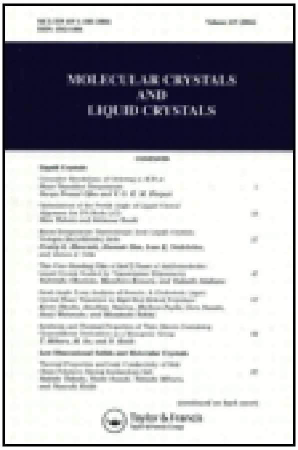

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The Metallic State of Doped Conjugated Polymers: ESR Studies

Patrick Bernier [a]
[a] GDPC - USTL, 34060, MONTPELLIER, Cédex, FRANCE

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THE METALLIC STATE OF DOPED CONJUGATED POLYMERS : ESR STUDIES

PATRICK BERNIER
GDPC - USTL, 34060 MONTPELLIER Cédex, FRANCE

Abstract We present ESR results obtained on highly doped polyacetylene and polyphenylene which bring some light on the magnetic and electronic properties of these systems, which are commonly assimilated to metals. We analyze the existing experimental data in terms of coexistence of Curie and Pauli type behaviours, and we show that ESR in the metallic state can be used to gain information on the dynamic properties of the electronic system.

INTRODUCTION

Classical materials with metallic behaviour are characterized by a state of high electrical conductivity associated with a temperature independant Pauli-type magnetic susceptibility[1]. Doped polyacetylene is a peculiar material in the sense that there is a wide range of dopant concentration (0.5 to 5 % mol) for which a negligible magnetic susceptibility is present with a rather high conductivity[2]. Then for concentrations above 5 % mol a significant Pauli susceptibility appears and the system is generally assimilated to a metal though the temperature dependence of the conductivity is not metal-like[3]. It is then interesting to investigate the magnetic properties and particularly their evolution upon doping up to the metallic state to obtain some information about the origin and nature of the electronic magnetism in these systems. For that purpose chemical doping of any conjugated polymer is not a very convenient technique. It generally yields inhomogeneous dopant distribution, the actual nature of the doping species is not always well established and the reversibility of the properties upon doping and dedoping cannot be checked [4] but ESR is easy to perform. On the contrary electrochemical doping allows a continuous study of the properties of the system. Transient as well as equilibrium states can be easily attained, and reversibility can be tested[5]. Nevertheless magnetic measurements during the electrochemical doping of any material is a delicate experiment to perform. In this paper we review some recent results obtained using ESR during the chemical or electrochemical doping of $(CH)_x$ and $(C_6H_4)_x$. The ESR parameters which will be considered are the g-value, the intensity I, the peak to peak linewidth ΔHpp of the absorption derivative, and the assymmetry ratio $A/_B$ of the spectrum, which have been studied versus the dopant concentration. Results are analyzed at the light of models which have been developped to describe the ESR magnetic properties of pure and impure metals[6] as well as highly doped semiconductors[7].

EXPERIMENTAL TECHNIQUES

The results described here are from various authors who used standard doping and experimental techniques[8,9,10]. One of our original contribution to the field concerns the use of electrochemical techniques to continuously study the evolution of the magnetic properties of $(CH)_x$ films during doping. The experimental conditions, in what concern the doping as well as the ESR recording, have been described elsewhere[11].

RESULTS AND DISCUSSION

g-value

In most cases (undoped or doped conjugated systems) the g-value is observed to be close to the free electron value g =2.0023, which confirm the fact that the resonance comes from electrons delocalised in the π-system[12,13]. For instance g presents no variation during the electrochemical Li doping of $(CH)_x$ and stays close to 2.0025[11]. Similarly there is an unsignificant variation of g when polyphenylene is doped with alkali metals, showing that there is a near zero contribution of the alkali metal spin-orbit coupling to the measured values[14]. On the contrary significant changes of g apparently occur when polyacetylene is doped with some transition metal halogenides like $FeCl_4^-$ [14] or $MoCl_5^-$ [15]. Nevertheless in these cases only the resonance of the transition metal ions Fe^{3+} ($g \sim 2.004$) and Mo^{5+} ($g \sim 1.8$) are observable while the π-electrons resonance is usually absent. Then in these cases the observed signal is not characteristic of the delocalized electrons system.

ESR intensity

The main difficulty if one wants to interpret the variations of the ESR intensity I comes from inhomogeneous doping. As I strongly depends on the dopant concentration, any inhomogeneity will distort the actual dependence. For instance it has been shown recently on electrochemically Li doped $(CH)_x$ that there exists a wide range of y values ($y < \sim 4$ %) for which I is almost zero and that I suddenly increases for $y > \sim 5$ %[8]. This result was made possible by a careful slow doping of a very thin film. On the other hand the same electrochemical Li-doping performed rapidly on a thick $(CH)_x$ film showed a continuous and monotoneous increase of I without any sharp increase for $y > \sim 5$ %[17].

The preceeding problem is connected with the question of the coexistence of Curie-type and Pauli-type spins in the system. If the dopant distribution is very inhomogeneous the undoped parts of the sample remain of the Curie-type while highly doped parts contribute to the total magnetization upon a Pauli form. On the contrary in the homogeneous case the Curie spins have disappeared during the first stages of the doping process and only remain the Pauli contribution which appears for $y > \sim 5$ %. It is then concluded that the apparent magnetic properties which appear for high doping levels strongly depend on the history of the system and on the kinetics of the doping process.

LINEWIDTH ΔHpp

The same difficulty exists in what concern the dependence with y of the linewidth ΔHpp. Inhomogeneous doping yields inhomogeneous broadening of the ESR spectrum which does not allow a quantitative analysis. When homogeneous doping can be achieved, the origin of the linewidth can be identified. If unresolved hyperfine coupling with the protons of the chains is the major contribution in undoped conjugated polymers, two other contributions have been identified in highly doped systems :

-spin orbit coupling on the dopant site. Recent experiments show that in alkali doped polyphenylene the linewidth ΔHpp increases with the atomic number of the dopant[14]. The same behaviour seems to be observed in doped polyacetylene[18].

-exchange between spins yielding a strong narrowing of the ESR spectrum. this effect applies mainly when the dopant concentration is high enough to favour an efficient exchange interaction between electron spins.

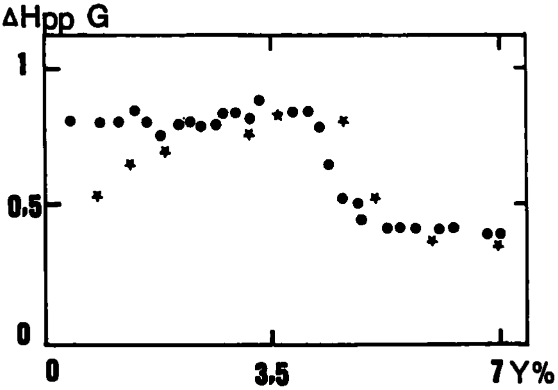

FIGURE 1 Variation of the ESR linewidth ΔHpp of $(CH)_x$ during the electrochemical Li doping, versus the dopant concentration y (● doping, ✱ dedoping).

In figure 1 is presented the variation of ΔHpp versus dopant con- concentration y for $(Li_yCH)_x$ electrochemically doped[17]. While the linewidth stays constant up to ~4.5 % a sudden decrease (by ~2) of ΔHpp is experienced at this concentration. This effect is roughly reversible and has to be related with the sudden increase of the ESR intensity I occuring at the same concentration and attributed to the appearance of a significant Pauli susceptibility[8].. In order to understand our linewidth data, we propose the following model :

When the dopant concentration y is varied, there is a competition between the number Nc of Curie spins (which decreases when y increases) and the number Np of Pauli spins (which increases when y increases)[19]. The transition occurs when Np suddenly increases ($y \sim 4$-5 %). The ESR characteristics reflect a Curie behaviour for $y < 4$-5 %) and a Pauli behaviour for $y > 4$-5 %. The linewidth ΔHpp follows the same rule with a dominant Curie character for the lowest concentrations, but becomes strongly exchange narrowed when Np increases significantly. For instance, a linewidth as small as 0.1 Gauss have been observed on a highly Li-doped (~ 10 % mol by electrochemical doping) $(CH)_x$ film[20], which is probably the smallest value obtained up to now on doped conjugated polymers. The temperature dependence of ΔHpp on highly Li-doped polyacetylene also suggest a metallic behaviour : the linewidth is roughly proportionnal to T, at least between 80 K and 370 K[21]. A similar behaviour has been obtained with K doped $(CH)_x$[22] and AsF_5 doped $(C_6H_4)_x$[9].

ASSYMETRY RATIO A/B

Resonance of conduction electrons in metals[23] or doped semiconductors[7] usually present an assymetry caracterized by the ratio A/B of the low field peak to the high field peak amplitudes. This effect is due to the existence of a skin depth caused by the high conductivity of the material (Dyson theory[24]). Simple geometries for the sample allow the use of analytical treatment and even with very inhomogeneous systems like doped polyacetylene or polyphenylene, typical Dysonian ESR spectra are commonly observed[13]. As in these systems the electronic mobility is expected to be very small, a comparison with the case of highly doped semiconductors is reasonable. Starting from the Dyson theory it is straightforward to predict the dependence of A/B versus d/δ where d is the thickness of the sample and δ the skin depth : A/B rapidly increases with d/δ , goes through a maximum for $d/\delta \sim 2.5$ and tends towards the limit value A/B $\sim$ 2.7[9,23]. A very good fit (Fig. 2) between theory and experiment has been obtained in case of $[(\mathrm{InCl}_4^-)_y\ \mathrm{CH}^{+y}]_x$ (Chemical doping)[26].

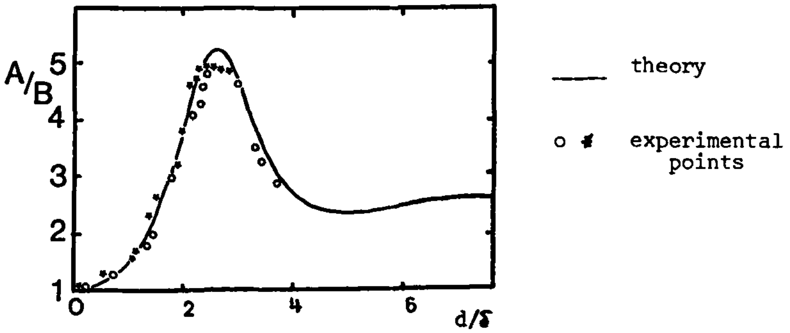

FIGURE 2 Variation of the assymetry ratio A/B of the ESR spectra on $[(\mathrm{InCl}_4^-)_{0.1}\ \mathrm{CH}]_x$, versus d/δ where d is the sample thickness and δ the skin depth.

From the comparison with the model developped by Pifer[7], values for the diffusion coefficient for the spins $\sim$ 0.25 cm^2/s are deduced and are in agreement with the starting hypothesis of poorly mobile spins. A similar result was recently obtained by Maurice et al on AsF_5 doped polyacetylene[9]. Nevertheless two remarks must be made :

- The above behaviour does not seem to be universal as A/B values as high as 16 could be observed which cannot be attained in the

Pifer model. It is not clear at the moment whether this is due to the existence of transitory conducting states with high mobility or to some anomalous dielectric behaviour of the material.

- During the electrochemical doping and dedoping of $(CH)_x$ the A/B variation is remarkably reversible and can be used to study the variation of the conductivity. Of course this has been already used to deduce the conductivity value of very reactive systems like $(Li_yCH)_x$ and is not restricted to electrochemical doping.

CONCLUSION

The last few years have seen a considerable improvement of our understanding of the magnetic properties of doped conjugated polymers, and ESR has been the main technique for that purpose. Combined with electrochemistry ESR represents a powerful way to investigate the properties of conducting polymers at the microscopic scale. Nevertheless many problems remain unsolved which are often related with the characteristics of the material itself : inhomogeneity, semy-cristallinity, unstability, etc... More data and a diversification of the materials to be investigated **are** necessary for further progress.

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