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CONDUCTION ELECTRON SPIN RESONANCE IN GRAPHITE AND ITS INTERCALATION COMPOUNDS: SURFACE AND INTERFACE SPIN RELAXATION EFFECTS

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INTRODUCTION

In all previous investigations of CESR phenomenon in graphite and graphite intercalation compounds (GICs) at the analysis of the resonance line shape the surface and interface spin relaxation effects were neglected. We have studied the dependences of lineshape, linewidth and intensity of CESR signal in HOPG and GICs on 1) sample dimensions, 2) microwave electromagnetic field configuration, 3) the frequency of modulation of constant magnetic field, H_0, 4) the time of graphite intercalation, and 5) the temperature. The results of these investigations unequivocally point to the presence of the strong surface and interface spin relaxation effects in samples investigated.

RESULTS AND DISCUSSION

The dependence of CESR line shape asymmetry parameter, A/B, and line width, ΔH, on graphite plate width, *l*, (Fig. 1A and 1B) differs from the known theoretical curves, calculated from the Dyson[1] CESR line shape expression without taking into account the effect of surface

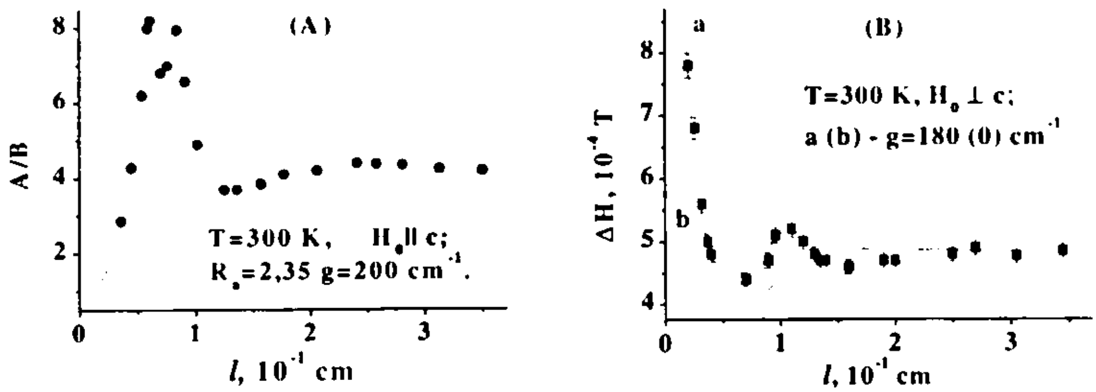

Fig. 1. The experimental (dots) and the theoretical (solid line) values of CESR line shape asymmetry parameter, A/B (A), and linewidth, ΔH (B), in HOPG plates vs. sample width *l*.

spin relaxation. First, the A/B(*l*) dependence has a three-peak form with the region of an 'inverted' line shape phase for the values of *l* between coordinates of these peaks (Fig. 1A). This is a characteristic property of the theoretical curves A/B(*l*) for the ratio $R_a=(T_{Da}/T_2)^{1/2}$ (where T_{Da} is the time of spin diffusion across the skin-depth δ_c governed by the σ_c – conductivity, and T_2 is the intrinsic spin-relaxation time) being less than 0,6[1-2], whereas for $l \gg \delta_c$ the experimental values of A/B are consistent with the theoretical values of this parameter for R_a>0.8[1-2] (Fig. 1A). Second, the values of A/B in the extrema of the experimental A/B(*l*) dependence differ considerably from those for the theoretical curves[2]. Third, at $l \to 0$ the experimental values of CESR linewidth tends to the infinity (Fig. 1B), whereas the corresponding theoretical curve tends to the finite value. (Fig. 1B). Additionally, the ΔH(T) dependence has a peak near 20 K (Fig. 2A), which can not be explained within the framework of existing theories of CESR linewidth in graphite.

Taken apart, the first particularity of the A/B(l) dependence in HOPG can be expla with the assumption that the density of microwave field is not uniform near the graphite plate surfaces and it depends on sample sizes. However, it is obvious that the second peculiarity of

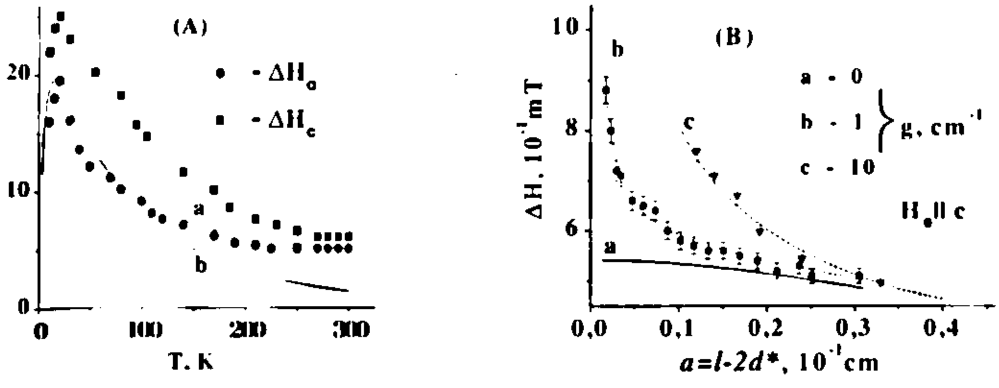

Fig. 2. The experimental (dots) and theoretical (lines) values of CESR linewidth, ΔH, in HOPG vs. temperature (A) and thickness, a, of the non-intercalated part of plate (for two different experiments of graphite intercalation by HNO_3) (B). In (A), the theoretical curve a (b) was calculated with constant value of intrinsic conduction electron spin relaxation time (using the Elliot[3] law for temperatures much less than the Debye temperature) and with Dyson[1] surface spin relaxation parameter g=200 cm^{-1}. In (B), $d^*=(2D_{int}\times\tau)^{1/2}$, where d^* is the thickness of the intercalated layer, D_{int} is intercalate two-dimensional diffusion constant.

this dependence and all peculiarities of ΔH(l) and ΔH(T) dependences can not be explained by such assumption. In Figs. 1A, 1B and 2A, the results of theoretical calculations, respectively, of A/B(l), ΔH(l) and ΔH(T) dependences in the frameworks of the Dyson[1] theory including surface spin relaxation effect of current carriers are presented. The A/B(l) curve was calculated taking into account the absorption of microwave field through all lateral surfaces both parallel and perpendicular to the c- axis and with the uniform distribution of microwave field. From Fig. 1A and 1B it can be seen that the theoretical curves with the value of Dyson[1] surface spin relaxation parameter $g=(3\varepsilon/4\Lambda_a)=200$ cm^{-1} (ε is a probability of spin reorientation during the collision of current carriers with the surface and Λ_a is a mean free path of current carriers in a basal plane) describes the experimental A/B(l) and ΔH(l) data well. The analysis have shown that the experimental curve ΔH(T) may be also explained well (Fig. 2.A) under the simultaneous presence of the following three factors: 1) surface spin relaxation of current carriers, 2) small amount of the localized spins (~1% of the current carrier concentration) with the value of g-factor being nearly equal to that for conduction electrons and 3) complete averaging of g-factors of the conduction electrons and localized spins.

In GICs with nitric acid the A/B(l) dependence has an additional weak extremum (from the direction of smaller l). In corresponding theoretical curves the similar peak appears only at the simultaneous presence of: 1) small amount of the localized spins and 2) surface spin relaxation effect of current carriers. But in this case the g-factors of spins localized near the sample surface and delocalized spins are not averaged.

The significant increase (decrease) of the graphite (GIC) CESR linewidth at the intercalation of the narrow HOPG plate by SbF_5, HNO_3, Br_2 and F_2 points out a non-zero probability of spin reorientation also during the collisions of current carriers with the interface between the intercalated and as-yet non-intercalated parts of plate (Fig.2B).

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