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Diffusion and intercalation of fluorine into highly oriented pyrolytic graphite: An *in situ* ESR study

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An *in situ* ESR study of specially cut highly oriented pyrolytic graphite (HOPG) indicates dramatic changes in the ESR line shape (A/B ratio) and intensity upon exposure to a fluorine atmosphere. The results can be interpreted by the formation of a macroscopic intercalation layer and the advance of a boundary separating the intercalated and nonintercalated HOPG. Using a theoretical model previously developed for the ESR of layer-substrate systems, we extract the thickness of the intercalated layer as a function of the exposure time and the diffusion coefficient of fluorine into the HOPG.

The intercalation process and staging phenomena have been the focus of much experimental and theoretical work during the past decade.[1,2] However, only little is known about the diffusion of the intercalate during the intercalation process. This diffusion was determined previously from kinetic studies and particularly by measuring the weight uptake of the highly oriented pyrolytic graphite (HOPG) material as a function of time.[3] These studies[1-3] clearly indicate that diffusion during the intercalation strongly depends not only on the nature of the intercalant species and the intercalant phase (solid, liquid, etc.), but also on surface barriers and the elastic strain field which acts during the opening of the graphite galleries. As such, it might be completely different from the diffusion coefficient of the intercalant in the equilibrium state.[4] This Rapid Communication presents an *in situ* ESR study of the intercalation of fluorine (and other fluorides) into HOPG. We use the fact that the ESR line shape and intensity of the bulk HOPG resonance vary strongly during the intercalation process. This is interpreted as being due to the formation of a macroscopic intercalation layer and the advance of the boundary separating this layer from the as-yet unintercalated HOPG. The advance of this front is attributed to diffusion of fluorine into the HOPG. Our work presents a new and powerful method to study diffusion coefficients during the process of intercalation.

The ESR measurements were carried out mostly at room temperature using an X-band E-line spectrometer. The HOPG samples were contained in Kel-F tubes connected via a valve to the fluorine reservoir.

Intercalation with fluorine is a relatively slow process[5] and probably requires the presence of minute quantities of impurities such as AsF_5, HF, etc. As will be demonstrated elsewhere,[6] the ESR results depend strongly on the fluorine pressure as well as on the size and shape of the HOPG samples. Here we shall emphasize our results for a particular HOPG slab with the following dimensions (see Fig. 1): $a = 1.5$ mm, $b = 7.5$ mm, and $c = 2$ mm; the fluorine pressure was 1300 Torr. The long b axis of the HOPG is along the axis of our TE_{011} cylindrical cavity. The ESR experiment was carried out with an applied magnetic field along the c axis of the HOPG slab. For this particular orientation the HOPG substrate exhibits a resonance at $g = 2.048$. This resonance does not interfere with the ESR spectrum induced by the intercalation and charge transfer [this spectrum is composed of lines at $g = 2$ and $g = 2.015$ (Ref. 5)]. It was easy, therefore, to investigate the effect of fluorine diffusion on the ESR line shape of the HOPG substrate. The most interesting feature of our experimental results is the variation of the line asymmetry and intensity upon intercalation. The line asymmetry (A/B) is defined[7] as the ratio of the maximum peak height to the minimum peak height, both measured with respect to the base line of the resonance derivative (see Fig. 2). In pure HOPG, $A/B \simeq 3$ (see Ref. 8). This A/B ratio is "normal" in the sense that the maximum peak height occurs at smaller magnetic fields. As the intercation process proceeds, the A/B ratio increases initially (but it is still "normal") reaching

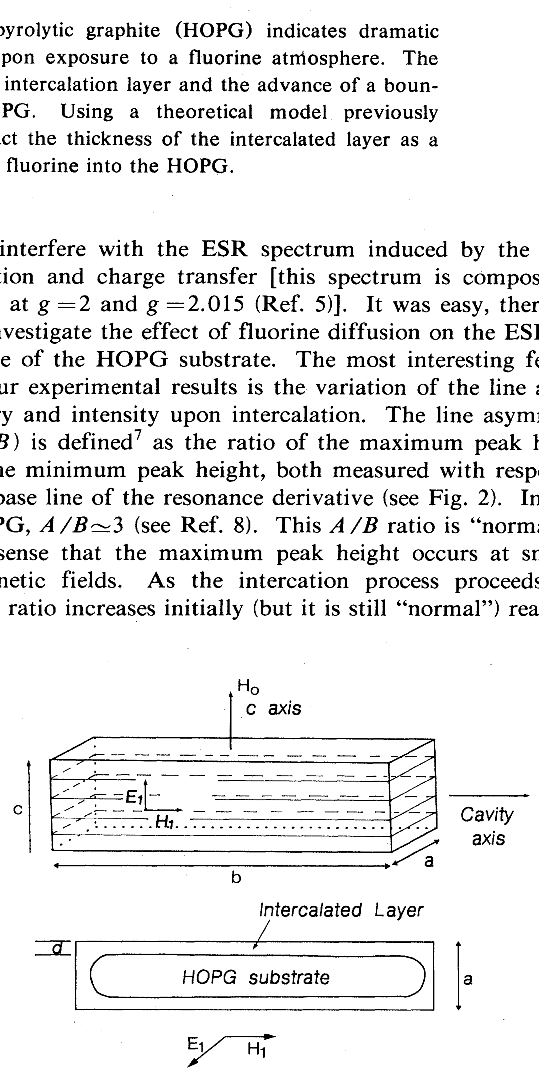

FIG. 1. The orientation of the HOPG slab with respect to the external magnetic field H_0 and the cavity axis. H_1 and E_1 are the magnetic and electric components of the rf field on the b-c face (actually, E_1 encircles the sample). The upper panel gives the dimensions of the HOPG slab ($a = 1.5$ mm, $b = 7.5$ mm, and $c = 2$ mm). Note that the b-c face (perpendicular to the a axis) is the largest, and consequently the microwave penetration is mainly via this face. E_1 is along the c direction, and the skin depth via the b-c face is determined, therefore, by the c-axis conductivity. The lower panel gives the a-b plane of a single graphite layer. d indicates the thickness of the intercalated layer; a is the thickness of the sample for microwave penetration via the b-c planes. H_1 is along the b axis and E_1 is along the c axis.

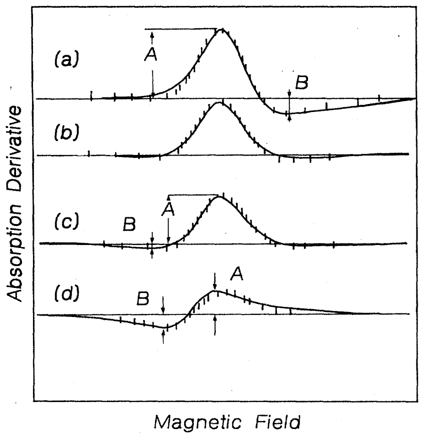

FIG. 2. Vertical segments indicate the experimental ESR line shape. (a) was measured at $t = 35$ min, (b) at $t = 3.1$ h, (c) at $t = 4.3$ h, and (d) at $t = 18.8$ h. Note that A/B (defined in the figure) changes from that of a normal line shape (a) to that of a reversed line shape [(c) and (d)]. Solid lines give the theoretical fits with Eqs. (5)–(7).

a maximal value of $A/B \simeq 8$. Upon further exposure to the fluorine atmosphere, the A/B ratio is "reversed" (minimum peak height occurs at lower fields) and its magnitude decreases. Figure 2 describes the ESR line shape for various exposure times. As seen, the A/B ratio varies from a normal phase to a "reversed" phase as a function of exposure time. The magnitude of the A/B ratio versus the exposure time is given in Fig. 3, upper panel; the maximum A/B corresponds to the time at which the phase reversal occurs. The lower panel of Fig. 3 shows the "intensity" [defined by the factor $(A+B)\Delta^2$, where Δ is the linewidth at $A/2$] versus the exposure time.

We believe that the exposure of the HOPG slab to the fluorine atmosphere results in the formation of an intercalated macroscopic layer and the diffusion of fluorine into the HOPG substrate.[9] The macroscopic thickness of this layer d increases with the exposure time; its conductivity is different from that of the HOPG starting material. The formation of an intercalation layer is consistent with the pioneering work of Hooley[2] and others.[1] The effect of a near-surface metallic layer on the ESR of localized spins in a metallic substrate was investigated previously both theoretically and experimentally.[10,11] The theoretical work clearly indicates dramatic changes of the A/B ratio as well as a "phase reversal" of the ESR line shape upon the increase of the layer thickness. This was attributed to microwave attenuation and reflections caused by the surface metallic layer. Consequently, we can adapt the theory of Zevin[11] to interpret our data. However, in the present case, the spins in consideration are mobile and the application of the theory[11] needs some justification.

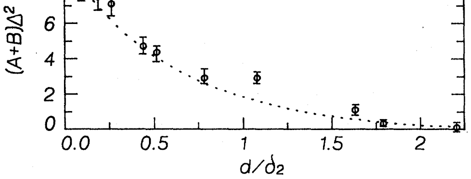

FIG. 3. Upper panel: A/B as a function of exposure time t and d/δ_2. Note that the time scale is not linear. The points a, b, c, and d correspond to the respective parts of Fig. 2. Dashed and solid lines indicate theoretical fit with Eqs. (5)–(7). Dashed line corresponds to the normal phase, solid line to the reversed phase. Lower panel: ESR intensity $(A+B)\Delta^2$ vs the exposure time t and d/δ_2. Dotted line gives the fit with theory, Eqs. (5)–(7).

Generally speaking, the ESR signal is due to microwave penetration via the b-c planes (perpendicular to the a axis) and a-b planes (perpendicular to the c axis, Fig. 1, upper panel). However, due to the large anisotropic conductivities, the skin depth δ ($\delta \simeq 1/\sqrt{2\pi\sigma\omega}$) for the microwave penetration via the b-c plane is significantly larger than that via the a-b plane for the configuration and microwave field described in Fig. 1. We estimate the skin depth for microwave penetration along the b-c face of our HOPG slab to be approximately 0.15 mm using the c-axis conductivity of HOPG and the X-band frequency. Thus, for the configuration and sample dimensions (note the relatively large area of the b-c face) described in Fig. 1, the ESR signal is almost completely due to microwave penetration via the b-c faces. Furthermore, due to the very large skin depth, we can demonstrate, in the framework of the theory of Dyson (see the work of Feher and Kip[7]), that the limit of spin localization is appropriate, although the spins are certainly mobile. This is due to the fact that it takes a time much larger than the longitudinal relaxation T_1 for the electron spins to cross the skin depth; i.e., the electron diffusion can be neglected. The observation of $A/B \simeq 3$ in the "pure" HOPG sample corresponds to the diffusionless limit in the theory of Feher and Kip[7] and strongly supports our arguments.

We shall briefly describe the calculation of Zevin.[11] The microwave absorption which determines the ESR line shape is related to the magnetic surface impedance Z^{mag} as follows:[10]

$$P = \frac{c}{16\pi} |H_1|^2_{z=0} Z^{\mathrm{mag}} \ , \tag{1}$$

where $|H_1|^2_{z=0}$ is the square of the oscillating magnetic field at the sample-vacuum interface ($z=0$). The surface impedance Z was calculated assuming that the solutions of the Maxwell equations are in the form of a plane wave, $\exp[-i(\omega t - kz)]$, where z is the direction of the wave propagation. Using the condition that the tangential components of H_1 and E_1 are continuous across the boundaries between the layer and the substrate (Fig. 1, lower panel), the surface impedance was calculated:

$$\begin{aligned} Z &= 2\mathrm{Re}\left(\left. \frac{E_1}{H_1} \right|_{z=0} \right) \\ &= 2\mathrm{Im}\left(\frac{ck_1}{4\pi i \sigma_1} \right) \left| \frac{R + \tan(k_1 d)\cot[k_2(a-d)]}{\cot[k_2(a-d)] - R\tan(k_1 d)} \right| \ . \end{aligned} \tag{2}$$

Equation (2) was calculated[11] under the assumption of a normal skin effect and takes into account that the constant magnetic field is in the plane of the rf field (Fig. 1). In this geometry $E_1 = E_x$, $H_1 = H_y$, and $R = \sigma_1 k_2 / \sigma_2 k_1$ with k_1 and k_2 defined as

$$k_1 = \frac{1+i}{\delta_1}; \quad \delta_1 = \frac{c}{\sqrt{2\pi\omega\sigma_1}} \; . \tag{3}$$

For our geometry (Fig. 1),

$$k_2 \simeq \frac{1+i}{\delta_2}\sqrt{1+2\pi\chi(\omega)}, \quad \delta_2 = \frac{c}{\sqrt{2\pi\omega\sigma_2}} \; . \tag{4}$$

Here σ_1 and σ_2 are the conductivities (along the c axis) of the intercalate layer and the HOPG substrate (Fig. 1), respectively, δ_1 and δ_2 are the appropriate skin depths, d is the thickness of the surface layer, $a-d$ is the thickness of the HOPG substrate (Fig. 1), and c is the light velocity.

The transverse susceptibility $\chi(\omega)$ is written in terms of its dispersion and absorption parts as $\chi(\omega) = \chi'(\omega) + i\chi''(\omega)$. Expanding the surface impedance in terms of $\chi(\omega)$, we find the magnetic surface impedance Z^{mag} as follows:[11]

$$Z^{\text{mag}} = \frac{\pi^2 \omega \delta_2 \chi_0 \omega_0}{c}[(\text{Re}\phi + \text{Im}\phi)\chi' + (\text{Re}\phi - \text{Im}\phi)\chi''] \; , \tag{5}$$

where ω_0 is the resonance frequency, χ_0 is the static susceptibility, Re and Im refer to the real and imaginary parts, and χ' and χ'' are the normalized line shapes given by

$$\chi' = \frac{1}{\pi}\frac{H_0 - H}{(H_0-H)^2 + \Delta^2}, \quad \chi'' = \frac{1}{\pi}\frac{\Delta}{(H_0-H)^2+\Delta^2} \; . \tag{6}$$

The values of H_0 and H are given by $H_0 = \hbar\omega_0 / g\mu_B$ and $H = \hbar\omega / g\mu_B$, respectively. The function ϕ, which determines the ratio between the absorption and the dispersion parts of the ESR signal, is given by Zevin.[11] In the limit $a > d$, ϕ can be expressed as

$$\phi \simeq 1/[\cos(k_1 d) - i\sqrt{\sigma_1/\sigma_2}\sin(k_1 d)]^2 \; . \tag{7}$$

We found that for the configuration described in Fig. 1, the approximation in Eq. (7) is justified, and the use of the more complete expression[11] of ϕ does not change the fitting or the parameters deduced by the fitting procedure.

Equations (5)–(7) indicate that the ESR line shape depends on the function ϕ and consequently on the two parameters d/δ_2 and σ_1/σ_2. In the fitting procedure we have assumed that σ_1/σ_2 (i.e., the ratio of the conductivities along the c axis) is time independent but d (the thickness of the intercalant layer) depends on the exposure time as $d^2 = 2Dt$, where D is the diffusion coefficient. The dashed and solid lines in Fig. 3 indicate the best fit of Eqs. (5)–(7) to the experimental line shape with the two parameters: $\sigma_1/\sigma_2 = 0.81$ and a (single!) diffusion coefficient $D = 1.45 \times 10^{-7}$ cm^2/min. Note that the theory correctly predicts the ESR line shape as a function of time, including the "phase reversal" phenomenon and the magnitude of A/B ratio (Fig. 2). Using the relation $d^2 = 2Dt$ ($D = 1.45 \times 10^{-7}$ cm^2/min), we have calculated the A/B ratio and intensity versus the parameter d/δ_2 (see Fig. 3). The fit with the experiment is very good (Fig. 3). In this fitting procedure, we have plotted the theoretical line shape using Eqs. (5)–(7) and have extracted the theoretical A/B ratio and intensity $(A+B)\Delta^2$ from the theoretical line shape.

The particular dependence ($d^2 = 2Dt$) of the layer thickness d on the fluorine exposure time t is a central point of our paper. It is consistent with the two-dimensional random-walk model and with the two-dimensional diffusion expected in intercalation compounds[1] and clearly indicates that the intercalation is dominated by a diffusion-controlled process. The observation of a single diffusion coefficient might indicate that the diffusion is independent of staging. We were not able to fit the data with different time dependences of d.

The value of σ_1/σ_2 extracted from our fitting is consistent with the fact that c axis conductivity decreases upon intercalation,[1] although the ratio is smaller than that expected from an intercalation compound with a well defined stage. This might indicate that at the very beginning of the intercalation process the stages are not well defined, probably due to disorder. This is consistent with the absence of $(00l)$ diffraction patterns associated with the staging phenomena at the beginning of the intercalation process. Thus, the nature of the "intercalation" layer is not clear. It is not clear also whether the diffusion front is sharp or the value of d represents only an average effective value of the thickness of the intercalation layer. This problem will be analyzed in more detail elsewhere. The value $D = 1.45 \times 10^{-7}$ cm^2/min measured in the present work is probably among the smallest diffusion coefficients in any intercalation compounds. Previous weight uptake studies of the intercalation of HNO_3 and Br_2 into an HOPG host showed that the magnitude of D depends strongly on the intercalate.[1,3] For example, for Br_2 at $T = 300$ K and at a pressure of 250 Torr, $D = 1.47 \times 10^{-6}$ cm^2/min, while for HNO_3 at $T = 300$ K and $p = 81$ Torr, $D = 203 \times 10^{-6}$ cm^2/min. The much higher value of D for HOPG-HNO_3 was attributed[3] to the liquid-like HNO_3 intercalate phase, while Br_2 intercalate forms an ordered phase at room temperature. Although a comparison might be meaningless due to the fact that D depends also on the shape and size of the HOPG host, the very small value of D for fluorine diffusion suggests a very strong coupling of the fluorine with the carbon layers. This is due to the fact that the fluorine is very electronegative. This conclusion is consistent with recent Raman studies.[12]

We have carried out also *in situ* ESR measurements[6] of the intercalation of the fluorides AsF_5 and MoF_6 into HOPG. Our preliminary studies clearly indicate dramatic changes of line shape of the HOPG signal upon exposure, including the increases and the decreases of A/B ratio and the phase reversal phenomenon. The value of D associated with AsF_5 diffusion was found to be significantly larger than that found for the fluorine diffusion. Thus, we believe that the experiment described here provides a powerful method to study diffusion coefficients in intercalation compounds.

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