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Metallic temperature dependence of resistivity in heavily doped polyacetylene by NMR

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Abstract

^{1}H-NMR spin-lattice relaxation rate T_1^{-1} of heavily doped polyacetylene was measured in an attempt to deduce the intrinsic resistivity of its metallic phase. Against our intention, in all of the samples a metallic behavior in the T_1^{-1} expected for a quasi-one-dimensional metal was not found for some period after doping, and it was revealed that those T_1^{-1}'s were governed by a relaxation mechanism due to residual Curie spins. In the bromine-doped sample, however, a change in the temperature dependence of T_1^{-1} from the non-metallic behavior to the metallic one was found as time passed. It was confirmed that this change was caused by the partial substitution of hydrogen atoms by bromine atoms in the polyacetylene chain. We succeeded in deducing the temperature dependence of intrinsic resistivity for metallic polyacetylene from the data of T_1^{-1}.

1. Introduction

The electrical resistivity of heavily doped polyacetylene measured by the ordinary four probe method is largely affected by the fibrillar morphology and/or the inhomogeneity of doping. It seems that the intrinsic resistivity of its metallic phase is never observed by the conventional method. There is a possibility to obtain the intrinsic resistivity of heavily doped polyacetylene utilizing a magnetic resonance technique. For heavily doped polyacetylene the ^{1}H-NMR T_1^{-1} is expected to be governed by the spin diffusion of its conduction electrons (or holes), and to be given by the following expression [1]:

$$T_1^{-1} = k_B T \chi_P \left\{ \frac{3}{5} d^2 f(\omega_N) + \left(a^2 + \frac{7}{5} d^2 \right) f(\omega_e) \right\}, \qquad (1)$$

where $\chi_P = \chi_P^{\text{molar}} / N_A (g\mu_B)^2$ is the normalized Pauli susceptibility, a and d are the isotropic and dipolar electron-proton hyperfine coupling constants, respectively, and ω_N and ω_e are the nuclear and electronic Larmor frequencies, respectively. For one-dimensional diffusive motion spectral density function $f(\omega)$ is expressed by

$$f(\omega) = 1 / \sqrt{2 D_{//} \omega} \qquad (2)$$

in terms of the intrachain diffusion rate $D_{//}$ which is related to the mean free path ℓ of the charge carriers by

$$\ell = 2\pi\hbar \chi_P D_{//} c_{//} , \qquad (3)$$

where $c_{//}$ is the intrachain carbon distance. As understood from Eqs.(1),(2) and (3), for metallic polyacetylene the ^{1}H-NMR T_1^{-1} is expected to show a temperature dependence different from the well-known Korringa relation: $T_1^{-1} \propto T$. For example, when the resistivity (inversely proportional to ℓ, and thus to $D_{//}$) increases with temperature obeying $\rho \propto T$, then T_1^{-1} increases obeying $T_1^{-1} \propto T^{1.5}$ in the frequency region where $f(\omega)$ is given by Eq.(2). We measured the ^{1}H-NMR T_1^{-1} in heavily doped polyacetylene with an intention to deduce the temperature dependence of the intrinsic resistivity of its metallic phase. In addition to ^{1}H-NMR T_1^{-1}, we measured the spin susceptibility which is necessary for deducing the resistivity by Schumacher-Slichter (ESR-NMR) method and SQUID susceptometer.

2. Experimental

Films synthesized by both the standard Shirakawa method and the non-solvent technique with heat treatment of catalyst similar to the Naarmann-Theophilou method were doped with FSO_3H, $HClO_4$, iodine, bromine and potassium in vapor phase. The ^{1}H-NMR T_1^{-1} measurement and the spin susceptibility measurement by Schumacher-Slichter method were carried out by homebuilt spectrometers with conventional methods.

3. Results and Discussion

The measured ^{1}H-NMR T_1^{-1}'s for all of the samples are shown in Fig.1 as functions of temperature. As reported previously [2,3], the expected metallic behavior of T_1^{-1} against the temperature was not found in all of the samples, at least for some period after the doping. All of the samples show a similar behavior to each other; T_1^{-1} increases from the smallest value at the lowest temperature and reaches a plateau around at 20~50K, then the plateau continues to a certain temperature. Because of this similarity, T_1^{-1} is considered to arise from an identical relaxation mechanism different from that of the metallic charge carriers. As shown in Fig.2, we found a correlation between T_1^{-1} and Curie spin concentration N_c in some temperature region and at several frequencies. From this fact we concluded that the measured T_1^{-1}'s were mainly governed by the relaxation mechanism due to the Curie spins which had been commonly ascribed to residual neutral solitons. Considering the circumstance in heavily doped polyacetylene, we could explain the experimental results by a model that the residual neutral solitons were confined in the limited undoped regions [4].

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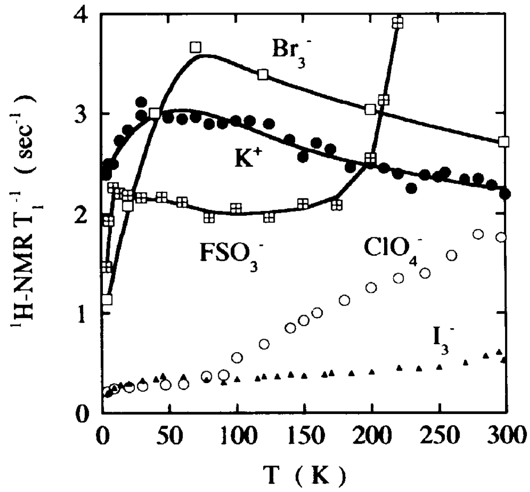

Figure 1. Temperature dependence of ^{1}H-NMR $T_1^{-1}$of $[CH(ClO_4^-)_{0.10}]_x$, $[CH(FSO_3^-)_{0.11}]_x$, $[CH(I_3^-)_{0.076}]_x$, $[CH(Br_3^-)_{0.15}]_x$ and $[CH(K^+)_{0.13}]_x$ measured at f_N=50.5MHz.

In the samples other than the bromine-doped one the T_1^{-1} had never shown the metallic behavior after all, while in the case of $[CH(Br_3^-)_{0.15}]_x$ the temperature dependence of T_1^{-1} had changed with time from the non-metallic one to the metallic one. Fig.3 shows the temperature dependence of T_1^{-1} in the sample annealed for 6 months after the doping at ambient temperature. It is found that above ~100K the T_1^{-1} increases obeying a power law: $T_1^{-1} \propto T^{1.5}$, as expected for a one-dimensional metal whose resistivity increases proportionally to temperature. Then, we confirmed that this change in T_1^{-1} was caused by the partial substitution of hydrogen atoms by the bromine atoms in the polyacetylene chain, reproducing similar results of T_1^{-1} for dehydrobrominated samples prepared by the thermal treatment described by Kletter et al. [5].

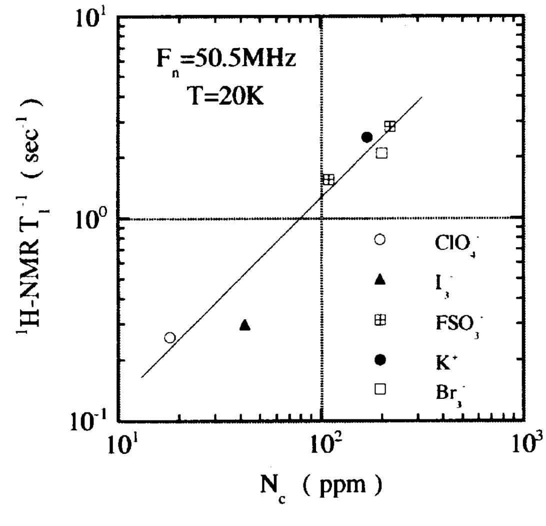

Figure 2. Correlation between ^{1}H-NMR T_1^{-1} and Curie spin concentration in the same samples as Fig.1.

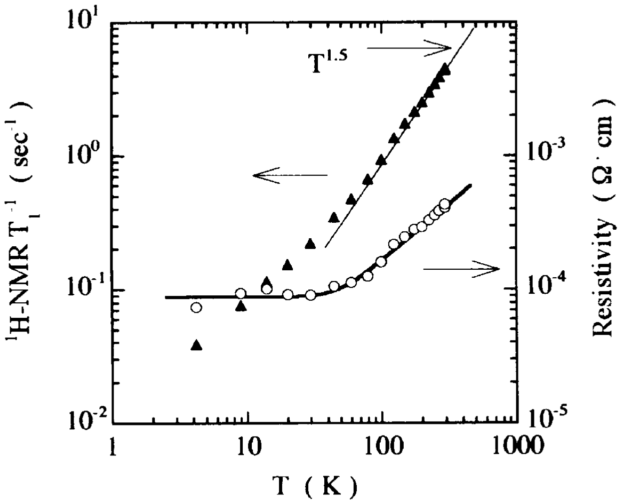

Figure 3. ^{1}H-NMR T_1^{-1} measured at f_N=50.5MHz and the resistivity deduced from them for $[CH(Br_3^-)_{0.15}]_x$ annealed for 6 months after the doping at room temperature. The solid curve shows eq.(5).

The resistivity deduced from the measured T_1^{-1} is also shown for $[CH(Br_3^-)_{0.15}]_x$ in Fig.3 as a function of temperature. The resistivity ρ_{ph} due to phonon scattering in the frame work of the undimerized SSH model is given by [4,6]

$$\rho_{ph}=\frac{\pi^2\hbar\Sigma}{e^2}\frac{\alpha^2 D(E_F)}{M\omega_0 v_F}\frac{1}{\cosh(\hbar\omega_0/2k_BT)\sinh(\hbar\omega_0/2k_BT)}, \qquad (5)$$

where Σ is the cross section per one chain, α the electron phonon coupling constant, ω_0 the phonon frequency causing carrier scattering and the other symbols have thier usual meanings. Generally, in a highly one-dimensional metal, if the phonon scattering is dominated only by a particular phonon, its resistivity due to phonon scattering has the same form as the above expression against the temperature. The sum of such a resistivity ρ_{ph} due to phonon scatterrig and a residual resistivity can reproduce the deduced resistivity well as presented by the solid curve in Fig.3, yielding $\hbar\omega_0/k_B$ =160K.

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