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Synthetic Metals 135–136 (2003) 431–432

SYNTHETIC METALS

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Charge transfer in heavily H_2SO_4-doped polyaniline

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Received 2 Jule 2002; accepted 5 Jule 2002

Abstract

140 GHz EPR study of dynamics of polarons in crystalline domains of heavily H_2SO_4-doped polyaniline is reported. Collective interaction of charge carriers with the lattice phonons is shown to determine the polymer conductivity. The parameters of spin and charge transfer in the polymer depend on its doping level.

Keywords: electron paramagnetic resonance, polyaniline and derivatives, conductivity

1. Introduction

The optical reflectance study of polyaniline (PANI) salts [1] have shown that H_2SO_4-doped PANI should be considered as Fermi glass in which the electronic states are localized due to disorder. From the analysis of the band structure it was concluded that PANI-H_2SO_4 can be considered as more metal than PANI-HCl but less metal then PANI doped with camphorsulfonic acid. The spin and charge transfer mechanisms in PANI-H_2SO_4 has not jet been studied.

We report here the first results of the high-frequency (140 GHz) EPR and conductivity study of PANI-H_2S0_4. As in case of PANI-HCl [2], at the doping the charge carriers start to scatter on the optical lattice phonons in 3D metal-like domains of PANI-H_2S0_4 [3]. In heavily doped PANI the charge carriers was shown to be transferred in framework of the variable range hopping (VRH) mechanism and undimerized Su Schrieffer Heeger (SSH) model.

2. Experimental

PANI powder-like samples were obtained by polymerization *via* a modification of the general oxidation route with $(NH_4)_2S_2O_8$ in 1.0 M hypochloric acid which were doped into solution of sulfuric acid in water with an appropriate *p*H value [4]. EPR experiments were performed using a 2-mm waveband (ν_e=140 GHz) EPR-05 spectrometer with 100 kHz *ac* modulation.

3. Results and Discussion

Room temperature EPR spectra of PANI-H_2SO_4 with different doping levels are presented in Fig.1. It was shown [3] that the Dyson-like line attributed to Pauli paramagnetic centers with isotropic g_{iso}=2.00314 depend on the doping

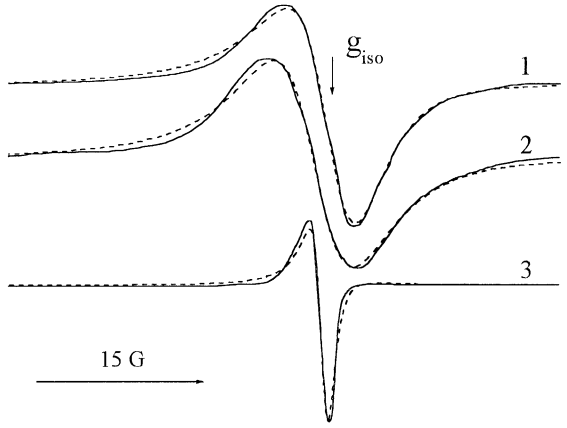

Fig.1. 140 GHz EPR absorption spectra of PANI-H_2SO_4 samples with doping level y = 0.21 (*1*), 0.42 (*2*), and 0.53 (*3*) registered at room temperature. By the dash lines are also shown the spectra calculated from Eq.(1) with D/A = 1.9 (above), 6.3 (middle), and 1.2 (below).

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0379-6779/03/$ – see front matter
doi:10.1016/S0379-6779(02)00554-4

level and temperature. Such spectrum consists of two contributions,

$$\frac{d\chi}{dB} = D(\sigma_{ac})g(\omega_e) + A(\sigma_{ac})g'(\omega_e), \quad (1)$$

where $D(\sigma_{ac})$ and $A(\sigma_{ac})$ are respectively the amplitudes of dispersion and absorption, σ_{ac} is the *ac* conductivity, and $g(\omega_e)$ is the line shape function.

The temperature dependences of the samples' *ac* conductivity due to diffusion of charge carriers determined from their Dyson-like EPR spectra according to the method described earlier [3] from Eq.(1) are presented in Fig.2.

The dependences of conductivity of PANI with y=0.21 and 0.42 shown in Fig.2 can be attributed to a collective interaction of charge carriers with the lattice phonons giving rise to conductivity [5]

$$\sigma_{ac}(T) = \sigma_0 T\left[\sinh\left(h\omega_{ph}/k_B T\right) - 1\right], \quad (2)$$

where h is the Plank constant, ω_{ph} is the angular frequency of the lattice optical phonons, and k_B is the Boltzmann constant. The Figure shows that the experimental σ_{ac} values obtained for these samples are fitted well by Eq.(2) respectively with $h\omega_{ph}$=0.017 eV and 0.013 eV.

The conductivity of heavily doped PANI sample demonstrates extremal temperature dependence with characteristic point $T_c \cong 200$ K that is typical also for PANI-HCl with $y \geq 0.4$ [2]. This fact can be explained by the above mentioned interaction of charge carriers with the lattice phonons at high temperatures (metallic regime) and their Mott's VRH with $\sigma_{ac} \propto T$ dependence at low temperatures (semiconducting regime). It is seen from Fig.2 that the function

$$\sigma_{ac}(T) = \left\{\sigma_{0_1}^{-1}T^{-1} + \sigma_{0_2}^{-1}T^{-1}\left[\sinh\left(h\omega_{ph}/k_B T\right) - 1\right]^{-1}\right\}^{-1} \quad (3)$$

with $h\omega_{ph}$=0.087 eV fits well the conductivity of heavily doped PANI-H_2SO_4 sample. The latter value is larger than $h\omega_{ph}$=0.018 eV determined for PANI-HCl [2] but lies near to $h\omega_0$=0.066 eV evaluated from the data obtained by Wang et al. [6]. RT *ac* conductivity of the heavily doped PANI-H_2SO_4 (about 110 S cm^{-1}) lies near that obtained for metal-like domains in other PANI-ES [7, 8].

The analysis of the data obtained allows to conclude that the doping changes the interaction of the charge carriers with the lattice phonons and therefore the charge transfer mechanism. In heavily doped PANI the charge carriers are transferred according to the VRH mechanism at low temperatures and are scattered on the lattice phonons at high temperatures. Such collective electron-phonon interaction is in agreement with the concept of 3D domains presence in PANI-ES [9,10] rather then the supposition of existing of 1D solitary conducting chains even in heavily doped PANI [11].

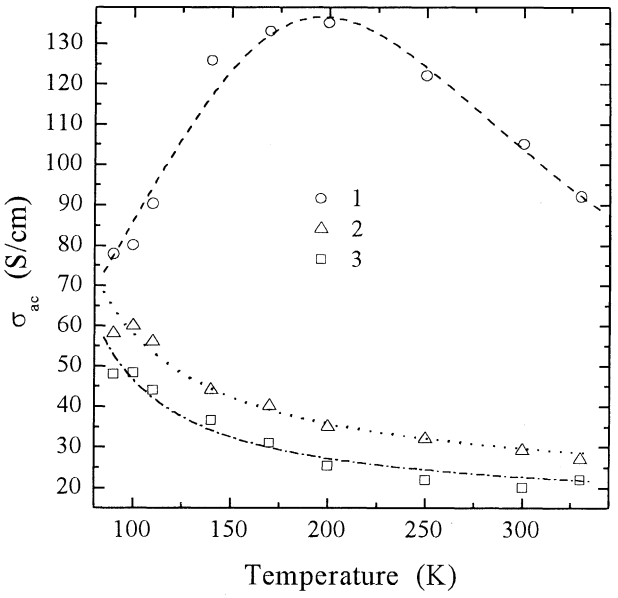

Fig.2. Temperature dependency of *ac* conductivity calculated from Dyson-like EPR line of H_2SO_4-doped PANI samples with y = 0.53 (*1*), 0.42 (*2*), 0.21 (*3*). The dependences calculated using Eq.(2) with σ_0=1.5·10^{-1} S·cm^{-1}·K^{-1} and $h\omega_{ph}$=0.013 eV (dotted line), σ_0=5.8·10^{-2} S·cm^{-1}·K^{-1} and $h\omega_{ph}$=0.017 eV (dash-dotted line) and Eq.(3) with σ_{0_1}=0.86 S·cm^{-1} K^{-1}, σ_{0_2}=2.1·10^{-2} S·cm^{-1}·K^{-1}, and $h\omega_{ph}$=0.087 eV (dashed line) are shown as well.

4. Acknowledgments

The authors are grateful to Dr. F. Lux for the preparation and distribution of the PANI samples. Partial financial support by RBRF Grant No 01-03-33255 is acknowledged.

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