PHYSICAL REVIEW B VOLUME 49, NUMBER 9 1 MARCH 1994-I

Paramagnetic susceptibility of highly conducting polyaniline: Disordered metal with weak electron-electron interactions (Fermi glass)

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(Received 18 August 1993)

Electron-spin-resonance studies of films of the conducting form of polyaniline (PANI), doped with camphor-sulfonic acid (CSA) and cast from metacresol solutions, show a temperature-independent Pauli susceptibility between 300 and 50 K; in PANI-CSA, there is no Curie contribution to the paramagnetic susceptibility at high temperatures. Below 50 K, a Curie-like contribution to the electronic susceptibility ($\chi \propto 1/T$) is observed, indicative of singly occupied states at the Fermi energy. Thus, at approximately 50 K, the electron-electron interactions are comparable to the thermal energy in this disordered metal near the boundary of the metal-insulator transition. We conclude from this crossover that the intrasite electron-electron interaction parameter U is $\sim$50–60 K ($\sim$4–5 meV). In many samples, evidence of a spin-glass transition is observed around 10 K due to spin-spin coupling between the singly occupied states. The average spin-spin coupling (random in sign) is thereby estimated to be 0.5–1 meV. The indirect exchange interaction between localized moments *via* π-electrons is proposed to dominate at these low temperatures.

INTRODUCTION

Electron-spin-resonance (ESR) measurements of the paramagnetic susceptibility continue to provide important information on the nature of the electronic states near the Fermi energy in highly doped, "metallic" conjugated polymers. The total electronic paramagnetic susceptibility can be written as

$$\chi_{\text{tot}}=\chi_{\text{Pauli}}+\chi_{\text{Curie}}=\chi_{\text{Pauli}}+C/T \ . \tag{1}$$

A Curie-like contribution ($\chi \propto 1/T$) to the magnetic susceptibility superimposed on a small, temperature-independent contribution has been quite generally observed in conducting polymers.[1–4] The temperature-independent part can be extracted from χ vs $(1/T)$ plots and is attributed to the Pauli contribution:

$$\chi_{\text{Pauli}}=2\mu_B^2 N(E_F) \ , \tag{2}$$

where $N(E_F)$ is the density of states (one sign of spin) at the Fermi energy. The Pauli contribution is, therefore, particularly important, for it provides a direct measure of $N(E_F)$. The Curie-like contribution arises from unpaired localized spins. For example, in a Fermi glass where the electronic states near the Fermi level are localized by disorder, states near E_F are singly occupied for $k_BT<U$ where k_B is the Boltzman constant, T is the temperature, and U is the intrasite electron-electron interaction parameter.[6]

Within the class of conducting polymer materials, polyaniline (PANI) is of special interest because of its excellent stability under ambient conditions. The metallic form of PANI, referred to as the "emeraldine salt" [Fig. 1(a)] can be obtained either by oxidation of the neutral "leucoemeraldine" [Fig. 1(b)] or by protonation of the "emeraldine base" form [Fig. 1(c)]. In the latter case, there is no change in the total number of π-electrons; the metallic state results from an internal redox reaction,[3,5] protonation-induced spin unpairing.[6] In an ordered structure, the metallic form has been described as a pola-

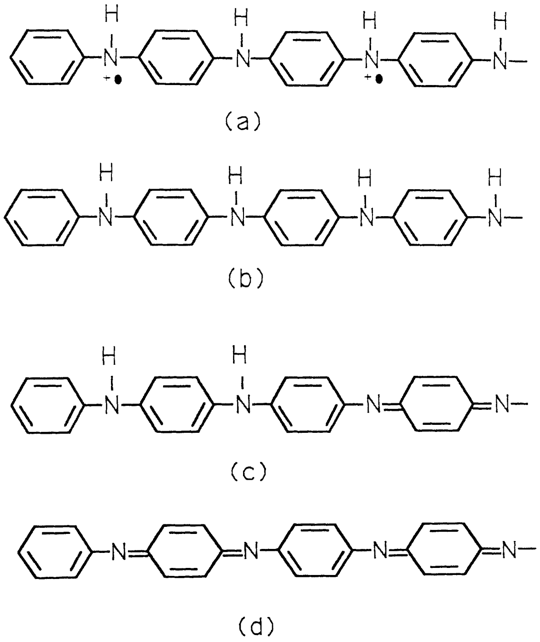

FIG. 1. Ideal structural formula of different forms of polyaniline: (a) emeraldine salt, (b) leucoemeraldine, (c) emeraldine base, and (d) pernigraniline.

ron lattice.[5,7] Further oxidation of the emeraldine salt leads to "pernigraniline" [Fig. 1(d)], a semiconducting degenerate ground-state polymer with all-imine nitrogens and with alternating benzenoid and quinoid ring structures.

The proposal of a metallic polaron lattice structure initiated controversy. The relatively large Curie-like contribution to the electronic susceptibility (even though a small Pauli term can be extracted as described above) implies a disordered electronic structure; a Fermi glass with Anderson-type localized states at the Fermi energy.[6] Genoud *et al.*[8] proposed a spinless bipolaron conduction mechanism and attributed the observed Curie contribution to the susceptibility in highly doped conducting PANI to defects; in their model there would be no intrinsic Pauli term.

Conduction by spinless bipolarons has been proposed for a number of nondegenerate ground-state conjugated polymers, since spin-resonance studies show an initial sharp increase in paramagnetic susceptibility upon doping (creation of isolated polarons) followed by a decrease upon doping to higher levels. The latter was interpreted as conversion of pairs of polarons into bipolarons.[1,2,8,9] A transition from localized polarons to a metallic polaron lattice would have a dramatic effect on the spin susceptibility: The temperature dependence would change from $\chi \propto 1/T$ to being temperature independent, and the magnitude would decrease by a factor of T/T_F, where T_F is the Fermi temperature. Such a qualitative change in behavior has been observed at the metal-insulator transition in doped polyacetylene; although in this case, the charge is primarily stored in spinless charged solitons at low doping levels.[10] This possibility was rejected for the emeraldine salt form of PANI on the basis of the measured susceptibility, which followed Eq. (1) with both a Curie-like contribution and a Pauli term.[5,6]

Recently, the use of functionalized protonic acids has been described as a means of doping PANI to the metallic state and, simultaneously, rendering the conducting polymer soluble in common nonpolar or weakly polar solvents. By utilizing such surfactant counterions, high electrical conductivities (100–400 S/cm) have been achieved in materials which exhibit temperature-independent magnetic susceptibility to temperatures as low as 80 K.[11–13]

In this study, we take a close look at the susceptibility (as measured by ESR) of PANI films and powders doped with camphor-sulfonic acid (CSA) over the temperature range 300–3 K. Between room temperature and 50 K, we find a temperature-independent Pauli susceptibility (with no detectable accompanying Curie-like contribution) corresponding to $N(E_F) \sim 1$ state/eV/two rings. Below 50 K, the susceptibility exhibits a Curie-like contribution corresponding to approximately $\sim 10^{20}$ localized spin-$\frac{1}{2}$ species per mol (two rings) of PANI. Thus, Eq. (1) is not valid over the entire temperature range; rather, there is a qualitative change in behavior at $T \sim 50$ K. Finally, in many samples a strong decrease in susceptibility is observed below 10 K. This decrease is observed in pure PANI-CSA and in dilute blends of PANI-CSA in other host polymers. The results are discussed in terms of a disordered metal near the metal-insulator transition with weak electron-electron interactions. The magnitude of the on-site electron-electron interaction parameter and the average spin-spin coupling constant (random in sign) are obtained by comparison with these characteristic temperatures. Furthermore, by measuring the susceptibility after recrystallization (from solution) of the same sample, we are able to directly demonstrate the effect of disorder on the electronic paramagnetic susceptibility.

RESULTS

The preparation of the PANI-CSA films has been described in earlier publications.[11–13] A Bruker 200 ESR spectrometer equipped with Oxford Instruments 900 cryogenic system was used for the ESR measurements. Sample tubes were sealed by melting under high vacuum. The susceptibility was measured by doubly integrating the ESR signal and calibrated with a Ruby reference at room temperature.

Figure 2 shows the ESR susceptibility for three different PANI-CSA films cast from metacresol solutions. The temperature-independent ESR susceptibility for $T > 50$ K and the sudden turn on of the Curie component below 50 K are clearly observable. The magnitude of the Pauli susceptibility is sample dependent with a mean value approximately 2×10^{-5} emu/mol (two rings). The corresponding density of states at the Fermi energy [as calculated from Eq. (2)] is $N(E_F) \approx 0.7 \pm 0.2$ states/eV/two rings. Residual solvent content and excess CSA in the material are the main sources of error (in determining the actual amount of PANI for calculating the absolute susceptibility). Because these error sources tend to

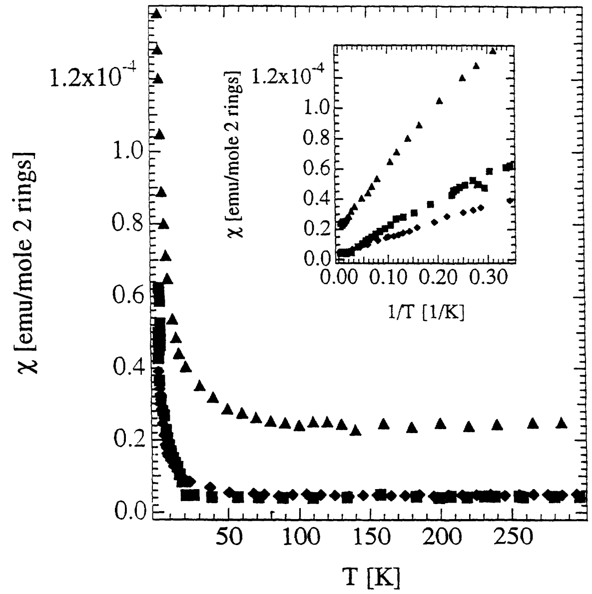

FIG. 2. ESR susceptibility vs temperature (inset versus inverse temperature) for three different kinds of PANI-CSA materials which represent three different transport regimes (Ref. 16), metallic (triangles), critical (diamonds), and insulating (squares).

overestimate the amount of PANI, we estimate $N(E_F) \sim 1$ state/eV/mol two rings, in agreement with earlier reports.[13]

The inset on Fig. 2 shows the susceptibility as a function of inverse temperature $(1/T)$ to emphasize the Curie-like behavior at low temperatures. There is no decrease in paramagnetic susceptibility at very low temperatures in these samples. However, as shown below, in many cases there is a relatively sharp decrease in $\chi(T)$ observable below 10 K.

Figure 3 shows the ESR susceptibility versus inverse temperature for different concentrations of PANI-CSA in blends with poly(methyl methacrylate), PMMA. The poorer signal-to-noise ratio is due to the small amount of PANI-CSA in the blends. After correction for the dilution factor, the magnitude of susceptibility and the density of states at E_F are quite similar to those obtained from pure samples. The susceptibility is nearly temperature independent down to approximately 50 K below which the onset of the Curie-like contribution to $\chi(T)$ is observed. Below 10 K there is a sharp decrease in the magnitude of the spin paramagnetism.

Figure 4 shows the temperature dependence of the normalized inverse susceptibility, $\chi(300K)/\chi(T)$, for *one and the same* PANI-CSA sample. The data shown in Fig. 4(a) were obtained from a PANI powder sample which has been equilibrated in a solution of CSA in ethanol without dissolving the polymer after doping. Thus, the structure of this polymer is determined during synthesis, and protonation occurs by diffusion of CSA into in a pre-existing solid-state morphology. The susceptibility of this polymer is as observed in earlier studies on PANI (Refs. 5–7) and consists of a combination of Curie and Pauli terms at all temperatures, as discussed in the Introduction [Eq. (1)]. After dissolving the same polymer in metacresol and casting the PANI-CSA as a film from solution ("recrystallization") the temperature dependence of the susceptibility changes dramatically [Fig. 4(b)]. The temperature-independent Pauli susceptibility dominates, and the Curie term takes over only below 100 K. At 10 K and lower, the paramagnetic susceptibility suddenly decreases. This low-temperature decrease in $\chi(T)$ is also observable (but less pronounced) in the powder sample [Fig. 4(a)].

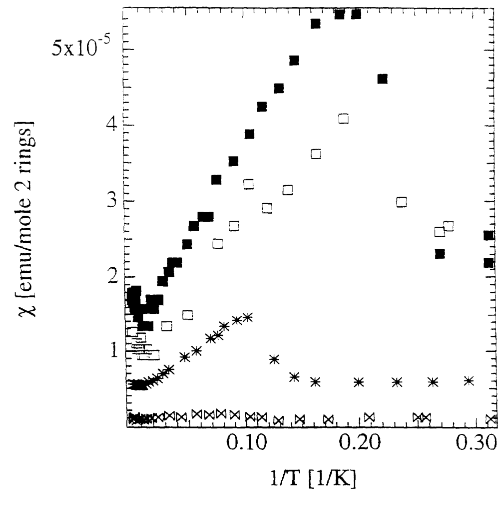

FIG. 3. ESR susceptibility versus inverse temperature for blends with different concentrations of PANI-CSA in PMMA, 0.64% (double-triangles), 1.24% (open squares), 9% (full squares), and 33% (stars).

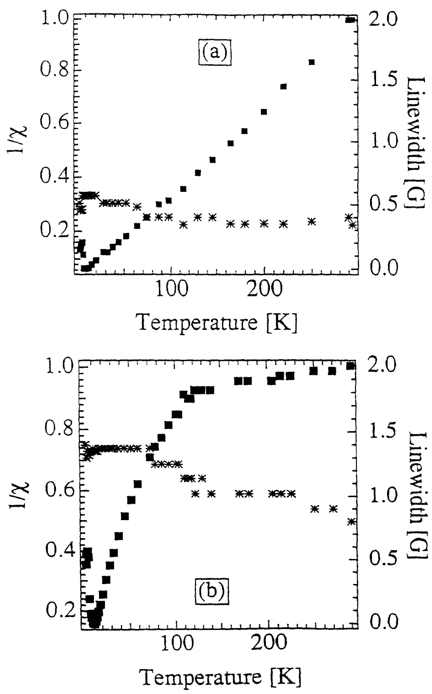

FIG. 4. Temperature dependence of the normalized inverse ESR susceptibility (full squares) and the peak to peak linewidth (stars): (a) Powder sample (protonated without dissolving) and (b) film cast from the metacresol solution of the sample in (a).

The peak-to-peak linewidth of the PANI-CSA powder is 0.35 G at room temperature and increases by less than a factor of 2 upon cooling to liquid-helium temperatures [Fig. 4(a)]. The peak-to-peak linewidth of the PANI-CSA film cast from solution in metacresol is also quite narrow, increasing from 800 mG at room temperature to 1.4 G at low temperatures. The relatively weak temperature dependence is consistent with that reported earlier.[13] The narrowing of the linewidth at high temperatures probably results from motional narrowing of the hyperfine fields due to increased thermal motion of the localized electrons in singly occupied states near the Fermi energy. There is no contribution from spin-orbit relaxation (a contribution to $1/T_1$ proportional to the temperature). Although such a contribution has been observed in polythiophene (as a result of the heavy sulfur atoms),[14,15] one would expect the spin-orbit coupling in polyaniline to be weak.

DISCUSSION

As shown by Reghu *et al.* in great detail,[16] charge transport in PANI-CSA is typical of that predicted for a disordered metal close in the critical regime of the metal-insulator (M-I) transition where the mobility edge is close to the Fermi energy. We, therefore, interpret the susceptibility data presented above in the context of the properties expected for a disordered metal close to the M-I transition. The general formula for the static spin susceptibility in the Anderson localized regime, as calculated by Kamimura, is the following:[17]

$$\chi(T)=2\mu_B^2/k_BT\Sigma_i\{2+\exp[\beta(\mu-\varepsilon_i-U)]+\exp[-\beta(\mu-\varepsilon_i)]\}^{-1}\ , \qquad (3)$$

where $\beta=1/k_BT$, μ is the chemical potential, ε_i are the energies of the localized states labeled by i, and U is the average intrasite electron-electron Coulomb interaction. The numerical solution of this general expression shows[17] that at temperatures sufficiently low that k_BT is less than U, states near the Fermi energy become singly occupied, and the spin susceptibility exhibits a Curie-law contribution

$$\chi(T)=\mu_B^2N_S/kT\ , \qquad (4)$$

where N_S is the number of singly occupied states (per unit volume) with spin $\frac{1}{2}$. Since there is a finite density of states at the Fermi energy, the low-temperature Curie contribution to the susceptibility arises from single occupancy of localized states near E_F.

When the Fermi energy is close to the mobility edge and much greater than the average on-site interaction U, the temperature dependence of the spin susceptibility gradually changes from Curie-law behavior to temperature-independent Pauli-type behavior with increasing temperature. Kamimura calls this transitional regime "a crossover region,"[17] which appears when $k_BT\cong U$. This crossover behavior is observed for PANI-CSA (see Fig. 2). From the slope of $\chi(T)$ versus $1/T$, the number of the singly occupied states at the Fermi energy is calculated to be $N_S\approx4\times10^{20}$ (per mol two rings) averaged over different samples. Thus, the fraction of the total number of states which are singly occupied (f_L) is small; $f_L=N_S/N_A\approx7\times10^{-4}$, where N_A is Avogadro's number. The same features are observed in the PANI-CSA blends (Fig. 3). Again, after correcting for the dilution and averaging over different samples, $N_S\approx4\times10^{20}$.

Due to the relatively sharp crossover from temperature-independent Pauli susceptibility to Curie-law behavior, the on-site interaction parameter can be readily extracted to be around $U\sim50$–60 K (~4–5 meV). This small value indicates the importance of "metallic" screening. Since the fraction of states which are singly occupied should be $f_L\approx UN(E_F)\approx U/\pi E_F$, this value of U implies $f_L\approx10^{-3}$, consistent in magnitude with the experimental value.

The spins in the localized, singly occupied states near E_F interact with one another. There have been several reports analyzing the low-temperature spin-spin interactions in conjugated polymers in terms of antiferromagnetic coupling.[18–20] We expect, however, that the indirect exchange coupling between localized electrons at a distance $\mathbf{R}_{ij}$ via the conduction electrons will be the dominant interaction. The effective spin-spin Hamiltonian is[21]

$$H_{\mathrm{IE}}=-\Sigma J(\mathbf{R}_{ij})\mathbf{S}_i\cdot\mathbf{S}_j\ , \qquad (5)$$

where the indirect exchange-coupling constant is

$$J(\mathbf{R}_{ij})=\Sigma J^2 2\cos\mathbf{q}\cdot\mathbf{R}_{ij}/[E(\mathbf{k}+\mathbf{q})-E(k)]\ , \qquad (6)$$

where the sum is over $\mathbf{k}$ and $\mathbf{q}$ with $k<k_F$ and $|\mathbf{k}+\mathbf{q}|>k_F$. In Eq. (6) J is the exchange interaction between localized spins in singly occupied states and the remainder of the π-electrons. Note that Eq. (8) oscillates in sign, typical of the Ruderman-Kittel-Kasuya-Yoshida spin polarization in metals.[21,22] Because of the random sign of the indirect interaction, the localized spins will lock into a spin-glass state at sufficiently low temperatures, i.e. at temperatures comparable to the root-mean-square average of the indirect exchange interaction. In one dimension, the indirect exchange falls off inversely with the distance,[23]

$$J(\mathbf{R}_{ij})\sim\frac{\cos 2k_FR_{ij}}{R_{ij}}\ . \qquad (7)$$

Thus, for quasi-one-dimensional conducting polymers, the interaction between localized spins can be sufficiently long range that collective behavior can be observed at a temperatures of order 10 K, even for concentrations as low as $N_S\sim4\times10^{20}$ per mole.

We have observed evidence of the spin-glass transition between 5–10 K (mean interaction energy of order 0.5–1 meV) in many PANI-CSA samples. Similar results have been reported for other conjugated polymers.[18] The transition in PANI-CSA is relatively sharp compared, for example, to that observed by Kispert *et al.* for poly(*para*-phenylene).[18] Kahol and Mehring[20] used the exchange-coupled model as described by Clark and Tippie for the random exchange Heisenberg antiferromagnet[24] for the explanation of the experimental data. Although they could fit the data reported in the literature satisfactorily (except for the sharp transition in polypyrrole[19]) by assuming a distribution of the coupling constants, indirect exchange [Eq. (7)] should be considered in greater detail as the possible origin of the distribution of coupling constants.

CONCLUSION

The results presented here have important implications for the understanding of the metallic nature of the conducting emeraldine salt form of PANI:

(1) The electronic paramagnetic susceptibility of PANI arises from a disordered metallic state close to the metal-insulator transition; i.e., a Fermi glass with finite density of states at the Fermi energy [$D(e_F)=1$ states/eV/two rings].

(2) The assignment of the observed spin susceptibility to leftover defects in PANI (Ref. 8) and the assumption that better material would give no spin signal is in contradiction to all experiments which show that PANI-CSA has improved physical properties: The conductivity is higher and shows a metallic temperature dependence,[26]

the thermopower is proportional to the temperature indicating a density of states at the Fermi energy comparable to that inferred from the Pauli susceptibility,[25] the photoinduced absorption spectrum shows sub-gap absorption features which are particularly well resolved,[26] and the infrared reflection is like that of a metal with mean free path comparable to a molecular repeat unit.[27]

(3) The crossover from temperature-independent susceptibility to Curie-law behavior below 50 K in PANI-CSA, and in dilute blends of PANI-CSA in PMMA is consistent with a disordered metal close to the critical regime of the metal-insulator transition with the Fermi energy close to the mobility edge. In such a Fermi glass, the states near the Fermi energy are localized with average on-site electron-electron interaction of $U \approx 50-60$ K (4–5 meV). The average indirect exchange coupling between localized spins is estimated as $J_{\mathrm{ind}} = 0.5-1$ meV.

(4) The intrinsic nature of the Pauli susceptibility and the linear (with temperature) thermopower indicate that PANI-CSA must be described as a degenerate electronic system with a finite density of states at the Fermi energy. These results demonstrate that models which assume transport by spinless bipolarons are not appropriate for the conducting emeraldine salt.

The conclusion that the electronic structure of the heavily doped state of conjugated polymers is that of a metal appears to be quite general.[28] In every case, as the material quality is improved, the magnitude of the Curie contribution decreases. Moreover, indications of "metallic" behavior with a finite density of states at the Fermi energy are shown by a variety of measurements, including the observation of thermopower which is linear in temperature[25,29] and the observation of an Overhauser shift (in heavily doped polythiophene).[14]

ACKNOWLEDGMENT

This research was supported by the MRL Program of the National Science Foundation under award No. DMR-9123048.

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