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An Analysis of Disordered Structures of *o*-Chlorobenzamide

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Crystals of the γ and δ forms of *o*-chlorobenzamide give diffraction patterns composed of sharp spots and continuous streaks along the row lines parallel to **a*** indicating one-dimensional disorder. These structures were solved on the basis of sharp spots from the 'averaged structure' and diffuse scattering due to the disorder; the stacking mode of layers is represented in terms of probabilities of finding a particular layer after the preceding one. Observed intensities were explained in terms of a random stacking of four types of double-layer units for the γ form and in terms of a random stacking of 16 types of four-layer units for the δ form. It was shown that the δ form has a tendency to degenerate into a superlattice having the sequence of one type of four-layer unit, while the γ form has a tendency to degenerate into two polymorphs having the repeat units corresponding to those of the α and β forms of *o*-chlorobenzamide.

Introduction

Diffracted intensities from a one-dimensionally disordered structure consist of Bragg reflexions from the 'averaged structure' and diffuse intensities which depend on the degree of disorder. Takaki & Sakurai (1975) derived an intensity formula for layer structures when the period of the 'averaged structure' is p times the thickness of one layer and each layer is either of two layers having different structure factors. The stacking mode of layers is represented in terms of the probabilities of finding a particular layer after the preceding one. The present paper deals with an application of this theory to disordered structures found in the γ and δ forms of *o*-chlorobenzamide.

In a previous paper (Kato, Takaki & Sakurai, 1974), it was reported that *o*-chlorobenzamide crystallizes in two polymorphic forms α and β, and in two disordered forms γ and δ. Detailed analyses of the α and β forms showed that they have both layer structures with almost the same cell dimensions, but differ from each other in the stacking mode of layers. In the α form, one layer, say A_1, is transferred to the next layer A_2 by centres of symmetry and this layer is further transferred to the third layer by the same symmetry operation, so that the stacking sequence $A_1A_2A_1A_2\ldots$ is formed. In the β form the stacking sequence is given by $A_1B_2A_1B_2\ldots$, in which the symmetry element relating successive layers is 2_1 parallel to **c**. As has already been pointed out, the results of these analyses suggest a possibility for some types of structural disorder to occur. This suggests, in turn, the fact that the disordered structures of *o*-chlorobenzamide might be explained in terms of the stacking disorder of four layer units, A_1, B_1, A_2 and B_2, where B_1 and B_2 are the mirror images of A_1 and A_2 across the (001) plane, respectively; the equivalent positions for them are as follows:

$$\begin{array}{lll} A_1: & x,y,z; & \bar{x},\tfrac{1}{2}+y,\bar{z}; \\ A_2: & x,\tfrac{1}{2}-y,\tfrac{1}{2}+z; & \bar{x},\bar{y},\tfrac{1}{2}-z; \\ B_1: & x,y,\bar{z}; & \bar{x},\tfrac{1}{2}+y,z; \\ B_2: & x,\tfrac{1}{2}-y,\tfrac{1}{2}-z; & \bar{x},\bar{y},\tfrac{1}{2}+z; \end{array}$$

where the fractional coordinate x is referred to the thickness of one layer, and x,y,z are the mean values of the corresponding values of the α and β forms.

Experimental

Crystals of the γ and δ forms were obtained accidentally from an aqueous solution. The crystal data of the two forms have already been given in the previous paper. Intensities were collected from zero-layer Weissenberg photographs about **b**, which are shown in Fig. 1.

Characteristics of the sharp spots and diffuse scattering from the two forms are as follows:

Sharp spots

(*a*) In the $h0l$ diffraction pattern of the γ form, the distribution of sharp spots indicates that the length a is almost equal to that of the α (or β) form.

(*b*) The $h0l$ diffraction pattern of the δ form contains extra spots showing the length a to be twice that of the γ form.

(*c*) Intensities of $h0l$ and $h0\bar{l}$ of the δ form are almost the same.

Diffuse scattering

(*a*) On the ($h0l$) photographs of the γ and δ forms, strong diffuse streaks appear along the lattice rows parallel to **a***.

(*b*) In the $0kl$ diffraction pattern of the γ form, diffuse streaks parallel to **a*** are associated with sharp spots with k odd.

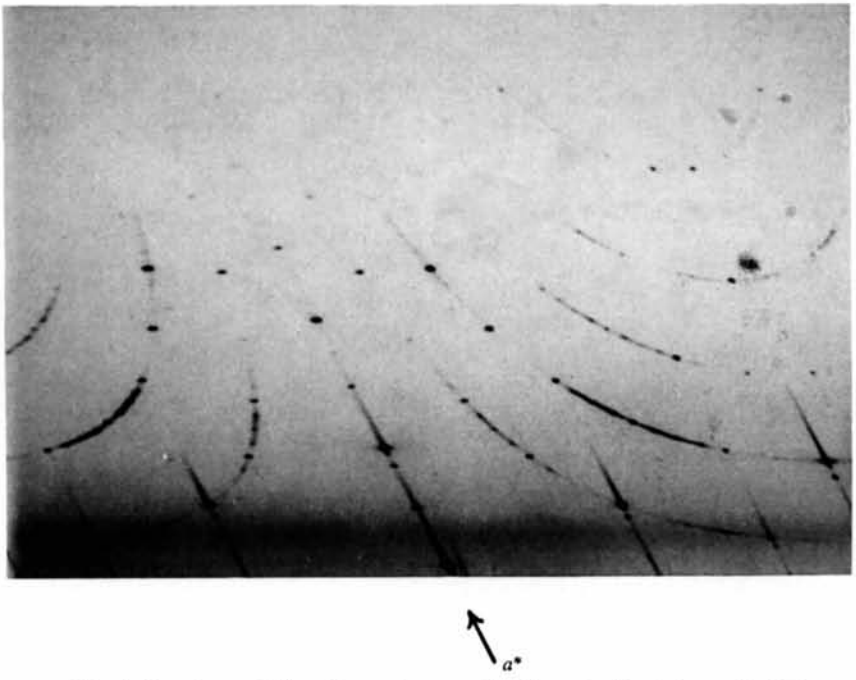

Fig. 1. Zero-layer Weissenberg photographs about **b**. (*a*) γ Form. (*b*) δ Form.

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Closer inspection of Fig. 1(*a*) (γ form) revealed that the sharp spots from the almost ordered domain with a structure very close to that of the α form are associated with the spots with $h+l$ even. Therefore great care was employed in the intensity estimation. On the other hand, the crystal of the δ form [Fig. 1(*b*)] contains small amounts of extra domains with two types of disorder; one is rather close to that of the γ form and the other is close to that of the δ form. However, no correction was made for the diffraction effects due to these small domains.

Observed intensities were estimated visually. The intensities of sharp spots were corrected by the usual method. The diffuse intensities were corrected for the polarization factor and for the geometrical factor given in Appendix II.

The scaling of the observed intensities (sharp spots) was done with the help of the $h00$ and $00l$ reflexions which are not affected by disordering, as will be seen later.

Disordered structure of the γ form

(1) *Bragg reflexions from the 'averaged structure'*

The arrangement of layers in the disordered structure of *o*-chlorobenzamide may be as follows: Assume the ith layer is A_1, then the $(i+1)$th layer is either A_2 or B_2, and the $(i+2)$th layer either A_1 or B_1, and so on.

As to the γ form [Fig. 1(*a*)], if the sharp spots are regarded as the Bragg reflexions from the averaged structure, its period along **a** should be twice the thickness of one layer. A model of the averaged structure of the γ form may then be given schematically as follows:

$$\begin{bmatrix} w_1 A_1 \\ w_2 B_1 \end{bmatrix} \quad \begin{bmatrix} w_1' A_2 \\ w_2' B_2 \end{bmatrix} \qquad ((a))$$

where w_1, w_2 are the probabilities of finding A_1, B_1 at the first layer, respectively, and w_1', w_2' are those of finding A_2, B_2 at the second layer, respectively. Therefore $w_1+w_2=1$ and $w_1'+w_2'=1$.

Taking the coordinates $(\xi 0 l)$ in reciprocal space such that the a axial length is the thickness of one layer, the structure factor for a $\xi 0 l$ reflexion from the averaged structure is given by

$$\bar{F}_a = F_{a1} + F_{a2} \exp(2\pi i \xi) \qquad (1)$$

with $F_{a1} = w_1 A_1 + w_2 B_1$ and $F_{a2} = w_1' A_2 + w_2' B_2$, where A_1, B_1, A_2, B_2 are the structure factors for the corresponding layer units.

By taking account of the equivalent positions given in the *Introduction*, the structure factors for the four layer units are given by

$$\left.\begin{aligned} A_1 &= 2N_2N_3 \sum f_j \cos 2\pi(\xi x_j + l z_j) \\ B_1 &= 2N_2N_3 \sum f_j \cos 2\pi(\xi x_j - l z_j) \\ A_2 &= (-1)^l A_1 \quad \text{and} \quad B_2 = (-1)^l B_1 \end{aligned}\right\} \qquad (2)$$

where N_2 and N_3 are the numbers of unit cells along **b** and **c**, respectively, and the atomic scattering factor f_j (with an isotropic temperature factor) is the mean value of those of the α and β forms.

The structure factors at the reciprocal lattice points are given as follows:

For $\xi = n$ (n integer) and l even, or $\xi = n+\frac{1}{2}$ and l odd,

$$F_a = (w_1 + w_1')(A_1 - B_1) + 2B_1 . \qquad (3)$$

For $\xi = n$ and l odd, or $\xi = n+\frac{1}{2}$ and l even,

$$F_a = (w_1 - w_1')(A_1 - B_1) . \qquad (4)$$

The values of w_1 and w_1' can be determined by comparing observed and calculated structure factors, but it was found that the agreement for the reflexions with $2\xi + l$ even was not so good as that for the reflexions with $2\xi + l$ odd. After some trials it became conceivable that the crystal might have a twinned structure composed of the structure ((a)) and its enantiomorph across (001) forming separate domains. The model of this enantiomorphic structure [structure ((b))] is represented by

$$\begin{bmatrix} w_1 B_1 \\ w_2 A_1 \end{bmatrix} \quad \begin{bmatrix} w_1' B_2 \\ w_2' A_2 \end{bmatrix} . \qquad ((b))$$

The structure factors for this model are given by

$$F_b = F_{b1} + F_{b2} \exp(2\pi i \xi) \qquad (5)$$

where $F_{b1} = w_2 A_1 + w_1 B_1$ and $F_{b2} = w_2' A_2 + w_1' B_2$.

The diffracted intensities from the composite structure are then given by

$$|\bar{F}|^2 = W|F_a|^2 + (1-W)|F_b|^2 \qquad (6)$$

Table 1. *Observed and calculated reflexion amplitudes* ($\times 5$) *for the γ and δ forms*

The indices h refer to the double-layer unit along **a** for the γ form and the four-layer unit for the δ form.

h	Fo	Fc	h	Fo	Fc	h	Fo	Fc	h	Fo	Fc	h	Fo	Fc	h	Fo	Fc	h	Fo	Fc
	γ Form		6	96	96	k,l=0,4			k,l=0,-6			31	12	12	6	170	134	20	50	64
			7	8	10	1	25	18	0	16	26	32	10	10	7	54	44	21	14	16
k,l=0,0			8	93	97	2	23	21	2	13	13	33	10	6	8	56	38	22	10	12
2	276	363	9	22	20	3	3	6	4	12	12	34	20	38	9	66	68	23	12	10
4	128	127	10	149	143	4	28	25	6	5	13	35	8	2	10	76	86	24	14	28
6	275	256	11	31	31	5	41	30							11	74	70	25	10	10
8	49	27	12	20	17	6	31	29					k,l=0,2		12	42	62	26	8	10
10	147	155	13	6	4	7	17	15		δ Form		0	532	506	13	50	48	27	8	12
12	62	59	14	11	11	8	17	5				1	16	14	14	62	58	28	8	16
14	31	33	15	6	6	9	7	11	k,l=0,0			2	20	16	15	14	18	29	6	12
16	10	20	16	18	30	10	29	40	4	518	706	3	16	4	16	16	6			
18	7	15				11	7	8	8	274	234	4	80	78	17	14	2	k,l=0,5		
			k,l=0,-2			12	9	19	12	520	512	5	66	58	18	50	36	1	10	6
k,l=0,1			0	250	253	13	8	7	16	92	54	6	60	92	19	14	2	2	106	90
1	105	118	2	32	30				20	308	310	7	106	118	20	12	4	3	14	12
2	21	22	4	116	105	k,l=0,-4			24	118	118	8	138	130	21	14	10	4	14	10
3	204	229	6	61	53	0	81	66	28	60	66	9	112	122	22	38	44	5	14	2
4	14	14	8	125	106	2	35	41				10	74	104	23	22	20	6	62	46
5	38	36	10	202	187	4	48	45	k,l=0,1			11	90	80	24	14	20	7	14	16
6	38	40	12	35	33	6	30	38	1	16	24	12	132	142	25	14	16	8	16	24
7	39	33	14	18	17	8	15	3	2	214	200	13	22	30	26	28	26	9	34	30
8	18	16	16	21	26	10	25	25	3	38	42	14	10	16	27	12	0	10	36	32
9	26	22				12	10	11	4	30	34	15	22	8	28	10	8	11	32	30
10	8	4	k,l=0,3			14	9	7	5	12	22	16	188	204	29	10	16	12	16	26
11	77	80	1	32	17				6	428	446	17	26	20	30	26	24	13	22	20
12	6	1	2	7	7	k,l=0,5			7	16	14	18	26	32	31	8	20	14	64	62
13	37	36	3	86	80	1	57	50	8	14	22	19	48	42	32	6	18	15	12	8
14	9	6	4	33	37	2	0	6	9	40	34	20	306	328				16	10	4
15	8	9	5	58	71	3	28	26	10	106	98	21	54	52	k,l=0,4					
16	6	6	6	38	40	4	14	15	11	54	58	22	36	48	0	178	132	k,l=0,6		
17	11	21	7	26	22	5	16	23	12	44	62	23	40	40	1	30	16	0	32	52
			8	6	3	6	15	17	13	64	60	24	44	42	2	26	28	1	10	4
k,l=0,-1			9	6	2	7	29	26	14	102	90	25	14	16	3	46	34	2	10	8
1	96	84	10	6	2	8	9	2	15	40	38	26	12	6	4	42	54	3	10	12
3	212	216	11	24	30				16	24	24	27	14	2	5	20	24	4	24	36
5	81	71	12	10	13	k,l=0,-5			17	18	12	28	30	28	6	12	10	5	14	16
7	75	67	13	12	10	1	49	41	18	50	44	29	12	10	7	14	8	6	14	16
9	28	23	14	5	5	3	30	20	19	12	4	30	10	10	8	68	68	7	14	14
11	79	77	15	9	12	5	40	24	20	10	6	31	12	8	9	48	38	8	24	32
13	37	35				7	37	38	21	14	6	32	40	56	10	40	46	9	16	10
15	14	9	k,l=0,-3			9	7	7	22	136	158	33	8	2	11	30	24	10	12	8
17	9	18	1	32	15				23	14	0	34	6	2	12	56	46	11	12	6
			3	66	55	k,l=0,6			24	12	2				13	28	34	12	8	28
k,l=0,2			5	61	44	1	6	6	25	14	2	k,l=0,3			14	18	22	13	6	0
1	19	11	7	45	43	2	15	25	26	64	70	1	10	2	15	14	10			
2	44	29	9	22	21	3	13	10	27	14	6	2	70	32	16	32	8			
3	60	60	11	17	16	4	16	22	28	12	8	3	12	6	17	14	12			
4	82	88	13	18	18	5	9	5	29	14	12	4	14	10	18	12	16			
5	73	68	15	21	20	6	9	15	30	16	12	5	28	18	19	14	18			

where W is the fraction of domains having the structure ((a)). Equation (6) gave a satisfactory agreement between observed and calculated intensities with the values $W=0{\cdot}8$, $w_1=0{\cdot}938$ and $w_1'=0{\cdot}531$. The conventional R index ($R=\sum||F_o|-|F_c||/\sum|F_o|$) was 0·14 for the $\xi 0l$ reflexions. Observed and calculated reflexion amplitudes are listed in Table 1.

(2) *Diffuse scattering*

According to Takaki & Sakurai (1975), the stacking mode of layers can be represented in terms of the probabilities α_{11}, α_{12}, etc., where α_{11} is the probability of finding A_1 after A_2 and α_{12} is that of finding B_1 after A_2, *etc.* This is shown in Table 2 as a probability matrix **P**.

Table 2. *Stacking mode in the γ form [structure* ((a))]

$$\begin{array}{cc|cccc} w & & A_1 & B_1 & A_2 & B_2 \\ w_1 & A_1 & & & \beta_{11} & \beta_{12} \\ w_2 & B_1 & & & \beta_{21} & \beta_{22} \\ w_1' & A_2 & \alpha_{11} & \alpha_{12} & & \\ w_2' & B_2 & \alpha_{21} & \alpha_{22} & & \end{array} \equiv \mathbf{P}$$

Introducing a matrix,

$$\mathbf{H}=\tfrac{1}{2}\begin{pmatrix} w_1 & w_2 & w_1' & w_2' \\ | & | & | & | \\ w_1 & w_2 & w_1' & w_2' \end{pmatrix}$$

we obtain the relation (Kakinoki & Komura, 1965):

$$\mathbf{HP}=\mathbf{PH}=\mathbf{H}\,.$$

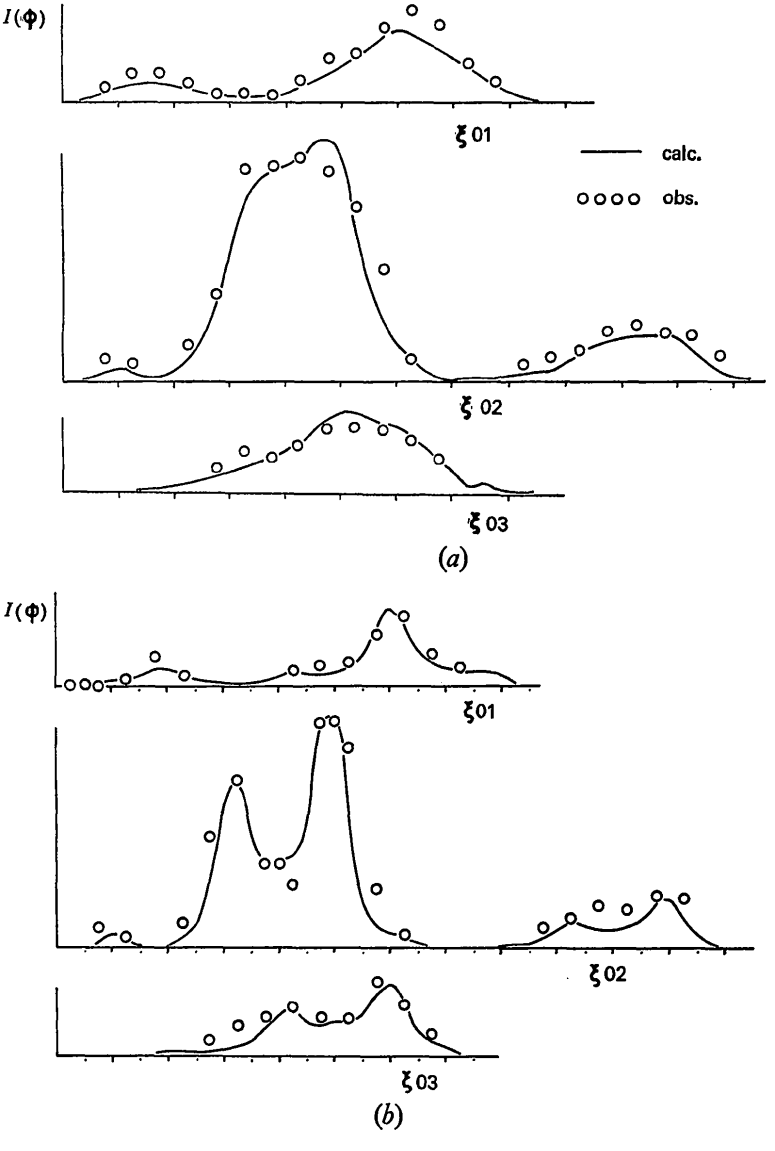

Fig. 2. Comparison of observed (circles) and calculated (full lines) diffuse intensities. (*a*) γ Form. (*b*) δ Form.

It can be shown that only two parameters, say α_{11} and β_{11}, are independent.

Substituting the parameters in Table 2 into the general intensity formula given by Takaki & Sakurai (1975) and remembering that $A_2=(-1)^l A_1$ and $B_2=(-1)^l B_1$, we obtain the intensity formula for the structure ((a)):

$$I_D(\varphi)=ND(\varphi)[R_o+2(1+X)^{-1}R_1\cos\varphi] \qquad (7)$$

where $\varphi=2\pi\xi$,
$X=(\alpha_{11}-\alpha_{21})(\beta_{11}-\beta_{21})$
$D(\varphi)=(1-X^2)/(1+X^2-2X\cos 2\varphi)$
$R_o=\frac{1}{2}(A_1-B_1)^2(w_1w_2+w_1'w_2')$
$R_1=\frac{1}{2}(-1)^l(A_1-B_1)^2$
$\times\{w_1w_2(\beta_{11}-\beta_{21})+w_1'w_2'(\alpha_{11}-\alpha_{21})\}$.

The intensity formula identical with (7) can be derived for the structure ((b)), since formula (7) is invariant with respect to interchanging A_1 with B_1. Therefore, the diffuse intensities from the γ form can be represented by (7).

Equation (7) gave the best intensity agreement using the values $\alpha_{11}=0{\cdot}938$ and $\beta_{11}=0{\cdot}531$. Comparison of observed and calculated intensities is shown in Fig. 2(*a*). The values of *w*'s and the matrix **P** for the structure ((a)) are given as follows:

$$w_1=0{\cdot}938,\ w_2=0{\cdot}062,\ w_1'=0{\cdot}531,\ w_2'=0{\cdot}469 \qquad (8)$$

$$\mathbf{P}=\begin{pmatrix} & & 0{\cdot}531 & 0{\cdot}469 \\ & & 0{\cdot}531 & 0{\cdot}469 \\ 0{\cdot}938 & 0{\cdot}062 & & \\ 0{\cdot}938 & 0{\cdot}062 & & \end{pmatrix} \qquad (9)$$

Disordered structure of the δ form

(1) *Bragg reflexions from the 'averaged structure'*

If the sharp spots in Fig. 1(*b*) are regarded as Bragg reflexions from the 'averaged structure', the period along **a** should be four times the thickness of one layer. Thus, as in the case of the γ form, a model of the averaged structure may be given by the scheme

$$\begin{bmatrix} w_1\mathrm{A}_1 \\ w_2\mathrm{B}_1 \end{bmatrix}\ \begin{bmatrix} w_1'\mathrm{A}_2 \\ w_2'\mathrm{B}_2 \end{bmatrix}\ \begin{bmatrix} \tilde{w}_1\mathrm{A}_1 \\ \tilde{w}_2\mathrm{B}_1 \end{bmatrix}\ \begin{bmatrix} \tilde{w}_1'\mathrm{A}_2 \\ \tilde{w}_2'\mathrm{B}_2 \end{bmatrix} \qquad ((c))$$

where $w_1+w_2=w_1'+w_2'=\tilde{w}_1+\tilde{w}_2=\tilde{w}_1'+\tilde{w}_2'=1$. The structure factor for a $\xi 0 l$ reflexion can be given by

$$F_c=F_{c1}+F_{c2}\exp(2\pi i\xi)+F_{c3}\exp(4\pi i\xi)+F_{c4}\exp(6\pi i\xi) \qquad (10)$$

where $F_{c1}=w_1A_1+w_2B_1$, $F_{c2}=w_1'A_2+w_2'B_2$, $F_{c3}=\tilde{w}_1A_1+\tilde{w}_2B_1$ and $F_{c4}=\tilde{w}_1'A_2+\tilde{w}_2'B_2$.

Since the intensities of $h0l$ and $h0\bar{l}$ reflexions from the δ form are almost the same (see *Introduction*), it was assumed that the crystal has the structure ((c)) and its enantiomorph [structure ((d))] across (001) in equal proportions. The model of the structure ((d)) was obtained from ((c)) by interchanging A_1 with B_1, *etc.* The intensity of a $\xi 0 l$ reflexion may then be given by

$$|\bar{F}|^2=\tfrac{1}{2}(|F_c|^2+|F_d|^2) \qquad (11)$$

where F_d is the structure factor for the structure ((d)).

The intensities at the reciprocal lattice points are given as follows:

For $\xi=n$ and l even, or $\xi=n+\frac{1}{2}$ and l odd
$|\bar{F}|^2=8(A_1^2+B_1^2)-(A_1-B_1)^2$
$\times(w_1+w_1'+\tilde{w}_1+\tilde{w}_1')(w_2+w_2'+\tilde{w}_2+\tilde{w}_2')$
for $\xi=n$ and l odd, or $\xi=n+\frac{1}{2}$ and l even
$|\bar{F}|^2=(A_1-B_1)^2(w_1+\tilde{w}_1-w_1'-\tilde{w}_1')^2$
for $\xi=n+\frac{1}{4}$ or $\xi=n+\frac{3}{4}$
$|\bar{F}|^2=(A_1-B_1)^2\{(w_1-\tilde{w}_1)^2+(w_1'-\tilde{w}_1')^2\}$ (12)

where the relations, $A_2=(-1)^lA_1$ and $B_2=(-1)^lB_1$ given in (2), are used. As only three equations are available, the values of *w*'s cannot be determined uniquely. Therefore, we tentatively put

$$w_1=\tilde{w}_1. \qquad (13)$$

This presumption was supported by the analysis of the diffuse intensities as shown later.

Using the above equations a satisfactory agreement was obtained between the observed and calculated intensities with the values $w_1=0{\cdot}813$, $w_1'=0{\cdot}187$, $\tilde{w}_1=0{\cdot}813$ and $\tilde{w}_1'=0{\cdot}813$. The conventional *R* index defined in the preceding section was 0·18 for $\xi 0 l$ reflexions. Observed and calculated reflexion amplitudes are listed in Table 1.

(2) *Diffuse scattering*

Similarly to the case of the γ form, the stacking mode of layers in the δ form is represented as shown in Table 3, where four parameters, say α_{11}, β_{11}, γ_{11} and δ_{11}, are independent. The same procedure as used in the case of the γ form gives the intensity formula

$$I_D(\varphi)=ND(\varphi)\times[R_o+2(1-X^2)^{-1}\sum_{m=1}^{3}(R_m-XR_{4-m})\cos m\varphi] \qquad (14)$$

where $X=(\alpha_{11}-\alpha_{21})(\beta_{11}-\beta_{21})(\gamma_{11}-\gamma_{21})(\delta_{11}-\delta_{21})$
$D(\varphi)=(1-X^2)/(1+X^2-2X\cos 4\varphi)$
$R_o=\frac{1}{4}(A_1-B_1)^2(w_1w_2+w_1'w_2'+\tilde{w}_1\tilde{w}_2+\tilde{w}_1'\tilde{w}_2')$
$R_1=\frac{1}{4}(A_1-B_1)^2(-1)^l\{w_1w_2(\beta_{11}-\beta_{21})+w_1'w_2'(\gamma_{11}-\gamma_{21})+\tilde{w}_1\tilde{w}_2(\delta_{11}-\delta_{21})+\tilde{w}_1'\tilde{w}_2'(\alpha_{11}-\alpha_{21})\}$
$R_2=\frac{1}{4}(A_1-B_1)^2\{w_1w_2(\beta_{11}-\beta_{21})(\gamma_{11}-\gamma_{21})+w_1'w_2'(\gamma_{11}-\gamma_{21})(\delta_{11}-\delta_{21})+\tilde{w}_1\tilde{w}_2(\delta_{11}-\delta_{21})\times(\alpha_{11}-\alpha_{21})+\tilde{w}_1'\tilde{w}_2'(\alpha_{11}-\alpha_{21})(\beta_{11}-\beta_{21})\}$
$R_3=\frac{1}{4}(A_1-B_1)^2(-1)^l\{w_1w_2(\beta_{11}-\beta_{21})(\gamma_{11}-\gamma_{21})\times(\delta_{11}-\delta_{21})+w_1'w_2'(\gamma_{11}-\gamma_{21})(\delta_{11}-\delta_{21})(\alpha_{11}-\alpha_{21})+\tilde{w}_1\tilde{w}_2(\delta_{11}-\delta_{21})(\alpha_{11}-\alpha_{21})(\beta_{11}-\beta_{21})+\tilde{w}_1'\tilde{w}_2'(\alpha_{11}-\alpha_{21})(\beta_{11}-\beta_{21})(\gamma_{11}-\gamma_{21})\}$.

Using this formula a satisfactory agreement was obtained between observed and calculated diffuse intensities with the values $\alpha_{11}=0{\cdot}813$, $\beta_{11}=0{\cdot}075$, $\gamma_{11}=0{\cdot}325$ and $\delta_{11}=0{\cdot}813$, as shown in Fig. 2(*b*). The values of the remaining parameters of Table 3 are as follows; $w_2=\tilde{w}_2=\tilde{w}_2'=0{\cdot}187$, $w_2'=0{\cdot}813$; $\alpha_{21}=\delta_{21}=0{\cdot}813$, $\alpha_{12}=\alpha_{22}=\delta_{12}=\delta_{22}=0{\cdot}187$, $\beta_{21}=\gamma_{12}=0{\cdot}675$, $\beta_{12}=\gamma_{21}=0{\cdot}925$, $\beta_{22}=0{\cdot}325$ and $\gamma_{22}=0{\cdot}075$.

Table 3. *Stacking mode in the δ form [structure ((c))]*

w		A_1 B_1	A_2 B_2	A_1 B_1	A_2 B_2
w_1	A_1		β_{11} β_{12}		
w_2	B_1		β_{21} β_{22}		
w_1	A_2			γ_{11} γ_{12}	
w_2	B_2			γ_{21} γ_{22}	
w_1	A_1				δ_{11} δ_{12}
w_2	B_1				δ_{21} δ_{22}
w_1	A_2	α_{11} α_{12}			
w_2	B_2	α_{21} α_{22}			

To examine the validity of the assumption $w_1 = \tilde{w}_1$ given in (13), we attempted to calculate the intensities for several sets of parameters obtained under the condition $w_1 \neq \tilde{w}_1$. However, it was found that the set of the parameters given above gives the best agreement.

Discussion

As can be seen in Figs. 2(*a*) and 2(*b*), the agreement between observed and calculated diffuse intensities is satisfactory. A remarkable feature found in the δ form is that the averaged structure [hereafter the structure ((c)) is considered] can be explained in terms of only the two types of four-layer units $A_1B_2A_1A_2$ and $B_1A_2B_1B_2$ with the weights 0·813 and 0·187, respectively. In the γ form [the structure ((a)) is considered], on the other hand, the averaged structure can be explained in terms of three types of double-layer units, say A_1A_2, A_1B_2 and B_1A_2, with the weights 0·469, 0·469 and 0·062, respectively.

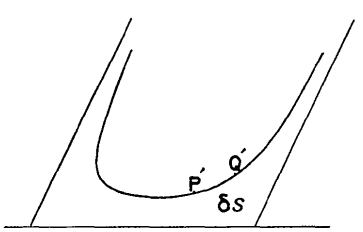

Fig. 3. The diagram of a Weissenberg photograph showing that the segment P′Q′ on the U-shaped curve corresponds to the segment PQ on the row line X′X″ in Fig. 4.

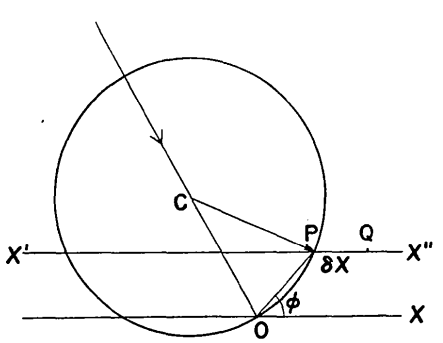

Fig. 4. The equatorial section of the reciprocal lattice.

The above results suggest that the multi-layer units play an important role in generating the disorder. To examine this we attempted to represent the disordered structures in terms of a stacking of double-layer units for the γ form and a stacking of four-layer units for the δ form. In the γ form the four types of double-layer units A_1A_2, A_1B_2, B_1A_2 and B_1B_2 were considered; the probabilities of finding these units in the crystal are 0·498, 0·440, 0·033 and 0·029, respectively (see Appendix I). The stacking mode of these units is shown in Table 4. The disordered structure of the γ form can be described in terms of a random stacking of the four double-layer units; the probability of finding a particular unit is independent of the preceding one (Appendix I).

Table 4. *Stacking mode of the double-layer units in the γ form [structure ((a))]*

W_j		A_1A_2	A_1B_2	B_1A_2	B_1B_2
W_1	A_1A_2	ϱ_{11}	ϱ_{12}	ϱ_{13}	ϱ_{14}
W_2	A_1B_2	ϱ_{21}	ϱ_{22}	ϱ_{23}	ϱ_{24}
W_3	B_1A_2	ϱ_{31}	ϱ_{32}	ϱ_{33}	ϱ_{34}
W_4	B_1B_2	ϱ_{41}	ϱ_{42}	ϱ_{43}	ϱ_{44}

In the same way the disordered structure of the δ form can be described in terms of a random stacking of the following units: They are $A_1B_2A_1A_2$, $A_1B_2A_1B_2$, $A_1B_2B_1A_2$, $A_1B_2B_1B_2$, $A_1A_2A_1A_2$, $A_1A_2A_1B_2$, $A_1A_2B_1A_2$, $A_1A_2B_1B_2$, $B_1B_2A_1A_2$, $B_1B_2A_1B_2$, $B_1B_2B_1A_2$, $B_1B_2B_1B_2$, $B_1A_2A_1A_2$, $B_1A_2A_1B_2$, $B_1A_2B_1A_2$ and $B_1A_2B_1B_2$ with the probabilities 0·566, 0·130, 0·046, 0·011, 0·016, 0·004, 0·033, 0·008, 0·046, 0·010, 0·004, 0·001, 0·033, 0·008, 0·069 and 0·016, respectively. Furthermore, if we assume the other combinations of the four-layer units $A_2A_1B_2A_1$, $A_2A_1B_2B_1$, *etc.*, the disordered structure can be described similarly in terms of a random stacking of 16 types of the four-layer units; the predominant stacking sequence is $A_2A_1B_2A_1$.

From the above results it may be concluded that the δ form has, as has been pointed out by Northolt & Alexander (1971), a tendency to degenerate into a superlattice with the sequence $A_1B_2A_1A_2$ (or $A_2A_1B_2A_1$), while the γ form has a tendency to degenerate into two polymorphs, of which the repeat units correspond to those of the α and β forms.

In another crystal sample of the γ form, the intensity distributions of sharp spots as well as diffuse scattering were found to be different, showing that the tendency to degenerate into the β form is stronger than that to degenerate into the α form.

Disorder phenomena similar to those of the δ form have been found in 1,8-diazacyclotetradecane-2,9-dione (Northolt & Alexander, 1971) and DL-norleucine (Mathieson, 1953); their disordered structures have both been explained in terms of the predominant stacking sequence of one type of four-layer unit determined from the analysis of sharp spots only.

APPENDIX I

The stacking mode of the double-layer units in the γ form

The stacking mode of the double-layer units A_1A_2, A_1B_2, B_1A_2 and B_1B_2 is shown in Table 4, where, for example, W_1 is the probability of finding A_1A_2 in the crystal and is given by $W_1=w_1\beta_{11}$, w_1 and β_{11} being given in Table 2; ϱ_{11}, for example, is the probability of finding A_1A_2 after A_1A_2 and is given by $\varrho_{11}=\alpha_{11}\beta_{11}$. The values of W_j and ϱ_{ij} are then obtained from (8) and (9): $W_1=0{\cdot}498$, $W_2=0{\cdot}440$, $W_3=0{\cdot}033$, $W_4=0{\cdot}029$; $\varrho_{11}=\varrho_{21}=\varrho_{31}=\varrho_{41}=0{\cdot}498$, $\varrho_{12}=\varrho_{22}=\varrho_{32}=\varrho_{42}=0{\cdot}440$, $\varrho_{13}=\varrho_{23}=\varrho_{33}=\varrho_{43}=0{\cdot}033$ and $\varrho_{14}=\varrho_{24}=\varrho_{34}=\varrho_{44}=0{\cdot}029$.

This model is equivalent to that shown in Table 2, because the intensity formula identical with (7) can be derived from this model.

APPENDIX II

Derivation of the geometrical factor

Zachariasen (1967) has given a general formula for the integrated intensity of the diffracted beam from a one-dimensionally disordered crystal when a convergent incident beam is used. This can be applicable to the case of the rotating crystal method. In our case (*b*-axis zero-layer Weissenberg method), if the total diffuse intensity $I_D(\xi 0l)$ associated with a given point ξ on a given diffuse rod X′X″ (Fig. 4) does not change appreciably over a segment PQ$(=\delta X)$ on the rod, the following formula can be obtained:

$$I(\xi 0l)=K\frac{\delta X}{\sin 2\theta}I_D(\xi 0l) \tag{15}$$

where K is a scale factor and $I(\xi 0l)$ is the integrated intensity recorded on a photographic film while the sphere of reflexion sweeps through the segment PQ.

If a segment P′Q′$(=\delta s)$ on the film shown in Fig. 3 corresponds to the segment PQ in the reciprocal space, the relation between δX and δs is given by

$$\delta X=\sin 2\theta\delta s/C\sqrt{\{\sin^2(\theta+\phi)+4\sin^2\theta\cos^2\phi\}} \tag{16}$$

where C is the camera constant and ϕ is the angle between OX and OP (Fig. 4).

In the actual intensity measurement, as the length δs is fixed, the formula (15) becomes

$$I(\xi 0l)=K'LI_D(\xi 0l) \tag{17}$$

where K' is a scale factor and

$$L=1/\sqrt{\{\sin^2(\theta+\phi)+4\sin^2\theta\cos^2\phi\}} \tag{18}$$

is the geometrical factor.

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