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

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Abstract: In all previous investigations of conduction ESR (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 line shape, line width and intensity of CESR signal in graphite and GICs on sample dimensions and experimental conditions and have shown the presence of the strong surface and interface spin relaxation effects in samples investigated.

Introduction

The method of conduction ESR (CESR) has been actively used in studies of graphite and graphite intercalation compounds (GICs) for determining the kinetic parameters of the spin carriers from an analysis of the CESR line shape [1-11]. For a long time the analysis of the CESR line shape for the graphite itself [1,2,11-14] and its intercalation compounds [3-10] was carried out using the well-known theory of Dyson [15] and Kaplan [16] not including the surface spin relaxation of current carriers by the standard procedures of Feher and Kip [17], Kodera [18], and Pifer and Magno [19]. However, in a strict sense, Dyson's theory [15] 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*. [20]. Saint Jean *et al*. [8] and Blinowski *et al*. [21] have studied this problem mathematically strictly using the Maxwell equations. To obtain the correct CESR line shape analysis in the case of anisotropic conductors, they have extended the Dyson theory [15] 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 spin relaxation effects. In this paper, we present the experimental results for the dependence of CESR signal parameters in highly oriented pyrolitic graphite (HOPG) and in GICs with nitric acid on sample dimensions and experimental conditions. The analysis of this results unequivocally points to the presence of the strong surface and interface spin relaxation effects in samples investigated.

Experimental

The CESR measurements were carried out at room temperature using an X-band E-line spectrometer in a rectangular cavity with TE_{102} mode. The constant magnetic field ($\mathbf{H}_0$) modulation frequency and amplitude were 2.5 kHz and ~0.1 mT, respectively. All plates for the experiments were cut from a single HOPG sample with the conductivity along (σ_a) and

perpendicular (σ_c) to the basal plane being equal to $(1.2\pm0.2)\times10^4$ S/cm and 7.7 S/cm at 300 K, respectively. They were in the shape of rectangular parallelepipeds with the dimensions: width (l)×height (h)×thickness (d)=l×0.355×0.072 cm^3, where $h\times l$ is the area of the basal plane. Synthesis of GICs $C_{10}HNO_3$ was carried out in liquid nitric acid with density $\rho\sim1.565$ g/cm^3. The stage of GICs was determined by X-ray diffractometer. The intercalation of narrow HOPG plate by HNO_3 was carried out on the sample with the dimensions: $2\delta_c\times0.4\times0.01$ cm^3 (δ_c is the skin-depth governed by the σ_c – conductivity) which was situated in a quartz tube connected via a valve to the reservoir with liquid nitric acid. During the measurements $\mathbf{H}_0$ (the magnetic component of the microwave field, $\mathbf{H}_{rf}$) was parallel (perpendicular) to the **c**-axis of the plates.

Results

Graphite.

For HOPG plates studied the CESR spectrum consists of a single line with the principal values of **g** – tensor determined by Feher-Kip [17] nomograms being equal to:

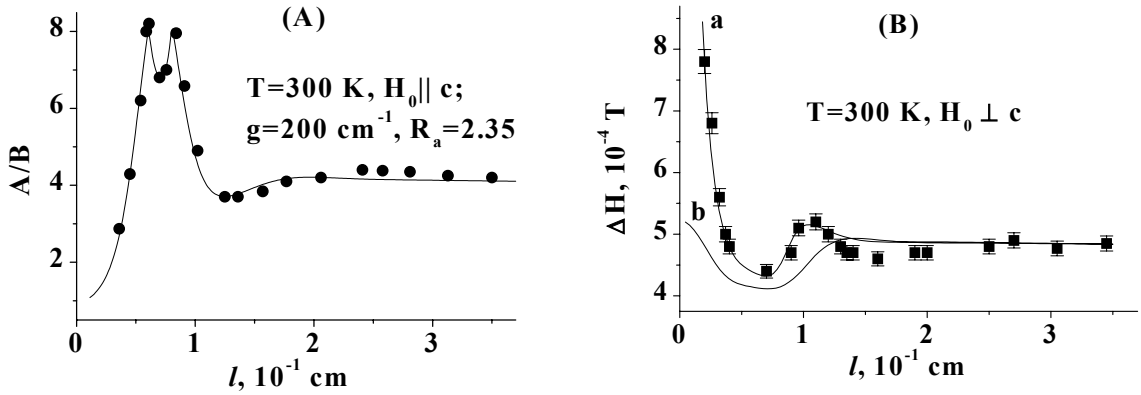

Fig. 1. The experimental (dots) and the theoretical (solid lines) values of CESR line shape asymmetry parameter, A/B (A), and line width, ΔH (B), in graphite vs. sample width l. In (B), curve a (b) corresponds to the value of Dyson [15] surface spin relaxation parameter g=200 (0) cm^{-1}.

$g_{\|}=2.0474\pm0.0002$ ($\mathbf{H}_0\|\mathbf{c}$) and $g_{\perp}=2.0029\pm0.0002$ ($\mathbf{H}_0\perp\mathbf{c}$). For the "thick" plates (d>0.045 cm) the dependence of asymmetry parameter, A/B, of the first derivative of CESR absorption line,
which is equal to the ratio of the peak intensity of the more intense wing, A, to that of the less intense wing, B, vs. l has three-peak form (Fig. 1A). In the interval $l_{1m}< l < l_{2m}$, where l_{1m} (l_{2m}) is the coordinate of the first (second) peak (in the direction of l increase) the line has an inverted line-shape phase – the A peak is located at a higher magnetic field than the B peak.
At l_{1m} and l_{2m} the line is symmetrical about the A peak, and the value of A/B is a maximum. The third, weak maximum is not associated with the change of phase of the line shape. At $l\rightarrow0$ the experimental values of CESR line width tends to the infinity (Fig. 1B). For all orientations of $\mathbf{H}_0$ relative to the **c**-axis the ΔH(T) dependence has a maximum near 20 K (Fig. 2A).

Graphite intercalation compounds: $C_{10}HNO_3$.

For all plates of GICs $C_{10}HNO_3$ studied, the CESR spectrum, as in graphite, consists of a single line with the axial angular dependence relative to the **c**- axis. The principal values of **g** – tensor are equal to $g_{\|}=2.0023\pm0.0002$ and $g_{\perp}=2.0028\pm0.0002$. The value of A/B does not depend on *d* and *h*. In a quasi-liquid phase of the intercalate subsystem ($T>T_c\approx250$ K) this dependence has qualitatively the same form as the corresponding dependence in graphite, except for the small extremum at $l^*\approx 0.06$ cm. This extremum is observed as well in a solid phase of the intercalate ($T<T_c$), where at $l>l^*$ the A/B(l) dependence has an one-peak shape.

Intercalation of graphite by HNO_3.

With the intercalation of HNO_3 into graphite the line width (the intensity), ΔH ($I=(A+B)\times\Delta H^2$), of the graphite CESR signal increases (decreases) monotonously (Fig. 2A).

At the beginning of the reaction, the A/B ratio of signal increases, but it is still 'normal' reaching a maximum value of A/B~13. The principal values of **g**-tensor for graphite (intercalated graphite) signal do not change up to its disappearance (up to the end of reaction).

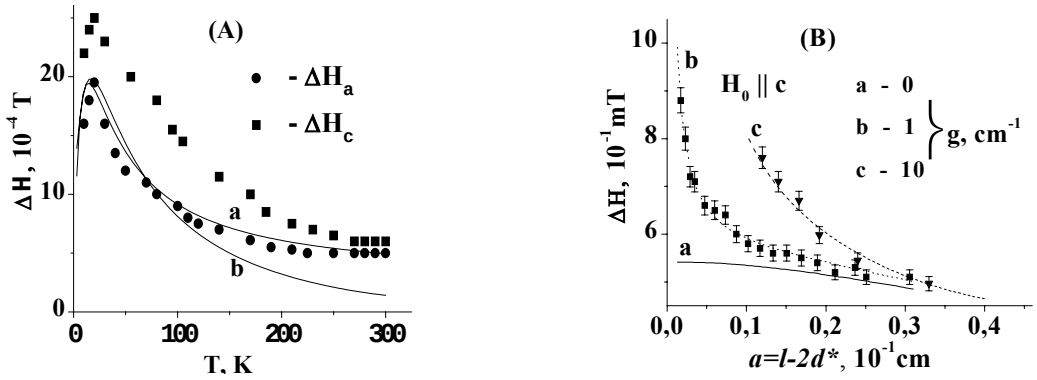

Fig. 2. The experimental (dots) and theoretical (lines) values of CESR line width, ΔH, in HOPG plates vs. temperature (A) and thickness, *a*, of the non-intercalated part of plate (for two different experiments of graphite intercalation by HNO_3) (B). In (A), the theoretical curve a (b) was calculated with constant value of intrinsic conduction electron spin relaxation time (using the Elliot [8] law for temperatures much less than the Debye temperature) and Dyson [15] surface spin relaxation parameter g=200 cm^{-1}.

Discussion

The dependence of CESR line shape asymmetry parameter and line width on graphite plate width (Fig. 1A and 1B) differs from the known theoretical curves, calculated from the Dyson [15] CESR line shape expression without taking into account the effects of surface spin relaxation. First, the presence of l values, for which the CESR line shape has an 'inverted' phase 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 [11,18], whereas the experimental values of A/B for $l >> \delta_c$ are consistent with the theoretical values of this parameter for $R_a>0.8$ [11,18] (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 [11,18]. Third, at $l\rightarrow0$ the experimental values of CESR line width tends to the infinity (Fig.

1B), whereas the corresponding Dyson [15] theoretical curve tends to the finite value, which differs from that for plates with $l >> \delta_c$ by 10% only (Fig. 1B). Additionally, the $\Delta H(T)$ dependence has a peak near 20 K (Fig. 2A), which can not be explained within the framework of existing theories of CESR line width in graphite.

In Figs. 1A, 1B and 2A, the results of theoretical calculations, respectively, of $A/B(l)$, $\Delta H(l)$ and $\Delta H(T)$ dependences in the frameworks of the Dyson [15] 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 [15] 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 $\Delta H(l)$ data well. The analysis have shown that the experimental curve $\Delta H(T)$ 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 or near one localized spin per 10^6 carbon atoms) 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.

The analyzis of origin of the additional weak extremum at $l^* \approx 0.06$ cm in $A/B(l)$ dependence for $C_{10}HNO_3$ has shown that the similar peak in corresponding theoretical curve appears only at the simultaneous presence of two factors in systems investigated: 1) small amount of the localized spins and 2) surface spin relaxation effect of current carriers. But in this case the g-factors of localized (near the sample surface) spins and delocalized spins are not averaged.

The invariability of g -values for graphite (intercalated graphite) up to the disappearance of graphite CESR signal (up to the end of reaction), indicates that the boundary, which separates the intercalated and as-yet the non-intercalated parts of sample may be considered as non-conductive. We suppose that the reason for the significant broadening of the graphite CESR signal is the collisions of current carriers with this non-conductive boundary. Using the relation $d^*=(2D_{int}\times\tau)^{1/2}$ (where d^* is the thickness of the intercalated layer, D_{int} is intercalate two-dimensional diffusion constant) the experimental dependence $\Delta H(\tau)$ (Fig. 2B) can be easily transformed into the dependence $\Delta H(a)$, where $a = l-2d^*$ is the thickness of the non-intercalated part of HOPG plate (Fig. 2B). The latter dependence can be calculated theoretically as well, using the Dyson[6] theory for the CESR in metals, including the effects of surface relaxation. It is shown in Fig. 2B, where the results of such analysis are presented, that the theoretical dependence of the graphite CESR line width, with Dyson [15] parameter g=1 cm^{-1} (curve b) and g=10 cm^{-1} (curve c) describes the experimental data well.

Acknowledgments

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