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ESR in polypyrrole with oxygen -Transport property in crystalline region-

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Abstract

Effect of oxygen on ESR linewidth in polypyrrole has been studied to obtain information on the on-chain diffusion rate through the Houze-Nechtschein relaxation mechanism. Alternatively, the amplitude of angular dependent ESR linewidth $A_{\Delta H}$ in partially aligned polypyrrole is analyzed to obtain $D_{//}$ through the Elliott broadening, which makes it possible to separate Pauli contribution by subtracting Curie one from the observed. Finally, $D_{//}$ is found to be nearly proportional to T^{-n}, n≈1/2, which can reproduce all the ESR linewidth data taken under He gas, air and oxygen atmospheres in the whole temperature-range.

Keywords: Electron spin resonance, Polypyrrole and derivatives

So far, intrinsic electrical resistivity within crystalline regions as a function of temperature is not known even in a high quality film because of heterogeneous structure of the polymer. In this aspect, a microscopic technique to study dynamics of charge carriers with spin is helpful, such as frequency dependence of ESR linewidth that makes possible to reveal interesting features for polyacetylene [1-3], polyaniline [4,5], polythiophene [6,7] and polypyrrole [3,7]. A voltage-shorted-compaction (VSC) study also gave interesting results consistent with the ESR ones [8-10].

It has been well known that ESR linewidth broadens reproducibly under the atmosphere containing oxygen [11]. New type of technique concerning with the spin carrier dynamics was proposed by Houzé and Nechtschein making use of this effect ascribed to an interaction between the spin carriers and oxygens adsorbed on the conducting polymers [12]. Such an extra broadening of the ESR linewidth was theoretically demonstrated to be proportional/inversely-proportional to the diffusion rate of the spin carriers in a strong/weak interaction regime. In this report, usefulness of this technique will be checked in the case of polypyrrole doped with PF_6^- ion. A point which should be stressed is that the discrimination if the actual cases were in the strong or weak interaction regime is impossible without knowledge on the electronic states of the material. In the present case, it can be concluded that the interaction strength between the spin carriers and the oxygens is in the strong regime based on its metallic electronic states deduced from other experimental evidences [13].

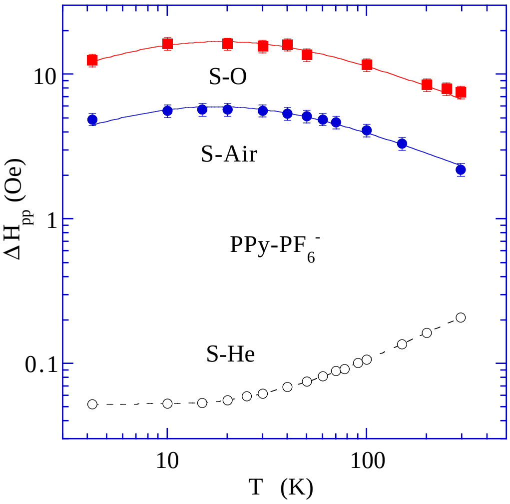

Fig.1 ESR linewidth in *S*-He (open circles), *S*-Air (closed circles) and *S*-O (closed squares) (from ref. [13]). The solid curves are the prediction by eq.(1) with $D_{//}$ deduced from the Elliott broadening analyzed from anisotropy of the linewidth.

Electrical conductivity of two-fold stretched film with a four-terminal method is 500 S/cm at 300 K and is finite even below 2 K (see, refs.[10,13] on sample and experimental). The temperature dependences of ESR linewidth are plotted for all the samples of *S*-He, *S*-Air and *S*-O (10 torr O_2 + He gas) in Fig.1. The ESR linewidth increasing with temperature for the *S*-He is a characteristic feature found commonly in PPy's doped with AsF_6^-, ClO_4^-, BF_4^-, TsO^- without oxygen [14]. On the other hand, the other samples with oxygen, *S*-Air and *S*-O, show a different behavior from *S*-He, that is, the linewidth shows a broad maximum around 15 K. This remarkable difference could be ascribed to an additional relaxation caused by the interaction between a mobile spin in the polymer backbone and one localized in the oxygen molecules adsorbed on the polymer. This additional relaxation rate is described by

$$\gamma \Delta H_{\rm HN} = pC_{\rm B}D_{//}/\ell, \qquad (1)$$

where $C_{\rm B}$ is the concentration of the relaxation centers (oxygen molecules in the present case), $D_{//}$ the diffusion rate along the polymer chain, γ the gyromagnetic ratio of the electron spin, ℓ the extension of the spin in the polymer and p the transition probability given by $p=(16/27)(3Jt_{\rm W}/2\hbar)^2/(1+(3Jt_{\rm W}/2\hbar)^2)$, where J is the interaction energy [12].

$\Delta H_{\rm HN}$ exhibits two different features in the two extreme conditions: (i) for the *weak coupling regime*, $3Jt_{\rm W}/2\hbar = 3J\ell^2/2\hbar D_{//} << 1$, it is proportional to the resistivity $\rho(T)$, $\Delta H_{\rm HN} \propto (J/\hbar)^2/D_{//} \propto \rho(T)$, and (ii) for the *strong coupling regime*, $3Jt_{\rm W}/2\hbar >> 1$, it is inversely-proportional to the resistivity $\rho(T)$, that is, proportional to the conductivity $\sigma(T)$, $\Delta H_{\rm HN} \propto D_{//} \propto 1/\rho(T) = \sigma(T)$. Thus, the contradictory conclusions can be attained with the same linewidth data, depending on the interaction strength, *weak or strong*. Here, it should be emphasized that based only on the linewidth data, one cannot conclude which regime the present systems belong to. To extract meaningful information from the linewidth data, other information on the electronic states is inevitable, such as metallic or semiconducting. Taking into account the several evidences for the metallic electronic states in the present system [10,14-18], the observed temperature dependences for the samples *S*-Air and *S*-O in Fig. 1 can be interpreted as an indication of the *strong* regime for the interaction with oxygens, since at least at T>15 K it behaves similarly to the metallic conductivity.

To examine the above conclusion in *S*-Air and *S*-O, $1/\Delta H_{\rm pp}$ is plotted in Fig.2 together with $\Delta H_{\rm pp}$ in *S*-He. This demonstrates that the temperature dependence of $1/\Delta H_{\rm pp}$ in *S*-Air and *S*-O is quite similar to $\Delta H_{\rm pp}$ in *S*-He at least above 50 K. Then, it is consistent with the conclusion that $\Delta H_{\rm pp}$ in *S*-He is metallic in $\rho(T)$ and $\Delta H_{\rm pp}$ in *S*-Air and *S*-O is metallic in $\sigma(T)$. Figure 2 suggests the intrinsic temperature dependence of electrical resistivity is described by $T^{1/2}$ above 50 K, which agrees with that observed in VSC resistance [3,7,10,14]. It is worthy to note that these data sets show a definite deviation from each other below 50 K. The origin of the deviation from $T^{1/2}$ dependence for *S*-He is due to a contribution of the Curie spins that is larger than the Pauli spins below 50 K. That for *S*-Air and *S*-O is due to a crossover of $\Delta H_{\rm HN}$ from the *weak* to the *strong* regime at the minimum temperature around 15 K demonstrated in Fig. 2. Such a behavior could be reproduced by eq.(1) with appropriate parameters as demonstrated by the solid curves in Fig. 1. The detailed discussion on $D_{//}$ deduced from the Elliott broadening through the anisotropy of the linewidth will appear elsewhere.

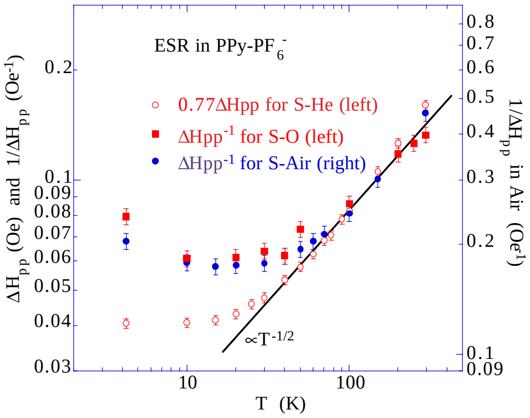

Fig.2 The temperature dependence of $\Delta H_{\rm pp}$ in *S*-He (open circles) is assigned to be Elliott (spin-phonon) broadening that is proportional to the electrical resistivity $\rho(T)$. (from ref. [13]) On the other hand, that of $\Delta H_{\rm pp}$ in *S*-Air (closed circles) and *S*-O (closed squares) is dominated by eq.(1) with a crossover around 15 K from the strong to the weak regime with decreasing temperature.

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