One-Dimensional Spin Diffusion in Polyacetylene, $(CH)_x$

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(Received 30 August 1979)

We report NMR experiments which imply that highly one-dimensional spin diffusion occurs in undoped *trans*-$(CH)_x$ and *trans*-$(CH(AsF_5)_{0.1})_x$. The corresponding anisotropy in the diffusion coefficient would be about 10^6.

Polyacetylene, $(CH)_x$, has recently been the subject of much experimental study.[1] The pristine (undoped) polymer is a direct-gap semiconductor of fundamental interest. Moreover, the polymer can be doped with donors or acceptors to give remarkable electrical properties.[2-5] Theoretical calculations[5] and experiments on partially oriented films[1] suggest an anisotropic band structure. However, the degree of one-dimensionality (1D) is not yet known. ESR[6] and magnetic susceptibility[7] experiments on the nondoped and lightly doped polymer have suggested that an unusual defect-spin mobility and doping mechanism exists in $(CH)_x$. Very recently a theory of domain-wall (soliton) formation in long-chain polyenes such as $(CH)_x$ has been proposed to explain these magnetic properties.[8]

In this paper, we present the first measurements of the hydrogen nuclear relaxation (T_1) and the dynamic nuclear polarization (DNP) of $(CH)_x$. Our DNP experiments prove that a mobile spin species exists in undoped *trans*-$(CH)_x$, while our measurements of T_1 as a function of static magnetic field suggest that extreme 1D spin diffusion exists in both undoped and heavily doped $(CH)_x$. These measurements are the first ones to give a quantitative estimate of the one-dimensionality in doped and undoped $(CH)_x$. Other experiments have been hampered by the random orientation of the fibrils in all $(CH)_x$ samples prepared to date. We find that the spin diffusion rate has a room-temperature value of $D \simeq 6\times10^{13}$ rad/sec.

The $(CH)_x$ samples were unoriented polycrystalline films prepared using techniques similar to those developed by Ito, Shirakawa, and Ikeda.[9] The films were never exposed to air and were converted to the all-*trans* isomer by heating at 140 °C for 1 h. We measured a room-temperature ESR linewidth of 1.2 G in agreement with previous results on undoped *trans*-$(CH)_x$. The proton nuclear relaxation time, T_1, was measured using a conventional $\pi, \pi/2$ pulse method over the frequency range 10–340 MHz. The recovery of the nuclear magnetization was quite exponential over a decade. The DNP measurements were performed in a fixed magnetic field of 2.92 kOe. The amplitude of the proton NMR signal was measured using a pulse technique as the microwave pumping frequency ω_p was changed point by point.

We first discuss the DNP results. This experiment consists of observing the NMR (at the nuclear Larmor frequency ω_N) while pumping with microwave power near the ESR Larmor frequency $\omega_e/2\pi = 8190$ MHz. Two limiting results may occur according to whether the electron nuclear coupling is static or dynamic.[10] In the static case, the electronic spin is fixed (at least its hopping frequency is less than ω_N) and forbidden transitions at $\omega_e \pm \omega_N$ can be induced. This is the so-called "solid-state effect" (SSE). On the other hand, if the electronic spin is moving such that a frequency component of motion exists at ω_e it is possible to enhance the NMR signal by pumping at the ESR frequency ω_e. This is the Overhauser effect (OE). In Fig. 1 we show the enhancement of the NMR signal obtained by pumping near ω_e for undoped $(CH)_x$ samples with different degrees of *cis-trans* content (as determined from ESR linewidth). In mixed samples, both OE and SSE

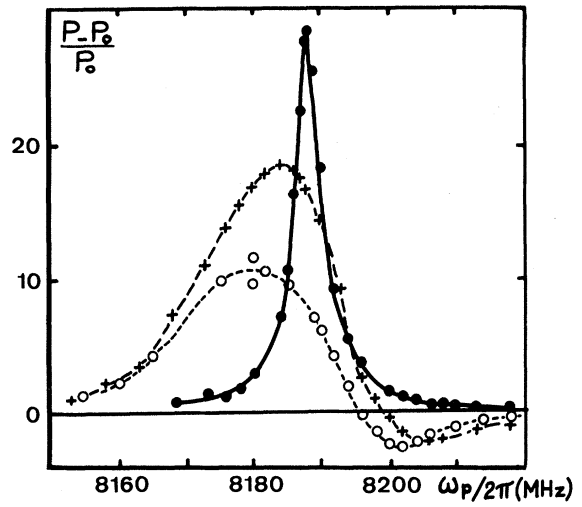

FIG. 1. Enhancement of proton NMR amplitude (P) as function of ω_p near $\omega_e/2\pi = 8190$ MHz for 50% (open circles), 65% (plusses), and 100% (closed circles) *trans*-content undoped $(CH)_x$. P_0 is the NMR signal amplitude without microwave pumping.

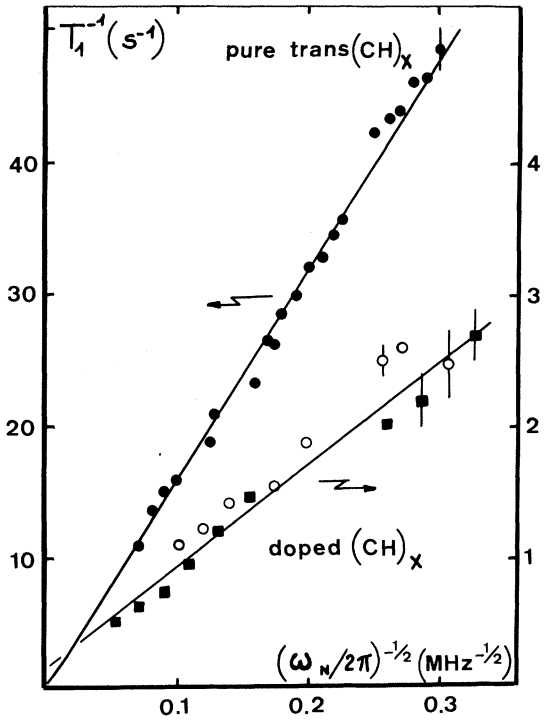

FIG. 2. Nuclear relaxation rate T_1^{-1} vs $(\omega_N/2\pi)^{-1/2}$ for undoped *trans*-$(CH)_x$ (left scale) and $(CH(AsF_5)_{0.1})_x$ (right scale). Closed squares and open circles refer to two different doped $(CH)_x$ samples. Solid lines correspond to Eqs. (1) and (2) as explained in the text.

are observed. The proportion of OE to SSE increases with the amount of *trans*-$(CH)_x$. In the all-*trans*-$(CH)_x$ a pure OE is seen which means that the electronic spins are moving with at least a frequency $\omega_e \simeq 5\times10^{10}$ rad/sec. This strongly supports the less definitive ESR evidence[6] for a mobile spin-$\frac{1}{2}$ defect and, moreover, gives a lower-limit estimate for the rate of motion. Our observation of a mixture of OE and SSE suggests that during the isomerization some localized spins are formed which eventually become mobile.

For our proton T_1 measurements, we expect the nuclear relaxation rate to be governed by the electronic spins. In that case,[11]

$$T_1^{-1} = k_B T\chi[\tfrac{3}{5}d^2 f(\omega_N) + (a^2 + \tfrac{7}{5}d^2) f(\omega_e)], \quad (1)$$

where χ is the normalized spin susceptibility $[\chi = \chi_{\text{molar}}/N(g\mu_B)^2]$, and a and d are the isotropic and dipolar electron-proton hyperfine couplings, respectively. The spectral density function, $f(\omega)$, reflects the electronic spin motion and depends sensitively on the dimensionality of the process. For 1D diffusion,

$$f(\omega) = (1/2D_{\parallel}\omega)^{1/2}, \quad (2)$$

where $D_{\parallel}$ is the intrachain diffusion rate. At low frequency, the 1D diffusion breaks down because of interchain hopping and 2D or 3D behavior is expected. In two dimensions, $f(\omega)$ displays a logarithmic divergence, while in three dimensions, it is nearly constant. The crossover between 1D and 2D or 3D regimes occurs at $\omega \simeq D_{\perp}$, $D_{\perp}$ being the interchain diffusion rate.

In Fig. 2, we show our most important results. It can be seen that for both undoped and heavily doped *trans*-$(CH)_x$, T_1^{-1} vs $\omega^{-1/2}$ is a straight line over our entire measurement range. *A priori*, different origins can be considered for explaining that frequency dependence. Such a behavior has been observed in solids with dilute *fixed* paramagnetic impurities.[10] Since in the present case the spins are mobile, at least at the rate of 5×10^{10} rad/sec, this possibility can be ruled out. More recently, a similar behavior has been suggested in spin-glasses at the freezing temperature.[12] However, it is clear from the susceptibility that $(CH)_x$ is in the paramagnetic regime at room temperature. Finally the $\omega^{-1/2}$ law can be attributed to a 1D spin diffusion. We favor this hypothesis which has explained successfully the T_1 experiments in the 1D tetracyanoquinodimethane (TCNQ) salts.[11,13,14] We cannot, however, rule out any process which causes a frequency-dependent D.

We first discuss the results for the undoped *trans*-$(CH)_x$. In that case, the data in Fig. 2 can be fitted with $T_1^{-1} = S(\omega_N/2\pi)^{-1/2}$. This implies that both $f(\omega_N)$ and $f(\omega_e)$ in Eq. (1) follow the 1D diffusive law [Eq. (2)]. From the slope S, an estimate can be obtained for $D_\parallel$. For the electron-proton scalar coupling a, we have used the value for a free spin in a carbon $2p_z$ orbital: $|a_{CH}/\gamma_e| = 23.4$ G.[15] The value of the dipolar coupling has been determined from the extrapolated Overhauser enhancement at infinite pumping power, namely 90 ± 20. We have found $d^2/a^2 \simeq \frac{1}{4} - \frac{1}{3}$, in excellent agreement with the d^2/a^2 ratio found for a $2p_z$ spin in the TCNQ salts.[16] We then find for the spin-diffusion rate $D \simeq 6 \times 10^{13}$ rad/sec. This appears to be a rather large value for an insulator since it is comparable with that found for conduction electrons in TCNQ metallic salts.[13,14] There is no evidence of 3D behavior at our lowest measuring frequency, and so we take this value as an upper limit for the interchain diffusion rate, i.e., $D_\perp \leq 6 \times 10^7$ rad/sec. This yields an anisotropy in spin diffusion of $D_\parallel/D_\perp \geq 10^6$. This result does suggest that undoped $(CH)_x$ may be much more one-dimensional than previously supposed.[5]

What is the origin of this remarkable spin diffusion? The only proposal to date is the motion of neutral spin-$\frac{1}{2}$ domain walls (solitons)[8] which are formed in the polymer chains during isomerization. The extreme 1D spin diffusion that we observe is consistent with this model; however, there is, to our knowledge, no estimate for the diffusion coefficient of these solitons. Using a relation found by Wada and Schrieffer[17] for the diffusion of domain walls in a 1D system we find $D \simeq 10^{13}$ rad/sec. This is in rather good agreement with the experimental value; however, the theoretical relation may not be valid at room temperature.

We now discuss our results on heavily doped (AsF_5) *trans*-$(CH)_x$. At the 10% doping level $(CH)_x$ is a metal and thus we expect the spin diffusion to be dominated by the conduction electrons (or holes). We notice in Fig. 2 that there is a positive intercept on the T_1^{-1} axis. This suggests that ω_N is located below the 3D crossover frequency [$f(\omega_N) \simeq$ const], while $f(\omega_e)$ remains governed by Eq. (2). By use of the measured Pauli susceptibility in heavily doped $(CH)_x$,[7] the intrachain diffusion rate is obtained from the slope: $D_\parallel = 1.7 \times 10^{17}$ rad/sec. On the other hand, we can obtain an upper bound for the interchain hopping rate from the absence of saturation of the relaxation rate at our lowest measuring frequency: $D_\perp \leq 4 \times 10^{10}$ rad/sec.

If the spin diffusion reflects the motion of the charge carriers, as it does in the conducting TCNQ salts,[13,14,18] one can deduce from $D_\parallel$ and $D_\perp$ both the intrachain mean free path (l) and the conductivity anisotropy. If one assumes a 1D metallic system, l is given by[14] $l = 2\pi\hbar\chi D_\parallel c_\parallel$, where $c_\parallel$ is the intrachain carbon distance, yielding $l \simeq 35 c_\parallel$. With l we can obtain a value for the intrinsic conductivity from the 1D relation[19] $\sigma_\parallel = 2e^2 l/\pi\hbar\Sigma$ where Σ is the cross section per $(CH)_x$ chain. We find $\sigma_\parallel \simeq 5 \times 10^4$ $(\Omega\ \mathrm{cm})^{-1}$. This is a much larger value than found in tetrathiafulvalene TCNQ[19] at 300 K and suggests that doped crystalline $(CH)_x$ would be a highly conducting material, perhaps somewhat like doped graphite. This value is consistent with an estimate from optical data.[20] The anisotropy of the conductivity is given by $\sigma_\parallel/\sigma_\perp = D_\parallel c_\parallel^2/D_\perp c_\perp^2 \geq 4 \times 10^5$. This degree of one-dimensionality is greater than the highest yet reported for a 1D conductor, $\sigma_\parallel/\sigma_\perp \simeq 10^5$ in $K_2[Pt(CN)_4]Br_{0.3} \cdot 3.2D_2O$ at room temperature.[21] However, our interpretation of the T_1^{-1} data for the *doped* $(CH)_x$ should be taken with some caution since such a relaxation could be caused by ~5% of the spins that were present in the undoped $(CH)_x$.

In conclusion, we have found that the spin diffusion in undoped and heavily doped *trans*-$(CH)_x$ is extremely one-dimensional at room temperature. This is consistent with the idea that neutral domain walls play an important role in the properties of $(CH)_x$ but more quantitative work is needed to prove it.

This work was partially supported by the U. S. Office of Naval Research. We acknowledge many useful discussions with K. Holczer.

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Integral Representation for Non-Planckian Distributions and the Cosmic Background Radiation

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(Received 17 September 1979)

A general result for the nonequilibrium distribution function for photons gives a greatest lower bound for the radiation flux spectrum. This inequality allows one to establish, from the recent measurements of the cosmic background radiation, that the observed spectrum arises from the superposition of single sources. Since the primeval fireball may be one of the single sources, it is inferred that the observed spectrum is consistent with a big-bang origin for the universe.

Some years ago,[1] the deviations of the cosmic background radiation (CBR) from an approximately 3-K blackbody were studied with the aid of the integral representation

$$F(\nu, t) = \frac{2\nu^3 h}{c} \int_0^\infty \frac{\sigma(T, t)dT}{\exp(h\nu/k_B T) - 1} \qquad (1)$$

for the photon flux spectrum, where the spectral function $\sigma(T, t)$ is positive definite. Such integral representations with $\int_0^\infty \sigma(T, t)dT = 1$ were obtained[2] by unifying the notions of the "approach to equilibrium" in quantum statistical mechanics and that of the asymptotic condition in axiomatic quantum field theory. The corresponding integral representation for non-Maxwellian distributions[2] was recently proved[3] for the spatially uniform Boltzmann equation for Maxwell models. It is interesting that the distribution (1) appears in an old work of Paley and Wiener[4] who generalize the integral equation of Laplace by replacing the Maxwell distribution by that of Planck. Paley and Wiener describe radiation from a source in approximate local equilibrium by (1), where $\sigma(T, t)$ denotes the "amount" of radiation coming from black bodies at temperature T; and, consequently, $\sigma(T, t)$ must be positive definite. With regard to the nature of the CBR in an expanding universe, the analysis with (1) results[1] in either (i) $\int_0^\infty \sigma(T, t) \neq 1$, and so to a CBR due to an aggregate of single sources distributed uniformly and isotropically in the expanding universe, or (ii) $\int_0^\infty \sigma(T, t)dT = 1$ in which case the radiation is solely due to the primeval fireball or else the CBR is due to a particular summation of discrete extragalactic sources[1] but with no primeval fireball. Notice that for the case $\int_0^\infty \sigma(T, t)dT \neq 1$, if the radiation resulting from the big bang, that is, the primeval fireball, is amongst the aggregate of single

