Magnetic behavior of the conducting polyaniline film $(PANI\text{-}DDoESSA)_{0.5}$ obtained from Electron Spin Resonance

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Introduction

Electron spin resonance (ESR) data obtained from a self-standing film of the doped plasticized polyaniline di-n-dodecyl ester of sulfosuccinic acid $(PANI\text{-}DDoESSA)_{0.5}$ are shown. The ESR experiments were performed with the magnetic field perpendicular and parallel to the film surface. The data could be fitted with a Dysonian line and a small Gaussian line [1]. Although due to its very small intensity, this work will focus on the behavior of the Dysonian line. In the thin sample limit of Dyson's theory ($d \leq \delta$) [2,3] this line can be represented by a combination of absorption and dispersion Lorentzian lines. The in-plane conductivity calculated via asymmetry of the line is of the same order of the in-plane DC conductivity. A small difference was observed in the behavior of the different orientations of the field showing that the experiment can identify the magnetic anisotropy at this value of magnetic field. A maximum is observed for the intensity for both directions around 7K and the intensity decreases for lower temperatures suggesting the depopulation of the excited triplet state of bipolarons [6] and consequently antiferromagnetically correlated polarons. Some evidences of a weak ferromagnetism below 6K are presented.

The sample

The film was prepared according to the synthesis procedure fully described in the reference [4]. 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 in in-plane alternate stacks of PANI chains and dopants bilayers while the stacking direction of PANI chains is mainly oriented out-of-plane. [4,5].

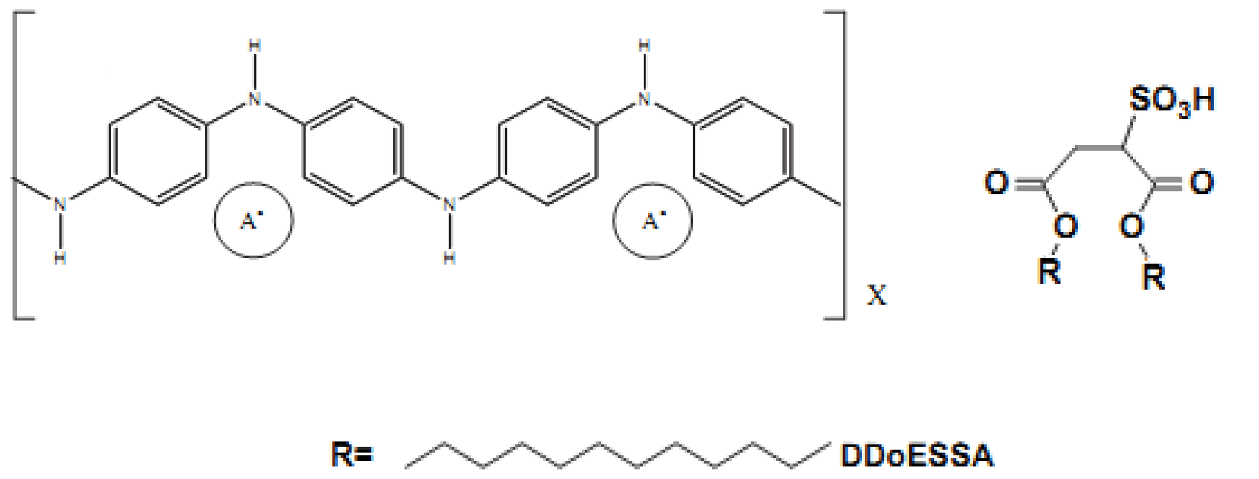

Fig. 1: Emeraldine salt form of PANI (conducting) and plastdopant di-n-dodecil ester of sulfosuccinic acid.

ESR measurments

A film (thickness d=49μm) of $(PANI\text{-}DDoESSA)_{0.5}$ was encapsulated in a special quartz tube of 2.0 mm inner diameter, in an argon atmosphere, after being evacuated and purged several times. X-band ESR experiments were performed in a Varian E-109 spectrometer equipped with an Oxford cryostat, from 4K to 300K , in two different configurations, with the magnetic field parallel and perpendicular to the plane of the film. A Cr^{3+} marker was placed close to the sample in order to obtain the actual g values.

Results

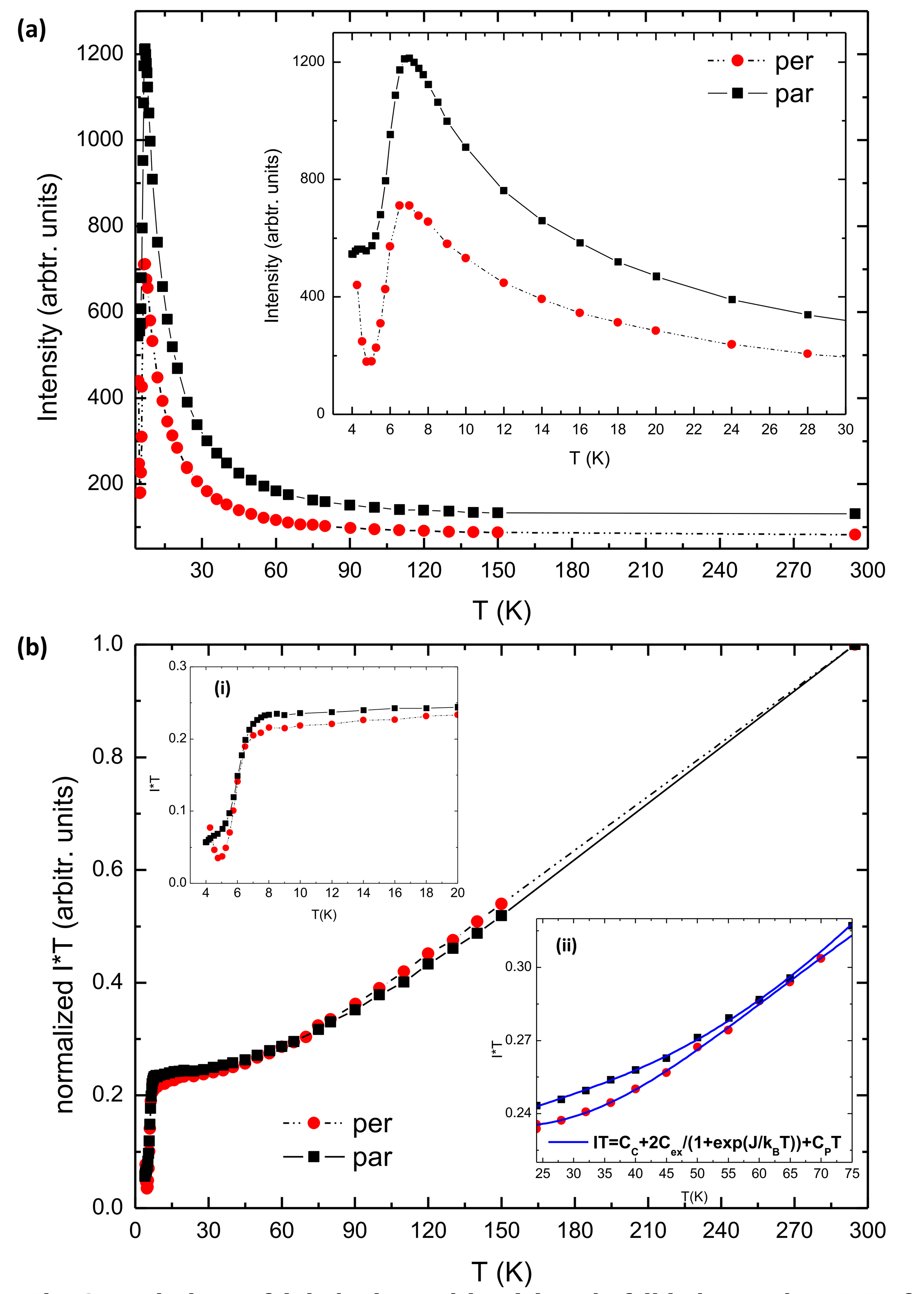

Fig. 2: Variations of (a) the intensities (I) and of (b) the product IxT of ESR lines as a function of the temperature at a 0.3G magnetic field parallel (black squares) and perpendicular (red circles) to the plane of the sample, obtained by double integration of the first derivative absorption line. Insets: (a) and (b)(i) span for lower temperatures; (b) (ii) adjust of ITxT data in the range 23K to 75K:

H_o orientation	C_C	C_{ex}	J/k_B	C_P
Parallel	0.22	0.55	262.4	$8.4x10^{-3}$
Perperndicular	0.23	0.32	146.9	0

where J is the exchange constant, k_B is the Boltzmann constant, C_C+C_{ex} is the Curie constant and C_P is the Pauli contribution for the magnetization.

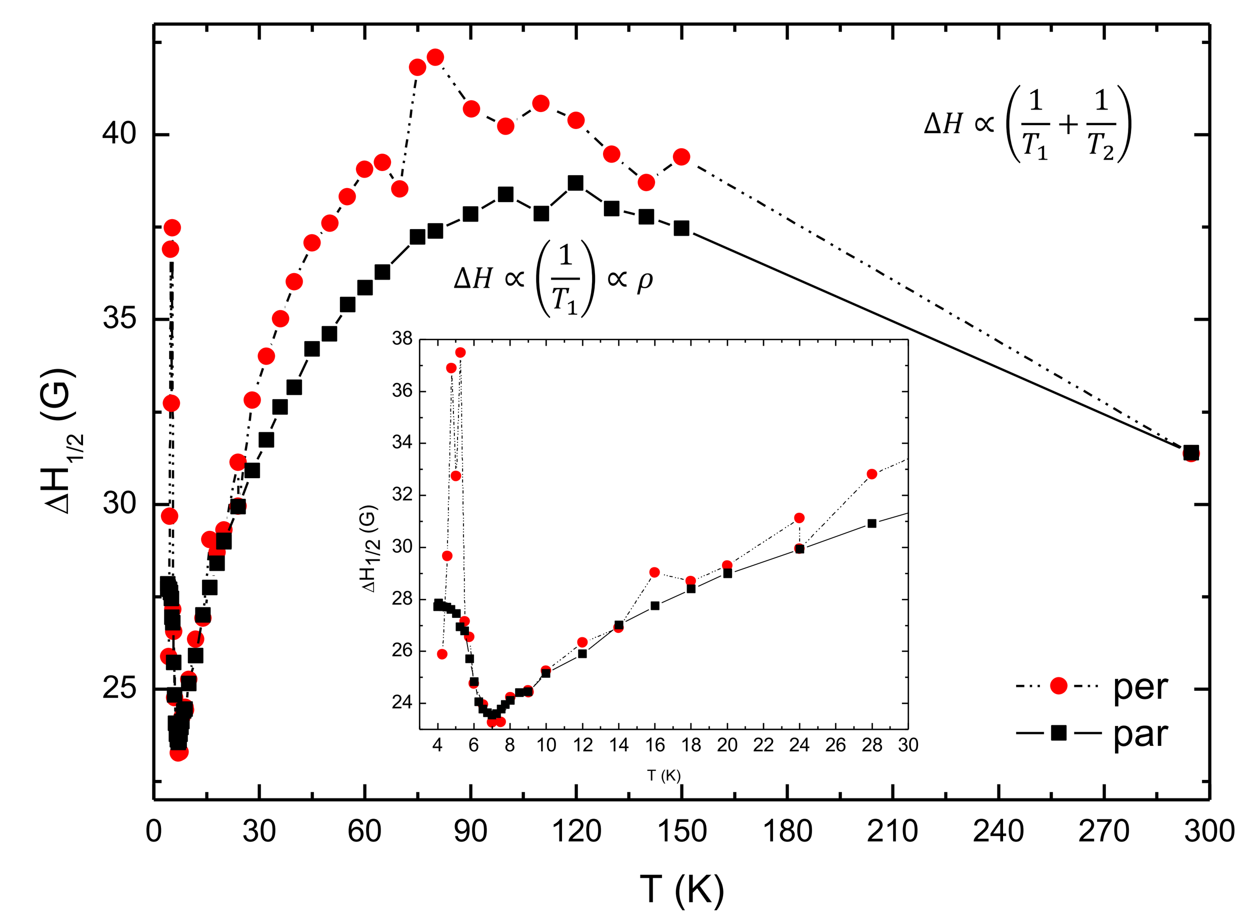

Fig. 3: Line width for both directions. ρ is the resistivity, T_1 corresponds to the spin-lattice relaxation time and T_2 stands for the spin-spin relaxation time [7]. Inset: span for lower temperatures.

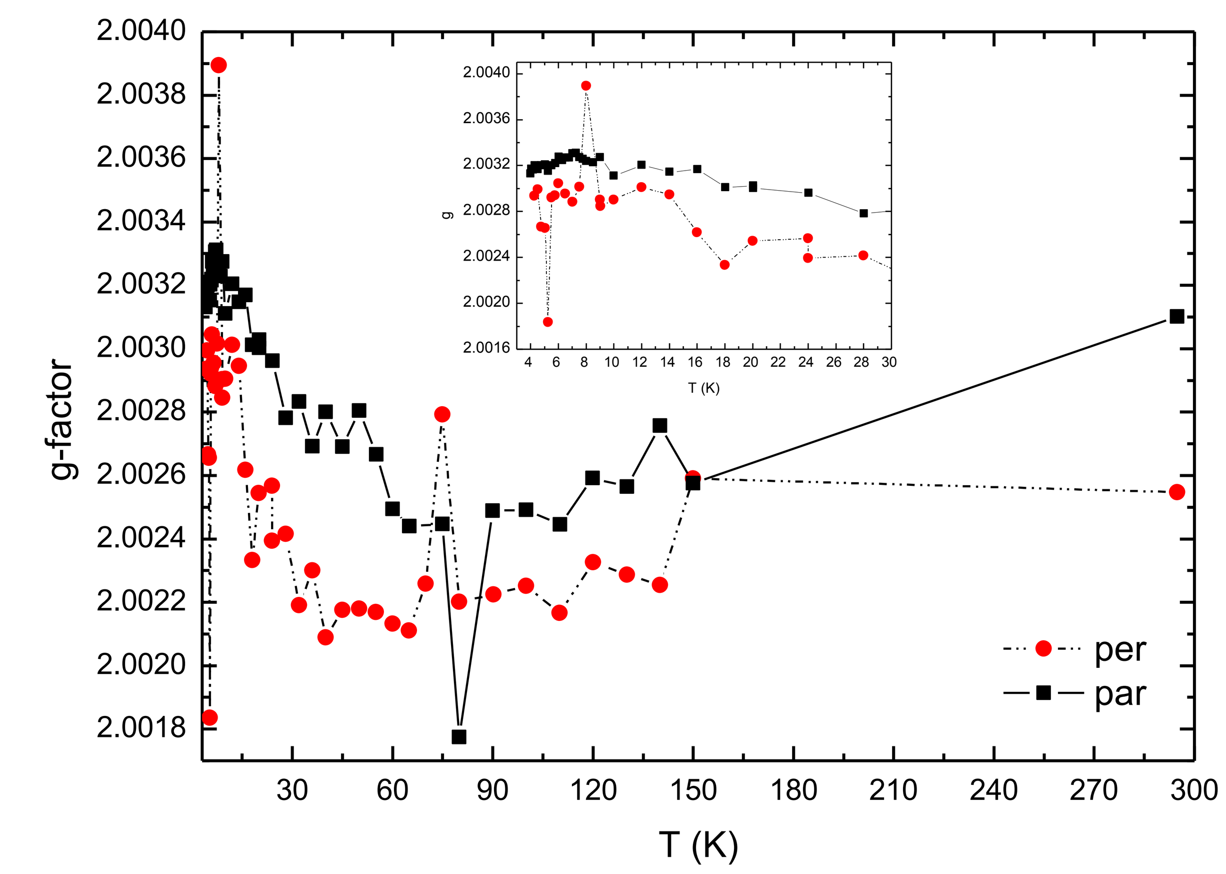

Fig. 4: An anisotropic g factor can be observed with the room temperature $g_{//}=2.0031$ (H_0 parallel to the plane of the film) and showing values higher than the free electron value $g_0=2.0023$ in the whole measured temperature range. A room temperature $g_{\perp}=2.0026$ is observed with the g-shift $(g-g_0)$ becoming negative in the range 110K-28K. Some kind of magnetic transition seems to appear at 75K.

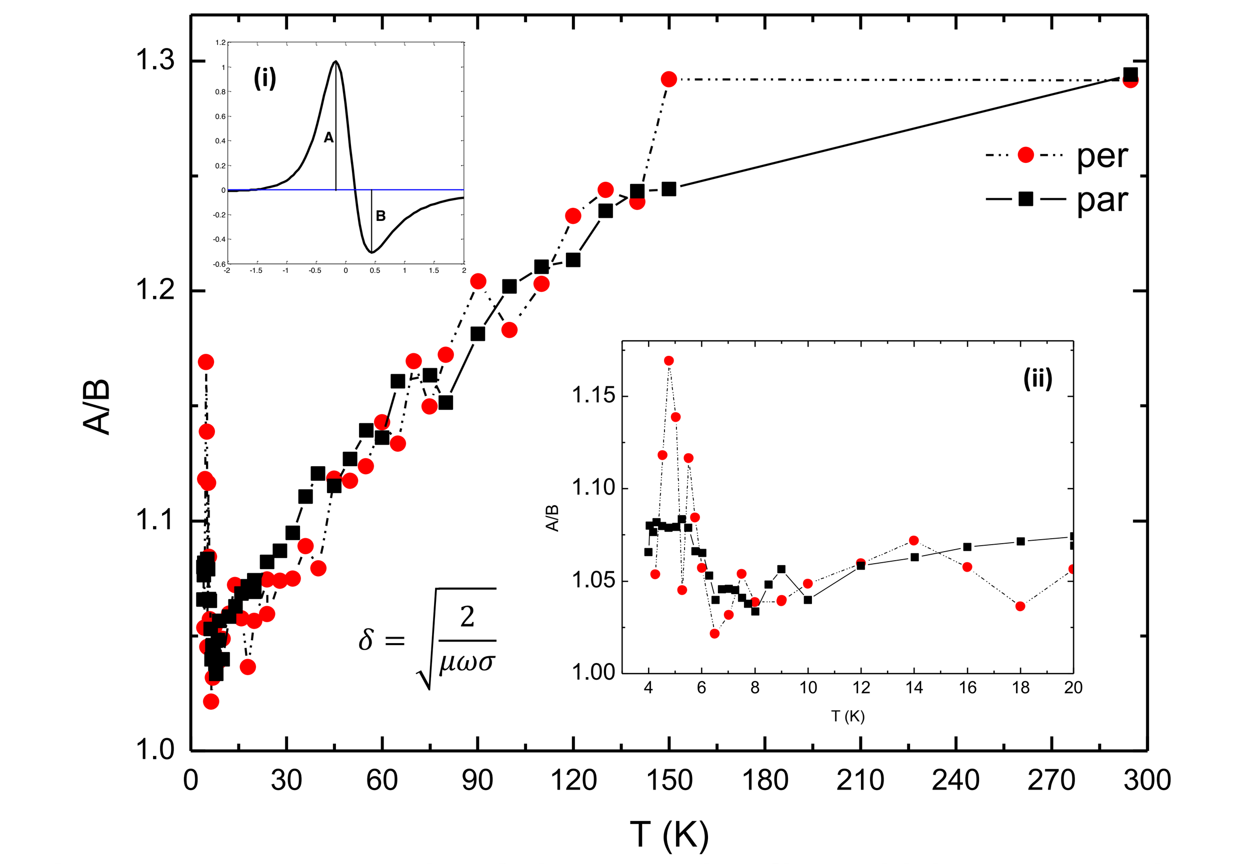

Fig. 5: Asymmetry ratio of the Dysonian line which corresponds to a ratio between the skin depth and the thickness of the sample. The different values for each direction at low temperature indicates a change of μ consistent with a weak ferromagnetic behavior. Inset: (i) illustrative A/B measurement; (ii) span for lower temperatures

Conclusions

An anisotropic exchange anti symmetric Dzyaloshinskii-Moriya term ($\hat{H} = \boldsymbol{D} \cdot (\vec{S_1} x \vec{S_2})$) mainly oriented perpendicular to the plane of the film, would explain the increase in ITxT, linewidth, A/B ratio and decrease in the g-value in the perpendicular direction, below 6K with the decrease of the temperature, as due to weak ferromagnetism.

It is interesting to note that we could extract such information in spite of the disorder of the system.

References

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