $(\omega_n)^{-1/2}$  by using<sup>14</sup>

$$T_{1n}^{-1} = \frac{k_B T \chi_m}{2\pi N (g\mu_B)^2 (2D_{||})^{1/2}} \times \left[ \frac{3}{5} d^2 (\omega_n)^{-1/2} + \left( a^2 + \frac{7}{5} d^2 \right) (\omega_e)^{-1/2} \right]. \quad (17)$$

Here  $\chi_m$  is the molar Pauli spin susceptibility,  $g$  is the electron  $g$  factor,  $\mu_B$  is the Bohr magneton,  $N$  is Avogadro's number, and  $k_B$  is Boltzmann's constant. Isotropic and anisotropic parts of the dipolar electron-nuclear hf interaction are again denoted by  $a$  and  $d$ , respectively.

#### IV. RESULTS AND DISCUSSION

ESE decay functions were measured over the temperature range of 140–300 K thus covering the highly conducting regime (I) and the semiconductor range (II) below the phase transition at 183 K. An electron-spin echo is displayed in Fig. 1, showing the characteristic relations of FID decay time, spectrometer dead time, and signal-to-noise ratio. Typical decay functions from (I) and (II) are depicted in Figs. 2 and 3. In order to show the characteristic behavior of  $\phi^{(e)}(2\tau)$  in (I), 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  $2\tau \leq 20 \mu\text{s}$ . The absence of experimental artifacts which might

impose a deviation from a simple exponential decay  $\exp(-2\gamma'\tau)$  was verified by lowering the sample temperature below the transition temperature of 183 K and recording ESE decays under identical experimental conditions. The observed echo decay then closely follows an  $\exp(-2\gamma'\tau)$  dependence (see Fig. 3). The metallic-phase decay functions were also least-squares-fitted, leading to exponents  $n=1.5(1)$  when varying the temperature between 183 and 300 K. The decay parameter  $\gamma \approx \Delta\omega$  is conveniently obtained from the  $1/e$  values of  $\phi^{(e)}(t)$ . Figure 4 shows the temperature dependence of  $\gamma$  within the metallic range. In the same temperature range no significant variation of  $t_0$  was detected.

For an estimate of  $D_{||}$  from Eq. (16), values for  $a$ ,  $d$ , and  $\sqrt{n}R$  must be adopted. In a recent experiment<sup>8</sup> Höptner *et al.* determined the spin concentration per fluoranthene molecule as  $n=1.2 \times 10^{-2}$  at  $T=285$  K. Although this value was determined for  $(\text{Fa}_2)^+ \text{PF}_6^-$ , we take the value as representative also for the  $(\text{Fa}_2)^+[(\text{PF}_6)_x(\text{SbF}_6)_{1-x}]^-$  crystals. Using the crystallographic data  $b_\mu=9.7 \text{ \AA}$  and  $c=3.3 \text{ \AA}$ , one obtains  $\sqrt{n}R=2 \times 10^8 \text{ rad/s}$ . This value can be interpreted as an average dipolar field of  $\sqrt{n}R/\gamma_e=11.5 \text{ G}$ .

The isotropic electron-nuclear hf couplings have been determined for the fluoranthene anion radical only. Taking these values as representative for the cation also, a second moment  $\langle a^2 \rangle^{1/2} \approx 1.6 \times 10^8 \text{ rad/s}$  is obtained.

The observed positive Overhauser enhancement of

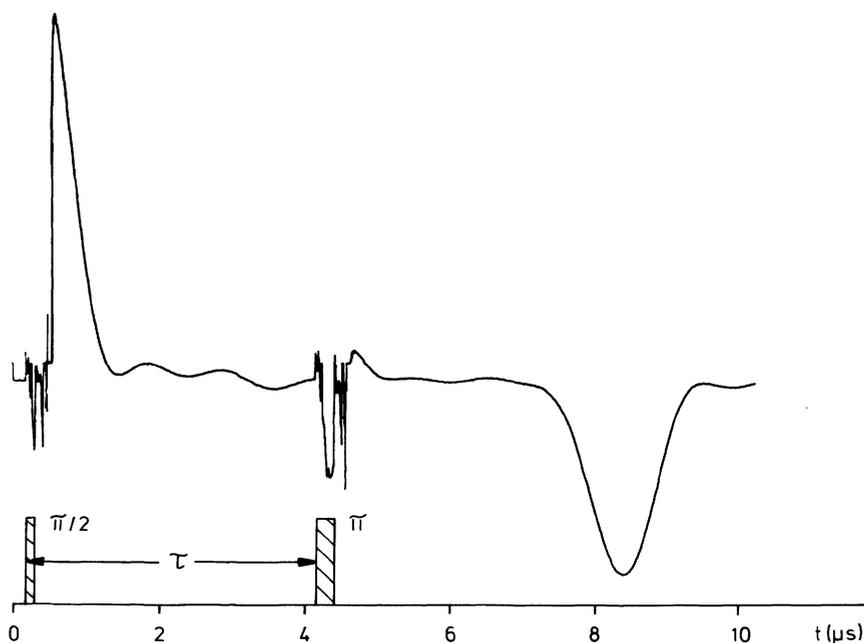


FIG. 1. Accumulated ESE signal (500 shots) of  $[(\text{fluorantheny})_2]^+ X^-$  using  $B_1^{\text{rot}} = 1 \text{ G}$ .

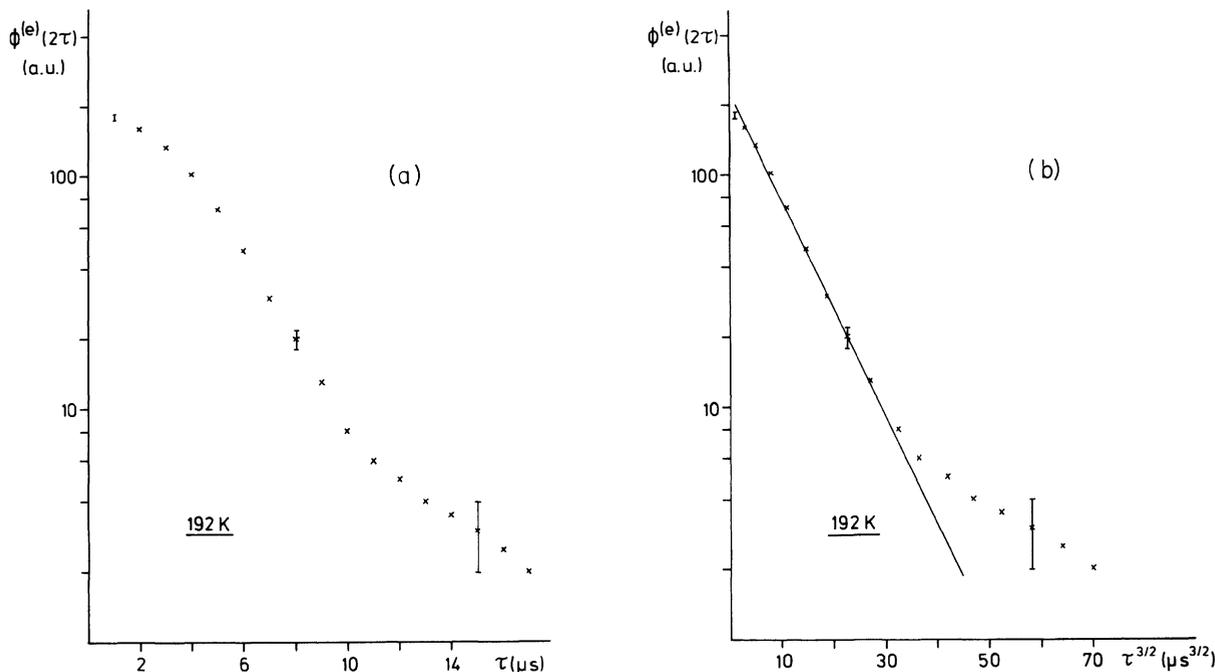


FIG. 2. ESE decay function  $\phi^{(e)}(2\tau)$  plotted vs (a)  $\tau$  and (b)  $\tau^{3/2}$ , respectively. The characteristic time  $t_0$  (see text) is obtained from  $\tau_0^{3/2} = 30 \mu\text{s}^{3/2}$ , at which  $\phi^{(e)}(2\tau)$  changes to a simple exponential.

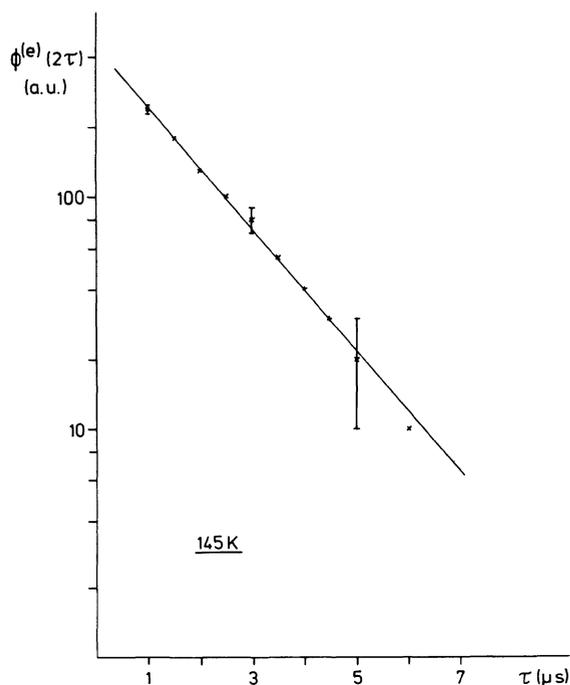


FIG. 3. ESE decay function  $\phi^{(e)}(2\tau)$  measured below the phase transition, exhibiting a purely exponential decay. Same sample and otherwise identical conditions were used as those leading to Fig. 2.

the proton NMR signal by a factor  $V \geq 50$ ,<sup>15</sup> when applying a saturating microwave field at the electronic Larmor frequency, proves the predominance of coupled electron-nuclear transitions via  $I_{\pm}S_{\mp}$  terms as compared to  $(I_{\pm}S_{\pm})$ -type transitions. Because both types of transitions are activated via the same spectral-density function  $\Gamma(\omega_e)$ , modulation of the isotropic hyperfine interaction (hfi) by the mobile electronic spins must be more effective for the coupled relaxation transitions than the modulation of the anisotropic hfi, thus allowing the conclusion  $a^2 > d^2$ . For the evaluation of the nuclear-spin-lattice relaxation rates, however, a predominance of the anisotropic parts of the hfi is expected for the following reasons. In aromatic C–H fragments,  $d$  is not much smaller than  $a$  and a relation of  $d^2 \approx 0.3-0.5a^2$  can safely be assumed. Owing to the diffusive  $\omega^{-1/2}$  dependence of the power spectral-density function, the contribution of the  $d$ -dependent term is selectively enhanced [see Eq. (17)]. Although the exact ratio  $\Gamma(\omega_n)/\Gamma(\omega_e)$  is not known yet, it is probably large enough to allow for the neglect of the  $a$ -dependent terms. [A limiting value  $\Gamma(\omega_n)/\Gamma(\omega_e) = (\gamma_e/\gamma_n)^{1/2}$  would emerge only if  $D_1 \ll \omega_n$ , and also if the presumably frequency-independent contributions of the electrons at the Fermi surface would vanish.]

With the use of  $\gamma = (2)^{-2/3}(4 \mu\text{s})^{-1}$  and  $\omega_p(\text{min}) = 22 \times 2\pi \times 10^6 \text{ rad/s}^{-1}$ , Eq. (16) leads to

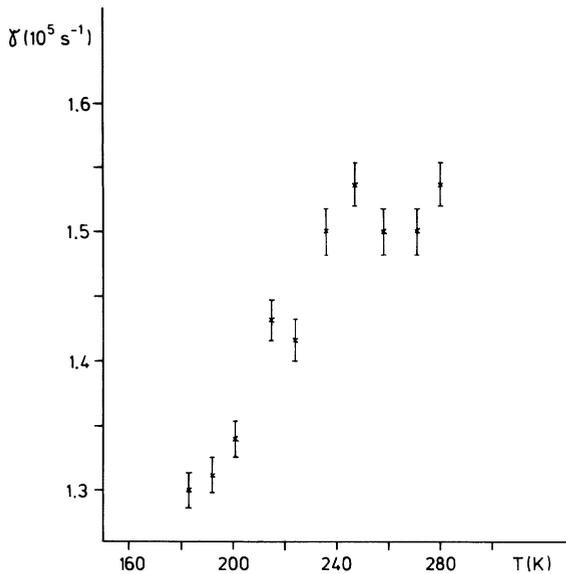


FIG. 4. ESE decay parameter  $\gamma$  as function of the absolute temperature in the "metallic" phase.

$$2 \times 10^{13} \leq D_{\parallel} \leq 2 \times 10^{16}, \quad (18)$$

in units of rad/s. From (18) and (12) an upper limit for  $D_{\perp}$  can be deduced when taking  $t_0 = 20 \mu\text{s}$ ,

$$D_{\perp} \leq 4 \times 10^7, \quad (19)$$

in units of rad/s. The values in (18) are extremely sensitive to the particular choice of  $a/\gamma_e$  and  $\sqrt{n}R/\gamma_e$  because these fluctuating fields enter bi-quadratically. The relation  $a \leq \sqrt{n}R$  is confirmed, however, by the observed temperature dependence of  $\gamma$ . The spin concentration  $n$  is expected to rise linearly with temperature because  $k_B T \ll E_F$ , the Fermi level.<sup>5</sup> If  $\sqrt{n}R \gg a$ , a linear increase of  $\gamma$  with temperature would be predicted from Eq. (14). Although such a linear increase is not observed over the whole temperature range, the positive slope nevertheless indicates  $\sqrt{n}R \geq a$ .

The deduced range for  $D_{\parallel}$  is confirmed by analyzing the proton spin-lattice rates  $T_{1n}^{-1}$  obtained recently for  $(\text{Fa}_2)^+\text{PF}_6^-$ .<sup>8</sup> For the two frequencies  $\omega_n$  used ( $\omega_n/2\pi = 22$  and  $44$  MHz), the rates  $T_{1n}^{-1}$  follow the  $(\omega_n)^{-1/2}$  dependence in the "metallic" range. With the use of the reported Pauli susceptibility  $\chi_m = 1.55 \times 10^{-5} \text{ cm}^3/\text{mole}$  (Fa) (Ref. 8) and the slope  $S$  of the  $(\omega_n)^{-1/2}$  dependence  $S = 3 \times 10^4 / \text{rad}^{1/2} \text{ s}^{-3/2}$ ,  $D_{\parallel} = 2 \times 10^{14} \text{ rad/s}$  is obtained, when using an average anisotropic proton hyperfine coupling (hfc)  $\bar{d}/\gamma_e = 1.5 \text{ G}$ . This value is estimated from the fluoranthene negative-ion values by taking  $d(n) = 0.7a(n)$  and

$$\bar{d} = \frac{1}{N} \sum_{n=1}^N d(n).$$

Such a definition clearly underestimates the relaxation rates for the strongly coupled protons [ $a(3,4)/\gamma_e = 5.2 \text{ G}$ ;  $a(1,6)/\gamma_e = 3.9 \text{ G}$ ]. Owing to the quadratic dependence of  $T_{1n}^{-1}$  on  $d$ , it is possible that proton spin relaxation predominantly occurs via these protons, a common spin temperature being established via nuclear spin diffusion. Assuming no bottleneck by proton spin diffusion at the observed low values of  $T_{1n}^{-1}$ , a more realistic choice of the relevant electron-nuclear coupling  $\bar{d}/\gamma_e \approx 3.5 \text{ G}$  leads to a value  $D_{\parallel} = 7 \times 10^{15} \text{ rad/s}$ , consistent with the upper limit of  $D_{\parallel}$  deduced from the  $\phi^{(e)}(t)$  decay.

In the deduction of  $D_{\parallel}$  from the observed ESE decay parameter  $\gamma$  it was assumed, that  $T_{1e}$  processes do not contribute significantly to the decay function. When using the conventional  $180^\circ\text{-}\tau\text{-}90^\circ$  pulse sequence, we did not observe a simple exponential longitudinal saturation recovery function. We attribute this fact to the nonvanishing inhomogeneous linewidth of our sample ( $\Delta\omega_i \approx 6 \times 10^6 \text{ rad/s}$ ) as compared to the field strength in the rotating frame expressed in rad/s. We therefore performed a spin-lock experiment in order to obtain a lower limit for  $T_{1e}$  by recording  $T_{1\rho}$ , the longitudinal magnetization-decay constant in the rotating frame. In such an experiment the magnetization is first rotated by  $90^\circ$  parallel to the  $y^{(r)}$  axis in the rotating frame, and then locked by a rf phase shift of  $90^\circ$  along the  $B_1$  field for an adjustable time  $\theta$ . The magnetization decay is observed by recording the ESE amplitude, which is obtained by refocusing the remaining magnetization after the end of the spin-lock pulse with another  $180^\circ$  pulse, being delayed by  $\tau'$  with respect to the end of the spin-lock pulse. Experimental artifacts are excluded by recording the ESE of the spin-locked magnetization with and without the first  $90^\circ$  pulse.

The decay functions obtained followed an exponential decay over an intensity range of 30:1 (see Fig. 5). The decay constant at room temperature was  $T_{1\rho}(290 \text{ K}) = 11.5(5) \mu\text{s}$ , increasing to  $20(1) \mu\text{s}$  close to the phase transition temperature, thus giving a lower limit to  $T_{1e}$ . At low temperatures the contributions of longitudinal relaxation to the observed magnetization-decay function  $\phi^{(e)}(t)$  are negligible. The mechanism leading to the comparatively short  $T_{1e}$ , however, is currently not understood. A careful measurement of the temperature dependence of  $T_{1e}$  exhibited a  $T_{1e}T = cT + c'$  dependence in contrast to the simple Korringa-type behavior reported by Sachs *et al.*<sup>7</sup>

If the *spin* diffusion also reflects the *charge* dif-

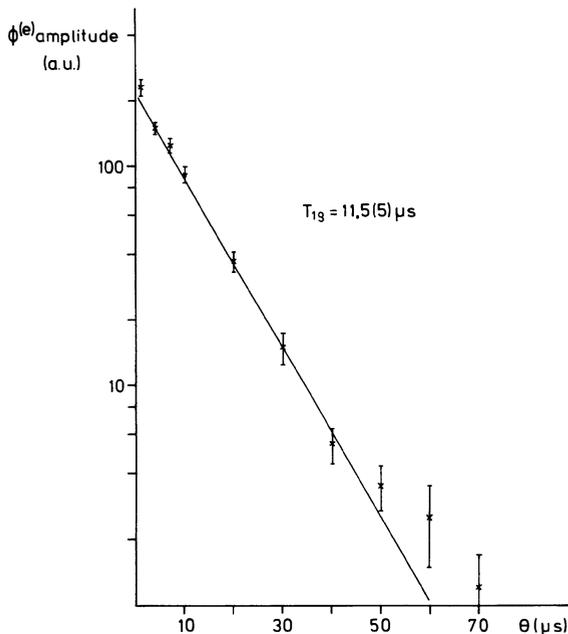


FIG. 5. ESE amplitude  $\phi^{(e)}$  as a function of the spin-locking time  $\theta$  for  $B_1^{\text{rot}} = 1.0$  G. Data were taken at room temperature.

fusion, an estimate of the mean free path  $l$  and the intrinsic one-dimensional conductivity can be obtained. With the use of<sup>14</sup>

$$l = 2\pi\hbar\chi_m N^{-1}(g\mu_B)^{-2}D_{||}c \quad (20)$$

and

$$\sigma_{||} = 2e^2 l / \pi\hbar b_{\mu}^2, \quad (21)$$

values of  $10^{-2}c \leq l \leq 10c$  and  $5 \leq \sigma_{||} \leq 5 \times 10^3 \Omega^{-1} \text{cm}^{-1}$  are obtained when using  $2 \times 10^{13} \leq D_{||} \leq 2.0 \times 10^{16} \text{rad/s}$ . This value has to be compared with the bulk one-dimensional conductivity at room temperature of  $\sigma_b = 10^1 - 10^2 \Omega^{-1} \text{cm}^{-1}$  which gives a lower limit to the intrinsic conductivity  $\sigma_{||}$ . Considering the lack of adjustable parameters, the agreement between  $\sigma_b$  and  $\sigma_{||}$  can be taken as evidence for similar spin- and charge-transport properties in the  $(\text{Fa}_2)^+X^-$  single crystals. Under this assumption the anisotropy of the conductivity can be deduced from  $\sigma_{||}/\sigma_{\perp} = D_{||}c^2/D_{\perp}b_{\mu}^2$  leading to  $6 \times 10^5 \leq \sigma_{||}/\sigma_{\perp} \leq 6 \times 10^7$ . This value is even larger than the highest values reported yet for  $\text{K}_2[\text{Pt}(\text{CN})_4\text{Br}_{0.3}] \cdot 3.2\text{H}_2\text{O}$  (Ref. 19) and  $(\text{CH})_x$ .<sup>14</sup>

## V. CONCLUSION

The interpretation of the echo-decay function  $\phi^{(e)}(t)$  using the model of one-dimensional spin diffusion leads to an *intrachain* diffusion rate in the range of  $2 \times 10^{13} - 2 \times 10^{16} \text{rad/s}$ . When interpreting  $D_{||}$  in terms of a free-electron model, a scattering time  $\tau_s$  of the conducting electrons can be estimated from the relation  $D_{||} = v_F^2 \tau_s c^{-2}$ . Relating the Fermi velocity  $v_F$  to the reduced susceptibility<sup>14</sup> by  $v_F = c(\pi\hbar 2\chi)^{-1}$ , the upper-limit value for  $D_{||}$  leads to  $\tau_s = 6 \times 10^{-15} \text{s}$ , close to the values observed for TTF-TCNQ [ $\tau_s(300 \text{K}) = 3.1 \times 10^{-15} \text{s}$  (Ref. 20)] and for the cation radical salt [(perylene)<sub>2</sub>]<sup>+</sup>X<sup>-</sup> {[C<sub>20</sub>H<sub>12</sub>]<sub>2</sub>]<sup>+</sup>X<sup>-</sup>} [ $\tau_s = 4.4 \times 10^{-15} \text{s}$  (Ref. 5)]. Since the upper-limit value also is in better agreement with the results from the dc-conductivity experiments, we suggest that the actual value of  $D_{||}$  is close to the upper limit given above.

The deduced mean free path of at most a few lattice constants renders the motion of the  $q \approx 0$  components diffusive along the chain, consistent with the basic assumption of our interpretation, that the  $q=0$  excitations of the charge-density wave dominate the  $q=2k_F$  excitations in their relaxation effects. Although probably the motion of electrons at the Fermi surface gives rise to a frequency-independent spectral-density function  $\Gamma_{2k_F}(\omega)$ , the relative magnitude of  $\Gamma_{2k_F}(\omega)$  and  $\Gamma_0(\omega)$  is strongly model dependent and yet unknown for  $(\text{Fa}_2)^+X^-$ .<sup>20</sup>

The ratio  $5 \times 10^6 \leq D_{||}/D_{\perp} \leq 5 \times 10^8$  for the *intra-* and *interstack* diffusion rates which emerges from the characteristic time  $t_0 \approx 20 \mu\text{s}$  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.

The estimated diffusion anisotropy is even larger than the value reported for *trans*-polyacetylene [*trans*-CH]<sub>x</sub>.<sup>14</sup> This increase of "one dimensionality," however, is not surprising when considering the crystal structure of both samples. Owing to the large distances between the aromatic stacks, the transverse  $\pi$  overlap integral  $t_t$  is significantly decreased, whereas the parallel stack value  $t_p$  is presumably only lower by a factor of 8, as deduced from the conduction-band width [ $W(\text{trans-polyacetylene}) = 8 - 10 \text{eV}$  (Ref. 21);  $W((\text{Fa}_2)^+X^-) \geq 1.2 \text{eV}$  (Ref. 22)]. Final confirmation of the deduced small value  $D_{\perp} \leq 4 \times 10^7 \text{rad/s}$  is expected from nuclear-spin-lattice relaxation experiments at low frequencies, which are currently under progress.

*Note added in proof.* According to W. H. Redstetter *et al.* [J. Org. Chem. **47**, 4873 (1982)], fluoranthene is a highly potent mutagen for human lymphoblasts, comparable in its potency to benzo( $\alpha$ )pyrene.

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