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Charge transport in slightly doped polyaniline

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Abstract

The results of an experimental study of d.c. and microwave (140 GHz) conductivities of slightly HCl-doped polyaniline are presented. It was found that charge carriers hop between polaron states according to the Kivelson's theory.

Keywords: Electron paramagnetic resonance, polyaniline

1. Introduction

In order to explain the temperature, pressure and frequency dependences of conductivity of lightly doped trans-polyacetylene (trans-PA) Kivelson have proposed [1] the model of isoenergetic phonon-assisted charge hopping between soliton bound states. Later he pointed out [2] that such a process might also be relevant in the other 1D semiconductors in which charge is transferred by soliton-like excitations or even in cis-PA with slightly nondege-nerate ground states. In this case the charge hopping would occur between bound soliton-antisoliton pairs such as polarons and bipolarons. As in the case of the intersoliton charge hopping, the activation energy for such an interpolaron charge transfer is small enough due to permanent number of polarons and bipolarons in the system. Since the quinoid-benzoid transition in organic conducting polymers is strongly modulated by the optical phonons, the probability P of a charge transfer between the polarons states is expected to be similar to that calculated for trans-PA [1], $P \propto \sigma_{dc}(T) \sim T^n$, where $n \approx 10$ is a constant. This model was successfully used in the study of trans-PA [3] and poly(p-phenylene) [4].

We present the first results on the investigation of the charge transport in slightly HCl-doped emeraldine salt form of polyaniline (PANI-ES) powder-like samples by d.c. conductometry and D-band (140 GHz) EPR spectroscopy.

2. Experimental

Emeraldine base form of polyaniline was synthesized according the method described in Ref.5. The protonation levels $y=[Cl]/[N] \approx 0.01$ and 0.03 (samples **I** and **II**, respectively) were reached by equalibrating of a sample with HCl solution of appropriate pH values for two days. The d.c. conductivity of the samples were measured at 77-340 K temperature region using four-points method. EPR measurements were performed using D-band EPR5-01 spectrometer. The relaxation times and the rates of a mobile spin diffusion along the chains D_{1D} and between them D_{3D} were measured separately using the steady-state saturation method at operation frequency ω_e and the Furier fluctuation power spectrum for 1D spin motion $\phi(\omega_e) = (2D_{1D}\omega_e)^{-1/2}$ at $D_{1D} > \omega_e > D_{3D}$ and $\phi(0) = (2D_{1D}D_{3D})^{-1/2}$ at $\omega_e \to 0$ [6,7].

3. Results and discussion

Figure 1 presents the temperature dependences of the D_{1D} and D_{3D} values. These parameters lie near to $D_{1D} \sim 10^{11}$ and $D_{3D} \sim 10^{9}$ rad/s at room temperature, respectively, and the first value is lower by approximately two orders of magnitude then that reported by Mizoguchi et al. [7] for PANI sample with doping level $y \leq 0.05$.

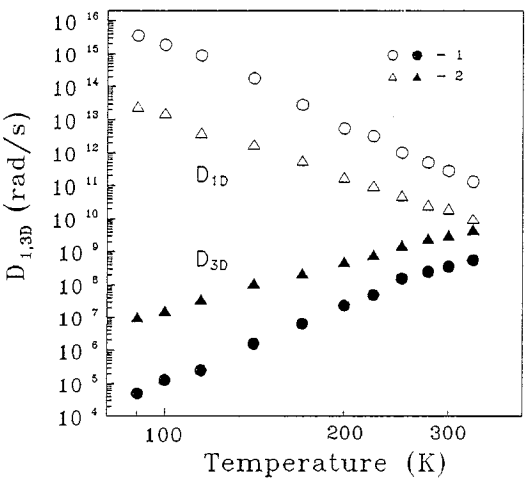

Fig.1. Temperature dependences of in-chain diffusion D_{1D} (open points) and interchain hopping D_{3D} (shaded points) rates of mobile paramagnetic centers in **I** (1) and **II** (2) samples.

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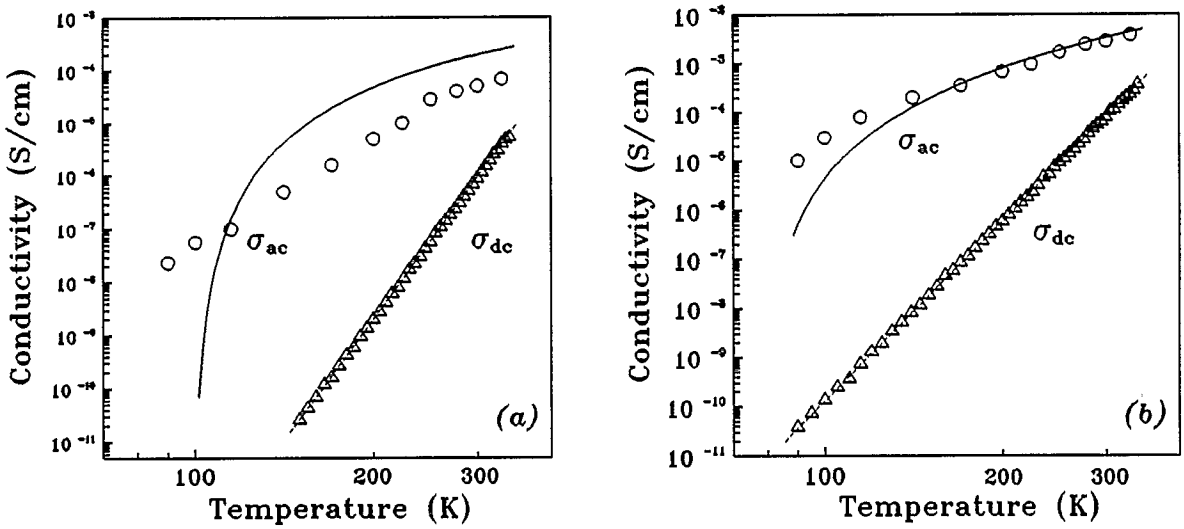

Fig.2. Temperature dependences of σ_{ac}(1) and σ_{dc}(2) determined for the samples I (a) and II (b) (points) and those calculated from Eqs.(2) and (3).

Interchain a.c. conductivity of the samples can be calculated from the data presented in Fig.1 as following

$$\sigma_{ac}=Ne^2D_{3D}b^2/(k_BT) \qquad (1)$$

where N is a total concentration of the mobile spin excitations and b is the interchain distance.

In contrast to the charge carriers in trans-PA both polarons and bipolarons are charged in PANI, so then Kivelson's equations for d.c. and a.c. conductivities one can write as [1,4]

$$\sigma_{dc}=\frac{k_1e^2\gamma(T)\xi\langle y\rangle}{k_BTR_0}\exp\left(-\frac{2k_2R_0}{\xi}\right) \qquad (2)$$

$$\sigma_{ac}=\frac{e^2N_i^2\xi_\parallel^3\xi_\perp^2\langle y\rangle\nu_e}{k_3k_BT}\left[\ln\frac{2\nu_e}{\gamma(T)\langle y\rangle}\right]^4 \qquad (3)$$

where k_1=0.45, k_2=1.39, and $k_3=6\bullet2^6$ are constants, $\xi=(\xi_\parallel\xi_\perp^2)^{1/3}$, $\xi_\parallel$ and $\xi_\perp$ are respectively the average, in-chain and out-of-chain electron decay lengths, $\gamma(T)=\gamma_0(T/300\,K)^{n+1}$ is the rate of a charge hopping between polaron and bipolaron states, $\langle y\rangle=y_py_{bp}(y_p+y_{bp})^{-2}$, y_p and y_{bp} are the concentrations of polarons and bipolarons, respectively, and $R_0=(4\pi N_i/3)^{-1/3}$ is the separation between charged impurities whose concentration is N_i.

Figure 2 shows σ_{ac}(T) dependence determined from Eq.(1), and σ_{dc}(T) one compared with the corresponding functions calculated from Eqs.(2) and (3) using b=3.39 Å, $\xi_\parallel$=11.9 Å, and $\gamma_0=3.5\cdot10^{19}$ s^{-1}, $\xi_\perp$= 0.79 Å, ξ=2.0 Å, $N_i=2.0\cdot10^{19}$ cm^{-1}, R_0=22.8 Å, $\langle y\rangle$=0.046, and n=15.2 for sample I and $\gamma_0=2.1\cdot10^{17}$ s^{-1}, $\xi_\perp$= 0.87 Å, ξ=2.1 Å, $N_i=8.4\cdot10^{19}$ cm^{-1}, R_0=13.7 Å, $\langle y\rangle$=0.081, and n=12.1 for sample II [8].

Fig.2,a shows an insufficient correspondence of an experiment to the theory in case of the first sample. Besides, the prefactor γ_0 is higher by approximately two order of magnitude compared with that estimated by Kivelson for trans-PA [1]. The better fitting of an experimental data to the Kivelson's theory is realized in case of sample II (Fig.2,b) evidencing for the charge phonon-assisted hopping between the mobile and pinned excitations in polymer II.

Acknowledgments

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References

[1] S. Kivelson, Phys. Rev. B, 25 (1982) 3798.
[2] S. Kivelson, Mol. Cryst., Liq. Cryst., 77 (1981) 65.
[3] A. J. Epstein, in Handbook of Conducting Polymers, T. E. Scotheim ed., Marcel Deccer, New York, 1986, p. 1041.
[4] P. Kuivalainen, H. Stubb, H. Isotalo, P. Yli-Lahti, and C. Holmström, Phys. Rev. B, (1985) 7900.
[5] P. Argirakis, L. W. Anacker, F. Zuo, M. S. Woo, D. B. Tanner, A. F. Richter, M. Angelopoulos, W. S. Huang, and A. G. MacDiarmid, Synth. Met., 21 (1987) 63.
[6] V. I. Krinichnyi, 2-mm Wave Band EPR Spectroscopy of Condensed Systems, CRC Press, Boca Raton, 1995.
[7] K. Mizoguchi, M. Nechtschein, J. -P. Travers, and C. Menardo, Phys. Rev. Lett., 63 (1989) 66.
[8] V. I. Krinichnyi, S. D. Chiremisow, and Ya. S. Lebedev (to be published).