yielded unsatisfactory results owing to considerable beam instabilities. Hence, the present work profited from a period of excellent ring operation with stable beam and electron current life times of up to 4h.

Applications of the method to other non-cubic structures with comparable properties are most likely to corroborate the optical model, and further experiments with new substances are planned.

Financial support, granted by the Bundesminister für Forschung und Technologie, is gratefully acknowledged.

References

ABRAHAMS, S. C. & MARSH, P. (1986). *Acta Cryst.* B**42**, 61-68.

ALEXANDER, E., FELLER, S., FRAENKEL, B. S. & PEREL, J. (1965). *Nuovo Cimento*, **35**, 311-312.

BELYAKOV, V. A. & DMITRIENKO, V. E. (1989). *Nucl. Instrum. Methods*, **282**, 526-528.

BLUME, M. & KISTNER, O. C. (1968). *Phys. Rev.* **171**, 417-425.

BONSE, U. & FISCHER, K. (1981). *Nucl. Instrum. Methods*, **190**, 593-603.

BONSE, U. & HENNING, A. (1986). *Nucl. Instrum. Methods*, A**246**, 814-816.

BONSE, U. & TEWORTE, R. (1982). *J. Phys. E*, **15**, 187-190.

BREFELD, W. (1989). Private communication.

BRÜMMER, O. & DRÄGER, G. (1966). *Phys. Status Solidi*, **14**, K175-K179.

COX, A. D. & BEAUMONT, J. H. (1980). *Philos. Mag.* B**42**, 115-126.

DMITRIENKO, V. E. (1983). *Acta Cryst.* A**39**, 29-35.

DMITRIENKO, V. E. (1984). *Acta Cryst.* A**40**, 89-95.

GUNTER, M. E. (1989). *Eur. J. Mineral.* **1**, 801-814.

HART, M. (1978). *Philos. Mag.* B**38**, 41-56.

HART, M. & RODRIGUEZ, R. D. (1981). *Philos. Mag.* B**43**, 321-332.

HART, M. & SIDDONS, D. P. (1981). *Proc. R. Soc. London Ser. A*, **376**, 465-482.

HEALD, S. M. & STERN, E. A. (1977). *Phys. Rev. B*, **16**, 5549-5559.

HURWITZ, H. & JONES, R. C. (1941). *J. Opt. Soc. Am.* **31**, 493-499.

JAMES, F. & ROOS, M. (1987). *MINUIT* Program. CERN Computer Centre, Program Library No. D506. CERN, Geneva, Switzerland.

JONES, R. C. (1941). *J. Opt. Soc. Am.* **31**, 488-493, 500-503.

JONES, R. C. (1942). *J. Opt. Soc. Am.* **32**, 486-493.

JONES, R. C. (1947). *J. Opt. Soc. Am.* **37**, 107-110, 110-112.

JONES, R. C. (1948). *J. Opt. Soc. Am.* **38**, 671-685.

JONES, R. C. (1956). *J. Opt. Soc. Am.* **46**, 126-131.

KÄNZIG, W. (1957). *Ferroelectrics and Antiferroelectrics.* London: Academic Press.

KIRFEL, A. & EICHHORN, K. (1989). HASYLAB/DESY Jahresbericht, pp. 383-384. HASYLAB, Hamburg, Federal Republic of Germany.

KIRFEL, A. & PETCOV, A. (1989). HASYLAB/DESY Jahresbericht, pp. 385-386. HASYLAB, Hamburg, Federal Republic of Germany.

KIRFEL, A., PETCOV, A., FISCHER, K. & EICHHORN, K. (1988). *Z. Kristallogr.* **185**, 160-161.

KIRFEL, A., PETCOV, A., FISCHER, K. & EICHHORN, K. (1989). *Z. Kristallogr.* **186**, 158-161.

KIRFEL, A., PETCOV, A., JAUCH, W. & PALMER, A. (1989). HASYLAB/DESY Jahresbericht, pp. 387-388. HASYLAB, Hamburg, Federal Republic of Germany.

KOLPAKOV, A. V., BUSHUYEV, V. A. & KUZ'MIN, R. N. (1978). *Sov. Phys. Usp.* **21** (11), 959-977.

PETCOV, A., KIRFEL, A. & FISCHER, K. (1988). *Z. Naturforsch. Teil A*, **43**, 388-390.

SHURCLIFF, W. A. (1966). *Polarized Light.* Harvard Univ. Press.

SMEND, F., SCHAUPP, D., CZERWINSKI, H., MILLHOUSE, A. H. & SCHENK-STRAUSS, H. (1984). DESY Internal Report SR-84-003. DESY/HASYLAB, Hamburg, Federal Republic of Germany.

TEMPLETON, D. H. & TEMPLETON, L. K. (1980). *Acta Cryst.* A**36**, 436-442.

TEMPLETON, D. H. & TEMPLETON, L. K. (1982). *Acta Cryst.* A**38**, 62-67.

TEMPLETON, D. H. & TEMPLETON, L. K. (1985*a*). *Acta Cryst.* A**41**, 133-142.

TEMPLETON, D. H. & TEMPLETON, L. K. (1985*b*). *Acta Cryst.* A**41**, 365-371.

TEMPLETON, D. H. & TEMPLETON, L. K. (1987). *Acta Cryst.* A**43**, 573-574.

TEMPLETON, D. H. & TEMPLETON, L. K. (1988). *Acta Cryst.* A**44**, 1045-1051.

TEMPLETON, D. H. & TEMPLETON, L. K. (1989). *Acta Cryst.* A**45**, 39-42.

Acta Cryst. (1990). A**46**, 763-772

On Differentiation of the Scattering Matrix in Dynamical Transmission Electron Diffraction

BY S. SPEER AND J. C. H. SPENCE

Department of Physics, Arizona State University, Tempe, AZ 85287, *USA*

AND E. IHRIG

Department of Mathematics, Arizona State University, Tempe, AZ 85287, *USA*

(*Received* 3 *January* 1990; *accepted* 9 *May* 1990)

Abstract

High-energy transmission electron diffraction from thin crystals under conditions of multiple scattering is considered. An expression is derived for the Jacobian of the scattering-matrix mapping, containing all partial derivatives of the scattering-matrix elements with respect to structure-matrix elements. (This structure matrix describes the scattering crystal and incident-beam direction). These results may be used

0108-7673/90/090763-10$03.00

to determine the regions of convergent-beam electron-diffraction (CBED) patterns which are most sensitive to changes in particular structure-factor amplitudes and phases (due, for example, to the effects of crystal bonding) and to develop more-efficient CBED algorithms based, for example, on a perturbation series in the incident-beam direction. A two-beam example is given.

1. Introduction

Scattering matrices in the form of a unitary transformation arise in many fields of physics. In this paper we analyse the scattering matrix **S** which describes the multiple elastic Bragg scattering of kilovolt electrons traversing a thin perfectly crystalline slab of thickness t. Our aim has been to derive a simple formula for the derivative $D\mathbf{S}_A$ of the scattering matrix **S** with respect to entries in the structure matrix **A**, where $\mathbf{S}(\mathbf{A}) = \exp(2\pi i\mathbf{A}t)$. The matrix **A** contains both the Fourier coefficients $V_{\mathbf{g}}$ of crystal potential and parameters $S_{\mathbf{g}}$ which specify the incident-beam direction and wavevector. $D\mathbf{S}_A$ is defined to be the unique linear map which gives the best approximation to the scattering matrix in a neighborhood of **A**. If **X** is an arbitrary (small) perturbation to **A** then Taylor's theorem gives

$$\mathbf{S}(\mathbf{A}+\mathbf{X}) \simeq \mathbf{S}(\mathbf{A}) + D\mathbf{S}_{\mathbf{A}}(\mathbf{X}).$$

Our results show that, provided the structure matrix **A** is both diagonalizable and invertible (conditions nearly always met with in practice), we have

$$D\mathbf{S}_{\mathbf{A}}(\mathbf{X}) = 2\pi i t\mathbf{S}(\mathbf{A})\mathbf{X}_1 + [\mathbf{S}(\mathbf{A})\mathbf{X}_3 - \mathbf{X}_3\mathbf{S}(\mathbf{A})]\mathbf{A}^{-1}.$$

Here, the matrices $\mathbf{X}_1$ and $\mathbf{X}_3$ are computed in terms of **X** by simple formulae given in equations (17), (18), (22a) below. It is a corollary of this general case that if **A** and **X** commute, then **A** is no longer restricted to be diagonalizable or invertible, and the formula simplifies to

$$D\mathbf{S}_A(\mathbf{X}) = 2\pi i t\mathbf{S}(\mathbf{A})\mathbf{X}.$$

Now let s_{ij}, a_{kl} be arbitrary elements of the $n \times n$ scattering and structure matrices, respectively. The map $D\mathbf{S}_A$ may be thought of as an $n^2 \times n^2$ matrix with $(ij)(kl)$th element $\partial s_{ij}/\partial a_{kl}$, $i, j, k, l = 1, \ldots, n$.

An explicit formula, amenable to numerical applications, is given for this $(ijkl)$th partial derivative [(29)] and we subsequently discuss how to use these quantities to derive expressions of physical significance, such as the total derivative $\mathrm{d}I/\mathrm{d}\theta$ of an observed beam intensity with respect to incident-beam orientation. A worked example is given in Appendix 4.

A second paper will apply our results to the analysis of the effects on convergent-beam electron-diffraction (CBED) patterns of small variations in $V_{\mathbf{g}}$ and $S_{\mathbf{g}}$ (such as those due to bonding in crystals or changes in beam direction). The results may also be used for the development of more-efficient algorithms for the rapid computation of CBED patterns, in which the dynamical intensities for one orientation are expressed in terms of those for a slightly different orientation. The Jacobian might also be used to determine *directly* the changes in structure factors due to crystal bonding from a comparison of measured CBED intensities with dynamical calculations for crystals containing unbonded atoms. Our approach is based on the methods of first-order perturbation theory, and includes all the parameters (*e.g.* beam direction) in the structure matrix.

The success of X-ray and neutron crystallography owes a great deal to the development of efficient computational algorithms. Using data from various experimental techniques such as powder diffraction, direct statistical methods, isomorphous replacement and Patterson maps, these algorithms have been refined over the years to the point where the solution of crystal structures with small and moderate-sized unit cells has become almost routine. These large software packages contain a vast amount of condensed crystallographic knowledge, including methods for the solution of the phase problem, symmetry information *etc.*

The complexity of the electron-diffraction problem (due to multiple scattering) has, however, so far prevented the development of efficient standardized software packages similar to those used in X-ray crystallography. Yet the advantages of electron crystallography provide a strong incentive for their development. These advantages include the ability to obtain atomic-resolution electron-microscope images of the same region as that analyzed by CBED (using the same instrument), the ability to obtain diffraction patterns from sub-nanometer-sized regions, and greater sensitivity to bonding and ionicity effects (Humphreys, 1979). In the past, CBED patterns have been used for the study of bonding in crystals (Voss, Lehmpfuhl & Smith, 1980; Zuo, Spence & O'Keeffe, 1988), for phase identification [based on their symmetry properties (Steeds, 1979)] and, in rare cases, for the solution of unknown crystal structures (Vincent, Bird & Steeds, 1984). The favored technique has become the convergent-beam electron-diffraction (CBED) method, in which a complete rocking curve is produced simultaneously in each diffracted order.

The traditional method of simulating CBED patterns has been based either on the multislice method (Buseck, Cowley & Eyring, 1989) or on the Bloch-wave method (Bethe, 1928). A Fortran listing of a typical Bloch-wave CBED program can be found in Zuo, Gjones & Spence (1989). For accurate quantitative work it is necessary in this method to diagonalize the structure matrix **A** for every point in the experimental diffraction pattern. For the refinement of structure factors needed in the study of bonding, this

tedious process must be repeated for many combinations of structure factors and other parameters (sample thickness, accelerating voltage, absorption coefficients) until good agreement with the experimental data is obtained. Our aim here is to speed up and automate this refinement process.

The effect of a perturbation in tilt on the scattering matrix has been discussed briefly in connection with the effect of small tilts on the reducibility of the scattering matrix to two-beam form, and the consequent periodicity in thickness of lattice images, by Anstis, Lynch, Moodie & O'Keeffe (1973).

2. The scattering matrix in transmission electron diffraction

We consider a plane-wave electron beam traversing a thin crystal of thickness t in Laue or transmission geometry. It is shown in texts on electron diffraction (Hirsch, Howie, Nicholson, Pashley & Whelan, 1977; Humphreys, 1979) that the solution of the one-electron Schroedinger equation for this problem gives the complex amplitude Φ_g of a diffracted Bragg beam $\mathbf{g}$ as

$$\Phi_g = \exp[2\pi i(\mathbf{K}+\mathbf{g})\cdot\mathbf{r})]\sum_i C_0^{i*} C_g^i \exp(2\pi i\gamma_i t). \quad (1)$$

Here, $\mathbf{K} = \mathbf{K}_t + K_z\mathbf{z}$ is the mean electron wavevector inside the crystal, whose magnitude is given by

$$K^2 = |\mathbf{K}|^2 = U_0 + 2m|e|E/h^2 \quad (2)$$

with E the accelerating voltage and electron structure factors $U_g = 2m|e|V_g/h^2$, where V_g is a Fourier coefficient of crystal potential in volts. Individual Bloch waves have labeling wavevectors $\mathbf{k}^{(j)}$ such that $\gamma_j = k_z^{(j)} - K_z (\simeq k_z^{(j)} - K)$. Boundary conditions appropriate to a thin parallel-sided slab of crystal are applied. We make the projection approximation [neglect of reflections in higher-order Laue zones (HOLZ)]. Backscattered waves are neglected. We assume that the incident-beam direction is close to the surface-normal direction. Values of the eigenvector elements C_g^j and eigenvalues γ_j are obtained from the eigenvalue dispersion equation

$$\mathbf{A}C^j = \gamma_j C^j. \quad (3)$$

Here the structure matrix $\mathbf{A}$ contains the electron structure factors $U_g/2|K|$ in off-diagonal positions, and quantities specifying the incident-beam direction

$$S_g = (-2\mathbf{K}_t\cdot\mathbf{g} - \mathbf{g}^2)/2K \quad (4)$$

on the diagonal, where S_g is the excitation error for beam $\mathbf{g}$ (positive for reciprocal-lattice points inside the Ewald sphere). We define the Laue circle as the intersection of the Ewald sphere with the plane of reciprocal-lattice points which passes through the origin (the ZOLZ). Then $\mathbf{K}_t(K_x, K_y)$ is a vector drawn from the center of the Laue circle to the origin of reciprocal space. It is the component of $\mathbf{K}$ in the zero-order Laue zone. The Bragg condition is satisfied if a reciprocal-lattice point falls on the Laue circle, so that $S_g = 0$.

Niehrs (1959) first showed that (1) may be written

$$\Phi(\mathbf{g}, \mathbf{K}_t) = \mathbf{S}\Phi_o \quad (5)$$

where the scattering matrix $\mathbf{S}$ is given by Hirsch *et al.* (1977, equation 12.17):

$$\mathbf{S}(\mathbf{A}) = \mathbf{S}(t, E, U_g, \mathbf{K}_t) = \mathbf{C}\{\mathbf{E}\}\mathbf{C}^{-1} = \exp[2\pi i\mathbf{A}(\mathbf{K}_t)t] \quad (6)$$

with $\mathbf{E}$ a diagonal matrix whose ith element is $\exp(2\pi i\gamma_i t)$.

3. Formal development

Background material for this section may be found in the texts by Lancaster & Tismenetsky (1985) and Shaw (1982). In the following formal development we use matrices $\mathbf{Z}$ and Δ. At the end of § 3 the results so obtained will be applied to corresponding structure matrices $\mathbf{A}$ (where $\mathbf{Z} \leftrightarrow 2\pi i t\mathbf{A}$) and perturbations $\mathbf{X}$ (where $\Delta \leftrightarrow 2\pi i t\mathbf{X}$), which may represent physical quantities. We consider the exponential mapping $\Phi: \mathbf{C}^{n\times n} \to \mathbf{C}^{n\times n}$ defined by

$$\Phi(\mathbf{Z}) = \exp(\mathbf{Z}) = \lim_{N\to\infty} \sum_{j=0}^{N} \mathbf{Z}^j/j! = (\mathbf{I} + \mathbf{Z} + \tfrac{1}{2}\mathbf{Z}^2 + \ldots),$$

where $\mathbf{C}^{n\times n}$ is the vector space of general complex $n\times n$ matrices, of which $\mathbf{Z}$ is an element. We use the results that the mapping $\Phi(\mathbf{Z}) = \exp(\mathbf{Z})$ is everywhere analytic, and hence continuously differentiable and uniformly convergent for all $\mathbf{Z}$ in any bounded region of $\mathbf{C}^{n\times n}$.

We now restrict the analysis to those matrices $\mathbf{Z}$ which are both diagonalizable and invertible. The generalization to arbitrary $\mathbf{Z}$ is noted subsequently. The derivative $D\Phi_Z$ of Φ at $\mathbf{Z}$ is defined to be the linear map $D\Phi_Z: \mathbf{C}^{n\times n} \to \mathbf{C}^{n\times n}$ satisfying

$$\lim_{\|\Delta\|\to 0} [\Phi(\mathbf{Z}+\Delta) - \Phi(\mathbf{Z}) - D\Phi_Z(\Delta)]/\|\Delta\| = 0. \quad (7)$$

Note that, although we are restricting the form of $\mathbf{Z}$, the argument Δ of $D\Phi_Z$ (*i.e.* the perturbation to $\mathbf{Z}$) may be any general complex matrix. $D\Phi_Z$ is unique if it exists, and its $n^2 \times n^2$ matrix representation on the standard basis of C^{n^2} is the Jacobian matrix of Φ evaluated at $\mathbf{Z}$. Thus if the n^2 elements of $\mathbf{Z}$ are arranged as a row vector of dimension n^2 in some arbitrary but fixed order, so that

$$\mathbf{Z} = (Z_{ij}) \leftrightarrow (z_1, \ldots, z_{n^2})$$

and the matrices $\mathbf{\Phi}, \mathbf{\Delta}$ are mapped into corresponding

vectors

$$\Phi = (\varphi_{ij}) \leftrightarrow (\varphi_1, \ldots, \varphi_{n^2}),$$
$$\Delta = (\delta_{ij}) \leftrightarrow (\delta_1, \ldots, \delta_{n^2}),$$

then $D\Phi_Z$ may be considered to be the $n^2 \times n^2$ matrix

$$D\Phi_Z = (\partial \varphi_k / \partial z_l)_{k,l=1,\ldots,n^2}$$

and, if

$$U = [\varphi_1(\mathbf{Z}+\Delta), \ldots, \varphi_{n^2}(\mathbf{Z}+\Delta)] - [\varphi_1(\mathbf{Z}), \ldots, \varphi_{n^2}(\mathbf{Z})],$$

then

$$\lim \frac{U - [D\Phi_Z(\delta_1, \ldots, \delta_{n^2})^t]^t}{|(\delta_1, \ldots, \delta_{n^2})|} = 0,$$

where the limit is taken as $|(\delta_1, \ldots, \delta_{n^2})|$ tends to zero, and the t denotes transpose.

This is the approach to be taken when interpreting the derivatives physically. For the purposes of deriving an expression for the value of the linear transformation $D\Phi_Z$ for an arbitrary perturbation Δ, we use the result that

$$D\Phi_Z(\Delta) = \lim_{h \to 0} [\Phi(\mathbf{Z} + h\Delta) - \Phi(\mathbf{Z})]/h \qquad (8)$$

where h is a scalar.

We now define the linear operator L with respect to $\mathbf{Z}$ by

$$L = L_z = L\colon C^{n \times n} \to C^{n \times n} \qquad (9)$$

$$L(\Delta) = \mathbf{Z}\Delta\mathbf{Z}^{-1} - \Delta. \qquad (10)$$

Appendix 1 establishes that

$$D\Phi_Z[L(\Delta)] = [\exp(\mathbf{Z}), \Delta]\mathbf{Z}^{-1} \qquad (11)$$

where square brackets are used to denote commutators.

Appendix 2 establishes that, provided $\mathbf{Z}$ is diagonalizable and invertible, every general complex matrix Δ has a unique decomposition as

$$\Delta = \Delta_1 + \Delta_2 \qquad (12)$$

where

$$L(\Delta_1) = 0 \qquad (13)$$

$$L(\Delta_3) = \Delta_2 \qquad (14)$$

for some (not necessarily unique) Δ_3.

Hence, by the linearity of the derivative,

$$D\Phi_Z(\Delta) = D\Phi_Z(\Delta_1 + \Delta_2) = D\Phi_Z(\Delta_1) + D\Phi_Z(\Delta_2). \qquad (15)$$

Now, from (13) and (10), $\mathbf{Z}\Delta_1\mathbf{Z}^{-1} = \Delta_1$, thus $[\mathbf{Z}, \Delta_1] = 0$. But it follows from (8) and the definition of the exponential mapping (see Appendix 1) that if $[\mathbf{Z}, \Delta] = 0$, then $D\Phi_Z(\Delta) = \exp(\mathbf{Z})\Delta$. Hence

$$D\Phi_Z(\Delta_1) = \exp(\mathbf{Z})\Delta_1.$$

In addition, for the second term in (15),

$$D\Phi_Z(\Delta_2) = D\Phi_Z\{L(\Delta_3)\} = [\exp(\mathbf{Z}), \Delta_3]\mathbf{Z}^{-1}.$$

Finally, we have

$$D\Phi_Z(\Delta) = (\exp \mathbf{Z})\Delta_1 + [\exp(\mathbf{Z}), \Delta_3]\mathbf{Z}^{-1}$$
$$= (\exp \mathbf{Z})\Delta_1 + \{(\exp \mathbf{Z})\Delta_3 - \Delta_3(\exp \mathbf{Z})\}\mathbf{Z}^{-1}. \qquad (16)$$

This establishes the result for all Δ, and for all matrices $\mathbf{Z}$ which are both diagonalizable and invertible. The derivative, however, exists continuously for all $\mathbf{Z}$ and Δ. For completeness, therefore, we include the following statement to extend our result to arbitrary matrices $\mathbf{Z}$: Both the diagonalizable and the invertible matrices comprise sets which are dense in $\mathbf{C}^{n \times n}$. By virtue of this fact, the derivative $D\Phi_Z(\Delta)$ evaluated at a matrix $\mathbf{Z}$ which fails to be diagonalizable or invertible or both may be defined precisely (and so computed) by a limiting process using (16) and a sequence $\{\mathbf{Z}_n\}$ of diagonalizable invertible matrices. That is, if $\lim_{n \to \infty} \mathbf{Z}_n = \mathbf{Z}$, then

$$D\Phi_Z(\Delta) = \lim_{n \to \infty} \{(\exp(\mathbf{Z}_n)\Delta_1 + [(\exp \mathbf{Z}_n)\Delta_3 - \Delta_3(\exp \mathbf{Z}_n)]\mathbf{Z}_n^{-1}\}.$$

4. Evaluation of Δ_1, Δ_2 and Δ_3

We define the diagonal matrix $\mathbf{D}$ of eigenvalues γ_j by

$$\mathbf{Z} = \mathbf{C}\mathbf{D}\mathbf{C}^{-1} \qquad (17)$$

where $\mathbf{C}$ is the $n \times n$ matrix of eigenvectors of $\mathbf{Z}$. Now define

$$\mathbf{Y} = \mathbf{C}^{-1}\Delta\mathbf{C} \qquad (18)$$

and the three matrices $\mathbf{Y}_1, \mathbf{Y}_2, \mathbf{Y}_3$ componentwise by

$$(\mathbf{Y}_1)_{ij} = (\mathbf{Y})_{ij}\delta\gamma_i\gamma_j \qquad (19)$$

$$(\mathbf{Y}_2)_{ij} = (\mathbf{Y})_{ij}(1 - \delta\gamma_i\gamma_j) \qquad (20)$$

$$(\mathbf{Y}_3)_{ij} = (\mathbf{Y})_{ij}(1 - \delta_{\gamma_i\gamma_j})/(\gamma_i/\gamma_j - 1). \qquad (21)$$

In these equations, $\delta\gamma_i\gamma_j$ is the Kronecker delta and, in (21), $(\mathbf{Y}_3)_{ij}$ is understood to be zero if $\gamma_i = \gamma_j$ (critical-voltage condition), despite the division by zero. The above expressions appear to be numerically awkward, involving as they do the discontinuous Kronecker delta and the diverging term $(\gamma_i/\gamma_j - 1)^{-1}$; fortunately, this awkwardness disappears, as it must, in the final results [(29)]. If an eigenvalue degeneracy is not present, $\mathbf{Y}_1 + \mathbf{Y}_2$ is just the decomposition of $\mathbf{Y}$ into diagonal and off-diagonal elements. We now define

$$\Delta_j = \mathbf{C}\mathbf{Y}_j\mathbf{C}^{-1}, \qquad j = 1, 2, 3. \qquad (22a)$$

It is verified in Appendix 3 that Δ_1, Δ_2, Δ_3 so defined give the desired decomposition of Δ, hence, the definition of $D\Phi_Z(\Delta)$ is complete.

Now consider the scattering-matrix mapping, defined by

$$\mathbf{S}(\mathbf{A}) = \exp(2\pi i \mathbf{A}t), \qquad (22b)$$

where **A** is the structure matrix, and suppose **A** is given a complex perturbation **X**. If **A** is diagonalized as $\mathbf{CDC}^{-1}$, then we have

$$\mathbf{A}^{-1} = \mathbf{CD}^{-1}\mathbf{C}^{-1}, \tag{23}$$

where $\mathbf{D}^{-1}$ is the diagonal matrix with jth diagonal element γ_j^{-1}. Making the appropriate substitutions in the results above, it is straightforward to verify that

$$\mathbf{DS}_{\mathbf{A}}(\mathbf{X}) = \mathbf{C}[2\pi it\mathbf{EY}_1 + (\mathbf{EY}_3 - \mathbf{Y}_3\mathbf{E})\mathbf{D}^{-1}]\mathbf{C}^{-1} \tag{24}$$

where $\mathbf{Y}_1$ and $\mathbf{Y}_3$ are defined as above, with

$$\mathbf{Y} = \mathbf{C}^{-1}\mathbf{XC}.$$

The derivative of the scattering matrix **S** is given in (24) entirely in terms of quantities derivable from the structure matrix **A** and the perturbation to it **X**. This equation [and (26)] may be used for computational purposes in analyzing the sensitivity of CBED patterns to experimental and crystal structure parameters.

By Taylor's theorem, the best linear approximation to the scattering matrix **S** in the neighborhood of a point **A** is then

$$\mathbf{S}(\mathbf{A}+\mathbf{X}) \simeq \mathbf{S}(\mathbf{A}) + D\mathbf{S}_{\mathbf{A}}(\mathbf{X}). \tag{25}$$

We stress that here, as below, the perturbation **X** can be any general complex matrix. In contrast to **A**, **X** is not restricted in any way. From (24), we have

$$\mathbf{S}(\mathbf{A}+\mathbf{X}) \simeq \mathbf{C}[\mathbf{E}(\mathbf{I}+2\pi it\mathbf{Y}_1) + (\mathbf{EY}_3 - \mathbf{Y}_3\mathbf{E})\mathbf{D}^{-1}]\mathbf{C}^{-1}. \tag{26}$$

5. Evaluation of the Jacobian

We have noted that $D\mathbf{S}_{\mathbf{A}}$ has a unique representation as the $n^2 \times n^2$ matrix

$$D\mathbf{S}_A = (\partial s_p/\partial a_q)_{p,q=1,\ldots,n^2} \tag{27}$$

where we reiterate here that the matrices **S** and **A** are understood to be vectorized in some arbitrary but fixed manner [see, for example, § 12.1 in Lancaster & Tismenetsky (1985)]. In addition, we have, from (24) an expression

$$D\mathbf{S}_{\mathbf{A}}(\mathbf{X}) = [(D\mathbf{S}_{\mathbf{A}}(\mathbf{X}))_{ij}]_{i,j=1,\ldots,n}$$

where

$$[D\mathbf{S}_{\mathbf{A}}(\mathbf{X})]_{ij} = \Gamma^{ij}_{11}X_{11} + \ldots + \Gamma^{ij}_{nn}X_{nn} \tag{28}$$

for some constants Γ^{ij}_{kl}, $k, l = 1, \ldots, n$. Identifying the expressions, we find that

$$\Gamma^{ij}_{kl} = \partial s_{ij}/\partial a_{kl}|_{\mathbf{A}}.$$

Moreover, a tedious but straightforward calculation from (24) shows that

$$\Gamma^{ij}_{kl} = \sum_{p=1}^{n} C_{ip}C^{-1}_{pk} \sum_{q=1}^{n} C_{lq}C^{-1}_{qj}\{2\pi itE_p\delta_{\gamma_p\gamma_q} + [(E_p - E_q)/(\gamma_p - \gamma_q)](1 - \delta_{\gamma_p\gamma_q})\}. \tag{29}$$

Equation (29) gives the derivative $\partial s_{ij}/\partial a_{kl}|_{\mathbf{A}}$ in a readily computable form, completely independent of any perturbation **X**. Moreover, this expression simplifies considerably in several significant special cases; for example, if $[\mathbf{A}, \mathbf{X}] = 0$, or if it can be determined that no eigenvalue degeneracies exist, or if absorption is ignored. (In that case, **A** is real symmetric, hence Hermitian, and $\mathbf{C}^{-1} = \mathbf{C}^{\prime}$.)

Given the structure matrix **A** and the crystal thickness t we can immediately compute the n^4 complex quantities Γ^{kl}_{ij}, $i, j, k, l = 1, \ldots, n$. In applications of the dynamical theory, however, many different 'degeneracies' (*i.e.* equal elements in **A**) are imposed by the structure of **A**, which depends on crystal symmetry and beam direction. For example:

(1) Centrosymmetric crystals without absorption in a single orientation (plane-wave illumination). Then the scattering mapping is from $\mathbf{R}^{(n^2-n)/2}$ into $\mathbf{C}^{(n^2+n)/2}$, with additional restrictions on the image space due to unitarity.

(2) Centrosymmetric absorbing crystals in any orientation. Here the mapping is from $\mathbf{R}^n$ into $\mathbf{C}^{(n^2+n)/2}$.

(3) In almost every case, the analysis is performed only on mappings into one column or row of **S**, since only a single column has physical significance. This restriction to one column of **S** distinguishes the electron-diffraction problem from that of the total exponential mapping in an important way.

Thus we are presented with the following problem: Given any auxiliary mapping $\tilde{\mathbf{S}}$: $\mathbf{C}^M \to \mathbf{C}^N$ associated with the mapping **S**, compute the Jacobian matrix

$$D\tilde{\mathbf{S}}_{\tilde{\mathbf{A}}} = (\partial \tilde{s}_i/\partial \tilde{a}_j|_{\tilde{\mathbf{A}}})|$$

for $i = 1, \ldots, N$ and $j = 1, \ldots, M$. Here $\tilde{\mathbf{A}}$ is the structure matrix, understood to contain only $M \le n^2$ independent elements, and $\tilde{\mathbf{S}}(\tilde{\mathbf{A}})$ is an ordered N-tuple ($N \le n^2$) containing the relevant elements of the scattering matrix.

This problem may be solved on a case-by-case basis, given the set $\{\Gamma^{ij}_{kl}\}_{i,j,k,l}$ and using the definition of the derivative. The procedure is essentially that followed above in obtaining the Γ^{ij}_{kl}, and in every case we find that $\partial \tilde{s}_i/\partial \tilde{a}_j$ is some easily computed linear combination of the Γ^{ij}_{kl}.

There are two additional points to be made. First, once $D\tilde{\mathbf{S}}_{\tilde{\mathbf{A}}}$ is found, the chain rule may be used to compute derivatives of functions of the vector $\tilde{\mathbf{S}}(\tilde{\mathbf{A}})$. For example, if experimental data are collected from convergent-beam patterns, then $\tilde{\mathbf{S}} = (s_1, \ldots, s_n)$ will contain the complex scattering data corresponding to a given crystal of constant thickness t covering a range of incident-beam directions indexed by θ. Then **A** has n variable elements $a_1, \ldots, a_n$ (the diagonal elements), which are each functions of θ only. If $|s_i|^2$ is the ith beam intensity and $\mathrm{Arg}(s_i)$ the ith beam phase, then $\mathrm{d}|s_i|^2/\mathrm{d}\theta$ and $\mathrm{d}[\mathrm{Arg}(s_i)]/\mathrm{d}\theta$ are computed readily in terms of $\partial s_i/\partial a_j$ using the

chain rule. Such computations, however, require that we have the real quantities $\partial(\mathrm{Re}\, s_i)/\partial(\mathrm{Re}\, a_j)$, $\partial(\mathrm{Re}\, s_i)/\partial(\mathrm{Im}\, a_j)$, $\partial(\mathrm{Im}\, s_j)/\partial(\mathrm{Re}\, a_j)$, $\partial(\mathrm{Im}\, s_i)/\partial(\mathrm{Im}\, a_j)$, rather than the single complex quantity $\partial s_i/\partial a_j$. This leads to our second point - since $\tilde{\mathbf{S}}$ is analytic, the Cauchy-Riemann equations will hold for every **A**. In that case, we have the following additional relationships:

$$\frac{\partial s_i}{\partial a_j}=\frac{\partial(\mathrm{Re}\, s_i)}{\partial(\mathrm{Re}\, a_j)}+i\frac{\partial(\mathrm{Im}\, s_i)}{\partial(\mathrm{Re}\, a_j)}$$

and

$$\frac{\partial(\mathrm{Re}\, s_i)}{\partial(\mathrm{Re}\, a_j)}=\frac{\partial(\mathrm{Im}\, s_i)}{\partial(\mathrm{Im}\, a_j)},$$
$$\frac{\partial(\mathrm{Re}\, s_i)}{\partial(\mathrm{Im}\, a_j)}=-\frac{\partial(\mathrm{Im}\, s_i)}{\partial(\mathrm{Re}\, a_j)}.$$

This represents a translation of the complex mapping into a real mapping; such a translation is best effected when defining the mapping $\tilde{\mathbf{S}}$.

6. Discussion

Equation (29) gives the partial derivative of every complex element of the scattering matrix with respect to every element of the structure matrix **A** in terms of the eigenvalues and eigenvectors of the unperturbed structure matrix **A**. Thus we may analyze: (1) The strength of dynamical interactions - the effect of changes in one structure factor on the intensity of a different (but coupled) beam. (2) The effect of small changes in sample thickness or accelerating voltage on dynamical intensities. [Only in the simplest two-beam cases is the optimum thickness for structure-factor refinement given by $t=(n+\xi_g/4)$, where the gradient of beam intensity with respect to change in structure factor is a maximum]. (3) The effects of small changes in orientation on diffracted intensities. (4) The effects of small changes in structure-factor phases in non-centrosymmetric crystals on CBED patterns. In this way, regions most sensitive to variations in the phase of particular structure factors, for example, might be identified under general n-beam conditions. The results of such a perturbation analysis may be presented by plotting $\partial\tilde{s}_i/\partial\tilde{a}_j$ over the surface of a CBED pattern (Hoier, 1989). Computational results of this type will be presented in a forthcoming publication. A two-beam example of the evaluation of these expressions is given in Appendix 4.

This work was performed at the NSF National Center for High Resolution Electron Microscopy at Arizona State University and was supported by NSF grant DMR88-13879 (JCHS).

APPENDIX 1

We will need the following simplification of the expression for the derivative given by (8), *viz*

$$D\Phi_Z(\Delta)=\lim_{h\to 0}\left(\frac{e^{Z+h\Delta}-e^Z}{h}\right)$$
$$=\lim_{h\to 0}\lim_{N\to\infty}\sum_{j=0}^{N}\frac{(Z+h\Delta)^j-Z^j}{hj!}$$
$$=\lim_{N\to\infty}\sum_{j=0}^{N}\left(\lim_{h\to 0}\frac{(Z+h\Delta)^j-Z^j}{hj!}\right).$$

Expanding $(Z+h\Delta)^j$ we see that the Z^j terms cancel, while all terms of order higher than one in Δ go to zero in the limit as $h\to 0$. Remaining are the terms linear in Δ; specifically, we have

$$D\Phi_Z(\Delta)=\lim_{N\to\infty}\sum_{j=1}^{N}(Z^{j-1}\Delta+Z^{j-2}\Delta Z+\cdots$$
$$+Z\Delta Z^{j-2}+\Delta Z^{j-1})(j!)^{-1}. \qquad (A1)$$

This is the expression from which lemmas 1 and 2 follow, essentially as computations.

Lemma 1: if $[\mathbf{Z},\Delta]=0$, then $D\Phi_Z(\Delta)=e^{\mathbf{Z}}\Delta$.

Proof: If **Z** and Δ commute, then Δ immediately comes out of the sum (A1) on either side, then out of the limit by virtue of uniform convergence. The jth term in the sum is seen by inspection to be the sum of j terms linear in Δ, whence

$$D\Phi_Z(\Delta)=\left[\lim_{N\to\infty}\sum_{j=1}^{N}\frac{jZ^{j-1}}{j!}\right]\Delta$$
$$=\left[\lim_{N\to\infty}\sum_{k=0}^{N-1}\frac{Z^k}{k!}\right]\Delta=e^Z\Delta$$

by definition of the matrix exponential.

Lemma 2: $D\Phi_Z[L(\Delta)]=[e^Z,\Delta]\mathbf{Z}^{-1}$.

Proof: first, we claim that the operators $D\Phi_Z$ and L commute: *i.e.*

$$D\Phi_Z[L(\Delta)]=L[D\Phi_Z(\Delta)].$$

For, by linearity of the derivative,

$$D\Phi_Z[L(\Delta)]=D\Phi_Z(\mathbf{Z}\Delta\mathbf{Z}^{-1})-D\Phi_Z(\Delta),$$

while, by definition of L,

$$L[D\Phi_Z(\Delta)]=\mathbf{Z}D\Phi_Z(\Delta)\mathbf{Z}^{-1}-D\Phi_Z(\Delta)$$

so it remains only to verify that

$$D\Phi_Z(\mathbf{Z}\Delta\mathbf{Z}^{-1})=ZD\Phi_Z(\Delta)Z^{-1},$$

which follows from (1). Now, we claim that

$$L[D\Phi_Z(\Delta)]=[e^Z,\Delta]\mathbf{Z}^{-1}.$$

This is seen as follows: using (A1) and noting that the operator comes inside limit and sum, consider the result of operating on the jth term in the sum with L. Premultiplying the term by $\mathbf{Z}$ and postmultiplying by $\mathbf{Z}^{-1}$ gives

$$(1/j!)(\mathbf{Z}^j\Delta\mathbf{Z}^{-1}+\mathbf{Z}^{j-1}\Delta+\mathbf{Z}^{j-2}\Delta\mathbf{Z}+\ldots+\mathbf{Z}^2\Delta\mathbf{Z}^{j-3}+\mathbf{Z}\Delta\mathbf{Z}^{j-2}),$$

whereas the identity operation gives

$$(1/j!)(\mathbf{Z}^{j-1}\Delta+\mathbf{Z}^{j-2}\Delta\mathbf{Z}+\ldots+\mathbf{Z}\Delta\mathbf{Z}^{j-2}+\Delta\mathbf{Z}^{j-1}).$$

Subtracting, we obtain after cancellation the following result for the jth term:

$$(1/j!)(\mathbf{Z}^j\Delta\mathbf{Z}^{-1}-\Delta\mathbf{Z}^{j-1})=(1/j!)(\mathbf{Z}^j\Delta-\Delta\mathbf{Z}^j)\mathbf{Z}^{-1}.$$

Splitting the combined summation and limit into the appropriate sum and removing Δ and $\mathbf{Z}^{-1}$ from the same, one gets

$$L[D\Phi_Z(\Delta)]=\left(\lim_{N\to\infty}\sum_{j=0}^{N}\frac{\mathbf{Z}^j}{j!}\right)\Delta\mathbf{Z}^{-1}-\Delta\left(\lim_{N\to\infty}\sum_{j=0}^{N}\frac{\mathbf{Z}^j}{j!}\right)\mathbf{Z}^{-1}$$

$$=[e^Z,\Delta]\mathbf{Z}^{-1}$$

by definition of the matrix exponential. The lemma now follows from our first claim.

APPENDIX 2

We give some useful notation and results from linear algebra: Let L be a linear operator on a vector space V.

Definition: the image of L, denoted here by Im (L), is the set of all vectors $\mathbf{v}$ in V having preimages in V; *i.e.* the set of all $\mathbf{v}$ in V such that there exists $\mathbf{w}$ in V satisfying $L(\mathbf{w})=\mathbf{v}$.

Definition: the kernel of L, denoted ker (L), is the set of all vectors $\mathbf{v}$ in V which are mapped to the zero vector by L; *i.e.* the set of all $\mathbf{v}$ in V such that $L(\mathbf{v})=0$.

Result: Im (L) and ker (L) are subspaces of V.

Notation: let S, P be subspaces of V. The sum $Q=S+P$ of S and P is defined in the obvious manner. If $S\cap P=0$, then we say the sum is direct and write $Q=S\oplus P$.

Hence: if $V=S\oplus P$, then any vector $\mathbf{v}$ in V has a unique decomposition as $\mathbf{v}=\mathbf{v}_1+\mathbf{v}_2$, where $\mathbf{v}_1$ is in S and $\mathbf{v}_2$ in P. The existence of such a decomposition follows from the definition of $S+P$; the uniqueness is seen by supposing that $\mathbf{v}_3+\mathbf{v}_4$ is another such decomposition. Then $\mathbf{v}_1-\mathbf{v}_3=\mathbf{v}_4-\mathbf{v}_2$, where $\mathbf{v}_1-\mathbf{v}_3$ is in S and $\mathbf{v}_4-\mathbf{v}_2$ in P, whence the conclusion $\mathbf{v}_3=\mathbf{v}_1$ and $\mathbf{v}_4=\mathbf{v}_2$.

Lemma 3: Let the matrix Z be diagonalizable as well as invertible. Then

$$C^{n\times n}=\text{Im}\,(L)\oplus\ker(L).$$

That is, every general complex $n\times n$ matrix Δ has a unique decomposition as $X=\Delta_1+\Delta_2$, where

(i) $L(\Delta_1)=0$;

(ii) there exists some $n\times n$ matrix Δ_3, not necessarily unique, such that

$$L(\Delta_3)=\Delta_2.$$

Discussion of proof: The proof of this lemma depends on two key elements as follows:

(i) The matrix representation of the linear operator L is an $n^2\times n^2$ matrix, which we denote also by L, which is diagonalizable whenever the matrix A is diagonalizable. This result follows directly from the developments given by Lancaster & Tismenetsky (1985) (Chap. 12); see in particular proposition 12.1.4 and theorem 12.2.1.

(ii) Since L is diagonalizable, $C^{n\times n}$ is decomposed as the direct sum of the eigenspaces of L [see Shaw (1982) (2.3)]. Thus

$$C^{n\times n}=\text{Im}\,(L)\oplus\ker(L),$$

since ker (L) is the zero eigenspace of L, and Im (L) is the direct sum of all the non-zero eigenspaces.

APPENDIX 3

Justification for the formulae giving Δ_1, Δ_2, Δ_3.

We are required to show three things:

(i) $\Delta=\Delta_1+\Delta_2$

(ii) $L(\Delta_1)=0$

(iii) $L(\Delta_3)=\Delta_2$.

That is, if (i)-(iii) can be shown to hold, then we are guaranteed that Δ_1 and Δ_2 give the unique decomposition, while Δ_3 is a suitable matrix for use in (16).

(i) follows immediately from the fact that $\mathbf{Y}=\mathbf{Y}_1+\mathbf{Y}_2$ by construction:

$$\Delta_1+\Delta_2=\mathbf{C}[\mathbf{Y}_1+\mathbf{Y}_2]\mathbf{C}^{-1}=\mathbf{CYC}^{-1}=\Delta,$$

by definition of $\mathbf{Y}$.

(ii) and (iii) both follow from the following derivation: Let $j=1$ or 3. Then

$$L(\Delta_j)=\mathbf{Z}\Delta_j\mathbf{Z}^{-1}-\Delta_j=\mathbf{CDY}_j\mathbf{D}^{-1}\mathbf{C}^{-1}-\mathbf{CY}_j\mathbf{C}^{-1}$$

$$=\mathbf{C}[\mathbf{DY}_j-\mathbf{Y}_j\mathbf{D}]\mathbf{D}^{-1}\mathbf{C}^{-1}.$$

Now suppose $j=1$. We need to show that $\mathbf{Y}_1$ and $\mathbf{D}$ commute; that is,

$$(\mathbf{DY}_1)_{ij}=\gamma_i(\mathbf{Y}_1)_{ij}=(\mathbf{Y}_1\mathbf{D})_{ij}=\gamma_j(\mathbf{Y}_1)_{ij}$$

for all $i, j=1,\ldots,n$. But this equation holds only if

$$(\mathbf{Y}_1)_{ij}=0 \quad \text{or } \gamma_i=\gamma_j$$

for all i, j, which is precisely the constraint place on

the elements of $\mathbf{Y}_1$ by the kronecker delta. Hence (ii) is verified. Finally, let $j=3$ above. We have

$$(\mathbf{DY}_3-\mathbf{Y}_3\mathbf{D})_{ij}=(\gamma_i-\gamma_j)(\mathbf{Y}_3)_{ij}=\begin{cases}0 & \text{if } \gamma_i=\gamma_j\\ \gamma_j(\mathbf{Y}_2)ij & \text{if } \gamma_i\neq\gamma_j\end{cases}$$

and it is easily seen that this product satisfies the definition of the product $\mathbf{Y}_2\mathbf{D}$, whence

$$L(\Delta_3)=\mathbf{CY}_2\mathbf{DD}^{-1}\mathbf{C}^{-1}=\mathbf{CY}_2\mathbf{C}^{-1}=\Delta_2.$$

APPENDIX 4

We illustrate some of the ideas developed in the text with the simplest possible example, that of the two-beam approximation.

1. *Solution of the two-beam case*

The development and notation here parallels that of Humphreys (1979). We begin with the general two-beam dispersion relation,

$$\begin{bmatrix}K^2-k_j^2 & U_{-g}\\ U_g & K^2-|\mathbf{k}_j+\mathbf{g}|^2\end{bmatrix}\begin{bmatrix}C_{1j}\\ C_{2j}\end{bmatrix}=\begin{bmatrix}0\\0\end{bmatrix} \quad (B1)$$

where we have denoted the Bloch-wave coefficients $C_{\mathbf{0}}^j$, $C_{\mathbf{g}}^j$ by C_{1j}, C_{2j}, respectively, for $j=1, 2$, in conformity with our notation.

With the assumptions of centrosymmetric crystal geometry ($U_{-g}=U_g$) and symmetrical Laue conditions ($g_z=0$), and neglecting backscattering *via* the high-energy approximation, we obtain the usual eigenvalue equation,

$$\frac{1}{2K}\begin{bmatrix}-k_t^2 & U_g\\ U_g & -|\mathbf{k}_t+\mathbf{g}|^2\end{bmatrix}\begin{bmatrix}C_{1j}\\ C_{2j}\end{bmatrix}=(k_z^j-K)\begin{bmatrix}C_{1j}\\ C_{2j}\end{bmatrix}. \quad (B2)$$

In general, $\mathbf{k}_t$ is antiparallel to $\mathbf{g}$ ($\mathbf{k}_t=-\mathbf{g}/2$ at the Bragg angle). Hence $-|\mathbf{k}_t+\mathbf{g}|^2=-(k_t^2-2k_tg+g^2)$. For simplicity, we bring the $k_t^2/2K$ term over to the right side of (2), making the eigenvalues

$$\gamma_j=k_z^j-K+k_t^2/2K.$$

Employing Humphreys's notation, we set

$$\xi_g=K/U_g$$

$$s=-(g/2K)(g-2k_t) \quad r=(s^2+1/\xi_g^2)^{1/2}.$$

Here ξ_g is the extinction distance, s the excitation error, and we have set r equal to Humphreys's quantity s'. In this notation, the eigenvalue equation we wish to solve is

$$\mathbf{A}\begin{bmatrix}C_{1j}\\ C_{2j}\end{bmatrix}=\gamma_j\begin{bmatrix}C_{1j}\\ C_{2j}\end{bmatrix}, \text{ where } \mathbf{A}=\begin{bmatrix}0 & \frac{1}{2\xi_g}\\ \frac{1}{2\xi_g} & s\end{bmatrix}.$$

The solution is straightforward by ordinary means, and is given by $\mathbf{A}=\mathbf{CDC}^t$, where $\mathbf{C}^t=\mathbf{C}^{-1}$ (since $\mathbf{A}$ is real Hermitian), and

$$\mathbf{D}=\begin{bmatrix}\gamma_1 & 0\\ 0 & \gamma_2\end{bmatrix}=\begin{bmatrix}-\frac{1}{2}(r-s) & 0\\ 0 & \frac{1}{2}(r+s)\end{bmatrix},$$

$$\mathbf{C}=\begin{bmatrix}-\dfrac{1}{\xi_gQ_1} & -\dfrac{1}{\xi_gQ_2}\\ \dfrac{r-s}{Q_1} & \dfrac{-(r+s)}{Q_2}\end{bmatrix}$$

where we have defined

$$Q_1=[\xi_g^{-2}+(r-s)^2]^{1/2}=[2r(r-s)]^{1/2}$$

$$Q_2=[\xi_g^{-2}+(r+s)^2]^{1/2}=[2r(r+s)]^{1/2}.$$

The scattering matrix is $\mathbf{S}(\mathbf{A})=(s_{ij})=\exp(2\pi i\mathbf{A}t)=\mathbf{CEC}^t$, where $\mathbf{E}$ is the diagonal matrix with jth diagonal element $\exp(2\pi i\gamma_j t)$ for $j=1, 2$. Performing the matrix multiplication, we find

$$\mathbf{S}(\mathbf{A})=\exp(\pi ist)\times\begin{bmatrix}\cos(\pi rt)-i(s/r)\sin(\pi rt) & (i/\xi_gr)\sin(\pi rt)\\ (i/\xi_gr)\sin(\pi rt) & \cos(\pi rt)+i(s/r)\sin(\pi rt)\end{bmatrix}. \quad (B2.5)$$

The beam intensities are then

$$I_g=|s_{21}|^2=\left(\frac{\pi}{\xi_g}\right)^2\left[\frac{\sin(\pi rt)}{\pi r}\right]^2$$

$$I_0=|s_{11}|^2=1-I_g. \quad (B3)$$

This completes the usual treatment of the two-beam case. The intent has been to fix notation.

2. *Computation of the Jacobian*

We wish to evaluate the 4×4 matrix $D\mathbf{S}$ at $\mathbf{A}$; *i.e.* we wish to calculate $D\mathbf{S}_\mathbf{A}$. We introduce the arbitrary vectorization

$$\mathbf{X}=(x_{ij})\rightarrow(\mathbf{X})_{vec}=(x_{11}, x_{21}, x_{12}, x_{22})^t$$

for any 2×2 matrix $\mathbf{X}$, where the t denotes transposition. Then from (27) and (28) we have

$$D\mathbf{S}_\mathbf{A}=2\pi it\exp(\pi ist)\begin{bmatrix}\Psi_{11}^{11} & \Psi_{21}^{11} & \Psi_{12}^{11} & \Psi_{22}^{11}\\ \Psi_{11}^{21} & \Psi_{21}^{21} & \Psi_{12}^{21} & \Psi_{22}^{21}\\ \Psi_{11}^{12} & \Psi_{21}^{12} & \Psi_{12}^{12} & \Psi_{22}^{12}\\ \Psi_{11}^{22} & \Psi_{21}^{22} & \Psi_{12}^{22} & \Psi_{22}^{22}\end{bmatrix}, \quad (B4)$$

where Ψ_{kl}^{ij} is evaluated at $\mathbf{A}$, and is defined by

$$\partial s_{ij}/\partial a_{kl}=2\pi it\exp(\pi ist)\Psi_{kl}^{ij}. \quad (B5)$$

Expanding (29) (remembering that $\mathbf{C}^{-1}=\mathbf{C}^t$), we find

$$\begin{aligned}\Psi_{kl}^{ij}=&\cos(\pi rt)(C_{i2}C_{j2}C_{k2}C_{l2}+C_{i1}C_{j1}C_{k1}C_{l1})\\&+i\sin(\pi rt)(C_{i2}C_{j2}C_{k2}C_{l2}-C_{i1}C_{j1}C_{k1}C_{l1})\\&+[\sin(\pi rt)/\pi rt](C_{i2}C_{j1}C_{k2}C_{l1}\\&+C_{i1}C_{j2}C_{k1}C_{l2}).\end{aligned}$$

Note that $\Psi_{kl}^{ij}=\Psi_{ij}^{kl}$; *i.e.* $D\mathbf{S}_\mathbf{A}$ is symmetric, so we need only specify the diagonal elements and the six elements in the upper triangle. The following relations are useful in computing the Ψ_{kl}^{ij}.

$$\det(\mathbf{C})=+1;\qquad Q_1Q_2=\frac{2r}{\xi_g};$$

$$\frac{1}{Q_1^2}+\frac{1}{Q_2^2}=\xi_g^2;\qquad \frac{1}{Q_1^2}-\frac{1}{Q_2^2}=\frac{s}{r}\xi_g^2$$

$$\frac{1}{Q_1^4}+\frac{1}{Q_2^4}=\left(1-\frac{1}{2\xi_g^2r^2}\right)\xi_g^4;\qquad \frac{1}{Q_1^4}-\frac{1}{Q_2^4}=\frac{s}{r}\xi_g^4.$$

After a tedious computation, we find that

$$\begin{aligned}\Psi_{11}^{11}&=[1-(2\xi_g^2r^2)^{-1}]\cos(\pi rt)-i(s/r)\sin(\pi rt)\\&\quad+(2\xi_g^2r^2)^{-1}\sin(\pi rt)/\pi rt;\\\Psi_{22}^{22}&=\Psi_{11}^{11}+2i(s/r)\sin(\pi rt);\\\Psi_{12}^{12}&=\Psi_{21}^{21}=(2\xi_g^2r^2)^{-1}\cos(\pi rt)\\&\quad+[1-(2\xi_g^2r^2)^{-1}]\sin(\pi rt)/\pi rt;\qquad (B6)\\\Psi_{21}^{11}&=\Psi_{12}^{11}=-(s/2\xi_gr^2)\cos(\pi rt)+(i/2\xi_gr)\sin(\pi rt)\\&\quad+(s/2\xi_gr^2)\sin(\pi rt)/\pi rt;\\\Psi_{22}^{21}&=\Psi_{22}^{12}=-\Psi_{21}^{11}+(i/\xi_gr)\sin(\pi rt);\\\Psi_{22}^{11}&=\Psi_{12}^{21}=\Psi_{12}^{12}-\sin(\pi rt)/\pi rt.\end{aligned}$$

3. *Examples*

We have remarked that if $\mathbf{X}$ is a perturbation to $\mathbf{A}$ satisfying $[\mathbf{A},\mathbf{X}]=\mathbf{0}$, then the expression for the derivative simplifies to

$$D\mathbf{S}_\mathbf{A}(\mathbf{X})=\mathbf{S}(\mathbf{A})\mathbf{X}=\exp(2\pi i\mathbf{A}t)\mathbf{X}.$$

For example, take $\mathbf{X}=c\mathbf{I}$, a constant complex multiple of the 2×2 identity matrix. Then certainly $[\mathbf{A},\mathbf{X}]=\mathbf{0}$, and

$$\begin{aligned}[D\mathbf{S}_\mathbf{A}(\mathbf{X})]_{\text{vec}}&=D\mathbf{S}_\mathbf{A}\begin{bmatrix}c\\0\\0\\c\end{bmatrix}\\&=(c)2\pi it\exp(\pi ist)(\Psi_{11}^{11}+\Psi_{22}^{11},\\&\quad\Psi_{11}^{21}+\Psi_{22}^{21},\Psi_{11}^{12}+\Psi_{22}^{12},\Psi_{11}^{22}+\Psi_{22}^{22})^t\\&=[\mathbf{S}(\mathbf{A})c\mathbf{I}]_{\text{vec}}=[\mathbf{S}(\mathbf{A})\mathbf{X}]_{\text{vec}},\end{aligned}$$

as we see by comparison with (*B*2.5).

Similarly, it is clear that the structure matrix $\mathbf{A}$ commutes with itself; accordingly, we expect that

$$[D\mathbf{S}_\mathbf{A}(\mathbf{A})]_{\text{vec}}=D\mathbf{S}_\mathbf{A}\begin{bmatrix}0\\1/2\xi_g\\1/2\xi_g\\s\end{bmatrix}=[\exp(2\pi i\mathbf{A}t)\mathbf{A}]_{\text{vec}}$$

and the verification is straightforward from (*B*2.5), (*B*4), (*B*5) and (*B*6). Now, denote by θ the angular deviation from vertical of the incident beam. Then all the angular dependence of the structure matrix is contained in k_t, *via* the relation $k_t=K\sin\theta$. Moreover, the $k_t^2/2K$ term which we have shuffled into the eigenvalues just adds an arbitrary multiplicative phase to the complex scattering data, so this θ dependence can be ignored for all physical purposes. Thus, $\mathbf{A}$ is dependent on θ only through the parameter s. Explicitly,

$$\begin{aligned}s=s(\theta)&=-g(g/2K-\sin\theta)\\&=g(\sin\theta-\sin\theta_b),\end{aligned}$$

where θ_b denotes the Bragg angle; $\sin\theta_b=g/2K$. Since $s=0$ when $\theta=\theta_b$, the matrix

$$\mathbf{X}=\begin{bmatrix}0&0\\0&s\end{bmatrix}$$

is a small perturbation to

$$\mathbf{A}(\theta_b)=\begin{bmatrix}0&1/2\xi_g\\1/2\xi_g&0\end{bmatrix}$$

for θ near θ_b. Setting $s=0$ in (*B*2.5), (*B*5) and (*B*6), we obtain a first-order approximation to the scattering matrix for orientations near Bragg incidence:

$$\begin{aligned}\mathbf{S}(\theta)&=\mathbf{S}[\mathbf{A}(\theta)]\\&\simeq\mathbf{S}[\mathbf{A}(\theta_b)]+D\mathbf{S}_{\mathbf{A}(\theta_b)}(\mathbf{X})\\&=\begin{bmatrix}\cos\left(\frac{\pi t}{\xi_g}\right)&i\sin\left(\frac{\pi t}{\xi_g}\right)\\i\sin\left(\frac{\pi t}{\xi_g}\right)&\cos\left(\frac{\pi t}{\xi_g}\right)\end{bmatrix}\\&\quad+\pi itg(\sin\theta-\sin\theta_b)\\&\quad\times\begin{bmatrix}\cos\left(\frac{\pi t}{\xi_g}\right)-\left(\frac{\pi t}{\xi_g}\right)^{-1}\sin\left(\frac{\pi t}{\xi_g}\right)&i\sin\left(\frac{\pi t}{\xi_g}\right)\\i\sin\left(\frac{\pi t}{\xi_g}\right)&\cos\left(\frac{\pi t}{\xi_g}\right)+\left(\frac{\pi t}{\xi_g}\right)^{-1}\sin\left(\frac{\pi t}{\xi_g}\right)\end{bmatrix}.\end{aligned}$$

Finally, to analyze rocking curves we want analytical expressions for the total derivatives $dI_0/d\theta$ and $dI_g/d\theta$. Consider $I_0 = |s_{11}|^2$. Let a superscript asterisk denote the complex conjugate. Then if $\mathbf{A} = (a_{kl})$, we have

$$\frac{dI_0}{d\theta} = \frac{d}{d\theta}|s_{11}|^2 = 2\,\mathrm{Re}\left(\frac{ds_{11}}{d\theta}\,s_{11}^*\right),$$

where

$$\frac{ds_{11}}{d\theta} = \sum_{k=1}^{2}\sum_{l=1}^{2}\frac{\partial s_{11}}{\partial a_{kl}}\frac{da_{kl}}{d\theta} = \frac{\partial s_{11}}{\partial s}\frac{ds}{d\theta},$$

since $s = a_{22}$ is the only element of $\mathbf{A}$ which depends on θ. Since

$$\frac{\partial s_{11}}{\partial s} = 2\pi i t \exp(\pi i s t)\Psi_{22}^{11} \quad \text{and} \quad \frac{ds}{d\theta} = g\cos\theta,$$

we compute immediately

$$\begin{aligned}\frac{dI_0}{d\theta} &= 2\,\mathrm{Re}\left(\frac{\partial s_{11}}{\partial s}\frac{ds}{d\theta}s_{11}^*\right)\\ &= \frac{-2\pi t g\cos\theta}{\xi_g^2 r^2}\left(\frac{s}{r}\right)\sin(\pi r t)\\ &\quad\times\left[\cos(\pi r t) - \frac{\sin(\pi r t)}{\pi r t}\right].\end{aligned}$$

By an exactly similar computation, we find

$$\frac{dI_g}{d\theta} = 2\,\mathrm{Re}\left(\frac{\partial s_{21}}{\partial s}\frac{ds}{d\theta}s_{21}^*\right) = -\frac{dI_0}{d\theta}.$$

The correctness of these expressions may be easily checked directly from (*B*3); it is much easier in this case to compute the total derivatives in this manner. When the dimension of the matrices exceeds two, however, it is in general impossible to perform the necessary analytical diagonalization of the structure matrix to obtain expressions for $I(\theta)$, so if the derivative is to be computed at all, it must ordinarily be approximated numerically by a difference quotient. In contrast to this, our method allows such derivatives to be calculated directly for matrices of any size.

References

ANSTIS, G. R., LYNCH, D. F., MOODIE, A. F. & O'KEEFFE, M. A. (1973). *Acta Cryst.* **A29**, 138-147.

BETHE, H. A. (1928). *Ann. Phys. (Leipzig)*, **87**, 55-129.

BUSECK, P., COWLEY, J. M. & EYRING, L. (1989). *High Resolution Electron Microscopy.* Oxford Univ. Press.

HIRSCH, P. S., HOWIE, A., NICHOLSON, R. B., PASHLEY, D. W. & WHELAN, M. J. (1977). *Electron Microscopy of Thin Crystals.* Florida: Robert E. Krieger.

HOIER, R. (1989). Private communication.

HUMPHREYS, C. J. (1979). *Rep. Prog. Phys.* **42**, 1825-1887.

LANCASTER, P. & TISMENETSKY, M. (1985). *The Theory of Matrices*, 2nd ed. New York: Academic Press.

NIEHRS, H. (1959). *Z. Naturforsch. Teil A*, **14**, 504-514.

SHAW, R. (1982). *Linear Algebra and Group Representations.* New York: Academic Press.

STEEDS, J. W. (1979). *Introduction to Analytical Electron Microscopy.* New York: Plenum Press.

VINCENT, R., BIRD, D. M. & STEEDS, J. W. (1984). *Philos. Mag.* **A50**(6), 745-763.

VOSS, R., LEHMPFUHL, G. & SMITH, P. J. (1980). *Z. Naturforsch. Teil A*, **35**, 973-984.

ZUO, J. M., GJONES, K. & SPENCE, J. C. H. (1989). *J. Electron Micros. Tech.* **12**, 29-55.

ZUO, J. M., SPENCE, J. C. H. & O'KEEFFE, M. (1988). *Phys. Rev. Lett.* **61**, 353-356.

SHORT COMMUNICATIONS

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible.*

Acta Cryst. (1990). **A46**, 772-776

The piezoelectric, elastic, photoelastic and Brillouin tensors for point groups with fivefold rotation axes.

By YI-JIAN JIANG, LI-JI LIAO and GANG CHEN, *Department of Applied Physics, Beijing Polytechnic University, Beijing*, 100022, *People's Republic of China*, and PENG-XIANG ZHANG, *Institute of Physics, Academia Sinica, Beijing*, 100080, *People's Republic of China*

(*Received* 6 *December* 1989; *accepted* 30 *April* 1990)

Abstract

The piezoelectric, elastic, photoelastic and Brillouin tensors for the point groups $5(C_5)$, $\bar{5}(S_{10})$, $\bar{1}0(C_{5h})$, $\bar{1}0m2(D_{5h})$, $52(D_5)$, $5m(C_{5v})$, $52m(D_{5d})$, $235(I)$ and $(2/m)\bar{3}\bar{5}(I_h)$ have been calculated and are tabulated here.

Introduction

Although periodic crystals with pentagonal symmetry in two dimensions and icosahedral symmetry in three dimensions cannot exist, there are both theoretical (Levine & Steinhandt, 1984) and experimental (Shechtmen, Blech,

0108-7673/90/090772-05$03.00