Magnetic Susceptibility Analysis of Conducting Polymers

S. Ayesh and P.K. Kahol

Department of Physics, College of Liberal Arts and Sciences

1. Introduction

The objective of this paper is to present a model which analyzes the magnetic susceptibility results in a large number of conducting polymers. We introduce this model, called the exchange coupled spin pairs model, for the following reasons. First, the conducting polymers polyaniline, polypyrrole and their derivatives have not been studied for their structural order, although many other studies of these polymers have been completed and reported in the literature [1]. Secondly, the simple interpretation of the linear part of the χT vs. T plots in terms of Pauli susceptibility has been recently questioned [2] especially for polyaniline and other less conducting polymeric materials because most of the spins are expected to be localized. Kahol and co-workers have shown that even the measured susceptibility of undoped polyaniline exhibits a Pauli-like behaviour, in spite of the fact that the samples are insulators with a DC conductivity of the order of 10^{-10} S/cm. [1]

The exchange coupled spin pairs model provides an indirect connection between the measured magnetic susceptibility and the degree of order or disorder in the sample. This connection allows a semi-quantitative study of magnetic susceptibility based on spin interactions and structural order in conducting polymers.

2. Model, results, discussion and significance

An inhomogeneous order-disorder model, according to which ordered regions in a polymer are surrounded by disordered regions, is normally used to analyze the magnetic susceptibility results of a number of conducting polymeric systems [3]. The magnetic susceptibility is believed here to arise from free spins in the ordered regions (Pauli susceptibility) and localized spins in the disordered regions (Curie susceptibility). Because disorder localizes electron spins and the conducting polymer systems exhibit significant disorder, we have applied an exchange coupled spin pairs model [4]. The disordered regions in this model exhibit intra-pair exchange couplings varying from J_1 to J_2. The larger the difference between J_1 and J_2, the more is the disorder in the system. The severely disordered regions exhibit a constant exchange coupling J_0. A small value of J_0 corresponds to localization and hence severe disorder. On the other hand, a relatively large value of J_0 arises due to increased wave function overlap, and thus it corresponds to spin pairs in more "ordered" regions.
The exchange coupled spin pairs model contains N/2 spin pairs with a random distribution of exchange couplings in the range of J_1 to J_2 according to a particular distribution function P(J). The expression for the magnetic susceptibility can then be obtained from the following integral [4]:

$$\chi_{PM} = \left(\frac{Ng^2\mu_B{}^2 C}{k_B T}\right)\cdot\int_{J_1}^{J_2}\left[3+\exp\left(\frac{-2J}{k_B T}\right)\right]^{-1} P(J)dJ;\quad \int P(J)dJ = 1\,, \tag{1}$$

where χ_{PM} is the magnetic susceptibility for a pair of spins, T is the temperature, N is the total number of spins in the system, μ_B is the Bohr magneton, k_B is Boltzmann constant, P(J) is the distribution function, the J couplings vary from a minimum J_1 to a maximum value J_2 and g is a dimensionless scalar called g-factor which has a value of approximately 2. Assuming that the distribution function P(J) is constant, the above equation becomes:

$$\chi_{PM}T = \left(\frac{Ng^2\mu_B{}^2}{k_B}\right)\cdot\left[k_B T\ln\left|3+\exp\left(\frac{-2J}{k_B T}\right)\right|+\frac{J}{3}\right]_{J_1}^{J_2}. \tag{2}$$

While this model can provide a reasonable overall fit, it is unable to account for the low temperature behavior. We argue that a fraction x_P of the spin pairs are coupled on the average with a single (small) exchange coupling, J_0, while the rest of the spin pairs exhibit a constant distribution of exchange couplings in the range J_1 to J_2. The spin pairs with J_0 exchange couplings

exist in the severely disordered regions and we will represent their magnetic behavior through the Bleany-Bowers equation[2,4]:

$$\chi_{BB}T = \frac{Ng^2\mu_B{}^2}{k_B}\cdot\left[3+\exp\left(\frac{-2J_0}{k_BT}\right)\right]^{-1}. \qquad (3)$$

So, our measured susceptibility will have the following expression:

$$\chi T = \left(\chi_{BB}T\right)\cdot x_P + \left(1-x_P\right)\cdot\left(\chi_{PM}T\right) \qquad (4)$$

The above expression was subjected to a non-linear regression of the data [5] with a computer program. Using all the above equations and the computer program, we found parameters for the 22 different samples (doped and undoped aniline oligomers, emeraldine base form of polyaniline and derivatives, polyaniline fibers, polyaniline nanotubes, polypyrrole and derivatives). [5] These parameters are the number of spins per mole, fraction of spin pairs coupled with a single exchange coupling, the value for J_0, the fraction of spins in pairs that exhibit a distribution of interactions, and finally, the values for J_1 and J_2 . We find that the above conducting polymers have a large amount of disorder, around 70-80%. The χT vs. T graphs show that the model calculations are almost identical to the experimental data, indicating that the exchange coupled spin pairs model can be applied to all the conducting polymers presented here. A representative χT vs. T graph model behavior for polypyrrole doped with DBSA is shown in Figure 1.

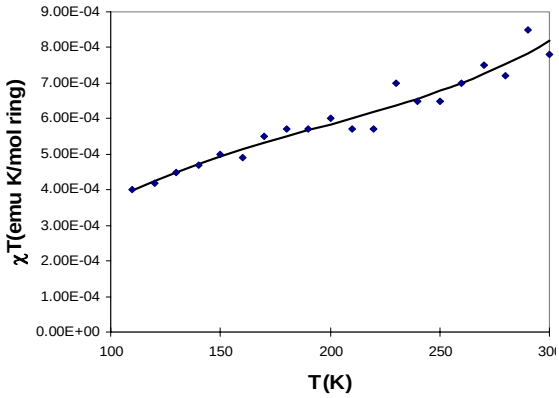

Fig.1. χT vs. T for DBSA doped polypyrrole.

3. Summary and Conclusions

The chemical and electrochemical syntheses of polymers lead to significant amount of disorder. Experiments show that the order or crystallinity in such systems is at the most fifty percent; typically, it is of the order of 10-20 percent. Because disorder localizes electron spins, we have applied an exchange coupled spin pairs model in the framework of the inhomogeneous disorder model. The model fits the experimental data well. However, given the complexity of spin interactions and the extent of disorder in conducting polymer systems, a quantitative study of the magnetic susceptibility data is still lacking.

4. References

[1] R.S. Kohlman and A.J. Epstein, in: R. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (Eds.), Handbook of Conducting Polymers, Marcel Dekker, New York, 1997, p.85.
[2] A. Raghunathan, P.K. Kahol, J. Ho, Y.Y. Chen, Y.D. Yao, Y.S. Lin, and B. Wessling, Phys. Review B58, R15955, (1998).
[3] J.M. Ginder, A.F. Richter, A.G. MacDiarmid, A.J. Epstein, Solid State Commun. 63, 97 (1987).
[4] P.K. Kahol and M. Mehring., Synthetic Metals 16, 257, (1986).
[5] S. Ayesh, MS. Thesis, Wichita State University, 2004.