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SURFACE AND INTERFACE SPIN RELAXATION OF CURRENT CARRIERS IN GRAPHITE AND ITS INTERCALATION COMPOUNDS

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The method of conduction ESR (CESR) has been actively used in studies of graphite, nano-graphite and graphite intercalation compounds (GICs) for determining the kinetic parameters of the spin carriers from an analysis of the CESR signal lineshape, linewidth and intensity [1,2]. For a long time the analysis of the CESR line shape for the graphite itself and its intercalation compounds was carried out using the well-known theory of Dyson [3] not including the surface spin relaxation of current carriers by the standard procedures. However, in a strict sense, Dyson's theory [3] of the CESR is applicable only for infinite metal plates of arbitrary thickness with isotropic conductivity and a single carrier type. Although experiments have shown the validity of using this theory for analyzing the CESR line shape in metal plates with finite dimensions, its applicability to the case of graphite and GICs with large anisotropy of skin depths, as well as anisotropy of carrier diffusion is not obvious. First, it was pointed out by Müller *et al.* [4]. To obtain the correct CESR line shape analysis in the case of anisotropic conductors, Blinowski *et al.* [5] have extended the Dyson theory [3] by taking into account the anisotropy of conductivity and diffusion. Herewith, authors, as well as all preceding researchers, implied that in GICs it is possible to neglect the surface and interface spin relaxation effects. In this paper, we present the experimental results for the dependence of CESR signal parameters in highly oriented pyrolitic graphite, pyrolitic graphite, acceptor and donor GICs on 1) sample dimensions, 2) microwave electromagnetic field configuration, 3) the frequency of modulation of constant magnetic field, 4) the time of graphite intercalation, and 5) the temperature. The analysis of these results unequivocally points to the presence of the *strong* surface and interface spin relaxation of current carriers in all samples investigated.

[1] M. Saint-Jean, C. Rigaux, B. Clejand, J. Blinowski, P. Kacman and G. Furdin. *Annales de Phisique*, **11**, 215(1986).
[2] A.M. Ziatdinov, *Molecular Physics Reports*, **18/19**, 149(1997).
[3] F.J. Dyson, *Phys. Rev.*, **98**, 349(1955).
[4] K.A. Müller, W. Berlinger, P. Pfluger, V. Geiser, and H.J. Güntherodt, *Solid State Commun.*, **55**, 803(1985).
[5] J. Blinowski, P. Kacman, C. Rigaux and M. Saint Jean, *Synth. Met.* 1985, **12**, 419(1985).

ESR IN NANOGRAPHITE AND ITS INTERCALATION COMPOUNDS

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The results of ESR investigation of nanographites - the structural elements (blocks) of activated carbon fibres (ACF). and their intercalation compounds with nitric acid are presented. According to our X-ray diffraction data the investigated nanographites consist of 5-6 graphen sheets and have an average in-plane size of $L_a \sim 30$ Å. The distance between carbon layers in nanographite is equal to 3.37 Å. that is much more. than in bulk graphite (3.354 Å).

The ESR spectrum of ACF consists of a single line. which g-factor value is close to the g-factor value for free electron. and with the peak-to-peak width ~6 mT. The EPR signal is practically symmetric. that specifies a weak anisotropy of the g-factor. At lowering of the temperature the ESR signal is narrowed at constant values of the g-factor and integral intensity.

The intercalation of nanographites by nitric acid molecules was carried out as by exposition of ACF in the intercalate atmosphere. and by the direct contact of ACF with the liquid intercalate. In both cases the spectrum of the final nanographite intercalation compounds consists of a single symmetric line with the g-factor value being close to the free electron value and with the linewidth ~1 mT. At the decreasing of temperature. the linewidth of ESR signal increases at constant values of the g-factor and integral intensity.

The distance between graphen sheets in nanographites decreases at the adsorption by ACF of water and some other molecules. Such compression of nanographites is accompanied by the change of g-factor and integral intensity of conduction ESR signal.

Reduction of the value and the anisotropy of g-factor in nanographite in comparison with the bulk graphite specify smaller value of the spin-orbit interaction for conduction electrons in nanographite. The most probable reason for this is the increase of intersheet distance in nanographites. resulting to the reduction of overlapping of conducting and valent π-zones. The value of ESR linewidth in nanographite on the order is more. than in bulk graphite. This fact contradicts to the well-known Elliott [1] theory of spin-lattice relaxation in bulk conductors, according to which the conduction ESR linewidth is proportional $(g-g_0)^2$. At the same time the specified result may be explained in the frameworks of the offered by author [2] model for the conduction electron spin-relaxation in carbon materials. In particular. according to this model in graphite an essential contribution of surface and interface spin relaxation into the total spin relaxation rate is present.

Note, that despite of an vicinity of $|g-g_0|$ values in nanographites and in their intercalation compounds with nitric acid the ESR signal in the former is much wider, than in the latter. Possible reason of this is the destruction of the edge-located magnetic states of nanographites at their intercalation by nitric acid molecules.

1. *Elliot R.J.* Phys. Rev. 1954. V.96, N 2. P.266-279.
2. *Ziatdinov A.M.* 1ˢᵗ World Conference on Carbon. Extended Abstracts. Berlin: Germany