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Magnetic field dependent magnetization of a conducting plasticized poly(aniline) film

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Abstract

We report magnetic data of free standing films of poly(aniline) (PANI) protonated with a plasticizing di-ester of succinic acid. The data have been obtained using the electron spin resonance (ESR) technique at two different frequencies, X-band (9.4 GHz) and Q-band (34 GHz), on one hand, and by magnetization measurements in broad ranges of temperatures and magnetic fields on the other hand. All the data can be explained assuming a transition as a function of temperature from delocalized magnetic moments in the valence band to localized positive polarons in several antiferromagnetically correlated bands. By increasing the magnetic field, the magnetic properties are affected in several ways. An intra-band admixture of states occurs; it contributes to increase the spins' localization and finally promotes an antiferromagnetic–metamagnetic transition.

1. Introduction

The magnetic properties of doped poly(aniline) (PANI) have been extensively studied by both electron spin resonance (ESR) and magnetization measurements using either vibrating sample magnetometer (VSM) measurements or superconductor quantum interferometer device (SQUID) measurements [1–7]. In most cases, the magnetic data were analyzed in terms of a temperature independent Pauli contribution and an inverse temperature Curie component. Kahol and Mehring [8] were the first to point out the importance of taking exchange into account in analyzing magnetic data in conducting polymers. Bussac and Zuppiroli [9] have calculated singlet and triplet states of a bipolaron with the adiabatic continuum model including short range Coulomb repulsions and the attraction of the doping counter-ions. A model of polaron clusters was also proposed by Zuppiroli *et al* [10] to explain evidence of polaron correlation from magnetoresistance data. Mizoguchi *et al* [11] introduced a spin exchange contribution to explain the spin diffusion process in poly(aniline) at low temperatures. They have estimated the low temperature limiting value of the ratio

of the intrachain exchange constant to the Boltzmann constant to be around 10 K. In a recent work, Nascimento *et al* [12] used the concept of bands of ferromagnetic and antiferromagnetic correlated polarons and singlet ($S = 0$) and triplet ($S = 1$) bipolarons to explain both the ferromagnetic behavior and the magnetic field dependence observed in pellets of doped poly(3-methylthiophene) and poly(pyrrole). Magnetic field dependent magnetic susceptibility data have also been reported in conducting poly(aniline) and poly(pyrrole) nanostructures [13]. In this work we discuss the magnetic data of a free standing conducting film ($\sim 13 \mu\text{m}$ in thickness) of poly(aniline) (PANI) protonated with the di-2-ethylhexyl ester of sulfosuccinic acid ($\text{C}_{20}\text{H}_{38}\text{O}_7\text{S}$, abbreviated as DEHESSA) (abbreviated as PANI(DEHESSA)_{0.5}, which means that one counter-ion for two benzene rings is present in the resulting conducting salt). They have been obtained by electron spin resonance (ESR) using two different frequencies, X-band (9.4 GHz) and Q-band (34 GHz). The total magnetization has been measured using a SQUID as a function of temperature for different values of magnetic fields and as a function of magnetic field at different temperatures. Magnetic transitions have been observed as a function of the temperature and

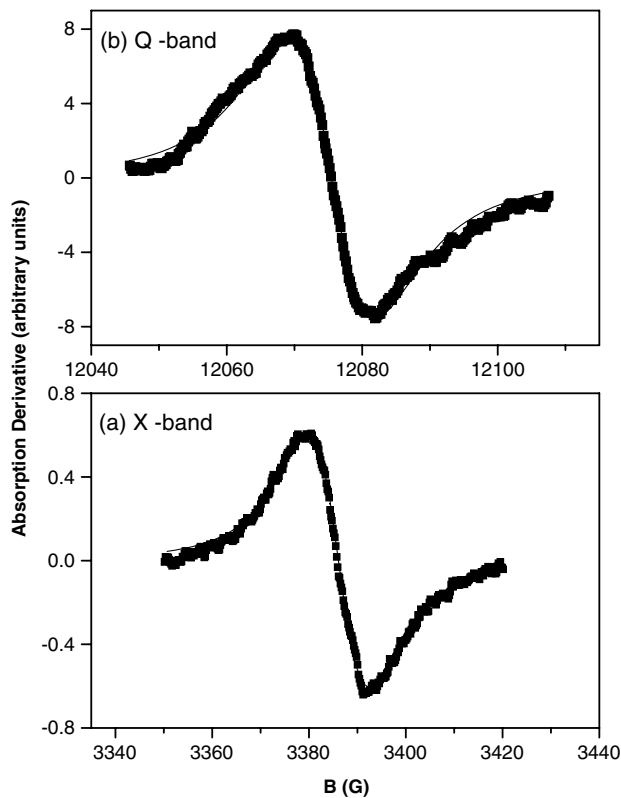


Figure 1. ESR lines recorded (a) at 4.2 K at 9.4 GHz (X-band) and (b) at 8 K at 34 GHz (Q-band).

magnetic field as well. We show that these transitions can be accounted for by introducing the concept of correlated polaronic bands.

2. Experimental details

The film was prepared according to the synthesis procedure fully described in [14]. The structure and the structural anisotropy of such films of 'plastdoped' PANI have been investigated by x-ray diffraction measurements. It has been shown that the structure of all these compounds consists of in-plane alternate stacks of PANI chains and dopant bilayers while the stacking direction of PANI chains is mainly oriented out of plane [14, 15]. It should be noted that such quite well defined structural features with a relatively high degree of ordering contrast with those of other doped PANIs, PANI doped with camphor-sulfonic acid for example, whose structure is much more ill defined [16, 17]. X-band (TE₁₀₂ rectangular cavity) and Q-band (TE₁₁₀ cylindrical cavity) ESR measurements were performed using a Bruker Elexsys spectrometer equipped with an Oxford helium gas cryostat. The PANI(DEHESSA)_{0.5} film was encapsulated in a special ESR tube of 2.0 mm diameter in an argon atmosphere, after being evacuated and purged several times. From both measurements, with the static magnetic field perpendicular to the film, at room temperature, a $g \sim 2.0$ and about 25 G wide Lorentzian resonance line was observed. Perpendicular resistivity (along the stacking direction of PANI chains) was measured at 300 Hz with a Solartron 1260 A

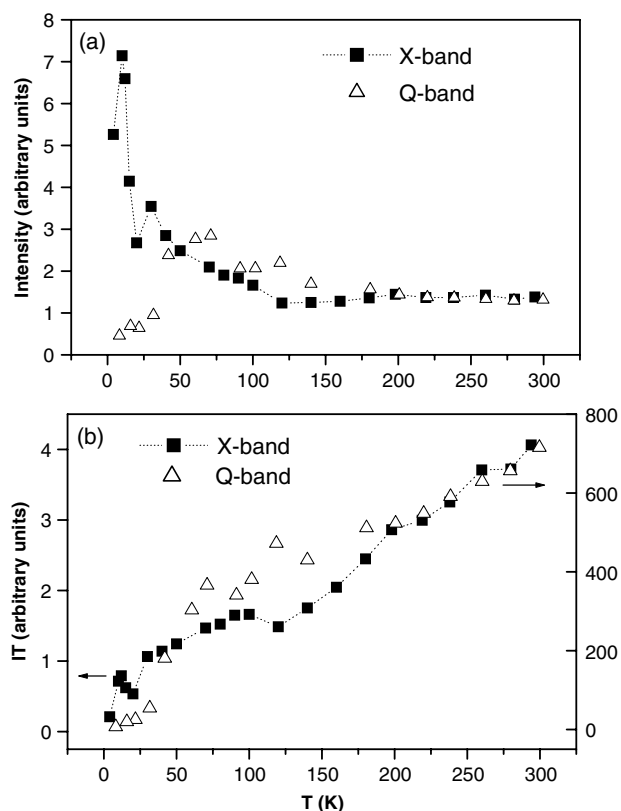


Figure 2. Variations of (a) the intensities (I) of ESR lines as a function of the temperature and (b) the product ($I \times T$) as a function of the temperature at low (3 kOe, closed squares and dotted line) and high (12 kOe, open triangles) magnetic field.

impedance analyzer with both faces of the film provided with vapor deposited gold contacts. The longitudinal global magnetization of a piece of film rolled around the direction of the applied magnetic field in between two non-magnetic plastic tubes has been measured under He atmosphere as a function of the temperature from 2 to 340 K at 3 and 50 kOe in a Quantum Design SQUID magnetometer model MPMSXL5. Similarly, the magnetization has also been measured at 50 and 2 K as a function of applied magnetic field from 0 to 50 kOe.

3. Results and discussion

3.1. Magnetic properties at low magnetic fields

In figure 1 the ESR spectra of both the X-band (a) and Q-band (b) are shown at 4.2 and 8 K respectively, both fitted as Lorentzian lines. In figure 2(a) we show intensity versus temperature ($I \times T$) data. The intensity data from both bands are not expected to be the same because they were obtained using different microwave cavities with different filling factors. For this reason, the Q-band data (open triangles) was normalized to coincide with the X-band data (full squares) in the temperature range in which Pauli susceptibility is observed. Starting with the X-band data, from 200 to 120 K a small decrease of the intensity is observed (figure 2(a)) before the delocalized-localized magnetic moment transition takes place. This type of behavior has been previously observed

Table 1. Parameters obtained from the fitting of equations (1)–(4).

Equation (1)	Equation (2)	Equation (3)	Equation (4)
$C_0 = 7.2 \times 10^{-2} \text{ emu g}^{-1} \text{ K}$	—	$M_p = 1.8 \times 10^{-3} \text{ emu g}^{-1}$	$M_0 = 2.1 \times 10^{-1} \text{ emu g}^{-1}$
$J_1/k_B = 12.7 \text{ K}$	$J_3/k_B = 219 \text{ K}$	—	$\lambda = 4.9 \times 10^{-2} \text{ G}^{-1}$

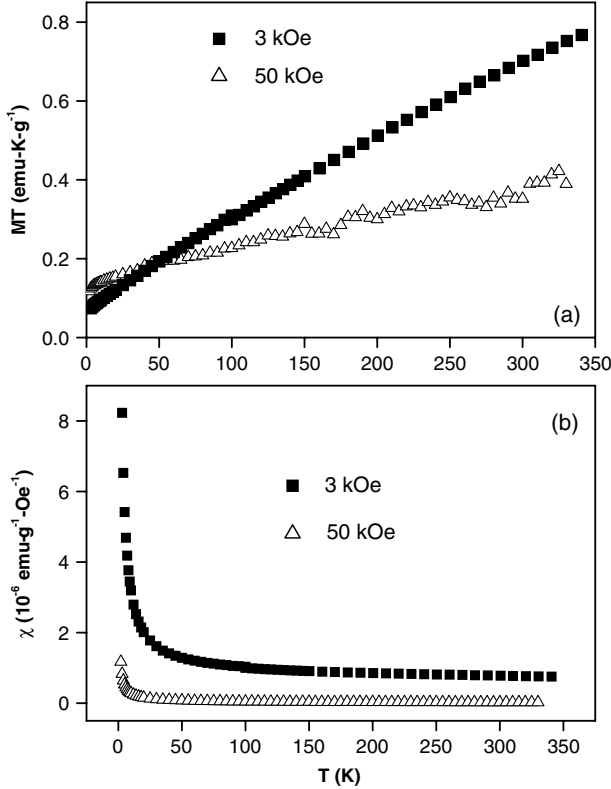


Figure 3. Magnetization measurements: (a) total magnetization per gram as a function of the temperature at 3 kOe (squares) and 50 kOe (triangles); (b) susceptibility as a function of the temperature for the same magnetic fields.

in other conducting polymers [18, 19]. In order to have a better understanding of the localized state, these data are plotted in figure 2(b) in the $IT \times T$ representation. Firstly it can be noticed that if the localized magnetic moments were not interacting, a pure Curie behavior should show up as a horizontal line. This behavior is clearly not observed and accordingly the localized magnetic moments are interacting. We assume that these magnetic moments are positive polarons and we will discuss which kind of interaction they are experiencing in the localized state. Still concerning the X-band data, we observe that around 10 K the intensity starts to decrease, with a small peak being first observed around 30 K. This decrease around 10 K has already been observed in films of poly(aniline) doped with camphor-sulfonic acid (PANI-CSA) by Sariciftci *et al* [20]. If we assume that polarons can interact to give a $S = 0$ singlet bipolaron or a $S = 1$ triplet bipolaron as discussed in [12], then the decrease in intensity is evidence that an $S = 0$ singlet bipolaron is the ground state, and this means we are dealing with an antiferromagnetic interaction. The role played by disorder was also discussed in [12]; we believe that disorder will prevent the complete

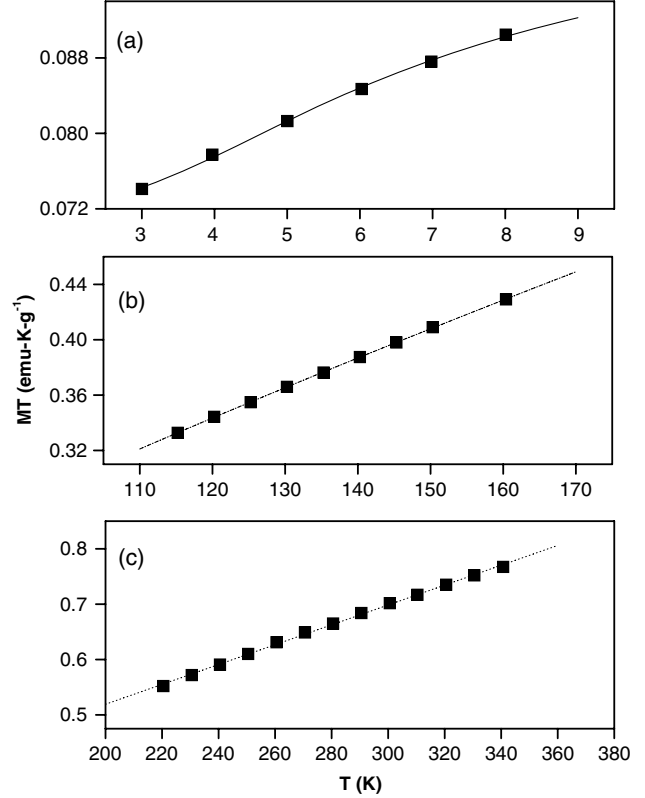


Figure 4. Fits of the different parts of the $MT \times T$ data obtained at 3 kOe according to the expressions (1), (2) and (3) (see text). The results of obtained fitting parameters are collected in table 1.

coupling of polarons into bipolarons and we assume that we have bands of antiferromagnetically coupled polarons.

Figure 3(a) shows magnetization data plotted as $MT \times T$ (zero field cooling) obtained applying a magnetic field of 3 kOe (full squares) and 50 kOe (open triangles). Figure 3(b) shows the susceptibility per gram for the same magnetization data. At very low temperatures, the temperature independent contribution in the $MT \times T$ data corresponds to the fraction of non-interacting polarons. The low temperature data of figure 3(a) for the magnetic field of 3 kOe was fitted using the expression [21]

$$MT = C_0 + 4C_1/(3 + \exp(J_1/k_B T)). \quad (1)$$

The constant C_0 is the Curie constant, and the parameter J_1 represents an average value of the exchange constant in the lowest band. If J_1 goes to zero in equation (1) the Curie behavior is recovered. The fitted data are shown in figure 4(a) and the fitting parameters are collected in table 1. The obtained value of $J_1/k_B = 12.7 \text{ K}$ is in reasonable agreement with the maximum observed around 10 K in the intensity of the X-band ESR data, suggesting that the excited

$S_1 = '1'$ state is found around this temperature. Above 10 K other bands of antiferromagnetically correlated polarons are expected but it is too arbitrary to determine their average values from the 3 kOe SQUID data and the X-band ESR does not have enough temperature points to allow a quantitative determination. We will refer to this collection of bands as band 2 of antiferromagnetically correlated polarons, in which, from the X-band ESR data, an $S = '1'$ state should be around 30 K. But the decrease in intensity observed from the X-band data below 200 K (figure 2(a)) suggests that another $S = '0'$ state is found close to the valence band, explaining the disappearance of magnetic moments. This happens when they leave the valence band and reach the $S_3 = '0'$ state. We can assume that in some range of temperatures the localized and delocalized states coexist. In figure 4(b) the 3 kOe magnetization $MT \times T$ data was fitted using the expression

$$MT = C + 4C_3/(3 + \exp(J_3/k_B T)) + M_P T. \quad (2)$$

In the above fitting expression the C constant has no real physical meaning because it does not represent the Curie contribution. M_P stands for the Pauli contribution and in order to correctly account for it in equation (2) we took its value from the linear fitting of the 3 kOe magnetization $MT \times T$ data:

$$MT = C_4 + M_P T. \quad (3)$$

Equation (3) was fitted in the range 220–340 K (figure 4(c)) in which we expect the Pauli contribution to be dominant. The value of M_P obtained for the Pauli contribution was replaced in equation (2) and a value of $J_3/k_B = 219$ K was obtained from the fitting (figure 4(b)) for the average value of band 3 of antiferromagnetically correlated polarons, in reasonable agreement with the X-band ESR data.

The parameters of both fittings are shown in table 1. It is interesting to observe that these results showing the contribution of localized and delocalized magnetic moments obtained at low magnetic field are in good agreement with the in-plane conductivity and absorbance data in PANI(DEHESSA)_{0.5} previously reported by Djurado *et al* [22]. Indeed, the metallic behavior of the in-plane conductivity has been observed in the same 220–300 K temperature range. From the extremely broad absorption tail extending towards the near infrared (NIR) domain, the coexistence of localized and delocalized states in the 200 K data could also be observed. An alternative way of discussing magnetic susceptibility data in terms of excited $S = 1$ triplet bipolarons was first suggested by Kahol *et al* [23] in the analysis of the data of several conducting polymers. It consists in using the magnetic susceptibility expression derived by Bussac and Zuppiroli [9] considering a random distribution of the dopants along the chains. They have used this model to fit the data of protonated poly(aniline) of Ginder *et al* [24]. However, the appearance of several clear defined steps in the susceptibility data can be observed, proving in our opinion the existence of several well defined small bands.

It is interesting to discuss the Pauli contribution ($M_P = 1.8 \times 10^{-3}$ emu g⁻¹) obtained from equation (3) and given in table 1. If we consider four benzene units and two dopants as

the repetition unit, we find a value of 7.2×10^{-4} emu mol⁻¹/4 rings for the Pauli susceptibility for a field of 3 kOe. This value is underestimated because we need to subtract the diamagnetic contribution, estimated from the Pascal constants for the sum of the elements to be of 7.8×10^{-4} emu mol⁻¹/4 rings. The corrected Pauli susceptibility at 3 kOe is then 1.5×10^{-3} emu mol⁻¹/4 rings.

3.2. The effect of a higher applied magnetic field

In order to understand the effect of a higher magnetic field on the magnetic properties of PANI(DEHESSA)_{0.5} we will discuss the Q-band ESR measurement with a resonance field around 12 kOe shown in figure 2 and the magnetization $MT \times T$ data obtained with a magnetic field of 50 kOe shown in figure 3. As already mentioned, in figure 2(a) it can be observed that for the Q-band data in the 200–120 K range, the decrease in intensity of the ESR line is not observed. Instead, Pauli susceptibility is observed but the delocalized–localized magnetic moment transition takes place at a higher temperature, i.e. around 180 K. We also observe from figure 2(a) that the intensity decreases at low temperatures from both X-band and Q-band data, but the temperature for which the intensity is maximal is not the same, being around 70 K for the Q-band and around 10 K for the X-band. We would like to understand these features applying the model of antiferromagnetic correlated bands of localized polarons and delocalized magnetic moments. One of the effects of a higher magnetic field, as previously discussed in [12], is to admix states with $S = 0$ with states with $S = 1$. This admixture of states will evidence the $S \neq 0$ state now observed from the Q-band data, in the range of temperatures where a decrease of intensity was observed in the X-band data, due to the $S_3 = '0'$ state. This admixture of bands also affects the temperature and magnitude of the intensity maxima in the Q-band data. For the same reason, the decrease in intensity at low temperatures happens at higher temperatures because the admixture of states increases the energy of the ground state of the antiferromagnetic correlated polarons, which is no longer a pure $S = 0$ state. Another consequence of the increase of the magnetic field is the additional reinforcement of localization. This can be nicely observed in the 50 kOe magnetization $MT \times T$ data in figure 3(a). The linear behavior observed for the high temperature range in the 3 kOe data (figure 4(c)) is at this field replaced by several small maxima, suggesting an increase in the contribution from the localized states until room temperature. The high magnetic field also increases the antiferromagnetic pairing, inducing a smaller susceptibility when compared with the 3 kOe susceptibility data. The $1/T$ Curie contribution is an approximation only satisfied for low magnetic fields and, in this way, it is only possible to obtain the Curie susceptibility for the 3 kOe magnetic field. Another interesting effect of the increase of the magnetic field can be observed in figure 5(a), in which SQUID magnetization data as a function of the magnetic field at 50 K are shown. A pronounced nonlinear behavior in the magnetization is observed for low magnetic fields. This contribution for the magnetization may come from the $S = '1'$

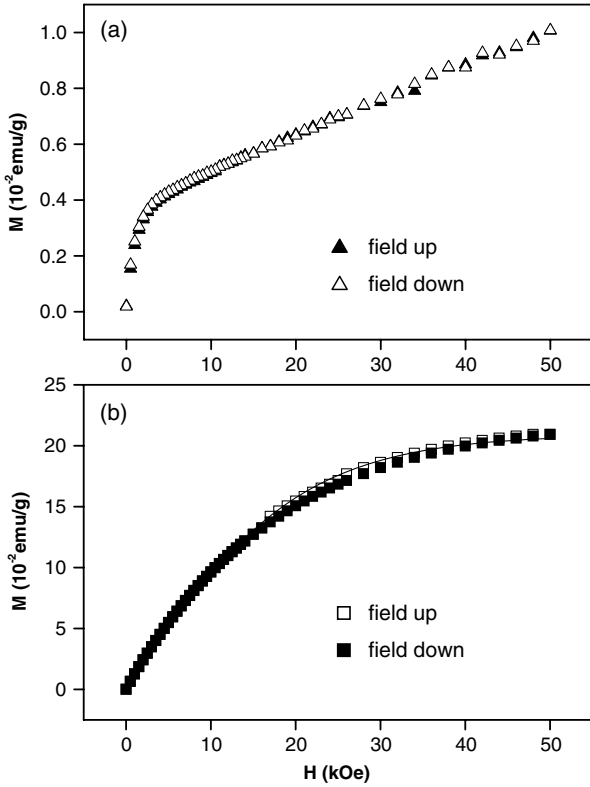


Figure 5. Total magnetization measured by SQUID as a function of the magnetic field at (a) 50 K and (b) 2 K. The solid line is the fitting of the 2 K down field data with the Brillouin spin 1/2 function.

excited triplet states. Above a magnetic field around 12 kOe a linear behavior is observed, signaling an antiferromagnetic–paramagnetic transition. This is the so-called metamagnetic transition, evidence of which was previously reported in conducting polymers [25]. The metamagnetic transition has been very well described by Hurd [26]. In a normal antiferromagnet the moments feel constraints due to exchange and crystal field anisotropy (D) that are far more substantial than the effects of any practical applied field. Below its Néel temperature a typical metamagnet is an antiferromagnet, but increasing the applied field strength can ultimately overcome the crystal anisotropy forces to change abruptly the internal magnetic structure. In some systems with large D the transition at low temperatures is to a saturated paramagnetic, sometimes called a ‘pseudo-ferromagnetic’, state. In figure 5(b) the same data are shown at 2 K and the saturated paramagnetic behavior can be clearly observed. In order to have a better understanding of the data of figure 5(b) we have performed a Brillouin spin 1/2 fitting:

$$M(H) = M_0 \tanh(\lambda H) \quad (4)$$

with

$$M_0 = N\mu \quad (5)$$

and

$$\lambda = \mu/k_B T. \quad (6)$$

Similar parameters were obtained for field up and for field down (full line shown). The parameters of the fitting are also reported in table 1. It is worth observing that the value

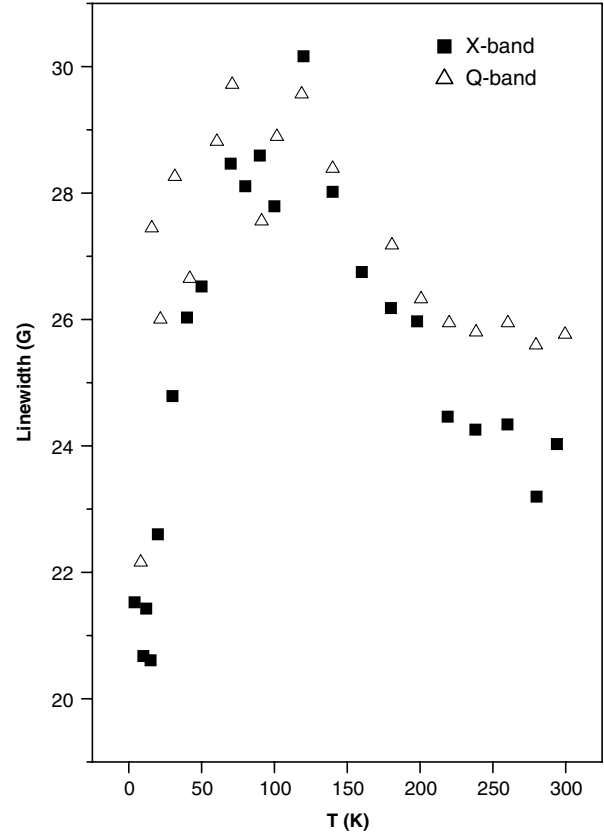


Figure 6. X- and Q-band ESR linewidth as a function of the temperature.

obtained for the parameter is higher than that we would find by simply assuming a Bohr magneton and a Curie behavior, i.e. $\lambda = 3.36 \times 10^{-5} \text{ G}^{-1}$. This fact suggests that a Curie–Weiss law is more appropriate and that an incipient ferromagnetic behavior is being observed. The magnetic moment obtained from the parameter assuming $T = 2 \text{ K}$ is $\mu = 13.6 \times 10^{-21} \text{ erg G}^{-1}$, a value slighter higher than that of the Bohr magneton, $9.27 \times 10^{-21} \text{ erg G}^{-1}$. If we want to compare the data obtained from equation (4) with the Curie constant C_0 obtained from equation (1) we have to write the linear approximation of the Brillouin function:

$$C_{\text{Curie}} = M_0 \mu H / k_B. \quad (7)$$

Replacing the values of M_0 and using $H = 3 \text{ kOe}$ we find $C_{\text{Curie}} = 6.2 \times 10^{-2} \text{ (emu g}^{-1}) \text{ K}$, in reasonable agreement with the value of C_0 obtained from equation (1).

3.3. The ESR linewidth

In figure 6, linewidth versus temperature ($H_{1/2} \times T$) for both X-band and Q-band data is shown. The data for both bands have similar magnitudes and temperature dependence in almost the whole temperature range. The ESR linewidth can show contributions of the spin–lattice relaxation time T_1 and the spin–spin relaxation time T_2 . Elliot’s mechanism of relaxation via the spin–orbit coupling in semiconductors [27] can be applied to understand the X-band linewidth data above 200 K.

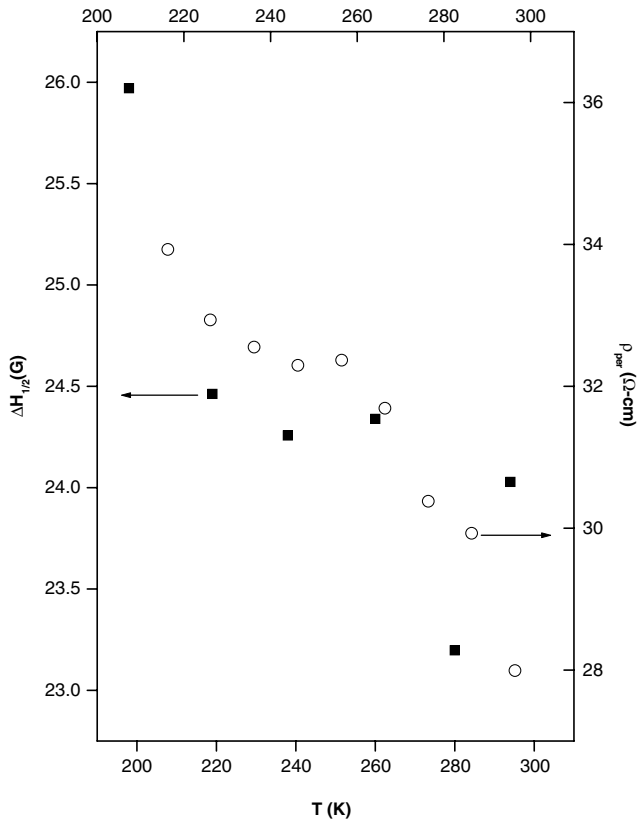


Figure 7. Comparison of X-band ESR linewidth data above 200 K (left scale) with the thermal variation of perpendicular DC resistivity in the same temperature range (right scale), evidencing that in this range the X-band ESR relaxation is dominated by Elliot’s mechanism.

According to [27] there is a relation of proportionality between the relaxation time τ_S associated with a scattering with spin flip and the relaxation time τ_R characteristic of the electrical resistivity. For a magnetic field applied perpendicular to the polymer film, the characteristic time involved is associated with the perpendicular resistivity, ρ_{per} . For the situation in which the temperature is higher than the Debye temperature, the linewidth can be written as

$$\Delta H \propto 1/\tau_R \propto \rho_{per}. \quad (8)$$

In figure 7 we have plotted X-band data $H_{1/2} \times T$ (full squares left scale) and perpendicular resistivity (open circles right scale) above 200 K. In spite of the scattering of the ESR data we can see a reasonable agreement between the two curves, suggesting that we are observing spin–lattice relaxation via Elliot’s mechanism. A similar agreement between resistivity data and linewidth for a low dimensional system was observed by Stein *et al* in graphite (HOPG) with the magnetic field applied parallel to the graphite layer [28]. Below 100 K, we observe a decrease in the linewidth when the temperature is decreased. In this temperature range the polarons are localized, they interact antiferromagnetically and we can assume that T_2 dominates and thus exchange narrowing is being observed. At very low temperatures, below 10 K for the X-band, there is an increase of the linewidth with the decrease of the

temperature. This increase reflects the increasing contribution of the uncorrelated polarons because the lowest $S = '1'$ state is being depopulated.

4. Conclusions

In this work we have shown ESR and magnetization data of PANI(DEHESSA)_{0.5}. All the data can be explained assuming a transition as a function of temperature from delocalized magnetic moments in the valence band to localized positive polarons in antiferromagnetic correlated bands. Concerning the stability of the sample, the encapsulated samples used in the ESR measurements always show reproducible data and are not suited to study aging effects. Magnetization data obtained with the MPMSXL5 magnetometer in a sample kept at ambient conditions shows a decrease of a factor around 2 in one year in the magnetization data values, without any particular feature around 100 K, suggesting that the small jump around this temperature seen in figure 3 is probably an artifact. It is interesting to discuss the differences observed in the intensity data taken from ESR (figure 2(a)) and susceptibility data taken from magnetization measurements (figure 3(b)). SQUID magnetization, being a volume measurement, does not ‘see’ very well the antiferromagnetic behavior because the net magnetization due to antiferromagnetic correlated polarons tends to zero. The SQUID technique ‘sees’ better the Curie behavior, and this Curie behavior is seen at low temperatures as an increase in the susceptibility. But the ESR technique, being a local technique, ‘sees’ both uncorrelated and antiferromagnetic correlated magnetic moments and can detect the signatures of the $S = 0$ states. The 30 K small maximum observed from the X-band ESR data also cannot be detected in the magnetization $MT \times T$ data at 3 kOe. But evidence of correlation close to this temperature for a magnetic field of 3 kOe can be observed in the $M \times H$ data at 50 K shown in figure 5(a). Another pertinent question concerns the difference of this system compared to the partially undoped poly(3-methylthiophene) (P3MT) pellets discussed in [12] in which a ferromagnetic correlation leaving a $S = 1$ triplet bipolaron ground state is proposed for the small crystalline portions of the polymer. For the disordered polymer antiferromagnetic correlated bands are proposed to explain the data above 20 K. The ferromagnetic–antiferromagnetic transition for that system around 20 K is probably a metamagnetic transition, because as shown in [25] the low magnetic field behavior is antiferromagnetic. In this way, for the system described in [12], small crystalline portions with ferromagnetic interaction are surrounded by the disordered polymer with antiferromagnetic interaction. It seems that this behavior is required by the balance of energy. The energy of the crystalline arrangement is lower, requiring the magnetic moment pairing to be of higher energy (ferromagnetic pairing) to match the energy of the surrounding disordered polymer. In the case of the sample studied in the present work, a highly doped and crystalline film of PANI(DEHESSA)_{0.5}, the magnetic moments delocalize in the crystalline and highly doped parts of the sample. In this way the balance of energy between the amorphous and crystalline

regions is provided by the kinetic energy. The effect of the increase of the magnetic field in the configuration measured in the present work points to a larger crystal field anisotropy D parameter and a more drastic antiferromagnetic–metamagnetic transition than that observed in the P3MT pellets studied in [25, 12]. In resumé, we believe that the present study proves that some conducting polymers can exhibit intrinsic magnetic behavior far more interesting than can be guessed by a simple Curie and Pauli term analysis.

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