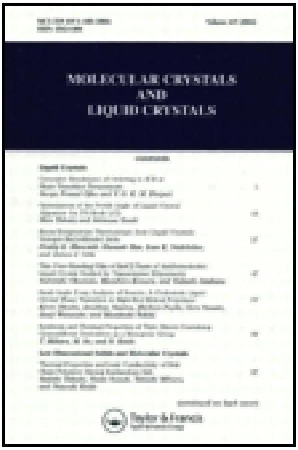

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NUMERICAL COMPUTATION OF GIC 00L REFLECTIONS CONSIDERING SLIGHT STAGE DISORDER

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Abstract The influence of slight stage disorder on the GIC 00L intensities and the structural parameters obtained from a structure refinement were determined by a computer simulation. Even for supposed pure stages with a stage fidelity more than 98% errors caused by this slight stage disorder have to be taken into account.

INTRODUCTION

Due to the structural properties of graphite intercalation compounds with stacking (translational) disorder the intensities of the 00L reflections are the only measurable integrated intensities which can be used to refine a model structure. One common kind of disorder that influences the integrated intensities of the 00L reflections is the stage disorder. This disturbance of the periodicity of the layers in the c-direction caused by layer units of higher or lower stage number results in a loss of intensity, a peakshift and a broadening of the diffraction peaks. These effects are well known[1] and some of them have been treated in the past.[2-7] Structural parameters obtained from the integrated intensities of obviously disordered compounds are expected to show a large error.

But even for supposed pure stages without any visible influence of stage disorder a very small fraction of stage impurities cannot be absolutely excluded. For these cases a computer simulation was written to calculate the 00L reflections of a model structure, which contained a slight degree of stage disorder. From these simulated peaks the integrated intensities and the profile parameters were extracted. With the integrated intensities the pure stage model was refined by a least-squares algorithm. Hence, the deviation of the structural parameters from those of the model chosen for the simulation could be obtained.

BASIS OF THE NUMERICAL COMPUTATION

In the simulation the intensity of the diffracted wave from one coherent domain is computed by addition of the diffracted waves from every single layer. The amplitudes A_i and the phases Φ_i of the single waves are calculated by

$$\Phi_i = \frac{\sin(\theta)\cdot 4\cdot\pi\cdot d_i}{\lambda} \quad ; \qquad A_i = f_i\left(\frac{\sin(\theta)}{\lambda}\right)\cdot \nu_i \quad ;$$

if the stoichiometric factors υ_i, the distance of the layer d_i from the origin, and the atomic scattering factors f_i are known for every layer in the domain from the chosen model (θ : diffraction angle, λ : wavelength).

Each domain consists of a fixed number of stage units. Stage disorder is simulated by adding randomly distributed extra graphene layers generating units with stage number S+1 or by substracting graphene layers generating units with S-1 (S referring to the pure stage). The resulting structure amplitude |F| for one domain is, e.g. in case of intercalates with the common triple layer stacking, given by

$$|F| = \sum_{i=1}^{n} \left[A_{Cl_1}\cdot e^{(i\cdot\phi_{Cl_1})} + A_{Me}\cdot e^{(i\cdot\phi_{Me})} + A_{Cl_2}\cdot e^{(i\cdot\phi_{Cl_2})} + \sum_{j=1}^{S} A_{C_j}\cdot e^{(i\cdot\phi_{C_j})} \right]$$

$$+ \sum_{j=1}^{m} A_C\cdot \exp\left(i\cdot\frac{\sin(\theta)\cdot 4\cdot\pi\cdot d_j}{\lambda}\right) + \sum_{l=1}^{k} -A_C\cdot \exp\left(i\cdot\frac{\sin(\theta)\cdot 4\cdot\pi\cdot d_l}{\lambda}\right)$$

where n denotes the number of stage units in the pure stage domain, m the number of added graphene layers , and k the number of subtracted graphene layers.

The intensity as a function of the diffraction angle is computed as the average of the $|F|^2$ values for a multiple number of domains. The obtained diffraction peaks are convoluted with a broadening instrumental function. The profile parameters and the integrated intensities are extracted.

RESULTS

An Indium(III)-chloride GIC stage 2 with the formula $C_{9.32+\Delta\upsilon(C)}In_{0.67+\Delta\upsilon(Me)}Cl_2$ [8] was chosen as the model compound. One layer unit consists of two chloride layers with a distance of z(Cl)=±150 pm from the central Indium layer and two graphene layers with z(C)=±475 pm. The peaks for the 00L reflections 001 to 00.10 were calculated for stage numbers from 1.9 to 2.1. Figure 1 shows as an example four simulated diffraction peaks of the 001 reflection with different stage numbers. Figure 2 shows the convoluted 003 and 004 reflections for stage numbers from 1.9 to 2.0. The well known[1] slight dependence of the 00(S+2) reflections on disorder compared to the strong dependence of the 00(S+1) reflection could be noticed.

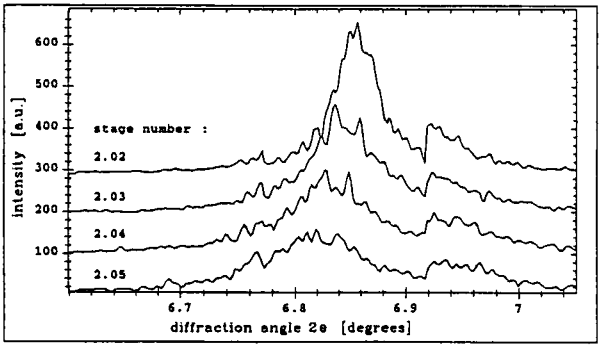

FIGURE 1 Simulated diffraction peak 001 of $InCl_3$ GIC with different degrees of disorder (Cu K_α, λ=154.2 pm).

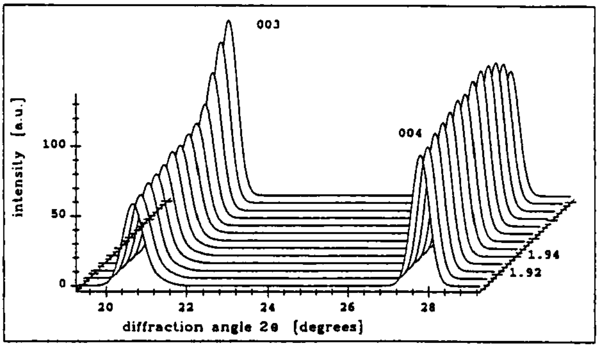

FIGURE 2 Simulated diffraction peaks 003 and 004 (CuK_α) convoluted by a broadening function; intensity modulation vs. stage number (1.9 to 2.0)

In Figures 3-5 the obtained profile parameters (area=integrated intensity, FWHM and peak position) in relation to the parameters of the pure stage (S=2) are plotted as a function of stage number. The alterations in peak position, FWHM, and intensity are characteristic of each type of 00L reflection, in agreement with earlier results obtained from an analytical expression.[1] The calculations are also in good accordance with parameters extracted from measured reflections.[2,9]

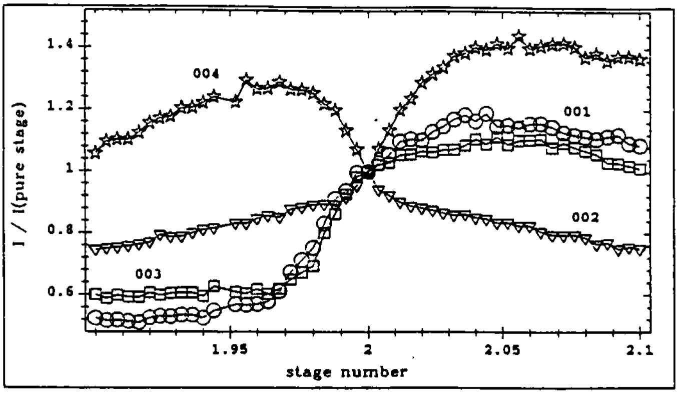

FIGURE 3 Relative 00L intensity alterations for different degrees of disorder.

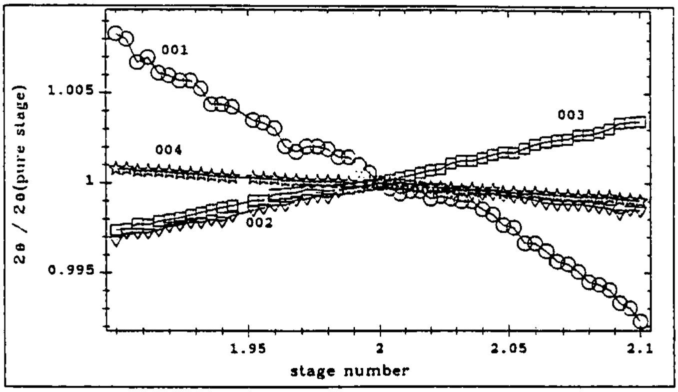

FIGURE 4 Relative 00L peak shift for different degrees of disorder

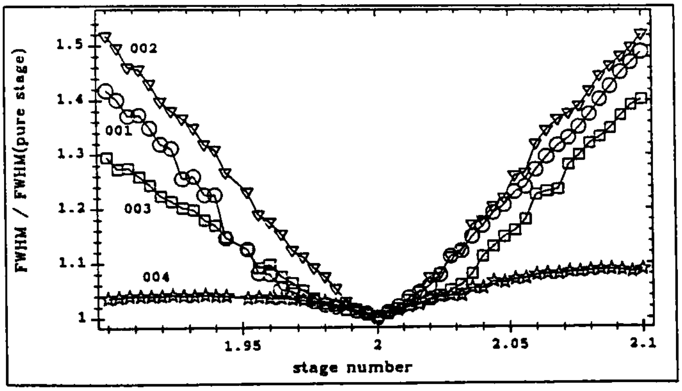

FIGURE 5 Relative FWHM alterations for different degrees of disorder

Figures 6-8 show the structural parameters of the pure stage model, which were refined with intensities obtained from the simulation for different degrees of disorder, represented by the stage number. The refined parameters were the distance of the chloride layer from the Indium layer z(Cl), the two additional stoichiometric factors for the Indium and the graphene layers $\Delta\upsilon(\mathrm{In})$ and $\Delta\upsilon(\mathrm{C})$ and the overall Debye-Waller factor.

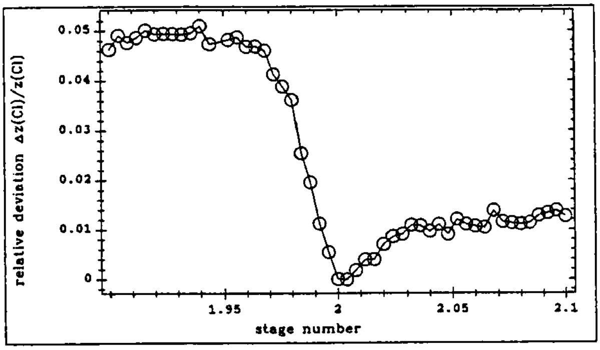

FIGURE 6 Relative deviation $\Delta z/z$ of the chloride layer at different degrees of disorder.

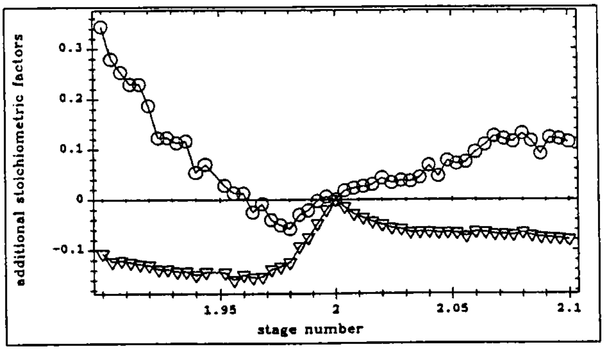

FIGURE 7 Additional stoichiometric factors (circle: $\Delta\upsilon(\mathrm{C})$, triangle: $\Delta\upsilon(\mathrm{In})$) at different degrees of disorder.

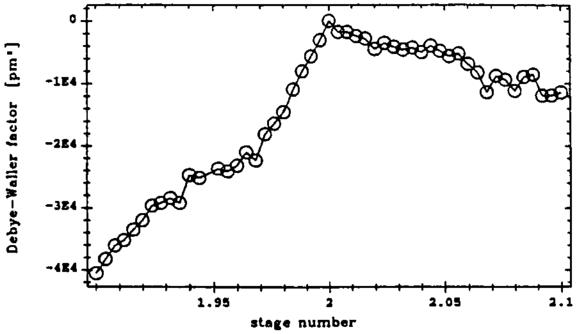

FIGURE 8 Additional overall Debye-Waller factor at different degrees of disorder.

It can be recognized that the dependence of the structure parameters on disorder is greater for compounds with a stage number less than the pure stage. For instance, a deviation in stage number of 0.03 leads to $\Delta z/z$ of nearly 5% in the lower stage and only 1% in the higher stage case. The negative values obtained for the additional Debye-Waller factor must be explained by a stronger dependence of high order reflections on stage disorder.

CONCLUSION

It could be shown that a stage fidelity of at least 99% is necessary to yield a precision of 1% in the z(Cl) value. Also the additional Debye-Waller factor and the stoichiometric factors show a strong dependence even on this slight disorder. It becomes also evident from the simulation, that a slight disorder (stage fidelity more than about 98%) cannot be recognized by a broadening or a shift of the diffraction peaks. Hence, the influence of slight stage disorder upon the structural parameters obtained from 00L intensities has to be taken into account even for supposed pure stages.

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