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Markovian growth mechanism for a layered material as revealed by diffuse x-ray scattering

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Abstract. Diffuse x-ray scattering lines observed from the layered material $\text{Cu}(\text{C}_6\text{H}_4(\text{OH})\text{COO})_2 \cdot (\text{H}_2\text{O})_2$ (DSC) reveal a considerable degree of short-range stacking order, indicating direct correlation between the first few neighbouring layers.

The data have been fitted to a 1D, two-parameter Markovian growth model, equivalent to a 1D Ising model involving nearest- and next-nearest-neighbour coupling. The disorder is caused by a combined effect of the one-dimensionality and the two coupling parameters, which are of the same sign. In the growth process the configuration of a given layer is influenced both by the previous layer configuration and the next previous one. Several samples from the same batch were studied, showing a considerable variation of the next-nearest-neighbour correlation parameters, indicating that the growth is very sensitive to the local external conditions (concentrations, impurities, temperature gradients, convection).

1. Introduction

Layered materials where the layer stacking sequence may vary, are often denoted *polytypic*, alluding to the fact that such materials occur in a variety of forms. Well-known and much studied examples are SiC and ZnS (Verma and Krishna 1966). In some cases the layer structure may be quite complicated, as in the material of the present study, yet the simplicity of the layer stacking is retained, effectively leaving only two energetically favourable nearest-layer configurations. Such cases are often describable by an Ising pseudo-spin picture (Yeomans 1988), where the various polytypes correspond to various stable spin solutions depending on details of the interaction parameters. These interaction parameters are thought to be fairly sensitive to the external conditions during the fabrication of the materials, leaving us with numerous varieties of superlattice structures, as for SiC.

It is also expected that under certain conditions fully or partially disordered materials may result, just as the Ising pseudo-spin system is disordered at sufficiently high temperatures or at low spatial dimensionalities. 1D Ising systems lack long-range order at all $T > 0$. Since the layer sequence, once realised during a given crystal growth process, can hardly transform to other sequences, the disorder will be retained at all temperatures. Thus, the study of the layer stacking is in fact a study of the growth sequencing process.

For a completely random case the probability P_i for a given layer ' i ' is only given by a constant, α , directly related to the mole fractions of the two configurations. However, in more realistic cases it may depend on the configuration x_{i-1} and x_{i-2} of the previous layers by

$$P_i = \alpha + \beta x_{i-1} + \gamma x_{i-2} + \dots$$

This picture may be extended to neighbours at greater distances as well, even including non-linear terms. Mathematically the approach corresponds to systems of Markov chains, which, as shown in an extensive work by Welberry (1985), may indeed be transformed into Ising models. In the present work we shall interpret the x-ray scattering from DSC in terms of layer-stacking disorder. The structure of DSC was determined by Jagner *et al* (1976).

The experimental details of the present x-ray work and the data processing are described in the preceding paper (Tjøtta *et al* 1991).

2. The Markovian growth process

A 1D picture presupposes that each layer member is fully ordered, and that there are two ways of adding layers on top of each other. According to Welberry (1985) the probability P_j for the choice of the ' j^{th} ' layer may be expressed by the discrete variable x_j ($x_j = 1$ for a '+ choice', $x_j = 0$ for a '- choice')

$$P_j = \alpha + \beta x_{j-1} + \gamma x_{j-2} + \delta x_{j-1} x_{j-2} + \dots \quad (1)$$

Welberry (1985) argues that the δ term is not essential for the form of the correlation function, and we shall neglect it here. Since our x-ray data show evidence for next-nearest-neighbour correlation, (but not necessarily for further neighbours) we shall keep only the three parameters α , β and γ .

Necessary formulation for the following discussion may be found in the Appendix. In a statistically random growth process no correlation will exist between neighbours, corresponding to $\beta = \gamma = 0$ and $\alpha = \frac{1}{2}$. Such a case gives rise to a uniform intensity distribution in a diffraction experiment (except for structure-factor variation due to the objects taking part in the growth (molecules, layers etc)). A process where the choice of a given layer is influenced by the previous layer only, corresponds to $\beta \neq 0$, $\gamma = 0$. Such a model may be qualitatively appropriate where the layer interaction is of short range, for instance through fitting of topological troughs and peaks on the layer surfaces. In this case the correlation between distant layers is transmitted equally by each intervening layer, leading to a simple form

$$C_n = \beta^n \quad (2)$$

for 'ferromagnetic' correlation $\beta > 0$, and peaks appear (A11) with maxima at integer indices l ('MDO₁ type'). 'Antiferromagnetic correlation', $\beta < 0$, would correspond to a preference for unequal nearest-neighbour pairing ('MDO₂ type'). In diffraction this case is revealed by peaking at half-integer l values. In either case a correlation range parameter ξ could be defined by

$$\beta = \pm e^{c/\xi} \quad (3)$$

and its value could be deduced from the peak width. In our case none of the samples could be described by a one-parameter fit only.

The other extreme case of $\beta = 0$, $\gamma \neq 0$ is less probable because it is hard to image a growth mechanism in which the nearest-neighbour plays no role while the next-nearest does. It is worthwhile to notice, though, that for such a case, $D_1 = -D_2$ (see (A4)), and (for real $D_{1,2}$) scattering peaks would occur with equal weight both at half-integer and integer values of l . The coupling parameter, γ , is positive for this case, leading to an enhanced probability of $(+) +$ or $(-) -$ next-nearest-neighbour pair occurrence. It is this cell-doubling tendency which explains the corresponding l index halving.

It turns out that our data can only be fitted by two non-equal D_1 and D_2 of opposite sign, corresponding to both β and γ finite.

3. Experiments and data fitting

Crystals were prepared at room temperature by adding 0.2 M CuSO_4 solution to the double volume of 0.2 M salicylic acid and 0.2 M NaOH. The solution was allowed to evaporate slowly over a few days, giving green crystals of size about $3 \times 1 \times 0.2$ mm, the shortest dimension corresponding to the layer normal axis c .

Four different crystals were picked out at random from the precipitate and studied by x-ray diffraction at room temperature as described in the preceding paper (Tjøtta *et al* 1991).

Table 1. Fitted parameters D_1 , D_2 with uncertainties, and derived coupling parameters α , β and γ and near-neighbour correlation functions C_n for the four samples, based on formulae given in the appendix.

| Sample | D_1 | D_2 | α | β | γ | C_1 | C_2 | C_3 |
|--------|--------------------|---------------------|----------|--------------------|----------------------|-------|-------|--------|
| Two | 0.12 ± 0.03 | -0.06 ± 0.03 | 0.4665 | 0.06 ± 0.04 | 0.007 ± 0.004 | 0.060 | 0.011 | 0.0012 |
| Three | 0.27 ± 0.02 | -0.14 ± 0.02 | 0.4160 | 0.13 ± 0.03 | 0.038 ± 0.008 | 0.135 | 0.055 | 0.0123 |
| Four | 0.30 ± 0.03 | -0.23 ± 0.03 | 0.4305 | 0.07 ± 0.04 | 0.069 ± 0.011 | 0.075 | 0.074 | 0.0104 |
| Five | 0.21 ± 0.02 | -0.12 ± 0.02 | 0.4425 | 0.09 ± 0.03 | 0.025 ± 0.005 | 0.092 | 0.033 | 0.0053 |

For each sample equation (A11) (with the corresponding (A4), (A5), (A6) and (A3)) was fitted by the least squares method to the scattering in the $l = 2.5\text{--}5.5$ region. The fitted parameters and corresponding correlation values are shown in table 1, and the experimental and fitted calculated intensity profiles are shown in figure 1. The fits are quite good in the actual fitted regions for all four samples. In fact, most of the apparent bad fitting seen on figure 1 is due to insufficiently precise structure-factor functions and is unimportant for the derived parameters of table 1 (see the preceding paper for discussion of this point). One notices that for sample four, peaking is observed and also reproduced both at integer and half-integer l -values. For samples three and five the fit is particularly good as far as peak shape and width are concerned, although there is a systematic deviation in the $l = 3.5$ region for samples four and five. The data statistics for sample two are somewhat inferior.

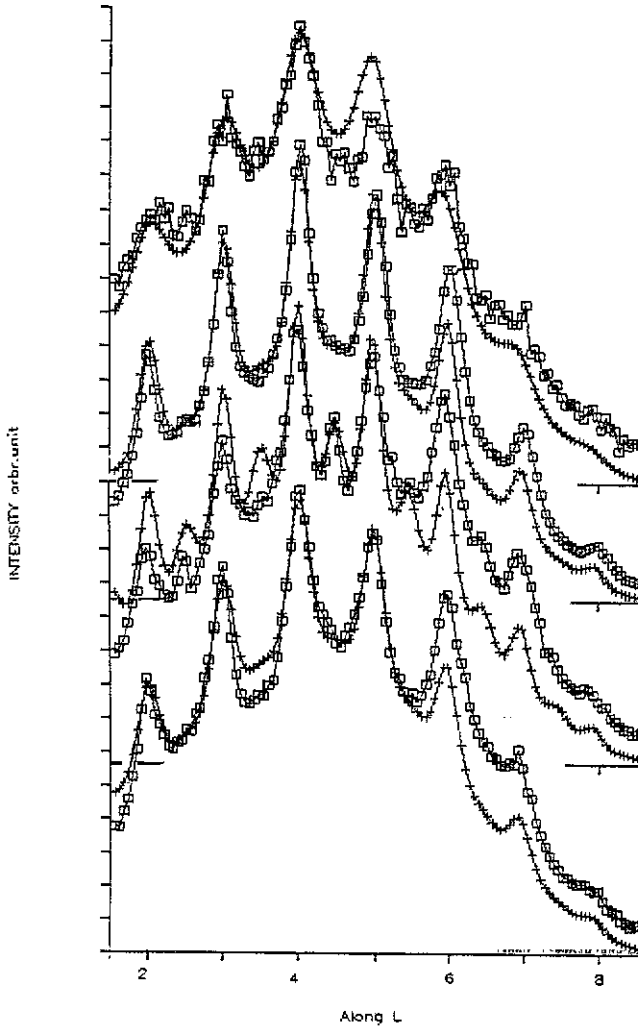


Figure 1. Observed (\square) and calculated (+) intensities along l for $[1\bar{1}l]$ for four different samples. The same, approximate layer structure factor is used for all four cases, and fitting is performed in the regime $l = 2.5-5.5$. Corresponding correlation parameters are given in table 1. Notice the shift of origin for the four samples (samples two to five from top to bottom).

4. Discussion

The values of β , γ , C_1 , C_2 and C_3 of table 1 show that the parameters vary considerably from sample to sample. Thus the coupling parameters of the Markovian chain are sensitive to the external growth conditions, such as temperature and concentration gradients, and other local parameters that may vary across the reaction beaker and during the time of growth. It is noteworthy, however, that β (and C_1) varies less than γ (and C_2) ($\beta \sim 0.09 \pm 0.04$). In other words, the guidance that a given layer obtains in its deposition process from the previously deposited one is less susceptible to disturbance

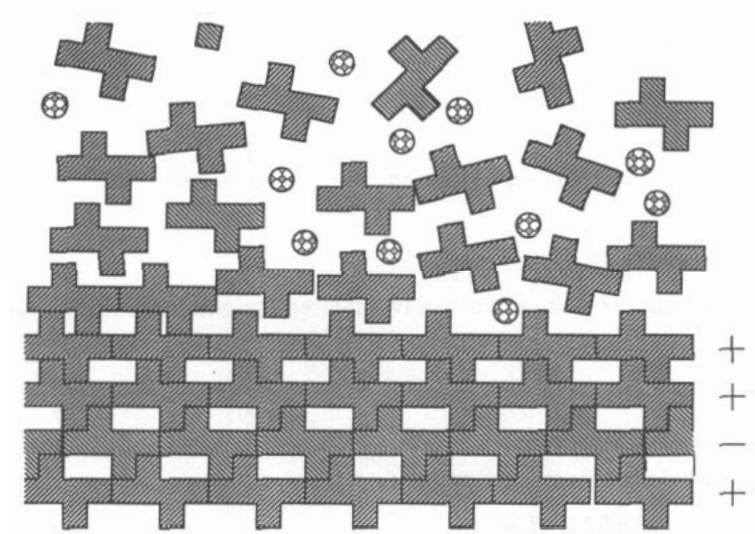


Figure 2. A schematic representation of the interface between solid and solution, indicating presolidification organization. The 'molecules' are given a shape to allow visualization of the alternative choice of layer orientation.

(by ion flow, convection etc.) than the corresponding one from the layer already one step further down. In our opinion this indicates that there is a transition region between the solid phase and the solution phase consisting of a few fairly well organised layers under formation (see a schematic picture in figure 2). It is within this transition region that the next-nearest-neighbour coupling must play its role, and where it is also most easily perturbed by the local flow conditions. The exact nature of this coupling is of course not known. The nearest-neighbour interaction is presumably of a short-range van der Waals type and, therefore, is influenced less by the local conditions of the solution phase. It would be interesting to study samples grown under strictly controlled, varied conditions to check the present conjecture. In our opinion it is striking that x-ray scattering studies on already-grown samples may be used to throw light on the growth mechanism.

Appendix

Welberry (1985) shows that for Markov chains the n th-neighbour correlation function C_n is in general expressible by the form

$$C_n = \sum_j c_j D_j^n \quad (\text{A1})$$

($-1 \leq D_j \leq 1$). For the case of only three parameters α , β and γ , one may show that $c_j = D_j = 0$ for $j > 2$, and that

$$D_{1,2} = \frac{1}{2}(\beta \pm \sqrt{K}) \quad (\text{A2})$$

$$K = \beta^2 + 4\gamma. \quad (\text{A3})$$

This solution implies that

$$\beta = D_1 + D_2 \quad (\text{A4})$$

$$\gamma = -D_1 D_2 \quad (\text{A5})$$

$$c_{1,2} = [1/(1 - \gamma)] [1 - 2\gamma(1 + \gamma)/(K \pm \beta\sqrt{K})] \quad (\text{A6})$$

and

$$c_1 + c_2 = 1. \quad (\text{A7})$$

One may, furthermore, show that the two nearest-neighbour correlations are

$$C_1 = \beta/(1 - \gamma) \quad (\text{A8})$$

$$C_2 = \beta^2/(1 - \gamma) + \gamma. \quad (\text{A9})$$

We notice that the parameter α does not enter these expressions. This parameter is determined by the average fraction m of + layers,

$$\alpha = m/(1 - \beta - \gamma). \quad (\text{A10})$$

For a disordered stacking sequence $m = 0.5$. (For a fully ordered case, $m = 1$ and a third solution $D = 1$ applies.)

In the preceding paper (Tjøtta *et al* 1990) we showed that the intensities of x-rays or neutrons scattered by the system are proportional to the Fourier transform of the correlation function C_n , giving for our case

$$I(Q) = c_1 (1 - D_1^2)/[1 + D_1^2 - 2D_1 \cos(Q \cdot c)] + c_2 (1 - D_2^2)/[1 + D_2^2 - 2D_2 \cos(Q \cdot c)] \quad (\text{A11})$$

with Q the scattering vector and c the growth direction repetition vector. The intensity is continuous in the growth direction index l ($Q \cdot c = 2\pi l$), with maxima and minima when l is an integer or half-integer for cases of real $D_{1,2}$. (Complex $D_{1,2}$ may be shown to give rise to 'satellite peaks'.)

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