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Moisture effects on the magnetic state in polyaniline

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Through magnetic-susceptibility measurements on samples of thermally aged polyaniline in the emeraldine-base form, Pauli and Curie susceptibilities are shown to depend sensitively on the presence of moisture. It is suggested that the same spin can contribute either to the Pauli susceptibility or Curie susceptibility depending upon its environment, or temperature, and that the presence of water even in trace amounts may determine the dynamical behavior of the spins.

The conductivity of emeraldine-base (EB) polyaniline has been ascribed to a "metallic state," which was described in terms of a metallic polaron lattice (with disorder).[1,2] This model was based on magnetic-susceptibility data on chemically prepared samples that showed the presence of significant Pauli susceptibility, which varied linearly with the degree of protonation. On the other hand, the origin of Curie spins and their variation with temperature and protonation level on chemical samples of EB polyaniline has been attributed to the localization of polarons and bipolarons at chain ends, surfaces, and within the small granular metal particles.[1] The strongest evidence in favor of three-dimensional metallic islands with associated percolation threshold in the range $y = 0.2$–0.3 (where $y = [\mathrm{Cl}]/[N_{\mathrm{total}}]$) comes from electron-spin resonance (ESR), magnetic-susceptibility, and x-ray structural studies[3] in polyaniline samples having much higher crystallinity and synthesized using *N*-methyl-2-pyrrolidone (NMP).[4] While the spin dynamics results of recent NMR and ESR investigations[5–7] may be seen[8] as confirming the above interpretation, an alternative explanation in terms of percolation between single-chain conducting islands has also been advanced.[5,6] At room temperature, the NMR- and ESR-deduced on-chain electron-spin diffusion rate $D_\parallel$ is found to be independent of the protonation level, while the transverse diffusion rate $D_\perp$ exhibits a sudden drop at $0.20 < y < 0.28$; these rates decrease with the decrease of temperature. Since $D_\parallel$ and $D_\perp$ decrease with the decrease of temperature[5,6] and the number of Curie spins increases with decrease of temperature,[1] we believe that the Curie and Pauli susceptibilities are interrelated and that the absorbed water may be influencing the dynamical behavior of the spins.

The research presented here was stimulated by the fact that the presence of water in EB polyaniline leads to enhanced conductivity.[9,10] Since it is very difficult to synthesize samples with no adsorbed or absorbed water, we thought it significant to remove water (rather than introduce more as in other studies[10]) and investigate the effect on the magnetic susceptibilities, with the expectation that removing water will decrease $D_\perp$ and $D_\parallel$, hence decreasing χ_P and increasing χ_C. In order to remove absorbed water and observe detectable changes in both χ_C and χ_P without changing the oxidation state and protonation, samples were subjected to heating *in vacua* (thermal aging). The χ measurements were made as a function of temperature on thermally aged samples under a vacuum of $\approx 50\times10^{-3}$ Torr. Heat treatment might also be thought to lead to the loss of chloride ions (or HCl) but thermogravimetric analysis (TGA) and thermal-decomposition measurements reported by various authors[11] indicate that significant loss of HCl occurs only after $T > 130\,^\circ\mathrm{C}$ (depending upon the protonation level) and that it is insignificantly small below $\approx 130\,^\circ\mathrm{C}$. Thermal aging at temperatures up to 100 °C–130 °C for a duration of 10–15 h thus leads essentially to the loss of absorbed water. This is supported by our χ vs T measurements made on samples aged at 150 °C, 200 °C, and 230 °C, which show continual decreases in Curie susceptibility beginning $\approx 150\,^\circ\mathrm{C}$, thus implying the loss of chloride ions or deprotonation of the polymer chains.

The EB polyaniline was synthesized by the standard method of oxidative polymerization of monomeric aniline with persulfate in acidic solution. Doping into a conducting state was accomplished by equilibrating samples in aqueous HCl.[12,13] *p*H values were determined with a *p*H meter after equilibration times of 50–60 h. Susceptibility measurements were made with a "force" magnetometer in a magnetic field of 5 kG.[14] The data have been corrected for any ferromagnetic impurities after calibrating the system with Pt and Al standards.

The measured susceptibility χ is the sum of χ_{core} $[=\chi_{\mathrm{core}}(\mathrm{BB})+\chi_{\mathrm{core}}(\mathrm{Cl})+\chi_{\mathrm{core}}(W)]$, χ_P and χ_C, where BB denotes the backbone of the polyaniline chain and W denotes water. Whilst χ_C can be obtained from the linear dependence of χ on $1/T$, χ_P can be determined only if an estimate of the amount of water present in the sample can be made. The mass of the chloride ions present in the thermally aged samples is assumed to be unchanged on aging up to $T \approx 130\,^\circ\mathrm{C}$ and any mass loss upon heating is attributed to water. Since the mass susceptibilities of water and Cl^- ions are nearly equal (to within 3%), error in the estimation of χ_P and χ_C due to errors in the masses of Cl^- and H_2O will be fairly small. We further argue that aging for ≈15 h at ≈230 K after having aged the same sample around 50 °C, 100 °C, 150 °C, and 200 °C removes almost all of the absorbed water and most of the chloride ions, and that the measured mass is only due to the backbone part of EB polyaniline, denoted as m_{BB}. The total measured susceptibility can therefore be written as

$$\chi=\frac{m_{BB}}{m_T}[\chi_{core}(BB)+\chi_C+\chi_P]+\frac{m_W}{m_T}\chi_{core}(W)+\frac{m_{Cl}}{m_T}\chi_{core}(Cl^-)\,, \qquad (1)$$

where m_T is the measured total mass of the sample, m_{BB} is the mass obtained after heating the sample at 230 °C, and $\chi_{core}(W)$ and $\chi_{core}(Cl)$ are taken from the literature. The value of 5.85×10^{-7} emu/g for $\chi_{core}(BB)$ was obtained from our measurements on a sample equilibrated at pH =7.1 where the doping level is zero. For each set of χ vs T measurements the value of measured susceptibility χ at 293 K was noted and a value of χ_C was obtained from the linear data in the range 250–293 K. With this information, it was then possible to obtain an estimate of χ_P from Eq. (1).

Figure 1 shows a plot of χ_C vs χ_P at room temperature for three samples of EB polyaniline equilibrated at pH =0.9, 1.6, and 2.7. Thermal aging temperature, its duration and mass of the sample after aging are listed for the three samples in Table I. It is found that the Curie susceptibility for all the samples increases on thermal aging as much as by a factor of 5 with accompanying decrease of Pauli susceptibility. On aging the samples above $T\approx150$ °C, χ_C however decreases along with much faster decrease of χ_P. It is important to remember that thermal aging was carried out in a vacuum of 50×10^{-3} Torr and the samples once loaded were not exposed to external environment. Coupled behavior of χ_P and χ_C is the most significant result of our measurements and analysis of the magnetic susceptibility data. This behavior is 70%–90% reversible for samples aged up to 130 °C–150 °C on exposing them to air for long periods. Aging above 150 °C, however, leads to deprotonation of the chains. The behavior below 150 °C is thus predominantly associated with the presence of absorbed water and the water molecules must thus be weakly bonded at specific sites to the polymer. Since the pH =7.1 sample showed neither significant change in sample mass on aging nor any change in the observed small Curie susceptibility ($\approx1.8\times10^{-8}$ emu/g), chloride ions seem to be playing a yet not understood role in bonding water molecules to the chains.

The most likely explanation for the observed decrease in χ_P with concomitant increase in χ_C (Fig. 1) appears to be in terms of the conversion of Pauli spins to Curie spins. Removal of water seems to lead to increased localization of the spins due to increased pinning of the charge as well as that of spin on the polymer backbone in the vicinity of

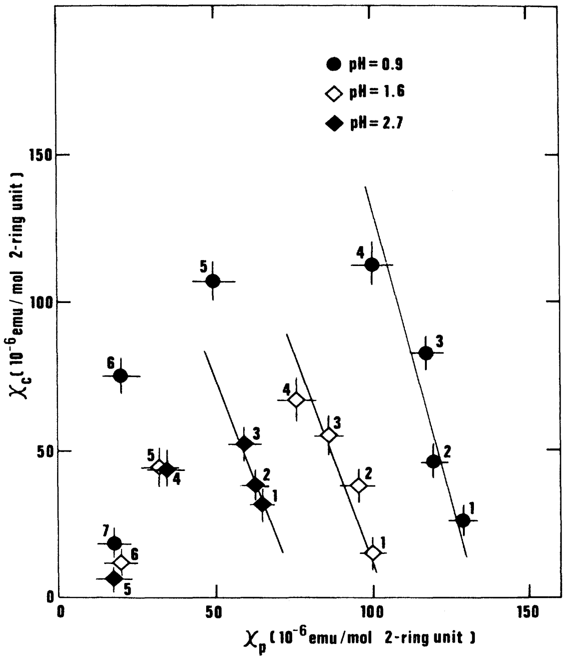

FIG. 1. χ_C vs χ_P at room temperature for three samples of emeraldine-base polyaniline (pH =0.9, 1.6, and 2.7). Numbers (1,2,...) next to the various data points correspond to thermal aging temperatures listed in column 2 of Table I.

TABLE I. Thermal aging temperature, duration and mass after aging of the four emeraldine-base polyaniline samples.

Sample	Aging temperature (°C)	Aging duration (h)	Mass after thermal aging (mg)
pH =0.9	(1) 23	· · ·	16.52
y =0.22 ± 0.01	(2) 50	14	15.88
	(3) 95	14	15.68
	(4) 135	19	15.19
	(5) 165	12	14.90
	(6) 200	12	14.12
	(7) 235	13	13.50
pH =1.6	(1) 23	· · ·	27.20
y =0.11 ± 0.01	(2) 50	20	26.51
	(3) 100	19	26.16
	(4) 150	20	25.08
	(5) 200	14	23.70
	(6) 230	18	22.30
pH =2.7	(1) 23	· · ·	21.41
y =0.06 ± 0.01	(2) 51	14	21.12
	(3) 102	12	20.63
	(4) 135	12	19.76
	(5) 235	14	18.28
pH =7.1	(1) 23	· · ·	13.00
y ≈ 0	(2) 62	14	12.96
	(3) 94	16	12.91
	(4) 150	16	12.83

the Cl^- anions. In other words, presence of water solvates the Cl^- anions, reduces the electrostatic interaction between the positive charge and the anions, and thereby leads to increased delocalization of the spins.[15] This interpretation is also consistent with increases of both the microwave conductivity and dielectric constant in $y \approx 0.50$ samples of EB polyaniline on exposure to moisture.[16,17] Role of moisture in the concept of textured metallic islands must therefore be included along with local order versus long-range disorder, delocalization versus incomplete localization, Coulomb correlations, and temperature.[16,17] It may be speculated that removal of water introduces more disorder leading to further localization of the spins, and that the effects observed here should be pronounced on samples with higher crystallinity.[4] Increase in χ_C with removal of water also correlates well with the observation that a heavily doped sample of EB polyaniline showed drastically increased EPR signals on pumping for about two days.[18] That the above may be a correct viewpoint is supported by 70%–90% reversibility of the magnetic susceptibility results on exposing the samples back to air for prolonged periods of time ($\approx$ 50–100 h). Further support for this picture comes from the linear least-squares fit of the χ_C vs χ_P data for aging temperatures up to 150 °C. Intercepts of the linear curves (Fig. 1) on the χ_C axis (i.e., for $\chi_P = 0$) were noted for the three samples, and converted to the number of spins per 2-ring unit. Values of the thus obtained spins are (0.40 ± 0.07) per 2-ring unit for the $p\mathrm{H} = 0.9$ sample, (0.20 ± 0.06) per 2-ring unit for the $p\mathrm{H} = 1.6$ sample, and (0.13 ± 0.06) per 2-ring unit for the $p\mathrm{H} = 2.7$ sample. These values compare very favorably with those deduced from pH versus doping level curves given by Chiang and MacDiarmid,[15] i.e., (0.44 ± 0.02), (0.22 ± 0.02), and (0.12 ± 0.02) per 2-ring unit, respectively.

We have also investigated at 100 K the χ_C vs χ_P behavior of the samples aged thermally up to 150 °C. As at room temperature χ_C is increased and χ_P is decreased on thermal aging. Linear regression of the data for the $p\mathrm{H} = 0.9$ and 1.6 samples yields (0.42 ± 0.12) and (0.25 ± 0.11) spins per 2-ring unit for $\chi_P = 0$. Although large errors in the above estimates forbid us to make any forceful claims, we can qualitatively discuss the observed behavior as follows. At 100 K, the number of Curie spins per 2-ring unit on the unaged sample at $p\mathrm{H} = 0.9$ is (0.055 ± 0.010), nearly three times larger than that at room temperature (0.021 ± 0.002); at temperatures lower than 100 K the number of Curie spins increases still further. Maximum number of Curie spins on the same but thermally aged sample is of the same order of magnitude (i.e., 0.080 ± 0.010) as at 100 K on the unaged sample. For the sample at $p\mathrm{H} = 1.6$, $n_C(100\ \mathrm{K}) \approx (0.040 \pm 0.008)$ to be compared with the maximum number of Curie spins on the aged sample as (0.053 ± 0.006). Similar results are obtained on samples equilibrated at other pH values. This leads us to the conclusion that absorbed moisture is the primary cause for the increase in the number of Curie spins with decrease in temperature.

In conclusion, we have shown via magnetic susceptibility measurements that both the Curie and the Pauli susceptibilities are dependent on the presence of small amounts of water, and that the removal of water results in the conversion of Pauli spins to Curie spins, confirming conclusions of other experimental investigations.[15–18]

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