SPIN DYNAMICS AND CONDUCTIVITY IN POLYANILINE: TEMPERATURE DEPENDENCE

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ABSTRACT

The relationship between spin dynamics and conductivity in polyaniline has been investigated as a function of temperature. The spin dynamics behavior has been studied from the frequency dependence of the ESR line width, which gives the electron spin-spin relaxation time (T_{2e}). The data can be explained in terms of quasi 1-D spin diffusion with two parameters: the intrachain ($D_{//}$), and the interchain ($D_{\perp}$) spin diffusion rates. Our remarkable finding is that the dc conductivity agrees quite well with the interchain diffusion rate $D_{\perp}$, both as a function of the protonation level y and as a function of temperature. Further, the charge carrier concentration is suggested to be temperature dependent.

INTRODUCTION

Polyaniline (PANI) is well known for its remarkable insulator-to-conductor transition as a function of protonation. Upon protonation of the emeraldine form of polyaniline the conductivity increases by 10 orders of magnitude while the number of electrons on the polymer chains remains constant [1]. Accompanying this transition a spin susceptibility appears [2], which is of Pauli type and is proportional to the protonation level [3]. Then, a granular polymeric metal model [3] has been proposed that the conducting state was made of metallic particles embedded in an unprotonated insulating sea. Besides, evidence for disorder has been pointed out, and it has been suggested that a description in terms of a Fermi glass might be more appropriate [4,5]. Recently it was confirmed by a spin dynamics technique with magnetic resonances that this insulator-to-conductor transition is percolative in origin, consistent with the granular model, but that "conducting island" consists of only single or very few polymer chain(s). Spin dynamics makes possible to study the spin motion of

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polaron having both spin and charge. Therefore, spin dynamics enables us to study the conductivity in a microscopic scale. Usefulness of spin dynamics has been shown in many cases investigating non-linear excitations in polymer; soliton [6,7] and polaron [8]. In a previous study, based on the parallel variation of the interchain spin diffusion rate $D_\perp$ and of the dc measured conductivity (σ) as a function of protonation, we have concluded that σ is dominated by interchain diffusion [9,10]. In the present paper we report further investigations of spin dynamics and conductivity in PANI. In particular, we show that the parallel variation of $D_\perp$ and σ is not only valid as a function of the protonation level, but also as a function of temperature.

EXPERIMENTAL

PANI powder was synthesized by well known technique reported by MacDiarmid et al [11]. After equilibrating it with ammonium solution, the sample with desired protonation level was prepared by equilibrating with HCl solution of appropriate pH. Protonation level y (=Cl/N) was determined by chemical analysis. ESR T_{2e} was determined with use of ESR line width at frequencies from 10 to 24,000 MHz by a home-built spectrometer [12].

RESULTS AND DISCUSSION

Figure 1 shows a typical experimental data for the ESR line width as a function of $1/\sqrt{f}$ at temperatures from 78 to 300 K, where the solid curves represent least square fits with the T_{2e}^{-1} expression

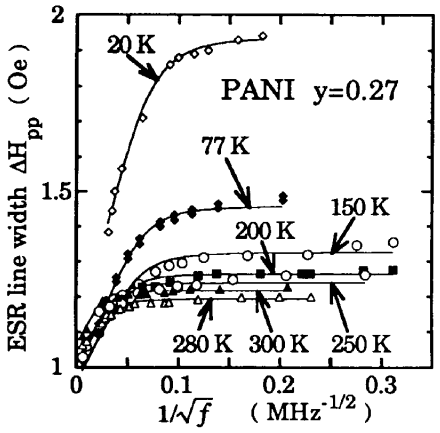
$$T_{2e}^{-1} = CR^2 [0.3f(0)+0.5f(\omega_e)+0.2f(2\omega_e)] \qquad (1)$$

where for the motion spectrum $f(\omega)$ a quasi 1-D diffusion behavior has been assumed;

$$T_1^{-1} \propto f(\omega) = \frac{1}{\sqrt{2D_\perp D_{//}}} \sqrt{\frac{1+\sqrt{1+(\omega/2D_\perp)^2}}{1+(\omega/2D_\perp)^2}}, \qquad (2)$$

where the result of anisotropic random walk model was used [13]. In the present analysis we use only the transverse diffusion rate $D_\perp$, which can be determined precisely only by the functional form of eqs.(1) and (2). This procedure suppresses the uncertainty related to the proportional coefficient in eq. (1). In the previous paper [9,10], it has been shown that the microscopic conductivity $\sigma_{D_\perp}$ deduced from $D_\perp$ as a function of the protonation level y agrees quite well with the measured σ. These facts strongly suggest that σ is dominated by interchain diffusion.

The temperature dependence of $D_\perp$ is shown in Fig. 2 and Fig. 3 for y=0.62 and 0.27, respectively. For y=0.62, the interchain diffusion rate $D_\perp$ agrees quite well with σ, but in the case y=0.27 a good agreement is found only for T > 250 K. At lower temperature the decay of $D_\perp$ for y=0.27 seems to saturate to a limiting value of ~10^{-9} rad/sec. This can be ascribed to a spin exchange contribution to the cutoff frequency



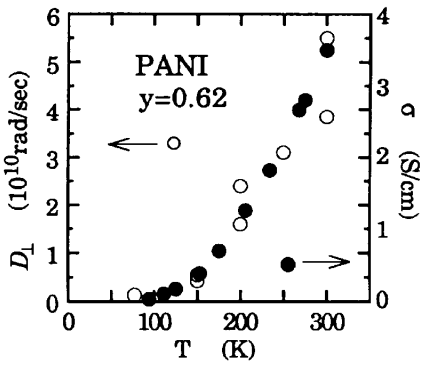
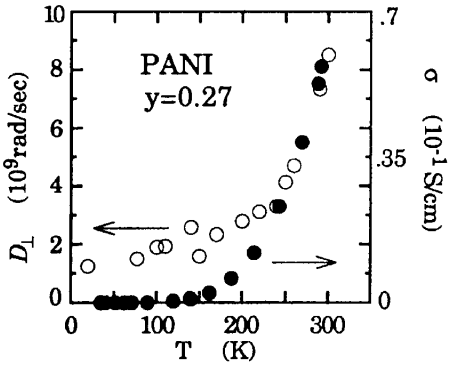


Fig. 1. (Left) ESR line width as a function of frequency. A least square fit was applied to determine ΔHpp.

Fig. 2. (Right) Temperature dependence of $D_\perp$ and (dc measured) σ for y=0.62.

of the 1-D diffusion. Spin exchange is expected to be independent of temperature and an increasing function of the spin concentration. For y=0.62, this effect is not noticeable because the diffusion rate $D_\perp$ is one order of magnitude larger. It is important to take into account the different contributions to $D_\perp$: interchain diffusion, interchain spin exchange, and (mainly intrachain) spin-spin dipolar coupling [14].

As in Ref. 9 we can estimate the microscopic conductivity from $D_\perp$ with the relation $\sigma_{D_\perp} = ne^2D_\perp/k_BT$, where n is the carrier concentration. Figure 4 shows the estimated conductivity $\sigma_{D_\perp}$ deduced from $D_\perp$ together with the measured σ, as a function of temperature for y=0.62, where the constant carrier concentration n=3.7×10^{21} (cm^{-3}) was used. For y=0.27, the parallel variation of $\sigma_{D_\perp}$ and σ is limited to the range T >



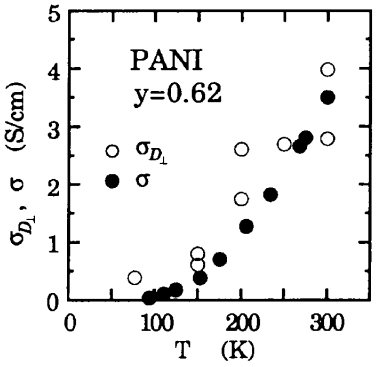


Fig. 3. (Left) Temperature dependence of $D_\perp$ and (dc measured) σ for y=0.27.

Fig. 4. (Right) Microscopic conductivity $\sigma_{D_\perp}$ calculated from $D_\perp$ and conductivity for y=0.62.

250 K (due to the influence of interchain spin exchange). We note that a better agreement for the temperature dependence is obtained between σ and $D_{\perp}$ than between σ and $\sigma_{D_{\perp}}$. This suggests that the effective charge carrier concentration could be temperature dependent (roughly $n \propto T$).

In conclusion, the present study in complement to earlier published data [9,10], supplies evidence that the conductivity in PANI is governed by the interchain charge hoppings. This may explain the moderate value of the conductivity usually measured.

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