Restricted Diffusion of the Conduction Electrons in Quasi-One-Dimensional Organic Conductors

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The spin-echo height in the electron spin resonance (ESR) of conduction electrons in the 1D organic metal $(FA)_2PF_6$, observed in static magnetic field gradients, exhibits a conspicuous curvature to a flatter slope after a faster decay for initial values of the pulse separation time. This curvature is explained by a model which takes into account restrictions to the free diffusional motion of electrons in the conducting channels of the system.

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The diffusional motion of charge carriers in the so-called 1D organic metals [1] is of paramount importance both theoretically and for practical purposes. Among the methods employed so far to study this diffusion in 1D conductors, perhaps the most direct one involves monitoring the influence of oriented static magnetic field gradient G on the ESR spin-echo decay [2,3] in such systems. Indeed, the microscopic diffusion constant $D_{\|}$ along the conducting channels as well as the anisotropic nature of the diffusion have been previously determined in several 1D conductors [4] by measuring the initial ESR spin-echo decay at time 2τ, as a function of the pulse separation time τ. Note, however, that Torrey's decay model [3] is valid only for free diffusional motion along G, whereas for any real 1D metal [5] the conducting channels are restricted to some final chain-length distribution dictated by the existence of impurities and other imperfections in the actual sample. Thus, the requirement of a relevant free diffusion component was met in the 1D conductors investigated so far only for initial τ values such that the precessing spins had no time to encounter a restriction along the channel, and the resulting diffusion parameters derived are valid only on a truly microscopic scale.

Presently we study the "quasimicroscopic" restrictions hindering the free diffusional motion along the conducting channels in real 1D organic metals. We demonstrate even larger deviation from Torrey's decay model by extending the experimental ranges of τ and G. A model calculation, based on analytical treatment [6] of diffusing spins in restricted geometries in static gradient, is used to derive from the measurements a unique channel-length distribution in $(\mathrm{fluoranthene})_2PF_6$. To our knowledge, this is the first reported observation of bounded-range electron diffusion detected by ESR echo attenuation, and the first direct determination of channel-length distribution in a 1D organic conductor.

Both static field gradient and pulsed gradient (PGSE) methods—see, for example, Refs. [7] and [8], respectively—have been used previously to study restricted diffusion of nuclei. However, the much shorter decay time associated with electron echoes, dictating gradient pulses in the μs range, ruled out PGSE with our experimental setup, and led us to select the static gradient approach.

A well-characterized single crystal sample [5] of the 1D organic conductor $(\mathrm{fluoranthene})_2PF_6$ was selected as a test case for the study. The size of the crystal was 3 mm × 1 mm × 0.8 mm. The stack axis of the fluoranthene molecules and therefore the direction of the conductivity and diffusion were oriented parallel to the long axis of the crystal. The sample was mounted in the probe head of a commercial electromagnet-based pulsed ESR spectrometer (Bruker ESP 300 E) operated at 9.5 GHz. The field gradient, directed along the conducting channels in the sample, was produced by two additional soft iron wedges located on the pole caps. Gradient intensity was varied by using wedge sets of different angles, and each gradient value was determined by a 1D ESR projection "imaging" of the sample along a known sample dimension. To avoid errors caused by insufficient excitation bandwidth, the imaging measurements were performed using a field sweep technique. Gradient values of $0.34\frac{T}{m}$, $0.57\frac{T}{m}$, $0.79\frac{T}{m}$, and $2.17\frac{T}{m}$ were thus determined.

The good conductivity of the organic metal causes a non-negligible skin effect, which leads to a preferential detection of the conduction electron spins in the sample surface region.

A sequence of two identical pulses was used for the measurements, which were performed at room temperature. The pulse separation time τ was varied between 320 ns and 8 μs. A phase cycling sequence was employed to prevent systematic errors caused by base line drifts, particularly for large τ values. The normalized echo heights, observed for each of the four gradient values, are shown as points in Fig. 1.

For unrestricted diffusion, the echo decay was analyzed already by Torrey [3]

$$E_u \sim \exp\left(-\frac{2\tau}{T_2} - \frac{2}{3}D\gamma^2G^2\tau^3\right), \qquad (1)$$

where T_2 is the transverse electron spin relaxation time and D is the microscopic diffusion constant of the spins.

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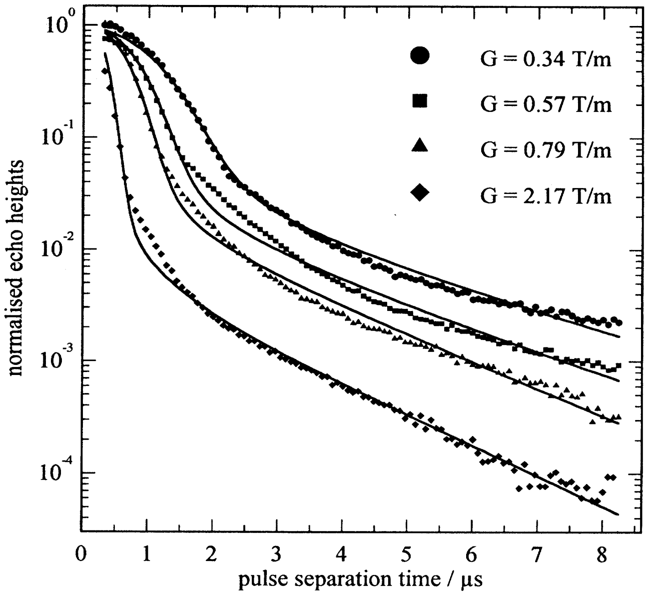

FIG. 1. ESR spin-echo height as a function of pulse separation at four gradient intensities. The solid lines represent a simultaneous fit for all four gradients. See text for details.

To treat restricted diffusion, we adopt a model [6] based on the method of phase accumulation of diffusing spins in field gradients. For the particular geometry of spins bounded between parallel planes separated by distance l and subjected to gradient G, the echo height E_r was derived analytically by Neuman [6] with the closed form solution

$$E_r \sim \exp\left[-\frac{2\tau}{T_2} - \frac{8\gamma^2 G^2 l^4}{D\pi^6} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^6} \times \left(2\tau - \frac{3 - 4e^{-Q\tau} + e^{-2Q\tau}}{Q}\right)\right], \quad (2)$$

with

$$Q = D\frac{(2n+1)^2\pi^2}{l^2}.$$

For larger τ values, Eq. (2) can be approximated by

$$E_r' \sim \exp\left[-\frac{2\tau}{T_2} - -\frac{\gamma^2 G^2 l^4}{120D}\left(2\tau - \frac{17l^2}{56D}\right)\right]. \quad (3)$$

Equations (2) and (3) have been derived assuming G is strictly perpendicular to the boundary planes, to prevent the free diffusional motion parallel to the planes from affecting E_r and E_r'. Turning to spins restricted to move along linear diffusion channels of length l, note that the transition from planar bounds allows us to relax some of the limitations on G. For the linear channel case, it is easily verified that the above derivation remains functionally valid for any direction of G, provided we use in Eq. (2) or (3) only the component of G along l. Finally, note also that in the large τ limit, E_r' decays once again exponentially, with a time constant $-(2/T_2) - 2\gamma^2 G^2 l^4/120D$ which in our experimental situation depends only slightly on G and l. This description agrees quite well with the experimental results. In a real (fluoranthene)$_2$PF$_6$ crystal there is a distribution of chain lengths rather than a single length. To compare the experimental data with the theory it is necessary to know the particular distribution. To derive such a distribution, we have simulated an ideal crystal in a Monte Carlo calculation, putting a large number of defects at random places along the chains. The resulting functional density distribution $P(l)$ was found to be exponential, $P(l) = e^{-l/\bar{l}}$. The normalized distribution, depending on the single parameter $\bar{l}$, is shown graphically in Fig. 2.

The contribution to the echo intensity from channels of length l is proportional to the "weight" function $lP(l)$, also shown in Fig. 2. To calculate the echo heights as a function of the pulse separation time, Eq. (2) was thus convoluted with the weight function and "best fitted" with the experimental data. Attempting first a fit with $\bar{l}$, D, and T_2 as the only free parameters, agreement with the data was only fair. It was concluded that the assumption of unique transverse relaxation time for all the spins is neither sufficient nor justified. The possibility of additional relaxation mechanisms caused by interactions with defects at the end of the chains would result in a faster effective relaxation rate for spins in very short

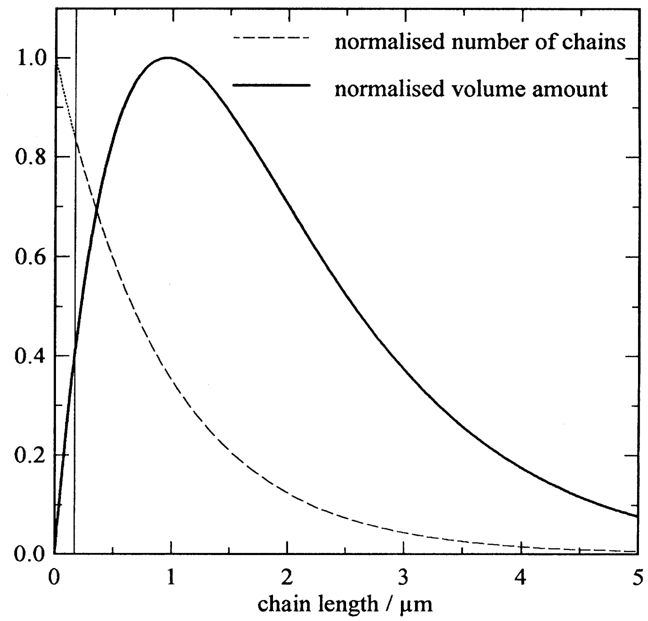

FIG. 2. The exponential chain length distribution, calculated with a Monte Carlo method (the dashed line) together with the volume amount (the thick line). The part on the left side of the "cut off" vertical line is substituted by nondiffusing spins (1.25% of the whole amount).

chains, compared with the "intrinsic" relaxation rate in long ones. To approximate this effect, the distribution $P(l)$ was cut off at some short chain length, and spins below the cutoff were assumed nondiffusing, with a unique shorter T_2 compared with the intrinsic value. A control calculation verified that the influence of diffusion in the short chains below the cutoff is sufficiently small to justify the substitution described above.

The solid curves in Fig. 1 represent the fitted result, obtained for $\bar{l} = 95.8\ \mu\text{m}$, $D = 1.8 \times 10^{-4}(\text{m}^2/\text{s})$, intrinsic value of $T_2 = 6.76\ \mu\text{s}$, cutoff length of $l = 17.0\ \mu\text{m}$, and a relaxation time of $3.0\ \mu\text{s}$ assigned to the small fraction of nondiffusing spins residing in chains below cutoff.

Apart from minor deviations for intermediate values of τ, the fit is in good agreement with the experimental data. The deviation is probably reflecting the existence of a distribution of relaxation rates in the real system, rather than just two distinct transverse relaxation times as assumed above. This distribution will depend on the average time a spin spends in the vicinity of a defect, and thus on the chain length in which the particular spin is located. The cutoff length quoted above implies a contribution of only 1.25% of nondiffusing spins to the initial spin echo. The fitted D value agrees well with that obtained by analyzing data points at short τ using the free diffusion model [Eq. (1)] in accord with the introductory discussion, and is also in conformity with former measurements [4]. The intrinsic transverse relaxation time fitted above is in very good agreement with the T_2 value obtained for the present sample in the absence of field gradient.

The nature of the assumed restriction is not revealed explicitly by the elementary model utilized above, but further insight into the physical processes involved can be obtained by considering previous experimental results. First, it can be concluded that nearly all of the charge carriers are reflected at the effective "restriction" without changing the spin state, i.e., only very little—if any—spin relaxation is caused by the chain edges. This is evidenced by the single-exponential relaxation observed in the absence of field gradient during the diffusion time [9] and by noting that the observed ESR susceptibility is essentially the same as the bulk dc susceptibility [10]. This conclusion is in accord with the present finding (Fig. 2) that only 1.25% of the spins are relaxing at higher than the intrinsic rate. A second, and somewhat subtler, refinement on the elementary model is related to the possible existence of some interchain carrier motion, manifested by perpendicular diffusion [4,5]. The perpendicular diffusion reported implies many interchain transitions during the observed intrinsic relaxation time T_2, leading to the conclusion that interchain motion occurs without loss of spin coherence, i.e., without additional damping of the echo decay. Thus, restrictions on individual conducting channels may be bypassed by the interchain motion of the spins, and for a restriction to be effective as a reflecting barrier in the present context, it must subtend a perpendicular dimension of the order of the perpendicular diffusion range during the observation time. Only an upper limit was reported for the perpendicular diffusion, which translates into an upper limit perpendicular motion of $1\ \mu\text{m}$ during the diffusion time window of $20\ \mu\text{s}$ used in the present experiment. Thus, we may conclude that the restricting objects inferred from our model calculation (with an average distance of $95\ \mu\text{m}$ along the chains) could be of any dimension between a single unit cell and up to $1\ \mu\text{m}$, depending on the real perpendicular diffusion constant. In the latter case, the restrictions could originate from grain boundaries of mosaiclike crystal structure and the model derived $D_{\parallel}$ is an effective diffusion constant representing a "composite" diffusion process in which carriers are bypassing single channel restrictions and are eventually reflected by the larger—and fewer—restrictions mentioned above.

The fitted mean chain length $\bar{l}$ of $95.8\ \mu\text{m}$ corresponds to an effective chain-end concentration of 3.5×10^{-6} per fluoranthene molecule. This concentration is 30 times smaller than the value quoted by Schimmel [11] for intrachain defects, obtained by comparing the conductivities in the optical and dc frequency range. One may only speculate that the smaller concentration deduced in the present study indicates indeed motion restricting entities that subtend many unit cells in the perpendicular direction.

In conclusion, we have used pulsed ESR techniques in combination with magnetic field gradient to study quasimicroscopic geometrical restrictions that influence the motion of electron spins in some solids. The current study involved a case representing just one particular group, the so-called 1D organic metals. However, on the basis of the present results it appears that similar techniques, perhaps using also the PGSE approach [8], may prove useful in the study of various mesoscopic semiconductor systems.

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