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Albert Ziatdinov [a] , Vladimir Kainara [a] & Aleksei Krivoshei [a]

[a] Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences, 159, Prosp. 100-letija, 690022, Vladivostok, Russia

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Conduction ESR and Surface Spin Relaxation in Graphite and Acceptor Graphite Intercalation Compounds

ALBERT ZIATDINOV, VLADIMIR KAINARA
and ALEKSEI KRIVOSHEI

Institute of Chemistry, Far Eastern Branch of the Russian Academy of Sciences. 159, Prosp. 100-letija, 690022 Vladivostok, Russia

Experimental results for the dependence of highly oriented pyrolytic graphite (HOPG) conduction ESR (CESR) line shape and in 2nd stage graphite intercalation compounds (GICs) with nitric acid ($C_{10}HNO_3$) on the sample sizes are presented. Both in HOPG and in GICs the theoretical description of these dependences is possible only if a certain probability of the reorientation of current carrier spins during their collisions with the sample surface is taken into account. The significant increase of the graphite CESR linewidth at the intercalation of the narrow HOPG plate by HNO_3 points out a nonzero probability of spin reorientation also during the collisions of electrons with the interface between the intercalated and the non-intercalated parts of the sample.

Keywords: graphite; graphite intercalation compounds; HNO_3; surface spin relaxation; conduction ESR

INTRODUCTION

The method of conduction ESR (CESR) has been actively used in studies of graphite and graphite intercalation compounds (GICs). The method is mainly used for determining the kinetic parameters of the spin carriers in these systems 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] has been carried out using the well-known theory of Dyson[15] and Kaplan[16] not including the surface relaxation of current carrier spins by the standard procedures of Feher and Kip[17], Kodera [18], and Pifer and Magno[19] However, in a strict sense, Dyson's theory 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 by taking into account the anisotropy of conductivity. Based on the results of such calculations, authors have proposed a procedure for analysis of the experimental CESR spectra in GICs, which allows to determine the physical characteristics related to the resonance. Herewith, authors, as well as all preceding researchers, implied that in GICs it is possible to neglect the surface relaxation of current carrier spins. In this paper, we present the new experimental results for the dependence of CESR line shape parameters in highly oriented pyrolitic graphite (HOPG) and in 2nd stage GIC with nitric acid ($C_{10}HNO_3$) on the sample dimensions. These data point out necessity of taking into account the presence of surface relaxation of current carrier spins at the analysis of the CESR signal lineshape in compounds investigated. The narrow HOPG plate CESR linewidth vs. time of intercalation by nitric acid pointing out the presence of a nonzero probability of the spin reorientation during the collisions of current carriers with the interface between the intercalated and the non-intercalated parts of the graphite plate is also presented.

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 are 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×l is the area of the basal plane. The accuracy in the determination of the dimensions was ~ 5×10^{-4} cm.

Synthesis of GIC $C_{10}HNO_3$ was carried out in liquid nitric acid with the density of ρ~1.565 g/cm^3. The stage structure of the GIC was analyzed 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 with the density of ρ~1.565 g/cm^3. Prior to the experiment, the system was evacuated to eliminate air and water.

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. The basal (l×h) and lateral sides (d×h) of the plates investigated were parallel to the $\mathbf{H}_{rf}$.

RESULTS

Graphite

For all studied graphite plates the CESR spectrum consists of a single line with the axial angular dependence relative to the **c**-axis. The principal values of **g** - tensor determined by Feher-Kip[17] nomograms or those of Kodera[18] are equal to $g_{\parallel}=2.0474\pm0.0002$ and $g_{\perp}=2.0029\pm0.0002$. 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. 1). 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.

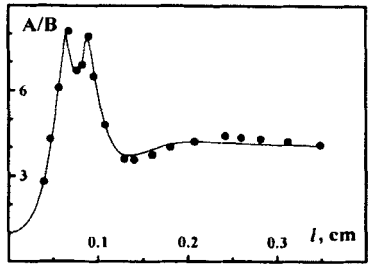

FIGURE 1 The experimental (dots) and the theoretical (solid line) values of A/B in HOPG plates vs. l. g=200 cm^{-1}, R_a=2.4, $\delta_c=2.6\cdot10^{-2}$ cm and $T_2=1.4\cdot10^{-8}$ s.

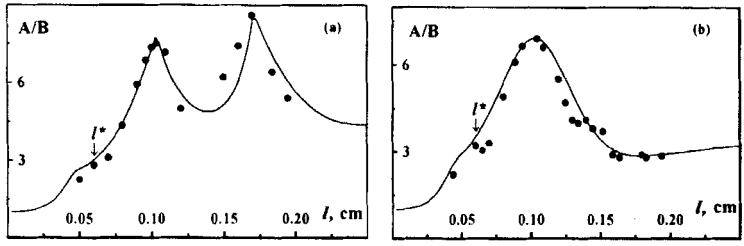

FIGURE 2 The experimental (dots) and the theoretical (solid line) CESR line shape asymmetry parameter A/B in $C_{10}HNO_3$ plates vs. l at $T>T_c$ (a) and $T<T_c$ (b). At $T>T_c$ [$T<T_c$] g, R_a, T_2 and δ_c are equal to 23 cm^{-1} [$(5.4+270\cdot\exp(-l/l_0))$ cm^{-1}, where l_0=0.025 cm], 1[1.5], 2.8[0.8]$\times10^{-7}$ s and 4.3[3.7]$\times10^{-2}$ cm, respectively.

Graphite intercalation compounds: $C_{10}HNO_3$

For all studied plates of GIC $C_{10}HNO_3$, 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±0.0002 and $g_{\perp}$=2.0028±0.0002. The value of A/B does not depend on *d* and *h*. The A/B(*l*) dependences in quasi-liquid ($T>T_c\approx250$ K) and in crystalline ($T<T_c$) phases of intercalate subsystem essentially differ from each other (Fig. 2). 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 $l^*\approx 0.06$ cm (Fig. 2a). 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. 2b).

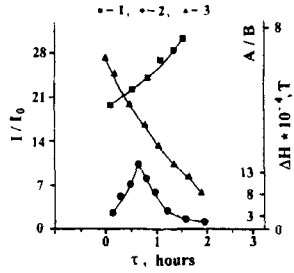

FIGURE 3 The narrow HOPG plate CESR signal parameters ΔH (1), A/B (2) and I/I_0 (3), vs. exposure time, τ, in HNO_3 atmosphere. I_0 is the intensity of the ESR signal in a standard sample.

Intercalation of graphite by HNO_3: CESR signal transformation

With the intercalation of HNO_3 into graphite the linewidth (the intensity), ΔH ($I=(A+B)\times\Delta H^2$), of the graphite CESR signal increases (decreases) monotonously (Fig. 3). 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. Later, the A/B ratio is 'reversed' (maximum peak height A occurs at higher magnetic field); the A/B maximum corresponds to the time when the phase reversal takes place.

DISCUSSION

The A/B(*l*) dependence of the graphite CESR signal (Fig. 1) differs from the well known corresponding theoretical curves, calculated from the classical Dyson line shape equation without taking into account effects of surface spin relaxation[8,9,11,15,18]. First, this dependence has a two-peak form with the region of an inverted line shape phase for the values of *l* between coordinates of these peaks. 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 spin diffusion time across the skin-depth δ_c, and T_2 is the interior spin-relaxation time) being less than 0,6[8,9,11,18]. Whereas for $l>>\delta_c$ the experimental values of A/B are consistent with the theoretical values of this parameter for $R_a>1$[8,9,11,18]. Second, in the extrema of the experimental A/B(*l*) dependence the values of A/B differ considerably from those for the theoretical curves[8,9,11,18]. Taken apart, the first particularity of the A/B dependence in graphite can be explained with the assumption that the density of the $\mathbf{H}_{rf}$ is not uniform near the sample surface and depends on the sample sizes. Notice that such nonuniformity of the $\mathbf{H}_{rf}$ near the graphite plate surfaces is expected because of the large value of the ratio σ_a/σ_c in graphite. However, it is obvious that the second peculiarity of this dependence can not

be explained within the framework of such assumption. Besides, in model with the nonuniform distribution of the $\mathbf{H}_{rf}$ near the HOPG plate surfaces the value of the current carrier diffusion constant in the basal plane, D_a, computed using the value of R_a (which was determined by an approximation of the experimental A/B(l) dependence) is larger by 2 orders of magnitude than its value deduced using the direct measurements of the σ_a - conductivity. All above problems can be solved if at calculations the surface spin relaxation effects of current carriers are taken into account.

In Fig. 1 the results of the theoretical calculations of the A/B(l) dependence in the framework of the Dyson theory [15] including surface spin relaxation effect of current carriers are presented. This curve was calculated taking into account the absorption of microwave field through all the lateral surfaces of plates: both parallel and perpendicular to the **c**- axis. Herewith, the density of the $\mathbf{H}_{rf}$ near these surfaces was considered equal. As can be seen from Fig. 1 the theoretical curve with the value of a Dyson[15] parameter $g=(3\varepsilon/4\Lambda)=200$ cm^{-1} (ε is a probability of spin reorientation during the collision of current carriers with the surface and Λ is a mean free path of current carriers) describes the experimental A/B data well. Besides, at the account of the surface spin relaxation effects, the difference between values D_a computed using the theoretical values R_a (Fig. 1) and determined using the direct measurements of the σ_a-conductivity decreases. Evidently, the strong effect of the surface spin relaxation on the graphite CESR parameters even at the room temperature is caused by the fact that the basal plane mobility of current carriers in it is larger by 2 orders of magnitude than that in simple metals.

The analysis had shown that the theoretical curves A/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. The presence a weak extremum at l^* in the experimental A/B(l) dependence for the $C_{10}HNO_3$ plates (Fig. 2) testifies that both these factors make a contribution to the ESR signal of GICs investigated. In the framework 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: $g=23$ cm^{-1} [$(5.4+270\cdot\exp(-l/l_0))$ cm^{-1}, where $l_0=0.025$ cm], N_{sl}/N_{sd} (the ratio of intensity of ESR signals of the localized and the delocalized spins)=0.15[0.3], T_{2sl}/T_{2sd} (the ratio of spin-lattice relaxation times for the localized and the delocalized spins)=0.75[1] and Δg_{ld} (the difference in **g** – values of the localized and delocalized spins)=6[6]$\times10^{-5}$ (Fig. 2). Note that the value N_{sl}/N_{sd} undergoes the step-wise changes at the aggregate phase transition in the intercalate subsystem. At the account of the surface spin relaxation effects, as well as in graphite, the difference between values D_a computed using the theoretical values R_a (Fig. 2) and determined using the direct measurements of the σ_a-conductivity decreases.

In the experiment on intercalation of the narrow ($l\sim2\delta_c$) HOPG plate by HNO_3 (Fig. 3) the whole volume of sample investigated is available for CESR

studies and a time of the graphite CESR signal disappearance corresponds approximately to the moment of contact of the counter (antiparallel) intercalation fronts. New and unexpected result of this experiment is the significant broadening of the CESR signal from the beginning to the end of this phase of intercalation (Fig. 3). We suppose that the reason for it is the collisions of current carriers with the interface between the intercalated and the non-intercalated parts of the plate. Indeed, when the intercalation front advances inside a plate the width of its non-intercalated part decreases and hereupon a frequency of collisions of spin carriers with the aforementioned interfaces increases. Therefore, at nonzero probability of spin reorientation during such collisions the increase of the total rate of spin relaxation of current carriers (and the CESR linewidth) with the time of intercalation can be observed.

Acknowledgments

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