Scattering of X-Rays by Parallel and Antiparallel Layers in Disordered Stacking and Statistical Layer Shift for α-Chitin

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Statistical Layer Shift, α-Chitin

The intensities scattered by antiparallel/parallel layers were calculated. Difference synthesis maps allowing for statistical layer shifts were computed for α-chitin. The results support the view that there may be antiparallel sequence with each layer displaced at random by +e or −e from a halving position in the x-direction. This is supported by greater breadth of certain reflection of the type 1kl compared to 0kl on the X-ray diffraction photograph. This gives strong evidence for some imperfection in the x-direction and the proposed indeterminacy ±e is one possible way in which this might arise.

Introduction

In the Carlstrom model[1] α-chitin may be thought of as a stack of parallel-chain sheets and arranged alternately parallel and antiparallel. The chains in the second layer were placed at $a/2$ with respect to in the first layer the interlayer spacing being $c/2$. The chain direction was taken parallel to oy and the sheets to be formed parallel to the plane xoy. The sheet structure is shown schematically in Fig. 1. Mering[2] calculated the diffraction from stacked layers taking account of the number of layers per stack. The result is a more general formula than that obtained by Hendricks *et al.*[3] for random stacks of an infinite number of layers. Mering[2] did not, however, include parallel/antiparallel layers amongst his examples.

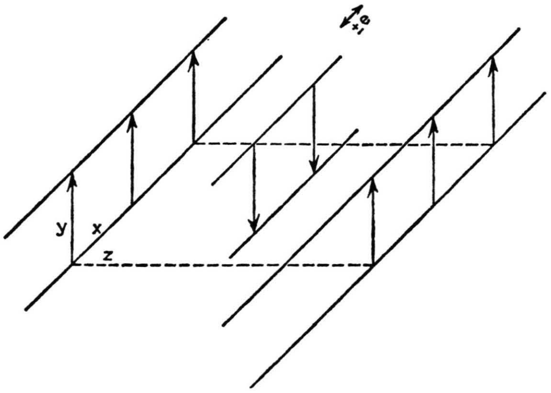

Fig. 1. The sheet structure of α-chitin.

The present work describes:

i) Calculation of intensity scattered by antiparallel layers/parallel layers.

ii) Computation of difference synthesis maps allowing for statistical layer shifts for α-chitin structure[4–6].

Calculation of Intensity Scattered by Antiparallel Layers / Parallel Layers

Parker (unpublished) considered the case of parallel and antiparallel layers. On purely theoretical grounds he thought that $a/2$ ($a = 4.76$ Å) was not necessary for the displacement of layers with respect to their first neighbour. He predicted that there could be two positions of the chains of equal energy. The potential energy when plotted as a function of intersheet displacement parallel to ox possess a symmetric character as shown in Fig. 2. Any of the potential energy curves A, B or in the Fig. 2 might occur, but that with two minimum is the possibility which interests us here. The relative position of the layers in the y-direction is exactly the same as in the R/c model[5], but in the x-direction each layer could be displaced from the preceeding one by $(a/2+e)$ Å or $(a/2-e)$ Å from the exact position in the R/c model. The total displacement after N layers is of the random walk type with N equal steps of $\pm e$.

Let the crystal consists of 2M layers or M repeats in the c direction. There are M up and M down layers as shown in Fig. 3. All the layers possess a unique glide plane parallel to their large dimension (xoy plane) and these are supposed to be spaced

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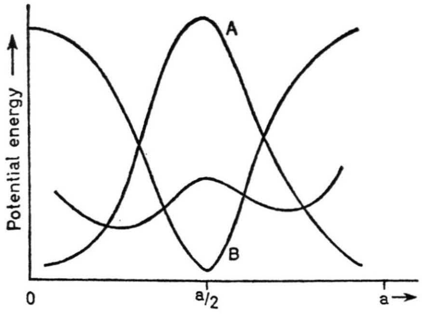

Fig. 2. Plot of potential energy as a function of intersheet displacement parallel to ox.

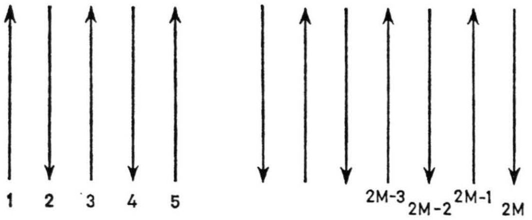

Fig. 3. Crystal consisting of M repeats in c direction. There are M up and M down layers and are supposed to be spaced precisely $c/2$ apart.

precisely $c/2$ apart. It is required to calculate the intensity scattered by all these layers.

The total intensity (I) can be calculated by adding

i) intensity for up-up layers;
ii) intensity for down-down layers;
iii) intensity for down-up layers;
iv) intensity for up-down layers.

$$I = \big((1-U^4)/(1+U^4-2U^2\cos 2\mu)\big)\,(\Phi_u\Phi_u^* + \Phi_d\Phi_d^*) + \big(2U(1-U^2)/(1+U^4-2U^2\cos 2\mu)\big)\,(\Phi_u\Phi_d^* + \Phi_u^*\Phi_d)$$

for M very large[3]

$$U e^{i\mu} = \sum_i p_i \exp 2\pi s\cdot r_i,$$

where

Φ_u = scattering factor of up layer;
Φ_d = scattering factor of down layer;
Φ_u^* = conjugate of Φ_u;
Φ_d^* = conjugate of Φ_d;

$s = (k-k_0)/\lambda$; k, k_0 are the unit vectors parallel to incident and scattered x-rays;

r_i = any one displacement vector between adjacent layers;

p_i = the probability of occurence of vector r_i.

In our case:

$$\begin{aligned} U e^{i\mu} &= \tfrac{1}{2}\exp i2\pi\,(h a^* + k b^* + \xi)\cdot(c/2+\varepsilon) \\ &\quad + \tfrac{1}{2}\exp i2\pi\,(h a^* + k b^* + \xi)\cdot(c/2-\varepsilon) \\ &= \tfrac{1}{2}\exp i2\pi\,(\xi\cdot c/2 + h a^*\cdot\varepsilon) + \tfrac{1}{2}\exp i2\pi\,(\xi\cdot c/2 - h a^*\cdot\varepsilon) \\ &= \tfrac{1}{2}\exp i2\pi\,\xi\cdot c/2\,\big(\exp i2\pi h e + \exp i2\pi h(-e)\big), \end{aligned}$$

where $a^*\cdot\varepsilon = \; = e$

$$= \exp i2\pi\,\xi\cdot c/2 \quad \cos 2\pi h e.$$

$$\therefore\; U = \cos 2\pi h e;$$
$$\mu = 2\pi\,\xi\cdot c/2;$$
ξ = normal to the plane.

The results are difficult to include in the structure determination for the following reasons:

The integrated intensities can not be measured directly from the x-ray diffraction photographs. The presence of a continuous background limits accurate determination of the intensities. The presence of background does not allow location of the base line of a reflection from microdensitometer curve. The effect of the randomness is contained in the quantity U^2. If $U \approx 1$ then the normal reflection curve is obtained (case A, Fig. 4). If however $U \ll 1$ then a flattened curve B is obtained. It turns out that the integrated areas of A and B differ only by a small, possibly negligible amount, but that a very considerable part of the area B is contained under the remote tails of the curve. When we apply the usual base-line correction to the densitometer traces of the reflection of type B the consequence must be to underestimate the area. Unfortunately it is hard to see how to allow for this effect with the x-ray photographs of α-chitin[5] where considerable overlapping occur. As a first approximation a correction factor for the peak height of the type $\cot^2(2\pi h e)$[3] could be applied to the calculated intensities, but this cor-

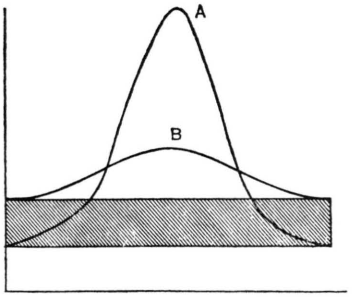

Fig. 4. A = normal curve ($U \approx 1$); B = Flattened curve ($U \ll 1$). (The effect of randomness is contained in the quantity U.)

rection was thought to be too drastic. Therefore another approximate correction factor of $\cos(2\pi h e)$ was applied to the calculated structure factors.

Computation of $\Delta\varrho_{X_0 Z_0}$ values[5] of 010 projection

The general expression for the calculations $\Delta\varrho_{X_0 Z_0}$ values[5] is given elsewhere. The method has been used by others for the refinement of single crystals for the location of atomic position in the unit cell and for the calculations of anisotropic temperature factors. The low resolution data from fibres do not permit the direct locating of individual atoms or the correction for the temperature factors[7]. It can permit one to gain only general idea about the position of the molecule in the unit cell. The most important reflections for use in difference synthesis are those for which observed structure factors are very small and calculated structure factors are very large. In this case the sign of calculated structure factors ($F c$) can be taken to calculate ($F o - F c$). It is difficult to decide upon the sign of those reflections for which observed structure factors ($F o$) are very small. The $\Delta\varrho_{X_0 Z_0}$ values were computed for the 010 projection. The calculated structure factors were adjusted to the shifted unit cell by multiplication by $\exp 2\pi i l/4$[5]. The calculated structure factors were then multiplied by the correction factor $\cos(2\pi h e)$ to allow for the statistical shift factor.

Results and Discussion

The $\Delta\varrho_{X_0 Z_0}$ values[5] were calculated at an interval of 1/10 in the X-axis direction and at an interval of 1/40 in the Z-axis direction. Contours in the map were drawn at an equal intervals. The α-chitin residue was plotted after translating in the Z-axis direction by $-1/4$. The maps were plotted for the correction factors $2\pi e = 0°, 54°, 57°, 60°, 63°$ and $72°$. These calculations indicated that the overall improvement for the projection may be at $2\pi e = 60°$. These calculations support the view that there may be antiparallel layer sequence with each layer displaced at random by $+e$ or $-e$ from a halving position in the x-direction. The $\Delta\varrho_{X_0 Z_0}$ maps obtained by using a correction factor of $\cos(2\pi h e)$ may improve the agreement between observed and calculated values. A value of $2\pi e = 60°$ was found to give best improvement. The x-ray diffraction photograph[5] shows that the 006 reflection is sharp as compared to the 104 reflection. It is seen that the width of the series of the reflections 101 increases from 101 to 104. The ratio of half widths of 104 and 006 given below:

h k l	ratio of half widths ($\nu_{1/2}\,104/\nu_{1/2}\,006$)
104	1.39
006	1.00

By extrapolation we might expect the 106 reflection to be still wider than 104. The 006 reflection is seen to be only about 0.7 the width of 104. Clearly the index $h = 1$ introduces a large amount of breadth into the reflection. This would be surprising if Carlstrom model[1] was exactly true. We might expect to find better crystal development in the a direction owing to the perfect H-bonding situation which can be present in which case index h would have a lesser broadening effect than index 1. The fact that the contrary is observed must be regarded as strong evidence for some imperfection in the a direction and the proposed indeterminacy $\pm e$ is one possible way in which this might arise. Model building shows that it is possible to form perfect H-bonding between $O_6 - H$ groups[5] of neighbouring layers if we do not insist on perfect $P2_12_12_1$ symmetry throughout. The $\pm e$ shifts are just what we expect if the development of H-bonding occurs. One feels that strong interlayer bonding of the kind mentioned above might well be present because of the very stable behaviour of α-chitin in the presence of water. X-rays, infrared and physical properties indicate little interaction with water contrasting markedly with the behaviour of β-chitin[8–10] which possesses the same layer structure.

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