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STRUCTURAL STUDY OF GRAPHITE OXYFLUORIDE AND THEIR DERIVATIVE COMPOUNDS

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Abstract From X-ray and ^{13}C NMR studies, a new structural model for graphite oxyfluorides and their related compounds, graphite oxide and graphite fluoride, is proposed. sp^3 and sp^2-hybridized carbon ratio are discussed for different compounds.

INTRODUCTION

For a long time it is well known that graphite can be strongly oxidized by fluorine (at high temperature) or oxygen (using oxygenated oxyacid) to form graphite fluoride (GF) or graphite oxide (GO), respectively. Both compounds show distorted layer structures and are characterized by C-F or C-O covalent bonds. Several structural models have been proposed[1,2], in particular, concerning the graphite oxide[3-5], because of the diversity of the bond nature, such as C=C, C-OH, and C-O-C.

Our recent success with the preparation of graphite fluoride at room temperature[6], in which the graphene layers remain planar and the C-F bond is semi-ionic, led us to investigate graphite oxyfluorides[7]. These compounds are noted hereafter GFO or GOF depending on their synthesis, either from oxygenation of GF or from fluorination of GO, respectively. In this paper, we present some structural models based on the observation of X-ray diffraction and ^{13}C NMR studies. In addition, concerning related GO and GF compounds, supplementary data was obtained suggesting a new structural model along the c axis.

EXPERIMENTAL

Graphite oxyfluorides GFO and GOF were prepared respectively by two different ways: 1- oxygenation of a fluorine-unsaturated GF. 2- fluorination of a oxygen-unsaturated GO. More details on the preparation and the characterisation of the compounds can be found in a previous publication[7]. The compounds obtained are washed several times with water and dried at 80 °C for one day. ^{13}C NMR measurements were carried out using MAS and CPMAS techniques. The spectra obtained by the two techniques were very similar.

RESULTS AND DISCUSSION

As previously mentioned[7], many different compositions of GFO and GOF compounds have been obtained. Table I collects those samples on which different measurements were performed for this study, namely, GOF, GFO, and their related compounds GO and GF respectively.

X-ray diffraction studies show very similar results for all compounds (GO, GOF, GF, and GFO) under different conditions. For example, Figure 1 represents three X-ray patterns for the same GOF sample at different steps: the first one corresponds to a freshly prepared untreated compound (Figure 1-a). It shows only one broad peak indicating high structural disorder along the c axis. In addition, the absence of 100 (d = 2.15 Å) and 110 (d = 1.24 Å) reflections of the host lattice indicate a planar disorder.

TABLE I Chemical formula of studied compounds.

Compound	Formula	C oxidation number
GO	$C_4O_{0.56}(OH)_{0.96}$	0.52
GOF	$C_4O_{0.92}F_{1.32}(OH)_{0.56}$	0.93
GF	$C_4F_{1.77}(HF)_{0.39}$	0.44
GFO	$C_4O_{0.12}F_{1.76}(OH)_{0.48}$	0.62

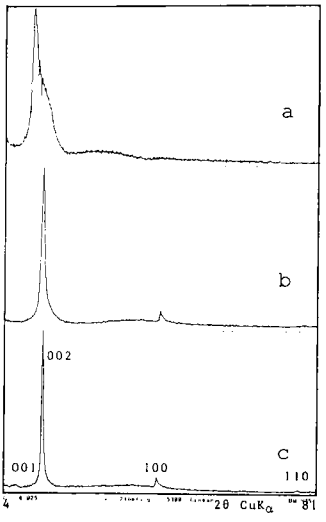


FIGURE 1 X-ray patterns of GOF.

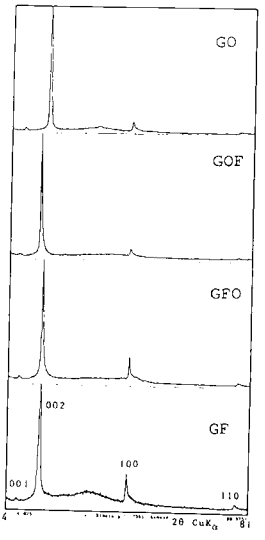


FIGURE 2 X-ray patterns

After washing with water and drying, the X-ray pattern (Figure 1-b) shows a higher crystallinity. The main peak at about 6.2 Å must correspond to the interlayer distance according to results reported in the literature for GO and first stage GF where it is systematically indexed as a 001 reflection. However, after a long conservation period of about two months in a dry atmosphere at room temperature (Figure 1-c), the X-ray pattern shows a narrower main peak and the appearence of a very weak one at about 12.40 Å. These features indicate a higher crystallinity of the compound suggesting that the main peak, at about 6.1 Å, may be indexed 002 (instead of 001) corresponding to I_c = 12.20 Å. Figure 2 exhibits patterns of all compounds (GO, GOF, GF, and GFO) obtained at this last step and the same interpretations can be proposed. The average values of I_c are 12 Å for GO, GOF, and GFO and 11.47 Å for GF.

If we now consider bond lengths and Van der Waals radii of the various atoms, we can calculate approximately the interlayer distance for oxygen and/or fluorine-saturated spaces: d_1 = 6.04 Å for GO, GOF, and GFO and 5.77 Å for GF.

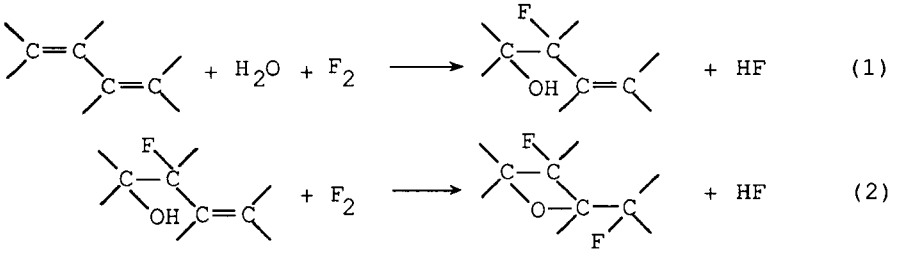
The d_2 values, for unsaturated systems are certainly lower[1]. This suggests a structural model along the c axis in which there is a sequence of two successive intercalated species layers of different densities or ratios. Accordingly, the I_c parameter is given by the sum of the interlayer spacing of higher density d_1 and that of the lower one d_2. This can well explain the presence of the first weak peak. This model can be supported by the fact that the compound is formed after an intermediate formation of a 2nd stage-GIC, as it has been found effectively during the formation of graphite oxide. For example, by Brodie method preparation, a second stage HNO_3-GIC is formed and, in the presence of $KClO_3$, the graphite oxygenation can be achieved starting by these occupied spaces and then in the unoccupied ones of the second stage GIC after HNO_3 intercalation. So, the oxygenation ratio of two successive interlayer spaces is kinetically different and it will have different densities.

The ^{13}C NMR spectra of all compounds are reported in Figure 3. Four lines labelled α, β, γ, and η are observed. A similar spectrum has been obtained for GO samples by other authors[5]. In agreement with their results, the α, β, and γ lines are assigned to carbon bonded to ether-oxygen (C-O-C), to hydroxyl groups (C-OH), and to sp^2-hybridized carbon (C=C), respectively. The GF compound exhibits two resonance lines; γ and η. The second line η can be assigned to carbon bonded to fluorine (C-F). Table II reports the chemical shifts for all compounds.

TABLE II Chemical shifts and assignment of NMR lines

Line	α	β	η	γ	
Carbon type	C-O	C-OH	C-F	C=C	
Chemical shift (ppm/TMS)	60	71		128	GO
	60	73	87		GOF
			84	132	GF
	60	70	83	133	GFO

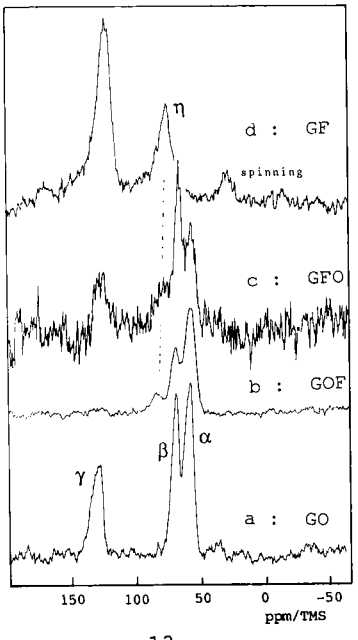
Figures 3-a and 3-b show the spectra of GO and that of fluorinated GOF in which the γ line completely disappears, and the η line appears. This is in agreement with the chemical composition of the compound and with the increase of carbon oxidation number which approaches 1 (0.93), the value for carbon aliphatic sp^3-hybridized. We can also clearly observe an increase of the α line relative to that of β indicating an increase of C-O-C carbon relative to C-OH carbon after fluorination of GO hydrated compound. This can be explained by the two following reactions (1) and (2):



On the contrary, the γ line does not disappear after oxygenation of GF as confirmed by chemical formula giving a carbon oxidation number much lower than 1 (0.62). In addition, it should not be ruled out that some fluorine, -F, may be replaced by -OH and -O- groups. Such phenomena occur easily with inorganic fluorides which hydrolyse to form oxyfluorides or oxides and hydroxides.

Finally, it seems that ^{13}C NMR measurements made with proton decoupling alone do not provide information on relative amounts of various carbon functions from the intensities of the corresponding lines for fluorine containing compounds. This requires joint fluorine decoupling that has not yet been accomplished.

In conclusion, for GO, GF, GOF, and GFO we propose a new structural model along the c axis based on a sequence of two successive intercalated species layers of different densities. Fluorination of oxygen-unsaturated GO gives GOF, a highly saturated compound; carbon is in sp^3-hybridized form. However, oxygenation of fluorine-unsaturated GF does take place but a large part of carbon remains in sp^2-hybridized



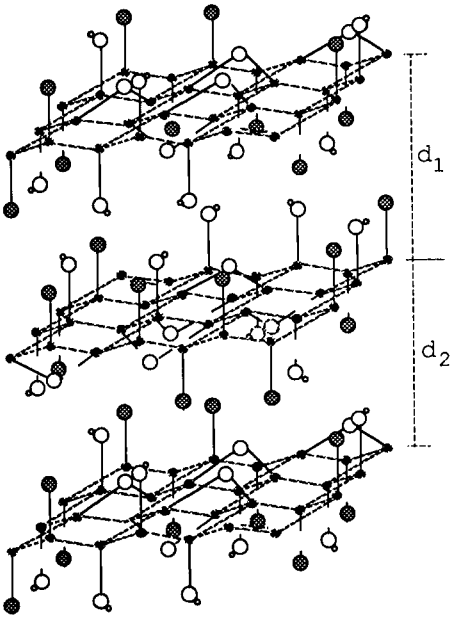


FIGURE 3 ^{13}C NMR spectra. FIGURE 4 Structural model.

●: F, o: O, ♂: OH

form. Finally, it seems that the C-F bond character is rather covalent in GOF and GFO. The presence of the covalent bond character environment of oxygen promotes this formation. All these considerations lead us to propose the structure shown in Figure 4.

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