Acta Cryst. (1964). **17**, 579

The Calculation of the Intensity of X-Rays Diffracted by Monodimensionally Disordered Structures

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(*Received* 6 *September* 1962 *and in revised form* 24 *June* 1963)

In this paper a new matrix method for the calculation of the intensity of X-rays diffracted by monodimensionally disordered structures is developed, which is to be regarded as derived from the method already given by Kakinoki & Komura. The present method allows simpler calculations in the case in which layers of different kinds are obtainable from one another by translation parallel to the layers. The subject is divided into two parts: in the first part the general theory for all possible cases is discussed, while in the second one some significant results are given.

1. Introduction

The problem of the calculation of the intensity of X-rays diffracted by monodimensionally disordered structures has been dealt with by a number of authors; we recall here the papers by Hendricks & Teller (1942), Wilson (1942), Mering (1949), Jagodzinski (1949*a*, *b*, *c*, 1954), Kakinoki & Komura (1952, 1954*a*, *b*, 1962), and Allegra (1961*a*, *b*, *c*, 1962).

Hendricks & Teller's method of solution is characterized by a matrix formulation of the problem. Wilson has given a different treatment, where a set of difference equations replaces the matrices introduced by Hendricks & Teller. Mering applies criteria analogous to those introduced by Hendricks & Teller to the study of natural silicates. Jagodzinski, who had first extended the difference-equation method to a greater generality (1949*a*, *b*) subsequently (1954) proposed an elegant formulation of the problem, resting upon the application of group theoretical considerations to the probabilities of sequence among the layers. Kakinoki & Komura subjected the matrix method and the difference-equation method to detailed analysis, demonstrating their substantial equivalence; moreover they obtained for the first time (1952) a significant simplification in Hendricks & Teller's mathematical procedure, allowing a lengthy matrix diagonalization to be avoided (Allegra, 1961*a*; Kakinoki & Komura, 1962). Moreover, Kakinoki & Komura extend the expression of the average diffracted intensity to the most general case of order of influence among layers ($s \geq 2$) even in the case in which layers are of different kinds (1954*a*, *b*).

The author has developed another method of mathematical formulation of the problem (Allegra, 1961*b*) which also extends the matrix formulation to the generality of cases; its relative convenience has allowed it to be applied to comparatively complicated cases (Allegra, 1961*c*, 1962). In the present paper a more complete mathematical exposition of the above method will be given. The subject is dealt with in the following two sections: in § 2 the general theory for all possible cases will be discussed, while in § 3 some significant results obtained by the theory of § 2 will be given.

2. General mathematical formulation

We will start from the fundamental conclusions arrived at by Kakinoki & Komura (1952, 1954*a*). Kakinoki & Komura have expressed the mean diffracted intensity by a monodimensionally disordered structure as a sum of terms each due to the mean interference effect between every layer and its nth neighbour (n comprised between 0 and $N \to \infty$, the total number of layers). We repeat here the following matrices, introduced by Kakinoki & Komura:

$$\mathbf{V} = \begin{vmatrix} S_1^* S_1 \mathbf{M} & S_1^* S_2 \mathbf{M} & \dots & S_1^* S_r \mathbf{M} \\ S_2^* S_1 \mathbf{M} & S_2^* S_2 \mathbf{M} & \dots & S_2^* S_r \mathbf{M} \\ \dots & \dots & \dots & \dots \\ S_r^* S_1 \mathbf{M} & S_r^* S_2 \mathbf{M} & \dots & S_r^* S_r \mathbf{M} \end{vmatrix}_R \tag{1}$$

$$\mathbf{F} = \begin{vmatrix} \mathbf{F}_1 & \dots & 0 \\ & \mathbf{F}_2 & \\ & \ddots & \\ 0 & \dots & \mathbf{F}_r \end{vmatrix}_R ; \quad \mathbf{F}_p = \begin{vmatrix} f_{(p-1)l+1} & \dots & 0 \\ & f_{(p-1)l+2} & \\ & \ddots & \\ 0 & \dots & f_{pl} \end{vmatrix}_l \tag{2}$$

$$\mathbf{Q} = \Phi \mathbf{P};$$

$$\Phi = \begin{vmatrix} \exp(-i\varphi_1)\mathbf{E}_l & \dots & 0 \\ & \exp(-i\varphi_2)\mathbf{E}_l & \\ & \ddots & \\ 0 & \dots & \exp(-i\varphi_r)\mathbf{E}_l \end{vmatrix}_R \tag{3}$$

$$\mathbf{P} = \begin{vmatrix} \mathbf{P}_{11} & \mathbf{P}_{12} & \dots & \mathbf{P}_{1r} \\ \dots & \dots & \dots & \dots \\ \mathbf{P}_{r1} & \mathbf{P}_{r2} & \dots & \mathbf{P}_{rr} \end{vmatrix}_R ;$$

$$\mathbf{P}_{pq} = \begin{vmatrix} p_{(p-1)l+1,(q-1)l+1} & \dots & p_{(p-1)l+1,ql} \\ \dots & \dots & \dots \\ p_{pl,(q-1)l+1} & \dots & p_{pl,ql} \end{vmatrix}_l \tag{4}$$

where:

r is the number of distinct kinds of layer;
s is the range of influence (Jagodzinski's 'Reichweite') among the layers;
$R=r^s$; $l=r^{s-1}$;
S_p is the form factor of the layer of pth kind, defined with respect to an intrinsic coordinate system;
$\mathbf{M}$ is a square matrix of order l, whose elements are all unity;
$\mathbf{F}_p$ is a diagonal matrix of order l, whose elements are the frequencies of occurrence of all the $l=r^{s-1}$ different groupings (complexions) of s successive layers, which terminate with the layer of pth kind;
$\mathbf{s}$ being the scattering vector ($|\mathbf{s}|=2\sin\theta/\lambda$), $\varphi_p=2\pi\mathbf{t}_p.\mathbf{s}$ is the phase shift corresponding to the vector $\mathbf{t}_p$, perpendicular to the layers, whose value measures the thickness of the layer of pth kind;
$\mathbf{E}_l$ is the unit matrix of order l;
$\mathbf{P}_{pq}$ is the square matrix whose elements are the probabilities that after every given complexion of s successive layers, terminating with a layer of the pth kind, there follows a complexion of the same order, terminating with a layer of the qth kind. Two adjacent complexions are defined as follows:

	kinds of layers
1st complexion	$(j_1, j_2, j_3, \ldots, j_{s-1}, p)$
2nd complexion	$(j_2, j_3, \ldots, j_{s-1}, p, q)$.

In this way the probability that the second complexion follows the first one is also the probability that a layer of the qth kind follows the first complexion $(j_1, j_2, \ldots, p)$ of s successive layers.

The mean interference term between nth neighbouring layers is expressed as follows according to Kakinoki & Komura:

$$\bar{I}(n)=\text{spur}\,\mathbf{VFQ}^n+\text{conjug.};\ (\bar{I}(0)=\text{spur}\,\mathbf{VF}) \quad (5)$$

and the total average intensity $\bar{I}$ diffracted by the structure is:

$$\bar{I}=\sum_{n=0}^{N}(N-n)\bar{I}(n)\,. \quad (6)$$

The summation indicated in (6) may be effected either by introducing the inverse matrix $(\mathbf{E}-\mathbf{Q})^{-1}$, as pointed out by Kakinoki & Komura (1952) and by the author (1961*a*), or by using the relations between the coefficients in the characteristic equation $\det(x\mathbf{E}-\mathbf{Q})=0$ and its roots and some other relations (Kakinoki & Kamura, 1961).

In the present paper a new matrix method is discussed, which may be considered as derived from the method given by Kakinoki & Komura, while a different method has been recently proposed by these two authors (1962). The present method also introduces the inverse matrix $(\mathbf{E}-\mathbf{Q})^{-1}$, and shows advantages in mathematical computation when two or more kinds of layer are obtainable from one another by simple displacement parallel to the layers. We will introduce, in the following, the expression *type of layer* in order to indicate all those kinds of layer which are reducible to only one kind when the above mentioned displacement is taken into account.

(*a*) *The layers are of m different types, and the order of influence s among layers is* ≥ 2

Let us first consider, as an example, a structure built up by layers of hexagonal symmetry and of only one type, which may occupy the three positions A, B and C, with respect to a fixed axis perpendicular to the layers (Fig. 1); moreover, for the sake of simplicity, we will suppose that no two adjacent layers can occupy the same position. It is well known that a number of disordered structures may be described as a proper statistical sequence of layers in these positions (Wilson, 1942*b*; Jagodzinski, 1949*b*, *c*, 1954; Kakinoki & Komura, 1954*b*; Allegra, 1962). It is apparent, from inspection of Fig. 1, that the vector displacement $\tau_1=\frac{2}{3}\mathbf{a}+\frac{1}{3}\mathbf{b}$ allows the change of A, B, and C into B, C and A respectively; while, conversely, the vector displacement $\tau_2=\frac{1}{3}\mathbf{a}+\frac{2}{3}\mathbf{b}$ changes B, C and A into A, B and C respectively.

Let us now represent, by the letters A, B and C, a complexion of adjacent layers, of any order:

$$ACBCBABA\ldots.$$

By simply shifting all the layers either by the vector

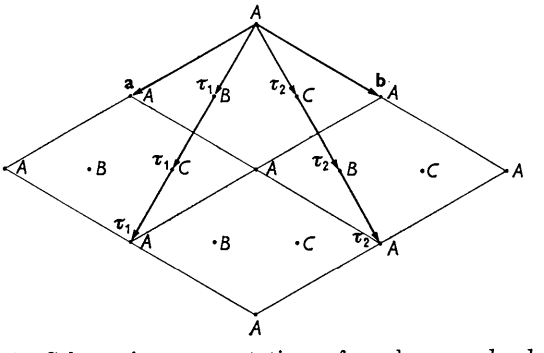


Fig. 1. Schematic representation of a hexagonal planar lattice, which may occupy the three positions indicated by A, B and C. The τ_1 and τ_2 vectors allow the three positions to be mutually interchanged.

τ_1 or by the vector τ_2, we obtain two other complexions:

$$\begin{array}{l} \qquad\qquad \tau_1 \nearrow BACACBCB\ldots \\ ACBCBABA\ldots \\ \qquad\qquad \tau_2 \searrow CBABACAC\ldots \end{array}$$

These three complexions of successive kinds of layer, formally distinct but physically identical, are equivalent to the unique complexion of the vectors connecting the origins of adjacent layers, considered as belonging to only one type. In other words, indicating by $\mathbf{c}$ a vector perpendicular to the layers, whose

modulus measures their constant thickness, the above said complexions may be described by:

$$\mathbf{t}_2\mathbf{t}_2\mathbf{t}_1\mathbf{t}_2\mathbf{t}_2\mathbf{t}_1\mathbf{t}_2\ldots \quad (\mathbf{t}_1=\mathbf{c}+\boldsymbol{\tau}_1;\ \mathbf{t}_2=\mathbf{c}+\boldsymbol{\tau}_2)$$

where the number of vectors is obviously equal to the number of layers minus 1.

The aim of this paper is to discuss briefly a matrix method in which the probability correlation of $(s-1)$ order among $\mathbf{t}_j$ vectors — or among related quantities, such as the phase shift factors $\exp[-i\varphi_j]=\exp[-2\pi i\mathbf{t}_j.\mathbf{s}]$ — will be considered instead of the analogous correlation of s order among kinds of layer; the $\mathbf{t}_j$ vectors must be always considered as the sum of a vector component perpendicular to the layers and a vector component parallel to them. As shown from the example referred to above, in fact, in some cases a reduction in the number of different complexions will arise; consequently, in these cases, a reduction in the order of the involved matrices, and therefore a simplification in the related calculations, will be achieved.

Such reduction and simplification have been achieved by Kakinoki & Komura (1954*b*) and Komura (1962). These authors reduced their large matrices by regarding these large matrices as consisting of minor matrices. But the present author will show that a new intensity equation containing only the reduced matrices can be directly derived.

Let us consider a monodimensionally disordered structure constituted by layers of m different types; the range of influence between layers is $s(\geq 2)$. Let V_j $(j=1, 2, \ldots, m)$ be the form factor of the layers of (j) type, defined with reference to an intrinsic origin. Moreover, let n_{jk} be the number of possible distinct vectors which connect the origins of two adjacent layers of types (j) and (k); the total number n of distinct vectors will be given by:

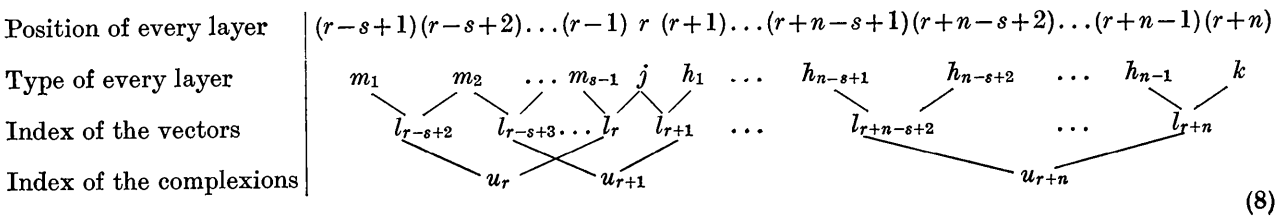
$$n=\sum_{j=1}^{m}\sum_{k=1}^{m} n_{jk}\,.$$

Let (l) be the index of the general vector $\mathbf{t}_l$; $\varphi_l=2\pi\mathbf{t}_l.\mathbf{s}$ will be the corresponding phase shift. Another index (r) will be added to the (l) index (l_r), if necessary, in order to specify the position in the structure of the second layer connected by the vector. Any complexion of (s) successive kinds of layer may be represented, in analogy to the example previously discussed, by the complexion of the $(s-1)$ successive vectors which connect every pair of adjacent layer types; we will indicate by (u) the index number of the general complexion, to which, when necessary, two other indices will be added in order to specify either the position, in the structure, or the type of the last layer connected by the vector complexion. As an example; $u_r(j)$ means: complexion of $(s-1)$ successive vectors, connecting (s) neighbouring layers of which the last is of jth type and in the (r) position. The index number (u) may assume all the integer values comprised between 1 and $\mathcal{N}$ — the total number of distinct vector complexions; the succession of the values of (u) will be ordered so that $u(j)>u(k)$ if $j>k$. Remembering that two adjacent vectors are subjected to the obvious condition that, if the first vector connects layers of types (k_1) and (k_2), the second one must connect layers of types (k_2) and (k_3), and so on, we may express the total number $\mathcal{N}(j)$ of complexions of the $u(j)$ class $(j=1, 2, \ldots, m)$ in the following way:

$$\mathcal{N}(j)=\sum_{k_1=1}^{m}\sum_{k_2=1}^{m}\ldots\sum_{k_{s-2}=1}^{m} n_{k_1k_2}n_{k_2k_3}\ldots n_{k_{s-2}j};$$

$$\mathcal{N}=\sum_{j=1}^{m}\mathcal{N}(j)\,. \qquad (7)$$

In order to evaluate $\bar{I}(n)$ (see (5)), we will now represent a group of neighbouring layers, with their corresponding types, vectors and complexions, by the following scheme:



(8)

Referring to the above diagram, with the known notations and representing by $\Delta\varphi_{jk}$ the phase shift between the nth neighbouring layers of types (j) and (k),

$$(\Delta\varphi_{jk}=2\pi(\mathbf{t}_{l_{r+1}}+\mathbf{t}_{l_{r+2}}+\ldots+\mathbf{t}_{l_{r+n}})\mathbf{s}$$
$$=\varphi_{l_{r+1}}+\varphi_{l_{r+2}}+\ldots+\varphi_{l_{r+n}})\,,$$

we will express $\bar{I}(n)$ as follows:

$$\bar{I}(n)=$$
$$\overline{V^{(j)}\exp(-i\Delta\varphi_{jk})V^{(k)*}}+\text{conjug.}=$$
$$\overline{V^{(j)}\exp(-i\varphi_{l_{r+1}}).\exp(-i\varphi_{l_{r+2}})\ldots\exp(-i\varphi_{l_{r+n}})V^{(k)*}}$$
$$+\text{conjug.} \qquad (9)$$

In (9), the bar indicates the operation of averaging effected either over the possible vectors between layers, with fixed (j) and (k), or over all possible (j) and (k). Introducing, in analogy to Kakinoki &

Komura, the symbols $f(u)$ and $p(uu')$ to indicate the frequency of occurrence of the (u) complexion, and the probability that a (u') complexion follows a (u) complexion, (5) becomes:

$$\bar{I}(n) = \sum_{j=1}^{m}\sum_{k=1}^{m}\Big\{\sum_{u_r(j)}\sum_{u_{r+1}}\cdots\sum_{u_{r+n(k)}} V^{(j)}f(u_r)p(u_r, u_{r+1}) \times \exp(-i\varphi_{l_{r+1}}).p(u_{r+1}, u_{r+2})\exp(-i\varphi_{l_{r+2}}) \times \ldots p(u_{r+n-1}, u_{r+n})\exp(-i\varphi_{l_{r+n}})V^{(k)*}\Big\} + \text{conjug.} \quad (10)$$

where the first and the last complexions indicated in the summation must belong to the $u(j)$ and the $u(k)$ classes, while the other complexions may assume all possible values.

The expression given above may be synthetically expressed by introducing the following vectors and square matrices of order $\mathcal{N}$:

$$\mathbf{V} = |\overbrace{V^{(1)}V^{(1)}\ldots V^{(1)}}^{\mathcal{N}(1)\text{ terms}}\ \overbrace{V^{(2)}V^{(2)}\ldots V^{(2)}}^{\mathcal{N}(2)\text{ terms}}\ \ldots\ \overbrace{V^{(m)}\ldots V^{(m)}}^{\mathcal{N}(m)\text{ terms}}|_{\mathcal{N}} \quad (11)$$

$\tilde{\mathbf{V}}$ = (the corresponding column vector)

$$F = |f(u)\delta^{(uu')}|_{\mathcal{N}} = \begin{vmatrix} f(1) & & & & 0 \\ & f(2) & & & \\ & & \ddots & & \\ & & & f(u) & \\ & & & & \ddots \\ 0 & & & & f(\mathcal{N}) \end{vmatrix}_{\mathcal{N}} \quad (12)$$

$$\mathbf{Q} = |Q(uu')|_{\mathcal{N}} = \begin{vmatrix} Q(11) & Q(12) & \ldots\ldots & Q(1\mathcal{N}) \\ Q(21) & Q(22) & \ldots\ldots & Q(2\mathcal{N}) \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\ Q(\mathcal{N}1) & Q(\mathcal{N}2) & \ldots\ldots & Q(\mathcal{N}\mathcal{N}) \end{vmatrix}_{\mathcal{N}};$$

$$Q(uu') = p(uu')\exp[-i\varphi_l], \quad (13)$$

where l is the index of the last vector in the (u') complexion.

Now it may be easily proved that (10) reduces to:

$$\bar{I}(n) = \mathbf{VFQ}^n\mathbf{V}^* + \text{conjug.}; \quad \bar{I}(o) = \mathbf{VFV}^*. \quad (14)$$

Formally this equation is the same as equation (5), because equation (1) can be factorized into

$$\mathbf{V} = \mathbf{S}^*\mathbf{M}_0\mathbf{S}$$

where

$$\mathbf{S} = \begin{vmatrix} S_1\mathbf{E}_l & & & \\ & S_2\mathbf{E}_l & & \\ & & \ddots & \\ & & & S_r\mathbf{E}_l \end{vmatrix}_R \quad \text{and} \quad \mathbf{M}_0 = \begin{vmatrix} \mathbf{M} & \mathbf{M} & \ldots & \mathbf{M} \\ \mathbf{M} & \mathbf{M} & \ldots & \mathbf{M} \\ \vdots & \vdots & & \vdots \\ \mathbf{M} & \mathbf{M} & \ldots & \mathbf{M} \end{vmatrix}_R$$

and hence

$$\text{spur}\,\mathbf{VFQ}^n = \text{spur}\,\mathbf{S}^*\mathbf{M}_0\mathbf{SFQ}^n = \text{spur}\,\mathbf{M}_0\mathbf{SFQ}^n\mathbf{S}^* = \mathbf{V}'\mathbf{FQ}^n\mathbf{V}'^*$$

where $\mathbf{V}$ is a vector whose s-component is the same as the ss-element of the diagonal matrix $\mathbf{S}$. The discrepancy exists in $\mathbf{Q}$, *i.e.* as seen from equation (3), $\mathbf{Q}^{(k)} = \Phi^{(k)}\mathbf{P}^{(k)}$ and $\Phi^{(k)}$ is a diagonal matrix,† while $\mathbf{Q}$ in equation (14) is not defined in a similar way, since $Q(uu') = p(uu')\exp(-i\varphi_1)$, and φ_1 contains two parts, one due to perpendicular displacement and the other due to parallel displacement. As a result of such a modification, the order of the matrices can be reduced and hence the calculation can be simplified, as the examples in the following paragraphs will show.

On the assumption that $\mathbf{Q}^n \to 0$ for $n \to N$ (very great), so that:

$$\sum_{n=0}^{N}(N-n)\mathbf{Q}^n = N(\mathbf{E}_{\mathcal{N}} - \mathbf{Q})^{-1}$$

where $\mathbf{E}_{\mathcal{N}}$ is the unit matrix of order $\mathcal{N}$, the value of the average intensity diffracted by the structure becomes:

$$\begin{aligned}\bar{I} &= \sum_{n=0}^{N}(N-n)\bar{I}(n) = N\mathbf{VF}\tilde{\mathbf{V}}^* \\ &\quad + \Big(\sum_{n=1}^{N}(N-n)\mathbf{VFQ}^n\tilde{\mathbf{V}}^* + \text{conjug.}\Big) \\ &= \mathbf{VF}\Big\{-\tfrac{1}{2}N\mathbf{E}_{\mathcal{N}} + \sum_{n=0}^{N}(N-n)\mathbf{Q}^n\Big\}\tilde{\mathbf{V}}^* + \text{conjug.} \\ &= N\mathbf{VF}\{-\tfrac{1}{2}\mathbf{E}_{\mathcal{N}} + (\mathbf{E}_{\mathcal{N}} - \mathbf{Q})^{-1}\}\tilde{\mathbf{V}}^* + \text{conjug.} \quad (15)\end{aligned}$$

I_{Av} (average diffracted intensity per layer)

$$= \bar{I}/N = \mathbf{VF}\{-\tfrac{1}{2}\mathbf{E}_{\mathcal{N}} + (\mathbf{E}_{\mathcal{N}} - \mathbf{Q})^{-1}\}\tilde{\mathbf{V}}^* + \text{conjug.} \quad (15a)$$

It is to be observed that, although the $\mathbf{Q}$ matrix is of order $\mathcal{N}$, most of its terms have zero value; in fact, a given probability $p(uu')$, in order to have physical meaning, must refer to two complexions u and u' such that the last $(s-2)$ vectors in the first complexion coincide with the first $(s-2)$ vectors in the second complexion, as is shown in (8).

We have seen that the convergence condition for the summation effected above is:

$$\lim_{n\to\infty}\mathbf{Q}^n = \mathbf{0}.$$

On the hypothesis that the $\mathbf{Q}$ matrix may be diagonalized by the similarity operation $\mathbf{Q} = \mathbf{A}\,\mathbf{\Lambda}\,\mathbf{A}^{-1}$, where

$$\mathbf{\Lambda} = \begin{vmatrix} \lambda_1 & \ldots\ldots & 0 \\ & \lambda_2 & \\ & \ddots & \\ 0 & \ldots\ldots & \lambda_{\mathcal{N}} \end{vmatrix},$$

† Superscript (k) is added to the matrices defined by Kakinoki & Komura in order to distinguish them from the corresponding ones used here by the present author.

then

$$\mathbf{Q}^n = \mathbf{A} \begin{vmatrix} \lambda_1^n & \cdots & 0 \\ & \lambda_2^n & \\ & & \ddots \\ 0 & \cdots & \lambda_{\mathcal{N}}^n \end{vmatrix} \mathbf{A}^{-1} .$$

For $n \to \infty$ the resulting matrix does not tend to $\mathbf{0}$ if and only if at least an eigenvalue of $\mathbf{Q}$ is equal to unity. This might be proved by the argument that the absolute value of any term of the $\mathbf{Q}^n$ matrix, say the term characterized by the indices (uu'), must not exceed the probability that the (u) complexion be followed by the (u') complexion, after (n) intermediate complexions, so that necessarily, in any case, $|\lambda_i| \leq 1$.

The mathematical condition which expresses the existence of an eigenvalue equal to unity is: $\mathrm{Det}\,(\mathbf{E}_{\mathcal{N}} - \mathbf{Q}) = 0$. If this condition is fulfilled, the summation indicated in (15) cannot be effected as shown; in these cases the diffracted intensity shows infinite peaks, as always occurs in a three-dimensionally regular crystal of infinite size.

We will recall here the algebraic relationships which connect the $p(uu')$ probabilities with the $f(u)$ frequencies. These are:

$$f(u') = \sum_{u=1}^{\mathcal{N}} f(u)p(uu') \quad (u' = 1, 2, \ldots, \mathcal{N}) \tag{16}$$

and may be derived by simple considerations. From the homogeneous system of linear equations (16), once $p(uu')$ are known, $f(u')$ can be easily obtained, using the obvious condition:

$$\sum_{u'=1}^{\mathcal{N}} f(u') = 1 . \tag{17}$$

A very frequent case is that of a disordered structure whose layers all belong to the same type. Denoting by V the layer form factor, and by $\mathbf{1}$ and $\tilde{\mathbf{1}}$ the row and column vectors, of order $\mathcal{N}$, whose elements are all unity, (15a) becomes:

$$I_{\mathrm{Av}} = VV^*\{\mathbf{1}\mathbf{F}[-\tfrac{1}{2}\mathbf{E}_{\mathcal{N}} + (\mathbf{E}_{\mathcal{N}} - \mathbf{Q})^{-1}]\tilde{\mathbf{1}} + \text{conjug.}\}. \tag{18}$$

Moreover we will observe that, if n is the number of possible translations between adjacent layers, the number $\mathcal{N}$ is given by (see (7)):

$$\mathcal{N} = n^{r-1}. \tag{19}$$

(*b*) *The layers are of m different types, and the order of influence s among layers is* 1

This case has been dealt with in detail by Hendricks & Teller (1942) and Kakinoki & Komura (1952). We will here show a useful simplification which arises when different vector translations between adjacent layers of given types are possible.

Let us introduce the following symbols:

$f^{(j)}$ = frequency of occurrence of the layers of (j) type $(j = 1, 2, \ldots m)$.

$l_r(jk)$ = index of the general vector between the layers of types (j) and (k), the latter being in the rth position. This index may vary from 1 to n_{jk}.

$p(l(jk))$ = probability that a layer of (j) type is followed by a layer of (k) type by the $l(jk)$ vector translation.

P_{jk} (overall probability that a (j) layer is followed by a (k) layer)

$$= \sum_{l(jk)=1}^{n_{jk}} p(l(jk)) .$$

$$f^{(k)} = \sum_{j=1}^{m} f^{(j)} P_{jk} .$$

Let us consider the general expression (9) for the total average diffracted intensity. The term under average operation may now be written in the following way:

$$\overline{V^{(j)} \exp(-i\Delta\varphi_{jk}) V^{(k)*}} = \sum_{j,r,s\ldots k=1,2\ldots m} \sum \sum \ldots \sum f^{(j)} V^{(j)} [\sum_{l_1(jr)} \sum_{l_2(rs)} \ldots \sum_{l_n(tk)} p(l_1(jr)) \times \exp(-i\varphi_{l_1}) . p(l_2(rs)) \exp(-i\varphi_{l_2}) \ldots p(l_n(tk)) \times \exp(-i\varphi_{l_n})] V^{(k)*} + \text{conjug.} \tag{20}$$

Let us make the substitution:

$$\alpha(rs) = \sum_{l(rs)=1}^{n_{rs}} p(l(rs)) \exp(-i\varphi_{l(rs)}) \tag{21}$$

and (20) reduces to:

$$\overline{V^{(j)} \exp[-i\Delta\varphi_{jk}) V^{(k)*}} = \sum_{j} \sum_{r} \ldots \sum_{k=1,2\ldots m} f^{(j)} V^{(j)} \alpha_1(jr)\alpha_2(rs) \ldots \alpha_n(tk) V^{(k)*} + \text{conjug.} \tag{22}$$

Let us define the following vectors and square matrices of m order: the row vector

$$\mathbf{V} = |V^{(1)} V^{(2)} \ldots V^{(j)} \ldots V^{(m)}| ,$$

and the corresponding column vector $\tilde{V}$; the diagonal matrix $\mathbf{F} = |F(jk)| = |f^{(j)}\delta^{(jk)}|$, and the matrix $\mathbf{Q} = |Q(jk)| = |\alpha(jk)|$.

The expression (22) may now be written:

$$\overline{V^{(j)} \exp(-i\Delta\varphi_{jk}) V^{(k)*}} = \mathbf{V}\mathbf{F}\mathbf{Q}^n\tilde{\mathbf{V}}^* + \text{conjug.} \tag{23}$$

and from the general expressions (6) and (9) we immediately derive the value of $I_{\mathrm{Av}}(N \to \infty, \mathrm{Det}(\mathbf{E} - \mathbf{Q}) \neq 0)$:

$$I_{\mathrm{Av}} = \bar{I}/N = \mathbf{V}\mathbf{F}\{-\tfrac{1}{2}\mathbf{E}_m + (\mathbf{E}_m - \mathbf{Q})^{-1}\}\tilde{\mathbf{V}}^* + \text{conjug.} \tag{24}$$

The order of the $\mathbf{Q}$ matrix here defined is never greater than the number of layer types; this implies, in general, a considerable simplification in carrying out the calculations with respect to the preceding matrix formulations.

In the particular case in which all layers are of the

same type ($m=1$), vectors and matrices above defined reduce to simple numbers. In particular:

$$\mathbf{V}(\tilde{\mathbf{V}}) \to V;\ \mathbf{F} \to 1 \text{ (in fact } f^{(j)}=f^{(1)}=1);$$

$$\mathbf{Q} \to \alpha = \sum_{l=1}^{n} p(l) \exp(-i\varphi_l) \quad (27)$$

and (26) reduces to:

$$I_{\mathrm{Av}} = VV^*\left\{-1+\frac{1}{1-\alpha}+\frac{1}{1-\alpha^*}\right\} = VV^*\frac{1-\alpha\alpha^*}{(1-\alpha)(1-\alpha)^*}. \quad (28)$$

The calculation by Warren & Warekois (1955) corresponds to this type.

3. Examples of calculation of the average diffracted intensity for some models of monodimensionally disordered structures

(*a*) We will first consider a structure constituted by layers of two types, I and II, which may follow statistically one on another with order of influence equal to 2. We will also assume that two adjacent layers of given kinds are connected by only one possible translation vector.

Let us indicate by 1 the index of the vector $\mathbf{t}_{\mathrm{I,I}}$.
Let us indicate by 2 the index of the vector $\mathbf{t}_{\mathrm{II,I}}$.
Let us indicate by 3 the index of the vector $\mathbf{t}_{\mathrm{I,II}}$.
Let us indicate by 4 the index of the vector $\mathbf{t}_{\mathrm{II,II}}$.

The complexion of $(s-1)$ neighbouring vectors reduces in this case ($s=2$) to the vectors themselves; therefore the (u) index varies from 1 to 4. The possible pairs of adjacent translations are 8: (11), (13), (21), (23), (32), (34), (42), (44). To these pairs the following probabilities (known numbers) correspond:

$$p(11)=q_1;\ p(13)=1-q_1;\ p(21)=q_2;\ p(23)=1-q_2$$
$$p(32)=1-q_3;\ p(34)=q_3;\ p(42)=1-q_4;\ p(44)=q_4. \quad (29)$$

It is apparent that from the four parameters q_1, q_2, q_3 and q_4 all possible probabilities may be deduced. In fact, by the solution of the system (16), we get:

$$f(1) = \frac{q_2(1-q_4)}{\Sigma};\ f(2)=f(3) = \frac{(1-q_1)(1-q_4)}{\Sigma};$$

$$f(4) = \frac{q_3(1-q_1)}{\Sigma};$$

$$\Sigma = (1-q_4)(1+q_2-q_1)+(1-q_1)(1+q_3-q_4). \quad (30)$$

The row vector $\mathbf{V}$ (see (11)) reduces to:

$$\mathbf{V} = |V^A V^A V^B V^B|; \quad (31)$$

V^A and V^B being the intrinsic form factors of the two types of layer. The $\mathbf{F}$ (expression (12)) and $\mathbf{Q}$ (expression (13)) matrices have the following form ($\varphi_i = 2\pi\mathbf{t}_i.\mathbf{s}$):

$$\mathbf{F} = \begin{vmatrix} f(1) & 0 & 0 & 0 \\ 0 & f(2) & 0 & 0 \\ 0 & 0 & f(3) & 0 \\ 0 & 0 & 0 & f(4) \end{vmatrix};$$

$$\mathbf{Q} = \begin{vmatrix} q_1e^{-i\varphi_1} & 0 & (1-q_1)e^{-i\varphi_3} & 0 \\ q_2e^{-i\varphi_1} & 0 & (1-q_2)e^{-i\varphi_3} & 0 \\ 0 & (1-q_3)e^{-i\varphi_2} & 0 & q_3e^{-i\varphi_4} \\ 0 & (1-q_4)e^{-i\varphi_2} & 0 & q_4e^{-i\varphi_4} \end{vmatrix} \quad (32)$$

and, substituting in (15*a*) and developing the calculations, we obtain:

$$I_{\mathrm{Av}} = 1/\Sigma\{(1-q_4)(1+q_2-q_1)V^AV^{A*} + (1-q)_1(1+q_3-q_4)V^BV^{B*} + \left[\frac{V^AV^{A*}\alpha+(V^AV^{B*}e^{i\varphi_2}+V^{A*}V^Be^{i\varphi_3})\beta+V^BV^{B*}\gamma}{e^{i(\varphi_2+\varphi_3)}(e^{i\varphi_1}-q_1)(e^{i\varphi_4}-q_4)-[(q_4-q_3)+(q_3-1)e^{i\varphi_4}][(q_1-q_2)+(q_2-1)e^{i\varphi_1}]}\right] + [\text{conjug.}]\} \quad (33)$$

in which

$$\alpha = (1-q_4)\{q_2e^{i(\varphi_2+\varphi_3)}(e^{i\varphi_4}-q_4)+[(q_1-q_2)(1+q_2-q_1)+(q_1-1)e^{i\varphi_1}][(q_4-q_3)+(q_3-1)e^{i\varphi_4}]\}$$
$$\beta = (1-q_4)(1-q_1)(e^{i\varphi_1}-q_1+q_2)(e^{i\varphi_4}-q_4+q_3)$$
$$\gamma = (1-q_1)\{q_3e^{i(\varphi_2+\varphi_3)}(e^{i\varphi_1}-q_1)+[(q_4-q_3)(1+q_3-q_4)+(q_4-1)e^{i\varphi_4}][(q_1-q_2)+(q_2-1)e^{i\varphi_1}]\}. \quad (34)$$

(*b*) A disordered structure constituted by layers of the same type, which may follow one on another by two possible translations ($\mathbf{t}_1$ and $\mathbf{t}_2$) with $s=2$, will be considered now.

This statistical model has been applied to a number of cases (Wilson, 1942; Hendricks & Teller, 1942; Mering, 1950; Kakinoki & Komura, 1954*b*). The new general formula which will be given here, in which the values of $\mathbf{t}_1$ and $\mathbf{t}_2$ are completely unspecified, has been applied in particular by Cesari, Morelli & Favretto (1961) to the structural study of some natural silicates.

In this case also the complexion of $(s-1)$ neighbouring translations reduces to the two translations themselves. We will indicate by:

q_1 the probability $p(11)$,
$(1-q_1)$ the probability $p(12)$,
q_2 the probability $p(22)$,
$(1-q_2)$ the probability $p(21)$.

By solving the system (16), we obtain, for the frequencies of occurrence of the two translations:

$$f(1) = \frac{1-q_2}{2-(q_1+q_2)};\ f(2) = \frac{1-q_1}{2-(q_1+q_2)} \quad (35)$$

while the $\mathbf{F}$ and $\mathbf{Q}$ matrices have the following form:

$$\mathbf{F} = \begin{vmatrix} f(1) & 0 \\ 0 & f(2) \end{vmatrix};\quad \mathbf{Q} = \begin{vmatrix} q_1e^{-i\varphi_1} & (1-q_1)e^{-i\varphi_2} \\ (1-q_2)e^{-i\varphi_1} & q_2e^{-i\varphi_2} \end{vmatrix} \quad (36)$$

We may now obtain the average diffracted intensity by the expression (18). The final result is:

$$I_{Av} = VV^* \times \frac{(q_1+q_2)(1-q_1)(1-q_2)[1-\cos(\varphi_1-\varphi_2)]}{[2-(q_1+q_2)]\{[1-(q_1+q_2)+(q_1^2+q_2^2+q_1q_2)] + [q_2-q_1-q_2(q_1+q_2)]\cos\varphi_1+[q_1-q_2-q_1(q_1+q_2)] \times\cos\varphi_2-[1-(q_1+q_2)]\cos(\varphi_1+\varphi_2)+q_1q_2 \times\cos(\varphi_1-\varphi_2)\}}. \quad (37)$$

If $q_1=1-q_2=1-\alpha$(put), $\varphi_1=\varphi-(2\pi/3)(h-k)$ and $\varphi_2=\varphi+(2\pi/3)(h-k)$ where $\varphi=2\pi l$, l being the continuous variable along c^* corresponding to one layer thickness, equation (37) becomes

$$I_{Av} = VV^* \frac{3\alpha(1-\alpha)}{2-3\alpha+3\alpha^2\pm\sqrt{3}(1-2\alpha)\sin\varphi+\cos\varphi}; \quad h-k=3n\pm1$$

which is the same as the result obtained by Paterson (1952) where $s=1$.

If $q_1=q_2=\alpha$(put), and φ_1 and φ_2 are the same as before, equation (37) becomes

$$I_{Av} = VV^* \frac{3\alpha(1-\alpha)}{4-8\alpha+5\alpha^2+4\alpha^2\cos\varphi-4(1-2\alpha)\cos^2\varphi}$$

which is the same as the result obtained by Wilson (1942), Hendricks & Teller (1942) and Kakinoki & Komura (1945*b*).

In Fig. 2, as an example, some curves are reproduced (by kind permission of Cesari *et al.*, 1962), showing the values of the function I_{Av}/VV^* against **s**, for appropriate values of the physical parameters. These curves have been calculated by the formula (37), in order to examine the type of disorder occurring in some clay minerals of the illite–montmorollonite type.

(*c*) The third case which will be considered now is given by a structure constituted by layers of the same kind, with hexagonal or trigonal symmetry. The layers may follow one on another by the two equivalent translations: $\mathbf{t}_1=\frac{2}{3}\mathbf{a}+\frac{1}{3}\mathbf{b}+\mathbf{c}$, $\mathbf{t}_2=\frac{1}{3}\mathbf{a}+\frac{2}{3}\mathbf{b}+\mathbf{c}$, where **a** and **b** are the repetition vectors of the bidimensional unit cell of the layer (Fig. 1) and **c** is the vector component perpendicular to the layers: the order of influence s is equal to 3. This statistical model, that may be applied in particular to a wide class of close-packed structures, has been already considered by Jagodzinski (1949*b*) and Kakinoki & Komura (1954*b*) with a different mathematical formulation; however, no compact formula for I_{Av} has been given until now.

The complexions of $2(=s-1)$ adjacent translations are 4, and will be labelled by the symbols I, II, III, and IV:

$$\text{I} \equiv (11);\ \text{II} \equiv (12);\ \text{III} \equiv (21);\ \text{IV} \equiv (22), \quad (38)$$

1 and 2 being the indices of the vectors $\mathbf{t}_1$ and $\mathbf{t}_2$.

By making use of symmetry considerations, we obtain the following relations among probability parameters:

$$p(\text{I}\ \ \text{I})=p(\text{IV IV})=1-\sigma;\ \ p(\text{I}\ \ \text{II})=p(\text{IV III})=\sigma;$$
$$p(\text{II III})=p(\text{III II})=1-\tau;\ \ p(\text{II IV})=p(\text{III}\ \ \text{I})=\tau. \quad (39)$$

Resolution of the system (16) leads to the following values for the frequencies of the four complexions:

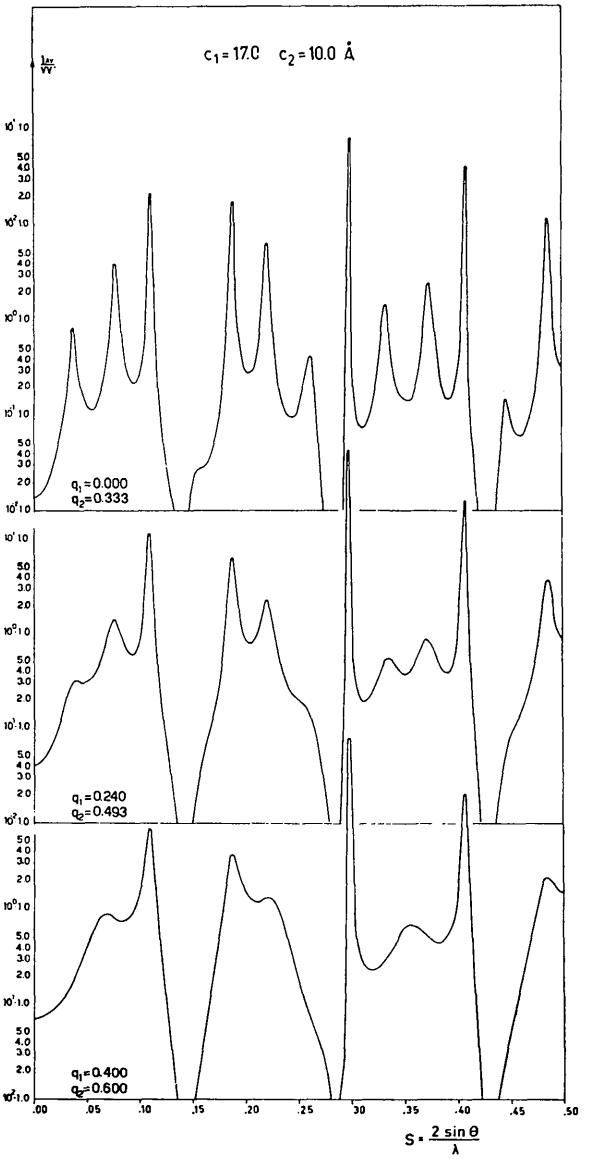


Fig. 2. Plots showing the interference function I_{AV}/VV^* against $\mathbf{s}(|\mathbf{s}|=2\sin\theta/\lambda)$ for a system constituted by two types of layers of different thickness (c_1 and c_2), and practically equal values of the layer form factor V. It is intended that the reciprocal vector **s** points perpendicularly to the layers. q_1 and q_2 represent the probabilities that the first- and second-type layers respectively follow layers of the same type. Formula (37) has been used (by kind permission of M. Cesari).

$$f(\mathrm{I})=f(\mathrm{IV})=\frac{\tau}{2(\sigma+\tau)}\,;\quad f(\mathrm{II})=f(\mathrm{III})=\frac{\sigma}{2(\sigma+\tau)} \tag{40}$$

and the **F** and **Q** matrices result:

$$\mathbf{F}=\begin{vmatrix} f(\mathrm{I}) & 0 & 0 & 0 \\ 0 & f(\mathrm{II}) & 0 & 0 \\ 0 & 0 & f(\mathrm{III}) & 0 \\ 0 & 0 & 0 & f(\mathrm{IV}) \end{vmatrix};$$

$$\mathbf{Q}=\begin{vmatrix} (1-\sigma)e^{-i\varphi_1} & \sigma e^{-i\varphi_2} & 0 & 0 \\ 0 & 0 & (1-\tau)e^{-i\varphi_1} & \tau e^{-i\varphi_2} \\ \tau e^{-i\varphi_1} & (1-\tau)e^{-i\varphi_2} & 0 & 0 \\ 0 & 0 & \sigma e^{-i\varphi_1} & (1-\sigma)e^{-i\varphi_2} \end{vmatrix}. \tag{41}$$

We may now use the expression (18), under the convergence condition Det $(\mathbf{E}-\mathbf{Q})\neq 0$. In particular, indicating by h, k and l the scalar products **a**.**s**, **b**.**s**, **c**.**s** respectively, the above condition is always satisfied, for non-particular values of σ and τ, in correspondence to those values of **s** for which $h-k=3n\pm 1$. Confining our attention to these values, we get, from (18):

$$\begin{aligned} I_{\mathrm{Av}} &= VV^*\frac{3\sigma\tau(2-\sigma-\tau)}{\sigma+\tau} \\ &\times\frac{[1+(1-\sigma-\tau)^2]+(1-\sigma-\tau)\cos 2\pi l}{[1+(1-\sigma)^2+(2-\sigma-\tau)^2(\sigma-\tau)^2+(1-\tau)^2(1-\sigma-\tau)^2} \\ &+(1-\sigma-\tau)^4]+2[(1-\sigma)+(1-\sigma)(2-\sigma-\tau)(\tau-\sigma) \\ &+(2-\sigma-\tau)(\tau-\sigma)(1-\tau)(\sigma+\tau-1)-(1-\tau) \\ &\times(\sigma+\tau-1)^3]\cos 2\pi l+2[(2-\sigma-\tau)^2(\tau^2-\sigma^2) \\ &+(1-\tau)(1-\sigma)(\sigma+\tau-1)]\cos 2\pi 2l+2(\sigma+\tau-1) \\ &\times[1-\tau-(1-\sigma)(\sigma+\tau-1)]\cos 2\pi 3l-2(\sigma+\tau-1)^2 \\ &\times\cos 2\pi 4l\,. \end{aligned} \tag{42}$$

In Fig. 3, as an example, some curves have been reported of the function I_{Av}/VV^* against 1, calculated by the formula (42) with different values of σ and τ.

By using the present theory, the author has carried out the calculation of the average diffracted intensity for some other models of monodimensionally disordered structures; the results have already been reported in another paper (Allegra, 1961*c*).

The author thanks Dr Kakinoki for very helpful discussions and important suggestions. He also acknowledges the constant help received from Prof. P. Corradini, of the University of Naples, Italy and the encouragement received from Prof. G. Natta.

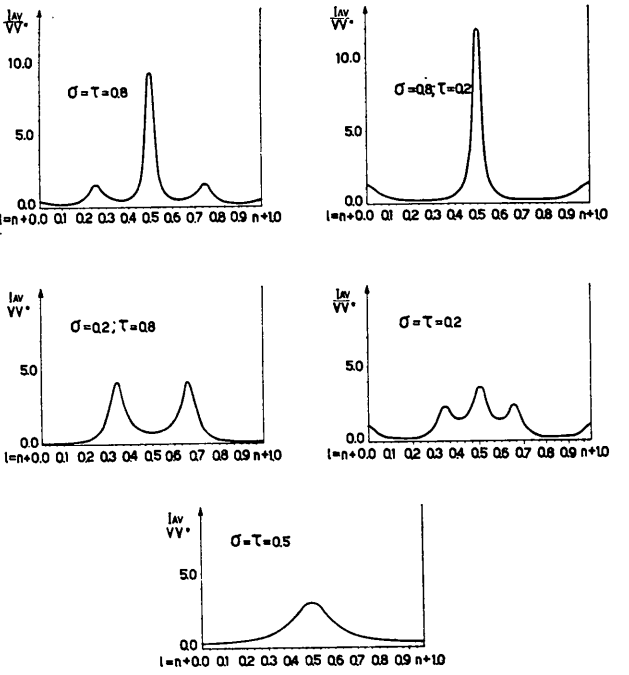


Fig. 3. Plots of the interference function I_{AV}/VV^*, against l, calculated by the formula (42) for different pairs of values of σ and τ.

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