ELSEVIER

Synthetic Metals 69 (1995) 243–244

SYNTHETIC METALS

MAGNETIC RESONANCE EVIDENCE FOR METALLIC STATE IN HIGHLY CONDUCTING POLYANILINE

N. S. Sariciftci[1], A. C. Kolbert[2], Y. Cao[3], A. J. Heeger[1] and A. Pines[2]

[1]Institute for Polymers and Organic Solids, University of California at Santa Barbara, Santa Barbara, CA 93106

[2]Department of Chemistry, University of California, Berkeley, CA 94720

[3] UNIAX Corp., 5375 Overpass Road, Santa Barbara, CA 93111

Abstract

Polyaniline doped with camphor sulfonic acid (PANI-CSA) has been shown to yield a material which, after processing from solutions in meta-cresol, exhibit a temperature independent magnetic susceptibility down to 50K. Below 50K a Curie like contribution sets in. We also report ^{13}C NMR experiments which clearly show that the ^{13}C spin lattice relaxation rates obey the Korringa relation for relaxation *via* the hyperfine coupling to conduction electrons.

1. INTRODUCTION

The electronic, paramagnetic susceptibility of heavily doped "metallic" conjugated polymers has been studied heavily during the last two decades. The total electronic paramagnetic susceptibility can be written as

$$\chi_{tot} = \chi_{Pauli} + \chi_{Curie} = \chi_{Pauli} + C/T \qquad (1)$$

A Curie-like contribution to the magnetic susceptibility superimposed on a small, temperature independent contribution has been quite generally observed in conducting polymer [1, 2]. The Curie contribution arises from localized spins and the Pauli contribution is directly proportional to the electronic density of states at the Fermi energy (E_F). For polyanilne (PANI) the metallic charge carriers were proposed to be spin=1/2 polarons exhibiting a metallic band structure ("polaron lattice") [3, 4]. On the other hand spinless bipolarons were suggested as the ground state charge carriers, which are created from isolated polarons upon heavy doping (polaron to bipolaron transition) [5, 6]. Clear evidence for metallic state can be obtained from the temperature independent Pauli susceptibility on and from the observation of Korringa relaxation of the nuclear spins.

Utilizing surfactant counterions to dope PANI renders solubility of the doped, metallic polymer in common nonpolar or weakly polar solvents. Upon processing from meta-cresol solutions PANI/CSA yields imporved mophology with high conductivities (100-400 S/cm) as well as a temperature independent magnetic susceptibility [7-10]. The metallic state of PANI/CSA can be described as in the critical regime of the disorder induced metal-insulator transition [9, 10]. In this contribution we present results of magnetic resonance studies on PANI/CSA. The magnetic susceptibility shows a temperature independent Pauli term down to low temperatures (50K). Below 50K, the suscepibility exhibits a Curie-like contribution corresponding to approx. 10^{20} localized spins per mole (two rings) of PANI/CSA [10]. The results are discussed in terms of a disordered metal near the mtal-insulator transition with weak electron-electron interactions. Furthermore, we report the nuclear magnetic resonance (NMR) evidence for relaxation of the ^{13}C nuclear spins *via* hyperfine coupling to conduction electrons (Korringa relation).

2. EXPERIMENTAL

The preparation of PANI/CSA films has been described in earlier reports [7, 8]. A Bruker 200 ESR spectrometer was used for electron spin resonance experiments. Sample tubes were sealed my melting under high vacuum. The susceptibility was measured by doubly integrating the ESR signal and calibrated with a Ruby reference at room temperature. NMR spin-lattice (T_1) relaxation experiments were performed on a Bruker MSL-400 spectrometer (9.4 T) equipped with variable temperature probe.

3. RESULTS AND DISCUSSION

3.1 ESR Susceptibility

The susceptibility *versus* temperature for different PANI/CSA samples show a temperature independent susceptibility persisting down to 50K [10]. The onset of the Curie term below 50K can be explained by the general formula for the static susceptibility in the Anderson localized regime of a

SSDI 0379-6779(94)02435-2

disordered metal in the critical regime of the metal-insulator transition as described by Kamimura [10, 11]. Details of this analysis is published elsewhere [10]. From the turn-on temperature for the Curie contribution one can directly deduce the on site electron-electron Coulomb correlation parameter, U, to be around 50-60K = 4-5 meV [10].

The intrinsic nature of the temperature independent Pauli susceptibility is demonstrated in Fig. 1. Here, we plot the inverse susceptibility as a function of temperature of *one and the same* sample, as-synthesized (powder) compared to films cast from meta-cresol solution. As clearly shown, the improvement of the material quality results in decrease of the Curie term and stabilizing of the Pauli term at high temperatures [10].

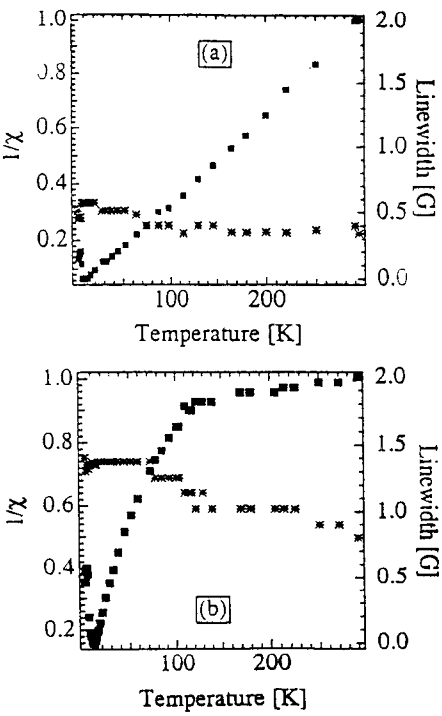

Figure 1: Temperature dependence of the normalized inverse ESR susceptibility(full squares) and the peak to peak linewidth (stars) a) PANI/CSA powder, b.) film cast from meta-cresol [10].

3.2 Korringa Relaxation

As shown in Fig. 2 the ^{13}C NMR spin-lattice relaxation rate is linear in temperature as for a metal (Korringa relation) [12]. Korringa enhancement factor has been estimated to be 10^2. Details are described in [12].

Acknowledgement:

This work is supported by the MRL program of the NSF under award No.DMR-9123048.A. C. K. is a fellow of the Miller Institute for Basic Research in Science.

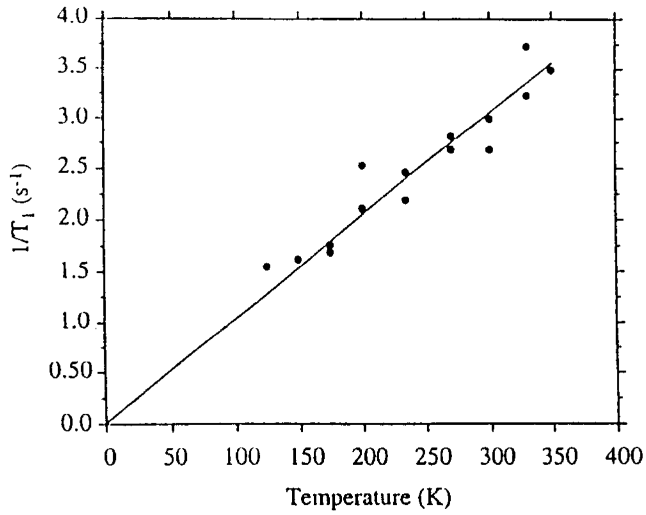

Figure 2: ^{13}C , T_1 relaxation rate *versus* temperature for a uniformly labeled PANI/CSA film.

References

1. *Handbook of Conducting Polymers*, edited by T. A. Skotheim (Marcel Dekker, New York, 1986).
2. A. J. Heeger, S. Kivelson, J. R. Schriefer, and S.P. Wu, Rev. Mod. Phys. 60 (1988) 781.
3. A. J. Epstein, J. M. Ginder, F. Zuo, R. W. Bigelow, H. S. Woo, D. B. Tanner, A. F. Richter, W. S. Huang and A. G. MacDiarmid, Synth. Met. 18 (1987) 303.
4. S. Stafstrom, J. L. Bredas, A. J. Epstein, H. S. Woo, D. B. Tanner, W. S. Huang and A. G. MacDiarmid, Phys. Rev. Lett. 59 (1987) 1464.
5. F. Genoud, J. Kruszka, M. Nechtschein, C. Santier, S. Davied and Y. Nicolau, Synth. Met. 41-43 (1991) 2887.
6. F. Devreux, F. Genoud, M. Nechtschein and B. Villeret in *Proceedings of the International Winterschool on Electronic Porperties of Polymers, Kirchberg/Tirol/Austria*, edited by H. Kuzmany, M. Mehring and S. Roth, Springer Series in Solid State Science, Vol. 76 (Springer, Berlin, 1987) p. 270.
7. Y. Cao, P. Smith and A. J. Heeger, Synth. Met. 48 (1992) 91.
8. Y. Cao and A. J. Heeger, Synth. Met. 52 (1992) 193
9. M. Reghu, Y. Cao, D. Moses and A. J. Heeger, Phys. Rev. B47 (1993) 1758.
10. N. S. Sariciftci, A. J. Heeger and Y. Cao, Phys. Rev. B49 (1994) 5988.
11. H. Kamimura, Philos. Mag. B42 (1980) 763.
12. A. C. Kolbert, S. Caldarelli, K. F. Thier, N. S. Sariciftci, Y. Cao and A. J. Heeger, Phys. Rev. B, submitted.