Low-temperature transport properties of poly(3-alkylthiophene)s doped with $FeCl_4^-$

1995 J. Phys.: Condens. Matter 7 L187

(http://iopscience.iop.org/0953-8984/7/14/002)

J. Phys.: Condens. Matter 7 (1995) L187–L191. Printed in the UK

LETTER TO THE EDITOR

Low-temperature transport properties of poly(3-alkylthiophene)s doped with $FeCl_4^-$

P Barta†, T Kaniowski†, W Łużny†, S Nizioł† and M Zagórska‡

† Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, PL-30059 Kraków, alica Mickiewicza 30, Poland

‡ Department of Chemistry, Technical University of Warsaw, PL-00664 Warszawa, ulica Noakowskiego 3, Poland

Received 18 January 1995

Abstract. This letter reports the results of temperature-dependent conductivity measurements performed for a conjugated polymer doped with magnetic complex. There, an abrupt decrease in conductivity was observed as temperature was lowered. The phenomenon is interpreted as the effect of the short-range magnetic order appearing and, consequently, affecting the transport processes by magnetic interactions mediated by charge-carrying species (polarons, bipolarons). In addition, results of x-ray diffraction experiments that were performed are discussed.

One of the major properties of classical polymers that distinguishes them from metals is their high electrical resistance. During the past two decades, however, a new class of conjugated, organic polymers capable of conducting electrical current has been developed. These novel polymers are often termed 'synthetic metals'. Only when MacDiarmid, Heeger and associates [1] reported their work on electrical conductivity arising in polyacetylene treated with strongly oxidizing or reducing reagents did the field of highly conducting polymers become a fashionable research subject. A number of other conjugated polymers were shown to exhibit similar electric properties after doping soon after. Room-temperature conductivity in the case of polyacetylene synthesized by Naarmann [2] has been increased to a real metallic value of up to 10^5 S cm^{-1}, roughly one-fifth that of copper. In general, transport processes responsible for such high conductivity are now well understood on the basis of one-dimensional models. In contrast, the nature of the interactions between guest molecules, introduced during doping into the polymer matrix, and charge-carrying species is still under investigation. In order to explain the role of dopant species in transport and magnetic properties of doped conjugated systems with short chains and/or conjugation lengths, a model (three-dimensional in its nature) of interchain polarons and bipolarons has been proposed recently [3]. The question about the influence of dopant species on transport or magnetic properties of doped polymer becomes crucial when ferric chloride is used as an oxidizing agent. This leads to the insertion of tetrachloroferrate, that is, the complex of the magnetic ion, into the polymer matrix. Note that the most important feature of the conjugated polymer doped with such an agent is its environmental stability.

The main goal of this work is to throw some light onto the nature of doping agent–charge-carrying species interactions by means of measurements of transport properties of the doped polymer. In particular, poly(3-alkylthiophene)s were subjected to conductivity measurements as a function of temperature. Moreover, temperature dependence studies

0953-8984/95/140187+05$19.50

of x-ray diffraction were carried out to determine the influence of doping on the polymer structure.

The exact procedure for the polymerization of poly(3-alkylthiophene)s and the doping procedure were reported by Kulszewicz-Bajer and coworkers [4]. The doping level of the free-standing films was determined from mass uptake and was verified by elemental analysis of selected samples. In passing, one important factor should be mentioned. Because doping with $FeCl_3$ produces $FeCl_2$ as a side product, this species as well as an excess of $FeCl_3$ should be removed after the doping process. Thus, the sample was washed in nitromethane and dried until a constant mass. Because both species mentioned are antiferromagnetic, the Mossbauer spectroscopy (ME) studies can indicate the presence of these antiferromagnetic 'contaminants'. The 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}. The DC conductivity measurements were carried out using the four-terminal van der Pauw method. Temperature setting was accomplished by means of a gas flow variable-temperature cryosystem with a film resistor as a heater. The temperature measurement accuracy was below 1 K. Finally, the x-ray diffraction experiments at low temperatures were carried out using equipment in the Institute of Low-Temperature and Structure Research of the Polish Academy of Science, Wrocław, Poland.

Measurements of temperature dependences of conductivity were inspired by previously reported results [5, 6] of experiments carried out in order to measure the magnetic properties of $FeCl_4^-$-doped P3ATs. Typical measured temperature dependences of the static magnetic susceptibility are plotted in figure 1(*a*), where a substantial departure from the typical paramagnetic behaviour can be observed at low temperature. The quenching of the magnetic signal at the lowest temperatures (i.e., at 3 K for poly(3-decylthiophene), P3DT, and at about 5 K for other samples) suggests that transition to a magnetic order occurs. The qualitative analysis of the experimental data (fitting the Curie–Weiss law to the paramagnetic part of the experimental data) showed that antiferromagnetic-like interactions were observed. In order to better illustrate this type of magnetic susceptibility behaviour, the decreasing of effective magnetic moment ($\mu_{\text{eff}} \sim (\chi T)^{1/2}$) with temperature is shown in figure 1(*b*), which indeed mimics that of common antiferromagnetic systems. Because the magnetic 'anomalies' were observed for systems doped with tetrachloroferrate and were not observed for systems doped with non-magnetic species, the phenomena should be related to the existence of the magnetic species within the polymer matrix. Consequently, due to the fact that the dopant species is involved in transport properties (as pronounced by Zuppiroli *et al* [3]), one may expect that the magnetic phenomena affect the transport processes. Therefore, for the same conjugated polymeric system, that is, P3AT doped with tetrachloroferrate, measurements of conductivity in a wide range of temperature (4–300 K) were performed. Typical results of the transport measurements were presented in figure 2. An abrupt decrease in the conductivity can be observed at low temperatures and the temperature of that sudden drop is similar to the temperature where anomalous magnetic behaviour was observed (see figure 1(*b*)). Thus, one can conclude that the magnetic phenomena observed are closely related to the transport processes in the doped π-conjugated system. In contrast, at temperatures above the transition temperature the conductivity dependence on temperature is apparently weak. This allows us to analyse the experimental data by means of typical models suggested for highly doped conducting polymers [7]. Consequently, the thermal fluctuation-induced tunnelling (TFIT) model [8] was fitted to the experimental data:

$$\sigma = \sigma_0 \exp\left(-\frac{T_1}{T + T_0}\right). \tag{1}$$

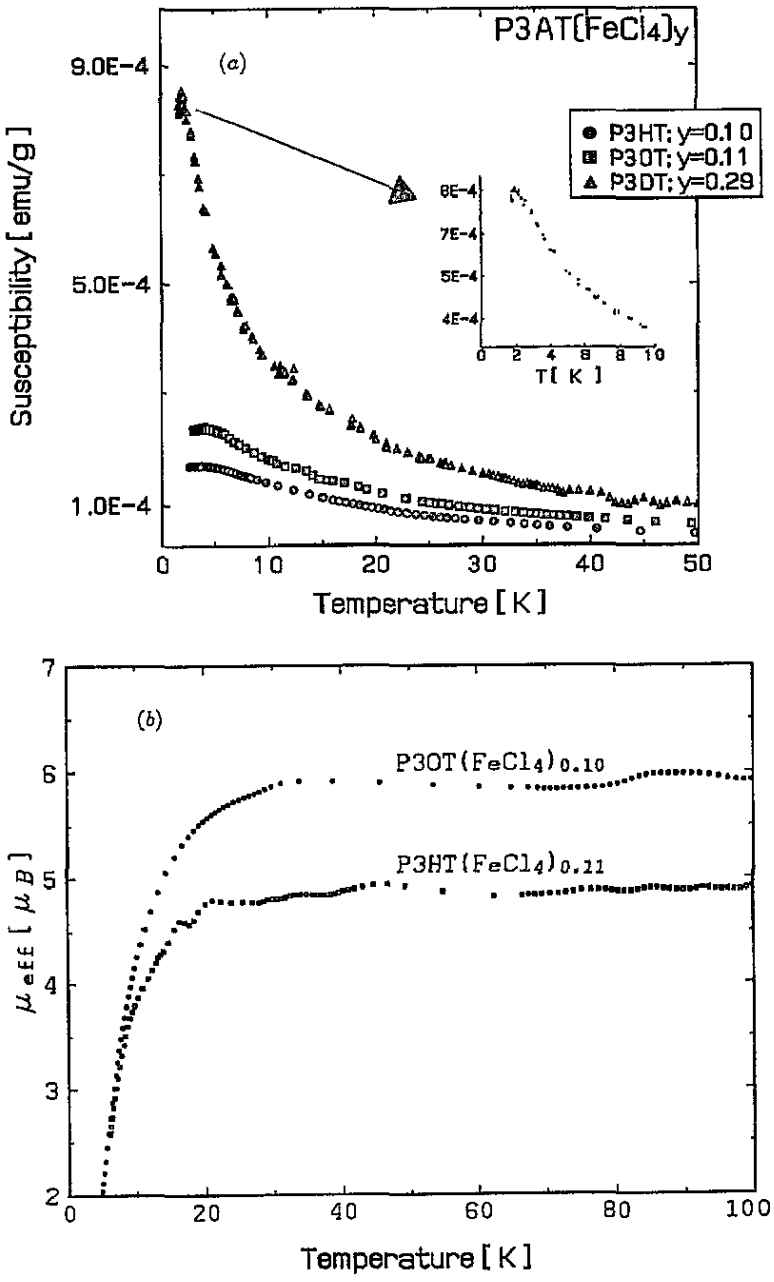
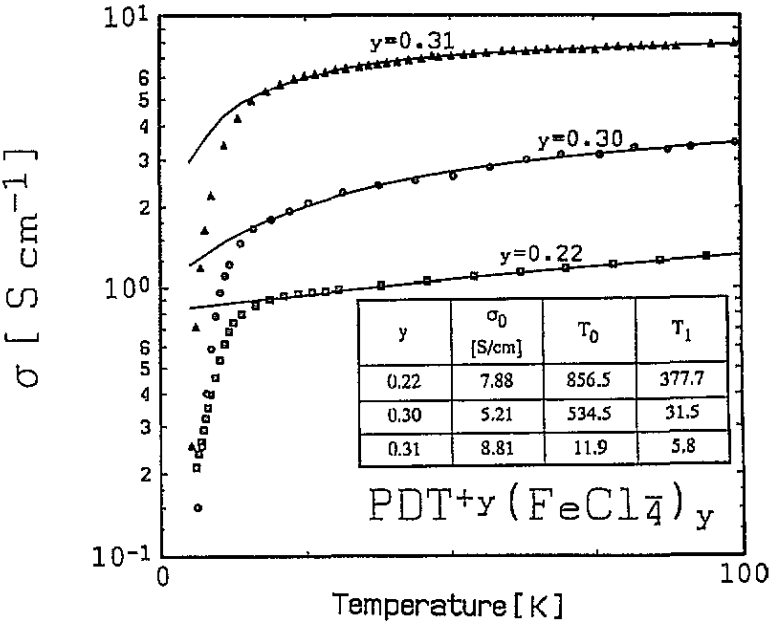


Figure 1. (*a*) Temperature dependences of the static magnetic susceptibility for $FeCl_4^-$-doped poly(3-alkylthiophene)s. Every third point is shown. (*b*) Temperature dependences of effective magnetic moment as derived from the Curie–Weiss law fitting [5].

The fitting procedure results are presented in figure 2 as the solid lines. The parameters of (1) derived from the fitting procedure are also included in figure 2.

In order to explain the magnetic and transport effects reported above, the McConnel [9] model can be considered. This model is based on the idea of mixing of the virtual triplet (or



y	σ_0 [S/cm]	T_0	T_1
0.22	7.88	856.5	377.7
0.30	5.21	534.5	31.5
0.31	8.81	11.9	5.8

Figure 2. Conductivity against temperature dependences. The parameters of the TFIT fitting (solid lines) are presented in the legend.

singlet) excited state with the ground state to stabilize ferro- (antiferro-) magnetic coupling. The new ground state lowered in energy is that one which has the greatest probability of admixing with the lowest-energy virtual charge transfer excited state. Of course, for each direction of the charge transfer the Hund rule can be applied to predict the lowest charge transfer excited state. In order to apply the above mechanism knowledge about the major features of the molecular orbitals is necessary. The iron exists in the tetrachloroferrate complex in the high-spin Fe(III) state and the d electrons of the iron are not involved in the bond formation between the central ion and the ligands. Thus, the five d orbitals are mainly localized on iron and they form the 2e (lower in energy) and $4t_2$ (higher in energy) occupied levels separated by the energy gap Δ. Note that the formal LUMO and HOMO are 2e and $4t_2$, respectively. Taking into account the splitting of the localized bipolaron (charge-carrying species in the high-doping-level regime) into two polarons [10] through the energy barrier of 0.2 eV one may suggest that the retro or virtual charge transfer occurs from/to dopant states to/from polaronic states. Both directions are allowed by the Hund rule. This, in turn, stabilizes the antiferromagnetic coupling. Consequently, this phenomenon results in a larger localization of the charge-carrying species (bipolarons, polarons) which leads to the abrupt decrease of conductivity. Note that the possibility of existence of interchain polaronic and bipolaronic clusters [3] invokes the idea that either non-local magnetic phenomena could be observed.

The structural investigation of doped poly(3-alkylthiophene)s performed by means of the x-ray diffraction technique at different temperatures has shown that between 300 K and 200 K some changes in the diffraction pattern were observed, probably as the effect of the glass transition. In the interesting temperature range (i.e., 15–100 K) no structural changes have been observed. This means that the observed transport and magnetic phenomena are not correlated with the evolution of the polymer structure. Moreover, the x-ray diffraction

experiments carried out for the neutral and doped samples showed [11] that dopant molecules are located between planes of polymer chains. That supports the idea of the virtual charge transfer between the dopant molecule and oxidized conjugated chain, especially when dopants are thought of as bridges for interchain hopping. The x-ray diffraction experiments allow us to estimate the crystallinity of the P3AT samples to be about 20%. Thus, having in mind the antiferromagnetic character of the magnetic response of the samples and the sudden drop in conductivity at low temperatures, the observed phenomena can be also interpreted in terms of the spin density waves (SDWs) [12]. It is expected that the magnetic response of the state characterized by means of the SDW is close to that of an antiferromagnet with a reduced magnetic moment. Decreasing of the saturation magnetic moment (μ_{sat}) for the doped P3OT sample was clearly observed during magnetization against external magnetic field measurements [6]. There μ_{sat} dropped from the value of $4.8\mu_B$/Fe ion measured at 4.2 K and above to the value $4.2\mu_B$/Fe ion at 2.1 K. That may support the idea of the SDW state developing in doped conjugated systems at low temperatures.

Results of the transport and structural experiments together with previously reported results of magnetic measurements allow us to draw the following conclusion: the presence of the magnetic complex as a dopant affects the transport processes. In the doped polymeric system interactions between the dopants may exist and the origin of these interactions may be interpreted on the basis of indirect exchange via charge-carrying species or (as a compliance of electrical transport and magnetic measurements) on the spin density wave ground state.

We are indebted to Professor A Proń for fruitful discussions. Very stimulating discussions with Professor A Oleś and Professor S Stafström are greatly appreciated. This work was financially supported by KBN grant No 3 P 405 057 07.

References

[1] Chiang C K, Fincher C R, Park Y W, Heeger A J, Shirakawa H, Louis E J, Gau S C and MacDiarmid A G 1977 *Phys. Rev. Lett.* **39** 1098
[2] Naarmann H 1987 *Synth. Met.* **17** 223
[3] Zuppiroli L, Bussac M N, Paschen S, Chauvet O and Forro L 1994 *Phys. Rev.* B **50** 5196
[4] Kulszewicz-Bajer I, Pawlicka A, Plenkiewicz J and Proń A 1989 *Synth. Met.* **30** 61
[5] Barta P, Nizioł S, Zagórska M, Proń A and Trybuła Z 1993 *Phys. Rev.* B **48** 243
[6] Barta P, Nizioł S, Le Guennec P and Proń A 1994 *Phys. Rev.* B **50** 3016
[7] Ehinger K and Roth S 1986 *Phil. Mag.* B **42** 799
[8] Paasch G 1992 *Synth. Met.* **51** 7
[9] Breslow R 1982 *Pure Appl. Chem.* **54** 927 and references therein
[10] Logdlund M, Lazzaroni R, Stafström S, Salaneck W R and Bredas J L 1989 *Phys. Rev. Lett.* **63** 1841
[11] Łużny W, Nizioł S, Straczyński G and Proń A 1994 *Synth. Met.* **62** 273
[12] Grüner G 1994 *Rev. Mod. Phys.* **66** 1