

SURFACE AND INTERFACE RELAXATION OF CURRENT CARRIER SPINS IN GRAPHITE AND ITS INTERCALATION COMPOUNDS

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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 Conduction ESR (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 pyrolytic graphite (HOPG) and in GICs with nitric acid on sample dimensions and experimental conditions. The analysis of this results uniquely points to the presence of the strong surface and interface spin relaxation effects in samples investigated.

Experimental

CESR measurements were carried using an Xband Eline spectrometer in a rectangular cavity with TE₁₀₂ mode. The

constant magnetic field (H_0) modulation frequency and amplitude were 2.5 kHz and 0.1 mT, respectively.

All experiments were carried out on samples in the shape of rectangular parallelepipeds with the dimensions: width (l)? height (h)? thickness (d), where $h \times l$ is the area of the basal plane. At the experiments, the basal $l \times h$ and lateral $d \times h$ sides were parallel and the c -axis was perpendicular to the magnetic component (H_{rf}), of the microwave field (Fig. 1). Note, that in the rectangular resonator, the structure of electromagnetic field of TE₁₀₂ mode has such a form that, at a conventional setting of the resonator, H_0 is parallel to the electrical component (E_{rf}) of microwave field (Fig. 1).

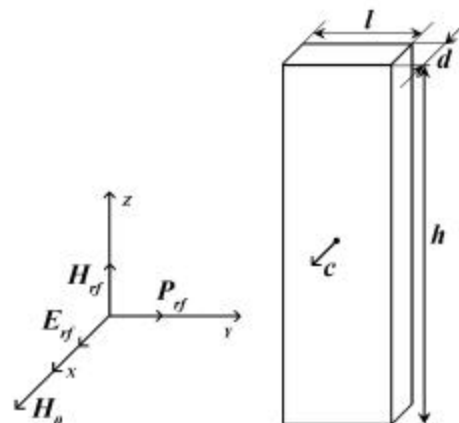


Figure 1. The orientation of the HOPG slab with respect to the external magnetic field H_0 and the cavity axis (X , Y and Z). H_{rf} , E_{rf} and P_{rf} are the magnetic and electric components of the radio-frequency field, and the Poynting vector in an unloaded rectangular cavity, respectively.

The study of dependences of graphite CESR lineshape parameters on sample dimensions were carried out on HOPG plates with dimensions: $l \times 0.355 \times 0.072 \text{ cm}^3$. The accuracy in the determination of the sample dimensions was $\sim 5 \times 10^{-4} \text{ cm}$.

Synthesis of the 2-nd stage GICs with nitric acid, $C_{10}HNO_3$, was carried out in liquid nitric acid with density $\rho = 1.565 \text{ g/cm}^3$ on HOPG plates with dimensions: $l \times 0.5 \times 0.01 \text{ cm}^3$. The stage structure of the GICs was determined by X-ray diffractometer.

The CESR study of graphite intercalation by nitric acid were carried out on HOPG plates with dimensions: $0.4 \times 0.04 \times 0.02 \text{ cm}^3$ and $0.4 \times 0.045 \times 0.03 \text{ cm}^3$. The HOPG samples were held in quartz tube connected via a valve to the reservoir with intercalate (liquid HNO_3 with density $\rho = 1.565 \text{ g/cm}^3$). Nitric acid vapours penetrated into the knee of reactor with the graphite sample through the hole with the size $8 \times 10^{-3} \text{ m}^2$ in the fluoroplastic diaphragm. Prior to the experiment, the system was evacuated to eliminate air and water. During the measurements, H_0 was applied along the graphite c -axis.

According to data of the four-probe method, at 300 K the c -axis conductivity (σ_c) of HOPG plate used is equal to $(7.7 \pm 0.8) \text{ S/cm}$. In the X-band experiment the value of the skin depth $\delta_c \sim 0.02 \text{ cm}$ corresponds to this conductivity, i. e. in experiments of graphite intercalation by nitric acid the whole volume of the HOPG plate investigated was available for the CESR studies.

The temperature studies of CESR spectra samples investigated were carried out in the temperature range from 100 K to 350 K. The temperature was varied by regulating the rate and temperature of nitrogen gas flow through the quartz dewar with the sample. The temperature was maintained and measured with an accuracy of $\sim 0.1 \text{ K/h}$ and $\sim 0.5 \text{ K}$, respectively.

Results

Graphite. The CESR spectrum of all HOPG plates investigated consists of a single asymmetric line determined by the Dyson-Kaplan mechanism [15, 16]. The spectrum is axial with respect to the c -axis and the principal values of g -factor determined by Feher-Kip [17] nomograms or those of Kodera [18] are equal to $g_c = 2.0474 \pm 0.0002$ and $g_a = 2.0029 \pm 0.0002$ for $H_0 \parallel c$ and $H_0 \perp c$, respectively.

For the "thick" plates ($l > 0.045 \text{ cm}$) 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. 2). 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, diffuse maximum is not associated with the change of phase of the line shape.

At $l \rightarrow 0$ the experimental values of CESR linewidth tends to the infinity (Fig. 3).

For all orientations of H_0 relative to the c -axis the ∂H increases first with decreasing temperature, forms a distinct peak at about 20 K and then falls off leftward (Fig. 4). The g -factor for $H_0 \perp c$ almost independent of temperature (Fig. 5). With the $H_0 \parallel c$, the g -value increases first with decreasing temperature, but it forms a distinct peak at about 20 K in a manner similar to that of the $\partial H(T)$ (Fig. 5).

Graphite intercalation by HNO_3 . After outflow of certain time (so-called "induction" time depending on sample size and experimental conditions) after the injection of HNO_3 gas into the part of the reactor with the HOPG plate, the CESR signal of graphite begins to transform and decrease in intensity until it fully disappears after ~ 3 hours (Fig. 6). Simultaneously a new signal with $g_c^* = 2.0019 \pm 0.0002$, and $g_a^* = 2.0030 \pm 0.0002$ appears in the spectrum (Fig. 7), where g_i^* ($i = a, c$) value is determined by the H_0 value at the point of intersection of the first derivative of CESR absorption line and the base line.

The linewidth (the intensity), ∂H ($I = (A+B) \partial H^2$), of the graphite CESR signal increases (decreases) vs. exposure time, τ , monotonously (Fig. 6 and 8). In an initial HOPG sample, which was used in experiment on intercalation, the CESR lineshape is 'normal' in the sense that the maximum peak height occurs at the lower magnetic fields. At the beginning of reaction the A/B ratio of graphite signal increases, but it is still 'normal' reaching a maximum value of $A/B > 8$. Later, upon further exposure in the intercalate atmosphere, the A/B ratio becomes 'reversed' (maximum peak height, A , occurs at higher magnetic fields than the peak B), and its magnitude decreases down to value less than 2.55; the A/B maximum corresponds to the moment when the 'reversal' of CESR lineshape takes place (Fig. 6). The g_i ($i = a, c$) value of graphite CESR signal does not change up to its disappearance.

For the CESR signal with g_i^* both the intensity, $I^* = (A^* + B^*) (\partial H^*)^2$, and linewidth, ∂H^* , dependences versus exposure time take a well-marked step-wise form (Fig. 7). At the moment of first observation the τ/τ^* value of this signal ~ 1 , then the value of asymmetry parameter increases up to 3.8, forms a distinct peak and decreases up to 2.2 to the end of reaction (Fig. 10). The g_i^* -values of this signal remain constant up to the end of intercalation.

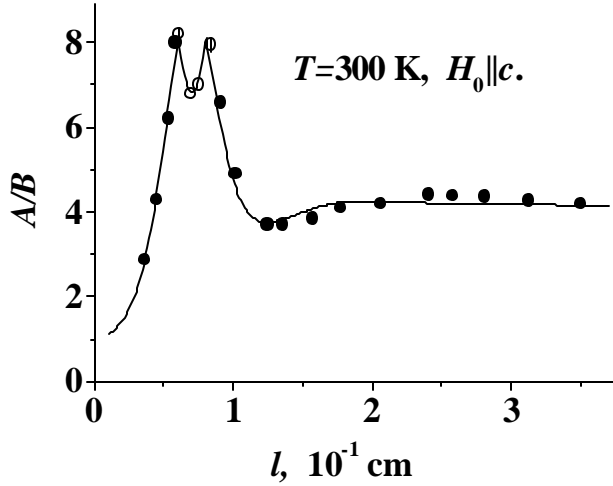


Figure 2. The experimental (dots) and the theoretical (solid line) values of CCSR line shape asymmetry parameter, A/B , in graphite vs. sample width l . The shaded and open dots are referred to the normal and 'reversed' lineshape, respectively; half-shaded dot corresponds to the lineshape with symmetric phase with respect to the A peak. $G_a=200 \text{ cm}^{-1}$, $R_a=2.35$, $R_c=6$, $T_2=1.16 \cdot 10^{-8} \text{ s}$. $R_i=(T_{Di}/T_2)^{1/2}$ (T_{Di} ($i=a, c$) is the time of spin diffusion across the skin-depth δ_i ($i=c, a$) governed by the δ_i - conductivity ($i=c, a$), and T_2 is the intrinsic spin-relaxation time), $\delta_i=0.02 \text{ cm}$. The X-band.

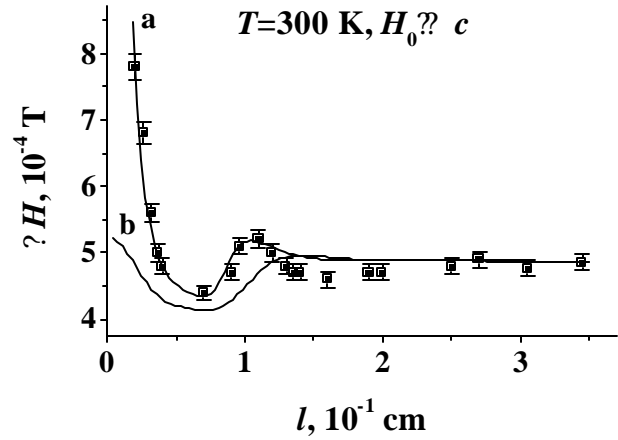


Figure 3. The experimental (dots) and the theoretical (solid lines) values of linewidth, δH , in graphite vs. sample width l . The curve a (b) corresponds to the value of Dyson [15] surface spin relaxation parameter $G_a=180$ (0) cm^{-1} . $R_a=2.5$, $R_c=6$, $T_2=1.38 \cdot 10^{-8} \text{ s}$. $R_i=(T_{Di}/T_2)^{1/2}$ (T_{Di} ($i=a, c$) is the time of spin diffusion across the skin-depth δ_i ($i=c, a$) governed by the δ_i - conductivity ($i=c, a$), and T_2 is the intrinsic spin-relaxation time), $\delta_i=0.02 \text{ cm}$. The X-band.

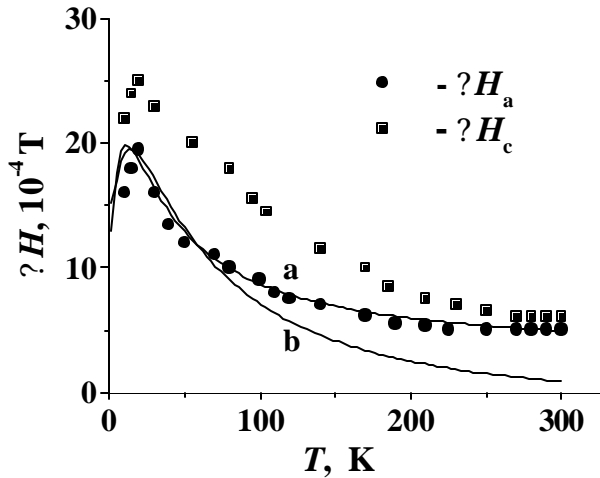


Figure 4. The experimental (dots) and theoretical (lines) values of CCSR linewidth, δH , in HOPG plates vs. temperature T . The theoretical curves (a) and (b) were calculated using the Exp. (2) with constant ($= 4.4 \cdot 10^{-4} \text{ T}$) and determined by the Exp. 4 values of linewidth (the intrinsic conduction electron spin relaxation time), respectively, and Dyson [15] surface spin relaxation parameter $G_a=180 \text{ cm}^{-1}$. The X-band.

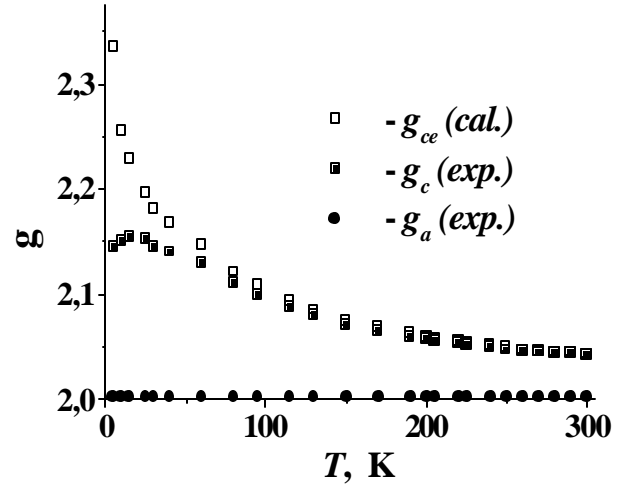


Figure 5. Experimental (solid dots) and calculated (open dots) values g -factor for CCSR signal in HOPG vs. temperature. The g_{ce} -values were extracted from the expression: $g_c(\text{exp}) = g_{ce}(\delta/\delta_c + \delta_s) + g_s(\delta/\delta_c + \delta_s)$, where g_{ce} , g_s are the values of g -shifts for the conduction electrons and the localized spins, respectively, both at $H_0 || c$. The X-band.

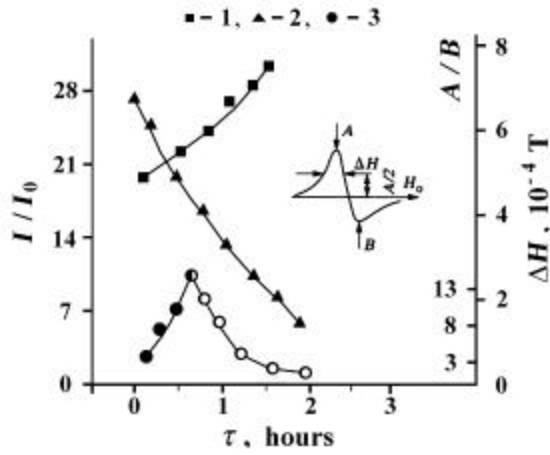


Figure 6. CCSR lineshape parameters for non-intercalated parts of the narrow ($l \sim 2\tau_c$) HOPG plate vs. exposure time, τ , in HNO_3 atmosphere. 1, 2 and 3 correspond to τH , A/B and I/I_0 , respectively ($I = (A+B)\tau^2 H^2$; I_0 is the intensity of the Mn^{2+} ESR signal of the standard sample: ZnS:Mn^{2+}). The shaded and open dots are referred to the 'normal' and 'reversed' lineshape, respectively; half-shaded dot corresponds to the lineshape with symmetric phase with respect to the A peak. The X-band; $T=300$ K.

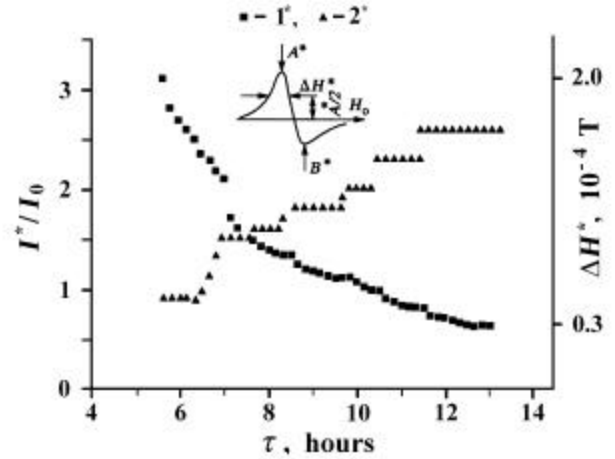


Figure 7. CCSR lineshape parameters for intercalated parts of the narrow ($l \sim 2\tau_c$) HOPG plate vs. exposure time, τ , in HNO_3 atmosphere. 1* and 2* correspond to τH^* , A^*/B^* and I^*/I_0 , respectively ($I^* = (A^*+B^*)\tau^2 (H^*)^2$; I_0 is the intensity of the Mn^{2+} ESR signal of the standard sample: ZnS:Mn^{2+}). The X-band; $T=300$ K.

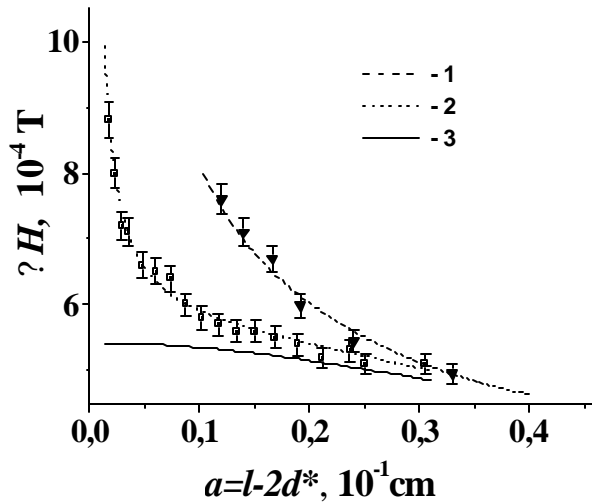


Figure 8. The experimental (dots) and theoretical (lines) values of CCSR linewidth, τH , vs. thickness, a , of the non-intercalated (by HNO_3) part of HOPG plate (for two different samples). 1: $G_a=30 \text{ cm}^{-1}$, $T_2=1.15 \cdot 10^{-8} \text{ s}$, $\tau_c=0.013 \text{ cm}$; 2: $G_a=2 \text{ cm}^{-1}$, $T_2=1.3 \cdot 10^{-8} \text{ s}$, $\tau_c=0.02 \text{ cm}$; 3: $G_a=0$, $T_2=1 \cdot 10^{-8} \text{ s}$, $\tau_c=0.02 \text{ cm}$. $H_0 \parallel c$, $T=300$ K.

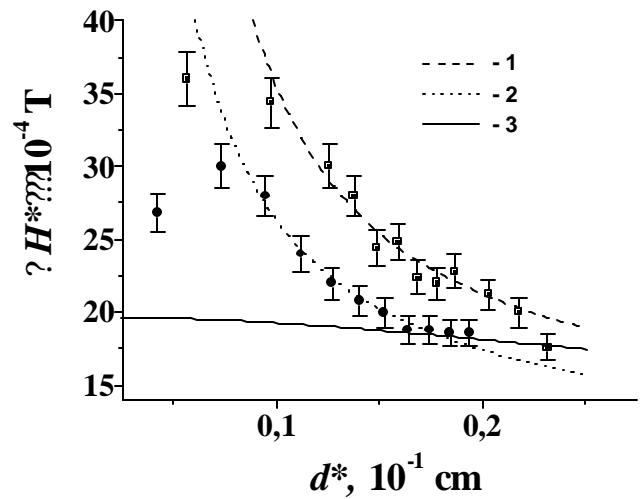


Figure 9. The experimental (dots) and theoretical (lines) values of CCSR linewidth, τH^* , vs. thickness, d^* , of the intercalated (by HNO_3) part of HOPG plate (for two different samples). 1: $G_a^*=180 \text{ cm}^{-1}$, $T_2^*=0.38 \cdot 10^{-8} \text{ s}$, $\tau_c^*=0.025 \text{ cm}$; 2: $G_a^*=70 \text{ cm}^{-1}$, $T_2^*=0.45 \cdot 10^{-8} \text{ s}$, $\tau_c^*=0.025 \text{ cm}$; 3: $G_a=0$, $T_2=0.35 \cdot 10^{-8} \text{ s}$, $\tau_c=0.025 \text{ cm}$. $H_0 \parallel c$, $T=300$ K.

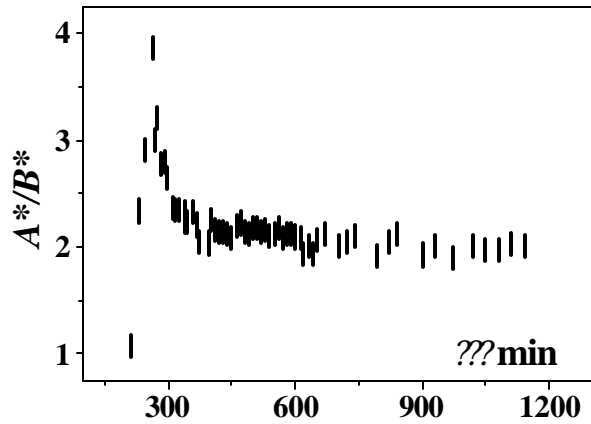


Figure 10. The CCSR lineshape asymmetry parameter, A^*/B^* , of the intercalated part of HOPG plate vs. exposure time, τ , in HNO_3 atmosphere. The X-band; $T=300$ K.

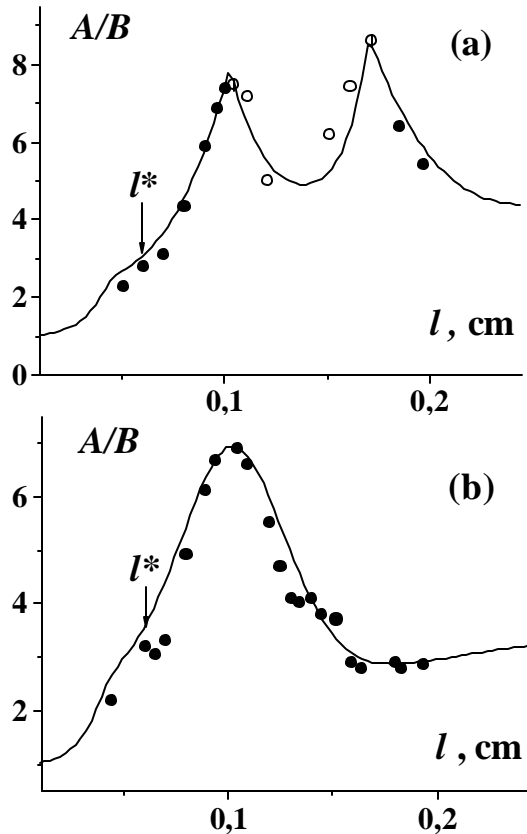


Figure 11. The experimental (dots) and the theoretical (solid line) values of the asymmetry parameter, A/B , in $\text{C}_{10}\text{HNO}_3$ plates vs. l at $T > T_c$ (a) and $T < T_c$ (b). At $T > T_c$ [$T < T_c$] G_a , R_a , T_2 and τ_c are equal to 23 cm^{-1} [$(5.4+270 \cdot \exp(-l/l_0)) \text{ cm}^{-1}$, where $l_0=0.025 \text{ cm}$], $1[1.5]$, $2.8[0.8] \cdot 10^{-7} \text{ s}$ and $4.3[3.7] \cdot 10^{-2} \text{ cm}$, respectively. The shaded, open and half-shaded dots are referred to the 'normal', 'reversed' and symmetric lineshapes with respect to the A peak, respectively. The X-band.

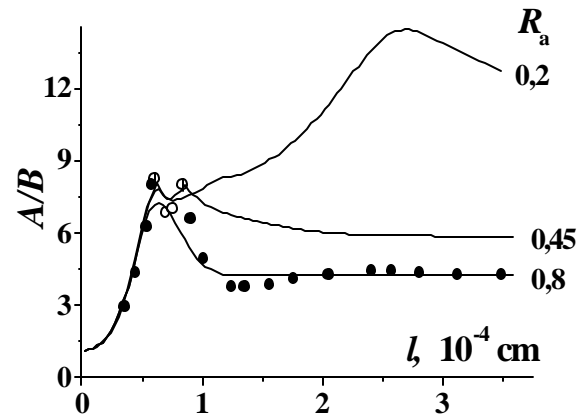


Figure 12. Experimental (dots) and theoretical (lines) values of CCSR lineshape asymmetry parameter, A/B , on sample thickness l . The theoretical curves were calculated using the Dyson [15] expressions for CCSR lineshape without taking into account the effects of surface spin relaxation of current carriers. The shaded and open dots are referred to the 'normal' and 'reversed' lineshape, respectively; half-shaded dot corresponds to the lineshape with symmetric phase with respect to the A peak. $R_a=(T_{\text{Da}}/T_2)^{1/2}$ (T_{Da} is the time of spin diffusion across the skin-depth τ_c governed by the τ_c – conductivity, and T_2 is the intrinsic spin-relaxation time).

Graphite intercalation compounds: $\text{C}_{10}\text{HNO}_3$. For all studied plates of GIC $\text{C}_{10}\text{HNO}_3$, the CCSR spectrum, as in graphite, consists of a single line with the axial angular dependence relative to the c -axis. The principal values of g -factor are equal to $g_c=2.0023 \pm 0.0002$ and $g_a=2.0028 \pm 0.0002$. The value of A/B does not depend on d and h . The $A/B(l)$ dependences in quasi-liquid ($T > T_c$; 250 K) and in crystalline ($T < T_c$) phases of intercalate subsystem essentially differ from each other (Fig. 11). In a quasi-liquid phase of the intercalate this dependence has qualitatively the same form as the corresponding dependence in graphite, except for the small extremum for $l^* \approx 0.06 \text{ cm}$ (Fig. 11a). This extremum is observed as well as in a solid phase of the intercalate, where at $l > l^*$ the $A/B(l)$ dependence has an one-peak shape (Fig. 11b).

Discussion

Graphite: dependences of CCSR lineshape and linewidth on sample size.

The dependences of CCSR lineshape asymmetry parameter A/B and linewidth ΔH on graphite plate width (Figs. 2 and 3) essentially differ from the known theoretical curves, calculated from the Dyson [15] CCSR lineshape expression without taking into account the effects of surface spin relaxation. First, the presence of l values, for which the CCSR lineshape 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 ℓ_c governed by the σ – conductivity, and T_2 is the intrinsic spin-relaxation time) being less than 0,6 (Fig. 12), whereas the experimental values of A/B for $l \gg \ell_c$ are consistent with the theoretical values of this parameter for $R_a>0.8$. Second, the values of A/B in the extrema of the experimental $A/B(l)$ dependence differ considerably from those for the theoretical curves (Fig. 12). Third, at $l \rightarrow 0$ the experimental values of CESR linewidth tends to the infinity (Fig. 3), whereas the corresponding Dyson [15] theoretical curve calculated from the Dyson [15] CESR lineshape expression without taking into account the effects of surface spin relaxation tends to the finite value, which differs from that for plates with $l \gg \ell_c$ by 10% only (Fig. 3).

The character of temperature dependence of CESR linewidth on l (Fig. 3) uniquely specifies the presence of the contribution of surface spin relaxation into total spin relaxation of current carriers in HOPG plates investigated. Basing on this conclusion the above peculiarities of experimental results were analyzed in the frameworks of the extended Dyson theory [15] including the effects of surface spin relaxation of current carriers. In Figs. 2 and 3, the results of theoretical calculations, respectively, of $A/B(l)$ and $\nu H(l)$ dependences in the frameworks of the extended Dyson [15] theory are presented. (At calculation of the theoretical curve $A/B(l)$, the absorption of microwave field through all lateral surfaces both parallel and perpendicular to the z - axis was taking into account and the uniform distribution of microwave field near the vertical surfaces of the plates was supposed). From Fig. 2 and 3 it can be seen that the theoretical curves with the value of Dyson [15] surface spin relaxation parameter $G_a=(3e/4\ell_a)\nu=200 \text{ cm}^{-1}$ (e is a probability of spin reorientation during the collision of current carriers with the surface and ℓ_a is a mean free path of current carriers in a basal plane) describes the experimental $A/B(l)$ and $\nu H(l)$ data well.

Graphite: the temperature dependence of CESR linewidth.

The first systematic study of temperature dependences of graphite CESR signal parameters was carried out as early as 1960 by Wagoner [1] using a natural single crystal specimen in the temperature range from 77 K up to 600 K. After Wagoner a number of authors [2, 11-14] conducted similar studies on a variety of well-defined specimens of graphite, and have obtained nearly the same results. In particular, in all samples investigated and for all orientations of H_0 relative to the c -axis the graphite CESR signal linewidth increases first with decreasing temperature. According to the data of Matsubara *et al.* [14], the $\nu H(T)$ -dependence forms a distinct peak near 20 K and then falls off.

At present there is no consensus between researchers on both the graphite CESR linewidth and its temperature dependence origin. Kawamura *et al.* [13] showed that at $H_0 \parallel c$ the Elliot's [22] expression for the CESR linewidth due to carriers interacting with phonons and/or impurities, which for $T \gg T_D$ (T_D is Debye temperature) can be written as:

$$\nu H_i = \text{const} (\nu g_i)^2 / \lambda m^* \nu(T) \quad (i=a, c) \quad (1)$$

($\nu g_i = g_i - g_0$ ($i=a, c$), where g_0 is the g -factor value for free electron, ν is the electronic gyromagnetic ratio, m^* is the carriers effective mass, and $\nu(T)$ is the carriers mobility), describes the graphite CESR linewidth in the interval 77-300 K qualitatively at least. Matsubara *et al.* [14] considered the temperature variation of graphite CESR linewidth at $H_0 \parallel c$ as a direct consequence of motional narrowing effect through an averaging process of g -values of scattered carriers over the Fermi surface in the limit of incomplete line averaging. In this limit the g -shift is averaged over all energy states of current carriers in k -space, but the linewidth contains the components which are proportional to the square of the microwave frequency. Kotosonov [12] pointed out that the small νH values of the spectral lines suggest complete averaging of the g -factor over all the energy states of current carriers during the spin-lattice relaxation. Thus, for example, in synthetic graphite samples the temperature change from 40 K to 100 K leads to the g_c changing by ~ 0.2 , which agrees with the resonance field shift by $\sim 3 \cdot 10^{-2}$ T, whereas the CESR linewidth remains within the limits of several oersteds.

According to the literature data [23, 24] the Debye temperature of graphite is nearly 400 K. Therefore the description of the graphite CESR linewidth temperature dependence by Exp. (1), proposed by Elliot for $T \gg T_D$, is not obvious. Furthermore, this expression does not explain the presence of linewidth temperature dependence at $H_0 \parallel c$ (Fig. 4) even at a qualitative level since in this orientation of H_0 the value of g_a does not depend on temperature (Fig. 5). The independence of the CESR linewidth on the microwave frequency shows that Matsubara's *et al.* [14] interpretation of the linewidth temperature dependence as a result of the motional narrowing of the incomplete averaging line is not correct also. Besides, the presence of low-temperature peak in $\nu H(T)$ curve also at $H_0 \parallel c$, where g -factor is temperature independent, shows that the origins of low-temperature peaks in $g_c(T)$ and $\nu H(T)$ dependences are different. The Kotosonov's [12] point of view does not contradict to the experimental data, but he did not consider the nature of linewidth temperature dependence.

Above, it was pointed out that the characters of the $\nu H(l)$ (Fig. 3) and $A/B(l)$ (Fig. 2) dependences of CESR line in graphite uniquely specifies the presence of the contribution

of surface spin relaxation into total spin relaxation of current carriers in samples investigated. Basing on this fact, we considered the temperature dependence of CESR linewidth in HOPG also in the frameworks of model including surface spin relaxation effects of graphite π -electrons. Additionally, we suppose the presence of a small amount of the localized spins (~1% of the current carrier concentration or near one localized spin per 10^6 carbon atoms) and complete averaging of g -factors of the conduction electrons and localized spins. In such case, the CESR linewidth ΔH_i ($i=a, c$) can be presented in the following form:

$$\Delta H_i = \Delta H_{ie}(\chi_e/\chi_e + \chi_s) + \Delta H_{is}(\chi_s/\chi_e + \chi_s) \quad (i = a, c), \quad (2)$$

where ΔH_{ie} and ΔH_{is} are the linewidths of CESR signal due to conduction electrons and localized spins, respectively;

$\Delta H_{ie} = \Delta H_{ie}^{\text{surf}} + \Delta H_{ie}^{\text{intr}}$, where $\Delta H_{ie}^{\text{surf}}$ and $\Delta H_{ie}^{\text{intr}}$ are contributions to the total conduction electron linewidth due to their interactions with sample surface and inner imperfections, respectively; χ_e and χ_s are the Curie and Pauli paramagnetic susceptibilities, respectively. At the calculations we assumed, that

$$\Delta H_{ie}^{\text{surf}} = a_{\gamma_i} \Delta H_{ai}(T) \quad (i=a, c), \quad (3)$$

where a_{γ_i} is a constant depending on physical properties of a sample surface and orientation of \mathbf{H}_0 relative to the c -axis. Because the Elliot's expressions [22] for the intrinsic spin relaxation of current carriers were calculated for the simple isotropic metals, their applications to the graphite is not obvious. Therefore, the calculations of ΔH_i were carried out by us with values of $\Delta H_{ie}^{\text{intr}}$ both independent, and dependent on temperature according to the Elliot [22] law for $T \ll T_D$:

$$\Delta H_i = \text{const} (\gamma_i)^2 T_D / \gamma_i \Delta H_{ai}(T) T^2 \quad (i = a, c). \quad (4)$$

Basing on the analysis of literature data on the temperature dependence of current carriers mobility in graphite basal plane [25] $\Delta H_{ai}(T)$ ($i = a, c$; this subindex was introduced for the account of dependence of carriers mobility on \mathbf{H}_0 -orientation) was approximated by the following expression

$$\Delta H_{ai}(T) = a_i + b_i/(c_i + T)^{1.6} \quad (i = a, c),$$

where a_i , b_i and c_i are the varied parameters; at calculations of ΔH_i for $\mathbf{H}_0 \parallel c$, their initial values were taken equal to $-4 \text{ m}^2/\text{Vs}$, $63 \cdot 10^3 \text{ m}^2 \cdot \text{K}^{1.6}/\text{Vs}$ and 55 K , respectively, for intrinsic linewidth temperature dependence determined by the Exp. 4 and were taken equal to $-0.4 \text{ m}^2/\text{Vs}$, $13.25 \cdot 10^3 \text{ m}^2 \cdot \text{K}^{1.6}/\text{Vs}$ and 24.5 K , respectively, for constant intrinsic

linewidth (in both cases, for the chosen values of parameters the $\Delta H_{ac}(T)$ -dependences approximately correspond to the in-plane mobility of carriers in the average on quality HOPG). Taking into consideration the data of irradiated graphite CESR-measurements [26] the values of g_s and ΔH_{is} were taken equal to $2,0023 \pm 0,25 \text{ mT}$, respectively. The values of a_{γ_i} in Exp. (3) and constants in Exp. (4) were calculated using the literature data on the value of $\Delta H_{ai}(T)$ in HOPG [25] and surface and intrinsic spin relaxations times at room temperature extracted from the analysis of experimental $\Delta H(l)$ data (Fig. 3), respectively.

The results of approximation of experimental temperature dependence of CESR linewidth at $\mathbf{H}_0 \parallel c$ by Exp. (2) are presented in Fig. 4. As it is seen from this figure, for both forms of temperature dependence of intrinsic spin relaxation rate the theoretical curve $\Delta H_i(T)$ contains the distinct peak near 20 K. At the same time, the theoretical analysis of Exp. (2) has shown, that this peak is absent if $\Delta H_{ie}^{\text{surf}} = 0$.

In the frameworks of the model considered in all temperature interval of investigations the best description of the experimental temperature dependence of CESR linewidth by Exp. (2) was achieved with temperature independent value of intrinsic spin relaxation rate (see Fig. 4). We believe that this fact has a physical sense and it is a consequence that in a real graphite the collisions of current carriers with the graphite crystallite boundaries introduce main contribution into intrinsic spin relaxation rate.

Evolution of CESR lineshape and linewidth at graphite intercalation by HNO_3 . With the configuration of our ESR experiment (Fig. 1) the microwave field penetrates into the HOPG plate mainly through its lateral sides, which are parallel to both the c -axis and \mathbf{H}_{rf} [11], i.e. through the lateral sides $h \parallel d$. Therefore, the evolution of graphite CESR signal of the sample investigated (Fig. 6) is mainly due to variations of the composition and properties of the HOPG plate at the surface areas from these sides. The dependence of the shape and intensity of graphite CESR signal on exposure time, t , of a sample in HNO_3 vapours is qualitatively identical to that of the ESR signal lineshape and intensity of the localized spins in a metallic substrate on the thickness of a spray-coated film of another metal [27]. In our case, the spins in consideration are certainly mobile, but for $l/\lambda_c < 2$ the CESR line shape does not depend on spin mobility [9,11], i.e., in the framework of the Dyson theory [15] in HOPG plate investigated the spin carriers may be considered as localized. Therefore, the variations of the shape and intensity of the graphite CESR signal (Fig. 6) may be considered as being due to the formation of a macroscopic 'intercalation' layer on the

HOPG plate (with conductivity being different from that of the initial material) and by advance of the interface separating this layer from as-yet the non-intercalated parts of sample (due to the diffusion of nitric acid molecules into the substrate along the graphite galleries). The invariability of the g -factor values for CESR signal from HOPG substrate (g_i) and that from 'intercalation' layer (g_i^*) up to the disappearance of signal and the end of reaction, respectively, indicates that the interface between 'intercalation' layer and as-yet the non-intercalated parts of sample may be considered as non-conductive. The non-conductivity of this interface may be caused by significant distortion of a carbon net near the intercalation front and/or by the presence of high phase-boundary electrostatic potential due to the different current carriers concentration in the intercalated parts of graphite and in the non-intercalated ones.

In the experiment under consideration, the whole volume of sample investigated is available for CESR studies. Therefore, the time of the graphite CESR signal disappearance corresponds approximately to the moment of contact of the counter (antiparallel) intercalation fronts. Let us assume, that the intercalation is determined by a two-dimensional diffusion-controlled process, i.e. the thickness of the intercalated layer, d^* , depends on the exposure time as $(d^*)^2 = 2D_{int}t$, where D_{int} is intercalate two-dimensional diffusion constant. In such a case, having substituted the value of time interval from the beginning of the graphite CESR signal transformation up to its disappearance, $t \approx 3$ h, and $d^* = l/2$ to this expression, it is easy to estimate the value $D_{int} \sim 2 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$. It is worth to note that this value of D_{int} well correlates with that obtained by high-resolution neutron scattering by Simon et al. [28]: $D_{int} \approx 4 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$.

A new and unexpected result of this experiment is the significant broadening of the graphite CESR signal from the beginning of the intercalation up to the contact of the counter intercalation fronts (Figs. 2 and 8). We suppose that the reason for it is the collisions of current carriers (at their diffusion along the graphite layers) with the non-conductive interface between the intercalated and the non-intercalated parts of the HOPG plate. Indeed, when the intercalation front advances into the HOPG plate (due to the diffusion of nitric acid molecules into the graphite along the graphite galleries) the width of its non-intercalated part decreases and, therefore, the frequency of collisions of graphite current carriers with these interfaces increases. Therefore, assuming the probability of spin reorientation of graphite current carriers during such collisions to be non-zero, the increase of the total rate of spin relaxation of graphite current carriers (the graphite CESR linewidth) with the time of intercalation can be observed. Note, that in all previous ESR experiments on graphite intercalation [4-9] which were carried out on

HOPG plates with $l \gg \lambda_c$, no broadening of the graphite CESR signal was observed. This indirectly supports our interpretation of the graphite CESR signal broadening at the intercalation of the narrow ($l \sim 2\lambda_c$) HOPG plate.

The increase of $A^*/B^*(\lambda)$ dependence at the beginning of intercalation from 1 until 3.7 (Fig. 10) corresponds to a theoretical $\lambda/B(\lambda)$ -dependence changing when increasing λ (λ is the ratio of a sample thickness to the skin-depth) [9, 11]. At the constant value of electrical conductivity along the c -axis of the forming GIC stage, this fact also points to the presence of the non-conductive barrier through the intercalation front and on its advance into sample. Under such understanding of the nature of $A^*/B^*(\lambda)$ -dependence (Fig. 10) a changing of the skin-depth governed by the c -axis conductivity of GICs from the beginning to the end of reaction may be easily determined by using the maximum and minimum values of A^*/B^* and the well known $\lambda/B(\lambda)$ -nomograms for different R -values [9, 11]. Such kinds of calculations show that the skin-depths of the initial 7-th stage and of the final 2-d stage of GICs differ approximately in 1.6 times.

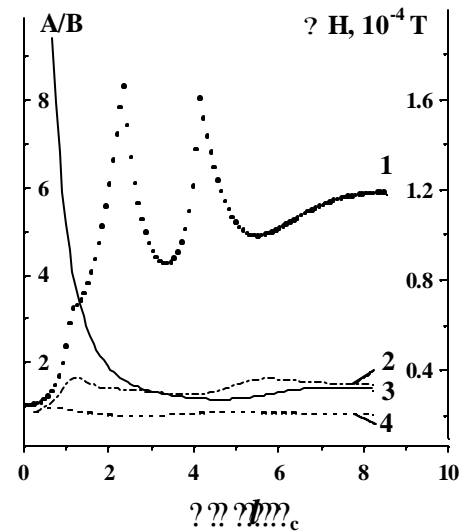


Figure 13. Calculated CESR lineshape asymmetry parameter, A/B (1), and linewidth, ΔH (2), vs. $\lambda = l/\lambda_c$ in GIC $C_{10}HNO_3$ at $T > T_c$ for the case of simultaneously presence in sample of localized spins and surface spin relaxation of current carriers. The curves 3 and 4 correspond to $\Delta H(\lambda)$ dependences for conduction electrons and localized spins, respectively. The X-band.

Using the relation $(d^*)^2 = 2D_{int}t$ the experimental dependence $\Delta H(\lambda)$ 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. 8). The latter dependence can be calculated theoretically as well, using the extended Dyson expressions for the CESR in metals

including the effects of surface spin relaxation [15]. (The analysis of the mentioned Dyson expression has shown that at given sample thickness the CESR linewidth increases with G value. For $G \rightarrow 0$, the value of CESR linewidth tends to the infinity at $l \rightarrow 0$). Obviously, if e is considered as an average value of probability of spin reorientation during collisions of graphite current carriers with the non-conductive phase boundary, then the extended Dyson expressions for the CESR in metals including the effects of surface spin relaxation of current carriers can be used for analysis of $H(a)$ dependence also. It is shown in Fig. 8, where the results of such analysis are presented, that the theoretical dependence of the graphite CESR linewidth, with non-zero values of G_a describes the experimental data well. The found value of $G_a = 1$ [10] cm^{-1} and the typical HOPG values of $G_a = (0.4 \div 1.6) \cdot 10^{-5}$ m [33] correspond to $l = (0.5 \div 2.1) \cdot 10^{-4}$ [(0.5 \div 2.1) $\cdot 10^{-3}$]. It is worth noticing that at present there are no data on interface spin relaxation in conductors in literature. There are only some published data on surface spin relaxation in simple metals. For comparison, the surface spin reorientation probabilities of conduction electrons in Cu and Li bulk samples are equal to $\sim 10^{-2}$ [34] and $\sim 5 \cdot 10^{-6}$ [35], respectively.

It is obvious, that the spins of current carriers colliding with the front of reaction from the intercalated part of graphite also have some probability of reorientation, β^* , during such collisions. Therefore, the analysis of $H^*(l)$ -dependence (Fig. 9) it is possible to execute on the same procedure, which above was used for the analysis of the $H(l)$ -dependence (Fig. 8). The application of the specified technique of the analysis to the experimental $H^*(l)$ -dependences (Fig. 9) give the G_7^* -values: ~ 180 cm^{-1} in one experiment and ~ 70 cm^{-1} in the other experiment. As we see, both values of G_7^* appreciably greater than the values of G_7 . If $\beta = \beta^*$, it means that already in the GIC stage originally forming the mean free path of current carriers in a basal plane appreciably shorter, than in initial graphite.

Graphite intercalation compounds ($C_{10}HNO_3$): CESR lineshape dependence on sample sizes. The analysis had shown that the theoretical curves $H/B(l)$ have an weak extremum (from the direction of smaller l) only under the simultaneous contribution to the ESR spectrum of the next two factors: 1) the surface spin relaxation of current carriers and 2) a small amount of the localized spins with the value of g - factor being nearly equal to that for conduction electrons but which spin-states are not average with spin-states of the conduction electrons. As seen from Fig. 13, the coordinates of first extremums of the $A/B(l)$ - and $H^*(l)$ -dependences approximately coincide.

The presence a weak extremum at l^* in the experimental

$A/B(l)$ dependence for the $C_{10}HNO_3$ plates (Fig. 11) testifies that both the surface spin relaxation and localized spins make a contribution to the ESR signal of GICs investigated. In the frameworks of this model we have been able to describe the experimental $A/B(l)$ dependence well above [below] T_c with the next set of parameters: $G_a = 23$ cm^{-1} [(5.4+270 \cdot exp(- l/l_0)) cm^{-1} , where $l_0 = 0.025$ cm], N_s/N_e (the ratio of intensity of ESR signals of the localized and the delocalized spins) = 0.15 (0.3), T_{2s}/T_{2e} (the ratio of spin-lattice relaxation times for the localized and the delocalized spins) = 0.75 (1) and β_{g_s-e} (the difference in g - values of the localized and delocalized spins) = 6 (6) $\cdot 10^{-5}$ (Fig. 11). It is worth to note that the change of ratio N_s/N_e at the aggregate phase transition in the intercalate subsystem follows from above calculations.

Conclusions

In graphite and its intercalation compounds the influence of sample size and experimental conditions on CESR signal lineshape and linewidth had been studied. The analysis of experimental results uniquely points to the presence of large contribution of surface spin relaxation effects into the total rate of spin relaxation (i.e. into the CESR linewidth) of current carriers in samples investigated. The contribution of collisions of the graphite and GIC current carriers with the intercalation front into their total spin relaxation rate (i.e. into the CESR linewidth) had been also revealed. Basing on the obtained results it may be supposed that many of existing problems connected with application of CESR technique to the study of graphite, GICs and other conducting carbon materials will be successfully solved after introducing into the consideration of surface and interface spin relaxation effects. The works in this direction are in progress.

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