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Conduction ESR Studies of Graphite Intercalation by Pentafluorides

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Abstract

Results of an *in situ* conduction ESR (CESR) study of SbF_5 and MoF_5 molecules intercalation into highly oriented pyrolitic graphite plates are presented. The narrowing (broadening) of the CESR signal from the intercalated (the non-intercalated) parts of the graphite plate during the advance of the reaction front into the graphite is explained by the non-zero probability of the spin reorientation at the collisions of current carriers with the intercalation front. The assumption was made that the reasons for step-wise increasing in the intensity of the CESR signal from the intercalated parts of the graphite plate during the reaction are the presence of the threshold intercalation potential and the periodical impoverishing of the adsorbed layers of the intercalate.

Keywords: graphite; intercalation; conduction ESR; SbF_5; MoF_5.

1. Introduction

Graphite intercalation compounds (GICs) form a large family of the layered intercalation compounds. The intercalation process and staging phenomena in GICs have been for a long time are in the focus of attention of researchers [1, 2].

The conduction ESR (CESR) technique is one of the most powerful methods for studying the graphite intercalation process, because shapes and intensities of the CESR signal from both non-intercalated and intercalated regions of graphite plate vary significantly during the intercalation. However, because of the difficulty of such experiments only a few CESR studies of graphite intercalation process have been undertaken [3-8] up to now.

This paper is devoted to the results of an *in situ* CESR study of SbF_5 molecules intercalation into highly oriented pyrolitic graphite (HOPG) plates with width being 1) comparable and 2) much more than the skin-depth, δ_c, governed by the *c*-axis conductivity σ_c. The experiments clearly show the step-wise nature of the intercalation and the large spin relaxation probability at collisions of current carriers with the intercalation front. Results of *in situ* conduction CESR measurements of MoF_5 (from liquid phase) intercalation into HOPG slabs are also presented.

2. Experimental

CESR measurements were carried out at room temperature using an X-band E-line spectrometer. The experiments were carried out on HOPG plates with height (h)×width (l)×thickness (d)=0.94×0.58×0.035 cm^3 (sample A) and 0.4×0.032×0.034 cm^3 (sample B), where $l \times h$ is the size of basal plane. The HOPG samples were held in a quartz tube connected via a valve to the reservoir with liquid SbF_5 with the vapour pressure ~1 Torr. During the measurements the constant magnetic field $\boldsymbol{H}_0$ was applied along the graphite ***c***-axis. According to data of the four-probe method, at 300 K the σ_c - conductivity of HOPG plate used is equal to ~7.7 $\Omega^{-1}\cdot cm^{-1}$. In the X-band the value $\delta_c \sim l/2$ corresponds to this conductivity, i. e. the whole volume of the sample B was available for the CESR studies.

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3. Results

The CESR spectrum of all HOPG plates investigated consists of a single asymmetric line determined by the Dyson mechanism [9]. The spectrum is axial with respect to the ***c***-axis and is characterized by g_c=2.0474±0.0002 and g_a=2.0029±0.0002. The lineshape asymmetry parameter, *A/B*, being determined as the maximum-to-minimum peak height ratio, both measured with respect to the base line of the first derivative of CESR absorption line, is 'normal' in the sense that the greater peak, *A*, occurs at the lower magnetic fields, than the smaller peak *B*.

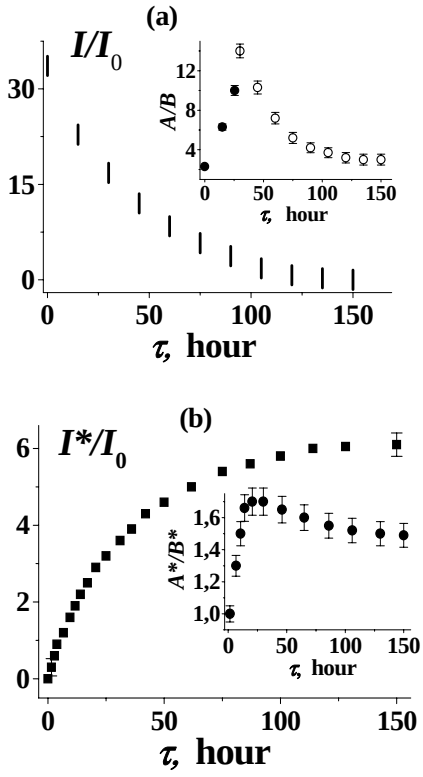

Fig. 1. The CESR lineshape parameters of non-intercalated (a) and intercalated (b) parts of HOPG plate (sample B) vs. exposure time, τ, in SbF_5 atmosphere. I_0 is the intensity of the standard ESR signal.

In certain time after the injection of SbF_5 gas into the knee of the reactor with the HOPG plate, the CESR signal of graphite begins to transform and decrease in intensity until it completely disappears (Figure 1a). Simultaneously a new signal with g_c*= 2.0025±0.0002, and g_a*= 2.0028±0.0002 appears in the spectrum (Figure 1b).

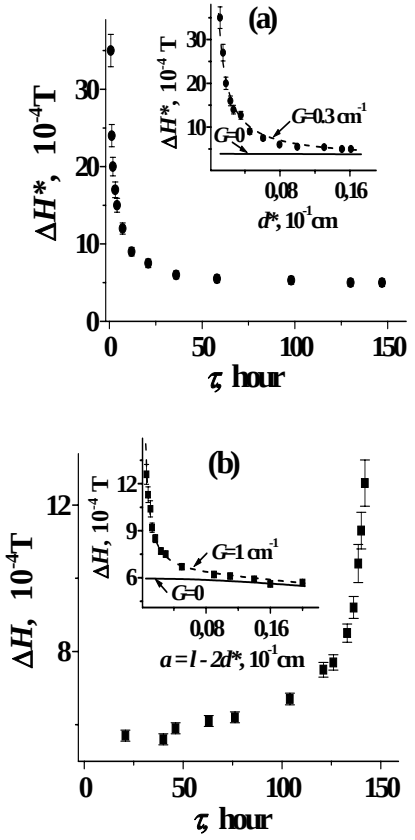

Fig. 2. The linewidth of CESR signal from non- (a) and intercalated (b) parts of HOPG plate (the sample B) vs. exposure time, τ, in SbF_5 atmosphere. The experimental (dots) and theoretical (lines) values of linewidth vs. thickness of the non-intercalated ($a=l-2d^*$) and the intercalated (d^*) graphite are presented in the corresponding inserts.

In both samples investigated the linewidth, ΔH^*, of CESR signal with g_i* monotonously decreases to the end of reaction (Figure 2a). In a sample A for any orientation of the ***c***-axis relative to the magnetic component of the microwave field, $\boldsymbol{H}_{rf}$, the dependence of intensity, $I^*=(A^*+B^*)\times\Delta H^{*2}$, of the CESR signal with g_i* on exposure time, τ, take a well-marked step-wise form (Figures 3, a and b). The g_i*-values of this signal remain constant up to the end of intercalation.

For both samples studied the intensity (the linewidth), $I=(A+B)\times\Delta H^2$ (ΔH), of the graphite CESR signal decreases (increases) vs. exposure time monotonously. In the sample A at the beginning of the reaction the *A/B* ratio of graphite signal increases, but it is still 'normal' reaching a maximum value of *A/B*~12. Later, upon further exposure in the intercalate atmosphere, the *A/B* ratio becomes 'reversed' (the maximum peak height, *A*, occurs at higher magnetic fields than the smaller peak *B*), and its magnitude decreases down to value ~5; the *A/B* maximum corresponds to the moment when the 'reversal' of CESR lineshape takes place (Figure 1a). The g_i (i=a, c) value of the graphite CESR signal does not change up to its disappearance.

In the sample B the character of the graphite CESR lineshape evolution is similar to that observed in the sample A, but in this sample to the moment of the graphite CESR signal disappearance the value of ΔH is much more than in the sample A at the corresponding time of the reaction.

At the intercalation of MoF_5, the changes in the graphite CESR signal parameters are similar to the corresponding dependences observed at graphite intercalation by SbF_5. But in this case, on the basic graphite signal, the additional narrow signal is observed. At the advance of the intercalation front into the HOPG slab, the intensities of this and basic signals decrease together, up to their complete disappearance. The assumption was made that the narrow signal corresponds to the localized spins, which appear on the intercalation front due to the strong distortion of graphite layers.

4. Discussion

In a traditional configuration of ESR-experiment the microwave field penetrates into HOPG plate mainly through its lateral sides, which are simultaneously parallel to both ***c***-axis and magnetic component of the microwave field $\boldsymbol{H}_{rf}$ [10], in our case through the lateral sides $h\times d$. Therefore, the evolution of graphite CESR signal of the samples investigated (Figures 1a, 2b and 3) is mainly due to variations of the composition and properties of the HOPG plate at the surface areas with the thickness ~δ_c from these sides due to the diffusion of SbF_5 molecules into the graphite. The dependence of the shape and intensity of graphite CESR signal on exposure time is qualitatively identical to that of the CESR signal lineshape and intensity of the conductive substrate on the thickness of a spray-coated film of another metal [11]. It allows us to make the conclusion that the changes of *A/B* and *I* of the graphite CESR signal are determined by the formation of a macroscopic 'intercalation' layer from the lateral sides of graphite plate, and by the advance of the boundary which separates its intercalated and non-intercalated regions.

The invariability of the *g*-factor values for the CESR signal from graphite (g_i) and that from the 'intercalation' layer (g_i*) up to the disappearance of the signal and the end of reaction, respectively, indicates that the interface between the 'intercalation' layer and as-yet the non-intercalated parts of sample may be considered as non-conductive.

In a sample B, the time of the graphite CESR signal disappearance corresponds approximately to the moment of contact of the counter (antiparallel) intercalation fronts. At the assumption that the intercalation is a two-dimensional diffusion process, the thickness of the intercalated layer, d^*, depends on the intercalation time, τ, as $(d^*)^2=2D_{int}\times\tau$, where D_{int} is intercalate two-dimensional diffusion constant. In such a case, substituting the value of the time interval from the beginning of the graphite CESR signal transformation up to its disappearance (Figure 1a) and $d^*=l/2$ to this expression, it is easy to estimate the value D_{int}~2.4×10^{-14} m^2 s^{-1}.

An unexpected result of our experiments is the significant narrowing of the CESR signal from intercalate layer at the beginning of the reaction (Figures 2a) and the significant broadening of the graphite CESR signal before the contact of the counter intercalation fronts (Figures 2b). We suppose that the reason for both these unusual lineshape dependencies is the collisions of current carriers with the interface between and the non- and intercalated parts of graphite plate.

Using the relation $(d^*)^2=2D_{int}\times\tau$, the experimental dependence $\Delta H(\tau)$ can be easily transformed into the dependence $\Delta H(a)$, where $a = l\text{-}2d^*$ is the thickness of the non-intercalated part of HOPG (Figure 2b). 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 [9]. From the insert of the Figure 2b, where the results of such calculations are presented, it can be seen, that the theoretical dependence of the graphite CESR linewidth with the non-zero value of Dyson spin-relaxation parameter $G=3\varepsilon/4\Lambda$ (ε is the surface spin reorientation probability, Λ is the mean free path of current carriers) describes the experimental data well. The found value of $G \equiv G_a=1$ cm^{-1} and the typical HOPG values of $\Lambda \equiv \Lambda_a=(0.4\text{-}1.6)\times10^{-5}$ cm^{-1} [12] correspond to $\varepsilon \equiv \varepsilon_a=(0.5\text{-}2.1)\times10^{-5}$.

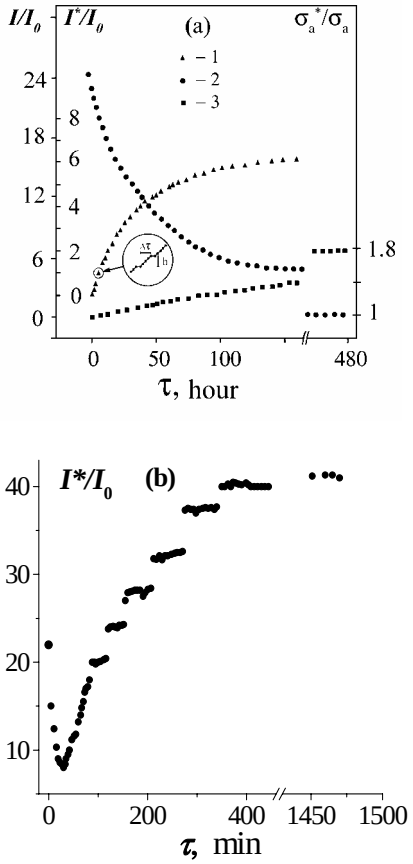

Fig. 3. The intensity of CESR signal from non- (I/I_0) and intercalated (I^*/I_0) parts of HOPG plate and σ^*_a (3) (the sample A) vs. exposure time, τ, in SbF_5 atmosphere. (a): $\boldsymbol{c}\perp\boldsymbol{H}_{rf}$; (b): $\boldsymbol{c}\|\boldsymbol{H}_{rf}$. I_0 (σ_a) is the intensity of a standard ESR signal (graphite basal plane conductivity).

The application of the above technique to the analysis of the experimental $\Delta H^*(d^*)$-dependence (insert of the Figure 2a) give the value of $G\equiv G_a^*\sim0.3$ cm^{-1}. I.e., the value of G_a^* appreciably smaller than the value of G_a. We believe that the reason for this discrepancy may be: 1) the strong spin-relaxation of the current carriers at their collisions with the GIC surface and/or 2) the asymmetry of the magnetic interactions for current carriers "swooping" on intercalation front from the graphite and GIC sides.

The step-wise increasing of the CESR signal intensity from the intercalated parts of the graphite plate (Figures 3, a and b) points to the repeated-batch insertion of the intercalate into sample. We assume that the reasons for such non-uniform insertion of the intercalate are the presence of the threshold intercalation potential and the periodical impoverishing of the adsorbed layers of the intercalate.

At the intercalation of MoF_5, the changes in the graphite CESR signal parameters are similar to the corresponding dependences observed at graphite intercalation by SbF_5. But in this case, on the basic graphite CESR signal, the additional narrow signal is observed. At the advance of the intercalation front into the HOPG slab, the intensities of this and basic signals decrease together, up to their complete disappearance. The assumption was made that the narrow signal corresponds to the localized spins, which appear on the intercalation front due to the strong distortion of graphite layers.

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References

[1] Dresselhaus MS, Dresselhaus G. Intercalation compounds of graphite. Adv. Phys. 1981; 30(2):139-326.

[2] Solin SA, Zabel H. The physics of ternary graphite intercalation compounds. Adv. Phys. 1988; 37(2):87-254.

[3] Davidov R, Milo O, Palchan I, Selig H. ESR study of graphite-fluorine and graphite-fluoride acceptor intercalation compounds. Synth. Met. 1983; 8:83-87.

[4] Palchan I, Davidov D, Zevin V, Polatsek G, Selig H. An in situ ESR study of the intercalation mechanisms: HOPG/fluorine and HOPG/HNO_3. Synth. Met. 1985; 12:413-418.

[5] Palchan I, Mustachi F, Davidov D, Selig H. ESR study of dulate intercalation compounds: C/F, C/K/F and C/Li/F. Synth. Met. 1984/85; 10:101-106.

[6] Nakajima M, Kawamura K, Tsuzuku T. ESR study of HNO_3 intercalation process of graphite. J. Phys. Soc. Jpn. 1988; 57(5):1572-1575.

[7] Ziatdinov AM, Mishchenko NM. In situ ESR study of the HNO_3-intercalate diffusion process in graphite intercalation compounds. J. Phys. Chem. Solids 1997; 58(7):1167-1172.

[8] Ziatdinov AM, Skrylnik PG. Graphite intercalation by nitric acid: conduction ESR and theoretical studies. Chem. Phys. 2000; 261(3):439-448.

[9] Dyson FJ. Electron spin resonance absorption in metals. II. Theory of electron diffusion and the skin effect. Phys. Rev. 1955; 98(2):349-359.

[10] Ziatdinov AM, Mishchenko NM. Electron spin resonance lineshape and kinetic parameters of the conduction electrons in highly anisotropic conductors: highly oriented pyrolitic graphite. Phys. Solid State 1994; 36(8):1283-1289.

[11] Zevin V, Suss JT. ESR in layer-substrate structures: The line shape and nondestructive contactless measurements of the layer conductivity. Phys. Rev. 1986; B34(10):7260-7270.

[12] Spain IL. Electronic transport properties of graphite, carbons, and related materials. Walker PL, Throweer Jr and PA, editors. Chemistry and physics of carbon, vol 8, New York:Dekker, 1973:119-305.