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The Dynamical Scattering Amplitude of an Imperfect Crystal. III. A Dynamical Diffraction Equation for Topography in the Spatial Coordinate Representation

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Based on a general dynamical theory of diffraction, an integral equation for dynamical diffraction in imperfect crystals is obtained in the spatial coordinate representation. This equation is derived for diffraction topography in the symmetrical Laue geometry from the basic dynamical equation of diffraction previously derived in the momentum representation. Discussion is presented on an interpretation of this integral equation beyond the given diffraction geometry. This equation can be considered as a basic equation for diffraction topography.

1. Introduction

It has been demonstrated in previous papers (Kuriyama, 1970, 1972, 1973) that a general dynamical theory of diffraction, *i.e.* the *quantum* theory (Ashkin & Kuriyama, 1966; Kuriyama, 1967*a*), can reproduce the *ray* theory (Penning & Polder, 1961, 1964; Kato, 1963, 1964*a*, *b*; Bonse, 1964; Kambe, 1965) as well as the *wave* theory (Takagi, 1962, 1969; Taupin, 1964). In so doing, the nature of the approximations inherent in the latter two theories has been clarified. Of these two, the *ray* theory has been proven to excel the other as theory. However, in order to apply this theory in a rigorous way, one has to find a set of canonical transformations without making an *ad hoc* choice for the ray trajectories. This creates a formidable computation problem. On the other hand, the *wave* theory, though containing theoretical deficiencies, had an appealing feature, in that it dealt with the wave fields directly and, in turn, with the amplitudes of the waves. It was also believed that the *wave* theory could easily be handled numerically. However, it has been subsequently shown that this theory, too, requires a large amount of work in its computation for a given set of atomic displacements in a crystal.

As a rule, regardless of the type of theory, it does not seem possible to calculate the intensity distribution in topographic images, unless a major computer effort is undertaken, case by case, for various types of crystal imperfections. It is, therefore, desirable to seek a more fundamental equation which is theoretically accurate or involves the least approximation in the fundamental process of its derivation, since the calculation has to be performed by a computer anyway.

Previously, such an equation was derived in the momentum representation (Kuriyama, 1970, 1972). However, the equation in the coordinate representation is much preferred, because the atomic displacements in a crystal are given as local functions. In the momentum representation, the geometrical factor has to be calculated first from these local functions to obtain the momentum representation of the displacements. This procedure is admittedly unappealing. In this paper the objective is, therefore, to present the basic equation of dynamical diffraction for imperfect crystals in the spatial coordinate representation.

2. The dynamical scattering amplitude for an imperfect crystal

In the scattering formalism of modern quantum theory, one deals with the exact quantum states of the system composed of the incoming particles and the scatterers. These states are called Heisenberg states and are given by the exact solution of the Schrödinger equation for the total Hamiltonian of the system. Dynamical variables such as field operators, therefore, obey the Heisenberg equation of motion. Before the incoming particles strike the scatterers, the exact Heisenberg state is called the *in* state, which implies that the incoming particles are free and the scatterers (for X-ray scattering, electrons in the crystal) occupy energy levels below the Fermi energy. This condition for the scatterers defines the ground state of the crystal. After the particles are scattered out of the crystal, one can define *out* states in a similar fashion. The *out* states represent the Heisenberg states in which the scattered particles are again free and the crystal can be either in its ground state or in one of the excited states. Obviously, the *out* state involving the ground state of the crystal leads to elastic scattering, while other *out* states are related to the processes of inelastic scattering (Kuriyama, 1971). In this paper, we confine ourselves to elastic scattering, since the dynamical diffraction effects in an imperfect crystal are our major concern here.

When the crystal diffracts the incoming particles and a detector receives the scattered particles, the state of the system changes from the *in* state to the *out* state. Therefore, there is a quantum transition from the *in* state to the *out* state associated with the diffraction phenomenon. The scattering amplitude of the system that is equivalent to the diffracted amplitude of the

outgoing particles is, in terms of the *in* to *out* transition, given (Ashkin & Kuriyama, 1966; Kuriyama, 1967*a*, *b*, 1968) by

$$\langle \Phi; \mathbf{k}'\nu'; \mathbf{R}'; \text{out} \,|\Phi; \mathbf{k}\nu; \mathbf{R}; \text{in}\rangle \equiv \langle \mathbf{k}', \mathbf{R}'; \text{out} \,|\mathbf{k}, \mathbf{R}; \text{in}\rangle . \quad (2.1)$$

Here the incoming particles having momentum $\mathbf{k}$ and polarization direction ν strike the crystal in its ground state (Φ) at position $\mathbf{R}$ and the particles come out at position $\mathbf{R}'$ with momentum $\mathbf{k}'$ and polarization direction ν', leaving the crystal in its ground state. This quantity can be written

$$\langle \mathbf{k}', \mathbf{R}'; \text{out} \,|\mathbf{k}, \mathbf{R}; \text{in}\rangle = \int \mathrm{d}^3p \int \mathrm{d}^3p' A^*(\mathbf{k}'\mathbf{p}'; \mathbf{R}') S(\mathbf{p}', \mathbf{p}) A(\mathbf{k}, \mathbf{p}; \mathbf{R}) , \quad (2.2)$$

in terms of the scattering matrix element $S(\mathbf{p}', \mathbf{p})$ and the spectral distributions A and A^* for the incoming and the outgoing particles (or the response of the detector) respectively.

It has been shown by Kuriyama (1970) that the scattering matrix element S can be given in a compact form for a crystal plate of thickness L:

$$S(\mathbf{p}', \mathbf{p}) = (p_z/|\mathbf{p}|)\delta(|\mathbf{p}'| - |\mathbf{p}|) \times \sum_{\mathbf{q}} \sum_{\mathbf{J}} \delta(\mathbf{p}_t + \mathbf{J}_t + \mathbf{q}_t - \mathbf{p}_t') [\mathsf{S}(\mathbf{p}')]_{\mathbf{0};\, -\mathbf{J}}^{\mathbf{0};\, -\mathbf{q}} , \quad (2.3)$$

where the subscripts t and z designate the tangential and normal components of a vector relative to the crystal surface. The S matrix is a super-matrix, *i.e.*, a matrix of matrices. The $(\mathbf{I}, \mathbf{J})$ element of a super-matrix is given by a matrix whose elements are specified by $(\mathbf{q}, \mathbf{q}')$. In this notation,† a super-matrix S is written $[\mathsf{S}]_{\mathbf{I};\, \mathbf{J}}^{\mathbf{q};\, \mathbf{q}'}$. The matrix S has the following form:

$$\mathsf{S}(\mathbf{p}) = \exp[-i\sigma_f \mathsf{M}(\mathbf{p})] , \quad (2.4)$$

where

$$\sigma_f = L/2k_z' , \quad (2.5)$$

and

$$[\mathsf{M}(\mathbf{p})]_{\mathbf{I},\mathbf{J}}^{\mathbf{q};\mathbf{q}'} = \frac{p_z}{(\mathbf{p}+\mathbf{I}+\mathbf{q})_z} \{(\mathbf{p}+\mathbf{I}+\mathbf{q})^2 - \mathbf{p}^2\} \delta_{\mathbf{q}\mathbf{q}'} \delta_{\mathbf{I}\mathbf{J}} - \frac{P_z}{(\mathbf{p}+\mathbf{J}+\mathbf{q}')_z} \gamma(\mathbf{I}+\mathbf{q}; \mathbf{J}+\mathbf{q}') .\dagger \quad (2.6)$$

The quantity γ is given by

$$\gamma(\mathbf{I}+\mathbf{q}; \mathbf{J}+\mathbf{q}') = \frac{1}{N} \sum_l v_l(\mathbf{I}+\mathbf{q}; \mathbf{J}+\mathbf{q}') \exp[-i\{\mathbf{I}+\mathbf{q}-\mathbf{J}-\mathbf{q}'\}\mathbf{R}_l] , \quad (2.7)$$

† The definition of the super-matrix element $[\mathsf{S}]_{\mathbf{I},\mathbf{J}}^{\mathbf{q};\mathbf{q}'}$ is different from the one described in previous papers (Kuriyama, 1970, 1972, 1973). The previous definition is obtained by changing the signs of I, J and q, q':

$$[\mathsf{S}]_{\mathbf{I},\mathbf{J}}^{\mathbf{q};\mathbf{q}'} \text{ (present)} \equiv [\mathsf{S}]_{-\mathbf{I},-\mathbf{J}}^{-\mathbf{q};-\mathbf{q}'} \text{ (previous)}.$$

See also the change in definition of the M matrix, equation (2.6).

where N is the total number of atoms in the crystal, v_l is the 'atomic' polarizability of the atom at the lth site, and $\mathbf{R}_l$ is the actual position of the lth atom, being displaced by $\mathbf{u}_l$ from its ideal position, $\mathbf{l}$. The set of $\mathbf{l}$'s forms the perfect lattice, conventionally called the perfect reference crystal. Since the matrices S and M are expressed as a super-matrix, one can identify $\mathbf{I}$ or $\mathbf{J}$ as a reciprocal-lattice vector defined in the perfect reference crystal. Consequently, the superscript, $\mathbf{q}$ or $\mathbf{q}'$, is thought of as a vector describing the deviation from a reciprocal-lattice point.

3. Spectral distributions for the incoming and the outgoing particles

In the calculation of the dynamical scattering amplitude of an imperfect crystal, equation (2.2), the incident particles are allowed to form a beam of any arbitrary shape falling upon a crystal at any desired position. These characteristics of the incident beam are described by the spectral distribution function A, which determines the momentum and the energy distribution (described by $\mathbf{p}$) as well as the geometrical position of the peak intensity (described by $\mathbf{R}$). As a result of the properties of the Fourier transform, the spectral function of a beam peaked at $\mathbf{R}$ is related to that of the beam peaked at $\mathbf{0}$ by the relation

$$A(\mathbf{p}, \mathbf{p}'; \mathbf{R}) = A(\mathbf{p}, \mathbf{p}'; \mathbf{0}) \exp[i(\mathbf{p}-\mathbf{p}')\mathbf{R}] \equiv A(\mathbf{p}, \mathbf{p}') \exp[i(\mathbf{p}-\mathbf{p}')\mathbf{R}] . \quad (3.1a)$$

Let us introduce the matrices, A and W, whose elements are defined by

$$[\mathsf{A}]_{\mathbf{p},\,\mathbf{p}'} \equiv A(\mathbf{p}', \mathbf{p}) \quad (3.2)$$

and

$$[\mathsf{W}(\mathbf{R})]_{\mathbf{p},\,\mathbf{p}'} \equiv \exp(i\mathbf{p}\mathbf{R})\delta_{\mathbf{p}\mathbf{p}'} . \quad (3.3a)$$

Then equation (3.1*a*) can be given by the matrix element

$$A(\mathbf{p}, \mathbf{p}'; \mathbf{R}) = [\mathsf{W}^{-1}(\mathbf{R})\mathsf{A}\mathsf{W}(\mathbf{R})]_{\mathbf{p},\,\mathbf{p}'} , \quad (3.1b)$$

where

$$\mathsf{W}^{-1}(\mathbf{R})\mathsf{W}(\mathbf{R}) = \mathsf{W}(\mathbf{R})\mathsf{W}^{-1}(\mathbf{R}) = \mathsf{I} . \quad (3.4)$$

In a similar fashion, we can identify A^* as a matrix associated either with the beam coming out of the crystal or with the detector system (slits, analysing crystals and a detector). In the original formulation of equation (2.2) by Ashkin & Kuriyama (1966), a complete orthonormal set of one-particle wave packets constructed from positive-frequency free-photon wave functions to represent possible free particle states was adopted. This treatment is equivalent to the physical situation in which the detecting system does not limit further the momentum and the energy response of the crystal to the incident beam. In this case, A^* in equation (2.2) is the complex conjugate of A. However, if additional slit systems are introduced to detect the

scattered beams, A^* can be replaced by a spectral function which characterizes the momentum and energy response of a detector and its location. This principle follows from the multiplicative property of the S matrices for successive events. In any case, the spectral distribution A^* is given by the matrix element

$$A^*(\mathbf{p},\mathbf{p}';\mathbf{R})=[\mathsf{W}^{-1}(\mathbf{R})A^*\mathsf{W}(R)]_{\mathbf{p},\mathbf{p}'}\,. \tag{3.5}$$

4. Matrix representation of the dynamical scattering amplitude

In diffraction problems, one can always distinguish each diffracted beam from others including the transmitted (**0**-diffracted) beam. It is, therefore, convenient to specify which diffracted beam is being observed. For this purpose, let us define the variables $\mathbf{p}$ and $\mathbf{p}'$ in terms of the reciprocal-lattice vectors and the deviations from the nearest reciprocal-lattice point, and let the momentum and the energy of the incident beam be dummy variables:

$$\mathbf{p}\equiv\mathbf{k}+\mathbf{q}_i \tag{4.1}$$

and

$$\mathbf{p}_\mathbf{J}\{\mathbf{q}\}\equiv\mathbf{p}+\mathbf{J}+\mathbf{q}=\mathbf{k}+\mathbf{J}+\mathbf{q}_i+\mathbf{q}\,. \tag{4.2a}$$

Then the scattering matrix S can be expressed in terms of these new variables as follows:

$$\begin{aligned}S(\mathbf{p}',\mathbf{p})&=\frac{p_z}{|\mathbf{p}|}\delta(|\mathbf{p}'|-|\mathbf{p}|)\sum_\mathbf{J}\sum_\mathbf{q}\delta(\mathbf{p}_t+\mathbf{J}_t+\mathbf{q}_t-\mathbf{p}_t')\\&\times[\mathsf{S}(\mathbf{p}')]^{\mathbf{0}}_{\mathbf{0};-\mathbf{J}}{}^{;-\mathbf{q}}\\&=\sum_\mathbf{J}\sum_\mathbf{q}[p_z/(\mathbf{p}_\mathbf{J}\{\mathbf{q}\})_z]\delta(\mathbf{p}'-\mathbf{p}_\mathbf{J}\{\mathbf{q}\})\\&\times[\mathsf{S}(\mathbf{k}+\mathbf{J}+\mathbf{q}_i+\mathbf{q})]^{\mathbf{0}}_{\mathbf{0};-\mathbf{J}}{}^{;-\mathbf{q}}\\&=\sum_\mathbf{J}\sum_\mathbf{q}[p_z/(\mathbf{p}_\mathbf{J}\{\mathbf{q}\})_z]\delta(\mathbf{p}'-\mathbf{p}_\mathbf{J}\{\mathbf{q}\})[\mathsf{S}(\mathbf{k})]^{\mathbf{q}_i+\mathbf{q},\,\mathbf{q}_i}_{\mathbf{J};\mathbf{0}},\end{aligned} \tag{4.3}$$

where we have made use of the following relations,

$$\begin{aligned}(p_z/|\mathbf{p}|)\delta(|\mathbf{p}'|-|\mathbf{p}|)\delta(\mathbf{p}_t+\mathbf{J}_t+\mathbf{q}_t-\mathbf{p}_t')\\=[p_z/(\mathbf{p}_\mathbf{J}\{\mathbf{q}\})_z]\delta(\mathbf{p}'-\mathbf{p}_\mathbf{J}\{\mathbf{q}\})\end{aligned} \tag{4.4}$$

and

$$[\mathsf{S}(\mathbf{p}+\mathbf{K}+\bar{\mathbf{q}})]^{\mathbf{q},\mathbf{q}'}_{\mathbf{I},\mathbf{J}}=[\mathsf{S}(\mathbf{p})]^{\mathbf{q}-\bar{\mathbf{q}};\,\mathbf{q}'-\bar{\mathbf{q}}}_{\mathbf{I}-\mathbf{K};\,\mathbf{J}-\mathbf{K}}. \tag{4.5}$$

The relation (4.5) can be easily proven from the property of the M matrix, (2.6), using the definition of matrix exponential (Kuriyama, 1972). Substituting the expressions (4.3), (3.1*b*) and (3.5) into (2.2), we obtain the scattering amplitude of an imperfect crystal

$$\begin{aligned}\langle\mathbf{k}',\mathbf{R}';\text{ out}\,|\mathbf{k},\mathbf{R};\text{ in}\rangle\\=\sum_\mathbf{J}\int\mathrm{d}^3q_i\int\mathrm{d}^3q\,\frac{(\mathbf{k}+\mathbf{q}_i)_z}{(\mathbf{k}+\mathbf{J}+\mathbf{q}_i+\mathbf{q})_z}\\\times[\mathsf{W}^{-1}(R')\mathsf{A}^*\mathsf{W}(R')]^{\varepsilon;\,\mathbf{q}+\mathbf{q}_i}_{\mathbf{K},\mathbf{J}}[\mathsf{S}(\mathbf{k})]^{\mathbf{q}+\mathbf{q}_i,\,\mathbf{q}_i}_{\mathbf{J},\mathbf{0}}\\\times[W^{-1}(\mathbf{R})\mathsf{A}W(\mathbf{R})]^{\mathbf{q}_i;\,\mathbf{o}}_{\mathbf{0};\,\mathbf{0}}\,,\end{aligned} \tag{4.6}$$

where the momentum of the outgoing beam is expressed by

$$\mathbf{k}'=\mathbf{k}+\mathbf{K}+\boldsymbol{\varepsilon}\equiv\mathbf{k}'_K \tag{4.2b}$$

in the same view as adopted for equation (4.1) and (4.2). The $\mathbf{K}$ is a reciprocal-lattice vector in the perfect reference crystal and implies that the **K**-Bragg diffracted beam is being observed.

If the experimental condition for detection of the diffracted beams allows us to assume

$$\frac{(\mathbf{k}+\mathbf{q}_i)_z}{(\mathbf{k}+\mathbf{K}+\mathbf{q}_i+\mathbf{q}_f)_z}=\frac{\mathbf{k}_z}{(\mathbf{k}+\mathbf{K})_z}\equiv\tau_\mathbf{K}\,, \tag{4.7}$$

then the scattering amplitude is written in a simple product form of matrices:

$$\langle\mathbf{k}'_\mathbf{K},\mathbf{R}';\text{ out}\,|\mathbf{k},\mathbf{R};\text{ in}\rangle=\tau_\mathbf{K}[\mathsf{F}]^{\varepsilon;\,\mathbf{o}}_{\mathbf{K},\mathbf{0}}\,, \tag{4.8}$$

where

$$\mathsf{F}(\mathbf{R}',\mathbf{R})=\mathsf{W}^{-1}(\mathbf{R}')\mathsf{A}^*\mathsf{W}(\mathbf{R}')\mathsf{S}(\mathbf{k})\mathsf{W}^{-1}(\mathbf{R})\mathsf{A}\mathsf{W}(\mathbf{R})\,. \tag{4.9}$$

It immediately follows that the matrix F becomes identical to S when the incident beam is an ideal plane wave and the spectral function for a detector has an ideal angular resolution.

However, a case of practical interest is found in topographical observations of the interior of the crystal. In this case, one uses a fairly well collimated, but well localized beam as an incident beam and observes the intensity distribution of a diffracted beam at a short distance from the crystal. Theoretically we identify this case as the 'spherical' wave case where the incident beam behaves almost like a spherical wave (the angular divergence of the beam is larger than the actual rocking curve width of the crystal), and the detector spectral function has a poor angular resolution, but a good resolution for locations.

For topography, one is not terribly concerned about the angular distribution of the outgoing beams, except for their general Bragg diffraction directions, for example, a transmitted direction and an **H**-Bragg diffraction direction. Therefore, the spectral function assumed above for the detector can be considered as reasonable. However, the above assumption for the incident beam is worthy of comment. In principle, the state of the incident beam is completely independent of the state of a scatterer crystal and the state of detecting systems. Therefore one can have, as an incident beam, an ideally well collimated beam which does not possess the angular divergence. In previous papers (Kuriyama, 1972, 1973) the scattering amplitude for such an ideal incident beam has been discussed. In this paper, however, we adopt the 'spherical' wave case for a mathematical reason. As will be seen later, one can calculate the scattering amplitude for an ideally well collimated incident beam on the same principle as that developed in this paper with a slight modification.

In the 'spherical' wave case, the spectral functions are given by the following matrix elements

$(\mathsf{A})_{\mathbf{p},\mathbf{p}'}=(\mathsf{A})^{\mathbf{q};\mathbf{q}'}_{\mathbf{I},\mathbf{J}}=A_0\delta_{\mathbf{I}0}\delta_{\mathbf{IJ}}$, regardless of $\mathbf{q}$ and $\mathbf{q}'$, (4.10*a*)

and

$(\mathsf{A}^*)_{\mathbf{p},\mathbf{p}'}=(\mathsf{A})^{\mathbf{q};\mathbf{q}'}_{\mathbf{I},\mathbf{J}}=A_{\mathbf{K}}\delta_{\mathbf{IK}}\delta_{\mathbf{IJ}}$, regardless of $\mathbf{q}$ and $\mathbf{q}'$. (4.10*b*)

Thus, the relevant matrix element of F is given by

$$[\mathsf{F}]^{\varepsilon;\,\mathbf{o}}_{\mathbf{K},\,\mathbf{0}}=A_0A_{\mathbf{K}}\exp(-i\varepsilon\mathbf{R}')\sum_{\mathbf{q}}\sum_{\mathbf{q}'}[\mathsf{W}(R')\mathsf{S}(k)\mathsf{W}^{-1}(R)]^{\mathbf{q};\mathbf{q}'}_{\mathbf{K},\mathbf{0}}\,. \tag{4.11}$$

5. Calculation of the F matrix

To obtain the matrix elements of F, we need to calculate the matrix S. In previous papers (Kuriyama, 1972, 1973), two attempts were made to calculate this matrix approximately. Although, then, the results were known not to be rigorous, it was believed that they were good enough for practical purposes and were easily understood intuitively by the traditional dynamical diffraction theory for a perfect crystal. These two attempts reproduced the ray theory (Kato, 1963, 1964*a*, *b*; Kambe, 1965, 1968) and the wave theory (Takagi, 1962, 1969; Taupin, 1964), and clarified the relationships among the existing phenomenological theories (Penning & Polder, 1961, 1964; Bonse, 1964; Wilkins, 1966; Balibar & Authier, 1967; Dederichs, 1966, 1967 and others). However, it was found that the phase modulation of the diffracted beams could not be dealt with properly without requiring an elaborate calculation. In this section, we therefore follow a standard mathematical procedure to obtain the S matrix (Neumann–Liouville expansion).

Before calculating the S matrix, we turn back to the definition of the W matrix, equation (3.3*a*). In the super-matrix representation where the index $\mathbf{p}$ is replaced by $\mathbf{p}'=\mathbf{k}+\mathbf{J}+\mathbf{q}$, as done in the previous sections, the W matrix can be defined in general by

$$[\mathsf{W}(\mathbf{R})]_{\mathbf{p},\mathbf{p}'}\rightarrow[\mathsf{W}(\mathbf{R})]^{\mathbf{q};\mathbf{q}'}_{\mathbf{I},\mathbf{J}}=\exp(i\mathbf{q}\,.\,\mathbf{R})\delta_{\mathbf{q},\mathbf{q}'}\delta_{\mathbf{IJ}}\,, \tag{3.3*b*}$$

whose diagonal elements are independent of $\mathbf{I}$. This change does not affect the definitions of the spectral functions, (3.1*a* and *b*). This can be easily assured by inspection especially for the explicit forms of A and A* defined by (4.10*a* and *b*).

From (2.4) and (2.5), the matrix $\mathsf{S}(\mathbf{k})$ is given by

$$\mathsf{S}(\mathbf{k})=\exp[-i\sigma_{\mathbf{K}}\mathsf{M}(\mathbf{k})]\,, \tag{5.1}$$

where

$$\sigma_{\mathbf{K}}=\tau_{\mathbf{K}}L/2k_z\,. \tag{5.2*a*}$$

For the sake of simplicity, we introduce the following three conditions. (1) The Fourier transform of the 'atomic' polarizability $v_l(\mathbf{I}+\mathbf{q};\mathbf{J}+\mathbf{q}')$ is approximated by $v_l(\mathbf{I}-\mathbf{J})$. Atoms in different unit cells are assumed to have the same scattering factor as in the perfect unit cell. (2) The quantities, $(\mathbf{q}-\mathbf{q}')\mathbf{u}_l$, are negligibly small, compared with $(\mathbf{q}-\mathbf{q}')\cdot\mathbf{l}$. (3) The geometrical factor, $p_z/(\mathbf{p}+\mathbf{J}+\mathbf{q})_z$, is approximated by $p_z/(p+J)_z$. In the following calculation, the conditions (2) and (3) are not really necessary, but have been adopted in order to avoid further complications in the mathematical manipulation.

In this approximation, the matrix M can be given in the following form:

$$\begin{aligned}[\mathsf{M}(k)]^{\mathbf{q};\mathbf{q}'}_{\mathbf{I},\mathbf{J}}=\{&\tau_Ih'_I(\mathbf{q})\delta_{IJ}\\&-\frac{1}{N}\sum_l\alpha\tau_Jv_l(\mathbf{I}-\mathbf{J})\exp[-i(\mathbf{I}-\mathbf{J})\mathbf{l}]\}\delta_{\mathbf{qq}'}\\&-\frac{1}{N}\sum_l\tau_Jv_l(\mathbf{I}-\mathbf{J})\{\exp[-i(\mathbf{I}-\mathbf{J})\mathbf{u}_l]-\alpha\}\\&\times\exp[-i(\mathbf{I}+\mathbf{q}-\mathbf{J}-\mathbf{q}')\mathbf{l}]\,,\end{aligned} \tag{5.3}$$

where

$$h'_I(q)=(\mathbf{k}+\mathbf{I}+\mathbf{q})^2-k^2. \tag{5.4}$$

We have used the property of the generalized Kronecker delta

$$\frac{1}{N}\sum_l\exp[-i(\mathbf{K}+\mathbf{q})\mathbf{l}]=\delta_{\mathbf{q}\mathbf{o}} \tag{5.5}$$

for a reciprocal-lattice vector $\mathbf{K}$. The quantity α is introduced as a renormalization factor, relating to the choice of the perfect reference crystal that is determined experimentally to be most appropriate (this can be understood in analogy to the mass and charge renormalization of electrons in field theory). If one wishes, one can set α equal to one. Using the matrix W defined by (3.3*b*), we can also express the matrix M as

$$\mathsf{M}=\sum_l\mathsf{W}^{-1}(l)\mathsf{M}_l\mathsf{W}(l)\,, \tag{5.6}$$

where

$$\begin{aligned}(\mathsf{M}_l)^{\mathbf{q};\mathbf{q}'}_{\mathbf{I},\mathbf{J}}=&\frac{1}{N}[\tau_Ih'_I(\mathbf{q})\delta_{\mathbf{IJ}}-\alpha\tau_Jv(\mathbf{I}-\mathbf{J})]\delta_{\mathbf{q},\mathbf{q}'}\\&-\frac{1}{N}\tau_Jv_l(\mathbf{I}-\mathbf{J})\{\exp[-i(\mathbf{I}-\mathbf{J})\mathbf{u}_l]-\alpha\}\,,\end{aligned} \tag{5.7}$$

and

$$v(\mathbf{I}-\mathbf{J})\equiv\frac{1}{N}\sum_l v_l(\mathbf{I}-\mathbf{J})\,. \tag{5.8}$$

In equation (5.3) and (5.6) the matrix M is given as a sum of two matrices, one of which is diagonal with respect to $(\mathbf{q},\mathbf{q}')$ elements. Therefore, the super-matrix M is written

$$\mathsf{M}=\mathsf{H}+\mathsf{V}\,, \tag{5.9*a*}$$

and

$$\mathsf{V}=\sum_l\mathsf{W}^{-1}(l)\mathsf{V}_l\mathsf{W}(l)\,, \tag{5.9*b*}$$

where

$$[\mathsf{H}]^{\mathbf{q};\mathbf{q}'}_{\mathbf{I},\mathbf{J}}=[\mathsf{h}(\mathbf{q})]_{\mathbf{I},\mathbf{J}}\delta_{\mathbf{q},\mathbf{q}'} \tag{5.10*a*}$$

and

$[\mathsf{V}_l]^{\mathbf{q};\mathbf{q}'}_{\mathbf{I},\mathbf{J}}=[\mathsf{v}(\mathbf{l})]_{\mathbf{I},\mathbf{J}}$, regardless of $\mathbf{q}$ and $\mathbf{q}'$. (5.10*b*)

The matrices expressed by lower case letters are ordinary matrices whose rows and columns are numbered by **I** and **J**. The upper case letters are used to describe the super-matrices. The (**I**,**J**) elements of the matrices, $\mathsf{h}(\mathbf{q})$ and v_l, are given from equation (5.3) or (5.6):

$$[\mathsf{h}(\mathbf{q})]_{\mathbf{I},\mathbf{J}}=\tau_{\mathbf{I}}h_I'(q)\delta_{\mathbf{IJ}}-\alpha\tau_{\mathbf{J}}v(\mathbf{I}-\mathbf{J}) \qquad (5.10b)$$

and

$$[\mathsf{v}(\mathbf{l})]_{\mathbf{I},\mathbf{J}}=-\frac{1}{N}\tau_{\mathbf{J}}v_l(\mathbf{I}-\mathbf{J})\,[\exp[-i(\mathbf{I}-\mathbf{J})u_l]-\alpha]\,. \qquad (5.11b)$$

Next we introduce the transformation matrix T which diagonalizes the H matrix:

$$\tilde{\mathsf{H}}=\mathsf{T}^{-1}\mathsf{H}\mathsf{T}\,. \qquad (5.12)$$

The matrix T is a diagonal matrix with respect to $\mathbf{q}$ and $\mathbf{q}'$, since the H has been diagonal with respect to $\mathbf{q}$ and $\mathbf{q}'$, and has the components

$$[\mathsf{T}]_{\mathbf{I},\mathbf{J}}^{\mathbf{q};\mathbf{q}'}=[\mathsf{t}(q)]_{\mathbf{I},\mathbf{J}}\delta_{\mathbf{q},\mathbf{q}'}\,. \qquad (5.13)$$

This matrix satisfies the following relations:

$$\mathsf{T}\mathsf{T}^{-1}=\mathsf{T}^{-1}\mathsf{T}=\mathsf{I} \qquad (5.14)$$

and

$$[\mathsf{T},\mathsf{W}(\mathbf{R})]=[\mathsf{T}^{-1},\mathsf{W}(\mathbf{R})]=[\mathsf{T},\mathsf{W}^{-1}(\mathbf{R})]=[\mathsf{T}^{-1},\mathsf{W}^{-1}(\mathbf{R})]=0\,. \qquad (5.15)$$

In this transformation, the matrix S is transformed into

$$\tilde{\mathsf{S}}=\mathsf{T}^{-1}\mathsf{S}\mathsf{T}\,. \qquad (5.16)$$

As shown in previous papers (Kuriyama, 1970, 1972, 1973), the matrix S satisfies the dynamical diffraction equation

$$\frac{\mathrm{d}\mathsf{S}(\sigma_K)}{\mathrm{d}\sigma_K}=i\mathsf{M}\cdot\mathsf{S}(\sigma_K) \qquad (5.17a)$$

or

$$\frac{\mathrm{d}\mathsf{S}(t)}{\mathrm{d}t}=(-i)\sigma_K\mathsf{M}\cdot\mathsf{S}(t)\equiv\lambda\mathsf{M}\cdot\mathsf{S}(t) \qquad (5.17b)$$

with the initial condition $\mathsf{S}(0)=\mathsf{I}$, where

$$(-i)\sigma_K=(-i)\tau_K L/2k\cos\varphi_K\equiv\lambda \qquad (5.2b)$$

as defined previously by (5.2*a*), and φ_K is the direction cosine of the propagation vector $\mathbf{k}'$. After $\mathsf{S}(t)$ is found from (5.17*b*), the value of t is set equal to one:

$$\mathsf{S}(\mathbf{k})=[\mathsf{S}(\mathbf{k};t)]_{t=1}\,. \qquad (5.18)$$

It follows from (5.16) and (5.14) that the equation (5.17*b*) is invariant under the transformation S to $\tilde{\mathsf{S}}$. Knowing that the matrix M is composed of the two parts as given by (5.9*a*), we transform $\tilde{\mathsf{S}}$ again into S^I:

$$\mathsf{S}^I=\exp[-\lambda\tilde{\mathsf{H}}\,t]\tilde{\mathsf{S}}\,. \qquad (5.19)$$

Then, substituting this into (5.17*b*), we obtain the new equation

$$\frac{\mathrm{d}\mathsf{S}^I(t)}{\mathrm{d}t}=\lambda\mathsf{V}^I(t)\mathsf{S}^I(t)\,, \qquad (5.20)$$

where

$$\mathsf{V}^I(t)=\exp(-\lambda\tilde{\mathsf{H}}t)\tilde{\mathsf{V}}\exp(\lambda\tilde{\mathsf{H}}t)=\exp(-\lambda\tilde{\mathsf{H}}t)\mathsf{T}^{-1}\mathsf{V}\mathsf{T}\exp(\lambda\tilde{\mathsf{H}}t)\,. \qquad (5.21)$$

In the Neumann–Liouville expansion, the solution of (5.20) is written

$$\begin{aligned}\mathsf{S}^I(t)&=\sum_{m=0}^{\infty}(-i\sigma_K)^m\int_0^t\mathrm{d}s_1\int_0^{s_1}\mathrm{d}s_2\ldots\int_0^{s_{m-1}}\mathrm{d}s_m\\&\quad\times V^I(s_1)\ldots V^I(S_m)\\&=\sum_{m=0}^{\infty}\left(\frac{1}{m!}\right)(-i\sigma_K)^m\int_0^t\mathrm{d}s_1\int_0^t\mathrm{d}s_2\ldots\int_0^t\mathrm{d}s_m\\&\quad\times P[V^I(s_1)\ldots V^I(s_m)]\\&=P[\exp\{(-i\sigma_K)\int_0^t V^I(s)\mathrm{d}s\}]\equiv P[\exp(\Phi)]\,,\end{aligned} \qquad (5.22)$$

where P indicates the operation that, in a product of coordinate, say s_n, labeled matrices, it rearranges them from right to left in the order of increasing s coordinates.

Using (5.22), (5.19), (5.16), the matrix F, (4.11), is now given by

$$[\mathsf{F}]_{\mathbf{K},\mathbf{0}}^{\boldsymbol{\varepsilon};\mathbf{0}}=A_0A_{\mathbf{K}}\exp(-i\boldsymbol{\varepsilon}\mathbf{R}')\sum_{\mathbf{q}}\sum_{\mathbf{q}'}[\mathsf{T}\mathsf{W}(\mathbf{R}')\times\{\exp[-i\sigma_K\tilde{\mathsf{H}}t]\}P[\exp(\Phi)]\mathsf{W}^{-1}(\mathbf{R})\mathsf{T}^{-1}]_{\mathbf{K},\mathbf{0}}^{\mathbf{q};\mathbf{q}'}\,. \qquad (5.23)$$

Substituting (5.9*b*) into (5.21), the matrix $\mathsf{V}^I(s)$ can be expressed, in terms of a lattice sum, by

$$\mathsf{V}^I(s)=\sum_l\exp(-\lambda\tilde{\mathsf{H}}s)\mathsf{T}^{-1}\mathsf{W}^{-1}(l)\mathsf{V}(l)\mathsf{W}(l)\mathsf{T}\exp(\lambda\tilde{\mathsf{H}}s)\,. \qquad (5.24)$$

Thus, the matrix F can be written in terms of the lattice sums:

$$[\mathsf{F}]_{\mathbf{K},\mathbf{0}}^{\boldsymbol{\varepsilon};\mathbf{0}}=\exp(-i\boldsymbol{\varepsilon}\mathbf{R}')\times\sum_{m=0}^{\infty}\frac{\lambda^m}{m!}\sum_{l_1}\ldots\sum_{l_m}\int_0^t\ldots\int_0^t\mathrm{d}s_1\ldots\mathrm{d}s_m\times\sum_{\mathbf{q}}\sum_{\mathbf{q}'}[\mathsf{A}_m(l_1,\ldots,l_m)]_{\mathbf{K},\mathbf{0}}^{\mathbf{q};\mathbf{q}'}\,, \qquad (5.25)$$

where, for convenience, A_0 and A_K are assumed to be one hereafter. Here

$$\mathsf{A}_m(l_1,l_2,\ldots l_m)=P[\mathsf{X}(0)\mathsf{V}(1)\mathsf{X}(1)\mathsf{V}(2)\ldots\mathsf{V}(m)\mathsf{X}(m)],\equiv\mathsf{A}_m(0,1,2,\ldots,m,m+1) \qquad (5.26)$$

where

$$\mathsf{X}(n)\equiv\mathsf{T}\mathsf{W}(\mathbf{l}_n)\exp\{\lambda\tilde{\mathsf{H}}(s_n-s_{n+1})\}\mathsf{W}^{-1}(\mathbf{l}_{n+1})\mathsf{T}^{-1}. \qquad (5.27)$$

In this notation, the P operates only on the s coordinates, although in (5.26) they are not written down separately from the l coordinates. Also, the variables, 0 and $m+1$, stand for the abbreviation of the sets of coordinates:

$$0\equiv(l_0,s_0)=(\mathbf{R}',t)\,, \tag{5.28a}$$

and

$$m+1\equiv(l_{m+1},s_{m+1})=(\mathbf{R},0)\,. \tag{5.28b}$$

It is known from (3.3b), (5.10) and (5.13) that the matrices, X, are diagonal with respect to $\mathbf{q}$ and $\mathbf{q}'$. It is also evident from (5.11) that all the $(\mathbf{q},\mathbf{q}')$ elements of the matrix V_l are equal to each other. Thus, we obtain

$$\sum_{\mathbf{q}}\sum_{\mathbf{q}'}[A_m(0,1,\ldots,m,m+1)]^{\mathbf{q},\mathbf{q}'} =P[\{\mathrm{Tr}\,\mathsf{X}(0)\}\mathsf{v}(1)\,\{\mathrm{Tr}\,\mathsf{X}(1)\}\ \ldots\ \mathsf{v}(m)\,\{\mathrm{Tr}\,\mathsf{X}(m)\}]\,, \tag{5.29}$$

where the trace of the matrix X is taken with respect to $\mathbf{q}$. The explicit expression of the trace is given through (5.27) by

$$[\mathrm{Tr}\,\mathsf{X}(m)]_{\mathbf{I},\mathbf{J}}=\sum_{\mathbf{q}}\sum_{i}t_{Ii}(\mathbf{q})t_{iJ}^{-1}(\mathbf{q})\exp[-i\sigma_K r_i(\mathbf{q}) \times(s_m-s_{m+1})+i\mathbf{q}(\mathbf{l}_m-\mathbf{l}_{m+1})]\,, \tag{5.30}$$

where $r_i(\mathbf{q})$'s are the diagonal elements of the matrix $\tilde{\mathsf{H}}$ that are the characteristic values of the matrix H. The operation P demands that the functions, $\mathrm{Tr}\,\mathsf{X}(m)$, be ordered from right to left in the increasing order of the s coordinates. By use of the step function $\theta(s)$, this operation can be performed to reduce (5.29) to

$$\sum_{\mathbf{q}}\sum_{\mathbf{q}'}[A_m(0,1,\ldots,m+1)]^{\mathbf{q},\mathbf{q}'}=\{\theta(s_0-s_1)\,\mathrm{Tr}\,\mathsf{X}(0)\} \times\mathsf{v}(1)\ \ldots\ \mathsf{v}(m)\,\{\theta(s_m-s_{m+1})\,\mathrm{Tr}\,\mathsf{X}(m)\}\,, \tag{5.31}$$

where

$$\left.\begin{aligned}\theta(s_n-s_{n+1})&=1\quad\text{for}\quad s_n-s_{n+1}>0\\&=0\quad\text{for}\quad s_n-s_{n+1}<0\end{aligned}\right\}. \tag{5.32}$$

Since the trace of $\mathsf{X}(m)$ is an exponential function of s_m-s_{m+1} as shown in (5.30), we can express the product of the step function and the matrix trace in the Fourier integral:

$$\theta(s_n-s_{n+1})\,\mathrm{Tr}\,\mathsf{X}(n)=\int_{-\infty}^{+\infty}(\mathrm{d}\omega_n/2\pi) \times\mathsf{g}(\omega_n;\,l_m-l_{m+1})\exp\{i\omega_n(s_n-s_{n+1})\}\,, \tag{5.33}$$

where the matrix g is defined by

$$[\mathsf{g}(\omega;l)]_{\mathbf{I},\mathbf{J}} =\sum_{\mathbf{q}}\sum_{i}t_{Ii}(\mathbf{q})\frac{(-i)}{\sigma_K r_i(\mathbf{q})+\omega-i\delta}t_{iJ}^{-1}(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{l}) \tag{5.34}$$

with an infinitesimally small, positive number δ. Substituting (5.33) into (5.31) and (5.25), we can perform the s-integrations and obtain

$$[\mathsf{F}]^{\varepsilon;\,\mathbf{0}}_{\mathbf{K},\mathbf{0}}=\exp(-i\varepsilon\mathbf{R}')\sum_{m=0}^{\infty}\frac{1}{m!}(-i\sigma_K)^m\int_{-\infty}^{+\infty}\mathrm{d}\omega_0\ \ldots \ldots\int_{-\infty}^{+\infty}\mathrm{d}\omega_m\exp(i\omega_0 s_0)\bar{\delta}(\omega_0-\omega_1)\ \ldots \ldots\bar{\delta}(\omega_{m-1}-\omega_m)\exp(-i\omega_m s_{m+1})\,[\mu_m(\omega_0,\ldots,\omega_m)]_{\mathbf{K},\mathbf{0}}, \tag{5.35}$$

where

$$2\pi\bar{\delta}(\omega)=\exp[-i(\omega t/2)]\sin(\omega t/2)/(\omega/2) \tag{5.36}$$

with $s_0=t$, being set equal to one in the final results, and $s_{m+1}=0$, and

$$\mu(\omega_0,\ldots,\omega_m)=\sum_{l_1}\ \ldots\ \sum_{l_m}\mathsf{g}(\omega_0;\,\mathbf{R}-\mathbf{l}_1)\mathsf{v}(\mathbf{l}_1) \times\mathsf{g}(\omega_1;\,\mathbf{l}_1-\mathbf{l}_2)\mathsf{v}(\mathbf{l}_2)\ \ldots\ \mathsf{v}(\mathbf{l}_m)\mathsf{g}(\omega_m;\,\mathbf{l}_m-\mathbf{R})\,. \tag{5.37}$$

Thus, the scattering amplitude for topography is given in terms of its moments.

6. A single symmetrical Bragg diffraction

The scattering amplitude for topography, (5.35), has been given by the products of matrices, which are no longer super-matrices, but the ordinary $(\mathbf{I},\mathbf{J})$ matrices. In this section, we deal with the diffraction condition, in which the diffracted beams are found only around the transmitted-beam direction and the **H**-Bragg diffracted direction with reference to the perfect reference crystal. In this condition, the scattering amplitude has a nonvanishing value for $\mathbf{K}=\mathbf{0}$ and $\mathbf{H}$. In this case, we can adopt an approximation to describe the $(\mathbf{I},\mathbf{J})$ matrices by the two by two matrices, where $\mathbf{I}$ and $\mathbf{J}$ take the value of $\mathbf{0}$ or $\mathbf{H}$. In this approximation, the matrices, h and v_l, are given by

$$\mathsf{h}(\mathbf{q})=\begin{pmatrix}h'_{\mathbf{0}}(\mathbf{q})-\alpha v(\mathbf{0}) & -\alpha\tau_{\mathbf{H}}v(-\mathbf{H})\\ -\alpha v(+\mathbf{H}) & h'_{\mathbf{H}}(\mathbf{q})-\alpha v(\mathbf{0})\end{pmatrix} \tag{6.1}$$

and

$$\mathsf{v}(\mathbf{l})=\left(-\frac{1}{N}\right)\begin{pmatrix}(1-\alpha)v(\mathbf{0}) & w_l(-\mathbf{H})\\ w_l(\mathbf{H}) & (1-\alpha)v(\mathbf{0})\end{pmatrix} \equiv\left(-\frac{1}{N}\right)\mathsf{w}(l)\,, \tag{6.2}$$

where $h'_{\mathbf{K}}(\mathbf{q})$ is given by (5.4), $v(\mathbf{0})$ by (5.8), and through (5.11)

$$w_l(\mathbf{K})=\{\exp[-i\mathbf{K}\cdot\mathbf{u}_l]-\alpha\}v_l(\mathbf{K})\,. \tag{6.3}$$

To avoid mathematical complications we assume further that (1) the diffraction condition is of the symmetrical Laue geometry, and (2) the classical flow vector, $\mathbf{j}$, satisfies the condition $\mathbf{j}\cdot\mathbf{q}\gg\mathbf{q}^2$ for any $\mathbf{q}$, where

$$\mathbf{j}=(k_z/k_z+q_z)\mathbf{k}+(k_z/k_z+H_z+q_z)\,(\mathbf{k}+\mathbf{H})\,.$$

This approximation enables us to write

$$\mathsf{h}(q)=\bar{\mathsf{h}}(q_t)+2k_z q_z\mathsf{I}\,, \tag{6.4}$$

where

$$\bar{h}(\mathbf{q}_t)=\begin{pmatrix}\bar{h}_0(\mathbf{q}_t) & -\alpha v(-\mathbf{H})\\ -\alpha v(+\mathbf{H}) & \bar{h}_{\mathbf{H}}(\mathbf{q}_t)\end{pmatrix} \quad (6.5a)$$

and

$$\bar{h}_{\mathbf{K}}(\mathbf{q}_t)=(\mathbf{k}+\mathbf{K})^2-\mathbf{k}^2-\alpha v(\mathbf{0})+2(\mathbf{k}+\mathbf{K})_t\cdot\mathbf{q}_t\,. \quad (6.5b)$$

Because of the property, (6.4), of the matrix h, the transformation matrix T can be chosen to be dependent only on $\mathbf{q}_t$ rather than on $\mathbf{q}$. Thus, the characteristic values of h which are the diagonal elements of the matrix $\tilde{\mathsf{h}}$ are given by

$$r_i(\mathbf{q})=\lambda_i(\mathbf{q}_t)+2k_zq_z\,, \quad (6.6)$$

where $\lambda_i(\mathbf{q}_t)$ are the characteristic values of the matrix $\bar{\mathsf{h}}$, and are given by

$$\lambda_i(\mathbf{q}_t)=-v(\mathbf{0})-\eta-(-1)^iR(\eta-\mathbf{q}_t\mathbf{H})\,. \quad (6.7)$$

Here the quantity η is related to the angular deviation of the incident beam from the Bragg angle expected for the perfect reference crystal:

$$2\eta=-[(\mathbf{k}+\mathbf{H})^2-\mathbf{k}^2]\,. \quad (6.8)$$

The function R is given by

$$R(x)=\sqrt{x^2+\beta^2}, \quad (6.9)$$

where

$$\beta^2=\alpha^2v(\mathbf{H})v(-\mathbf{H})\,. \quad (6.10)$$

The subscript i represents the mode of the dynamical diffraction; the anomalous transmission mode is chosen for $i=1$.

In terms of these characteristic values, the transformation matrix T can be given by

$$\mathsf{t}(\mathbf{q}_t)=\frac{-1}{v(-\mathbf{H})}\begin{pmatrix}v(-\mathbf{H}) & v(-\mathbf{H})\\ \lambda_1-\bar{h}_0(\mathbf{q}_t) & \lambda_2-\bar{h}_0(\mathbf{q}_t)\end{pmatrix}, \quad (6.11a)$$

while the inverse transformation is given by

$$\mathsf{t}^{-1}(\mathbf{q}_t)=\frac{1}{\lambda_1-\lambda_2}\begin{pmatrix}\lambda_2-\bar{h}_0(\mathbf{q}_t) & -v(-\mathbf{H})\\ \lambda_1-\bar{h}_0(\mathbf{q}_t) & v(-\mathbf{H})\end{pmatrix}, \quad (6.11b)$$

Thus, if we define the matrix composed of the dynamical field functions (Kuriyama, 1969) by

$$[\mathsf{D}^{(i)}]_{\mathbf{I},\mathbf{J}}=t_{Ii}t_{i\mathbf{J}}^{-1}\,, \quad (6.12)$$

then this matrix is given in the present approximation by

$$\mathsf{D}^{(i)}(q_t)=\begin{pmatrix}\frac{1}{2}\left[1-(-1)^i\frac{\eta-Hq_t}{R}\right] & (-1)^i\frac{v(\mathbf{H})}{2R}\\ (-1)^i\frac{v(-\mathbf{H})}{2R} & \frac{1}{2}\left[1+(-1)^i\frac{\eta-Hq_t}{R}\right]\end{pmatrix}. \quad (6.13)$$

The function (5.34) is now written

$$\mathsf{g}(\omega,l)=\frac{V}{(2\pi)^3}\times\sum_j\int d^3q\,\mathsf{D}^{(j)}(q_t)\frac{(-i)}{\sigma_K[\lambda_j(\mathbf{q}_t)+2k_zq_z]+\omega-i\delta}\times\exp(i\mathbf{q}\cdot\mathbf{l})\,, \quad (6.14)$$

where the sum over $\mathbf{q}$ is replaced by the integral and V is the volume of the crystal given by Nv_c in terms of the unit-cell volume of the perfect reference crystal v_c. This integral can be performed first over q_x, and then over q_z by a contour integration. Since the imaginary part of $v(\mathbf{0})$ is positive (Ashkin & Kuriyama, 1966), the pole is found on the upper half of the complex plane:

$$q_P=\frac{1}{2k_z}\,\mathrm{Re}\,[v(\mathbf{0})+\eta-(-1)^iR(\eta-q_tH)]-\frac{\omega}{2\sigma_Kk_z}+i\frac{1}{2k_z}\,\mathrm{Im}\,[v(\mathbf{0})-(-1)^iR(\eta-q_tH)]\,, \quad (6.15)$$

which is equivalent to the solution of the dispersion equation with the boundary conditions in the traditional dynamical diffraction theory. An advantage in the contour integration is found in the fact that absorption is automatically taken care of. Thus, the matrix g is given by

$$\mathsf{g}(\omega;\mathbf{l})=\sum_i\frac{V}{(2\pi)}\delta(l_x)\frac{1}{2\sigma_Kk_z}\theta(l_z)\times\int dq\,\mathsf{D}^{(i)}(q)\exp[i\{ql_t+q_Pl_z\}]\,. \quad (6.16)$$

The integral in (6.16) is a familiar one in the dynamical diffraction theory for a perfect crystal when the incident wave is treated as a spherical wave. Kato (1968) calculated this integral. If we adopt Kato's notations,

$$v(\mathbf{H})=\beta\exp(i\delta_+);\ v(-H)=\beta\exp(i\delta_-)\,, \quad (6.17a)$$

$$\alpha=(l_z/2k_z)=(l_z/2k\cos\theta_B) \quad (6.17b)$$

and

$$q=(l_t/H)=(l_t/2k\sin\theta_B)\,, \quad (6.17c)$$

then we can define the matrix U by

$$\mathsf{U}=\begin{pmatrix}U_0 & U_{\mathbf{H}}\\ U_{-\mathbf{H}} & U_0\end{pmatrix}, \quad (6.18a)$$

where the elements $U_{\mathbf{K}}$ are given by Kato's U_g functions as $U_g=\theta(\alpha-|q|)U_K$:

$$U_0(\alpha,q)=\pi\beta[(\alpha-q)/(\alpha+q)]^{1/2}J_1[\beta(\alpha^2-q^2)^{1/2}] \quad (6.18b)$$

$$U_H(\alpha,q)=\pi i\beta\exp[i\delta_+]J_0[\beta(\alpha^2-q^2)^{1/2}] \quad (6.18c)$$

$$U_{-H}(\alpha,q)=\pi i\beta\exp[i\delta_-]J_0[\beta(\alpha^2-q^2)^{1/2}]\,. \quad (6.18d)$$

In terms of this matrix U, we obtain

$$\mathsf{g}(\omega;\mathbf{l})=\left(\frac{V}{2\pi L}\right)\left(\frac{1}{2k\sin\theta_B}\right)\times\delta(l_t)\theta(l_z)\theta(\alpha-|q|)\mathsf{U}(l)\exp\left[i\kappa(\omega,\mathbf{l})\right],\quad(6{\cdot}19)$$

where

$$\kappa(\omega,\mathbf{l})=\{v(\mathbf{0})+\eta\}\alpha+\eta q-(l_z/L)\omega\qquad(6.20)$$

and

$$H=2k\sin\theta_B\,.$$

Substituting this expression for g into equation (5.37), we obtain

$$\begin{aligned}\mu_m(\omega_0,\omega_1,\ldots\omega_m)=&\left(\frac{V}{2\pi L}\right)^{m+1}\left(\frac{1}{2k\sin\theta_B}\right)^{m+1}\\&\times\sum_{\mathbf{l}_1}\ldots\sum_{\mathbf{l}_m}\delta(R'_x-l_{1x})\ldots\delta(l_{mx}-R_x)\\&\times\theta(R'_z-l_{1z})\ldots\theta(l_{mz}-R_z)\\&\times\theta(\alpha_0-\alpha_1-|q_0-q_1|)\ldots\\&\ldots\theta(\alpha_m-\alpha_{m+1}-|q_m-q_{m+1}|)\\&\times\mathsf{U}(\mathbf{R}'-\mathbf{l}_1)\mathsf{v}(\mathbf{l}_1)\mathsf{U}(\mathbf{l}_1-\mathbf{l}_2)\ldots\mathsf{v}(\mathbf{l}_m)\mathsf{U}(\mathbf{l}_m-\mathbf{R})\\&\times\exp\left[i\{\kappa(\omega_0;\mathbf{R}'-\mathbf{l}_1)\right.\\&\left.+\kappa(\omega_1;\mathbf{l}_1-\mathbf{l}_2)+\ldots+\kappa(\omega_m;l_m-l_{m+1})\}\right],\end{aligned}\qquad(6.21)$$

where α_n and q_n are defined by (6.17) and therefore are related to $\mathbf{l}_n$. Because of the property of the $\bar{\delta}$ function, (5.36), we assume that all the ω_n's can be replaced by ω_0. The permutation of these ω_0 yields the same term $m!$ times, cancelling the factor of $(1/m!)$ in (5.35). At this stage, we replace the lattice sums by the integrations over the crystal volume, and change the variables $\mathbf{l}_n$ to α_n and q_n using the relations (6.17*b* and *c*). We also use the matrix w defined by (6.2). Through these processes, the higher-order factors involving V, L, N, $k\sin\theta_B$ and $k\cos\theta_B$ become unity. Thus we obtain

$$\begin{aligned}[\mathsf{F}]^{\mathfrak{E}\cdot\mathfrak{o}}_{\mathbf{K},\mathbf{0}}=&N_{\mathbf{K}}\exp\left[i\phi(\mathbf{R}',\mathbf{R})\right]\sum_{m=0}^{\infty}\left(\frac{i}{2\pi}\right)^m\\&\times\int\ldots\int\mathrm{d}\alpha_1\mathrm{d}q_1\mathrm{d}\alpha_2\mathrm{d}q_2\ldots\mathrm{d}\alpha_m\mathrm{d}q_m\\&\times\theta(\alpha_0-\alpha_1)\theta(\alpha_1-\alpha_2)\ldots\theta(\alpha_m-\alpha_{m+1})\\&\times\theta(\alpha_0-\alpha_1-|q_0-q_1|)\ldots\\&\ldots\theta(\alpha_m-\alpha_{m+1}-|q_m-q_{m+1}|)\\&\times\mathsf{U}(\alpha_0-\alpha_1,q_0-q_1)\mathsf{w}(\alpha_1,q_1)\mathsf{U}(\alpha_1-\alpha_2,q_1-q_2)\ldots\\&\ldots\mathsf{w}(\alpha_m,q_m)\mathsf{U}(\alpha_m-\alpha_{m+1},q_m-q_{m+1}),\end{aligned}\qquad(6.22)$$

where the normalization factor $N_{\mathbf{K}}$ and the phase factor $\varphi(\mathbf{R}',\mathbf{R})$ are defined by

$$N_{\mathbf{K}}=\frac{A_0A_KV}{2k\sin\theta_B}\delta(R'_x-R_x)\delta(R'_z-R_z-L)\qquad(6.23)$$

and

$$\varphi(\mathbf{R}',\mathbf{R})=\left(\frac{v(0)+\eta}{2k\cos\theta_B}\right)(R'_z-R_z)+\frac{\eta}{2k\sin\theta_B}(R'_t-R_t)\,.\qquad(6.24)$$

Owing to the presence of the step functions, the range of each integral is limited within the diffracting domain of atoms (Kuriyama, 1968, 1969). The entire domain of diffraction in which atoms can participate in this scattering is shown in Fig. 1. The domain is bounded by four planes: two of them intersect at $t=R_t$, $z=0$, the other two intersect at $t=R'_t$, $z=L$ and the angles between these two planes are equal to $2\theta_B$, making an angle of θ_B with the diffracting plane in both directions.

7. Dynamical diffraction equation in the spatial coordinate representation

We introduce the set of new variables (x_n,y_n) by the transformation

$$\begin{pmatrix}x_n\\y_n\end{pmatrix}=\frac{1}{\sqrt{2}}\begin{pmatrix}1&1\\1&-1\end{pmatrix}\begin{pmatrix}\alpha_n\\q_n\end{pmatrix}.\qquad(7.1)$$

Then the diffracting domain is represented by a rectangle in the xy plane as shown in Fig. 2. The range of each two-dimensional integral in (6.22) is, in turn, represented by rectangles possessing a common corner at (x_0,y_0) that is the observation point: the range of (x_n,y_n) is given by

$$x_{n+1}<x_n<x_0;\ y_{n+1}<y_n<y_0\,,\qquad(7.2)$$

and all the variables are also limited within the diffracting domain. Thus the integrals over α and q are expressed, in terms of x and y, by

$$\begin{aligned}\int\ldots\int\mathrm{d}\alpha_1\mathrm{d}q_1\ldots\mathrm{d}\alpha_m\mathrm{d}q_m\to(-\sqrt{2})^m\int_{x_{m+1}}^{x_0}\mathrm{d}x_m\\\times\int_{y_{m+1}}^{y_0}\mathrm{d}y_m\int_{x_m}^{x_0}\mathrm{d}x_{m-1}\int_{y_m}^{y_0}\mathrm{d}y_{m-1}\ldots\int_{x_2}^{x_0}\mathrm{d}x_1\int_{y_2}^{y_0}\mathrm{d}y_1\,,\end{aligned}\qquad(7.3)$$

where

$$x_{m+1}<x_m<\ldots<x_1<x_0;\ y_{m+1}<y_m<\ldots<y_1<y_0\,.\qquad(7.4)$$

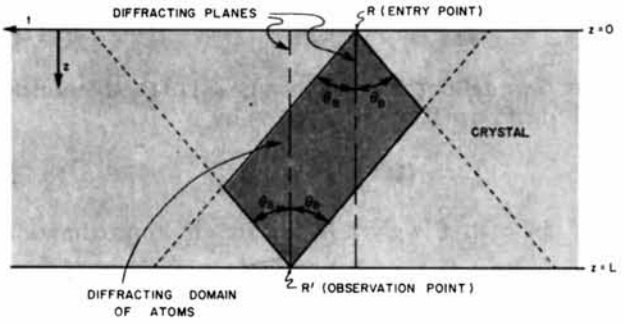

Fig. 1. A diffracting domain of atoms in the symmetrical Laue geometry. **R** and **R'** are the entry position of the X-ray beam and an exit (or observation) position of the diffracted X-ray beam. The shaded area represents the diffracting domain. θ_B is the Bragg angle.

The integral ranges in (7.3) are equivalent to the following one

$$(-i/2)^m \int_{x_{m+1}}^{x_0} dx_1 \int_{x_{m+1}}^{y_0} dy_1 \int_{x_{m+1}}^{x_1} dx_2 \int_{x_{m+1}}^{y_1} dy_2 \cdots \cdots \int_{x_{m+1}}^{x_{m-1}} dx_m \int_{y_{m+1}}^{y_{m-1}} dy_m , \quad (7.5)$$

since the range of x_n, for example, is given by

$$x_{m+1} < x_n < x_0 ; \; x_{n+1} < x_n , \quad (7.6)$$

and is depicted by a shaded area in Fig. 3.

For convenience, we write the scattering amplitude (4.8) as

$$\langle k'_{\mathbf{K}}, \mathbf{R}' ; \text{out} \, |\mathbf{k}, \mathbf{R} ; \text{in} \rangle = \tau_K N_K \exp [i\varphi(\mathbf{R}', \mathbf{R})] \, [\Psi(\mathbf{R}', \mathbf{R})]_{\mathbf{K},0} , \quad (7.7)$$

where the matrix Ψ represents the sum of the terms

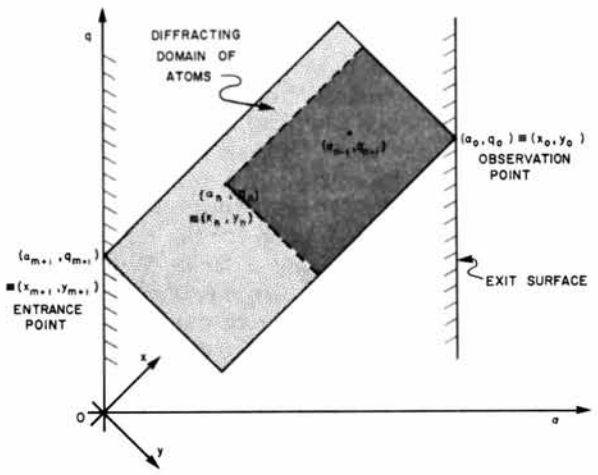

Fig. 2. The diffracting domain in a transformed coordinate system.

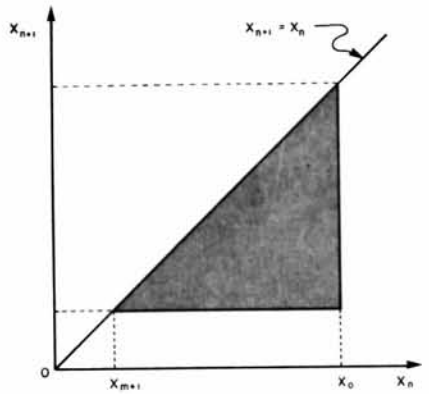

Fig. 3. Illustration of the integral ranges in the scattering amplitude.

involving multiple integrals given by (6.22). Then the matrix Ψ is written, based on the discussion above,

$$\Psi(x-x_e, y-y_e) = \sum_{m=0}^{\infty} \left(\frac{-i}{\sqrt{2\pi}}\right)^m \int_{x_e}^{x} d\xi_1 \int_{y_e}^{y} d\eta_1 \times \int_{x_e}^{\xi_1} d\xi_2 \int_{y_e}^{\eta_1} d\eta_2 \cdots \int_{x_e}^{\xi_{m-1}} d\xi_m \int_{y_e}^{\eta_{m-1}} d\eta_m \times \mathsf{U}(x-\xi_1, y-\eta_1)\mathsf{w}(\xi_1\eta_1)\mathsf{U}(\xi_1-\xi_2, \eta_1-\eta_2) \times \mathsf{w}(\xi_2\eta_2) \cdots \mathsf{w}(\xi_m\eta_m)\mathsf{U}(\xi_m-x_e, \eta_m-y_e) , \quad (7.8)$$

where the coordinate (x_e, y_e) represents the entry point of the incoming beam that is equivalent to $\mathbf{R}$ in the crystal coordinate system, and the variables (ξ_n, η_n) are related to the crystal coordinates by the transformations defined by (7.1) and (6.17*a* and *b*). To obtain the scattering amplitude (7.7) the coordinate (x, y) should be set at the observation point $\mathbf{R}'$. However, we can consider that the matrix Ψ is a function of the continuous variables x and y, the ranges of which are bounded within the interior (including the crystal surfaces) of the crystal.

Equation (7.8) can be looked at from a different point of view. The mathematical form of (7.8) is none other than the solution of an integral equation in an infinite series expansion. Therefore, we can conclude that the function $\Psi(x, y)$ satisfies the integral equation

$$\Psi(x-x_e, y-y_e) + \left(\frac{i}{\sqrt{2\pi}}\right) \int_{x_e}^{x} d\xi \int_{y_e}^{y} d\eta \times \mathsf{U}(x-\xi, y-\eta)\mathsf{w}(\xi, \eta)\Psi(\xi-x_e, \eta-y_e) = \mathsf{U}(x-x_e, y-y_e) . \quad (7.9)$$

The elements of the matrix $\mathsf{U}(x-\xi, y-\eta)$ are obtained from equations (6.18*a*, *b* and *c*) using the transformation (7.1) as follows

$$\mathsf{U}(x, y) = \begin{pmatrix} U_0(x, y) & U_H(x, y) \\ U_{-H}(x, y) & U_0(x, y) \end{pmatrix} , \quad (7.10a)$$

where

$$\left.\begin{aligned} U_0(x, y) &= \pi\beta (y/x)^{1/2} J_1(\beta\sqrt{xy}) \\ U_{\pm H}(x, y) &= i\pi\beta \exp [i\delta_{\pm}] J_0(\beta\sqrt{xy}) \end{aligned}\right\} \quad (7.10b)$$

for positive values of x and y, and U_0 and $U_{\pm H}$ become zero in the negative ranges of x and y. The matrix w is obtained from equation (6.2) and (6.3) by transforming the crystal coordinate to the (x, y) coordinate.

The scattering amplitude of an imperfect crystal for a single symmetrical Bragg diffraction has, therefore, been expressed by the matrix Ψ which satisfies the integral equation given by (7.9). This equation has been expressed in the spatial coordinate system (x, y) which is directly related to the actual coordinate system of the crystal. With this view, we can consider the integral equation (7.9) as the dynamical diffraction equation for imperfect crystals in the spatial coordinate representation. The dynamical diffraction equation (Kuriyama, 1970, 1972, 1973) previously mentioned in (5.17) still remains as the basic equation for dynamical dif-

fraction in imperfect crystals when one uses the momentum representation.

8. Discussion

The dynamical diffraction equation for imperfect crystals has been derived in the spatial coordinate representation for a single symmetrical Bragg diffraction. Because of the generality of its mathematical form, this integral equation can be considered to hold also for more general diffraction conditions. For instance, asymmetrical diffraction conditions can be accommodated if one replaces the matrix U by calculating the propagators $g(\omega; l)$ in (5.34) for a given geometry. However, the transformation from the crystal coordinate to the (x,y) coordinate system would become more complicated. In a similar way, the multiple Bragg diffraction conditions can be treated by replacing the two-by-two matrices, U and w, by matrices of higher rank. Again a more complicated transformation from the crystal coordinate system to the (x,y) coordinate system would be expected.

As long as one can find the proper transformation to the (x,y) coordinate system, the dynamical diffraction equation for these general geometrical and diffraction conditions takes the same form, an integral equation, as obtained in the previous section. Therefore, it can be concluded that the integral equation of the matrix Ψ is, indeed, a basic dynamical diffraction equation for imperfect crystals. In view of this, this equation is equivalent to the dynamical diffraction equation derived previously in the momentum representation (Kuriyama, 1970, 1972, 1973).

Although it may seem strange, it is true that in this paper we arrived at the integral equation after the solution of this equation had been found. This chronology was unavoidable at that time, since our interest was primarily to solve the dynamical diffraction equation in the momentum representation, (5.17), and express the solution as a function of position within the crystal in terms of the given spatial displacements of atoms. Since (7.7) has been found to be the solution of the integral equation, although expanded in an infinite series, one may wonder if the equation (7.9) is of any significance. Indeed, (7.7) can be a sufficient expression of the solution, if the series converges very rapidly within the first few terms for particular sets of atomic displacements.

For example, imperfections that are well localized and isolated from each other provide an example for which (7.7) is an adequate expression (Kuriyama, 1969). Another example can be found in the case where imperfections are again local (or given by a well defined function), and are statistically distributed over the entire crystal (Kuriyama, 1967; Kuriyama & Miyakawa, 1969). However, when imperfections are linked with each other or spread over a relatively large portion of the diffracting domain, the first few terms may not be sufficient to represent the series. Since the matrix U represents the propagation of scattered waves inside the perfect reference crystal, the terms, U w U, U w U w U, *etc.*, correspond to the one-collision, two-collision, *etc.* processes where after each collision, the waves propagate again as if they are in the perfect reference crystal.

It is therefore obvious that the multiple-collision processes (higher-order terms in the series) cannot be neglected for imperfections that occupy a large portion of the diffracting domain. In this case, an infinite series expansion of the solution is not convenient. Once the specific set of atomic displacements is given everywhere inside the diffracting domain, one can seek the solution analytically or numerically in the most convenient form for the given set by starting with the integral equation, thus avoiding a slowly converging form of the solution. In this sense, the integral equation of dynamical diffraction offers a larger latitude than its solution in the form of a series expansion.

Among several phenomenological theories of dynamical diffraction in imperfect crystals, the *wave* theory (Takagi, 1962, 1969; Taupin, 1964) was being rapidly accepted without careful theoretical justification (Kuriyama, 1972). Undoubtedly it was easily understood in terms of the then existing knowledge of the dynamical theory for perfect crystals if the concept of the local reciprocal lattice was accepted. In addition, with the use of computers, the *wave* theory was thought to be easily solvable, case by case, for various specific types of imperfection. It has, however, become obvious that solving the equation for the *wave* theory is quite cumbersome, requiring a large effort in computer calculation even for a single realistic type of imperfection. The situation in the case of the *ray* theory is just as bad. If one has to solve equations by computers anyway, then one should start with the most fundamental equation which, from a theoretical point, has far fewer restrictions on its validity. The integral equation derived in the previous section is one of such fundamental equations.

When the fundamental dynamical diffraction equation is expressed in the momentum representation, as given by (5.17), and accompanied by its initial condition [$S(t_0,t_0)=I$, where $t_0=0$ in (5.17)], the S matrix becomes what is known as the matricant of the system, which will be written at the coordinate t as $S(t,t_0)$ in terms of t_0. Owing to the properties of matricants (Gantmacher, 1959), the S matrix at the coordinate t is given by

$$S(t,t_0)=S(t,t_n)S(t_n,t_{n-1})\ \ldots\ S(t_2,t_1)S(t_1,t_0) \qquad (8.1)$$

as the product of the matricants between any two points ordered along the path from t_0 to t, where

$$t>t_n>t_{n-1}>\ \ldots\ >t_1>t_0\,. \qquad (8.2)$$

By contrast, the Ψ matrix in the spatial coordinate representation does not possess this property. The integral equation cannot even be reduced to a convenient differential equation. This mathematical complexity

doubtlessly creates difficulty in solving the intensity distribution in diffraction topographs for various types of imperfection. This complexity merely reflects the fact that, in an imperfect crystal, the beams tend to spread out as they scatter from different places in the crystal, and conversely, the beams at one point are under the influence of many beams created at different locations before they reach that point.

If one can assert that the beams inside the crystal proceed along a path, then the integral equation (7.9) can be reduced to a differential equation and the Ψ matrix becomes the matricant of the system. In this case, the determination of the path itself becomes a separate problem. For instance, in the calculation of the propagator g in § 6, one could have employed the approximation of the stationary phase, as demonstrated previously by Kuriyama (1968). Then, by retaining only the anomalous transmission mode, a path could have been established. Along this path, the final equation could have assumed a differential equation form, making the Ψ matrix a matricant. The diffraction conditions in high-energy electron diffraction make this approximation practical, since the Bragg angles are extremely small.

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The Use of X-ray Anomalous Scattering for the Detection of Small Deviations from Centrosymmetry*

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A quantitative relation is obtained between Bijvoet differences and the deviations from centrosymmetry of a structure. An expression is derived for the root-mean-square value of Δ, where

$$\Delta=[I(\mathbf{H})-I(\bar{\mathbf{H}})]/\sigma_N^2,\ \sigma_N^2=\sum_{j=1}^{N} f_j^2,$$

in terms of $\langle|\Delta\mathbf{r}_j|\rangle$ and k'' where $\Delta\mathbf{r}_j$ are the deviations in atomic coordinates from ideal centrosymmetry, and $k''=\Delta f''/f'$. Curves are given connecting r.m.s. Δ with $\langle|\Delta\mathbf{r}_j|\rangle$ for a two-dimensional hypothetical model. When $\langle|\Delta\mathbf{r}_j|\rangle$ is small the r.m.s. Δ is quite sensitive to $\langle|\Delta\mathbf{r}_j|\rangle$ with a moderate anomalous scatterer present in the structure. The behaviour of the Bijvoet ratio is also studied empirically.

1. Introduction

In a recent paper from this laboratory (Srinivasan & Vijayalakshmi, 1972) the use of X-ray anomalous scattering as a sensitive tool for resolving the space-group ambiguity of dibenzyl disulphide was discussed. The use of X-ray anomalous scattering effects for space group determination is well known (Okaya & Pepinsky, 1961; Ramachandran & Parthasarathy, 1963; Parthasarathy & Ramachandran, 1963). However, it has not been apparent that it could be used successfully in cases where the distinction between alternate space groups is a subtle one involving small deviations from centrosymmetry. This was in fact the case with dibenzyl disulphide where it was shown that if the

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