

Triplet Paramagnetic Centers in Conducting Polymers – Study by ESR and SQUID

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1. Introduction

Conducting polymers, *viz.*, polyaniline, polyacetylene, polypyrrole, polythiophene, polyphenylene, and many others, are interesting due to their unusual physical properties and a possibility of their diverse practical use. Researchers pay attention mainly to studies of luminescence and conductivity and their applications in microelectronic devices, photodiodes, sensors, batteries, technological membranes, *etc.* Magnetic properties are of a special interest, being tightly related to the nature of charge carriers and to fine features of polymer structure.

The frequently observed experimental linear temperature dependence of the product of magnetic susceptibility by temperature

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

makes it possible to divide the susceptibility into two components: the temperature-independent part χ_P and the part obeying the Curie law $\chi = C/T$ (see, *e.g.*, data for polyaniline (Wang et al., 1992; Ranganathan et al., 1999; Kahol et al., 2005a), polythiophene (Kahol et al., 2005a), and polypyrrole (Joo et al., 2001)). The origin of these two components is usually explained within the framework of the "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, some experimental facts do not obey this scheme. (i) It is natural to expect that ESR lines of defects and metallic regions are of different widths but, in most cases, ESR lines of conducting polymers exhibit no superposition of the lines with different widths. (ii) Magnetic susceptibility is observed for both doped and undoped polymers (with odd and even number of electrons per polymer units), and in some cases, the $\chi T - T$ plots are not linear, *i.e.*, the susceptibility cannot be presented as the sum of two components: the Pauli and Curie susceptibilities. For instance, some samples of undoped polyaniline possess a weak susceptibility with the nonlinear $\chi T - T$ dependence (Kahol et al., 2004a). Polyacetylene and polythiophene demonstrate unusual magnetic properties. Polyacetylene (Ikehata et al., 1980; Masui et al., 1999) has a weak susceptibility in both doped and undoped states with the nonlinear $\chi T - T$ dependence. The magnetic properties of polythiophene depend on the nature of substituents in the ring. The susceptibility of undoped

polythiophene is low and increases upon doping (Chen et al., 1986), whereas the susceptibility of undoped alkyl -substituted polythiophenes is high and decreases upon doping (Colaneri et al., 1987; Čík et al., 2005), and the $\chi T - T$ plots are nonlinear in many cases. (iii) There is no correlation between the degree of crystallinity and the value of χ_p .

The existence of the Pauli susceptibility is considered to serve as a strong argument in favor of the metallic regions. However, many data show nonmetallic character of conductivity. It is asserted (Lee et al., 2006) that metallic polyaniline was first synthesized only in 2006.

If conducting polymers are nonmetals, we should search for another interpretation of the frequently observed linear dependences $\chi T - T$. The linear dependence $\chi T - T$ for undoped polyaniline and doped polyaniline with low conductivity has earlier been explained by the model of exchange - coupled polaron pairs (Kahol et al., 2004a; Kahol et al., 1999; Ranghunathan et al., 1998). The integration of susceptibility of antiferromagnetically bound pairs over broad distribution of the exchange interaction (from 0 to a maximum, with a constant weight) was shown to give the quasi-Pauli susceptibility. The ground state of these pairs is singlet, the singlet-triplet splitting is determined by the value of exchange interaction. This model can also explain the nonlinear $\chi T - T$ dependences and requires high values of the exchange interaction, up to 1000 K. In our opinion, these values are unrealistically high. We have previously shown (Kulikov et al., 2005) that the maximum known value for the exchange interaction (~ 1 K) is observed for distance between polyaniline chains of ~ 0.6 nm. We believe that the model of exchange - coupled polaron pairs remains valid under suggestion that the singlet-triplet splitting is not caused by the exchange interaction between two isolated centers, but it is a property of a particular polymer fragment, for example, tetramer, and cannot be interpreted as a result of the interaction of isolated spins. Our quantum chemical calculations of tetramer dication showed (Kulikov et al., 2007a) that for different conformations the singlet-triplet splitting can vary from -10 to $+30$ kJ mol $^{-1}$ (from -1000 to 3000 K). The authors (Kahol et al., 2004a; Kahol et al., 1999; Ranghunathan et al., 1998) decided that their model cannot be applied to high-conducting polymers, because both ESR and measurements of the low-temperature thermal capacity give close values for the density of electron states at the Fermi level (Kahol et al., 2005a,b). This conclusion seems unreliable because of difficulties in separating the thermal capacities of lattice and electrons due to an unclear anomaly of the temperature dependence of the thermal capacity at 2 K.

To explain all features of magnetic properties of conducting polymers, we proposed the "triplet" model and confirmed it by an analysis of our and literature data obtained by ESR and SQUID (Kulikov et al., 2007b, 2008, 2010a,b, 2011). According to the "triplet" model, conducting polymers consist of fragments only in singlet or triplet state (no doublet states) with wide distribution of the singlet-triplet splitting, and magnetic properties of conducting polymers are described by an integral of fragment magnetization over this distribution.

This Chapter is a mini-review of our papers (Kulikov et al., 2005, 2007a,b, 2008, 2010a,b, 2011). The most convincing confirmation of the "triplet" model gives an analysis of the dependence of magnetization of polymers at helium temperatures on magnetic field. Most of the field dependences are simulated by the Brillouin function with spin $S \approx 1$, whereas the widespread "metallic" model predicts $S = 1/2$.

2. The "triplet" model of paramagnetic centers in conducting polymers

We suppose that conducting polymers consist of fragments with close angles between the planes of adjacent rings. The fragments are separated from each other by sharp changes in these angles, and there is a set of conformations of these fragments resulting in variation of

the singlet–triplet splitting in a wide range (Kulikov et al., 2007a). The authors (Misurkin et al, 1994, 1996) pioneered in concluding that chains of conducting polymers are divided by chain defects into conjugated fragments of a final length. A hypothesis about the triplet nature of paramagnetism in conducting polymers was advanced in papers (Berlin et al., 1972; Vinogradov et al., 1976). Fragmentary structure of polythiophene was proposed (see (Čík et al., 2005) and references cited therein), according to which the polymer consists of fragments with parallel adjacent rings, and the coplanar character of the rings is violated by their turns relative to each other.

In our “triplet” model, the temperature and field dependences of magnetization of conducting polymers are analyzed on the basis of the scheme of energy levels shown below.

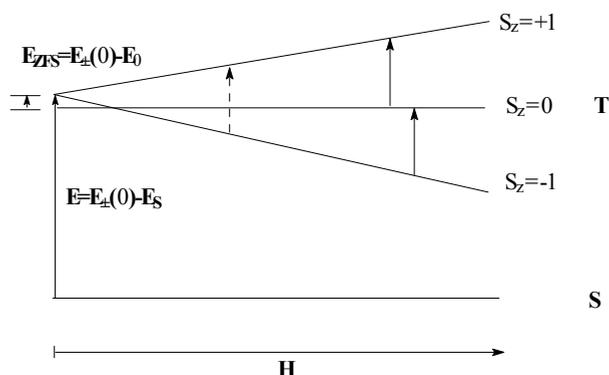


Fig. 1. Energy levels of a polymer fragment in magnetic field H . S and T denote singlet and triplet states, E is the singlet-triplet splitting, E_{ZFS} is the zero-field splitting, arrows show two allowed and one forbidden ESR transitions (Kulikov et al., 2008).

Magnetization (or magnetic moment) M of one mole of polymer elementary units is calculated by equation

$$M = \frac{g\mu_B N_A}{L} \int_{E_1}^{E_2} \frac{\exp(\frac{g\mu_B H}{kT}) - \exp(-\frac{g\mu_B H}{kT})}{\exp(\frac{g\mu_B H}{kT}) + \exp(-\frac{g\mu_B H}{kT}) + \exp(\frac{E_{ZFS}}{kT}) + \exp(\frac{E}{kT})} F(E) dE \quad (2)$$

where g is g -factor, μ_B is the Bohr magneton, N_A is the Avogadro number, H is magnetic field, k is the Boltzmann constant, $F(E)$ is the density of distribution of E , L is the number of polymer elementary units in polymer fragments. If $g\mu_B H/kT \ll 1$, $M = \chi H$, where χ is susceptibility.

Eq. (2) is easily derived on the basis of the scheme of energy levels if to take into account the Boltzmann distribution of level populations. Eq. (2) includes the length of fragments L (in elementary units). As a rule, the experimentally measured magnetization and susceptibility are normalized on one mole of elementary units of polymers; for instance, the unit of polyaniline holds two benzene rings. The susceptibility of fragment depends only on E and is independent of L . Therefore, with the increase in L the number of moles of fragments decreases and, hence, the susceptibility decreases.

The results of calculation of χT vs. T by Eq. (2) are shown in Fig. 2. The uniform function $F(E)$, which is constant between E_1 and E_2 and zero at other values of E , was used. Fig. 2

shows both linear and nonlinear curves, resembling experimental ones. At negative E_1 values, the plots are close to straight lines, and both the susceptibility components, the temperature-independent component and that obeying the Curie law, are described in the unified manner. It becomes clear why ESR lines do not reveal in most cases the superposition of two lines with different widths: both the components are of the same triplet nature. The nonlinear $\chi T - T$ dependences correspond to the case of $E_1 > 0$. The integral in Eq. (2) can be taken in the explicit form, if the uniform (rectangular) distribution function $F(E)$ is used and $g\mu_B H/kT \ll 1$ and $E_{ZFS}=0$. The explicit expression of the integral facilitates simulation of experimental data; curves in Fig. 2 were calculated by this expression. Qualitatively the same dependences, obtained for the uniform distribution of the E value and presented in Fig. 2, can be obtained numerically for the Gaussian distribution of E . Below all simulations by Eq. (2) are carried out at $E_{ZFS}=0$. For paramagnetics with $S \geq 1$ the nonzero value of E_{ZFS} results in the splitting of allowed ESR lines and arising of the weak forbidden ESR line at the half-field (see Fig. 1). The lack of the half-field forbidden transition and ESR line splitting (see Fig. 1) suggests that the zero-field splitting is less than 1 mT, or 0.01 J mol^{-1} (Kulikov et al., 2005, 2007a, 2010b).

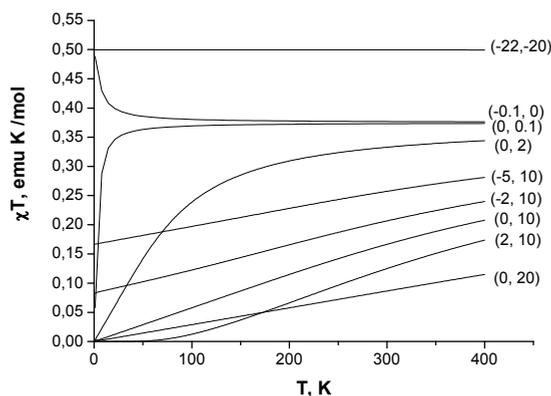


Fig. 2. Temperature dependences of the product χT calculated by Eq. (2) at $L=2$, $E_{ZFS}=0$ and the uniform function $F(E)$ with different values of E_1 and E_2 given in parentheses in kJ/mole (Kulikov et al., 2008).

3. Analysis of temperature dependences of magnetic susceptibility of conducting polymers in the framework of the “triplet” model

This part contains an analysis of our (Section 3.1) and literature (Section 3.2) temperature dependences for conducting polymers in the framework of the “triplet” model.

3.1 Effect of synthesis features, gases and heating on solutions and powders of polyaniline salts

The temperature plots of χT for polyaniline solution in *m*-cresol before and after heating at 423 K are presented in Fig. 3. The emeraldine base was dissolved during a month, and polyaniline transformed into the doped (protonated) form PANi(*m*-cresol)_{0.5} (Kulikov et al., 2005). In Fig. 3, 4 and 5 the triangles oriented down, up, and sideways correspond to temperature decrease from 293 K to minimum, then to increase to 423 K, and to return to

room temperature, respectively. ESR line of the solution shows no superposition of two lines and the line width is ~ 1 mT, which (according to (Kulikov et al., 2005)) indicates unfolded chain conformation. Characteristics of the solution remain unchanged for many months. Thus, this is a true solution of unfolded chains containing no metallic regions. Nevertheless, the linear dependence (see Fig. 3, plot 1) is observed below room temperature, and according to Eq. (1), one could formally determine $\chi_P = 1.2 \times 10^{-4}$ emu mol $^{-1}$ and the number of Curie spins (~ 0.1) per one elementary unit containing two benzene rings. The small temperature hysteresis near room temperature and the decrease in the susceptibility on heating above this temperature can be explained in the framework of the spin crossover phenomenon (Kulikov et al., 2007a). The freezing point of m-cresol is 8–10 °C.

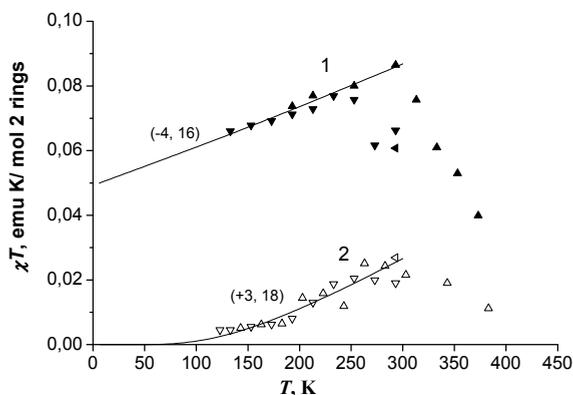


Fig. 3. Temperature dependences of χT for solution of polyaniline in m-cresol before (1) and after (2) heating at 423 K. Solid lines were calculated by Eq. (2) for $L = 4$ and the E_1 and E_2 values given in parentheses. The values of χ were measured by ESR (Kulikov et al., 2008).

After heating of the solution for 15 min at 423 K, the susceptibility decreases and the temperature dependence below room temperature becomes nonlinear (see Fig. 3, plot 2). After heating, the susceptibility returns at room temperature slowly (for 1 month) to the initial value (Kulikov et al., 2007a).

The nonlinear dependences cannot be explained in the framework of the "metallic" model. Plots 1 and 2 in Fig. 3 can naturally be explained in the framework of the "triplet" model. The heating changes conformations of fragments and, as a consequence, changes the distribution of the singlet–triplet splitting. Solid lines in Fig. 3 were calculated by Eq. (2) for $L = 4$ and the E_1 and E_2 values given in parentheses. The heating increases E_1 from -4 to $+3$ kJ mol $^{-1}$ at an almost unchanged E_2 value (16 and 18 kJ mol $^{-1}$).

If experimental $\chi T - T$ plots are nonlinear, all parameters of the "triplet" model, E_1 , E_2 and L , can be determined from approximation of $\chi T - T$ plots by Eq. (2) (Kulikov et al., 2008). For polyaniline, L is 2–4; these values are close to values $L=2-6$ determined for polyaniline by the method of thermodestruction (Ivanov, 2007).

The plot $\chi T - T$ for powder of doped polyaniline PANi(ClO $_4$) $_{0.5}$ synthesized at -20° C is given in Fig. 4. The plot *in vacuo* differs from that in air. This can be explained by the change in the distribution of the singlet–triplet splitting after adsorption of dioxygen on the polymer.

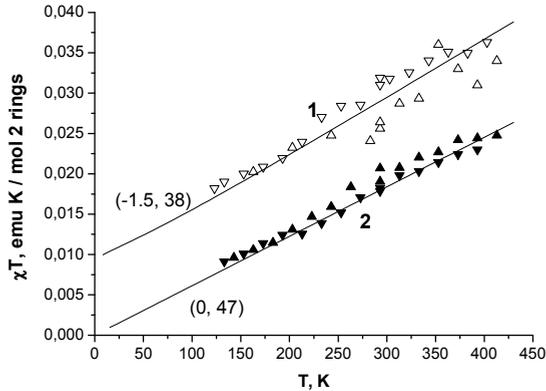


Fig. 4. Temperature dependences of the product χT for powder of doped polyaniline PANi(ClO₄)_{0.5} *in vacuo* (1) and in air (2). PANi was synthesized at -20° C. Solid lines were calculated by Eq. (2) for $L=4$ and values of E_1 and E_2 given in parentheses. The values of χ were measured by ESR (Kulikov et al., 2008).

Fig. 5 shows $\chi T - T$ plots *in vacuo* and in air for PANi(ClO₄)_{0.5} synthesized at room temperature. These plots differ from those shown in Fig. 4. Thus, synthesis conditions affect the conformations of polyaniline fragments and, as a consequence, the distribution of the singlet – triplet splitting.

Plot 1 in Fig. 5 is nonlinear and cannot be simulated by Eq. (2). Plot 1 can be explained under assumption that for 3% of polymer fragments E_1 and E_2 values are negative and much lower than kT , and for remaining fragments E_1 and E_2 are 6 and 35 kJ mol⁻¹, respectively (at $L = 4$). In other words, we assume that the distribution of singlet-triplet splitting $F(E)$ is the sum of two rectangular functions. This kind of the distribution function was used also for simulation of $\chi T - T$ plots measured by SQUID (see below). Plot 2 in Fig. 5 measured in air is linear and can be simulated by Eq. (2) at $L = 4$, $E_1 = 0$, and $E_2 = 27$ kJ mol⁻¹.

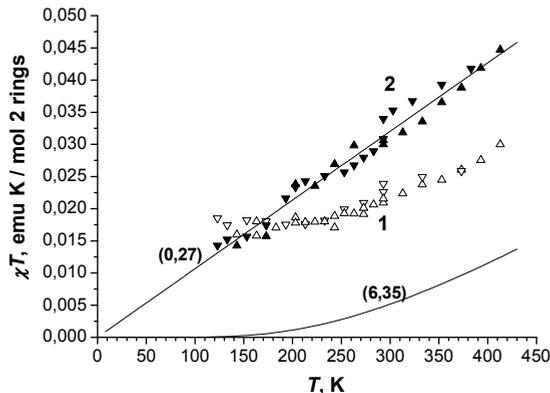


Fig. 5. Temperature dependences of the product χT for powder of PANi(ClO₄)_{0.5} *in vacuo* (1) and in air (2). PANi was synthesized at room temperature. Solid lines were calculated by Eq. (2) for $L = 4$ and the E_1 and E_2 values indicated in parentheses. The values of χ were measured by ESR (Kulikov et al., 2008).

3.2 Literature temperature dependences for polythiophene and polyacetylene

Fig. 6 shows analysis of data (Šeršeň et al., 1996) on susceptibility of poly(3-dodecylthiophene) in the framework of our model. The authors assumed that the polymer consists of fragments, susceptibility of each fragment obeys the Curie law, but the number of fragments decreases with decreasing temperature due to recombination of fragments. They succeeded in good approximation of experimental data by formula $\chi \sim \sum \exp(-E_i/kT)/T$ (solid line in Fig. 6a). However, their model is not realistic because the twist of thiophene rings required for recombination of fragments is improbable in films at low temperatures. Eq. (2) with $E_1=0.7$ kJ/mol, $E_2=8.2$ kJ/mol and $L=78$ describes well their data (solid lines in Fig. 6b). Uncertainties in values of E_1 , E_2 and L are given in Fig. 6b. Our model does not require temperature changes in chain conformation.

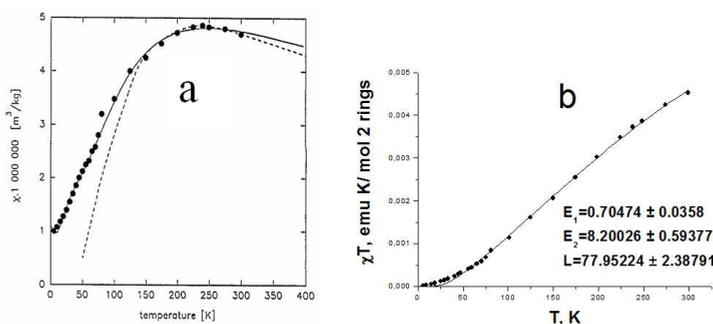


Fig. 6. Temperature dependence of magnetic susceptibility of film of poly(3-dodecylthiophene). (a) The dependence χ - T taken from (Šeršeň et al., 1996). (b) Simulation of this dependence in coordinates χT - T by Eq. (2) (Kulikov et al., 2007b). The values of E_1 and E_2 are given in kJ mol⁻¹. The values of χ were measured by a magnetometer.

Fig. 7 shows analysis of data (Masui & Ishiguro, 2001) on susceptibility of *v*-trans-polyacetylene in the framework of our model. The authors explain the appreciable “spin gap” below 200 K by “spin-charge separation”. Our analysis (Fig. 7b) did not reveal any phase transitions. It is worthwhile to mention that for all doping degrees except 6.6% the ESR lines are Lorentzian, without indications of superposition of lines from metallic and amorphous regions.

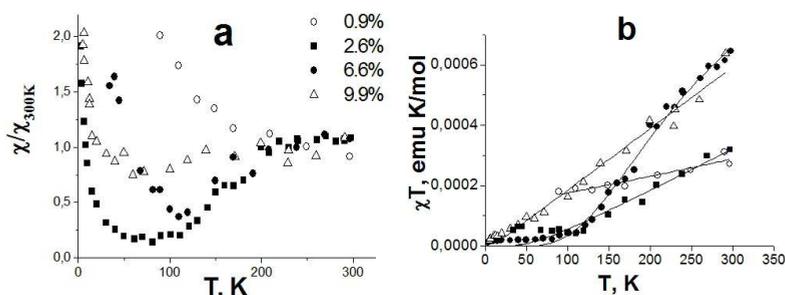


Fig. 7. Temperature dependences of magnetic susceptibility of *v*-trans-polyacetylene at various degrees of doping. (a) Data taken from (Masui & Ishiguro, 2001). (b) Simulation of these data by Eq. (2) with parameters given in Table 1 (Kulikov et al., 2007b). The values of χ were measured by ESR.

Uncertainties of the parameters for polyacetylene are not given in Table 1; they are much higher than those for polythiophene because the experimental data are of bad quality and some plots in Fig. 7b are close to straight lines.

Doping, %	E_1 , kJ/mol	E_2 , kJ/mol	L
0.9	-2.4	145	126
2.6	1.2	87	94
6.6	4.1	4.3	540
9.9	0.2	88	64

Table 1. Parameters of Eq. (2) used for simulation of data in Fig. 7b.

4. Analysis of field dependences of magnetization of polyaniline and polypyrrole in the framework of the "triplet" model

Combined measurement of temperature and field dependences of magnetization is a severe exam for the "triplet" model. 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 the unified explanation for these components by Eq. (2). One can decide between the "metallic" and "triplet" models by analyzing the field dependence of magnetization of conducting polymers at low temperatures. If the "metallic" model is valid, mainly defects in amorphous domains should be observed at low temperatures because the Curie component increases at lowering temperature as $1/T$, and the field dependences at helium temperature should be described by the Brillouin function (see, for instance, (Carlin et al., 1986)) with spin $S=1/2$:

$$M(\eta) \sim (S+0.5) \text{cth}[(S+0.5)\eta] - 0.5 \text{cth}(\eta/2) \quad (3)$$

where $\eta = g\mu_B H/kT$.

However, if the "triplet" model holds, the field dependences should be described taking into account the distribution of the singlet-triplet splitting. In this case, the field dependences may be described by the Brillouin functions with $S \leq 1$.

The $\chi T - T$ dependence for the polyaniline powder PANi(m-cresol)_{0.5} is shown in Fig. 8. It is almost linear, as predicted by the "metallic" model; a slight deviation from linearity is observed at $T < 10$ K. This deviation was also reported by other authors for polyaniline and poly(ethylenedioxythiophene) (Kahol et al., 2004b, 2005a; Sitaram et al., 2005) but no explanation was given. Figure 9 demonstrates the field dependence of magnetization of polyaniline powder PANi(m-cresol)_{0.5} at $T = 2$ K.

Data in Fig. 8 and 9 were corrected for the diamagnetic core by Pascal rules (see, for instance, (Carlin, 1986; Selwood, 1956)).

The temperature dependence of χT is rather well simulated by Eq. (2) (Fig. 8, solid line). To achieve a good simulation of experimental data at $T < 10$ K, the distribution function $F(E)$ was chosen as the sum of two rectangular functions. Parameters of the distribution function were determined automatically by the Microcal Origin software.

The field dependence given in Fig. 9 is well simulated by the Brillouin functions with $S=0.30$ (not shown). This value of S is smaller than predicted by the "metallic" model ($S=1/2$). The theoretical field dependence (solid line) is similar in shape to the experimental one, and only by $\sim 10\%$ smaller in amplitude. Note that absolute (not relative) values of χT and M were calculated in Fig. 8 and 9 by Eq. (2).

The value $S=0.3$ is rather close to $S=1/2$ predicted by “metallic” model, and this looks not very convincing, therefore we continued our experiments and searched for field dependences in literature.

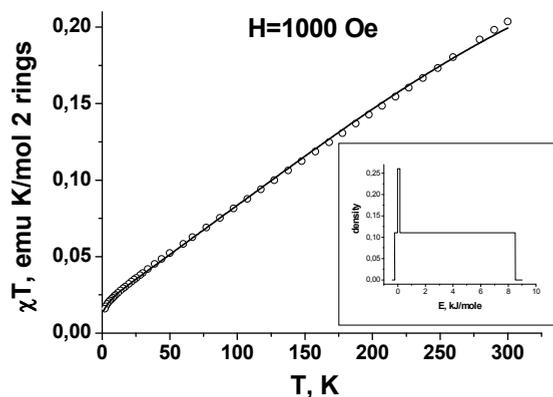


Fig. 8. Temperature dependence of χT for PANi(m-cresol)_{0.5} polyaniline powder. Open circles are experimental data, solid line is the simulation of experimental data by Eq. (2) at $E_{ZFS} = 0$ and $L = 2$ for the distribution function $F(E)$ shown in the Insert. The values of χ were measured by SQUID (Kulikov et al., 2010b).

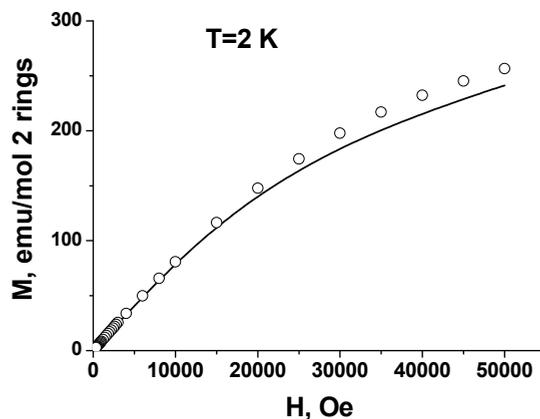


Fig. 9. The field dependence of magnetization of polyaniline powder PANi(m-cresol)_{0.5} at $T = 2$ K. Open circles are experimental data; solid line is simulation by Eq. (2) at $E_{ZFS} = 0$, $L = 2$ and $T = 2$ K for the same distribution function $F(E)$, as in Fig. 8. The values of M were measured by SQUID (Kulikov et al., 2010b).

At present, we know only four field dependences of magnetization at low temperatures for conducting polymers. Fig. 10 shows two our measurements for polyaniline (including one given in Fig. 9), and two literature data for polyaniline and polypyrrole. Results of simulation of these field dependences by the Brillouin function are given in Table 2. Three field dependences are simulated by the Brillouin function with $S \approx 1$, and one our previous

measurement is simulated with $S=0.3$. We think that this is a strong evidence in favor of the “triplet” model. In the frame of this model, the value of S is close to 1, if the share of polymer fragments with ground triplet levels ($E<0$) is high. Note that the “triplet” model can also explain the value $S=0.3$.

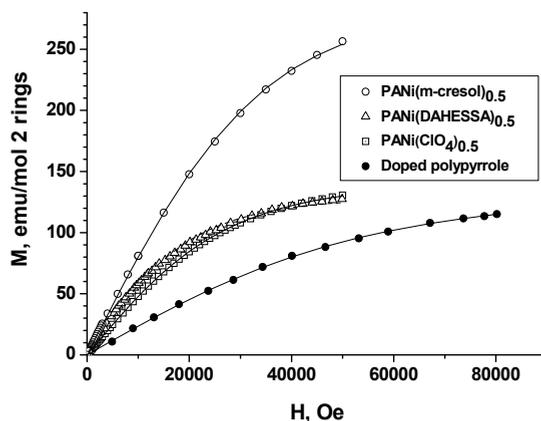


Fig. 10. Field dependences of magnetization for powders of polyaniline and polypyrrole at helium temperatures. Solid lines are simulation of the experimental results by the Brillouin function. Temperatures of measurements, values of S and references are given in Table 2. All data were obtained by SQUID. This Figure can be found in (Kulikov et al., 2010a, 2011).

Sample	Temperature, K	S	Reference
PANi(m-cresol) _{0.5}	2.0	0.30	Kulikov et al., 2010b
PANi(DAHESSA) _{0.5}	2.0	1.15	Djurado et al., 2008
PANi(ClO ₄) _{0.5}	2.6	1.05	Kulikov et al., 2011
Doped polypyrrole	5.0	1.01	Long et al., 2006

Table 2. Parameters of the Brillouin function used for simulation of data in Fig. 10.

The authors of paper (Djurado et al., 2008) were sure that the “metallic” model is true, and simulated the field dependence for polyaniline by the Brillouin function with $S=1/2$, but they were forced to increase the Bohr magneton by a factor of ≈ 1.5 . If do not make this strange increase of the universal constant, the field dependence is simulated with $S=1.15$. This value is a little bit higher than 1, maybe because the authors did not correct their data for the diamagnetic core. The field dependence for polypyrrole (Long et al., 2006) was not simulated by the authors.

5. Problems of the “triplet” model

Conducting polymers show no forbidden half-field ESR line and no splitting of allowed ESR lines which are typical for triplet states. Thus, for these polymers the zero-field splitting is small. Forty years ago it was explained qualitatively by the triplet state delocalization (Berlin et al., 1972). At present, the value of E_{ZFS} can be calculated by methods of quantum chemistry. We tried to calculate this splitting for doped tetramer and octamer of polyaniline by software package ORCA (Kulikov et al., 2011). It is known that magnetic properties of

doped conducting polymers depend on the nature of counter-anions (Long et al., 2006), therefore we added to structures of tetramer and octamer two or four various counter-anions respectively and carried out calculations for zero net charge of these complexes. Unfortunately, the optimization procedure for these complexes without covalent bonds oligomer-counteranions was not converged.

Experimental data, for instance values of $S \approx 1$ for majority of samples, show that there is no fragments in doublet state, *i. e.*, all fragments contain even number of electrons. Maybe, the absence of fragments with odd number of electrons is due to instability of polymer structure like the Peierls instability. The Peierls' theorem states that a polymer chain with alternating spaces between adjacent elements is energetically more favorable than the chain with equal spaces. Probably, conducting polymers with even number of electrons in fragments are more stable.

SQUID and ESR are main methods of studying magnetic properties of conducting polymers. In contrast to ESR, SQUID permits to measure both temperature and field dependences of magnetization. However, magnetization measured by SQUID includes not only spin contribution described by Eq. (2) but other contributions. The "triplet" model describes only spin contribution, therefore other contributions have to be subtracted from the total magnetization. In all papers only correction for the diamagnetic core by Pascal rules is carried out. However, there is the Van Vleck paramagnetism (Van Vleck, 1932).

Both the diamagnetic and Van Vleck susceptibilities are characteristic for substances with singlet ground state and do not depend on temperature and magnetic field. These susceptibilities are of different signs and comparable absolute values, and are not detected by ESR. Paper (Kahol et al., 2004a) states that SQUID and ESR give close values of susceptibilities for one sample of polyaniline, therefore for this sample the Van Vleck susceptibility is small. However, in our work (Kulikov et al., 2011) a comparison of ESR and SQUID data for one sample of polyaniline revealed a temperature-independent contribution which is not diamagnetic one. This may be explained by appreciable the Van Vleck contribution.

The diamagnetic and Van Vleck contributions are not important at helium temperatures, because they are temperature-independent and the Curie contribution proportional to $1/T$ dominates at low temperatures.

At present, we used only two methods, ESR and SQUID, to prove the "triplet" model. Other methods are required for further proof and study of details of this model. Two methods could be used for this purpose. (i) In the "triplet" model, all variety of experimental temperature dependences of χT are explained by variety of the distribution functions $F(E)$, therefore it is important to measure this function by direct methods. Low-lying triplet levels ($10 \text{ kJ/mol} \sim 1000 \text{ cm}^{-1}$) could be detected as a low-intensive broad phosphorescence in IR region. (ii) There are other direct methods of determining the value of spin S by pulsed ESR. For instance, the spin multiplicity was confirmed by nutation spectroscopy to be $S=1/2$ for spin soliton in a π -conjugated ladder polydiacetylene (Ikoma et al., 2002). It would be interesting to compare results of study of a conducting polymer by nutation spectroscopy and SQUID (field dependence).

6. Conclusion

To explain all features of magnetic properties of conducting polymers, we proposed the "triplet" model and confirmed it by analysis of our and literature data obtained by ESR and

SQUID. According to the “triplet” model, conducting polymers consist of fragments only in singlet or triplet state (no doublet states) with wide distribution of singlet-triplet splitting, and magnetic properties of conducting polymers are described by an integral of the fragment magnetization over this distribution. The “triplet” model is alternative to the “metallic” model which is commonly accepted.

The most plain, convincing and reliable evidence in favor of the “triplet” model gives an analysis of our and literature data for polyaniline and polypyrrole. The analysis shows that the field dependences of magnetization of conducting polymers at helium temperatures are often described by the Brillouin function with $S \approx 1$, whereas the widespread “metallic” model predicts $S = 1/2$. The “triplet” model describes only spin contribution, therefore other contributions have to be subtracted from the total magnetization. At helium temperatures, other contributions are insignificant.

In the “metallic” model, the ratio of the Pauli to Curie contributions of susceptibility is experimental fact and is determined by the share of metal and amorphous regions in a polymer. The “triplet” model simulates in the unified way both the temperature and field dependences; the absolute values of magnetization at various temperatures and fields are simulated rather than shapes of the dependences.

The “triplet” model is able to explain such features of temperature dependences of χT for polyaniline, polyacetylene and polythiophene, as nonlinearity of these dependences, and the effect of heating and gases on these dependences.

7. References

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