Study of the diffusion of localized spin states with $S = 1/2$ and crystalline polyacetylene

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(Submitted 3 December 1989; resubmitted 4 April 1990)
Zh. Eksp. Teor. Fiz. **98**, 567–570 (August 1990)

To refine the nature of localized spin states, the shape of esr lines in crystalline polyacetylene has been studied. The quasi-1-D character of spin diffusion along the chain has been established for the orthorhombic modification. The rate of spin diffusion $D_{\parallel}$ has been determined to be in the range of values 3×10^8 rad/sec $< D_{\parallel} < 10^{10}$ rad/sec. The absence of 1-D motion of spins in amorphous polyacetylene and in polyacetylene synthesized by Shirakawa's method is due to the presence of a large number of structural defects.

An effective method of detecting solitons in polyacetylene is to study the nature of the motion of the spins along and across the chains. This is because the electron spin resonance (esr) line shape is substantially determined by the dimensionality of the system, by the spin–spin interactions, and by the degeneracy of the hyperfine structure. Thus, the degree of electron delocalization electron is characterized by the line width, and the dimensionality of the system is characterized by the arms of the line profile.

In general, the shape of the esr absorption curve can be used to determined the dynamics of the spin system of the substance studied. At first the absorption line was predicted to have a Gaussian shape for freely moving solitons.[1] However, owing to the randomization of the soliton motion due to the interaction with the random fields of protons, the shape of the central peak of the dynamic magnetic susceptibility $\chi''(\mathbf{q},\omega)$ is fairly complex. We put forward some estimates that make it possible to reproduce the laws of motion of solitons with spin $S = 1/2$ from the line shapes of the central peak. These estimates are based on a relationship defined by the high-temperature correlation function $G(t)$ of the magnetization $M_x(t)$. From the fluctuation–dissipation theorem, this relationship is given by the expression

$$G(t) = \frac{k_B T V}{\pi} \int_{-\infty}^{+\infty} \frac{\chi''(\omega)}{\omega}{}^{s} e^{-i\omega t}\, d\omega,$$

where s is an index corresponding to the symmetric part of the dynamic magnetic susceptibility matrix, V is the volume of the substance, and k_B is Boltzmann's constant. Since the correlation function can be represented in the form (see Ref. 2)

$$G(t) = \langle M_x(t) M_x(0) \rangle \to \frac{\mathrm{Tr}\{M_x(t) M_x(0)\}}{\mathrm{Tr}\{I\}}$$

$$\sim \exp\left[i\omega_0 t - \int_0^t (t-\tau) \langle \omega(0)\, \omega(\tau) \rangle d\tau \right],$$

the shape of the line is ultimately specified by the local-field correlation function

$$\Psi(\tau) = \langle \omega(0)\, \omega(\tau) \rangle,$$

which obeys the 1-D diffusion equation, i.e., $\Psi(\tau) \propto \tau^{-1/2}$. From this we obtain the following estimate of the correlation function:

$$G(t) \propto \exp(i\omega_0 t) \exp(-\gamma t^{3/2}).$$

Since the central absorption peak is proportional to $\chi''(\omega)/\omega$, then, introducing the variable $\Omega = \omega_0 - \omega$, after the Fourier transformation $G(t) \to G(\Omega)$, we have

$$\chi''(\Omega)/\omega_0 \propto \Omega^{-5/2},$$

or, for the derivative of the absorption function, $Y(\Omega) \propto \Omega^{-7/2}$. In an actual experimental situation, in the case of 1-D motion, the function $\Omega^3 Y(\Omega)$ should be linearly dependent on $\Omega^{-1/2}$.

In accordance with this result, an analysis of the shape of the esr resonance lines of crystals of various modifications was carried out. The studies involved the use of a standard method employing an RE 1306 spectrometer with wavelength $\lambda = 3.0$ cm. The polyacetylene was synthesized by the method described in Ref. 5.

Figure 1 shows curves of $H^3 Y$ as a function of $H^{-1/2}$ for polyacetylene synthesized by Shirakawa's method (SPA) (Fig. 1), and crystalline polyacetylene (CPA), which is the subject of the present study (Fig. 1). Note that in contrast to SPA (Fig. 1), for one of the CPA modifications (orthorhombic)[5,6] 1-D diffusion is observed, a plot of whose dependence on $H^{-1/2}$ is characterized by the presence of a

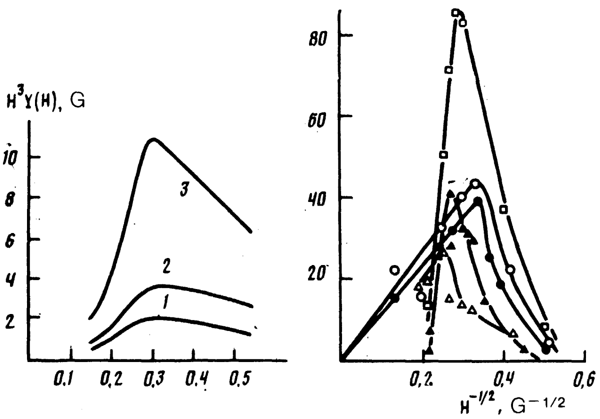

FIG. 1. $H^3Y(H)$ vs $H^{-1/2}$. (a) for polyacetylene samples synthesized by Shirakawa's method, having different line widths: $\Delta H_{pp} = 0.44$ (1), 0.85 (2), 2.5 (3) G. (b) for samples of initial CPA: 1(□), 2(○), 3(●)—partially crystalline, 4(▲)—crystalline, 5(△)—slightly doped.

0038-5646/90/080315-03$03.00

straight segment passing through the origin (Fig. 1, curves 2 and 3).

Next, by analogy with the analysis of esr absorption line width made for SPA in Ref. 3, where the diffusion rate $D_\parallel$ was estimated, we estimate this rate for CPA. We present the main calculations and results for SPA. We know that the line width is determined by the following relation:

$$\Delta\omega={}^1/_8(a^2+{}^4/_5d^2+nR^2)\,(D_\parallel\omega_c)^{-1/2}, \tag{1}$$

where a and d are, respectively, the constants of the isotropic and anisotropic hyperfine interactions, n is the spin concentration

$$R^2=({}^9/_{10}\sqrt{2})\sum_\mu R_\mu^2$$

(R_μ will be defined below), and ω_c is the threshold frequency. For $\omega_c\sim\Delta\omega$, Eq. (1) becomes self-consistent in $\Delta\omega$

$$\Delta\omega={}^1/_4(a^2+{}^4/_5d^2+nR^2)^{2/3}D_\parallel^{-1/3} \tag{2}$$

In accordance with Refs. 3 and 7, we choose $|a/\gamma_e| = 23.4$ G, $d=0.25a^2$, $n=1/1400$, $\Delta\omega=\gamma_e\Delta H=0.35$ G. To determine $D_\parallel$ from Eq. (2), all one has to do is calculate the value of R, which is determined in terms of the coefficient of dipole interactions between spins of adjacent chains by spatial averaging:

$$R_\mu^2=5\left\langle\left|\sum_{\lambda'}^{\mu}R_{\lambda\lambda'}^M(h)\right|^2\right\rangle,$$

where h is the direction of the magnetic field, and $R_{\lambda\lambda'}^M$ is given by

$$R_{\lambda\lambda'}^M(h)=(4\pi/5)^{1/2}R_{\lambda\lambda'}Y_2^M(h).$$

Here $R_{\lambda\lambda'}=\hbar\gamma_e/r^3_{\lambda\lambda'}$, $r_{\lambda\lambda'}$ is the distance between the nodes of λ and λ', and $Y_2^M(h)$ is a spherical harmonic function. (Our line of reasoning is illustrated in Fig. 2.) Then

$$R_\mu^2=\sum_{\lambda'\lambda''}^{\mu}R_{\lambda\lambda'}R_{\lambda\lambda''}P_2[\cos(\lambda\lambda',\lambda\lambda'')], \tag{3}$$

where $P_2(x)=(1/2)(3x^2-1)$. It also follows from Fig. 2 that $(\lambda\lambda',\lambda\lambda'')=\theta_{\lambda''}-\theta_{\lambda'}$, $\cos\theta_{\lambda'}=b_\mu/r_{\lambda\lambda'}$, $\sin\theta_{\lambda'}=c\lambda'/r_{\lambda\lambda'}$ and Eq. (3) can be written in the form

$$R_\mu^2={}^1/_2\hbar^2\gamma_e^4(3S_1^2+3S_2^2-3S_3^2),$$

where

$$S_1=\sum_{\lambda'}b_\mu^2/r_{\lambda\lambda'}^5,\quad S_2=\sum_{\lambda'}(\lambda'c)^2/r_{\lambda\lambda'},\quad S_3=\sum 1/r_{\lambda\lambda'}^3.$$

Evaluation of these sums yields

$$R_\mu=2\hbar\gamma_e^2/(3^{1/2}b_\mu^2c).$$

Now, assuming that a given chain is surrounded by six equivalent small chains with $b_\mu=4.4$ Å and $c=1.2$ Å, we obtain an estimate of the SPA diffusion rate

$$10^{12}(\Delta H)^{-2}<D_\parallel<3\cdot10^{12}(\Delta H)^{-3},$$
$$8\cdot10^{12}\ \text{rad/sec}<D_\parallel<8\cdot10^{13}\ \text{rad/sec},$$

which is in good agreement with the NMR results of Ref. 3, $D_\parallel=6\times10^{13}$ rad/sec.

Similar calculations carried out for the orthorhombic modification of CPA [$c=4.0$ Å, $b_\mu=7.9$ Å, $\Delta H\simeq7$G. (Refs. 5 and 6)] give for the spin densities $\sim10^{16}$–10^{18} cm^{-3}, which are values characteristic of their CPA modification, and a diffusion rate range 3×10^8 rad/sec $<D_\parallel<10^{10}$ rad/sec. Below 3×10^8 rad/sec, quasi-1-D motion can no longer be distinguished, since th line width is determined by diffuse hyperfine structure from the protons at the nodes. In this case, the lines assume a Gaussian shape, which is typical of CPA with an ideal spatial packing of the chains and the crystalline potential makes a real contribution to the diffusion rate. A shift of the chains along the c axis results in attenuation of the crystal field and an increase of the diffusion rate, and is directly reflected in the shape of the esr lines, while the nature of the motion becomes clearly one-dimensional.

Still unclear is the question of the relationship between the long spin-lattice relaxation times T_1 and the diffusion mechanism for the motion of solitons of spin 1/2. Actually, at the lowest diffusion rates $\sim3\times10^8$ rad/sec, the time of travel of a soliton along a chain is $\sim10^{-7}$–10^{-6} sec. The spin should then either scatter on the ends of the chain and cross over to an adjacent chain, or become fixed to the end of the chain, or reflect from the end of the chain and oscillate with a characteristic time $\sim10^{-6}$–10^{-5} sec. The spin should then either scatter on the ends of the chain and cross over to an adjacent chain, or become fixed to the end of the chain, or reflect from the end of the chain and oscillate with a characteristic time $\sim10^{-6}$–10^{-5} sec. Apparently, only the later situation permits an explanation of the observation of long times T_1 in CPA. In general, this situation is entirely realistic in the presence of CH_3 and CH_2 end groups.[6] Since in a neutral chain the solitons are usually produced in pairs, it follows that in all probability, breathers are formed here. In the second situation, one of the solitons may become fixed to the end of the chain, and a second soliton executes oscillations along the chain.

Thus in crystalline or partially crystalline polyacetylene with strong "insulated" chains, for example, in crystals of orthorhombic symmetry, the soliton motion is essentially unidimensional. The appearance of defects due to the irregularity of the structure of the individual molecules or their 3-D packing leads to localization of the spins and to the possibility of their crossover to neighboring chains.

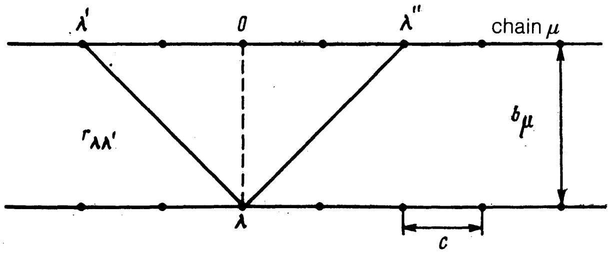

FIG. 2. Schematic representation of polyacetylene chains with the notation used in the calculation of R.

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Translated by Adam Peiperl