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ELECTRON PARAMAGNETIC RESONANCE IN AsF_5 DOPED POLYPARAPHENYLENE

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Abstract Polyparaphenylene, PPP, has been polymerized from benzene, as described by Kovacic, and heavily doped in AsF_5 vapour. The spin susceptibilities were about 10^{-6} emu/mole carbon for the Pauli part, plus one Curie spin per 1000 carbon atoms. The asymmetry of the EPR signal of pellets was found to be in good agreement with Dyson's theoretical predictions for slowly diffusive spins in the case of aged samples. On the other hand, the occurence of exchange interactions gave rise in freshly doped samples to enhanced magnetization diffusion rates, and then to more asymmetrical EPR lines.

EXPERIMENTAL

PPP was synthesized from benzene, $CuCl_2$, and dry $AlCl_3$ (1). P-type doping was accomplished by exposing the PPP powder (2) to a 100 mb vapour pressure of AsF_5. The 3 hours doping time led to a concentration of one AsF_6^- anion per 3 phenyls (3).

The DC conductivity of the doped material pressed to pellets felt between 200 and 260 S cm^{-1}.

The EPR was observed on a conventional X band spectrometer with field modulation frequencies of 100 and 4 kHz, equipped with a continuous helium flow cryostat.

EPR RESULTS

Susceptibility

0.1 mg of PPP powder was deposited around a small glass cylinder (1.5 mm diameter) enclosing a ruby standard (4), and placed in the bottom of an EPR tube. Doping was made in situ, and the EPR tube was then sealed. The EPR signal was symmetric, since the sample

thickness was only one tenth of the skin-depth, and lorentzian.

The spin susceptibility was measured between liquid helium and room temperature. The concentration of Curie spins was about 1000 ppm (per carbon atom), instead of 2 ppm in the undoped polymer, and the Pauli susceptibility was about 10^{-6} emu/mole carbon.

Study of Dyson effect on pellets

Dyson has calculated the EPR line shape for conduction electrons in metals (5), giving an analytical formula in the case of flat plates : the absorption line asymmetry can be described by the ratio A/B of the derivative extrema. It depends on Θ/δ, ratio of the plate thickness over the skin-depth, and on T_D/T_2, ratio of the diffusion time through the skin-depth over the spin-spin relaxation time (fig. 1).

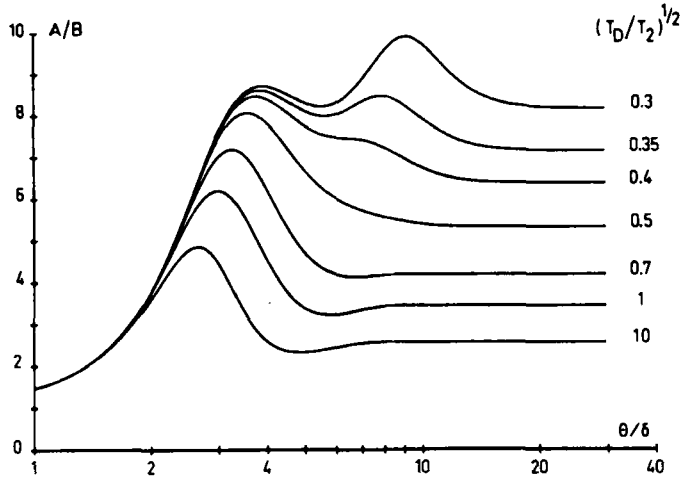

FIGURE 1 Asymmetry A/B as a fonction of Θ/δ for different values of $(T_D/T_2)^{1/2}$

The same results were found by Kaplan (6) who used the phenomenological Bloch equations modified to include diffusion of the magnetization and conductivity. Thus the paramagnetic centers are not necessarily the charge carriers. Bernier et al. have investigated the Dyson effect in metallic $(CH)_x$ films (7), and have found a good agreement with theory.

We have pressed doped PPP powder into pellets of various thicknesses and DC conductivities, obtained by aging in dry box. Figure 2 gives the results of EPR measurements which are well fitted by the theoretical curve for slowly diffusive spins ($T_D/T_2 > 100$) without any adjustable parameter.

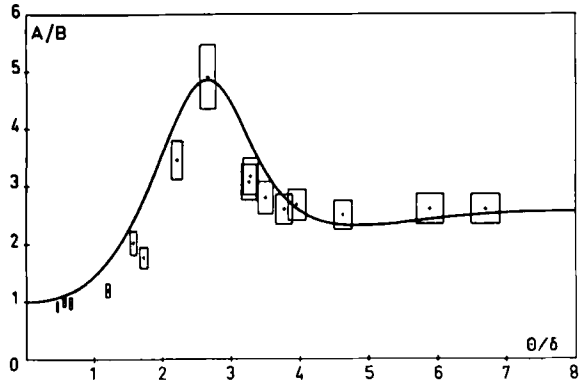

FIGURE 2 Asymmetry ratios A/B for aged PPP samples (8). The solid line is theoretical for $T_D/T_2 \to \infty$.

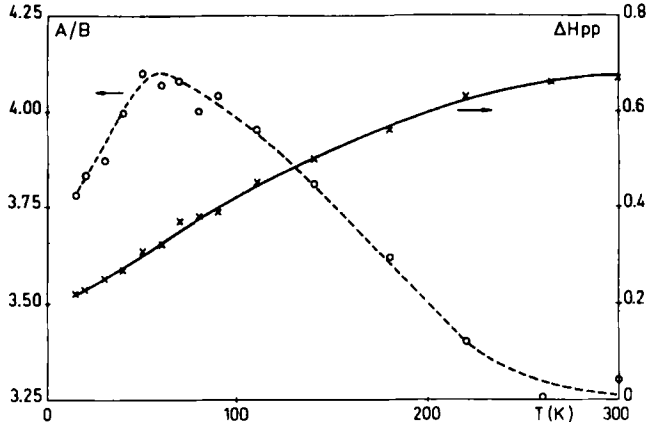

FIGURE 3 Asymmetry ratio A/B, (---), and linewidth ΔHpp (—), vs temperature for a freshly doped thick sample.

Importance of exchange interactions

The EPR of a freshly doped, thick ($\Theta/\delta = 28$) PPP sample shows evi-

dence for exchange interactions :
i/ Narrow line (ΔHpp = 0.23 G.), with extended wings.
ii/ No saturation at low temperature (P = 10 mW) : the spin system is more efficiently coupled to the lattice by fast magnetization diffusion through exchange (9).
iii/ The narrowing of the EPR line on cooling (fig. 3) would be inconsistent with motional narrowing.
iiii/ The asymmetry ratio is higher than the theoretical value of 2.55 for non diffusive spins. The diffusion coefficient it implies is too high ($\sim$ 50 cm^2/s) to be related to real motion of the spins, but rather to diffusion of the magnetization through exchange.

Then the increase of the asymmetry ratio and the narrowing of the line on cooling would indicate more exchange at low temperature.

CONCLUSION

The spin susceptibilities in AsF_5 doped polyparaphenylene are in good agreement with those reported earlier by Kume et al (10), but differ from those measured in the SbF_5 doped material (11). The Curie spins might be related to polarons in poorly doped regions (12). The strength of exchange interactions progressively weakens after doping leaving the expected Dysonian line shapes. We are working at determining whether this evolution should be linked to a slow diffusion and homogenization of the dopant anions, or to a degradation of the doped polymer.

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