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Magnetic susceptibility of polyaniline and polyaniline-polymethylmethacrylate blends

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While heat-capacity measurements on polyaniline yield density of states at the Fermi level \(N(E_F)\) of the order of 3 states/(eV·2 rings), a value of 16 states/(eV·2 rings) was reportedly found from magnetic susceptibility measurements. We report here our magnetic susceptibility measurements, which, in agreement with the heat-capacity results, yield \(N(E_F)\) of the order of 2 states/(eV·2 rings). These results firmly establish the metallic nature of charge carriers in the polyaniline family.

In an earlier paper, we presented results of a low-temperature heat-capacity study of \(p\)-toluenesulfonic acid (PTSA) doped polyaniline (PANI), and PTSA doped polyaniline-polymethylmethacrylate (PANI-PMMA) blends. The specific heat \(C\), which is related to heat capacity \(c\) as 
\[
C = c/(m/M)
\]
with \(m\) and \(M\) being the sample mass and molecular mass, respectively, was represented at low temperatures by the expression 
\[
C = A + \gamma T + \beta T^3
\]
for PANI and by the expression 
\[
C = \gamma T + \beta T^3
\]
for PANI-PMMA blends; here, \(\gamma T\) and \(\beta T^3\) are the electronic and lattice contributions, respectively, to specific heat. Since \(\gamma\) is related to the density of states at the Fermi level as \(N(E_F)\) (in states/eV·mole) \(= 0.212\gamma\) (in mJ/mole·K²), analysis of the specific-heat data gave \(N(E_F)\) values of 3 states/(eV·2 rings) for PANI, 17 states/(eV·2 rings) for PANI(40%)-PMMA(60%) (abbreviated as PP4060), and 17 states/(eV·2 rings) for PANI(33%)-PMMA(67%) (abbreviated as PP3367). These heat-capacity obtained values of \(N(E_F)\) were then compared with those obtained by another group from magnetic susceptibility \((\chi)\) measurements using the relation 
\[
N(E_F) = \chi_P/\mu_B^2
\]
where \(\chi_P\) is Pauli susceptibility and \(\mu_B\) is Bohr magneton. While the agreement between the \(N(E_F)\) values obtained from these two different techniques was semiquantitative for PP4060 and PP3367, magnetic susceptibility obtained \(N(E_F)\) for PANI was larger by a factor of 7 compared to its value from heat-capacity measurements.

The purpose of this paper is to present our own magnetic susceptibility measurements on PANI in view of the above difference between the heat capacity obtained (3 states/eV 2-rings) and the magnetic susceptibility determined (21 states/eV 2-rings) values of \(N(E_F)\). It is significant to note that a typical value of \(N(E_F)\) reported by various groups on variously synthesized PANI is around 3 states/(eV·2 rings). Two samples of PANI from two different batches and one

FIG. 1. \(\chi T\) as a function of \(T\) for two samples of polyaniline. Least-squares fit of the data is shown by lines passing through the data.

FIG. 2. \(\chi T\) as a function of \(T\) for the polyaniline-polymethylmethacrylate (40:60) blend. The line through the points shows least-squares fit of the data.
sample of PP4060 were therefore obtained from Ormecon Chemie Gmbh & Co—the same supplier of earlier samples as well. $\chi$ measurements were made at 5 kG with a “force” magnetometer on PANI and PP4060 samples, which were pressed in the form of a parallel pipe and had a mass in the range 80–100 mg. The pressed samples were attached directly to a fine quartz fiber, whose other end connected to the electromicrobalance for force measurements; this arrangement avoided applying any addendum corrections due to the sample holder.

In the free-electron model, slope and intercept of the $\chi T$ vs $T$ plot yield Pauli susceptibility ($\chi_P$) and Curie constant ($C$), respectively. Figure 1 therefore shows data in the $\chi T$ vs $T$ form for the two PANI samples. In obtaining this plot, the diamagnetic core susceptibility and the molecular mass were taken as $-203.2 \times 10^{-6}$ emu/(mole 2-rings) and 373, respectively. A simple analysis of the data shown in Fig. 1 gives the following values for $\chi_P$ and $C$: $66 \times 10^{-6}$ emu/(mole 2-rings) and 0.0037 for sample 1, and $73 \times 10^{-6}$ emu/(mole 2-rings) and 0.0059 for sample 2. $N(E_F)$ values obtained from these Pauli susceptibilities are 2.1 and 2.3 states/(eV 2-rings). These values are in disagreement with the one reported earlier, but in agreement with the value obtained from our heat-capacity measurements.

The $\chi T$ vs $T$ behavior for the PP4060 sample was also obtained which is shown in Fig. 2. Values of $-319.4 \times 10^{-6}$ emu/(mole 2-rings) and 653 were used, respectively, for the diamagnetic core susceptibility and the molecular mass in obtaining the shown behavior. The plot yields a $\chi_P$ of $420 \times 10^{-6}$ emu/(mole 2-rings) or 14 states/(eV 2-rings) for $N(E_F)$, which is in agreement with the previously reported value.

In conclusion, the results from heat-capacity and magnetic susceptibility experiments, in spite of different sensitivities of these techniques, have been shown to yield nearly the same corresponding values of $N(E_F)$ for polyaniline and polyaniline-methylmethacrylate systems. It therefore seems clear that theoretical models or experimental analyses which do not require the existence of free-electron spins or Pauli susceptibility may not correctly describe the underlying physics of systems in the polyaniline family.

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