Doping-induced magnetic phase transition in poly(3-alkylthiophenes)

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The dopant-agent$-\pi$ system magnetic interactions in $FeCl_4^-$-doped poly(3-alkylthiophenes) (PAT's) have been studied. In particular, PAT's were subjected to magnetic susceptibility and magnetization measurements. The main goal of the experiments was to obtain temperature and magnetic-field dependencies of the above-mentioned magnetic quantities. The PAT samples were doped with ferric trichloride to different doping levels. The susceptibility and magnetization studies have shown that in the doped conjugated system the transition from a paramagentic phase to an ordered phase occurs as the temperature is lowered. The magnetic interactions observed are associated with the dopant-agent$-$charge-carrying-species antiferromagnetic coupling. The coupling is stabilized by a retro or forward virtual charge transfer between the impurity molecule and the polymer chain.

I. INTRODUCTION

Conjugated polymers have been extensively studied in the last 17 years, mainly due to their interesting physics but also because of a wide range of possible industrial applications of these compounds. Unfortunately, the majority of conjugated polymers, in their doped state, suffer from a lack of environmental stability. Substituted polythiophenes distinguish themselves from other members of conducting polymer families in the respect that they are reasonably stable and soluble in commonly used solvents. This last property strongly facilitates their processing and characterization. Undoped conjugated polymers are insulators, and the state of high conductivity in these materials is usually achieved by the so-called doping reaction. A good doping process ought to be reproducible and easy to perform. One of the most common doping agents is ferric chloride, which leads to the insertion of $FeCl_4^-$ ions to the polymer matrix. The insertion of magnetic counter ions such as ferric tetrachloroferrate anions also seems to be very important from an experimental point of view. This is because magnetic experiments might be very useful as a source of information about the nature of the dopant-agent$-\pi$-system interactions. This, in turn, can contribute to an understanding of the transport properties in conducting polymers.

Results of measurements of static magnetic susceptibility, magnetization, and electron-spin resonance (ESR) were reported in our previous papers.[1,2] Poly (3-alkylthiophenes) (PAT's) doped with $FeCl_3$ were chosen as the system subjected to the experiments mentioned. An analysis of the data presented has shown that at low temperature an indirect magnetic interaction between the

Fe^{+3} ion mediated via the bipolaron affects the magnetic response of the sample measured. This, in turn, can lead to a localization of states of the charge-carrying species (bipolarons). In such cases, the existence of a "short-range" magnetic ordering can therefore be expected at temperatures below 20 K. Moreover, magnetization measurements have shown that magnetization curves plotted against a B/T (external magnetic field to temperature) ratio changed their slope below that temperature, and the $M = f(B/T)$ dependence did not follow the Brillouin shape. The phenomena described were confirmed by means of conductivity versus temperature measurements,[3] where an abrupt decrease in conductivity below a certain temperature was observed. The experiments mentioned above were carried out only under low-magnetic-field conditions, and therefore it was impossible to measure the value of the magnetization in the saturation state.

In this paper results of measurements of magnetization as a function of external magnetic field and temperature are reported. Poly(3-alkylthiophenes) doped with ferric chloride were subjected to magnetic experiments in high magnetic fields sufficient to achieve the saturation state. The paper is structured in the following way: in Sec. II a brief description of the sample preparation is given: a description of the experimental techniques used is also included. Section III is devoted to a description of the experimental results with a short recollection of previously obtained results. In Sec. IV an interpretation of the observed phenomena is suggested. The experimental results are discussed in view of the McConnell's virtual charge-transfer model. Finally, in Sec. V, a summary of the work is given.

II. EXPERIMENT

The monomers for the polymerization, i.e., 3-alkylthiophenes, were prepared from 3-bromothiophene by Grinard coupling.[4] The monomers were then polymerized with $FeCl_3$ to the corresponding polymer. The exact procedure for the preparation of PAT's used in the present studies can be found in the paper by Kulszewicz-Bajer et al.[5] The polymer was checked for iron contamination after synthesis, and was found to be essentially iron free. Free-standing thin films of the undoped sample were prepared by casting from chloroform solutions. The films were doped with $FeCl_3$ to give $[PAT(FeCl_4)_y]_n$, where y is the dopant concentration defined as the number of dopant anion species per monomer of the polymer. The doping level was controlled by the soaking time. After doping the samples were washed repeatedly to remove any excess doping agent, and then dried in vacuum to a constant mass. The doping levels were determined from mass uptake and verified by elemental analysis for selected samples. The relative error of the dopant concentration determination was estimated to be below 10% for all samples tested. Based upon the elemental analysis of the selected samples, the estimated dopant levels should be regarded as the higher bounds. It should be noted here that doping with $FeCl_3$ produces $FeCl_2$ as a side product. The existence of the reduced species as well as an excess of $FeCl_3$ was verified by Mossbauer-spectroscopy (ME) studies, as reported by Proń et al.[6] Because both species are antiferromagnetic below their Neel temperatures, ME measurements indicate the presence of "antiferromagnetic contaminants." ME studies of selected samples have shown that the weight ratio of the contaminants to the "dopant iron" is of the order of 10^{-2}, and hence cannot affect the observed magnetic response of the samples. The thin free films of the polymer subjected to the magnetic measurements were cooled down to liquid-nitrogen temperature, mechanically divided into small flakes, and mounted into a copper/glass holder. The high-magnetic-field measurements were carried out at the International Institute of High Magnetic Fields and Low Temperatures, Wrocław, Poland. The apparatus used consists of Bitter magnets, and the installation allows for the induction method of the magnetization measurements to be used. The field stability was estimated to be about 10^{-3} T, and the apparatus sensitivity was about 0.1 emu/g.

Magnetic susceptibility measurements were also performed by means of a superconducting quantum interference device (SQUID) magnetometer in C.E.N., Grenoble. The total sensitivity of the apparatus for a total change of the magnetic moment of a sample was about 10^{-8} emu. Temperature setting in the experiments was accomplished either by a continuous-flow cryostat or by a bath cryostat. The temperature was controlled by a $Au+Fe$-chromel thermocouple, and the temperature stability was below 1 K with a temperature measurement accuracy of about 0.1 K.

III. DESCRIPTION OF THE EXPERIMENTAL RESULTS

Similarly as in our previous papers,[1,2] magnetic-susceptibility measurements were carried out for samples with different lengths for the alkyl group, namely hexyl-C_6H_{13}, octyl-C_8H_{17} and decyl-$C_{10}H_{21}$, that is PHT, POT, and PDT, respectively. The samples were doped to dopant concentrations corresponding to medium and high doping levels. The typical temperature dependence for the static magnetic susceptibility determined experimentally is shown in Fig. 1, where static magnetic susceptibility is plotted as a function of absolute temperature. A substantial departure from the typical paramagnetic behavior is more evident for the PDT sample, and is
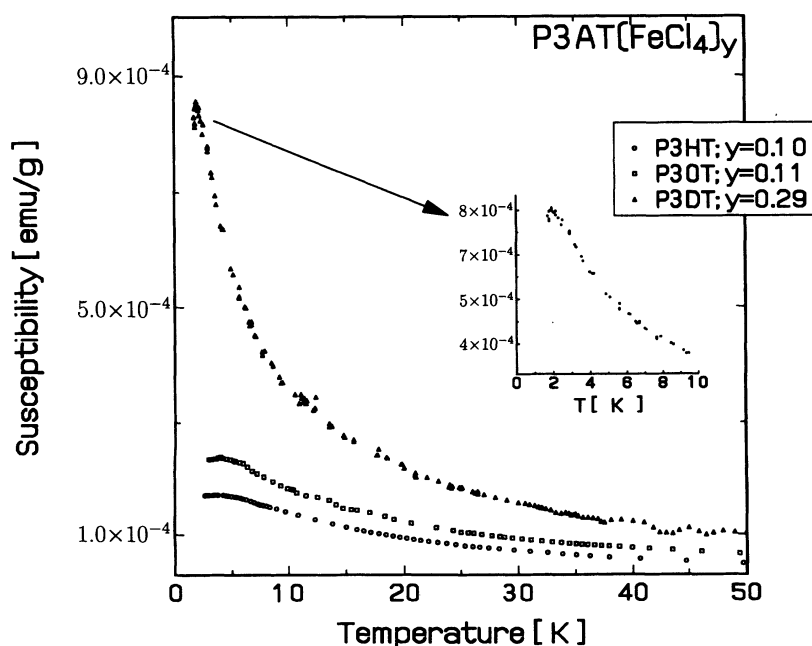

FIG. 1. Temperature dependence of the static magnetic susceptibility for $FeCl_4^-$-doped poly(3-alkylthiophene)s. Curves for PHT and POT are taken from Ref. 1. Every third point is shown.

TABLE I. Magnetic parameters derived from the Curie-Weiss law fitting above T_a.

Sample	PHT			POT			PDT	
Doping level y	0.10	0.42	0.11	0.29[a]	0.41	0.10	0.27[a]	0.29
T_a [K]	22.8	20.8	31.3	32.7	33.6	32.4	30.4	33.6
Θ [K]	1.79	1.81	1.11	0.86	1.72	1.45	0.95	1.24
C [emu K/Fe mol]	2.98	3.32	4.27	3.84	3.36	3.52	3.2	3.29
μ_{eff} [μ_B/Fe ion]	4.89	5.16	5.85	5.23	5.19	5.34	5.1	5.12
δ_μ [μ_B/Fe ion]	0.56	0.33	0.34	0.24	0.17	0.27	0.18	0.18

[a] The experiments performed by means of SQUID.

shown in the inset of Fig. 1. The quenching of the magnetic signal as temperature is lowered (i.e., at about 3 K in case of PDT and at about 5 K for other samples), typical of magnetic ordering transitions. Note that the temperatures mentioned are well below the Neel temperatures for $FeCl_3$ and $FeCl_2$, which are 15 and 22.5 K, respectively.

In order to verify qualitatively the agreement of the temperature dependence of the susceptibility with the Curie-Weiss law, the following formula was fitted to the experimental data over the entire temperature range:

$$\chi(T) = \chi_0 + \frac{C}{T-\theta} , \qquad (1)$$

where the temperature-dependent part comes from the Curie-Weiss law, and χ_0 is the sum of all temperature-independent contributions, i.e., the core diamagnetism of the polymer chains and of the dopant molecules. Moreover, the Pauli susceptibility for the charge carriers should be taken into account in the temperature-independent part of Eq. (1). In general, a good correlation coefficient (of 0.999) was obtained only in the high-temperature range of the susceptibility data. Below a certain temperature, which we define as T_a, the static magnetic susceptibility did not follow the Curie-Weiss law. The value of the effective magnetic moment μ_{eff} in the paramagnetic phase and its error δ_μ were estimated

from the Curie coefficient C obtained in the fitting procedure. All fit parameters obtained and values derived are shown in Table I. It should be stressed here that the influence of the error of the dopant concentration determination on the estimated values of the magnetic moment errors was most pronounced for the lowest dopant concentrations. In spite of the errors, the values of μ_{eff} shown in Table I are smaller than those expected for a pure spin state ($\mu_{eff} = 5.92$). This is *probably* caused by incomplete quenching of the orbital angular momentum of ferric ion because of a small distortion of the tetrahedral ligand arrangement. As was mentioned above, at temperatures below T_a the temperature dependence of the static magnetic susceptibility does not follow the Curie-Weiss law. In addition, the dependence of T_a on the length of the alkyl group is clearly observed. This behavior will be discussed further. For all samples the values of Θ obtained are all positive and are of the same order of magnitude as the estimated temperature error. Hence the existence of positive values of the factor representing magnetic interactions cannot be interpreted as an effect of ferromagnetic interactions in the polymer samples. In order to summarize our susceptibility data reported previously, the temperature dependence of $(\chi - \chi_0)(T - \Theta)$, i.e., a quantity proportional to the effective magnetic moment, is shown in Fig. 2 to better illustrate the magnetic-susceptibility deviation from the
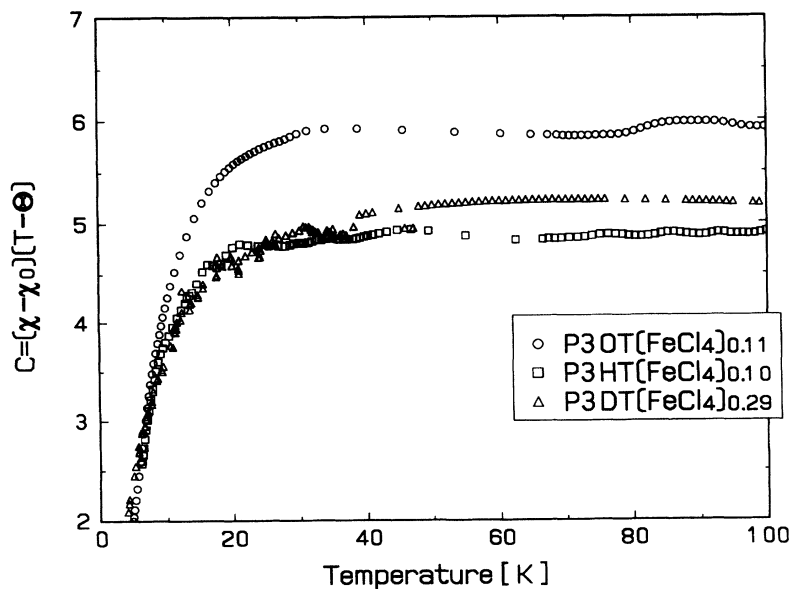

FIG. 2. Curves of $(\chi - \chi_0)(T - \Theta)$ vs temperature are shown for selected PHT, POT, and PDT samples. The nonlinear parts illustrate the discordance with the fitted Curie-Weiss law. Curves for PHT and POT are taken from Ref. 1.

Curie-Weiss law. The shape of the susceptibility curves compared to the Curie-Weiss law fitted in the high-temperature range (see Fig. 1) suggests rather antiferromagneticlike interactions. Furthermore, the measured effective magnetic moment μ_{eff} is lower than that expected for a pure paramagnetic dopant species. In order to verify the data obtained, susceptibility measurements were also carried out using the SQUID magnetometer. Two samples doped with ferric trichloride were subjected to experiments, namely POT ($y = 0.29$) and PDT ($y = 0.27$). The results of the measurements confirm results obtained by means of the static magnetic measurements carried out on a Faraday-type magnetic balance. The SQUID magnetic-susceptibility data are included in Figs. 1 and 2, the parameters derived in fitting procedure of Eq. (1) are given in Table I.

Consider now the behavior of paramagnetic spins in high magnetic fields at low temperatures. In such a case, magnetization per unit volume can be described by the following formula:

$$M = NgJ\mu_B B_J \left[\frac{gJ\mu_B H}{k_B T} \right] , \quad (2)$$

where B_J is the Brillouin function

$$B_j(\eta) = \frac{1}{J} \left[(J + \tfrac{1}{2})\coth(J + \tfrac{1}{2})\eta - \tfrac{1}{2}\coth\frac{\eta}{2} \right] , \quad (3)$$

where

$$\eta = \frac{g\mu_B H}{k_B T} J , \quad (4)$$

and B_J describes the saturation of paramagnetic moments of the total quantum number J. Therefore, if one assumes that the ferric ion acts as a pure paramagnetic ion, a similar dependence of the magnetization can be observed as a function of the ratio H/T independent of temperature. In such a case, even if accessible magnetic

fields are not sufficient to reach the saturation state, the magnetization ought to follow the onset of the Brillouin function, especially at low temperatures. Any disagreement observed in the H/T dependence of the magnetization may be caused by the effect of magnetic interactions. If J is very large ($J \to \infty$), the Brillouin function can be approximated by

$$B_{J \to \infty}(\eta) = L(\eta) = \coth(\eta) - \frac{1}{\eta} , \quad (5)$$

where $L(\eta)$ is the Langevin function. The approximation $J \to \infty$ means that in the presence of applied magnetic field any arrangement of magnetic moment is possible. The Langevin function describes the magnetization dependence on magnetic field and temperature for clusters with a large individual magnetic moment.

Accordingly, for two samples PHT ($y = 0.42$) and POT ($y = 0.41$), static magnetization measurements were carried out as a function of magnetic field at five temperatures below T_a. In order to obtain a strong and pronounced magnetic signal in a weak magnetic field, samples with the highest dopant concentration were chosen. Measurements were performed in magnetic fields from 0 to 0.5 T. A typical magnetization dependence on the H/T ratio for POT are shown in Fig. 3. The measured dependence of the magnetization on the ratio of magnetic field and absolute temperature should have followed the linear onset of the Brillouin function, if the paramagnetic state had been achieved. In fact, it can be seen that the magnetization increases linearly with the H/T ratio at higher temperatures, with a slope depending on the measurement temperature. This means that magnetic phenomena can be roughly described by the Curie law, as these are approximated in the magnetization formula. The effective magnetic moment, evaluated from the highest temperature results ($\mu_{\mathrm{eff}} = 5.30$ and 5.64 for PHT and POT, respectively), is close to the value obtained from the temperature dependence of the susceptibility.
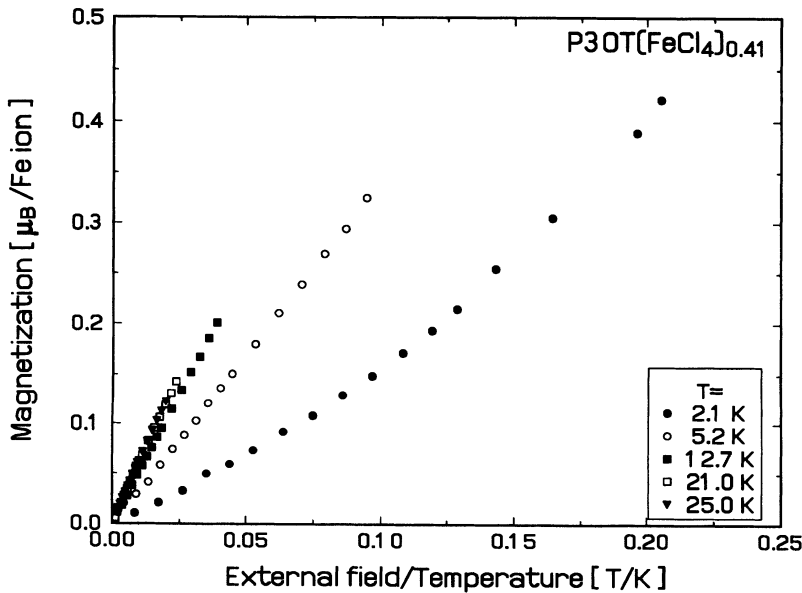

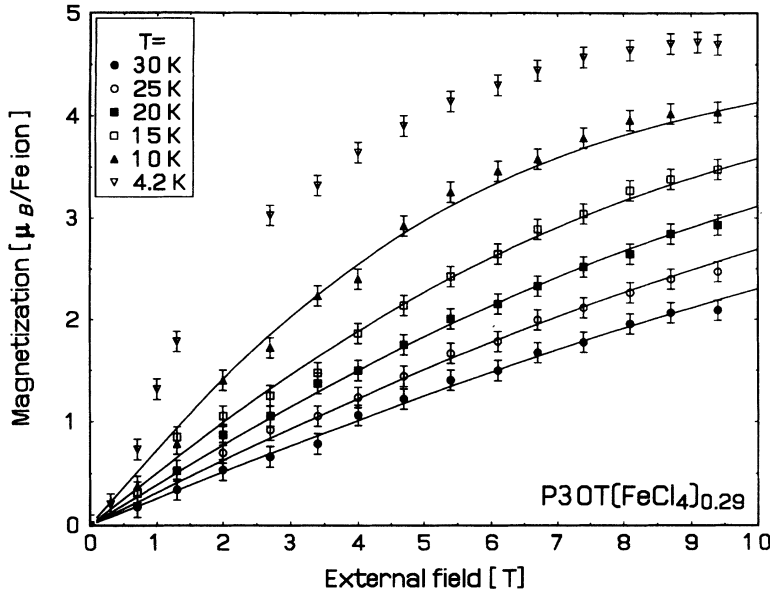FIG. 3. Curves of the magnetization dependence on the H/T ratio for doped POT (data taken from Ref. 1).

FIG. 4. Magnetization vs external magnetic field for the POT sample measured under different temperature conditions.

The fact that the slope of the magnetization curve depends on temperature leads to the following conclusion: the paramagnetic response of the sample is affected by the response of a state in which short-range magnetic order exists. The explanation is reasonable, especially due to the nonlinear behavior of the magnetization at the lowest measurement temperature. Thus the static magnetic measurements suggest an accentuation of magnetic interactions at low temperatures.

In general, the magnetization (M) possesses a characteristic field dependence which enables a qualitative determination of the magnetic behavior. However, in order to compare the experimentally measured field dependence of the magnetization with theoretical curves, high-magnetic-field experiments should be carried out. Hence such measurements have been performed at different temperatures for two samples, i.e., poly(3-octylthiophene) and poly(3-decylthiophene), doped to high dopant concentrations (0.29 and 0.25, respectively). The results for POT are presented in Fig. 4. The experimental points obtained at temperatures above the transition temperature suggested should follow the magnetic-field dependence of the magnetization described by Eq. (2). In fact, as can be observed in Fig. 4, the fitting procedure shows quite a good agreement for the experimental data with the theoretical dependence expected. The parameters obtained during fitting are presented in Table II. The data given in that table shows that at high temperatures the field dependence of the magnetization data follows the Brillouin dependence characteristic for noninteracting ions with $S_i = \frac{5}{2}$, i.e., Fe(III) ions in the high-spin state. For low temperature the data-fitting procedure of the Brillouin function has not been successful. In spite of the fact that "low-field" and "high-field" experiments were performed using different equipment a good correlation between these two data sets can be observed. Keeping in mind that errors of magnetization measurements using Bitter magnets (high-field regime) were larger than those obtained using Cahn balance (low-field regime) it can be

assumed that experimental data follow smooth curves, as is illustrated in Fig. 5. The errors approximated are also given in these figures as error bars. The analysis of the experimentally obtained $M = f(H)$ curves allows us to draw the conclusion that a magnetic transition can be observed that is similar to a field-dependent transition from an antiferromagnetic state to a high-moment ferromagnetic state. Moreover, a decrease in the saturation magnetic moment for the POT sample is clearly observed in Fig. 5 at temperatures below 4 K. The same kind of measurements were performed by means of the SQUID magnetometer. However, under high-magnetic-field conditions the measurements could be carried out only at temperature $T \geq 4$ K. The magnetization data plotted vs applied magnetic field are presented in Fig. 6. The Brillouin function [Eq. (3)] and the Langevin function [Eq. (5)] were used to fit the $M = f(H/T)$ dependence [see Eq. (2)] to the experimental points. Thus it can be concluded that these two functions could approximate the data with the same accuracy. The fact that the Langevin function can also describe the experimental points may suggest that a

TABLE II. g and J ($=S$) parameters derived from fitting of Eqs. (2)–(4) to data obtained during the magnetization measurements.

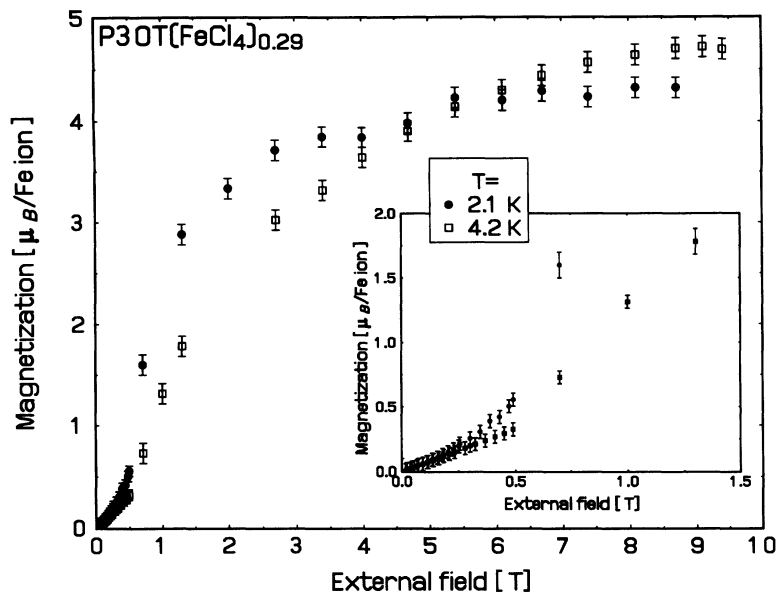| Sample	Temperature [K]	g	S
	30	2.02	2.50
	25	2.02	2.50
P3OT(FeCl$_4^-$)$_{0.29}$	20	2.02	2.50
	15	2.00	2.45
	10	2.02	2.42
	40	2.00	2.50
	30	2.00	2.50
P3DT(FeCl$_4^-$)$_{0.25}$	20	2.02	2.50
	15	2.02	2.50
	10	2.00	2.46

FIG. 5. Magnetization vs magnetic field for the POT sample at low temperature. The same dependence for the lowest magnetic-field values is shown in the inset (see Fig. 3). The same shape of the curve can be observed for PDT.

superparamagnetic behavior of the sample is observed. This means that clusters with spontaneous magnetization can exist within the sample.

IV. DISCUSSION AND THEORETICAL CONSIDERATIONS

Many works were devoted to the nature of the impurity molecule when diluted ferric chloride is used during doping. It was found that a tetrahedral $FeCl_4^-$ complex is formed as a counter ion.[7] In this complex the iron ion exists in the high-spin Fe(III) form. Because the molecular-orbitals (MO) structure is the key point in understanding magnetic interactions, a brief description of the major features of molecular orbitals of $FeCl_4^-$ will be given below.

In the case of a D-state ion, the fivefold orbital degeneracy of the ion in the gaseous state is partially removed in a tetrahedral crystal field. A simple scheme for the molecular-orbital energy levels[8,9] is presented in Fig. 7. Only the atomic orbitals expected to make the largest contribution to each molecular orbital are shown. The main contribution to the delocalized bonding orbitals comes from the occupied orbitals of the ligands and from $4s$ and $4p$ orbitals of the transition-metal ions. The d electrons responsible for magnetic behavior are not involved in the bond formation between the transition-metal ion and the ligands. Therefore, the five d orbitals
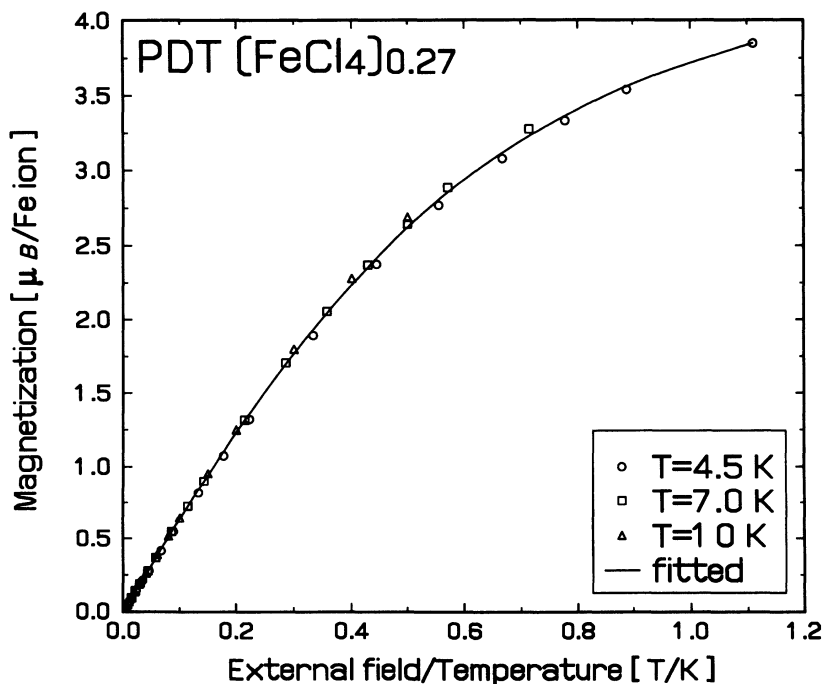

FIG. 6. Magnetization vs external magnetic field divided by temperature under different temperature conditions. The experiment performed by means of SQUID.
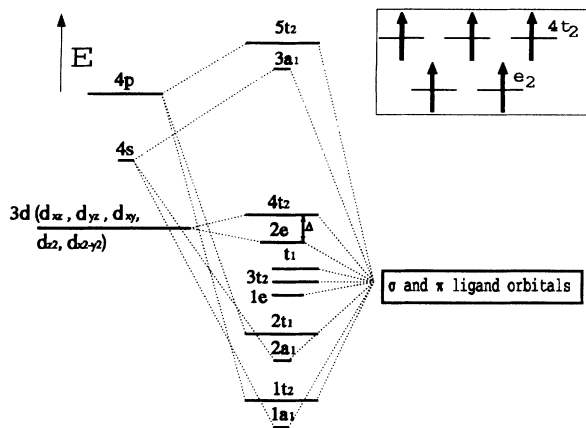
FIG. 7. A qualitative energy-level diagram for the molecular orbitals in a tetrahedral chloroferrate complex. A scheme for the high-spin state containing only unpaired spins is given in the inset.

are localized mainly on metal. The energy gap between $4t_2$ and $2e$ levels (ligand field splitting Δ) is small, because of the character of the ligands.[10] These levels are the highest occupied molecular orbitals housing five electrons (formal oxidation state of the metal) in the *predominantly* nonbonding levels. Indeed, the proximity of the g value of the ferric complex observed in the ESR experiment[10] to the free-electron value (2.0023) indicates that the five unpaired d electrons are not used as a bonding orbital in the $FeCl_4^-$-complex. If any were, the special case of the half-filled shell would be destroyed and the ESR spectrum altered. Note that the formal HOMO (highest occupied molecular orbital) is the $2e$ orbital, and the LUMO (lowest unoccupied molecular orbital) is the $4t_2$ orbital. In this case, however, Hund's rule applies, i.e., the state with the maximum spin multiplicity has the lowest energy. For this reason the $4t_2$ level is also occupied, and the molecule is in the high-spin state. The half-filled shell of the high-spin $3d^5$ ion implies that the ground state will be an orbital singlet, that is, $^6S_{5/2}$. Because further discussion deals mainly with these highest occupied states ($4t_2$ and $2e$), a simple scheme of the energy levels is presented in the inset of Fig. 7.

In order to explain the magnetic results reported above, the McConnell[11] model can be considered. Briefly, this model is based on the idea of an admixing of a virtual triplet (or singlet) excited state (ES) [with $m_s = 1$ (or 0) arising from either $m_s = 1$ (or 0) donor or $m_s = 1$ (or 0) acceptor, but not both], formed by virtual charge transfer, with the ground state (GS) for stabilizing ferro-(antiferro-) magnetic coupling. The model is usually used in order to explain the bulk ferromagnetism in the new class of organic materials.[12] In a simple picture, if spin interactions are not considered, the acceptor (A^-)/donor (D^+) pair behaves as a simple paramagnet. This is because in this system two ground states equal in energy exist; that is, the ferromagnetic GS_{FM} and the antiferromagnetic GS_{AFM}. The spin interactions, however, lead to lowering of either GS_{FM} or GS_{AFM} and to the ferromagnetic (or antiferromagnetic) coupling. It is clear

that, due to the Pauli exclusion rule, one of the ground states may be not stabilized in the course of the charge-transfer process, and corresponding magnetic coupling can be ruled out. In order to predict the magnetic coupling in a real system, however, a more detailed inspection of possible electron configurations is necessary. Moreover, when two possible directions of the charge transfer is allowed, only experimental results can be helpful with pointing out a more probable configuration.

Keeping in mind the admixing mechanism described above, and the electron configuration of the polymer guest molecules, an explanation of the magnetic interactions in low magnetic field in a doped conjugated system can be suggested. In order to better understand that phenomenon, it is convenient to remind the reader of the mechanism of recombining two interacting polarons into a bipolaron. A schematic picture of this mechanism is presented in Fig. 8(a). In the case of the dilute dopant concentration, polarons can exist separately. Increasing the doping level, however, leads to the polaron wavefunction overlapping, i.e., polaron interactions. Consequently, midgap polaronic states combine to form additional bonding and antibonding states. These states are equivalent to a double-charged bipolaron, which is the lowest energy charge storage configuration in the intermediate doped polythiophene.[13] Indeed, bipolarons are energetically favored over polarons[14,15] by approximately 0.2 eV. Increasing the dopant concentration leads to
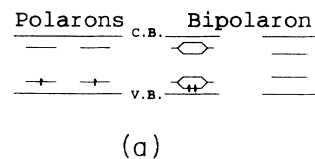
(a)
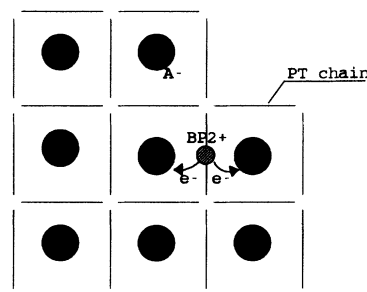
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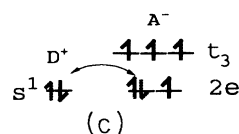
(c)

FIG. 8. (a) Schematic drawing of a recombination of two polarons into a bipolaron. (b) Scheme of a plane projection of channel structure of a doped polythiophene. This structure can be associated with the *P4mm* 2D space group. The possible virtual forward charge transfer is also illustrated. (c) The possible virtual charge transfer (CT) is illustrated. Both directions of CT stabilize the AFM coupling.

overlapping of the bipolaron wave functions, and midgap bipolaronic states become bipolaron bands. The transition between noninteracting and overlapping regimes occurs at a doping level of $y = 0.20$; that is, one bipolaron per ten thiophene rings.[14] This value was obtained theoretically. Note that the inhomogeneity of the doping is likely to lower this value. Further doping leads to the bipolaron lattice, which is assumed to be a representative band configuration for the saturation doping level.[15] At the saturation doping level, however, there is a possibility (suggested theoretically) that the bipolaron lattice may revert to a polaron lattice. This bipolaron lattice-polaron lattice crossover can be driven by Coulomb-type interactions.

The single, noninteracting double-charged bipolarons are delocalized over 6-thiophene rings. When the dopant concentration is sufficient for the bipolaron wave functions overlapping, bipolarons can be delocalized over a whole polythiophene chain. Further increasing of the doping level results in the delocalization of bipolarons over several polythiophene (PT) chains. A good solubility of the alkyl-substituted polythiophene, however, suggests relatively weak interchain electronic transfer interactions; that is, the electronic structure is highly anisotropic or is quasi-one-dimensional. Moreover, the transport properties depend strongly on the length of the alkyl chain, i.e., the distance between the neighboring chains.[16] This is consistent with the suggestion that the interchain transfer integral $(t_\perp)$ is smaller than the intrachain (nearest-neighbor) transfer integral $(t_\parallel)$. Consequently, the electronic motion along the conjugated chain is the dominant transport mechanism. To the best of our knowledge, there are no theoretical estimations of the values of these integrals for the polythiophene system. This is because the largest effort has been made to understand the transport processes in the polyacetylene system. Therefore, we should assume that $t_\parallel$ and $t_\perp$ are of the same order as the polyacetylene case,[17–19] that is, 0.1 and 2.5 eV in the absence of dopants, respectively. In the real system, however, the presence of the interstitial dopant ions should be also taken into account. Hopping through the emptied acceptor level of the impurity is negligible, since the level is about several eV above the π orbitals of the PT chain.[20]. The presence of the acceptor can, however, affect the values of $t_\parallel$ and $t_\perp$. The on-chain hopping parameter $(t_\parallel)$ is approximately four times larger than that calculated by Bussac and Zuppiroli[21] for an impurity-free case. Moreover, as was reported,[21] the chain-impurity molecule transfer integral (t_1) is of the same order as the interchain transfer integral $t_\perp$ (0.1 eV $< t_1 < 0.3$ eV). Accordingly, in the presence of the dopants the parameters for the on-chain hopping $(t_\parallel)$ and the interchain hopping $(t_\perp)$ are changed, and the dopants give rise to localized bond defects (due to modulation of $t_\parallel$). The dopants, on the other hand, may be thought of as bridges for interchain hopping. It should be also taken into account that decreasing temperature leads to increasing the localization of the charge-carrying species.[22] Therefore, at a sufficiently low temperature, charged bipolarons are localized mainly on the polymer chain, and because of a dopant attraction they are located at sites close to the charged impurities.

The results of structural investigations showed that a doped polymer adopts a channel structure with polymer chains surrounding the dopant ions.[23] The number of neighboring chains depends on the size of the dopant molecule. This situation is illustrated schematically in Fig. 8(b). Consequently, even if the polymer possesses a disordered structure in the macro scale it is justifiable to treat the doped conjugated system as an ordered system (charge-transfer complex) in the micro scale. Hence the McConnell model can be used to explain the magnetic phenomena observed. When a charged bipolaron is localized on the site close to the acceptor (A^-), the system may lower the total energy by the virtual forward charge transfer from a polymer chain to a free $2e$ state. In order to do that, an energy barrier of 0.2 eV should be tunneled to convert the bipolaron to two polarons. However, the barrier is of the order of the magnitude of the chain-impurity transfer integral t_1 (see Sec. II above). Moreover, this barrier can be lowered by Coulomb repulsion between two adjacent, overlapping bipolarons. Following this idea, an additional charge-transfer complex comes into being, i.e., $PT^{2+}(FeCl_4^{2-})$. The forward charge transfer stabilizes the antiferromagnetic coupling between the polaron state and the tetrachloro-ferrate complex. According to the McConnell model, however, retro virtual charge transfer is also possible. The diagram of both, that is, the forward and the retro charge transfers, is shown in Fig. 8(c). Accordingly, the virtual charge transfer in both directions stabilizes the antiferromagnetic coupling. Consequently, this phenomenon results in a larger localization of the charge-carrying species which, in turn, leads to abrupt decrease of the conductivity.

From the point of view of the model suggested, it is possible to explain the T_a temperature dependence on the length of the alkyl chain group (see Table I). The longer the alkyl chain group, the longer the interchain distance which, in turn, lowers the interchain transfer integral $t_\perp$. Therefore, the bipolarons are more localized on a single chain. Consequently, the charge-transfer process can occur at higher temperature, sufficient for bipolaron localization.

The fact that the T_a temperature (see Table I) does not depend on the dopant concentration can be explained by the fact that the samples were doped to medium and high regimes. Since doping is inhomogeneous and only bulk doped samples were subjected to the measurements, the dopant anions are located within areas with different dopant concentrations. Some areas within a sample are doped to a high (saturation) level, while others are doped to a doping level well below the average estimated for a bulk sample. The size of the these highly doped "clusters" increases upon doping, with an almost constant dopant concentration within an individual "cluster." Thus the molar magnetic response of a single cluster should not depend upon the dopant concentration.

V. CONCLUSION

The results of magnetic measurements suggest that at low temperatures (below the temperature denoted as T_a)

a pairwise magnetic interaction exists. The temperature dependence of the susceptibility provides evidence that there exists an antiferromagneticlike coupling. Moreover, the magnetization studies show that a transition from a paramagnetic phase to an ordered phase also takes place. The magnetization dependence on the H/T ratio for the lowest measurement temperature is reminiscent of the effect of a ferrimagneticlike interaction. Keeping in mind that the guest ions are arranged in "channels" parallel to the polymer chain axes,[23] the following conclusions can be drawn.

(i) Under low-magnetic-field conditions the magnetic interactions observed are associated with the dopant-agent–charge-carrying species antiferromagnetic coupling. The coupling is stabilized by a retro or forward virtual charge transfer between the impurity molecule and the polymer chain. In order to lower the total energy of the system by means of the antiferromagnetic coupling, a splitting of the bipolaron to polarons occurs. This results in an abrupt decrease in the conductivity[3] at the temperature at which the transition is observed. Such a situation is more favorable in systems with a large distance between the adjacent chains; that is, when the interchain transfer integral is of the same order (or lower) as the chain-impurity transfer integral. This induces a larger localization of the charge-carrying species on a single chain. Because of the higher mobility of the charge carriers at higher temperatures, the doped polymer

behaves like a paramagnetic material above the T_a temperature. However, an apparent reduction of the effective magnetic moment of the $FeCl_4^-$ complex in the paramagnetic phase can be observed. The nature of this phenomenon is not entirely understood. It is suggested that future closer examination of the doped system should take into account the incomplete quenching of the orbital angular momentum.

(ii) Decreasing the saturation magnetic moment (see Fig. 5) suggests that long-range order is observed under high-magnetic-field conditions. This phenomenon can be related to ferromagneticlike interpair interactions. Consequently, a transition to the magnetically ordered phase induced by magnetic field can be observed.

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