Nature of paramagnetic centers in polyaniline as studied by SQUID magnetometry

A. V. Kulikov and M. N. Shishlov*

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow region, Russian Federation.
Fax: +7 (496) 515 3588. E-mail: kulav@icp.ac.ru

The temperature and field dependences of the magnetic moment of polyaniline powder doped by *m*-cresol were measured by SQUID magnetometry in the temperature range 2—300 K at 1000 Oe and in the range 0—50000 Oe at 2 K, respectively. The field dependence is not described by the Brillouin function for spin 1/2, as is expected in the framework of a commonly accepted "metallic" model. Both dependences are quite correctly described by a "triplet" model using a distribution of singlet-triplet splitting (E) with the density distribution function having a narrow peak near $E = 0$.

Key words: polyaniline, magnetic moment, SQUID magnetometry, singlet-triplet splitting.

Conducting polymers including polyaniline, polyacetylene, polythiophene, polypyrrole, poly(*para*-phenylene vinylene), *etc*. possess unusual physical properties and can be used in various fields. Practically, the emphasis is placed on the studies of their luminescence and conductivity. Investigations of the magnetic properties occupy a special position because these properties are intimately related to the nature of charge carriers and to subtle features of the polymer structure.

Often, the experimentally observed linear dependence of the product of the paramagnetic susceptibility of conducting polymers by the temperature (χT) on temperature

$$\chi T = \chi_P T + C \qquad (1)$$

allows one to divide the magnetic susceptibility into two components, *viz.*, the temperature-independent component χ_P and the component obeying the Curie law $\chi = C/T$ (see, *e.g.*, the data for polyaniline and its derivatives,[1—4] poly(ethylenedioxythiophene),[1] and polypyrrole[5]). The origin of these two components is usually explained within the framework of a "metallic" model, which treats doped conducting polymers (in the form of both powders and films) as highly ordered metallic domains "immersed" into amorphous domains. The metallic domains are associated with the temperature-independent component (the Pauli susceptibility) while defects in the amorphous domains are responsible for the Curie susceptibility.

However, a number of experimental facts do not obey the pattern mentioned above. For instance, it is unclear why the EPR lines of metallic and amorphous domains characterized by different widths do not overlap. In addition, it is difficult to explain the frequently observed nonlinear dependences $\chi T—T$ in the framework of the "metallic" model. We have proposed a "triplet" model for paramagnetic centers in conducting polymers.[6] According to this model, conducting polymers comprise relatively short periodic fragments with close values of the angles between neighboring ring planes. These fragments are separated from one another by abrupt changes in these angles, each fragment can be in the triplet or singlet state, and there is a number of fragment conformations, which leads to variation of the singlet-triplet splitting (E) over a wide range. In this case, the magnetic susceptibility can be described by an integral of the Bleaney—Bowers equation over the E distribution. For some fragments, triplets lie lower than singlets; these fragments are responsible for the Curie-like contribution to the magnetic susceptibility. In the "metallic" model, this contribution is interpreted as defects in amorphous domains. Using a rectangular density distribution having a constant value in the interval from E_1 to E_2, we have explained the temperature dependence of the magnetic susceptibility of polyaniline (see Ref. 6) and nonlinear temperature dependences $\chi T—T$ obtained for polyacetylene and a polythiophene derivative.[7]

One can decide between the "metallic" and "triplet" models by analyzing the field dependence of the magnetic moments of conducting polymers at low temperatures. If the "metallic" model is valid, mainly defects in amorphous domains should be observed at low temperatures and the field dependences should be described by the Brillouin function for the spin (S) 1/2. However, if the "triplet" model holds, the field dependences should be

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described taking into account the distribution of the singlet-triplet splitting. In this case, the field dependences cannot be described by the Brillouin functions for the spin 1/2 or 1.

As far as we know, there is a single study in which the field dependence of the magnetic moment of a conducting polymer was measured at low temperatures.[8] It was concluded that the field dependence of the magnetization of polyaniline at $T = 2$ K is described by the Brillouin function for the spin $S = 1/2$. In the text below, we will analyze the results obtained in Ref. 8 and show that this conclusion is incorrect.

In the present work, we measured the temperature and field dependences of the magnetic moment of a polyaniline powder. Approximation of the field dependence at $T = 2$ K by the Brillouin function gives $S = 0.30$, which is much smaller than the value predicted by the "metallic" model ($S = 0.5$). At the same time, the "triplet" model correctly describes both the temperature and field dependences using the distribution density with a narrow peak near $E = 0$. The "triplet" model also provides a reasonable explanation for the temperature and field dependences presented in Ref. 8.

Experimental

In choosing the polyaniline sample, we were guided by the following considerations. First, the constant C in Eq. (1) should be large; in this case, the "metallic" model predicts predominance of the Curie spin susceptibility at low temperatures. Second, molecular oxygen should not affect the EPR spectrum. Oxygen molecules ($S = 1$) can add to polymers and thus change their paramagnetic properties. SQUID magnetometry measurements are carried out in helium atmosphere; therefore, a decrease in the concentration of sorbed oxygen and some changes in the magnetic properties of the sample can occur.

Polyaniline was synthesized by oxidative polymerization at −20 °C as described earlier.[6] The precipitate of polyaniline salt was washed with an alkali and water and dried at room temperature. The polyaniline base powder thus obtained is EPR silent. The powder (25 mg) was dissolved in *m*-cresol (3 mL) over a period of a month and then dried at room temperature over a period of a month. According to published data,[9] *m*-cresol acts as a dopant, *i.e.*, protonates the polyaniline base which thus becomes a paramagnetic salt characterized by a large constant C. The powder exhibits an intense EPR signal (g-factor 2.0028, width 0.37 mT) at room temperature. The large width of the signal suggests that polyaniline chains are extended.[9] Molecular oxygen does not broaden the EPR spectrum of the doped polymer.

The magnetic moment of the polyaniline powder (23.8 mg) was measured on a Quantum Design MPMS 5XL SQUID magnetometer. Corrections for the magnetic moment of the sample holder and diamagnetism of polyaniline were applied. The molecular weight of a virtual complex comprising two aniline units and one *m*-cresol anion is 289. In the text below, this polyaniline powder is denoted as PANi(*m*-cresol)$_{0.5}$. The magnetic moment was normalized per mole of the complex ($(23.8 \cdot 10^{-3}$ g$)/289 = 8.24 \cdot 10^{-5}$ mol). The diamagnetic contribution to the magnetic susceptibility of polyaniline (with *m*-cresol anion) calculated from the Pascal rule is $-1.73 \cdot 10^{-4}$ electromagnetic units (emu) per mole of the complex.

Results and Discussion

The experimental temperature and field dependences of the magnetic moment of polyaniline powder were analyzed using the energy level scheme shown in Fig. 1. The magnetic moment M per mole of substance was calculated using the expression

$$M = \frac{g\mu_B N_A}{L} \int_{E_1}^{E_2} AF(E)dE, \qquad (2)$$

where $A = \dfrac{\exp\left(\frac{g\mu_B H}{kT}\right) - \exp\left(-\frac{g\mu_B H}{kT}\right)}{\exp\left(\frac{g\mu_B H}{kT}\right) + \exp\left(-\frac{g\mu_B H}{kT}\right) + \exp\left(\frac{E_{ZFS}}{kT}\right) + \exp\left(\frac{E}{kT}\right)}$;

g is the g-factor, μ_B is the Bohr magneton, N_A is the Avogadro constant, H is the magnetic field, k is the Boltzmann constant, $F(E)$ is the distribution density of the quantity E, E_{ZFS} is the zero-field splitting, and L is the number of the monomer units in the periodic fragment. The distribution functions used are shown in Fig. 2. $F(E) = 0$ for $E < E_1$ and $E > E_2$,

$$\int_{E_1}^{E_2} F(E)dE = 1.$$

The magnetic moment M was calculated numerically except for some cases stated below. Calculations were carried out at $g = 2.0028$. At rather small H, the following relation is valid:

$$M = \chi H,$$

where χ is the molar susceptibility.

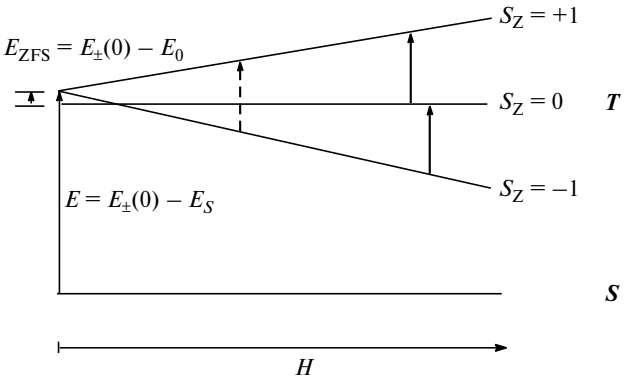

Fig. 1. Energy levels of a polymer fragment in a magnetic field, ***S*** and ***T*** denote the singlet and triplet states, respectively. E is the singlet-triplet splitting and E_{ZFS} is the zero-field splitting. Solid and dashed arrows indicate the allowed and forbidden transitions, respectively.

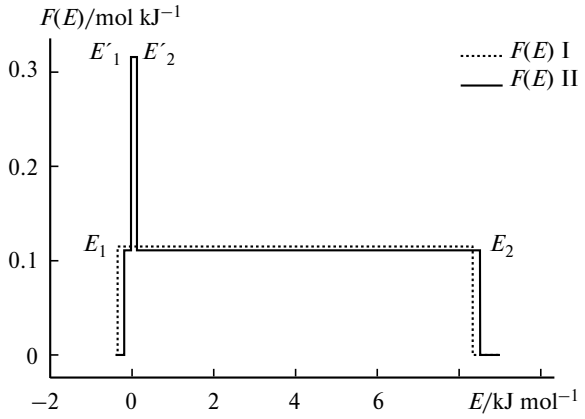

Fig. 2. The singlet-triplet splitting distribution functions ($F(E)$).

The singlet-triplet splitting E depends on the conformation of the polymer fragment and, according to quantum chemical calculations of polyaniline tetramer, varies from −10 to 30 kJ mol^{-1} (see Ref. 10).

The χT—T dependence for the polyaniline powder PANi(m-cresol)$_{0.5}$ is shown in Fig. 3. It is almost linear, as predicted by the "metallic" model; a slight deviation from linearity is observed at $T < 10$ K. This behavior of polyaniline and poly(ethylenedioxythiophene) was also reported by other authors[1,3,4] but no explanation was given. Figure 4 demonstrates the field dependence of the magnetic moment of polyaniline powder at $T = 2$ K. Experimental data are well approximated by the Brillouin formula[11]

$$B_S(\eta) \approx (S + 0.5)\mathrm{cth}[(S + 0.5)\eta] - 0.5\mathrm{cth}(\eta/2),$$

where $\eta = g\mu_B H/kT$, at $T = 2$ K, and $S = 0.30$. The best S value ($S = 0.30$) was determined using the Microcal

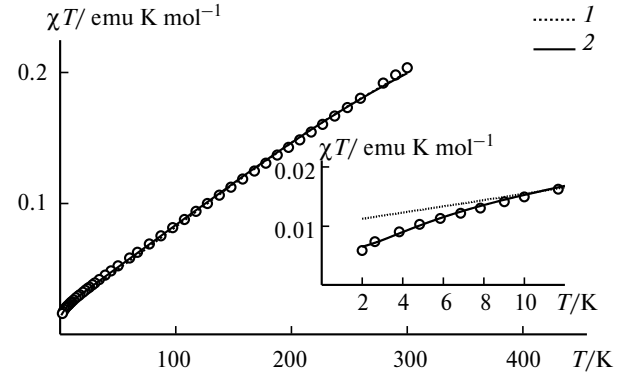

Fig. 3. Temperature dependence of χT for PANi(m-cresol)$_{0.5}$ polyaniline powder: open circles denote experimental data in the temperature interval 2—300 K at a magnetic field strength of 1000 Oe; *1* and *2* denote the results of calculations using relation (2) at $E_{ZFS} = 0$ and $L = 2$ for the distribution functions $F(E)$ I and II, respectively. The inset shows the low-temperature portion of the curve.

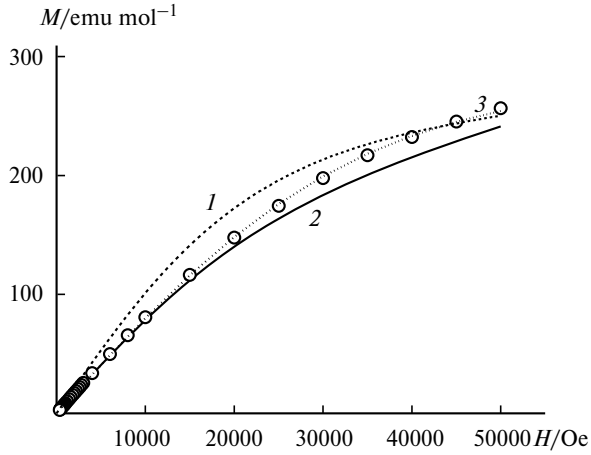

Fig. 4. The field dependence of the magnetic moment of PANi(m-cresol)$_{0.5}$ polyaniline powder at $T = 2$ K: open circles denote experimental data; *1* and *2* denote the results of calculations using relation (2) at $E_{ZFS} = 0$, $L = 2$ and $T = 2$ K for the distribution functions $F(E)$ I and II, respectively; *3* is the Brillouin function with $S = 0.30$ and $T = 2$ K.

Origin 6.0 software. This is much smaller than the value predicted by the "metallic" model ($S = 0.5$).

The dependence χT—T (see Fig. 3, experimental data) was calculated using expression (2) at $E_{ZFS} = 0$ and $L = 2$ with the rectangular distribution function $F(E)$ I (Fig. 2). The E_1 and E_2 values for this function (see Table 1) were determined as follows. At $E_{ZFS} = 0$, $T > 2$ K, and $H = 1000$ Oe, the integrand in relationship (2) is similar to the known Bleaney—Bowers function and in the case of rectangular distribution the integral can be calculated in explicit form reported earlier.[6] Using this explicit form of the integral with $L = 2$ and the Microcal Origin 6.0 software, we processed the experimental data and determined the values E_1 and E_2. According to the "triplet" model, L can take only even values. Approximation with $L = 4$ poorly describes the experimental data. The polyaniline monomer unit comprises two benzenoid rings; therefore, at $L = 2$ the polymer chain fragment includes four rings. Expression (2) with the distribution density I (see Table 1) poorly describes both the temperature dependence of the magnetic susceptibility at $T < 10$ K (see Fig. 3) and the field dependence (see Fig. 4).

Table 1. Parameters of the distribution function

$F(E)$	$-E_1$	E_2	E_1'	E_2'	Area under narrow peak
	kJ mol^{-1}				
I	0.351	8.337	—	—	—
II	0.192	8.52	0.023	0.122	0.030
III	0.415	13.7	0.022	1.37	0.042

* E is the singlet-triplet splitting of the main rectangular function (E_1 and E_2) and the narrow peak (E_1' and E_2') (see Fig. 2)

Table 2. Experimental S values and results of calculations using relation (2) for the field dependences at $T = 2$ K

Sample	S				
	Experiment	$E_{ZFS} = 0^a$			$E_{ZFS} = 15^{a,b}$
		$F(E)$ I	$F(E)$ II	$F(E)$ III	
PANi(m-cresol)$_{0.5}$	0.30	0.83	0.35	—	0.24
PANi(DEHESSA)$_{0.5}$	1.14	—	—	0.72	—

[a] The E_{ZFS} values are given in J mol^{-1}.
[b] Calculated using the rectangular distribution function $F(E)$ with $E_1 = -0.4$ and $E_2 = 0.85$ kJ mol^{-1}

For convenient comparison of the accuracy of different approximations of the field dependences, the results obtained were approximated by the Brillouin function at $T = 2$ K (Table 2). The accuracy of this procedure can be evaluated by comparing the S values for the experimental and theoretical dependences; the closer the corresponding values the higher the accuracy.

The marked deviation of the χT—T dependence from linearity at $T < 10$ K can be explained as follows. Earlier,[6] the temperature dependences were reported for the χT quantity calculated as the Bleaney—Bowers integral over the singlet-triplet splitting distribution for a rectangular distribution function from E_1 to E_2. If $E_1 = 0$ and $E_2 \approx 0.1$ kJ mol^{-1}, the product χT rapidly increases from zero and reaches a maximum as T increases from 0 to 10 K. Therefore, the distribution function was assumed to be the sum of two rectangular distribution functions of which one is narrow and $E_1 \approx 0$. We thus determined the parameters of the distribution function $F(E)$ II at which expression (2) correctly describes the temperature behavior of χT in the whole temperature interval (see Table 1 and Fig. 2). Relationship (2) used with this distribution function correctly describes both the temperature dependence χT—T at all temperatures including the interval $T < 10$ K (see Fig. 3) and the field dependence (see Fig. 4 and Table 2).

The theoretical field dependence is similar in shape to the experimental dependence, the corresponding values being only about 10% smaller in amplitude. The E distribution function is determined by the approximation of the temperature dependence of the absolute value of χT and is thus affected by the errors in determination of the sample weight, molecular weight, and diamagnetic correction; as a consequence, this introduces errors in calculations of the field dependence using relation (2).

Significant deviation of the dependence χT—T from linearity at $T < 10$ K can also be explained in another manner. Up to this point, we assumed $E_{ZFS} = 0$ in relation (2). When using a rectangular distribution function with $E_1 = -0.4$ kJ mol^{-1} and $E_2 = 8.5$ kJ mol^{-1}, expression (2) at $E_{ZFS} = 15$ J mol^{-1} and $L = 2$ correctly describes both the dependence χT—T in the whole temperature interval and the field dependence (see Table 1). These parameters were determined using the trial and error method. However, the E_{ZFS} value is too large and does not agree with EPR data. The lack of half-field forbidden transitions and EPR line splitting (see Fig. 1) suggests that the zero-field splitting is less than 1 mT, or 0.01 J mol^{-1} (see Refs 6 and 9).

Earlier,[8] the temperature and field dependences for films of polyaniline doped with bis(2-ethylhexyl)-sulfosuccinate ($C_{20}H_{38}O_7S$ (DEHESSA)$_{0.5}$) were measured (see Figs 5 and 6). The plots from Ref. 8 were digitized using the Graph Digitizer 1.8 software. The magnetic moment and susceptibility normalized[8] per gram were recalculated with per mole assuming that the molecular weight of a virtual complex comprising two aniline units and one DEHESSA ion is 604.

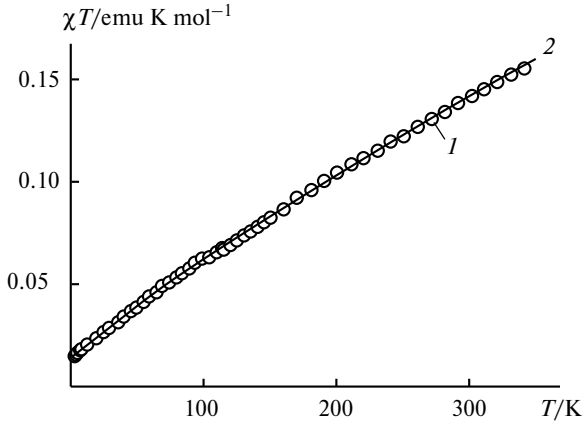

Fig. 5. Temperature dependence of χT for PANi(DEHESSA)$_{0.5}$. Open circles denote experimental data (see Ref. 8); the solid line denotes the results of calculations using relation (2) at $E_{ZFS} = 0$ and $L = 2$ for the distribution function $F(E)$ III.

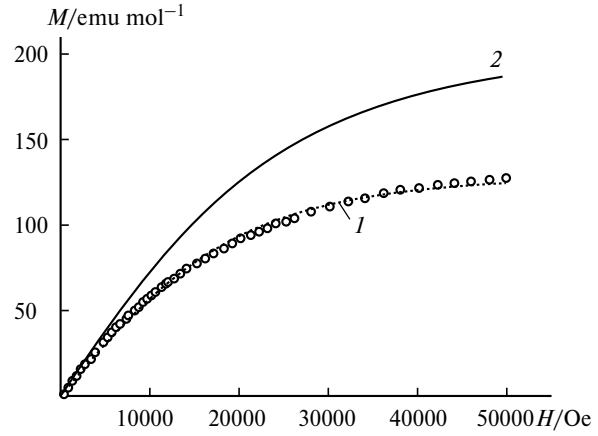

Fig. 6. The field dependence of the magnetic moment of PANi(DEHESSA)$_{0.5}$ film at $T = 2$ K: Open circles denote experimental data (see Ref. 8); *1* is the Brillouin function for $S = 1.14$; *2* denotes the results of calculations using relation (2) at $E_{ZFS} = 0$ and $L = 2$ for the distribution function $F(E)$ III.

The field dependence shown in Fig. 6 was approximated[8] by the Brillouin function for $S = 0.5$; however, in that case the μ_B was forcedly increased by a factor of 1.5. Ignoring this quite unusual admission, the field dependence is described by the Brillouin function for $T = 2$ K and $S = 1.14$ (see Fig. 6 and Table 1).

The dependence $\chi T—T$ is well described by expression (2) with the sum of two rectangular distribution functions $F(E)$ III (see Fig. 5 and Table 1). Approximation of the field dependence by relation (2) with this distribution function is shown in Fig. 6. The differences between the experimental data and results of calculations for PANi(DEHESSA)$_{0.5}$ are larger than for PANi(*m*-cresol)$_{0.5}$. This can be due to various reasons. For instance, it is unclear whether the corrections for diamagnetism of the sample and sample holder were applied. These corrections are significant in high fields and calculations ignoring them may lead to an increase in the parameter S of the Brillouin function. Our analysis shows that the "triplet model" correctly describes the temperature dependence of the magnetic susceptibility and reasonably describes the field dependence of the magnetization of PANi(DEHESSA)$_{0.5}$.

Conclusion

Summing up, we have shown that the "triplet" model provides a better description of the dependence of the magnetic moment of doped polyaniline powder at 2 K. Approximation of the field dependence by the Brillouin function gives a spin value of 0.30, which is much smaller than the value $S = 0.5$ predicted by the "metallic" model. At the same time, the "triplet" model without zero-field splitting correctly describes both the temperature and field dependences if one uses the singlet-triplet splitting distribution density with a narrow peak near $E = 0$.

The field and temperature dependences are correctly described using a rectangular distribution with a zero-field splitting of 15 J mol^{-1}; however, the large splitting contradicts the EPR data.

The "triplet" model satisfactorily describes the field dependence for the PANi(DEHESSA)$_{0.5}$ film.[8]

Note that in the "metallic" model the ratio of the temperature-independent component to the Curie component of the paramagnetic susceptibility is an experimental fact, whereas the "triplet" model provides a unified explanation for not only these components, but also the nonlinear character of the temperature dependence $\chi T—T$ at $T < 10$ K.

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