

Intensities of X-ray Scattering from a One-Dimensionally Disordered Crystal Having the Multilayer Averaged Structure

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A general formula for the intensity of X-ray scattering from a one-dimensionally disordered layer structure is given in matrix form when sharp spots and diffuse streaks are observed along the reciprocal lattice rows. The intensity formula with 'Reichweite'=1 is expressed in the form $I(\varphi) = I_L(\varphi) + I_D(\varphi)$, where the first term gives intensities of Bragg reflexions due to the 'averaged layer structure' whose period is p times the thickness of one layer, and the second those of diffuse scattering due to the disorder. A solution is given for a model in which each layer site of the p layers is occupied by either of two layers with different structure factors. It is shown that in this model no continuous peak shift occurs regardless of the degree of disorder. Solutions for the cases where each layer site is occupied by one of three or four layers with different structure factors are also given.

Introduction

On many photographs obtained from layer structures having one-dimensional disorder, one may often find continuous diffuse streaks along the lattice rows between spots of sharp reflexions. Examples are DL-norleucine (Mathieson, 1953), 1,8-diazacyclotetradecane-2,9-dione (Northolt & Alexander, 1971), *o*-chlorobenzamide (Kato, Takaki & Sakurai, 1974), sodium 2-oxocaprylate (Pant, 1964) and hexagonal $\text{CaAl}_2\text{SiO}_8$ (Takéuchi & Donnay, 1959).

With regard to the analysis of disordered crystals such as those mentioned above, a detailed treatment of intensities will be presented on the basis of the matrix method given by Kakinoki & Komura (1965) (hereinafter KK), when sharp spots can be regarded as Bragg reflexions due to the 'multilayer averaged structure'.

The intensity formula for X-ray scattering from a one-dimensionally disordered crystal with equal thickness of layers is given, in electrons, by Hendricks & Teller (1942) and KK as

$$I(\varphi) = NJ_0 + \sum_{m=1}^{N-1} (N-m)J_m \exp(-im\varphi) + \text{conj.} \quad (1)$$

with

$$J_m = \text{Tr } \mathbf{VWP}^m \quad \text{and} \quad J_0 = \text{Tr } \mathbf{VW} \quad (2)$$

where conj. means the complex conjugate of the foregoing term; N is the number of layers; $\varphi = 2\pi\xi$, ξ being the continuous variable in the reciprocal space related to the scattering vector by

$$(\mathbf{s} - \mathbf{s}_0)/\lambda = \xi \mathbf{a}^* + K\mathbf{b}^* + L\mathbf{c}^*,$$

where K, L are integers and $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ the reciprocal vectors, in which \mathbf{a}^* is referred to a corresponding to the thickness of one layer. The elements of the

matrices \mathbf{V} , \mathbf{W} and \mathbf{P} (order τ) are as follows:

$$(\mathbf{V})_{kl} = F_k^* F_l, \quad (\mathbf{W})_{kl} = w_l \delta_{kl} \quad \text{and} \quad (\mathbf{P})_{kl} = \alpha_{kl}$$

where δ_{kl} is Kronecker's delta; F_k is the structure factor of the layer F_k ($k=1, \dots, \tau$); w_l is the probability of finding the layer F_l in a certain layer position (existence probability of F_l); α_{kl} is the probability of finding the layer F_l after the layer F_k . Relations between w_l and α_{kl} are given by KK,

$$\mathbf{HP} = \mathbf{PH} = \mathbf{H} \quad (3)$$

where $(\mathbf{H})_{kl} = w_l$.

Intensity formula

Let us construct a model of the 'averaged layer structure' on the following assumptions: (i) The thickness of each layer is the same. (ii) The period of the averaged structure is p times the thickness of one layer. (iii) The j th site of the p layers is occupied by $F_l^{(j)}$ ($l=1, \dots, t$) with a probability $w_l^{(j)}$, where

$$\sum_{l=1}^t w_l^{(j)} = 1. \quad (4)$$

The model of the averaged structure may be given schematically as follows:

$$\begin{bmatrix} w_1^{(1)} F_1^{(1)} \\ \vdots \\ w_t^{(1)} F_t^{(1)} \end{bmatrix} \begin{bmatrix} w_1^{(2)} F_1^{(2)} \\ \vdots \\ w_t^{(2)} F_t^{(2)} \end{bmatrix} \cdots \begin{bmatrix} w_1^{(p)} F_1^{(p)} \\ \vdots \\ w_t^{(p)} F_t^{(p)} \end{bmatrix} \cdot$$

1st site 2nd site pth site

The structure factor for a ξKL reflexion from the averaged structure is then given by

$$\mathbf{F} = \sum_{j=1}^p \mathbf{F}^{(j)} \exp\{i(j-1)\varphi\} \quad (5a)$$

where

$$\bar{F}^{(j)} = \sum_{i=1}^t w_i^{(j)} F_i^{(j)} \quad (5b)$$

which denotes the averaged structure factor for the j th layer.

If $\alpha_{kl}^{(j)}$ is defined as the probability of finding $F_l^{(j)}$ after $F_k^{(j-1)}$, the matrices \mathbf{P} , \mathbf{W} and \mathbf{V} necessary for the calculation for the above model may be written as follows:

$$\mathbf{P} = \begin{bmatrix} & \mathbf{p}_2 & & & \\ & & \mathbf{p}_3 & & \\ & & & \ddots & \\ & & & & \mathbf{p}_p \\ \mathbf{p}_1 & & & & \end{bmatrix} \quad (6a)$$

with

$$\mathbf{p}_j = \begin{bmatrix} \alpha_{11}^{(j)} & \dots & \alpha_{1t}^{(j)} \\ \vdots & \ddots & \vdots \\ \alpha_{t1}^{(j)} & \dots & \alpha_{tt}^{(j)} \end{bmatrix} \equiv \begin{bmatrix} \alpha_{11} & \dots & \alpha_{1t} \\ \vdots & \ddots & \vdots \\ \alpha_{t1} & \dots & \alpha_{tt} \end{bmatrix}^{(j)\dagger} \quad (6b)$$

$$\mathbf{W} = \frac{1}{p} \begin{bmatrix} w_1 & & & \\ & \ddots & & \\ & & \ddots & \\ & & & w_p \end{bmatrix} \quad \text{with } w_j = \begin{bmatrix} w_1 \\ \vdots \\ w_t \end{bmatrix}^{(j)} \quad (7)$$

and

$$\mathbf{V} = \begin{bmatrix} v_{11} & \dots & v_{1p} \\ \vdots & \ddots & \vdots \\ v_{p1} & \dots & v_{pp} \end{bmatrix} \quad (8a)$$

with

$$v_{ij} = \begin{bmatrix} F_1^{*(i)} F_1^{(j)} & \dots & F_1^{*(i)} F_t^{(j)} \\ \vdots & \ddots & \vdots \\ F_t^{*(i)} F_1^{(j)} & \dots & F_t^{*(i)} F_t^{(j)} \end{bmatrix} \quad (8b)$$

As an example, the 'P-table' (see Kakinoki, 1967) for $p=3$ and $t=2$ is shown in Table 1.

† In this paper this type of representation is used for simplicity.

Table 1. The 'P-table' for $p=3$ and $t=2$

	$F_1^{(1)}$	$F_2^{(1)}$	$F_1^{(2)}$	$F_2^{(2)}$	$F_1^{(3)}$	$F_2^{(3)}$
$w_1^{(1)}$	$F_1^{(1)}$		$\alpha_{11}^{(2)}$	$\alpha_{12}^{(2)}$		
$w_2^{(1)}$	$F_2^{(1)}$		$\alpha_{21}^{(2)}$	$\alpha_{22}^{(2)}$		
$w_1^{(2)}$	$F_1^{(2)}$				$\alpha_{11}^{(3)}$	$\alpha_{12}^{(3)}$
$w_2^{(2)}$	$F_2^{(2)}$				$\alpha_{21}^{(3)}$	$\alpha_{22}^{(3)}$
$w_1^{(3)}$	$F_1^{(3)}$	$\alpha_{11}^{(1)}$	$\alpha_{12}^{(1)}$			
$w_2^{(3)}$	$F_2^{(3)}$	$\alpha_{21}^{(1)}$	$\alpha_{22}^{(1)}$			

Substituting the matrices \mathbf{P} , \mathbf{W} and \mathbf{V} given above into (1), we can obtain the intensity formula for our model. The next problem is to express this formula in terms of Laue and diffuse terms. Let us put

$$\alpha_{kl}^{(j)} = w_l^{(j)} + \beta_{kl}^{(j)} \quad (9)$$

then

$$\mathbf{p}_j = \mathbf{h}_j + \mathbf{r}_j \quad (10)$$

where

$$\mathbf{h}_j = \begin{bmatrix} w_1 & \dots & w_t \\ \vdots & \ddots & \vdots \\ w_1 & \dots & w_t \end{bmatrix}^{(j)} \quad \text{and} \quad \mathbf{r}_j = \begin{bmatrix} \beta_{11} & \dots & \beta_{1t} \\ \vdots & \ddots & \vdots \\ \beta_{t1} & \dots & \beta_{tt} \end{bmatrix}^{(j)} \quad (11)$$

The matrix \mathbf{P} is then written as

$$\mathbf{P} = \mathbf{K} + \mathbf{R} \quad (12)$$

where

$$\mathbf{K} = \begin{bmatrix} & \mathbf{h}_2 & & \\ & & \mathbf{h}_3 & \\ & & & \ddots \\ & & & & \mathbf{h}_p \\ \mathbf{h}_1 & & & & \end{bmatrix} \quad (13)$$

and

$$\mathbf{R} = \begin{bmatrix} & \mathbf{r}_2 & & \\ & & \mathbf{r}_3 & \\ & & & \ddots \\ & & & & \mathbf{r}_p \\ \mathbf{r}_1 & & & & \end{bmatrix} \quad (14)$$

Here, we give some important relations which are necessary for further development of our theory. From (4), (7) and (11) we have

$$\text{Tr } w_j = \text{Tr } \mathbf{h}_j = \text{Tr } \mathbf{W} = 1 \quad (15a)$$

and

$$\mathbf{h}_i \mathbf{h}_j = \mathbf{h}_j \quad (i=1, \dots, t). \quad (15b)$$

Using the relation $\mathbf{HP} = \mathbf{PH} = \mathbf{H}$, where

$$\mathbf{H} = \frac{1}{p} \begin{bmatrix} \mathbf{h}_1 & \dots & \mathbf{h}_p \\ \vdots & \ddots & \vdots \\ \mathbf{h}_1 & \dots & \mathbf{h}_p \end{bmatrix} \quad (16)$$

we have

$$\left. \begin{aligned} \mathbf{h}_j \mathbf{p}_{j+1} &= \mathbf{h}_{j+1} \\ \mathbf{p}_i \mathbf{h}_j &= \mathbf{h}_j \end{aligned} \right\} \quad (17)$$

Further, from (12), (13) and (14), we obtain the following relations:

$$\left. \begin{aligned} \mathbf{HK} = \mathbf{KH} = \mathbf{H} \\ \mathbf{HR} = \mathbf{RH} = \mathbf{0} \end{aligned} \right\} \quad (18)$$

from which we have

$$\left. \begin{aligned} \mathbf{h}_j \mathbf{r}_{j+1} = \mathbf{0} \\ \mathbf{r}_i \mathbf{h}_j = \mathbf{0} \end{aligned} \right\} \quad (19)$$

and hence

$$\mathbf{KR} = \mathbf{RK} = \mathbf{0} \quad (20)$$

which leads to the following result:

$$\mathbf{P}^m = \mathbf{K}^m + \mathbf{R}^m \quad (m \geq 1). \quad (21)$$

Hence

$$\mathbf{J}_m = \mathbf{K}_m + \mathbf{R}_m \quad (22a)$$

where

$$\mathbf{K}_m = \text{Tr } \mathbf{VW}\mathbf{K}^m \text{ and } \mathbf{R}_m = \text{Tr } \mathbf{VW}\mathbf{R}^m. \quad (22b)$$

These equations are rewritten as (Appendix I)

$$\mathbf{K}_m = \frac{1}{p} \sum_{j=1}^p \text{Tr } \mathbf{v}_{j+m, j} \mathbf{w}_j \mathbf{h}_{j+m} \quad (23)$$

and

$$\mathbf{R}_m = \frac{1}{p} \sum_{j=1}^p \text{Tr } \mathbf{v}_{j+m, j} \mathbf{w}_j \mathbf{r}_{j+1} \dots \mathbf{r}_{j+m} \quad (24)$$

where $\mathbf{v}_{s+p, j} = \mathbf{v}_{s, j}$, $\mathbf{h}_{j+p} = \mathbf{h}_j$ and $\mathbf{r}_{j+p} = \mathbf{r}_j$. Equation (23) is further reduced to

$$\mathbf{K}_m = \frac{1}{p} \sum_{j=1}^p \mathbf{F}^{*(j+m)} \mathbf{F}^{(j)} \quad (25)$$

where $\mathbf{F}^{(j)}$ is defined by (5b) and $\mathbf{F}^{(j+p)} = \mathbf{F}^{(j)}$.

Referring to (25), let us define

$$\mathbf{K}_0 = \frac{1}{p} \sum_{i=1}^p |\mathbf{F}^{(i)}|^2; \quad (26)$$

then

$$\begin{aligned} \mathbf{R}_0 &= \mathbf{J}_0 - \mathbf{K}_0 \\ &= \frac{1}{p} \sum_{j=1}^p \sum_{k < l}^{t-1} w_k^{(j)} w_l^{(j)} |\mathbf{F}_k^{(j)} - \mathbf{F}_l^{(j)}|^2. \end{aligned} \quad (27)$$

By the use of (22), (26) and (27) a general intensity formula may be given by

$$I(\varphi) = I_L(\varphi) + I_D(\varphi) \quad (28a)$$

where

$$I_L(\varphi) = N\mathbf{K}_0 + \sum_{m=1}^{N-1} (N-m)\mathbf{K}_m \exp(-im\varphi) + \text{conj.} \quad (28b)$$

and

$$I_D(\varphi) = N\mathbf{R}_0 + \sum_{m=1}^{N-1} (N-m)\mathbf{R}_m \exp(-im\varphi) + \text{conj.} \quad (28c)$$

In these formulae, as will be seen in the following sections, $I_L(\varphi)$ gives the intensity of Bragg reflexions from the averaged structure and $I_D(\varphi)$ gives the intensity of diffuse scattering.

Calculation of $I_L(\varphi)$

Putting $N=pM$ and $m=\lambda+pr$ ($0 \leq \lambda \leq p-1$) and substituting into (28b), we have

$$I_L(\varphi) = -NK_0 + \sum_{\lambda=0}^{p-1} K_\lambda \exp(-i\lambda\varphi) \sum_{r=0}^{M-1} (N-pr-\lambda) \times \exp(-ipr\varphi) + \text{conj.} \quad (29)$$

After the summation with respect to r we have (Appendix II)

$$I_L(\varphi) = G(\varphi) [pK_0 + \sum_{m=1}^{p-1} (p-m)K_m \times \exp(-im\varphi) + \text{conj.}] \quad (30)$$

where λ is replaced by m for convenience and

$$G(\varphi) = (\sin^2 N\varphi/2) / (\sin^2 p\varphi/2). \quad (31)$$

By comparing (30) with (1), it is seen that the formula in square brackets of (30) corresponds to the averaged intensity of scattering when the number of layers is p and the structure factor of the j th layer is $\mathbf{F}^{(j)}$ [see (25)].

Therefore, formula (30) can be rewritten in the form

$$I_L(\varphi) = \frac{1}{p} G(\varphi) \left[\sum_{r=0}^{p-1} \left| \sum_{j=1}^p \mathbf{F}^{(j+r)} \exp\{i(j-1)\varphi\} \right|^2 \right] \quad (32)$$

where $\mathbf{F}^{(j+p)} = \mathbf{F}^{(j)}$. At a reciprocal lattice point having a coordinate $\xi = H/p$ (H integer), (32) becomes

$$I_L(2\pi H/p) = p^{-2} N^2 \left| \sum_{j=1}^p \mathbf{F}^{(j)} \exp\{2\pi i H(j-1)/p\} \right|^2.$$

Hence, if N is sufficiently large, (32) may be replaced by

$$I_L(\varphi) = G(\varphi) |\bar{\mathbf{F}}|^2 \quad (33)$$

with

$$\bar{\mathbf{F}} = \sum_{j=1}^p \mathbf{F}^{(j)} \exp\{i(j-1)\varphi\}$$

which is identical with (5).

Consequently, it may be concluded that $I_L(\varphi)$ gives the intensity of Bragg reflexion from the averaged structure given in the preceding section.

Calculation of $I_D(\varphi)$ for $t=2$

The matrices \mathbf{v}_{ij} , \mathbf{w}_j , \mathbf{r}_j and \mathbf{p}_j for $t=2$ are as follows:

$$\begin{aligned} \mathbf{v}_{ij} &= \begin{bmatrix} F_1^{*(i)} F_1^{(j)} & F_1^{*(i)} F_2^{(j)} \\ F_2^{*(i)} F_1^{(j)} & F_2^{*(i)} F_2^{(j)} \end{bmatrix}, \quad \mathbf{w}_j = \begin{bmatrix} w_1 & 0 \\ 0 & w_2 \end{bmatrix}^{(j)} \\ \mathbf{r}_j &= \begin{bmatrix} \beta_{11} & \beta_{12} \\ \beta_{21} & \beta_{22} \end{bmatrix}^{(j)}, \quad \mathbf{p}_j = \begin{bmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{bmatrix}^{(j)}. \end{aligned}$$

Note that the parameters $\alpha_{ki}^{(j)}$ are restricted by the relation $\mathbf{HP} = \mathbf{PH} = \mathbf{H}$, so that p parameters, say $\alpha_{11}^{(j)}$ ($j=1, \dots, p$), are independent if the existence probabilities $w_1^{(j)}$ (and $w_2^{(j)}$) have been determined from the analysis of sharp reflexions.

The following intensity calculation was carried out on the assumption that N is sufficiently large and the value of R_m falls off rapidly with increasing m . Intensity formula (28c) may then be approximated by

$$I_D(\varphi) = NR_0 + N \sum_{m=1}^{N-1} R_m \exp(-im\varphi) + \text{conj.} \quad (34)$$

For $t=2$, R_m and R_0 given by (24) and (27), respectively, may further be reduced to

$$R_m = \frac{1}{p} \sum_{j=1}^p w_1^{(j)} w_2^{(j)} (F_1^* - F_2^*)^{(j+m)} (F_1 - F_2)^{(j)} \times \prod_{v=1}^m (\alpha_{11} - \alpha_{21})^{(j+v)} \quad (35a)$$

with

$$R_0 = \frac{1}{p} \sum_{j=1}^p w_1^{(j)} w_2^{(j)} |F_1^{(j)} - F_2^{(j)}|^2 \quad (35b)$$

by the use of the following relations:

$$\left. \begin{aligned} \mathbf{r}_j \mathbf{r}_i &= (\alpha_{11} - \alpha_{21})^{(i)} \mathbf{r}_j \\ \mathbf{w}_j \mathbf{r}_{j+1} &= w_1^{(j)} w_2^{(j)} (\alpha_{11} - \alpha_{21})^{(j+1)} \begin{bmatrix} 1 & -1 \\ -1 & 1 \end{bmatrix} \end{aligned} \right\} \quad (36)$$

which can be derived from (19) and (11).

Let us now put $N = pM$ and $m = \lambda + pr$ ($0 \leq \lambda \leq p-1$). Then (34) becomes

$$I_D(\varphi) = -NR_0 + N \sum_{\lambda=0}^{p-1} \exp(-i\lambda\varphi) \sum_{r=0}^{M-1} R_{\lambda+pr} \times \exp(-ipr\varphi) + \text{conj.} \quad (37)$$

From (35) the following relation may be obtained:

$$R_{\lambda+pr} = R_\lambda X^r$$

with

$$X = \prod_{v=1}^p (\alpha_{11} - \alpha_{21})^{(v)}. \quad (38)$$

Substituting into (37) and summing up with respect to r , we have the final result after neglecting X^M , giving

$$I_D(\varphi) = ND(\varphi) [R_0 + (1-X^2)^{-1} \sum_{m=1}^{p-1} (R_m - XR_m^*) \times \exp(-im\varphi) + \text{conj.}] \quad (39a)$$

where λ is replaced by m for convenience, and

$$D(\varphi) = (1-X^2)/(1+X^2-2X \cos p\varphi). \quad (39b)$$

For $p=1$, the following intensity formula should be used:

$$I_D(\varphi) = ND(\varphi) w_1 w_2 |F_1 - F_2|^2. \quad (39c)$$

Consequently, the intensity of diffuse scattering can be calculated from (35), (38) and (39) when the 'P-table' has been given.

It is noteworthy that, if the absolute value of X is not small compared with unity, the variation of the function in the square brackets of (39a) with respect to ξ is much slower than that of $D(\varphi)$, and the latter will be

the only factor which governs the positions of peak maxima. Thus, depending on whether X takes positive or negative values, the diffuse maxima occur at the positions $\xi = H/p$, where H is an integer, or $(2H+1)/2p$; *i.e.* there is no continuous peak shift regardless of the value of X .

In concluding this section, we show below the intensity formulae when $p=3$ and $t=2$ (see Table 1).

$$I_L(\varphi) = |\bar{F}|^2 (\sin^2 N\varphi/2) / (\sin^2 3\varphi/2)$$

where

$$\bar{F} = \sum_{j=1}^3 \bar{F}^{(j)} \exp\{i(j-1)\varphi\}$$

with

$$\bar{F}^{(j)} = w_1^{(j)} F_1^{(j)} + w_2^{(j)} F_2^{(j)}.$$

$$I_D(\varphi) = ND(\varphi) [R_0 + (1-X^2)^{-1} \sum_{m=1}^2 (R_m - XR_{3-m}^*) \times \exp(-im\varphi) + \text{conj.}]$$

where $X = (\alpha_{11} - \alpha_{21})^{(1)} (\alpha_{11} - \alpha_{21})^{(2)} (\alpha_{11} - \alpha_{21})^{(3)}$

$$D(\varphi) = (1-X^2)/(1+X^2-2X \cos 3\varphi)$$

$$R_0 = \frac{1}{3} \sum_{j=1}^3 w_1^{(j)} w_2^{(j)} |F_1^{(j)} - F_2^{(j)}|^2$$

$$R_m = \frac{1}{3} \sum_{j=1}^3 w_1^{(j)} w_2^{(j)} (F_1^* - F_2^*)^{(j+m)} (F_1 - F_2)^{(j)} \times \prod_{v=1}^m (\alpha_{11} - \alpha_{21})^{(j+v)}.$$

It is to be noted that if $F_k^{(j)} = F_k$ and $w_k^{(j)} = w_k$ ($k=1,2$; $j=1,2,3$) in Table 1, the period of the averaged structure may be reduced to the thickness of one layer, *i.e.* the period of \mathbf{p}_j becomes three times that of the averaged structure. In general, the value of p can be chosen to be an integral multiple of the period of the averaged structure when diffuse maxima appear at $\xi = H/p$ or $(2H+1)/2p$.

Calculation of $I_D(\varphi)$ for $t \geq 3$

The treatment of diffuse intensity by the present method generally becomes very complicated when $t \geq 3$, except in the case where matrices \mathbf{V} , \mathbf{W} and \mathbf{R} have some special symmetries. In general cases, one should apply the 'third method' given by KK.

By diagonalizing the matrix \mathbf{R} we may write R_m in the form

$$R_m = \sum_{v=1}^{pt} d_v x_v^m. \quad (40)$$

Here x_v is the v th root of a characteristic equation

$$F(x) = \det(x\mathbf{E} - \mathbf{R}) = 0 \quad (41)$$

where \mathbf{E} is the unit matrix of order pt . The expansion for $t=3$ is given by

$$F(x) = x^p \{x^{2p} + a_p x^p + a_{2p}\} = 0 \quad (42)$$

with

$$a_p = -\text{Tr}(\mathbf{Q}_1 \dots \mathbf{Q}_p) \quad \text{and} \quad a_{2p} = \det(\mathbf{Q}_1 \dots \mathbf{Q}_p)$$

where \mathbf{Q}_j is a 2×2 matrix with the elements $(\mathbf{Q}_j)_{kl} = (\alpha_{kl} - \alpha_{3l})^{(j)}$ ($k, l \leq 2$). From (42), x_v ($v = 2p + 1, \dots, 3p$) can be chosen to be zero. Hence

$$R_m = \sum_{v=1}^{2p} d_v x_v^m \quad (43a)$$

with

$$R_0 = \frac{1}{3} \sum_{j=1}^p \sum_{k < l}^2 \sum_{l}^3 w_k^{(j)} w_l^{(j)} |F_k^{(j)} - F_l^{(j)}|^2. \quad (43b)$$

Using the method given by KK [see their equation (45)] we have the following intensity formula:

$$I_D(\varphi) = N \frac{\sum_{m=0}^{p-1} \{R_m + (a_p R_m + R_{p+m}) \exp(-ip\varphi)\} \exp(-im\varphi)}{1 + a_p \exp(-ip\varphi) + a_{2p} \exp(-2ip\varphi)} + \text{conj.} - NR_0. \quad (44)$$

A similar procedure can be followed when $t \geq 4$. The expansion of the characteristic equation may be given by

$$F(x) = x^p \{x^{(t-1)p} + a_p x^{(t-2)p} + \dots + a_{tp-p}\} = 0. \quad (45)$$

The diffuse intensity is then given by

$$I_D(\varphi) = N \frac{\sum_{m=0}^{p-1} \exp(-im\varphi) \sum_{n=0}^{t-2} \exp(-inp\varphi) \sum_{l=0}^n a_{np-lp} R_{m+l p}}{\sum_{m=0}^{t-1} a_{mp} \exp(-imp\varphi)} + \text{conj.} - NR_0 \quad (46)$$

with $a_0 = 1$. Here, we give only the expansion of the characteristic equation for $t = 4$. It is:

$$F(x) = x^p \{x^{3p} + a_p x^{2p} + a_{2p} x^p + a_{3p}\} = 0 \quad (47)$$

with

$$a_p = -\text{Tr}(\mathbf{Q}_1 \dots \mathbf{Q}_p),$$

$$a_{2p} = \text{Tr}(\mathbf{C}_1 \dots \mathbf{C}_{2p})$$

and

$$a_{3p} = -\det(\mathbf{Q}_1 \dots \mathbf{Q}_p)$$

where \mathbf{Q}_j is a 3×3 matrix with the elements $(\mathbf{Q}_j)_{kl} = (\alpha_{kl} - \alpha_{4l})^{(j)}$ ($k, l \leq 3$) and $(\mathbf{C}_j)_{kl}$ is the cofactor of the element $(\mathbf{Q}_j)_{kl}$, i.e. \mathbf{C}_j is the adjoint of the matrix \mathbf{Q}_j .

The value of R_m may be calculated from (22b) or (24). However, the resulting formula is usually lengthy and complicated. Therefore it is tedious to rearrange it into compact form. In such a case one should use the formulae given in Appendix III.

Application to sodium 2-oxocaprylate

In this section, we give an application of our theory to the disordered structure of sodium 2-oxocaprylate

(Pant, 1964). This example is chosen because we found that the intensity formula derived by our theory based on the model given by Pant is different from that derived by Pant.

According to Pant, the model of the disordered structure is constructed from four kinds of layers, namely A_1 , A_2 , B_1 and B_2 , and the rule of arrangement of these layers is as follows. If the i th layer is $A_1(A_2)$, the $(i+1)$ th layer is either B_1 or B_2 , the probabilities of finding B_1 and B_2 after $A_1(A_2)$ being $1-\alpha$ (α) and $\alpha(1-\alpha)$, respectively; in the same way, if the $(i+1)$ th layer is $B_1(B_2)$, the $(i+2)$ th layer is either A_1 or A_2 , the probabilities of finding A_1 and A_2 after $B_1(B_2)$ being $1-\alpha$ (α) and $\alpha(1-\alpha)$, and so on. This stacking mode of layers corresponds to the case where $p=2$ and $t=2$ in our theory. The 'P-table' is shown in Table 2.

Table 2. The 'P-table' for the disordered structure of sodium 2-oxocaprylate (Pant, 1964)

w	A_1	A_2	B_1	B_2
$\frac{1}{2} A_1$			$1-\alpha$	α
$\frac{1}{2} A_2$			α	$1-\alpha$
$\frac{1}{2} B_1$	$1-\alpha$	α		
$\frac{1}{2} B_2$	α	$1-\alpha$		

From the consideration of symmetry relations between the four layers (see Tavale, Pant & Biswas, 1964; Pant, 1964), we find the following relations when $K+L$ odd:

$$\left. \begin{aligned} B_1 &= A_1^* \exp(i\varphi), \\ B_2 &= A_2^* \exp(i\varphi) \end{aligned} \right\} \quad (48)$$

and

$$A_1 - A_2 = B_1 - B_2$$

where A_1 , A_2 , B_1 and B_2 are the structure factors for the corresponding layers. Using these relations and substituting the parameters in Table 2 into (35), (38) and (39), we find

$$I_D(\varphi) = ND(\varphi) [R_0 + (1-X^2)^{-1}(R_1 - XR_1^*) \times \exp(-i\varphi) + \text{conj.}] \quad (49)$$

where $X = (1-2\alpha)^2$, $R_0 = |A_1 - A_2|^2/4$, $R_1 = R_1^* = |A_1 - A_2|^2(1-2\alpha)/4$ and $D(\varphi) = (1-X^2)/(1+X^2-2X \cos 2\varphi)$. This formula is further reduced to

$$I_D(2\pi\xi) = N|A_1 - A_2|^2 Q \quad (50)$$

with

$$Q = D(2\pi\xi) \{(1-2\alpha) \cos^2 \pi\xi + \alpha^2\} / \{1 + (1-2\alpha)^2\}$$

where φ is replaced by $2\pi\xi$.

On the other hand, Pant (1964) has derived the intensity formula by the method given by Wilson (1962). His calculation was made on the basis of the model of arrangement of four types of double-layer units, namely A_1B_1 , A_2B_1 , A_1B_2 and A_2B_2 , which can be deduced from Table 2. However, he has made two

fundamental errors. First, the equivalent positions of B_1 and B_2 with respect to those of A_1 and A_2 are in error. Second, the calculation of J_m^\dagger and J_0 is in error. If these errors are corrected, it can be shown that an intensity formula identical with (50) can be obtained by his method.

The present theory has also been successfully applied to the analysis of the disordered structures of *o*-chlorobenzamide (Takaki, Kato & Sakurai, 1975).

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APPENDIX I

Derivation of equations (23) and (24)

Let us introduce a matrix

$$\mathbf{G} = \begin{bmatrix} \mathbf{I} & & & \\ & \cdot & & \\ & & \cdot & \\ & & & \mathbf{I} \\ \mathbf{I} & & & \end{bmatrix} \quad \text{with } \mathbf{G}^p = \mathbf{E} \quad (51)$$

where \mathbf{I} and \mathbf{E} are unit matrices of orders t and pt , respectively. The matrices \mathbf{K} and \mathbf{R} are then written as

$$\mathbf{K}_0 = \mathbf{G}\mathbf{K} \quad \text{and} \quad \mathbf{R} = \mathbf{G}\mathbf{R}_0 \quad (52)$$

where

$$\mathbf{K}_0 = \begin{bmatrix} \mathbf{h}_1 & & & \\ & \cdot & & \\ & & \cdot & \\ & & & \mathbf{h}_p \end{bmatrix} \quad \text{and} \quad \mathbf{R}_0 = \begin{bmatrix} \mathbf{r}_1 & & & \\ & \cdot & & \\ & & \cdot & \\ & & & \mathbf{r}_p \end{bmatrix}.$$

Substituting the relation $\mathbf{R} = \mathbf{G}\mathbf{R}_0$ into (22b) we have

$$\begin{aligned} R_m &= \text{Tr } \mathbf{V}\mathbf{W}(\mathbf{G}\mathbf{R}_0)^m \\ &= \text{Tr} \begin{bmatrix} \mathbf{r}_{2-m} \cdots \mathbf{r}_1 & & & \\ & \cdot & & \\ & & \cdot & \\ & & & \mathbf{r}_{p+1-m} \cdots \mathbf{r}_p \end{bmatrix} \mathbf{V}\mathbf{W}\mathbf{G}^m \\ &= \frac{1}{p} \sum_{j=1}^p \text{Tr } \mathbf{v}_{j+m, j} \mathbf{w}_j \mathbf{r}_{j+1} \cdots \mathbf{r}_{j+m} \end{aligned} \quad (53)$$

where $\mathbf{r}_{j+p} = \mathbf{r}_j$. The same procedure gives

$$\begin{aligned} K_m &= \frac{1}{p} \sum_{j=1}^p \text{Tr } \mathbf{v}_{j+m, j} \mathbf{w}_j \mathbf{h}_{j+1} \cdots \mathbf{h}_{j+m} \\ &= \frac{1}{p} \sum_{j=1}^p \text{Tr } \mathbf{v}_{j+m, j} \mathbf{w}_j \mathbf{h}_{j+m} \end{aligned} \quad (54)$$

where relation (15b) is used.

† This error was corrected by Pant (1973, private communication).

APPENDIX II

Summation of equation (29) with respect to r

Equation (29) may be rewritten as

$$\begin{aligned} I_L(\varphi) &= pK_0 \left[-M + \sum_{r=0}^{M-1} (M-r) \exp(-irp\varphi) + \text{conj.} \right] \\ &+ \left[\sum_{\lambda=1}^{p-1} K_\lambda \exp(-i\lambda\varphi) \sum_{r=0}^{M-1} (N-pr-\lambda) \right. \\ &\quad \left. \times \exp(-irp\varphi) + \text{conj.} \right]. \end{aligned} \quad (55)$$

The summation of the first term gives apparently $pK_0G(\varphi)$ with $G(\varphi)$ given by (31). Using the relation $K_\lambda^* = K_{p-\lambda}^\dagger$ we have

$$\begin{aligned} I_L(\varphi) &= pK_0G(\varphi) + \sum_{\lambda=1}^{p-1} K_\lambda \exp(-i\lambda\varphi) \left[\sum_{r=0}^{M-1} (mp-pr-\lambda) \right. \\ &\quad \left. \times \exp(-irp\varphi) \right. \\ &\quad \left. + \sum_{r=0}^{M-1} (mp-p-pr+\lambda) \exp\{i(1+r)p\varphi\} \right] \\ &= G(\varphi) \left[pK_0 + \sum_{\lambda=1}^{p-1} (p-\lambda)K_\lambda \exp(-i\lambda\varphi) \right. \\ &\quad \left. + \sum_{\lambda=1}^{p-1} \lambda K_\lambda \exp\{i(p-\lambda)\varphi\} \right] \\ &= G(\varphi) \left[pK_0 + \sum_{\lambda=1}^{p-1} (p-\lambda)K_\lambda \exp(-i\lambda\varphi) + \text{conj.} \right]. \end{aligned} \quad (56)$$

APPENDIX III

Calculation of R_m for $t \geq 3$

For $p=1$

Formula R_m for $p=1$ is given by

$$R_m = \text{Tr } \mathbf{V}\mathbf{W}\mathbf{R}^m \quad (57)$$

where $(\mathbf{V})_{kl} = F_k^* F_l$, $(\mathbf{W})_{kl} = w_l \delta_{kl}$ and $(\mathbf{R})_{kl} = \beta_{kl}$. This formula can be rewritten in the form

$$R_m = \frac{1}{2} \text{Tr } (\mathbf{V} + \mathbf{V}^T)\mathbf{W}\mathbf{R}^m + \frac{1}{2} \text{Tr } (\mathbf{V} - \mathbf{V}^T)\mathbf{W}\mathbf{R}^m \quad (58)$$

where \mathbf{V}^T is the transpose of \mathbf{V} . From the definition of \mathbf{V}

$$\mathbf{V}^T = \tilde{\mathbf{V}}$$

where $\tilde{\mathbf{V}}$ is the complex conjugate of \mathbf{V} . Therefore the first term of (58) is the real part of R_m and the second one the imaginary part.

Let us introduce matrices \mathbf{U} and \mathbf{M} with the elements

$$(\mathbf{U})_{kl} = |F_k|^2 \quad \text{and} \quad (\mathbf{M})_{kl} = 1 \quad (59)$$

$$\begin{aligned} \dagger K_\lambda^* &= \frac{1}{p} \sum_{j=1}^p \bar{F}^{(j+\lambda)} F^{*(j)} = \frac{1}{p} \sum_{s=1}^p \bar{F}^{*(s-\lambda)} F^{(s)} \\ &= \frac{1}{p} \sum_{s=1}^p \bar{F}^{*(s+p-\lambda)} F^{(s)} = K_{p-\lambda}. \end{aligned}$$

respectively. Then using the relation $\mathbf{KR}=0$ given in (20) we have

$$\mathbf{UWR} = \begin{bmatrix} |F_1|^2 & & & \\ & \ddots & & \\ & & \ddots & \\ & & & |F_t|^2 \end{bmatrix} \mathbf{MWR} = \begin{bmatrix} |F_1|^2 & & & \\ & \ddots & & \\ & & \ddots & \\ & & & |F_t|^2 \end{bmatrix} \mathbf{KR} = 0.$$

Hence

$$\text{Tr } \mathbf{UWR}^m = 0. \quad (60a)$$

A similar procedure gives

$$\text{Tr } \mathbf{U}^T \mathbf{WR}^m = 0. \quad (60b)$$

Combining (58) and (60) we have

$$\begin{aligned} R_m &= -\frac{1}{2} \text{Tr} \{ \mathbf{U} + \mathbf{U}^T - \mathbf{V} - \mathbf{V}^T \} \mathbf{WR}^m \\ &\quad - \frac{1}{2} \text{Tr} \{ \mathbf{U} - \mathbf{U}^T - \mathbf{V} + \mathbf{V}^T \} \mathbf{WR}^m \\ &= -\frac{1}{2} \text{Tr } \mathbf{SWR}^m - \frac{1}{2} \text{Tr } \mathbf{TWR}^m \end{aligned} \quad (61)$$

where $(\mathbf{S})_{kl} = |F_k - F_l|^2$ and $(\mathbf{T})_{kl} = (F_k^* + F_l^*) (F_k - F_l)$.

For $p \geq 2$

In the same way as described above, (24) can be rewritten in the form

$$\begin{aligned} R_m &= \frac{1}{2p} \sum_{j=1}^p \text{Tr} (v_{j+m,j} + v_{j+m,j}^T) w_j r_{j+1} \cdots r_{j+m} \\ &\quad + \frac{1}{2p} \sum_{j=1}^p \text{Tr} (v_{j+m,j} - v_{j+m,j}^T) w_j r_{j+1} \cdots r_{j+m}. \end{aligned} \quad (62)$$

Let us introduce a matrix $\mathbf{u}_{j+m,j}$ with the elements $(\mathbf{u}_{j+m,j})_{kl} = |F_k^{(j+m)}|^2$. Following the same procedure

as in the preceding paragraph we have

$$\left. \begin{aligned} \text{Tr } \mathbf{u}_{j+m,j} w_j r_{j+1} \cdots r_{j+m} &= 0 \\ \text{and} \\ \text{Tr } \mathbf{u}_{j+m,j}^T w_j r_{j+1} \cdots r_{j+m} &= 0 \end{aligned} \right\} (63)$$

where the relations in (19) are used. Combining (62) and (63) we obtain the resultant formula:

$$\begin{aligned} R_m &= -\frac{1}{2p} \sum_{j=1}^p \text{Tr } \mathbf{s}_{j+m,j} w_j r_{j+1} \cdots r_{j+m} \\ &\quad - \frac{1}{2p} \sum_{j=1}^p \text{Tr } \mathbf{t}_{j+m,j} w_j r_{j+1} \cdots r_{j+m} \end{aligned} \quad (64)$$

where

$$(\mathbf{s}_{j+m,j})_{kl} = (F_k^* - F_l^*)^{(j+m)} (F_k - F_l)^{(j)}$$

and

$$(\mathbf{t}_{j+m,j})_{kl} = (F_k^* + F_l^*)^{(j+m)} (F_k - F_l)^{(j)}.$$

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