Structural Determination of Graphite
FeCl₃, ZnCl₂ using (001) X-ray Diffraction

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Analysis of the (001) x-ray diffractograms of well staged graphite-FeCl₃, stages **n**=2,3,4,5 and graphite-ZnCl₂, stages **n**=4,5 compounds reveals important structural information concerning these compounds. The I_c separation between intercalated layers is observed. The FWHM for analysed intercalated specimen were found not to be significantly different from the values for pristine graphite. Connections of results from the (001) x-ray diffraction with the I_c values for the reflection with maximum intensity may be used as a rapid method for stage identification.

I. Introduction

Using x-ray diffraction techniques it is possible to obtain the stage index n of Graphite Intercalated Compounds (GIC)[1] which is defined as the number of carbon layers between two intercalated layers. Information concerning sample homogeneity anù stage fidelity[2] can be obtained from the positions and linewidths of (001) diffraction profiles. The in-plane ordering and intercalate stacking can be identified[3] from the (hk0) reflections. Using (001) integrated intensities[4] one can obtain information about the inner structure of a multilayer intercalant (ex. AlCl₃, FeCl₃) and a qualitative analysis of these integrated intensities can be used to characterize the separation $c_0 + 2d_i$ between the intercalated layer and the two adjacent carbon layers.

In this work, we present the GIC structure factor and scattered intensity calculations. We also report the following, from (001) x-ray experimental data in GIC-FeCl₃, ZnCl₂: (a) the repeat distance **I,**; (b) the extent of stage fidelity through the intensity of maxima identified with secondary stages; (c) the sample homogeneity as determined by the half-widths of the reflections and (d) a simple procedure to identify the stage index n of any GIC from scattered integrated intensity data.

II. GIC Structure factor calculations

Contributions of **s** atoms in the unit cell to the structure factor F(hkl) is given by:

$$F(\vec{G}) = \sum_{j=1}^{\mathbf{s}} f_j \exp(i\vec{G} \cdot \vec{r_j}) , \qquad (1)$$

where $\vec{G}$ is the reciprocal lattice vector, $\vec{r_j}$ denotes the coordinates of the j-th atom in the unit cell. f_j is the scattering factor if the j-th atom, given by:

$$f_j = f_j^0 \exp\left(-B_j \frac{sin^2\theta}{\lambda^2}\right) , \qquad (2)$$

where B_j is the Debye-Waller temperature factor, λ denotes the incident wavelength and f_j^0 is the scattering factor for the atom at rest.

Considering only reflections in the basal planes, we can evaluate contributions to the structure factor of the intercalated atoms and also those contributions due the carbon atoms.

Fig.1 shows a simplified model of a GIC structure. Taking the system origin on the intercalated layer,

$(r_j)_i = 0$ and considering the same scattering factor f_i for the intercalated atoms, we have:

$$F_i(00l) = N_i f_i \qquad (3)$$

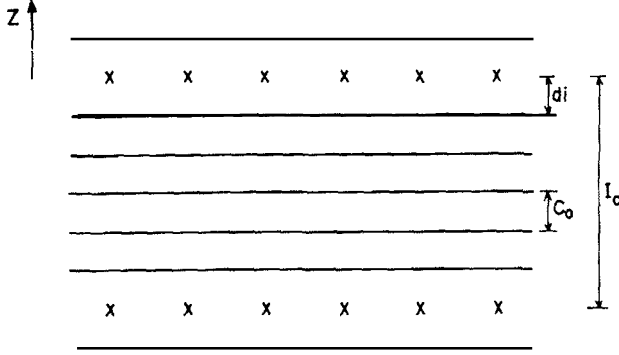where N_i is the number of intercalant atoms per unit cell.

Figure 1. Simplified model of a GIC Structure. X represents the intercalated layer and the heavy line denotes the carbon layer. d_i is the separation between an intercalant and adjacent carbon layers. The c_0 and I, parameters are, respectively, the separation between two graphite and intercalated layers.

This is the contribution of intercalant atoms, which are supposed to be monoatomic, to the total structure factor. The contribution due to carbon atoms is

$$F_c(00l) = (-1)^l N_c f_c \frac{sin(n\pi xl)}{sin(\pi xl)} \ , \qquad (4)$$

where N_c is the number of carbon atoms per unit cell, $x = c_0/I_c$. $c_0 = 3.35$Å is the separation between two graphite layers and I, is the intercalant repeat distance, along c-axis. The parameter I, is related with the stage n, as:

$$I_c = 2d_i + (n-1)c_0 \ , \qquad (5)$$

where d_i is the separation between an intercalated layer and the adjacent carbon layer. Experimentally, I, can be measured from the positions of diffraction peaks, using Bragg's law,

$$l\lambda = 2I_c sin\theta_l \ , \qquad (6)$$

where θ_l is the diffraction angle. Taking $\xi = N_i/N_c$ as the intercalated density in the unit cell, the GIC structure factor is given by:

$$F(00l) = \xi f_i + (-1)^l f_c \frac{sin(n\pi xl)}{sin(\pi xl)} \qquad (7)$$

The reflection intensities are proportional to $\| F(00l) \|^2$. In practice, some corrections are necessary to reduce the integrated intensities to $\| F(00l) \|^2$ due to the combined Lorentz and polarization effects, C_L, x-ray beam absorption by the sample, C_A and a scale factor S. Hence, we obtain

$$\| F(00l) \| = [SI(00l)/C_L C_A]^{1/2} \ . \qquad (8)$$

Eq. (8) obviously does not give information about the atomic ordering in the intercalating layer. However, one can get qualitative information about (001) reflections related with the intensities for any intercalated specimen (mono or multi-layered) and also about the stage n by neglecting f_i in the Eq. (7). This approximation is valid when the intercalant species has small atomic number or for cases where N_i is small compared with N_c.

Using only Lorentz and polarization corrections[5] in Eq. (8), we have the following approximate expression for the scattered intensities:

$$\eta_n(y) = \frac{(1 + cos^2 2\theta_l)}{sin2\theta_l} f_c^2 \frac{sin^2 ny}{sin^2 y} \qquad (9)$$

where $y = \pi xl/I_c$.

Taking 1 as a continuum variable, the above equation means that for a given wavelength λ, the relative intensities for any GIC, for a given stage n, is related with a single plot of $\eta(y)$ versus y. Hence, if we know the y-values for each (001) reflection and the I, parameter, we can find out the maximum relative intensity and compare it to the most intense (001) diffraction maximum obtained by experimental data.

III. Experimental

Samples were prepared using Highly Oriented Pyrolytic Graphite (HOPG) as a host material. The graphite specimens were cut to typical dimensions $5.0 \times 6.0 \times 0.4$ mm^3. The GIC-FeCl$_3$, ZnCl$_2$ samples used in this work were prepared using the conventional two zone phase growth method[6]. The stage for each sample was determined by measuring the (001) X-ray diffraction peaks from a conventional $\theta - 2\theta$ scan, at room temperature. CuKα radiation ($\lambda = 1.542$Å) from a Phillips PW 1380/60 generator was used and a Na(I)

scintillation detector was selected to provide discrimination of the incident X-ray energy.
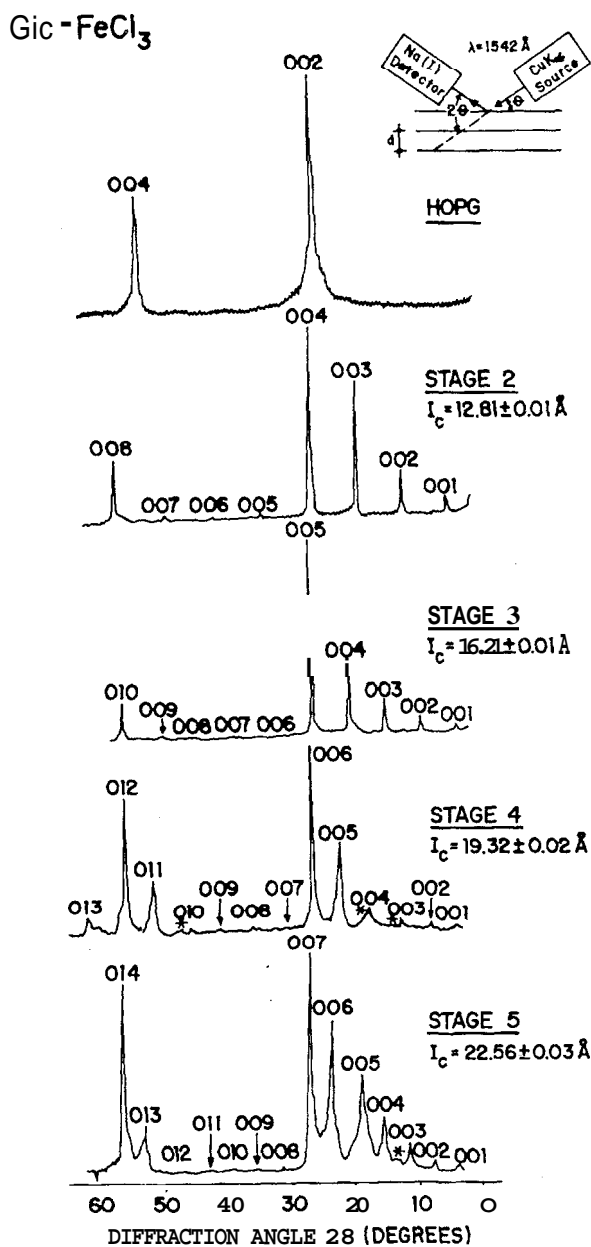
Gic - ZnCl₂

Gic - FeCl₃

Figure 2. Stage characterization using X-ray cliffraction for stages n = **2, 3,** 4 and 5 graphite-FeCl₃ compounds. The intercalated repeat distance I_c and stage index are given on the right. Reflections due to aclmixed stages are indicated by (*). Tlie HOPG diffractogram is included for comparision. The diffractograms were taken with a CuK_α, X-ray source and a Na(I) detector.
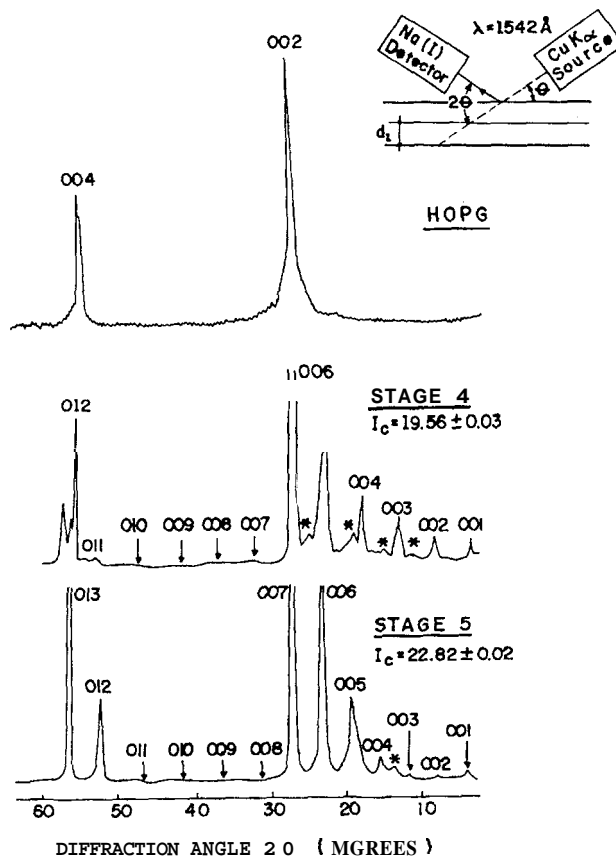

Figure 3. X-rap stage characterization for stages n = 4 and 5 for graphite-ZnCl₂ compounds. Reflections due to admixecl stages are indicated by (*). Tlie stage and the separation between two intercalated layers are indicated on the right.

Fig. 2 and Fig. 3 show the recordecl diffraction patterns for GIC-FeCl₃ and GIC-ZnCl₂ samples, respectively. Also shown in the figures are values for the corresponding intercalant repeated distance I_c, from Bragg's law analysis. We noted the appearance of some small secondary maxima (labeled by an asterisk in Fig. 2 and Fig. **3)** for *graphite*-FeCl₃ stages 4 and 5, and for *graphite*-ZnCl₂ stages 4 and 5 compounds, indicating the presence of admixed stage in those samples. However, these secondary maxima are not significant (5.0%, at maximum) compared to the primary peaks. At this level, we can consider the samples as having a goocl stage homogeneity.

IV. Discussion

Metz and Hohlwein[2] have shown that, other than the absence of secondary peaks, a random spacing between intercalated layers shifts the positions of the

diffraction peaks and increases the Full Width at Half Maximum (FWHM) of these peaks relative to tlie single stage material.

In Fig. 4, we have plottecl the FWHM for EIOPG and for the intercalated samples used in this work, in units of $\Delta(sin\theta/l)$ versus $sin\theta/l$. The figure revcals that the FWHM of tlie reflections for intercalation compounds is not significantly different from those for HOPG. Comparing tlie results, we conclude that tlie samples, not only are well-staged (with tlie exceptions of $FeCl_3$ stage 4 and $ZnCl_2$ stage 4 and 5 graphite compounds) but also have little statistical disorcler after intercalation.
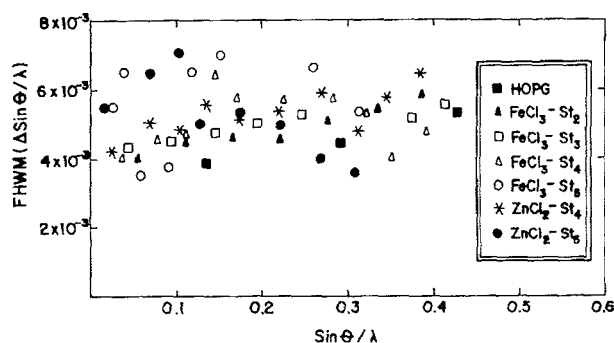

Figure 4. Plot of tlie Full Width at Half Maximum (FWHM) of the (001) reflections in units of $\Delta(\sin\theta/l)$ versus $\sin\theta/l$ for HOPG, ancl graphite-$FeCl_3$, $ZnCl_2$ compounds.

Small observed differences relative to EIOPG are mainly due to minor variations in the structure of tlie host material upon intercalation.

In tlie Fig. 5 ancl Fig. 6 we have plotted tlie results of Eq. (9) for the various samples. We have used tlie scaterring factor f_c froin reference[7], to estimate $\eta(y)$. We also show the relative intensities $I(00l)$ for *graphite*-$FeCl_3$ and *graphite*-$ZnCl_2$ obtained from cliffraction peaks.

With regard to GIC - $FeCl_3$, tlie tlieoretical curve for $\eta(y)$, in Fig. 5, shows that for n = 2,3,4 and 5 tlie intensity maximafrom (001) reflections are (004), (005), (006) and (007), respectively. On the other hand, for GIC- $ZnCl_2$, it is founcl tliat for n = 4 and 5, reflections corresponcl to (006) ancl (007), respectively

If tlie most intensive (001) diffraction peak is assumed to be (0,0,n+m), wliere **n** is the stage index and m is an integer, we have tliat for a given stage index n, the subsidiary maxima for increasing values of 2θ will be (n+m)-fold. Here **in** is cleterinined empirically

as being the nearest integer which is approximated by $(d_s - c_0)/c_0$, where d_s is tlie sandwich thickness (the distance separating two carbon layers between which, tlie intercalant is sandwiched)[2−4]. Values for m=2 have been found for both, $FeCl_3$ and $ZnCl_2$, intercalants.

For *graphite*-$FeCl_3$ and *graphite*-$ZnCl_2$ compounds, their respective most intense (001) diffraction peak occurs for l = n+2. This **n** value agrees with our experimental results, using calculated values for I, shown in Fig. 2 and Fig. 3. The good agreement between theoretical ancl experimental values shows that it is correct to neglect ξf_i in Eq. (7). We argue this fact based on stoichiometric calculations. For $ZnCl_2$, a stage **3** intercalated componnd, yields tlie formula $C_{16.5}ZnCl_{5.1}$[8]. On tlie other hand, for $FeCl_3$, tlie stoichiometry of such an intercalatecl procluct is $C_{12.5}FeCl_3$ and $C_{26}FeCl_3$[9−10] ln the second ancl third stages, respectively. Consequently, tlie highel the stage index, the smaller the ratio of N_i to N. As this ratio decreases, tlie contribution of ξf_i to the GIC structure factor given in Eq. (7) becomes less important.

Furthermore, the validity of this approximation lias already been shown for GIC-K,-Cs, stage 2[3]. Neglecting ξf_i in Eq. (7) also sliows that Eq. (9) can be valid for monoatomic as well as poliatomic intercalants.

Therefore, tlie method above can be used as a rapid and simple method for stage iclentification of graphite intercalation compoiinds.

V. Conclusions

(a) We have obtained information ahout the repeat distance I_c between two intercalated layers, tlie stage **n** and tlie liomogneity of GIC-$FeCl_3$ and GIC-$ZnCl_2$. It must be stressecl that for the first time GIC-$ZnCl_2$ stages n = 4 ancl 5 were prepared; (h) All structural information in this work was analysed from angular positions, linewidths and integrated intensities of (001) diffraction peaks, cleterminecl by X-ray diffraction techniques; (c) A more complete determination concerning structural inforination for compounds presented in this work, can be obtained using the (hkl) reflection lines, from which we can obtain experimentally the intercalation densities ancl in-plane lattice parameters. In relation to *graphite*-$ZnCl_2$, very little has been published so far along these lines.
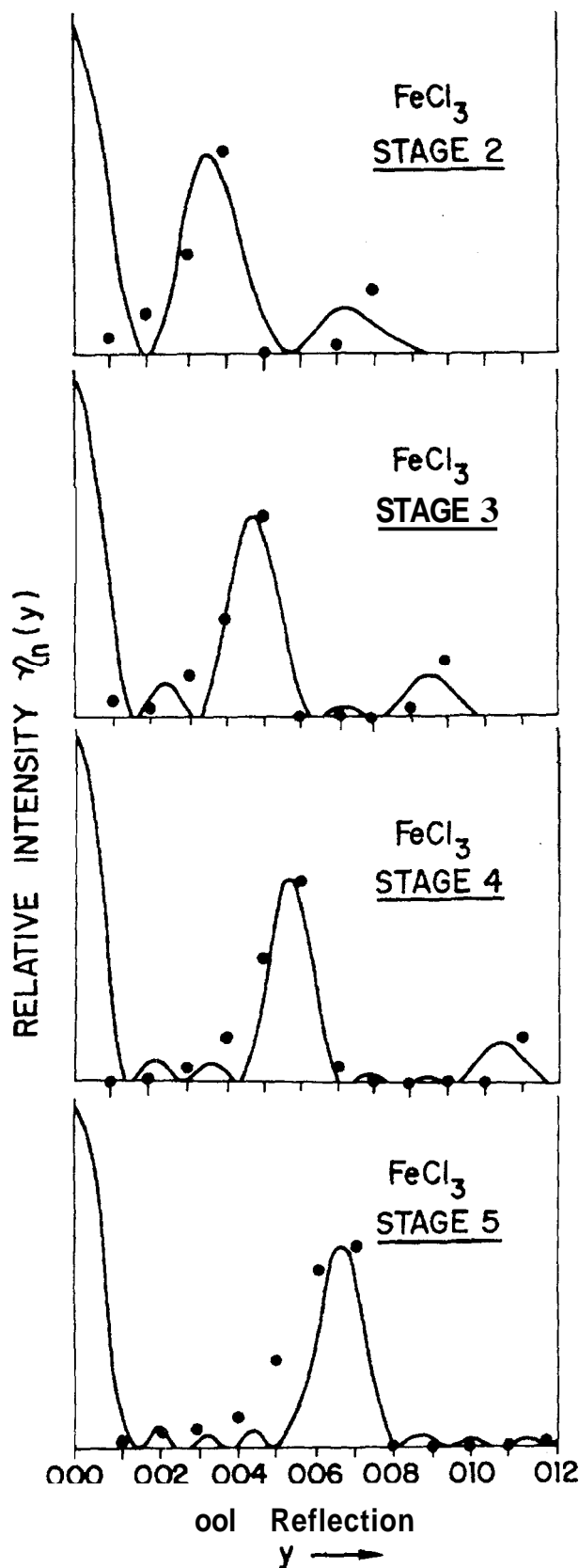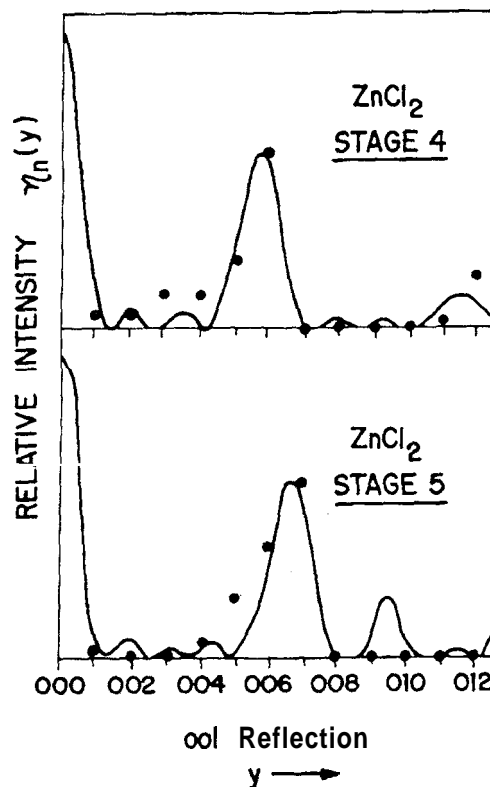
Figure 6. Plots for relative X-ray peak intensity $\eta_n(y)$ versus y, for stages n=4 and 5 graphite-$ZnCl_2$ compounds. The dots represent experimental (001) intensity data.

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Figure 5. Plots for relative X-ray intensities $\eta_n(y)$ versus y. The dots denote measured (001) intensities foi GIC-$FeCl_3$, stages n = 2,3,4 and 5.

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