Acta Cryst. (1979). A**35**, 803–810

Application of the Matrix Method to the Calculation of Diffuse Scattering in Linearly Disordered Crystals

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(*Received* 6 *November* 1978; *accepted* 2 *April* 1979)

Abstract

The matrix method for the calculation of diffuse scattering has been applied to linearly disordered crystals. Although it is shown that the matrix method and the difference formula are equivalent for equal length cells, the algebraic and computational advantages of the matrix method are stressed and are illustrated by the example of short-range order in hollandite, $K_{1\cdot54}Mg_{0\cdot77}Ti_{7\cdot23}O_{16}$.

1. Introduction

Recent interest in highly conducting molecular systems has resulted in the synthesis of many new quasi one-dimensional crystalline materials (Keller, 1977; Miller & Epstein, 1976; Marks, 1978). Many of these systems exhibit diffuse scattering characteristic of linear disorder (Endres, Keller, Megnamisi-Belombe, Moroni, Pritzkow, Weiss & Comès, 1976; Smith & Luss, 1977; Huml, 1967; Herbstein & Kapon, 1972; Cowie, Gleizes, Grynkewich, Kalina, McClure, Scaringe, Teitelbaum, Ruby, Ibers, Kannewurf & Marks, 1979). It is therefore necessary to interpret the diffuse as well as the Bragg scattering in order to understand fully the structures of these new systems. The theoretical framework for the calculation of the diffraction of X-rays from systems displaying planar disorder has received a great deal of attention. The two general methods developed are the difference equation (Jagodzinski, 1949*a*,*b*,*c*; Wilson, 1942) and the matrix method (Kakinoki & Komura, 1952; Hendricks & Teller, 1942; Takaki & Sakurai, 1976). However, there have been relatively few general discussions in the literature of linear disorder (Guinier, 1963) and none, as far as we know, of the application of the matrix method to such systems. In the present paper we treat by the matrix method the problem of diffuse scattering from a linearly disordered crystal and point out in several examples the calculational advantages of the method over the difference equation.

We restrict ourselves to systems where the probabilities of finding a particular atom or group of atoms in position $n + 1$ depends at most on the particular atom or group at position n. Much of the work on the matrix method for planar disorder (Takaki & Sakurai, 1976 and references therein) has centered on a formalism where finding a particular layer to follow the nth also depends on the $n - 1$ and more remote neighbors; this sort of extension is also possible for the linear case.

2. Derivation of the general formula

Consider a crystal to be made up of a series of parallel columns; the two primitive intercolumn vectors are $\mathbf{a}$ and $\mathbf{b}$. The vector from the origin to the kth atom in the nth column is

$$\mathbf{R}_{n,k} = n_1\,\mathbf{a} + n_2\,\mathbf{b} + x\,\mathbf{a} + y\mathbf{b} + Z_{n,k}\,\hat{\mathbf{c}},$$

where $\hat{\mathbf{c}}$ is a unit vector in the column direction, n refers to the two whole numbers n_1, n_2 and x, y are the usual fractional coordinates. Letting $\mathbf{s} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\hat{\mathbf{c}}^*$ be the scattering vector, α, β, γ being continuous variables in reciprocal space, the diffracted field from all atoms in the crystal becomes

$$\varepsilon = \sum_n \exp\,[2\pi i\mathbf{s}\,.\,(n_1\,\mathbf{a} + n_2\,\mathbf{b} + x\,\mathbf{a} + y\mathbf{b})] \times \sum_i f_{n,i} \exp\,[2\pi i\mathbf{s}\,.\,\hat{\mathbf{c}}Z_{n,i}],$$

where $f_{n,i}$ is the atomic scattering factor. If we define the structure factor of the nth column as $C_n = \sum_n \sum_i f_{n,i} \exp\,(2\pi i\mathbf{s}\,.\,\hat{\mathbf{c}}Z_{n,i})$, the expression for the intensity is:

$$I(\mathbf{s}) = \varepsilon\varepsilon^* = \sum_n \sum_{n'} \exp\,[-2\pi i\mathbf{s}\,.\,(\mathbf{t}_{n'} - \mathbf{t}_n)]\,C_n\,C^*_{n'}, \quad (1)$$

where $\mathbf{t}_n = n_1\,\mathbf{a} + n_2\,\mathbf{b}$. If all terms in the double sum that contain the vector $\mathbf{t}_m = (n'_1 - n_1)\mathbf{a} + (n'_2 - n_2)\mathbf{b} = m_1\,\mathbf{a} + m_2\,\mathbf{b}$ are grouped together, (1) becomes:

$$I(\mathbf{s}) = \sum_m \left(\sum_n C_n\,C^*_{n+m}\right) \exp\,(-2\pi i\mathbf{s}\,.\,\mathbf{t}_m). \quad (2)$$

0567-7394/79/050803-08$01.00

For a sufficiently large number of terms, the sum over n becomes $K_m\langle C_n C^*_{n+m}\rangle$, where K_m is the number of terms in the sum and is numerically equal to $AA(\mathbf{t}_m)/\sigma$. Here, A is the cross-sectional area of the crystal, $\sigma = \mathbf{a}.\mathbf{b}$ and $AA(\mathbf{t}_m)$ is the area common to the crystal and an identical crystal displaced by vector $\mathbf{t}_m$. For a parallelepiped crystal with N_1 cells along $\mathbf{a}$ and N_2 cells along $\mathbf{b}$, (2) becomes:

$$I(\mathbf{s}) = \sum_{m_1}\sum_{m_2}(N_1-|m_1|)(N_2-|m_2|)\langle C_n C^*_{n+m}\rangle \times \exp(-2\pi i\mathbf{s}.\mathbf{t}_m). \tag{3}$$

If we let $\langle C_n C^*_{n+m}\rangle = |\langle C_n\rangle|^2 + \Omega_m$, (3) becomes:

$$\begin{aligned} I(\mathbf{s}) = {} & |\langle C_n\rangle|^2 \sum_{m_1}\sum_{m_2}(N_1-|m_1|)(N_2-|m_2|) \\ & \times \exp(-2\pi i\mathbf{s}.\mathbf{t}_m) \\ & + \sum_{m_1}\sum_{m_2}\Omega_m(N_1-|m_1|)(N_2-|m_2|) \\ & \times \exp(-2\pi i\mathbf{s}.\mathbf{t}_m). \end{aligned} \tag{4}$$

The sum over m can be evaluated explicitly for the first term and (4) becomes:

$$\begin{aligned} I(\mathbf{s}) = {} & |\langle C_n\rangle|^2 \left\{\frac{\sin^2(\pi\alpha N_1)}{\sin^2(\pi\alpha)}\right\}\left\{\frac{\sin^2(\pi\beta N_2)}{\sin^2(\pi\beta)}\right\} \\ & + \sum_{m_1}\sum_{m_2}(N_1-|m_1|)(N_2-|m_2|)\Omega_m \\ & \times \exp(-2\pi i\mathbf{s}.\mathbf{t}_m). \end{aligned} \tag{5}$$

The first term in (5) is small unless α and β are integral and then it expresses Bragg's law for the *ab* plane. The quantity $|\langle C_n\rangle|^2$ is an implicit function of γ, and the interference along the average column (if any) will determine the c spacing. The second term in (5) contains all of the information on the diffuse scattering. In this paper we shall be concerned with the evaluation of this term when there is no correlation between columns. In this instance, $\langle C_n C^*_{n+m}\rangle = |\langle C_n\rangle|^2$ for $m \neq 0$, and the diffuse term in (5) is

$$I_2(\mathbf{s}) = N_1 N_2\{\langle C_n C^*_n\rangle - \langle C_n\rangle\langle C^*_n\rangle\} = N_1 N_2 \Omega_0. \tag{6}$$

Since Ω_0 is not a function of α or β (neglecting the λ^{-1} $\sin\theta$ dependence), experimentally we expect planes of diffracted intensity, a result which is well-known (Guinier, 1963). We now proceed to evaluate the two terms in (6).

2.1. *Evaluation of* $\langle C_j C_j^*\rangle$

Suppose that each of the columns C_j can be constructed by stacking N shorter segments linearly. Let there be R types of shorter segments each with a specified length $|\mathbf{c}_\nu|$, $\nu = 1, 2, \ldots R$, containing q_ν atoms. The structure factor for a segment (hereafter called a cell) is

$$F_\nu = \sum_{j=1}^{q_\nu} f_{\nu,i}\exp(2\pi i\mathbf{s}.\mathbf{c}_\nu Z_{\nu,j}), \quad \nu = 1, 2, \ldots R.$$

The structure factor of a column (neglecting a possible net phase shift) is

$$C = \sum_{n=1}^{N} F_{u_n}\exp(2\pi i\Phi_n), \tag{7}$$

where $u_n = 1, 2, 3, \ldots R$, Φ_n is the phase shift resulting from the preceding $n-1$ cells, and N is the number of cells. Letting $\varphi_\nu = 2\pi\gamma\, c_\nu$, $\nu = 1, 2, \ldots R$, we see that $\Phi_n = \sum_{l=1}^{n-1}\varphi_{u_l}$ and therefore Φ_n depends on the lengths of the preceding $n-1$ cells. With (7), we have

$$\langle C_j C_j^*\rangle = \left\langle\sum_n\sum_{n'} F_{u_n}F^*_{u_{n'}}\exp(i\Phi_n)\exp(i\Phi_{n'})\right\rangle. \tag{8}$$

If we group all terms in the sum with the phase Φ_m, $\Phi_{n'} = \Phi_n + \Phi_m$, then (8) becomes

$$\langle C_j C_j^*\rangle = \sum_n\sum_m\langle F_{u_n}F^*_{u_{n+m}}\exp(-i\Phi_m)\rangle. \tag{9}$$

If we denote by $I^{(m)}$ an expression for $\langle F_{u_n}\, F_{u_{n+m}}$ $\exp(-i\Phi_m)\rangle$ which is independent of n, then (9) may be written

$$\langle C_j C_j^*\rangle = \sum_{m=-(N-1)}^{N-1}(N-|m|)I^{(m)}. \tag{10}$$

Derivation of an expression for $I^{(m)}$ closely follows that given by Kakinoki & Komura (1952) for planar disorder. The result is simply stated here.

Let the probability of finding the nth cell in a column of type s, $s = 1, 2, \ldots R$, be ε_s (the existence probability). Let P_{st} be the probability that the $(n+1)$th cell in a column is of type t, *given that* the nth cell is of type s. If $P_{st} \neq \varepsilon_t$, the cells which make up the column are said to be correlated. If we define the following $R \times R$ matrices:

$$\mathsf{E} = \begin{pmatrix} \varepsilon_1 & 0 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & \varepsilon_2 & 0 & 0 & \cdot & \cdot & 0 \\ \vdots & & & & & & \vdots \\ 0 & \cdots & \cdots & \cdots & \cdots & \cdots & \varepsilon_R \end{pmatrix},$$

$$\mathsf{F} = \begin{pmatrix} F_1^*F_1 & F_1^*F_2 & \cdots & F_1^*F_R \\ F_2^*F_1 & F_2^*F_2 & \cdots & F_2^*F_R \\ \vdots & & & \vdots \\ F_R^*F_1 & F_R^*F_2 & \cdots & F_R^*F_R \end{pmatrix},$$

$$\mathsf{P}=\begin{pmatrix} P_{11} & P_{12} & \cdots & P_{1R} \\ P_{21} & P_{22} & \cdots & P_{2R} \\ \vdots & & & \vdots \\ P_{R1} & \cdots & \cdots & P_{RR} \end{pmatrix},$$

$$\Phi=\begin{pmatrix} e^{-i\varphi_1} & 0 & 0 & 0 & \cdot & \cdot & \cdot & 0 \\ 0 & e^{-i\varphi_2} & 0 & \cdot & \cdot & \cdot & \cdot & 0 \\ \vdots & & & & & & & \vdots \\ 0 & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & e^{-i\varphi_R} \end{pmatrix},$$

$$\mathsf{Q}=\Phi\mathsf{P}. \tag{11}$$

Then,

$$I^{(m)}=\mathrm{Tr}\,\mathsf{FEQ}^m, \tag{12}$$

where for the special case, $m=0$,

$$I^{(0)}=\mathrm{Tr}\mathsf{FE}. \tag{12a}$$

In (12), matrix products are implied and $\mathsf{Q}^m=\mathsf{Q}.\mathsf{Q}.\mathsf{Q}$, m times. With (12), (10) becomes:

$$\langle C_j C_j^*\rangle = N\mathrm{Tr}\mathsf{FE}+\sum_{m=1}^{N}(N-m)\mathrm{Tr}\mathsf{FEQ}^m+\text{conj.} \tag{13}$$

If $(\Pi-\mathsf{Q})$, where Π is the unit matrix, is not singular ($|\Pi-\mathsf{Q}|\neq 0$), the sum over m can be performed in general, and (13) becomes:

$$\langle C_j C_j^*\rangle = N\mathrm{Tr}\mathsf{FE}+N\mathrm{Tr}\mathsf{FEQ}(\Pi-\mathsf{Q})^{-1} + \mathrm{Tr}\mathsf{FE}(\mathsf{Q}^{N+1}-\mathsf{Q})(\Pi-\mathsf{Q})^{-2}+\text{conj}, \tag{14}$$

where $\mathsf{Q}^{-2}=\mathsf{Q}^{-1}.\mathsf{Q}^{-1}$.

2.2. *Evaluation of* $\langle C_j\rangle\langle C_j^*\rangle$

Except for a phase shift, the structure factor of the jth column is given by (7). Let a column begin with a certain cell type, s. If there are n_s phase shifts possible for each cell of type s, then let these phase shifts be denoted $\psi_{s,j}$, $j=1,2,\ldots,n_s$, $s=1,2,\ldots,R$. Let the probability that the column experiences a shift of $\psi_{s,j}$ be $\mu_{s,j}$, then $\sum_{j=1}^{m_s}\mu_{s,j}=1$ and $\sum_{j=1}^{n_s}\mu_{s,j}\,\psi_{s,j}=\Psi_s$. The probability of finding a column with a phase shift $\Psi_{s,j}$ with the specific sequence of N cells being $F_s\,F_{u_1}\,F_{u_2}\,F_{u_3}\ldots F_{u_{N-1}}$ is:

$$\mu_{k,s}A_{su}=\mu_{k,s}\,\varepsilon_s\,P_{su_1}\,P_{u_1u_2}\ldots P_{u_{N-2},u_{N-1}}.$$

In addition to the phase shifts $\psi_{s,j}$, we include an addition set of phase shifts Λ_j, which do not depend on the particular type of beginning cell. Since the Λ_j can be averaged independently, the contribution of a single column to $\langle C\rangle$ becomes

$$\langle\Lambda\rangle A_{s,n}\,\Psi_s[F_s+F_{u_1}\exp(-i\varphi_s)+\ldots]. \tag{15}$$

Summing (15) over all s and u yields $\langle C\rangle$, which can be written in expanded form as

$$\langle\Lambda\rangle\Big\{\sum_s\sum_{u_1}\ldots\sum_{u_{N-1}}A_{su}\,\psi_s\,F_s+\sum_s\sum_{u_1}\ldots\sum_{u_{N-1}}A_{su}\,\psi_s\,F_{u_1} \times\exp(-i\varphi_s)+\ldots+\sum_s\sum_{u_1}\ldots\sum_{u_{N-1}}A_{su}\,\psi_s\,F_{u_{N-1}} \times\exp[-i(\varphi_s+\varphi_{u_1}+\ldots+\varphi_{u_{N-2}})]\Big\}. \tag{16}$$

The first sum in (16) is

$$\langle\Lambda\rangle\Big\{\sum_s\sum_{u_1}\sum_{u_2}\ldots\sum_{u_{N-1}}F_s\,\varepsilon_s\,\psi_s\,P_{su_1}\,P_{u_1u_2}\ldots P_{u_{N-2},u_{N-1}}\Big\} =\langle\Lambda\rangle\langle F_s\,\Psi_s\rangle, \tag{17}$$

since $\sum_j P_{ij}=1$.

If we define the following $R\times R$ matrix,

$$\mathsf{V}=\begin{pmatrix} F_1\,\Psi_1 & F_1\,\Psi_2 & \ldots & F_1\,\Psi_R \\ F_2\,\Psi_1 & F_2\,\Psi_2 & \ldots & F_2\,\Psi_R \\ \vdots & & & \vdots \\ F_R\,\Psi_1 & \cdots & \cdots & F_R\,\Psi_R \end{pmatrix}, \tag{18}$$

(17) becomes $\langle\Lambda\rangle$TrVE. Similarly, the general expression for the $(k+1)$th term in (16) is:

$$\sum_s\sum_{u_1}\ldots\sum_{u_k}\Psi_s\,F_{u_k}\exp[-i(\varphi_s+\varphi_{u_1}+\ldots+\varphi_{u_{k-1}})] \times\varepsilon_s\,P_{su_1}\,P_{su_2}\ldots P_{u_{R-1}}\,P_{u_R}, \tag{19}$$

since the sums over u_{k+1}, $u_{k+2}\ldots u_{N-1}$ are all unity. In terms of the matrix elements of Q and VE (equations 11, 18), (19) becomes

$$\langle\Lambda\rangle\Big\{\sum_s\sum_{u_1}\sum_{u_2}\cdots\sum_{u_k}(\mathsf{VE})_{u_{k,s}}\,\mathsf{Q}_{su_1}\,\mathsf{Q}_{u_1u_2}\ldots\mathsf{Q}_{u_{k-1}u_k}\Big\},$$

which by analogy with (12*a*) is:

$$\langle\Lambda\rangle\mathrm{Tr}(\mathsf{VEQ}^k). \tag{20}$$

With (18) and (20), $\langle C\rangle$ becomes:

$$\langle C\rangle=\langle\Lambda\rangle\Big\{\mathrm{Tr}(\mathsf{VE})+\sum_{k=1}^{N-1}\mathrm{Tr}(\mathsf{VEQ}^k)\Big\} \tag{21}$$

and

$$\langle C\rangle\langle C^*\rangle=\langle\Lambda\rangle\langle\Lambda^*\rangle\Big\{\mathrm{Tr}(\mathsf{VE}) +\sum_{k=1}^{N-1}\mathrm{Tr}(\mathsf{VEQ}^k)\Big\}\{\text{conj}\}. \tag{22}$$

In a similar manner to (14), if $|\mathsf{Q}-\Pi|\neq 0$:

$$\langle C\rangle=\langle\Lambda\rangle[\mathrm{Tr}\mathsf{VE}+\mathrm{Tr}\mathsf{VEQ}(\mathsf{Q}^{N-1}-\Pi)(\mathsf{Q}-\Pi)^{-1}]. \tag{23}$$

2.3. *Matrix formulation of the diffuse scattering from a linearly disordered crystal with no correlation between chains*

With (13), (22), and (6), the expression for the diffuse intensity becomes

$$I_2(\mathbf{s}) = N\mathrm{Tr(FE)} + \sum_{m=1}^{N-1} (N-m)\mathrm{TrFEQ}^m + \mathrm{conj}$$
$$- \langle \Lambda \rangle \langle \Lambda^* \rangle \left\{ \mathrm{Tr(VE)} + \sum_{m=1}^{N-1} \mathrm{TrVEQ}^m \right\} \{\mathrm{conj}\}. \tag{24}$$

If the determinant, $|\Pi - \mathrm{Q}|$, is not equal to zero, the sums over m in (24) can be taken explicitly and from (14) and (23) we have,

$$\begin{aligned} I_2(\mathbf{s}) = {} & N\mathrm{TrFE} + N\mathrm{TrFEQ}(\Pi - \mathrm{Q})^{-1} \\ & + \mathrm{TrFE}(\mathrm{Q}^{N+1} - \mathrm{Q})(\Pi - \mathrm{Q})^{-2} + \mathrm{conj} \\ & - \{\langle \Lambda \rangle [\mathrm{TrVE} + \mathrm{TrVEQ}(\mathrm{Q}^{N-1} - \Pi) \\ & \times (\mathrm{Q} - \Pi)^{-1}]\}\{\mathrm{conj}\}. \end{aligned} \tag{25}$$

3. The connection between the matrix method and the difference formula

If for each cell type s, $c_s = n_s c$, where n_s is an integer, it is possible to fragment each cell into n_s subcells and thus, $e^{-i\varphi_s} = e^{-i\varphi}$ for all s. The difference equation (Jagodzinski, 1946*a*,*b*,*c*; Wilson, 1942) for the diffuse intensity can then be written as follows:†

$$\begin{aligned} I_2(\mathbf{s}) = {} & \sum_{m=-N}^{N} \langle F_n F^*_{n+m} \rangle (N - |m|) e^{-im\varphi} \\ & - \langle \Lambda \rangle \langle \Lambda^* \rangle \langle \Psi \rangle \langle \Psi^* \rangle \langle F \rangle \langle F^* \rangle \\ & \times \sum_{m=-N}^{N} (N - |m|) e^{-im\varphi}. \end{aligned} \tag{26}$$

Let us write (24) symbolically as

$$I_2(\mathbf{s}) = A - BB^*.$$

It has been shown by Kakinoki & Komura (1952) that

$$\langle F_n F^*_{n+m} \rangle = \mathrm{TrFEP}^m, \tag{27}$$

and therefore putting $\Phi = e^{-i\varphi}\,\Pi$, the first sum in (26) becomes identical with the A term in (24). Also, since multiplication by the unit matrix is commutative, the B term in (24) becomes

$$\mathrm{TrVEQ}^m = e^{im\varphi}\, \mathrm{Tr}\Pi\mathrm{VEP}^m. \tag{28}$$

If we define the diagonal $R \times R$ matrix

$$\mathrm{V}_0 = \begin{pmatrix} F_1 \Psi_1 & 0 & 0 & \cdots & 0 \\ 0 & F_2 \Psi_2 & 0 & \cdots & 0 \\ \vdots & 0 & & \ddots & \vdots \\ 0 & \cdots & \cdots & \cdots & F_r \Psi_n \end{pmatrix},$$

it can be seen that $\mathrm{V}_0 \mathrm{M} = \mathrm{V}$, where M is an $R \times R$ matrix with all elements equal to one. Kakinoki & Komura (1952) have shown that $\mathrm{MEP}^n = \mathrm{ME}$. With this, (28) is

$$\mathrm{TrVEQ}^m = e^{-im\varphi}\, \mathrm{TrVE}. \tag{29}$$

With (28), the BB^* term in (24) can be rearranged to be identical with the second term in (25). Hence the difference formula (26) is identical with the matrix formulation (24) for all $\varphi_s = \varphi$. However, the labor involved in using (26) without the aid of (27) is often prohibitive, since for each problem of interest recursion relationships must be derived for the $\langle F_n F^*_{n+m} \rangle$. In final form these must give the same result as (27). Moreover, the matrix equation in the form of (24) or (25) can obviously be incorporated into a general computer program, thus allowing one to test with relative ease a large number of models.

4. The special case of no correlation between the cells in a column

If the cells making up any column are not correlated (*i.e.* $\mathrm{P}_{st} = \varepsilon_t$), the A term in (24) becomes (Kakinoki & Komura, 1952):

$$\begin{aligned} \langle C_j C_j^* \rangle = N \Bigg\{ & \langle F_s F_s^* \rangle + \frac{\langle F_s^* \rangle \langle F_s \varphi_s \rangle}{1 - \langle \varphi \rangle} \\ & + \frac{\langle F_s \rangle \langle F_s^* \varphi_s^* \rangle}{1 - \langle \varphi_s^* \rangle} \Bigg\} \\ & + \langle F_s^* \rangle \langle F_s \varphi_s \rangle \frac{\langle \varphi_s \rangle^N - 1}{(1 - \langle \varphi_s \rangle)^2} \\ & + \langle F_s \rangle \langle F_s^* \varphi_s^* \rangle \frac{\langle \varphi_s^* \rangle^N - 1}{(1 - \langle \varphi_s^* \rangle)^2}, \end{aligned} \tag{30}$$

where

$$\begin{aligned} \langle F_s F_s^* \rangle &= \sum_{s=1}^{R} \varepsilon_s F_s F_s^*, \\ \langle F_s \rangle &= \sum_{s=1}^{R} \varepsilon_s F_s, \\ \langle \varphi_s \rangle &= \sum_{s=1}^{R} \varepsilon_s e^{-i\varphi_s}, \\ \langle F_s \varphi_s \rangle &= \sum_{s=1}^{R} \varepsilon_s F_s e^{-i\varphi_s}. \end{aligned} \tag{31}$$

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† In the conventional notation for the difference equation, $\langle F \rangle$ includes the phase shifts. Here we choose to define $\langle F \rangle = \sum_{s=1}^{R} \varepsilon_s F_s$.

Similarly, it can be shown that the B term in (24) may be written

$$\langle C\rangle = \langle \Lambda\rangle [\langle F_s F_s^*\rangle + \langle F_s\rangle\langle \Psi_s \varphi_s\rangle \left\{ \frac{\langle \varphi_s\rangle^{N-1} - 1}{\langle \varphi_s\rangle - 1} \right\},$$

where $\langle F_s \Psi_s\rangle = \sum_{s=1}^{R} \varepsilon_s \Psi_s$, $\langle \Psi_s \varphi_s\rangle = \sum_{s=1}^{R} \varepsilon_s \Psi_s e^{-i\varphi_s}$. (32)

From (30), (32), and (24) we obtain

$$I_2(\mathbf{s}) = N\left\{\langle FF^*\rangle + \frac{\langle F^*\rangle\langle F\varphi\rangle}{1-\langle\varphi\rangle} + \frac{\langle F\rangle\langle F^*\varphi^*\rangle}{1-\langle\varphi^*\rangle}\right\} + \frac{\langle F^*\rangle\langle F\varphi\rangle(\langle\varphi\rangle^N - 1)}{(1-\langle\varphi\rangle)^2} + \frac{\langle F\rangle\langle F^*\varphi^*\rangle(\langle\varphi^*\rangle^N - 1)}{(1-\langle\varphi^*\rangle)^2} - \langle\Lambda\rangle\langle\Lambda^*\rangle\left\{\langle F\Psi\rangle + \langle F\rangle\langle\Psi\varphi\rangle\frac{\langle\varphi\rangle^{N-1} - 1}{\langle\varphi\rangle - 1}\right\}\{\mathrm{conj}\}, \qquad (33)$$

where subscripts have been omitted. Except for the case $\langle\varphi\rangle = 1$, the terms with N as an exponent are of the order of unity, and for large N the diffuse scattering can be represented by the first term in curly brackets.

Let us consider the case $\langle\varphi\rangle = 1$. If at some $\gamma = \Gamma(\mathbf{s} = \alpha\mathbf{a} + \beta\mathbf{b} + \gamma\mathbf{c}^*)$, $\varphi_s = 2\pi\gamma c_s = 2\pi m_s$, where m_s is any integer, (33) becomes indeterminate. The limit of (33) as $\gamma \to \Gamma$ is:

$$I_2(\Gamma) = N^2\langle F\rangle\langle F^*\rangle + N(\langle FF^*\rangle - \langle F\rangle\langle F^*\rangle) - \langle\Lambda\rangle\langle\Lambda^*\rangle\{\langle F\Psi\rangle + \langle F\rangle\langle\Psi\rangle(N-1)\} \times \{\langle F^*\Psi^*\rangle + \langle F^*\rangle\langle\Psi^*\rangle(N-1)\}. \qquad (34)$$

If $R = 1$, and we are therefore dealing with ordered columns containing only one cell type, $\langle F\rangle = F$ and essentially all of the diffuse scattering is concentrated in the planes $\gamma = \Gamma$, and (34) reduces to:

$$I_2(\Gamma) = N^2 FF^*(1 - \langle\Lambda\rangle\langle\Lambda^*\rangle\,\Psi\Psi^*). \qquad (35)$$

If the cell lengths, c_s, implicitly contained in (33) are integral multiples of some length c, then (24) could be used instead with

$$\exp(-2\pi i\varphi_s) = \exp(-2\pi i\varphi) = \exp(-2\pi i\mathbf{s}.\mathbf{c}).$$

We illustrate this in the next section.

4.1. *A simple illustration*

Consider a simple case in which each column consists of a random mixture of two types of cells, I and II, with lengths c and $2c$, having one and two atoms, respectively (Fig. 1). For a column composed of these two cells, the average site to site distance is c; the average displacement is zero.

For this case the Bragg diffraction pattern will have a period $c^* = 1/c$. In the c direction the thermal motion of the one atom per cell will appear to be abnormally high owing to the displacements which form the diatomics in group II.

We now wish to apply (24) and (33) to this case and compare results. Intuitively, we expect the same result as (33) is a special case (no correlation between cells in a column) of (24). For (30) we have

$$\langle F\rangle = \varepsilon_{\mathrm{I}} F_{\mathrm{I}} + \varepsilon_{\mathrm{II}} F_{\mathrm{II}},$$

$$\langle\varphi\rangle = \varepsilon_{\mathrm{I}} \exp(-2\pi i\mathbf{s}.\mathbf{c}) + \varepsilon_{\mathrm{II}} \exp[-2\pi i\mathbf{s}.(2\mathbf{c})], \qquad (36)$$

$$\langle F\varphi\rangle = \varepsilon_{\mathrm{I}} F_{\mathrm{I}} \exp(-2\pi i\mathbf{s}.\mathbf{c}) + \varepsilon_{\mathrm{II}} \mathrm{F}_{\mathrm{II}} \exp[-2\pi i\mathbf{s}.(2\mathbf{c})],$$

where $\mathbf{s} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$, $F_{\mathrm{I}} = 1$, $F_{\mathrm{II}} = 2\cos[2\pi\mathbf{s}.\mathbf{c}(1-d)]$. As stated above, it is also possible to use (24) with all $\varphi_s = \varphi$. In order to do this, we consider cell II to be two cells each with length c and thus for all cells $\varphi = 2\pi i\mathbf{s}.\mathbf{c}$. The existence probabilities ε_1, ε_2, ε_3 for the individual atom approach can be expressed in terms of group existence probabilities as follows:

$$\varepsilon_1 = \varepsilon_{\mathrm{I}}/(\varepsilon_{\mathrm{I}} + 2\varepsilon_{\mathrm{II}}), \quad \varepsilon_2 = \varepsilon_3 = \varepsilon_{\mathrm{II}}/(\varepsilon_{\mathrm{I}} + 2\varepsilon_{\mathrm{II}}). \qquad (37)$$

The inverse relations are:

$$\varepsilon_{\mathrm{I}} = \varepsilon_1/(\varepsilon_1 + \varepsilon_2), \quad \varepsilon_{\mathrm{II}} = \varepsilon_2/(\varepsilon_1 + \varepsilon_2). \qquad (38)$$

The other necessary quantities for (24) are:

$$F_1 = 1, \quad F_2 = \exp(2\pi i\mathbf{s}.\mathbf{c}d), \quad F_3 = \exp(-2\pi i\mathbf{s}.\mathbf{c}d);$$

$$\varphi_j = 2\pi i\mathbf{s}.\mathbf{c}, \quad j = 1, 2, 3;$$

$$\langle\Lambda\rangle = 1, \quad \Psi_{\mathrm{I}} = 1, \quad \Psi_{\mathrm{II}} = \cos(2\pi\mathbf{s}.\mathbf{c});$$

$$\mathsf{Q}^m = \Pi e^{-im\varphi}\,\mathsf{P}^m.$$

The elements of P can be deduced from Fig. 1. Given that we are on atom 3, the probability that atom 2 will be the next atom is unity. Thus, $P_{32} = 1$, $P_{31} = P_{33} = 0$. Given that we are on atom 1 or 2 the probability that 1 will be the next atom is ε_{I}. Therefore, $P_{11} = P_{21} = \varepsilon_{\mathrm{I}}$

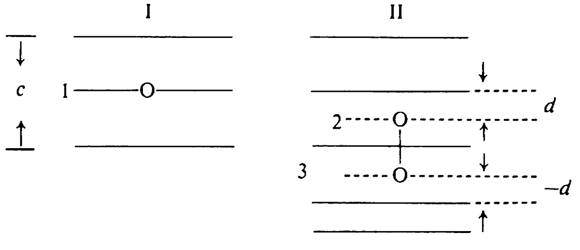

Fig. 1. Atomic and group labeling scheme for a linear lattice of mono- and diatomics.

and $P_{31} = 0$. Similarly, $P_{13} = P_{23} = \varepsilon_{\rm II}$ and $P_{33} = 0$. The probability matrix is then

$$\mathsf{P} = \begin{pmatrix} \varepsilon_{\rm I} & 0 & \varepsilon_{\rm II} \\ \varepsilon_{\rm I} & 0 & \varepsilon_{\rm II} \\ 0 & 1 & 0 \end{pmatrix}, \tag{40}$$

or from (38), (40) may be written

$$\mathsf{P} = \begin{pmatrix} \varepsilon_1/(\varepsilon_1+\varepsilon_2) & 0 & \varepsilon_2/(\varepsilon_1+\varepsilon_2) \\ \varepsilon_1/(\varepsilon_1+\varepsilon_2) & 0 & \varepsilon_2/(\varepsilon_1+\varepsilon_2) \\ 0 & 1 & 0 \end{pmatrix}.$$

Inspection of (40) reveals that $|\Pi - \mathsf{P}| = 0$ and therefore we cannot evaluate the sums in (24) explicitly [*e.g.* as in (25)]. As pointed out by Hendricks & Teller (1942), the evaluation of (24) then becomes very complex. However, the singularity of $|\Pi - \mathsf{P}|$ presents no practical difficulties, as (24) can be summed numerically on a digital computer for any case of interest.

It is possible to sum (20) in the present case for $\gamma = 0$. Here, Φ is the unit matrix, $\mathsf{F} = \mathsf{M}$, and $\mathrm{Tr}\mathsf{FEP}^n = \mathrm{Tr}\mathsf{MEP}^n = \mathrm{Tr}\mathsf{ME} = 1$. Thus, (24) becomes:

$$I_2(\gamma = 0) = N + 2\sum_{m=1}^{N-1}(N-m) - \left\{N + \sum_{m=1}^{N-1}\right\}^2 = 0. \tag{41}$$

This result is to be expected since it is well known that for purely displacive disorder there is no diffuse scattering around the origin (see, for example, Guinier, 1963).

On the other hand, in terms of the quantities in (30) we have $F_{\rm I} = 1$, $F_{\rm II} = 2$, and $\langle\varphi\rangle = 1$ at $\gamma = 0$ and (33) becomes $I_2(\gamma = 0) = N(\langle FF^*\rangle - \langle F\rangle\langle F^*\rangle) = N\varepsilon_{\rm I}\varepsilon_{\rm II}$, an obviously erroneous result for $\varepsilon_{\rm I}$ or $\varepsilon_{\rm II} \neq 0$. The origin of this problem is apparently the tacit assumption in (10) that each column contains the same number of cells. Of necessity, then, each column would contain a different number of atoms which is not the case we are treating. Yet (24) works because there is no distinction between the number of atoms and the number of cells. Application of (33) fails only when $\langle\varphi\rangle = 1$ (often these are the Bragg positions) and thus most of the scattering pattern is predicted correctly by the first term in (33). It is interesting to note that the limit of this first term in (33), which is

$$\lim_{\gamma\to\Gamma}\left[\langle FF^*\rangle + \frac{\langle F^*\rangle\langle F\varphi\rangle}{1-\langle\varphi\rangle} + \frac{\langle F\rangle\langle F\varphi^*\rangle}{1-\langle\varphi^*\rangle}\right] = \langle FF^*\rangle + \frac{\langle F\rangle\langle F^*\rangle\langle c_s^2\rangle - \langle c_s\rangle(\langle F\rangle\langle F^*c_s\rangle + \langle F^*\rangle\langle Fc_s\rangle)}{\langle c_s\rangle^2}, \tag{42}$$

gives the correct result for purely displacive disorder and $\gamma = 0$. We speculate that (42) may yield the correct result for all $\gamma = \Gamma$ since this is known to be the case for the corresponding term for planar disorder (Kakinoki & Komura, 1952). However, there are no practical difficulties as the troublesome points may be evaluated with the use of (24).

5. Comparisons with experiment

5.1. *Bis(benzoquinone dioximato)nickel* 0·5 *iodide*

In the quasi one-dimensional material $\mathrm{Ni(bqd)_2I_{0\cdot5}}$, (bqd = 1,2-benzoquinone dioximate), the iodine atoms reside in channels formed by the benzo groups of the metal complex (Endres, Keller, Moroni, & Weiss, 1975). This material exhibits diffuse scattering which has been interpreted in terms of disorder of the iodine chains (Endres *et al.*, 1976) which are shown to contain $\mathrm{I_3^-}$ ions. As a very simple illustration of how the formalism of the previous sections may be applied, we derive the scattering expression for this problem. The displacement scheme which leads to the formation of the triiodide ions is shown in Fig. 2. In addition to this displacement, each chain undergoes separate displacement of $\pm d_2$, as a unit. Since $R = 1$ and $e^{-i\varphi_s} = e^{-i\varphi}$ ($\varphi = 2\pi 3c$, where c is the average site to site distance), the diffuse scattering then is concentrated in the planes, $\Gamma = n/3c$. From Fig. 2, we have $F = (1 + 2\cos[2\pi l'(\frac{1}{3} - d_1)]$, where $l' = \Gamma/3c$ and d_1 is the fractional coordinate in the cell of length $3c$. Since relative to some fixed origin, any atom in the cell can be the first in the column,

$$\Psi = \tfrac{1}{3}[1 + \exp(-2\pi i l'/3) + \exp(+2\pi i l'/3)],$$

and since any chain must have an additional phase shift of $\pm d_2$,

$$\langle\Lambda\rangle = \tfrac{1}{2}[\exp(-2\pi i l' d_2) + \exp(+2\pi i l' d_2)].$$

With the above, (35) becomes

$$I_2(\Gamma)/N^2 = \{1 + 2\cos[2\pi l'(\tfrac{1}{3} - d_1)]\}^2 \times (1 - (\tfrac{1}{9})\{\cos^2[2\pi l' d_2]\}\{1 + 2\cos[2\pi l'(\tfrac{1}{3})]\}^2). \tag{43}$$

Endres *et al.* (1976), using a structure factor formalism, arrive at an expression which on rearrangement is identical with (43). However, (43) is much more easily obtained.

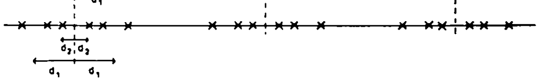

Fig. 2. Model with displaced symmetrical $\mathrm{I_3^-}$ groups for $\mathrm{Ni(bqd)_2I_{0\cdot5}}$. ○ Averaged position after forming $\mathrm{I_3}$ by displacement d_1. ⊗ New positions after shift of d_2. ○ Local atomic sites of one $\mathrm{I_3^-}$ unit (from Endres *et al.*, 1976).

5.2. *Short-range order in hollandite*

As an example of the applicability of the matrix method to more complex problems, we will consider a case in which there is more than one type of column cell.

The diffuse scattering arising from linear disorder in the material $K_{1\cdot54}Mg_{0\cdot77}Ti_{7\cdot23}O_{16}$, hollandite, has recently been interpreted in terms of a four-cell model with no correlations between cells (Beyeler, 1976). Although no details are given, the model was derived from the difference formula method.

The diffuse scattering in this material results from a combination of displacive and substitutional disorder in the potassium ion chain. The average site to site distance is 2·90 Å = c. The reported model involves four cells of length $3c$, $4c$, $5c$, and $6c$; the atomic displacement parameters and vacancy scheme for each cell are given in Fig. 3.

In terms of the parameters in (33) we have the following from Fig. 3:

$$c_1 = 3c, \quad c_2 = 4c, \quad c_3 = 5c, \quad c_4 = 6c;$$

$$\varepsilon_1 = 0{\cdot}15, \quad \varepsilon_2 = 0{\cdot}37, \quad \varepsilon_3 = 0{\cdot}37, \quad \varepsilon_4 = 0{\cdot}11;$$

$$F_1 = \exp[q(3/2 - x)] + \exp[q(5/2 + x)],$$

$$F_2 = \exp[q(3/2 - x)] + \exp[5q/2] + \exp[q(7/2 + x)],$$

$$F_3 = \exp[q(3/2 - x)] + \exp[q(5/2 - y)] + \exp[q(7/2 + y)] + \exp[q(9/2 + x)],$$

$$F_4 = \exp[q(3/2 - x)] + \exp[q(5/2 - z)] + \exp[7q/2] + \exp[q(9/2 + z)] + \exp[q(11/2 + x)],$$

where $q = -2\pi i\mathbf{s}\,.\,\mathbf{c}$.

Since $P_{ij} = \varepsilon_j$ for this case, we use (33) (neglecting terms of order one) to calculate all points $0 \le \gamma \le 2{\cdot}4$, except those for which $\langle\varphi\rangle = 0$, ($\gamma = 0$, $1c$, $2c$); these were calculated by (42). The resulting scattering pattern (actually the interference function) is compared with that reported by Beyeler (1976) in Fig. 4. The agreement with experiment is good. However, there is a great reduction in labor involved in application of the matrix method (equation 33) rather than the difference method (equation 26). Thus, the four model cells contain 17 atoms (a vacancy can be considered an atom with a form factor of zero), and to evaluate $\langle F_n F^*_{n+m}\rangle$ in (20) is equivalent to manipulating the elements of a 17 × 17 matrix (equation 27). With the use of the matrix formulation (equation 33), setting up the problem, as illustrated above, is trivial.

It should be pointed out that there are several qualitative differences between the scattering expected for an ordered linear lattice (equation 35) and for one in which $R > 1$, *e.g.* hollandite. The intensity for the case $R = 1$ is of the order of N^2, while that for $R > 1$ (and $e^{i\varphi_s}$ not all equal) is of the order of N. The profiles of the planes of diffracted intensity for $R = 1$ are a sharp function of γ, and can be indexed on a single repeat distance. For $R > 1$, the diffuse planes can sometimes be indexed approximately (see for example Beyeler, 1976), but are not periodic in the same sense as those for $R = 1$. The profiles predicted by (33) for $R > 1$ are often appreciably larger than those for the Bragg peaks. These conclusions are not peculiar to the case of linear disorder, but can be reached for disorder problems of any dimensionality (Guinier, 1963).

6. Conclusions

The number of linearly disordered systems involving well-defined groups of atoms is increasing rapidly (see, for example, Miller & Epstein, 1976). In particular, the use of iodine or bromine as an oxidant to bring about high conductivity in stacked metal systems is of increasing importance (Marks, 1978). Although spectroscopic methods provide some clues as to halogen species present in the chains (*e.g.* I^-, I_2, I_3^-, I_5^-) and hence to the formal oxidation state of the metal, diffuse scattering of X-rays is much more sensitive to the state of order of the chains. The matrix method offers some very real advantages over the difference equation method in the interpretation of diffuse scattering from these and other systems in which there is linear disorder. One advantage is the natural way in which rigid linear groups are incorporated into the

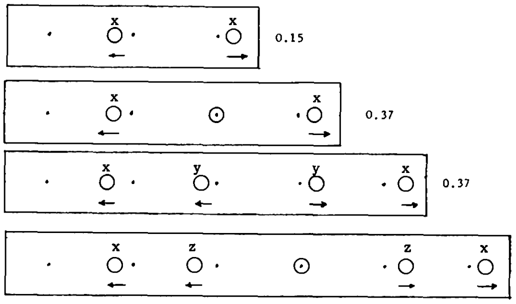

Fig. 3. Vacancy and displacement scheme for a four-cell model of the state of order of the potassium ion chain in hollandite. Group existence probabilities are also given.

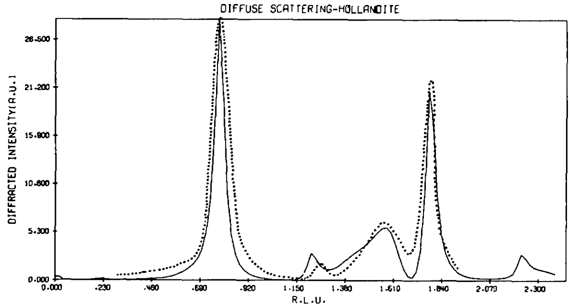

Fig. 4. Comparison of the experimental (···) and calculated (equation 33) interference function in hollandite. The experimental values are from Beyeler (1976).

formalism by allowing for cells of different lengths. This is in contrast to the difference equation method where each member of a group must be treated separately. Another advantage of the matrix method is its ready adaptability to computational methods. With the matrix method the diffuse scattering for a given model is readily calculated throughout reciprocal space. On a high speed computer the model is readily varied. Attempts are underway to refine such scattering models, based on the matrix method and diffuse X-ray data collected by counter methods.

This research was supported under the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR76-80847).

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Phase Extension and Refinement of Bence–Jones Protein Rhe (1·9 Å)

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(*Received* 17 *October* 1978; *accepted* 1 *May* 1979)

Abstract

A procedure is described whereby crude atomic coordinates obtained from a medium-resolution electron density map (~3–4 Å) with the aid of Watson–Kendrew models may be refined to native data of near-atomic resolution using only a limited subset of the data and non-interactive computer graphics. This refinement procedure for the Bence–Jones protein Rhe included phase extension from 3·0 to 1·9 Å and led to an improved crystallographic sequence for the protein. The structure was refined, by a stereochemically restrained least-squares technique in reciprocal space, to a residual value $R_F = 0{\cdot}284$ for a model consisting of 795 non-hydrogen protein atoms with an overall thermal factor using data with d ranging from 5·0 to 1·9 Å. Relative weights for the structure factor and stereochemical-restraint observations were determined empirically and the optimum weights were found to be those which yield values of $W|F_o - F_c|^2$ which are typically 4 to 6 times the value of $W|d_o - d_I|^2$, where d_o and d_I are the current and ideal values for the stereochemically restrained parameters. It was found that reasonable refinement may be obtained with only 32% of the observed data.

Introduction

In the application of the method of multiple isomorphous replacement, MIR, to the structure determination of macromolecules, one is often confronted

0567-7394/79/050810-08$01.00