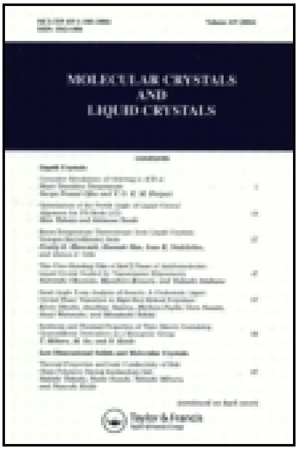

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Solitons in Polyacetylene Induced and Probed by Positive Mupons

K. Ishida [a], K. Nagamine [a], T. Matsuzaki [a], K. Nishiyama [a], Y. Kuno [a], T. Yamazaki [a] & H. Shirakawa [b]

[a] Meson Science Laboratory, University of Tokyo, Bunkyo-ku, Tokyo, Japan

[b] Institute of Materials Science, University of Tsukuba, Sakura-mura, Ibaraki, Japan

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SOLITONS IN POLYACETYLENE INDUCED AND PROBED BY POSITIVE MUONS

K. ISHIDA, K. NAGAMINE, T. MATSUZAKI, K. NISHIYAMA, Y. KUNO and T. YAMAZAKI
Meson Science Laboratory, University of Tokyo, Bunkyo-ku, Tokyo, Japan

H. SHIRAKAWA
Institute of Materials Science, University of Tsukuba, Sakura-mura, Ibaraki, Japan

Abstract Positive muons were injected into both trans- and cis- $(CH)_x$ as well as $(CD)_x$. In cis-polyacetylene, the μ^+ was found to form a radical state with an unpaired electron localized near the μ^+. In trans-polyacetylene, the longitudinal μ^+ spin relaxation rate at 293 K showed $H^{-1/2}$ dependence on the applied field H. After considering possible mechanisms, we concluded that it is due to the soliton-like one-dimensional motion of induced unpaired electron.

INTRODUCTION

Trans-polyacetylene has been attracting theoretical and experimental interests because of the proposed existence of the soliton[1]. There have been many experimental studies by magnetic resonances and other methods, but some basic properties like soliton formation or its dynamics seem to remain unclear. In this study, we probed this celebrated system by the μ^+SR method[2]. Preliminary results have been reported elsewhere[3].

EXPERIMENTAL METHOD

Positive muon, μ^+ is an unstable elementary particle with spin 1/2, mass of about 1/9 times proton mass and with the magnetic moment about 3.2 times that of proton. Polarized μ^+ is naturally available even after thermalization in the matter. When μ^+ decays with the life-time τ_μ of 2.2 μs, it emits a positron asymmetrically about the muon spin direction at that moment. Thus, time-dependent measurements of the angular asymmetry of these decay positrons provide the relaxation of the muon spins due to local magnetic interactions. The role of μ^+ is quite significant in the studies of polyacetylene: it is well known that μ^+, when stopped in a hydrocarbon with double bonds, generally forms a muonium radical; the relaxation phenomena can be used to probe the location or the dynamics of the unpaired spin in a chain of polyacetylene.

The experiment was carried out at Meson Science Laboratory, University of Tokyo[4]. Pulsed (50 ns width and 50 ms separation) and polarized (80%) muons were stopped in the polyacetylene target of a stack of thin films(in total, 4 cm x 4 cm x 1 g/cm^2). We used a standard μSR set up, where longitudinal magnetic field can be applied along the initial spin direction of μ^+. We detected decay positrons by scintillation counter telescopes in both forward and backward directions to the beam[3,4]. Under zero or longitudinal fields, the number of positrons $N(t,\theta)$ is expressed as $N_o \exp(-t/\tau_\mu) \times [1 + AG_z(t) \cos\theta]$, for the forward ($\theta$=0) and backward ($\theta=\pi$) counters, where A is the asymmetry at t=0 and $G_z(t)$ is the longitudinal relaxation function of the muon spin.

EXPERIMENTAL RESULTS

In our study, the longitudinal relaxation of μ^+ was measured under various longitudinal fields. The result is shown in Fig. 1, where the decay e^+ asymmetry is displayed as a function of time, representing a relaxation function $G_z(t)$.

As clearly seen in Fig. 1a, the μ^+ asymmetry in cis-isomer is recovered with the increase of the applied field, where almost no damping is seen in the time spectra. The result is consistent with a typical decoupling pattern of the muonium ($Mu=\mu^+e^-$)-like paramagnetic state. Our results suggest the following picture: the μ^+ picks up an electron during the slowing-down processes; then, during thermalization this Mu is attached to one of the π-bonds of cis-polyacetylene, and forms a pair bonding with one of the π-electrons, and the other left-out π-electron becomes unpaired, forming a Mu radical (see lower part of Fig. 1a).

As shown in Fig. 1b, in trans-isomer, the μ^+ asymmetry at t=0 stays almost constant with the applied field, while relaxation rates remarkably depend on the field. We consider that this difference between cis- and trans-polyacetylene is related to a mobility of the induced unpaired electron: in cis-isomer, the unpaired spin is almost fixed to the carbon next to the muon, while in trans-isomer, it can diffuse along the chain because of the degenerate structure between two phases of bond alternation.

The observed time spectra for trans-polyacetylene were fitted by the equation, where we assumed an exponential type relaxation function for $G_z(t)$: e^{-t/T_1}. The relaxation rates (T_1^{-1}) are shown in Fig. 2, as a function of the applied field. We found that the relaxation rate can be represented by $H^{-1/2}$ for the external field H from 10 to 3000 G at 293 K for both trans- $(CH)_x$ and $(CD)_x$. Its rate was $3.2(2) \times 10^5\ H^{-1/2}\ s^{-1}$ for $(CH)_x$ and $2.3(2) \times 10^5\ H^{-1/2}\ s^{-1}$ for $(CD)_x$, where H is given is Gauss. These values are two orders of magnitudes larger than those of ^1H NMR, which is $2.4 \times 10^3\ H^{-1/2}\ s^{-1}$.

μ^+ SPIN RELAXATION IN trans- POLYACETYLENE

To explain these $H^{-1/2}$ dependences, three relaxation mechanisms should be considered, namely, a) due to the nuclear dipolar field, b) by cross relaxation to the fixed paramagnetic defects similar to the nuclear spin diffusion, and c) by the one-dimensional diffusion of spins like soliton.

The effect of the nuclear dipolar field on the longitudinal relaxation of the μ^+ was calculated by the Monte-Carlo calculation. In this calculation, about ten nearest protons were included and

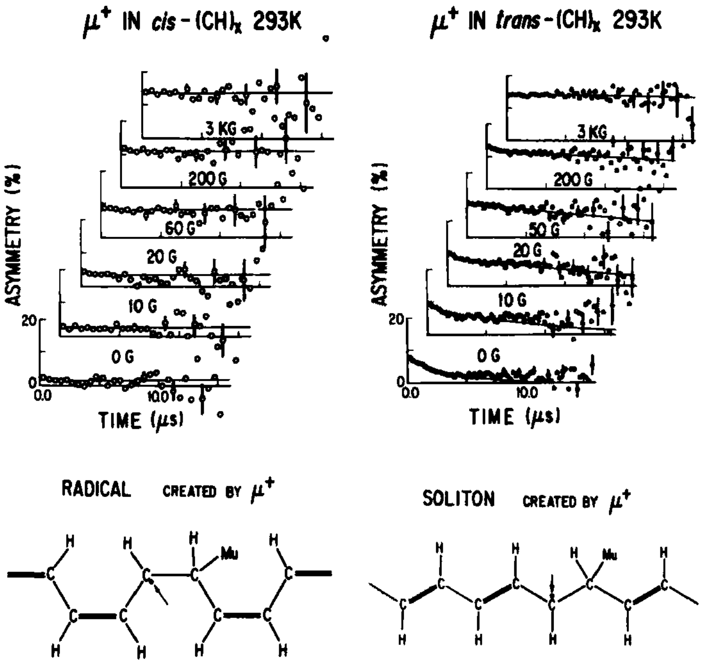

FIGURE 1 Time spectra of decay positron asymmetry for μ^+ in cis- $(CH)_x$ (a) and trans- $(CH)_x$ (b) at 293 K for various applied longitudinal fields, and the curves are best-fitted exponential relaxation functions.

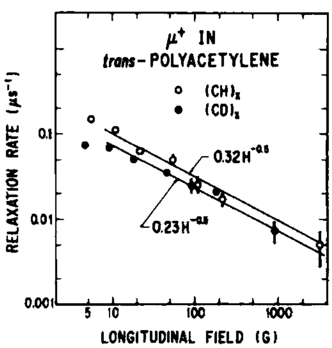

FIGURE 2 The relaxation rates versus external field for μ^+ in trans- $(CH)_x$ and trans- $(CD)_x$ at 293 K.

the directions of the crystal and the initial proton spins to the applied field were randomly taken. Time evolution of the spins were calculated by solving Bloch equations, for each time step of 0.05 μsec. The dynamical effect of the protons was included by a strong collision model, where the proton spin is reoriented randomly without any memories after some time interval τ_c. It was found that this dipolar effect can be almost completely decoupled by the longitudinal field above 10 G. Again, this effect does not explain the observed similar relaxation rates for $(CH)_x$ and $(CD)_x$ inspite of the factor 3 difference in the dipolar width.

The contribution similar to the nuclear spin diffusion is expected to produce $H^{-1/2}$ dependence. In μSR, however, this mechanism does not work at all; the muon is a perfectly dilute impurity (10^3 muons in 10^{23} carbons). The only effect we have to consider is the direct dipolar coupling between the muon and the paramagnetic spin. But, again, this does not explain the measured $H^{-1/2}$ dependence.

Therefore, only one mechanism that can explain the $H^{-1/2}$ dependence is the one-dimensional spin diffusion. In this case, the spin-lattice relaxation for the ^{1}H NMR $T_1(p)^{-1}$ can be expressed as[5] $(1/4)n_s[\frac{3}{5}d^2 f(\gamma_p H) + (a^2 + \frac{7}{5}d^2)f(\gamma_e H)]$, where a and d are the isotropic and the dipolar hyperfine couplings between the electron and the proton, respectively, γ_e and γ_p are the electron and proton gyromagnetic ratios, n_s is the density of unpaired spin per carbon atom and $f(\omega)$ is the spectral density function written as $1/(2D_{//}\omega)^{1/2}$ for one-dimensionally diffusing electron spins with diffusion constant $D_{//}$. The observed $T_1(\mu)^{-1}$ for the μ^+ is two orders of magnitude larger than $T_1(p)^{-1}$ at the same external field. If one of the proton is replaced by the muon, the ratio of $T_1(\mu)^{-1}$ and $T_1(p)^{-1}$ should be scaled by the square of the gyromagnetic ratio γ^2_μ/γ^2_p which is almost 10. After this correction there still remains an order of magnitude difference in the ratio of T_1^{-1}.

Here, we introduce the picture of unpaired-spin formation by the muon, which yields enhancement due to the increased density of the soliton at the μ^+: the μ^+ produces a soliton on the same chain, namely, soliton/probe is nearly 1, while in ^1H NMR, proton spins are relaxed by isothermally produced solitons at specific chains; soliton/probe is $1/n_c$, where n_c is estimated to be around 6, by considering the chain length and the paramagnetic spin concentration. Thus, this enhanced soliton density can explain the difference in T_1^{-1}.

In conclusion, we have found a new interesting phenomena of μ^+ induced soliton. The $H^{-1/2}$ dependence of $T_1(\mu)^{-1}$ can be solely attributed to the one-dimensional diffusion of soliton, induced by the muon itself.

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