ELECTRON PARAMAGNETIC RESONANCE STUDY ON BALL-MILLED NANOGRAPHITES

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We present the results of an Electron Paramagnetic Resonance study, a part of a joint Raman-EPR study on nanographites obtained by ball-milling of graphite pristine for different times [1].
Electron paramagnetic resonance (EPR) has long provided a valuable tool for probing the electronic properties of carbon-based materials with extended π-electron systems [see for example 2,3]. The dominant EPR signal in graphitic systems containing flat or rolled graphene sheets is given by the itinerant π-carriers in the conduction band, which give a characteristically asymmetric type of spectrum, with the so called *dysonian* lineshape. A further EPR signal of interest is that due to the electron spins localized on open edges of nanographenes with zigzag-type edges. According to the theoretical predictions, flat sheets of nanographene have non-bonding-electron states with energy levels at the contact point between the π- and π^*-bands, and electron density localized around the zigzag edge region [4].
We have studied samples of graphite powder obtained from Aldrich and ball milled for 90, 360 and 1200 minutes. All the samples give EPR signals only at resonance fields corresponding to carbon paramagnetic species. Therefore we can exclude any contribution from other contaminant paramagnetic species produced by the ball miller, which would be characterized by different g values.
The typical EPR spectrum is an asymmetric band with superimposed a narrow lorentzian line, as shown in Figure 1.
The EPR spectra have been simulated accurately by taking into account contributions of gaussian and dysonian broad components inhomogeneously broadened by the anisotropy of the **g** tensor, and of a narrow lorentzian line. The broad bands are attributed to the itinerant conduction electrons, and the lorentzian line to the π electrons on the zigzag edges. The linewidth of this line is exchange narrowed by the interaction with the itinerant electrons. Its intensity follows the Curie-Weiss behaviour with a small (few degrees) antiferromagnetic Weiss constant.
The trend on increasing the milling time is the following:
i. a progressive "symmetrization" from dysonian to gaussian of the broad EPR bands attributed to the shrinking of the graphite crystals;
ii. an increase of the homogeneous linewidth attributed to an increasing spin-lattice relaxation rate caused by the formation of new edges;
iii. a growing g anisotropy due to the disorder of the stacking of the graphene layers;
iv. an increasing contribution of the lorentzian line, due to the formation of new zigzag edges.

It should be noted that the trends of g anisotropy and of spinlattice relaxation rate with the milling time reported in Table 1 can be nicely correlated with the Raman results, see [1] and the abstract by Zerbi and Tommasini presented in this Graphita workshop.

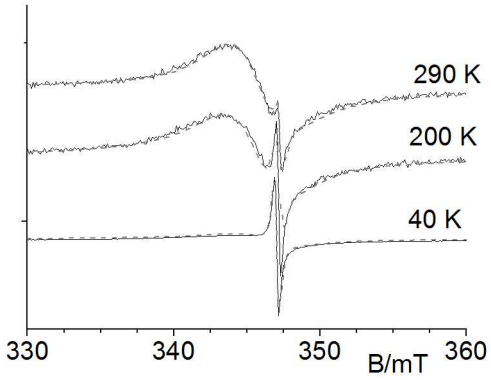

Figure 1: EPR spectra at three different temperatures of the sample ball-milled for 360 minutes. Continuous line, experimental spectra, broken line, simulations.

Sample	Γ/mT	$1/T_1$ /s^{-1}	Δg *100
GP	3.8	$2.3x10^9$	1.27
G90	4.5	$2.7x10^9$	1.7
G360	9	$5.5x10^9$	2.5
G1200	45	$27x10^9$	28

Table 1: Linewidths Γ, spin-lattice relaxation rates $1/T_1$ and g anisotropy of the EPR band due to the mobile electrons. GP= graphite pristine, G_{xx}= graphite milled for xx minutes.

References

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