

VERY LOW TEMPERATURE NUCLEAR SPIN DIFFUSION IN TRANS-POLYACETYLENE

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Abstract

We have carried out a study of the frequency ($23 \text{ MHz} < f < 35 \text{ MHz}$) dependence of the proton spin lattice relaxation time, T_1 , of *trans*-(CH)_x for temperatures $0.33 \text{ K} < T < 4.2 \text{ K}$. We find that within this range T_1 can be expressed as an activated quantity, $T_1 = A \exp(-\Delta/k_B T)$, with $\Delta = g\mu_B H$ (A and g constant). The observed effective g factor of 3.3 for the activation energy suggests that we are nearly in the low-temperature high-field limit ($g\mu_B H/k_B T > 1$) for one-dimensional nuclear spin diffusion to fixed electron spins. We show that assuming proton relaxation is due to mobile neutral solitons leads to a one-dimensional diffusion constant that increases with decreasing temperature and has an activated behaviour *i.e.*, $D = D_0 \exp(\Delta'/k_B T)$ with $\Delta' = 1.1 \text{ K}$. However, this latter model is in contradiction with the reported solid state effect at low temperatures.

1. Introduction

Polyacetylene, (CH)_x, has been the subject of much recent work [1, 2]. For isolated chains of the *trans* isomer, there are two degenerate phases of bond alternation. In undoped (CH)_x, the soliton or domain wall which separates regions of different phase is neutral with spin 1/2. Earlier experiments that have studied the motion of the neutral soliton and its coupling to the (CH)_x chain have been in the temperature range from room temperature to 4.2 K, where the magnetic spin energy, $\mu_B H$, is much less than the thermal energy, $k_B T$.

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We report here measurements at lower temperatures where the magnetic spin energy becomes comparable to or larger than $k_B T$. The temperatures and frequencies covered in this study significantly extend the limit of present measurements to larger $g\mu_B H/k_B T$ and overlap with previous measurements at higher temperatures. We find that T_1 is thermally activated with a field-dependent activation energy. These results are consistent with a model of relaxation where the nuclear magnetization diffuses to fixed electron spins; the fixed spins being associated with neutral solitons [1 - 3].

Earlier nuclear magnetic resonance (NMR) and dynamic nuclear polarization (DNP) measurements have demonstrated that solitons are mobile and diffuse in one dimension along the chain at room temperature. Nechtschein and coworkers [3] found that

$$T_1^{-1} \propto (D_{\parallel} \omega)^{-1/2} \quad (1)$$

where ω is the nuclear Larmor frequency. They obtained a room temperature diffusion constant, for one-dimensional motion of the soliton diffusing along the chain, of $D_{\parallel} \sim 6 \times 10^{14} \text{ s}^{-1}$. Observation of the Overhauser Effect (OE) in the DNP experiments supports the one-dimensional soliton diffusion model at high temperatures. Measurements by Clark *et al.* [4] have shown that interchain diffusion does not become important until very low frequencies for temperatures from room temperature to 4 K. In contrast, at 100 K and below [5], DNP experiments show a solid state effect (SSE), which indicates that the soliton is becoming localized. In this case nuclear relaxation will occur through diffusion of the nuclear magnetization along the $(\text{CH})_x$ chain to the fixed soliton.

2. Theory

As long as the electron and nuclear Zeeman energies, ω_e and ω_n respectively, are much smaller than $k_B T$, the nuclear relaxation rate is [6]

$$T_1^{-1} = \pi/5 [6\langle D^2 \rangle \phi^z(\omega_n) + (7\langle D^2 \rangle + 5\langle A^2 \rangle) \phi^+(\omega_e)] \quad (2)$$

where $\langle A^2 \rangle$ and $\langle D^2 \rangle$ are the mean squares of the scalar and dipolar parts of the hyperfine coupling and ϕ^z and ϕ^+ are the Fourier transforms of the local electronic spin autocorrelation functions at the site of the nuclear spin:

$$\phi^z(t) = \langle S^z(t) S^z(0) \rangle$$

$$\phi^+(t) = \langle S^+(t) S^-(0) \rangle$$

At high temperatures in the isotropic paramagnetic region, one has $\phi^+ = 2\phi^z$. For an electron spin moving with one-dimensional diffusive behaviour the spectral density, ϕ^z , is given by

$$\phi^z(\omega) = C/2\pi(2D\omega)^{-1/2} \quad (3)$$

where C is a normalization constant. Equation (3) is valid when the electron spin diffuses quickly on the time scale of the nuclear relaxation.

As the Zeeman energy of the electron spin becomes comparable to the thermal energy, eqn. (2) is no longer valid since electron spin flips, described by ϕ^+ , are no longer effective in relaxing the nuclear spins. There are two possible behaviours for the relaxation rate for a diffusing soliton. (1) If the soliton remains freely diffusing at low temperatures, then the $T_1 \sim \omega^{-1/2}$ dependence of eqn. (1) remains valid, but the proportionality constant differs from the high temperature value, reflecting the loss of the spin flip contribution to the relaxation process. (2) If the diffusion rate becomes slow compared to the nuclear spin-spin relaxation time, effects due to the finite extent of the soliton become important. In this case the relaxation rate is [7]

$$T_1^{-1} = \alpha \omega^{-1/2} - \beta \quad (4)$$

where α and β are temperature dependent. As in the high temperature case, α is proportional to $D^{-1/2}$ while the second term, β , is proportional to D^{-1} .

Alternatively, the DNP experiments at low temperatures suggest that the soliton is localized and that relaxation proceeds via one-dimensional diffusion of the nuclear magnetization to the fixed soliton, *i.e.*, nuclear spin diffusion. If the electron relaxation time is faster than the nuclear spin diffusion time, the relaxation rate is given by [8]

$$T_1^{-1} = 4\pi/3C(\mu_B/\gamma_n)^{1/2}D^{3/4}\omega^{-1/2}\tau^{-1/4} \quad (5)$$

where C is the soliton concentration, D is the nuclear spin diffusion constant, and τ is the electron relaxation time.

At very low temperatures [5] and high magnetic fields, the electron relaxation time becomes longer than the nuclear spin diffusion time so that the nuclear spin system is always in internal equilibrium. The electron spin is the bottleneck in the relaxation process, leading to a relaxation rate given by [5]

$$T_1^{-1} \propto C(\langle S_z^2 \rangle - \langle S_z \rangle^2)\tau(1 + \omega^2\tau^2)^{-1} \quad (6)$$

where $\langle \rangle$ is a thermal average and S_z refers to the electron spin. In the low-temperature high-field limit ($g\mu_B H/k_B T \gg 1$) both the electron spin relaxation rate and the difference $\langle S_z^2 \rangle - \langle S_z \rangle^2$ should be thermally activated:

$$\langle S_z^2 \rangle - \langle S_z \rangle^2 \propto \exp(-g_e\mu_B H/k_B T) \quad (7)$$

$$\tau \propto \exp(g_e\mu_B H/k_B T) \quad (8)$$

The activation energy for both quantities is $g_e\mu_B H$, where g_e is the free electron g factor. When $\omega\tau \gg 1$ (very slow electron relaxation), then the quantity $\tau/(1 + \omega^2\tau^2)$ may be replaced with $1/\omega^2\tau$ and the relaxation rate is

$$T_1^{-1} = \frac{A}{\omega^2} \exp(-g_{\text{eff}}\mu_B H/k_B T) \quad (9)$$

where g_{eff} , the effective g factor, is $2g_e$ and A is a constant.

3. Experimental details

The polyacetylene films used in this work were prepared using the technique of Shirakawa [9]. The *cis-trans* isomerization was carried out at 180 °C for 20 minutes *in vacuo*. The samples were stored in an inert gas atmosphere until needed and exposure to air during mounting was limited to less than 10 minutes, after which the sample was pumped below 10^{-4} Torr for several hours to remove oxygen contamination. Thermal contact between the $(\text{CH})_x$ film and the mixing chamber of a dilution refrigerator was established by including liquid ^3He in the cell containing the sample. The initial magnitude of the free induction decay, which is proportional to the static nuclear magnetization along the applied field, followed Curie law behaviour for all temperatures and fields studied, indicating that sufficient thermal contact was obtained with this method.

The relaxation rate was measured using a conventional π - τ - $\pi/2$ pulse sequence. The magnetization recovery after a π pulse was followed over two orders of magnitude and could be described by a single exponential over that whole range. At the highest temperatures studied in this work, our measurements are in good agreement with both the relaxation rate [10] and the lineshape [11] found in previous studies.

4. Results and discussion

The results of our measurements [12] of the relaxation time T_1 from 23 MHz $< f < 35$ MHz and 0.3 K $< T < 4.2$ K are shown in Fig. 1. These measurements cover the range $0.3 < g_e\mu_B H/k_B T < 3.0$, which includes the interesting region where $g_e\mu_B H/k_B T$ is approximately one.

In the very low-temperature high-field limit, the relaxation rate is given by the activated form of eqn. (9). Figure 1 shows fits of the data to this thermally activated form. The measured activation energy, shown in Fig. 2 and Table 1, depends linearly on the magnetic field, to within experimental uncertainties, and is given by

$$\Delta = g_{\text{obs}}\mu_B H \quad (10)$$

where the observed g factor, $g_{\text{obs}} = 3.3$. In the very low-temperature high-field limit g_{obs} should be equal to $g_{\text{eff}} = 4.0$, (twice the free-electron g factor), while our measured value is 3.3. (Similar values have been reported by Clark *et al.* [5].) In addition, our results for the prefactor in eqn. (9) (given in Table 1), which should vary as ω^{-2} in the low-temperature high-field limit, are consistent with variations between $\omega^{-1/2}$ and $\omega^{1/2}$.

Our experiments were performed in the range $0.3 < g_{\text{eff}}\mu_B H/k_B T < 0.3$, and significant deviations from the low-temperature high-field limit can be expected. The reduced value of g_{eff} and the weak frequency dependence of the prefactor suggest that our measurements are not entirely in the region where the very low temperature limit is valid. Instead our measurements

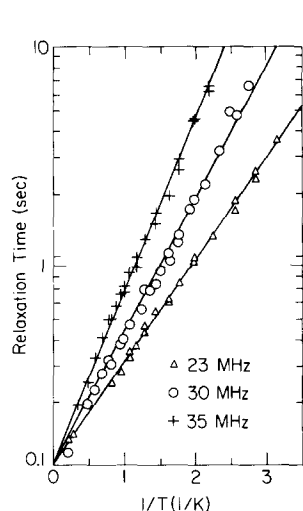


Fig. 1. Proton relaxation time as a function of T^{-1} at different frequencies.

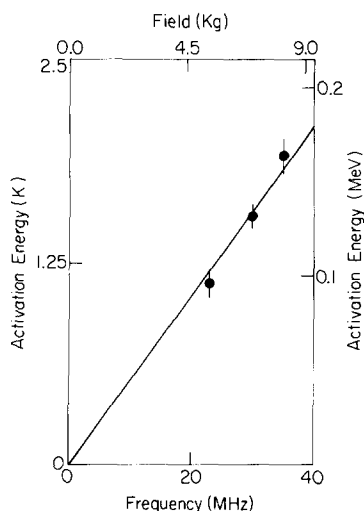


Fig. 2. Activation energy as a function of magnetic field or frequency.

TABLE 1

Measured activation energy and prefactor

f (MHz)	H (kg)	T (K)	A (s)
23	5.40	1.12 ± 0.1	0.099 ± 0.015
30	7.05	1.54 ± 0.1	0.099 ± 0.017
35	8.22	1.90 ± 0.1	0.099 ± 0.015

span the range between eqns. (5) and (9). In this region $\omega\tau \sim 1$ and $\tau/(1 + \omega^2\tau^2)$ varies as τ . This gives a thermally activated form for the relaxation rate, with a prefactor that is approximately frequency independent and an activation energy of $g_e\mu_B H/k_B T$.

As an alternative approach, we may consider the case where the soliton remains freely diffusing. Evidence that the electron spins are not freely diffusing at low temperatures is obtained from observation of the SSE in DNP experiments [13] and by nuclear relaxation experiments on ^{13}C -enriched [14] and D-enriched [15] samples. However, in the light of earlier work by Maki [16] and Devreux *et al.* [7], it is also instructive to examine our results in terms of the one-dimensional soliton diffusion model. Figure 3 presents the experimental results in a form that shows their one-dimensional soliton diffusion character. The solid lines in Fig. 3 are fits to eqn. (4), the low-temperature one-dimensional diffusion result. The fitting parameters are summarized in Table 2. The intercept, β , is inversely proportional to the slope, α , as predicted by Devreux.

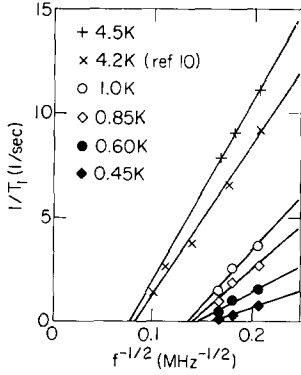


Fig. 3. Proton relaxation rate as a function of $f^{-1/2}$ at different temperatures.

TABLE 2

Fit parameters for eqn. (4) and the calculated diffusion constant

T (K)	α (MHz ^{1/2} /s)	β (s ⁻¹)	D (s ⁻¹)
4.5	110.3	11.1	2.4
1.0	52.2	7.17	10.9
0.85	41.3	5.83	17.5
0.60	25.5	3.72	45.9
0.45	16.4	2.61	110.9

A diffusion can be obtained from α and we find that this diffusion constant increases with decreasing temperature. Only relative values of D_{\parallel} are obtained in our experiment, but absolute values can be obtained by matching the results of Nechtschein *et al.* [7] to our highest temperature points. These values are listed in Table 2. Below 1 K, the diffusion constant can be fitted to a thermally activated form:

$$D = D_0 \exp(\Delta'/k_B T) \quad (11)$$

where Δ'/k_B , the activation energy for diffusion, is 1.10 K and D_0 is $4.8 \times 10^{10} \text{ s}^{-1}$. This sort of behaviour has been theoretically predicted by Maki [16] using a model in which the solitons propagate ballistically at low temperatures. However, the predicted activation energy (approximately 10 K) is much larger than the observed activation energy of 1.10 K. Moreover the SSE observed at low temperatures indicates that the soliton is localized, in disagreement with the Maki model.

5. Summary

We have found that both the low-temperature high-field model for nuclear spin diffusion and the slowly diffusing one-dimensional soliton

model describe the experimental results well. Using the low-temperature high-field model, the observed g factor is somewhat smaller than expected and the exponential prefactor has a weaker frequency dependence than expected. This discrepancy is consistent with $g_{\text{eff}}\mu_B H/k_B T$ not being sufficiently large for the model to be completely valid.

Alternatively, the data have been analysed in terms of the one-dimensional soliton diffusion model. Although the results can be shown to agree with this model, it is in contradiction with many [1, 2] recent experiments which show that the soliton is localized.

We conclude, therefore, that the low-temperature spin-lattice relaxation behaviour in *trans*-(CH)_x is dominated by the diffusion of nuclear magnetization to fixed paramagnetic centres. The relaxation time of the impurity, τ , is found to follow a thermally activated form.

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