

Materials Science Forum  
Volumes 91-93 (1992) Pt. 2

# Intercalation Compounds ISIC-6

Pt. 2



Guest Editors: D. Tchoubar and J. Conard

Trans Tech Publications

## IN SITU ESR-STUDIES OF INTERCALATION OF $SbF_5$ MOLECULES INTO HIGHLY ORIENTED PYROLYTIC GRAPHITE

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### ABSTRACT

ESR-studies in situ of intercalation of  $SbF_5$ -molecules into plates of high oriented pyrolytic graphite (HOPG) from gaseous phase have been carried out. Axis  $\bar{c}$  of plates in the process of the reaction were placed perpendicular and parallel to magnetic component ( $\vec{H}$ ) of microwave field (MWF). It allowed to "observe" processes of intercalation both from basic and lateral sides of plates. Analysis of variations of spectra on exposure time, points at the presence of slow diffusion of intercalate through sides parallel to  $\bar{c}$ -axis in the whole thickness of a sample and succession of relatively faster discrete and identical acts of nucleation of new phase (intercalated regions).

### INTRODUCTION

In spite of numerous publications devoted to study of various aspects of structure and properties of graphite intercalation compounds (GIC) [ 1,2 ] there is a lack of information concerning character of diffusion of "guest" molecules into graphite in the process of its intercalation especially in the beginning of the reaction. ESR method proved itself to be one of the most effective methods of study of initial moments of graphite intercalation owing to high sensitivity and selective capability [ 3,4 ]. If the character of interaction of MWF with conductive graphite plates is known, it's possible, by selecting geometry and orientation of a sample in the MWF, "to observe" intercalation process from the basic or lateral sides parallel to  $\bar{c}$ -axis of graphite. In the present paper we give an account of the results of ESR-studies in situ of intercalation from gaseous phase of  $SbF_5$  molecules into plates of HOPG with various geometrical shape at the orientation of  $\bar{c}$ -axis a) perpendicular and b) parallel to  $\vec{H}$

## EXPERIMENT

ESR-studies of intercalation of  $\text{SbF}_5$  molecules from gaseous phase into HOPG plates at vapour pressure ( $\sim 1$  Torr) and room temperature were carried out in rectangular resonator of X-band with the  $\text{TE}_{102}$  mode at 100 kHz modulation with 0.1 mT amplitude. Plates with two geometrical forms were used for studies. The plate in the shape of parallelepiped (sample 1) with the sides  $0.58 \times 0.94 \times 0.035 \text{ cm}^3$  ( $0.58 \times 0.94 \text{ cm}^2$ -square of a basic side) was placed in the resonator in such a way that two long lateral sides were parallel to  $\vec{H}$ .  $\vec{c}$ -axis of plate lied in the horizontal plane and parallel to constant magnetic field  $\vec{H}$  and electric component  $\vec{E}$  of MWF. It is worth nothing that  $\vec{H}$  and  $\vec{E}$ -are the orientations of MWF in the cavity before introducing the conductive plate of HOPG. A plate with disk-shaped form (sample 2), diameter 0.27 cm and thickness 0.014 cm, was placed in the process of the reaction in such a way that its  $\vec{c}$ -axis was parallel to  $\vec{H}$  and perpendicular to  $\vec{E}$ . Measurements of conductivity along carbonic layers ( $\sigma_a$ ) in the process of intercalation of  $\text{SbF}_5$  into HOPG were controlled with the help of the device of uncontact measurement of electric conductivity analogous to one described in [ 5 ].

## RESULTS

All HOPG plates emit a signal of ESR of conduction electrons (CESR) with axial angular dependence relative to  $\vec{c}$ -axis and  $g_{\parallel} = 2.0474 \pm 0.0001$ ,  $g_{\perp} = 2.0029 \pm 0.0001$ , defined according to Feher and Kip methodics [ 6 ]. The parameter of asymmetry of the first derivative of ESR absorption line  $A/B$  of samples defined in the way

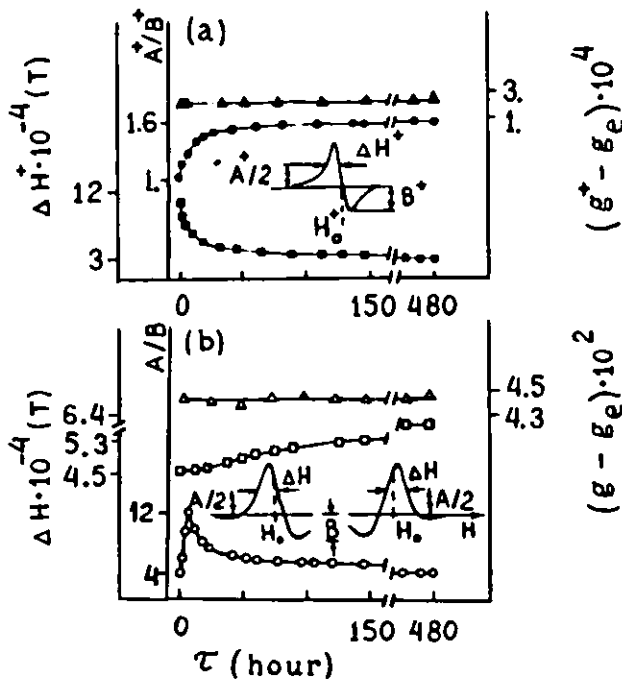


Fig.1  $g$ -factor and parameters of the shape of ESR line of intercalated (a) and non-intercalated (b) parts of graphite changes versus exposure time ( $\tau$ ) of sample 1 in  $\text{SbF}_5$  vapours.

$\Delta$  ( $\blacktriangle$ ) -  $g_{\parallel}$  ( $g_{\parallel}^+$ ),  
 $\square$  ( $\blacksquare$ ) -  $\Delta H$  ( $\Delta H^+$ ),  
 $\circ$  ( $\bullet$ ) -  $A/B$  ( $A^+/B^+$ ).  
 Symbol "+" marks the parameters of resonance line from intercalated parts of graphite.

$T=300\text{K}$ ,  $f=9.5\text{GHz}$ .  
 $\vec{c} \parallel \vec{H}, \perp [\vec{E} \times \vec{H}]$ .

indicated for left\_CESR line in the Fig. 1b, depends on  $\bar{c}$  orientation relative to  $\tilde{H}$ . However at  $\bar{c} \perp \tilde{H}$ , this parameter is always more than 2.55- value typical for localized magnetic moments in thick metallic films with isotropic conductivity. Shape of line is "normal" - in the sense that A peak occurs at smaller magnetic fields comparative with B peak.

If  $\bar{c}$ -axis of HOPG is oriented along  $\tilde{H}$  (sample 2) resonance signal is characterized by:  $1 < A/B < 2.55$ . Several investigations showed that when decreasing thickness of these plates A/B of the signal aspired to  $\rightarrow 2.55$ . This fact proves that A/B decrease in this orientation is accounted for increase in relative contribution to resonance of small graphite crystallites and surface  $p_z$  radicals, for which  $A/B \sim 1$ .

After filling of test-tube with  $SbF_5$  vapour new signal has been emerged with conditional parameter,  $g_{\parallel}^+ (g_{\perp}^+) = 2.0025 (2.0028) \pm 0.0001$  - defined by  $\tilde{H}$  at the point of intersection of the first derivative of ESR absorption and zero line Fig.1a. Rate of intensity growth has a saturated nature. A/B of the mentioned signal is  $\sim 1$  at the moment of its rise. By the end of the experiment this parameter comes to  $\sim 1.6$ . The line is fluently becoming  $\sim 3$  times narrower (Fig.1). Peculiarity of evolution of the mentioned line is unmonotonous growth of its intensity. In fact, curve 1 (Fig.2)

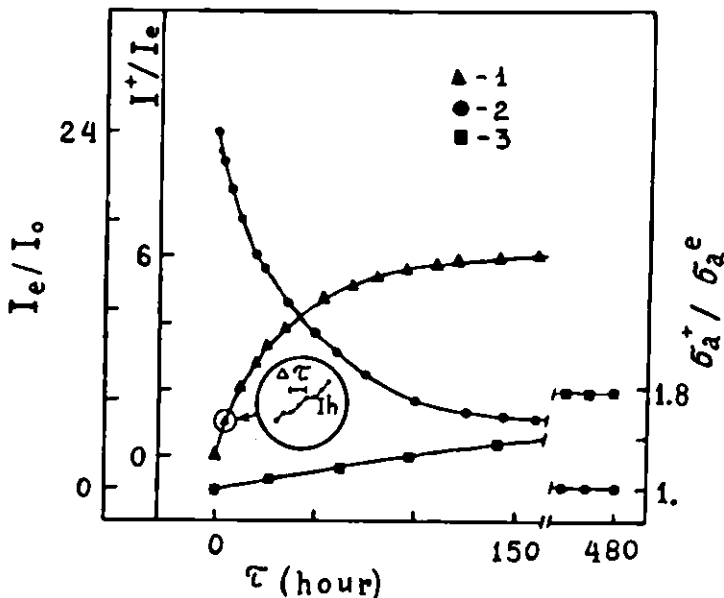


Fig.2. Ratio intensities of ESR lines of GIC ( $I^+$ ) and conduction electrons of HOPG ( $I_e$ ) (curve 1), conduction electrons and manganese in the standard sample  $ZnS:Mn^{2+}$  ( $I_0$ ) (curve 2) and ratio conductivities in basic plane in plate studied ( $\sigma_a^+$ ) and in standard HOPG sample ( $\sigma_a^e$ ) (curve 3) for sample 1 versus exposure time ( $\tau$ ) of HOPG in  $SbF_5$  vapour.  $I_e = (A+B) \cdot (\Delta H)^2$ ,  $I^+ = (A^+ + B^+) \cdot (\Delta H^+)^2$ . Section of the curve 1. is depicted in circle in increased ( $\Delta \tau \times 45$ ,  $I^+ / I_e \times 38$ ).  $T=300K$ ,  $\nu=9.5$  GHz,  $\bar{c} \perp \tilde{H}$ ,  $\perp [ \tilde{E} \times \tilde{H} ]$ .

consists of a number of small "steps" - alternating series of small sections with different "slopes". By prolongation of exposure time the length of the "steps" increased and its height (h) decreased. However, both parameters were changing rather slow, so it was possible to select such intervals of time to place several identical "steps" (Fig.2 curve 1).

Intensity of CCSR line of the sample 1 fluently decreases up to complete disappearance during the reaction (Fig.2, curve 2). Its width increases  $\sim 1.4$  times, as for A/B, at first it shows an increase which reaches in  $\sim 4.5$  hour its maximum ( $\approx 12$ ) and fluently decreases to  $\sim 4.5$ . At the maximum of A/B the line is symmetric relative to A peak and then, up to its disappearance, A peak is situated in the larger magnetic field in comparison with B peak (Fig.1) - it has a "reversed" shape. Described variations of ESR spectrum are accompanied by a fluent increase of  $\sigma_a^+$  in  $\sim 1.8$  times the HOPG value (Fig.2, curve 3).

Variation of the shape and intensity of CCSR line in the opposite orientation (Fig.1) relative to its temporary transformations were observed by decrease of width of the sample 1, exposed in  $\text{SbF}_5$  vapour during  $2 \cdot 10^3$  hours by means of cutting identical narrow pieces from vertical sides. Symmetrical line relative to A peak with  $A/B \approx 9$  was observed at width of a plate 0.25 cm. Plate splitting with this width on 3 parts with approximately identical width (0.01cm) along basic plane resulted in disappearance of CCSR signal from the extreme plates at invariable shape of ESR line with  $g_{\parallel}$  and restoration in the middle plate of the shape of CCSR line with traces of the line with  $g_{\perp}$ .

Process of intercalation in the sample 2 was registered by variations of intensity, width and A/B resonance signal. In the process of the reaction width of this signal increased 2 times, peak intensity  $\sim 6$  times. A/B variation have more complicated n-shaped form with gently sloping right maximum (Fig.3).

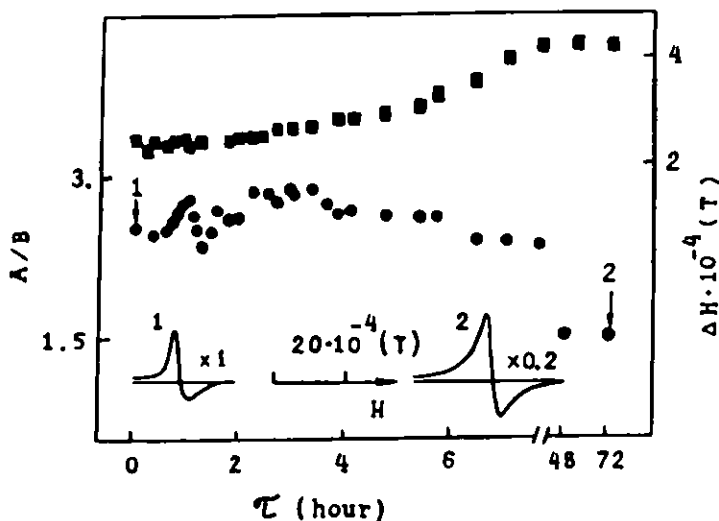


Fig.3. A/B (●) and  $\Delta H$  (■) parameters of the shape of ESR line changes on exposure time ( $\tau$ ) of sample 2 in  $\text{SbF}_5$  vapours.  $T=300\text{K}$ ,  $\nu=9.5\text{GHz}$ ,  $c \perp H$ ,  $\perp [E \times H]$ .

## DISCUSSION

At  $\vec{c} \perp \vec{H}$  MWF penetrates into HOPG samples mainly through its lateral sides parallel to  $\vec{c}$  and  $\vec{H}$  [ 7,8 ] (through vertical lateral sides, in our case ). Therefore, evolution of ESR spectrum of the sample 1 is conditioned by variations of composition and properties of HOPG plate at surface areas from lateral sides of that with thickness of order of skin depth corresponding to the conductivity of the plate along  $\vec{c}$  ( $\approx 2.2 \cdot 10^6$  A ). It's necessary to note that dependence of shape and intensity of CESR line on exposure time of samples in  $\text{SbF}_5$  vapour is qualitatively identical to dependence of corresponding characteristics of CESR line of conductive substrate on thickness of a film made of another metal [ 9 ] . It allows to make a conclusion that variations of shape and intensity of CESR line of HOPG are conditioned by diffusion of intercalate molecules into graphite " galleries " through its lateral sides. This diffusion leads to formation of a surface layer with increasing thickness and conductivity different from graphite conductivity. ESR data of intercalated graphite areas confirm of such surface layer. In fact, asymmetrization of the shape of ESR line of intercalated parts of graphite with  $g_{\parallel}^+$  points at increase (from lateral sides) of ratio thickness of intercalated area and of skin depth corresponding to conductivity along  $c$  in this area of material or otherwise, advancement of intercalate molecules along " galleries " deep into plate. Restoration of shape and intensity of CESR line at decrease of width of the plate agrees with interpretation of their changes at increase of exposure time. ESR data of various parts of a product of interaction of HOPG+ $\text{SbF}_5$  point also at the presence of " galleries " filled with intercalate in areas adjoining exposed basic sides of the plate and only partial filling of " galleries " situated in depth.

At  $\vec{c} \parallel \vec{H}$  MWF penetrates into HOPG plate mainly through basic sides. Conductivity along  $\vec{c}$ -axis is low ( $\approx 7 \cdot 10^4 \text{ Ohm}^{-1} \cdot \text{cm}^{-1}$  [ 10 ] ), therefore , in the time scale of ESR spins are localized in two-dimensional graphite layers and their signal is characterized by the same value  $A/B \approx 2.55$  as the signal of localized spins. Temporary transformation of ESR signal of the sample 2 agrees with intercalation mechanism proposed for explanation of spectrum evolution of the sample 1. In fact, the contribution of near surface intercalated layers of plate to intensity of ESR signal is bigger in comparison with non-intercalated correspondent sizable graphite areas increases in comparison with one of corresponding in sizes non-intercalated graphite areas because of great density of "holes" at Fermi surface of GIC. Therefore, only in the beginning of the reaction character of A/B variation defines variation of corresponding parameter of graphite line (the first maximum). Increase in contribution of signal from GIC must lead to increase of A/B up to 2.55 . Final A/B value is lower than 2.55. It's conditioned by increase of a plate thickness, firstly in the edges, in the process of intercalation.

Gentle sloping section of the curve 1 (Fig.2) corresponds to low diffusion of  $\text{SbF}_5$  in HOPG simultaneously along whole thickness of sample. Faster discrete acts of intercalation into graphite " galleries " take place parallel with a slow diffusion of intercalate and are shown on the curve as section with larger steepness. It's possible that each section corresponds to formation of a separate layer of intercalate or domains of GIC. A such interpretation of origin of " stepped " growth of signal intensity with  $g_{\parallel}^+$ , increase with time ( $\Delta \tau$ ) is conditioned by increase of activation

barrier of this process which depends on advancement of area of discrete nucleation of intercalated regions deep into the plate in c direction. Decrease of h parallel with increase of exposure time of a sample is, apparently, results in fluent diffusion of intercalate along whole thickness of the plate. It leads to gradual decrease of addition to intensity of GIC signal from each act of discrete intercalation because of the presence of a skin depth.

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