JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 17, SUPPLEMENT B-II, 1962
PROCEEDINGS OF INTERNATIONAL CONFERENCE ON MAGNETISM AND CRYSTALLOGRAPHY, 1961, VOL. II

Electron Diffraction Intensities from Thick Crystals

L. STURKEY

The Dow Metal Products Company, Metallurgical Laboratory
Midland, Michigan, U.S.A.

Using the scattering-matrix formulation, electron diffraction intensities have been computed for two cases in which many simultaneous reflections are considered. In one case five reflections are treated in 100Å steps to 2000Å of crystal thickness and in the other twenty-one reflections are calculated in 50Å steps to 1500Å.

The results show that all intensities are roughly periodic with thickness, but the periods and relative intensities are greatly different from those calculated from a simple two-beam case. Forbidden reflections remain significant even for very thick crystals.

Two reliable approximations are presented and their range of validity demonstrated. A satisfactory method for introducing absorption is given, and the application to electron microscopy is described.

The "scattering-matrix" method provides the most convenient and rigorous system for considering the multiple interactions that occur in electron transmission diffraction patterns:

$$\begin{pmatrix}\phi_0(y)\\ \phi_1(y)\\ \phi_2(y)\\ \cdot\\ \cdot\end{pmatrix}=\exp(iy)\begin{pmatrix}k_0-k_y(0) & r_{0,1} & r_{0,2} & \cdot & \cdot\\ r_{1,0} & k_0-k_y(1) & r_{1,2} & \cdot & \cdot\\ r_{2,0} & r_{2,1} & k_0-k_y(2) & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\\ \cdot & \cdot & \cdot & \cdot & \cdot\end{pmatrix}\cdot\begin{pmatrix}1\\ 0\\ 0\\ \cdot\\ \cdot\end{pmatrix}$$

where y=plate thickness, $k_0=2\pi/\lambda$,

$$k_y(i)=(2\pi/\lambda)\cos\theta_i,\quad r_{i,0}=\pi\frac{V_{i,0}}{E}$$

$V_{i,0}$ = Fourier coeff. of potential for scattering from direction θ_0 to direction θ_i,
E=acc. voltage of electrons used.

The intensity of a reflection is given by

$$I_i(y)=\phi_i(y)\phi_i^*(y)$$

For thick crystals there is no obvious criterion for deciding which reflections are to be considered, and the very slow convergence of the exponential function of the matrix for even moderate thickness makes the expansion into a power series relatively useless. Therefore, it seems advisable to make some calculations for thick crystals considering many reflections to obtain some idea of the mathematical properties of the formulation. Such calculations are especially desirable to place the electron microscope study of imperfections in thin films on a sound basis.

Since the expression $\exp(i\boldsymbol{M}ny)=[\exp i\boldsymbol{M}y]^n$, the complete matrix for a small thickness $[\exp i\boldsymbol{M}y]$ was calculated, and intensity values for integral multiples of y were obtained by raising the matrix to successively higher powers. For each power higher than the first, only the first column was necessary.

Case I: In order to separate the effects of variations in Fourier coefficients from variations in angles of incidence, the following hypothetical matrix equation was calculated up to twenty powers:

$$\begin{pmatrix}\phi_0(100\text{ n})\\ \phi_1(100\text{ n})\\ \phi_2(100\text{ n})\\ \phi_3(100\text{ n})\\ \phi_4(100\text{ n})\end{pmatrix}=\left\{\exp i\begin{pmatrix}.628 & .333 & .333 & .333 & .333\\ .333 & 0 & .333 & .333 & .333\\ .333 & .333 & .628 & .333 & .333\\ .333 & .333 & .333 & 2.51 & .333\\ .333 & .333 & .333 & .333 & 2.51\end{pmatrix}\right\}^n\begin{pmatrix}1\\ 0\\ 0\\ 0\\ 0\end{pmatrix}$$

The results for the transmitted intensity and the reflection set at the Bragg angle, I_2, are shown in Fig. 1. along with the intensity of one of the other reflections.

The average intensities and periodicities of all the beams were computed and compared with those calculated from a two-beam approximation. These results are shown in the

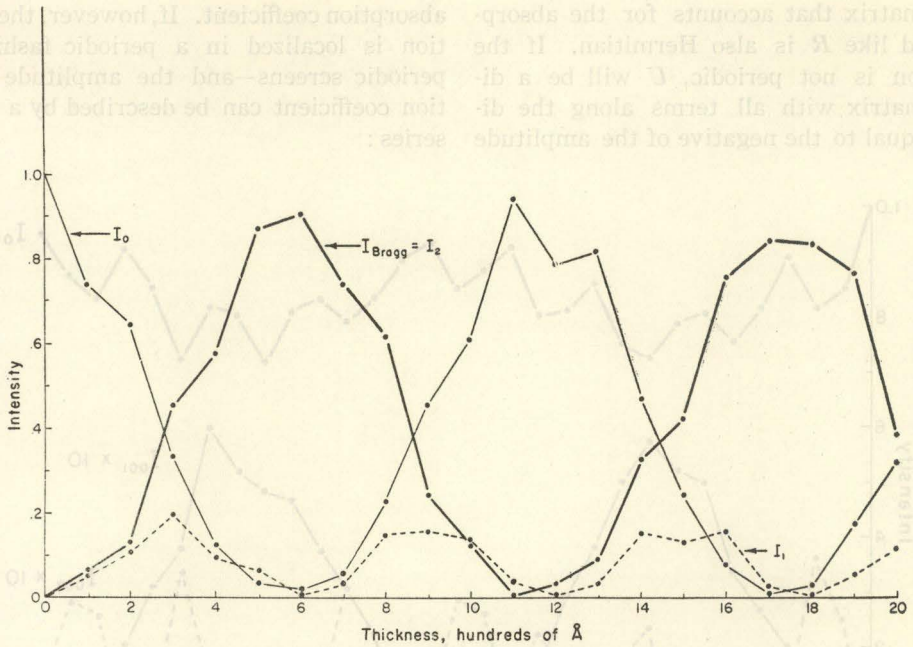

Fig. 1. Variation of intensity with thickness of transmitted intensity I_0, Bragg reflection I_2, and another reflection I, for matrix of Case I.

following table:

	I_0	I_1	$I_2=\theta_B$	$I_3=I_4$
Av. Int. 0~2000Å	.356	.085	.458	.050
Av. Int. 2-Beam	.500	.106	.500	.032
Periodicity 0~2000Å	1100Å	600Å	1100Å	270Å
2-Beam Periodicity	943Å	685Å	943Å	314Å

$I_0=\psi_0\psi_0^*$ $I_1=\psi_1\psi_1^*$, etc. I_2=Bragg reflection

Case II: Twenty-one simultaneous reflections were considered for the magnesium structure with incident beam (1) exactly parallel to a close packed direction, i.e. perpendicular to a (110) plane; and (2) then tilted slightly so Bragg conditions for (002) reflection were satisfied. The elementary matrix was for a thickness of 50Å, λ=0,5Å. E=60kV. Thirty powers of exponential of this matrix were calculated to give intensities in 50Å up to 1500Å. For the case of normal incidence (1) on the (110) plane the results are shown in Fig. 2. The case for Bragg reflection from the (002) plane is shown in Fig. 3. In all cases studied, the intensity of the directly transmitted beam plus that of the Bragg reflection accounts for only about 80 % of the total intensity. All reflections are approximately simply periodic with periods greatly different from those expected for a 2-beam case.

Approximations: The best approximation found to-date that preserves the metric of the space is of the form:

$$e^{A+B+C} \doteqdot e^{C/4}e^{B/2}e^{C/4}e^{A}e^{C/4}e^{B/2}e^{C/4}$$

$$AB \neq BA, \quad \text{etc.}$$

If the central core is the exponential of the 2×2 matrix containing the incident and Bragg-reflection beams, the approximation will be a good one. The periodicities computed in this way will not necessarily be accurate, but the average intensities over a range of thickness will be close to the true values.

The approximation discussed at the Montreal Symposium in 1957[1] has been found to be most useful in deciding how many terms are to be included in the scattering matrix and in discussing the formulation theoretically.

Absorption: For the case of true absorption, the scattering-matrix formulation is:

$$\begin{pmatrix} \phi_0(y) \\ \phi_1(y) \\ \phi_2(y) \\ \vdots \end{pmatrix} = \exp\left[(i\boldsymbol{R}+\boldsymbol{U})y\right] \begin{pmatrix} 1 \\ 0 \\ 0 \\ \vdots \end{pmatrix}$$

$\boldsymbol{U}$ is a matrix that accounts for the absorption, and like $\boldsymbol{R}$ is also Hermitian. If the absorption is not periodic, $\boldsymbol{U}$ will be a diagonal matrix with all terms along the diagonal equal to the negative of the amplitude absorption coefficient. If, however, the absorption is localized in a periodic fashion—i.e. periodic screens—and the amplitude absorption coefficient can be described by a Fourier series:

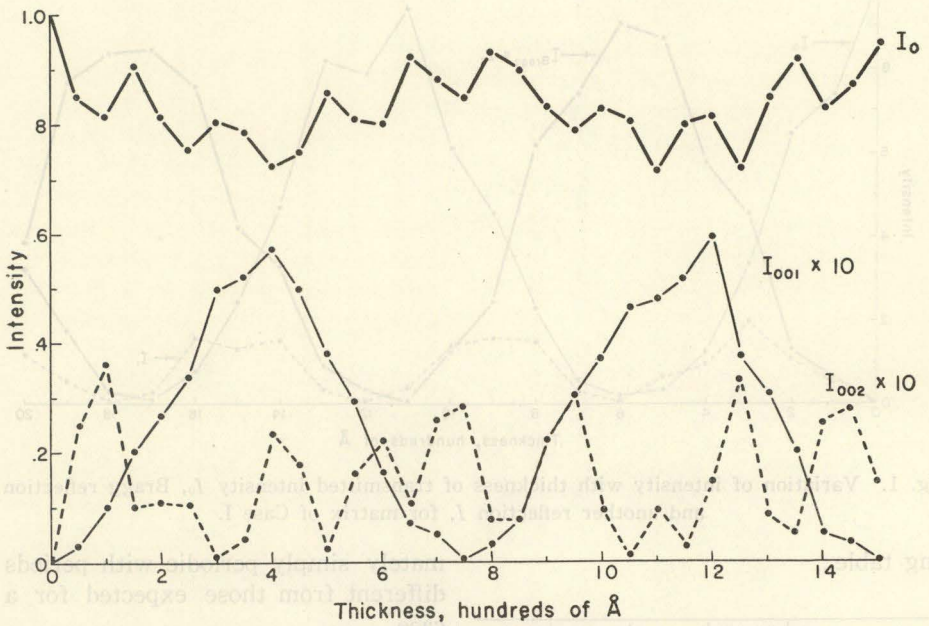

Fig. 2. Variation of intensity with thickness for electron beam normal to (110) plane of magnesium. Shown are transmitted beam I_0, the basal reflection $I_{(002)}$, and the forbidden reflection $I_{(001)}$. Case II-1.

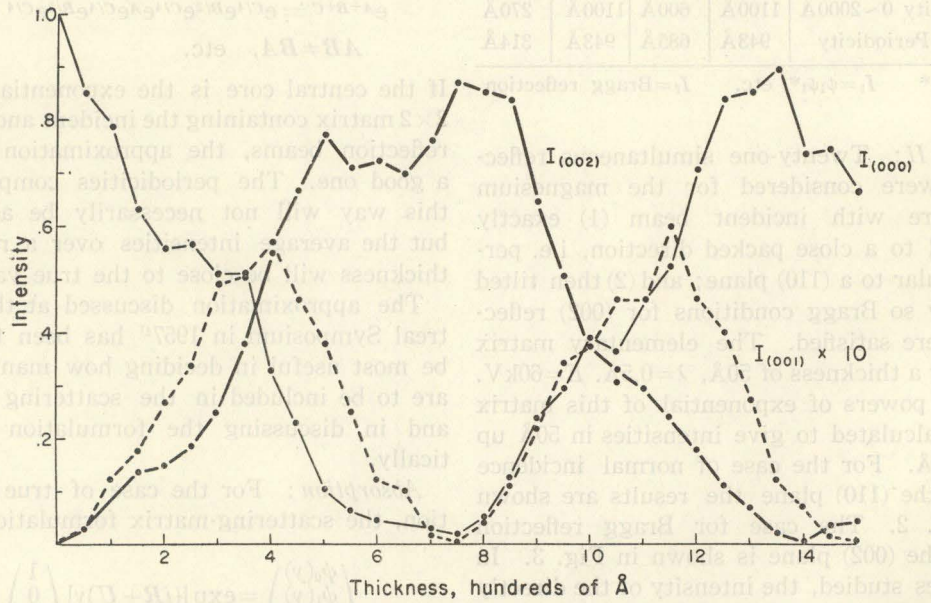

Fig. 3. Variation of electron diffracted intensity with thickness for Bragg reflection from basal plane of magnesium. Shown are transmitted intensity I_0, Bragg reflection $I_{(002)}$, and forbidden reflection $I_{(001)}$. Case II-2.

$$\mu=\mu_0+\sum_{hkl}|\mu_{khl}|-\sum_{hkl}\mu\, e^{i2\pi/\lambda\, g\cdot r}$$

the components of the absorption matrix are:

$$U_{k,k}=-(\mu_0+\sum_i|\mu_i|)$$

$$U_{\substack{jk\\ i\neq k}}=\mu_{j-k}=\mu^*_{k-j}$$

For the two-beam case, with one periodic scattering coefficient and one periodic absorption coefficient, the transmitted and reflected intensities for exact Bragg incidence are:

$$I_{\text{trans.}}=e^{-(2\mu_0+4\mu_1)t}\{\cos^2(rt)+\sinh^2(\mu_1 t)\}$$

$$I_{\text{refl.}}=e^{-(2\mu_0+4\mu_1)t}\{\sin^2(rt)+\sinh^2(\mu_1 t)\}$$

Electron Microscope Applications: The scattering matrix method is particularly useful in deriving the transmitted intensity observed in electron microscope studies of thin films, since any sequence of disorders may be conveniently described by a sequence of exponentials of scattering matrices:

$$\begin{pmatrix}\psi_0\,(t_1+t_2+t_3)\\ \psi_1\,(t_1+t_2+t_3)\\ \psi_2\,(t_1+t_2+t_3)\\ \cdot\\ \cdot\end{pmatrix}=e^{iR_3t_3}e^{iR_2t_2}e^{iR_1t_1}\begin{pmatrix}1\\0\\0\\ \cdot\\ \cdot\end{pmatrix}$$

The phases of the components of the various matrices must then all be referred to the same basis.

For a fault planes of phase displacement α at a thickness t_1, where the total film thickness is t_1+t_2, the two-beam results for exact Bragg incidence are:

$$I_{\text{trans.}}=\cos^2\alpha/2\cos^2 r(t_1+t_2)+\sin^2\alpha/2\cos^2 r(t_1-t_2)$$

$$I_{\text{refl.}}=\cos^2\alpha/2\sin^2 r(t_1+t_2)+\sin^2\alpha/2\sin^2 r(t_1-t_2)$$

The intensity contours are thus symmetrical about the center of the fault. The inclusion of a periodic absorption does not change this symmetry for a material containing only one kind of atom. Since the center of a dislocation may be considered as a fault displacement of π, the beaded appearance of a dislocation is obviously explained by the same equations. Many other intensity variations in electron microscope images are thus easily explained, However, observed periodicities must be used with caution, since these are not usually the simple two-beam periodicities.

Reference

1 L. Sturkey, *Acta Cryst.* **10** (1957) 858.

DISCUSSION

H. Niehrs: I should like to give only a general suggestion on the application of the matrix formulation, not especialy relating to Dr. Sturkey's paper. Usually the case of only one incident primary beam is considered, but the same scattering matrix may generally be operated on a superposition of several coherent primary beams. This alone would be of no practical importance. However, the position of the first component corresponding to the one primary beam may be displaced to another position within the 1-columned matrix of the primary amplitudes, and such a displacement would practically be useful in solving the diffraction problem for a *different* angle of incidence with the *same* scattering matrix.

L. Sturkey: I quite agree with Dr. Niehrs. However, the matrix should be large enough so that the incident beam is approximately equally surrounded by considered reflections in such cases.

A. F. Moodie: For the case of a heavy atom structure analysis, the phase grating approximation, which may be regarded as an approximation to the scattering matrix theory, seems to offer a more convenient method for numerical computation.

L. Sturkey: For a heavy atom structure it is true of course that the exponential of the scattering matrix converges more slowly, since the Fourier coefficients are large for comparable thickness. In addition, as the atom gets heavier and heavier, more and more terms are required in the scattering matrix to be sure it has not been cut off too soon. However, the computation procedure is no more complicated, and whether an approximation used is a good one or not can be in any cases judged only by actual checking as I have done with my approximations.

M. J. Whelan: I should like to remark that Dr. Howie and myself have performed

numerical calculations of the systematic reflections due to the 111 row of reciprocal lattice points in two metals, aluminium and gold, by working out the fundamental linear equations of the dynamical theory, with the only approximation due to the truncation of the matrix. (Reported at the Delft Conference and at Cambridge a year ago). In the computer programme we could specify the size of matrix and the position of the zero order diagonal element, and examined the covergence of the intensities of the stronger beams for matrices up to size 12×12. The intensities of the beams corresponding to the core of the matrix are not appreciably affected by adding more elements to the perimeter of the matrix for size 7×7, but those of weak beams near the perimeter of the matrix may suffer from truncation error. In calculations for 3 beams only (e.g. 111, $\bar{1}\bar{1}\bar{1}$ and 000 in f.c.c. crystal), serious errors in form of the dispersion surface, such as its non-periodicity in reciprocal space, were found. These errors would be expected to occur if the zero order term on the diagonal is too near the corner of the matrix. I suspect the Case I of Dr. Sturkey might suffer from this defect.

The values of V_g assumed for aluminium were: $V_{111}=6.25\,\mathrm{V}$, $V_{222}=2.52\,\mathrm{V}$, $V_{333}=1.5\,\mathrm{V}$, $V_{444}=0.9\,\mathrm{V}$, $t_0^{(111)}$(extinction distance)$=586$Å, (2-beam value 640Å).

For gold: $V_{111}=22.6\,\mathrm{V}$, $V_{222}=11.6\,\mathrm{V}$, $V_{333}=6.8\,\mathrm{V}$, $V_{444}=4.35\,\mathrm{V}$, $t_0^{(111)}=135$Å, (2-beam value 180Å).

7-beams were used in the calculations.

For aluminium (Fig. 1), the peaks of 000 and 111 reflection do not all rise to unity, but the two-beam theory gives a very good description. In the calculations for gold (Fig. 2), the weak beams $\bar{1}\bar{1}\bar{1}$ and 222 are no longer negligible, and the two-beam

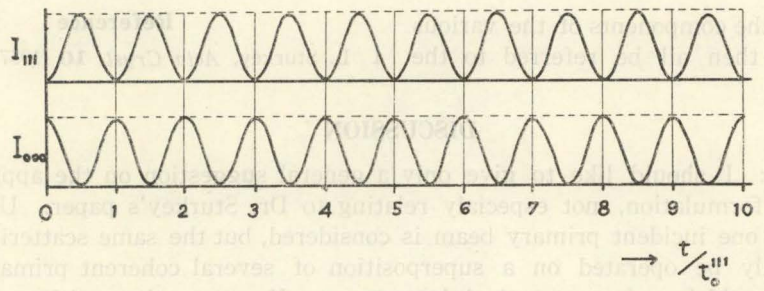

Fig. 1. Aluminum, 7-systematic reflections.

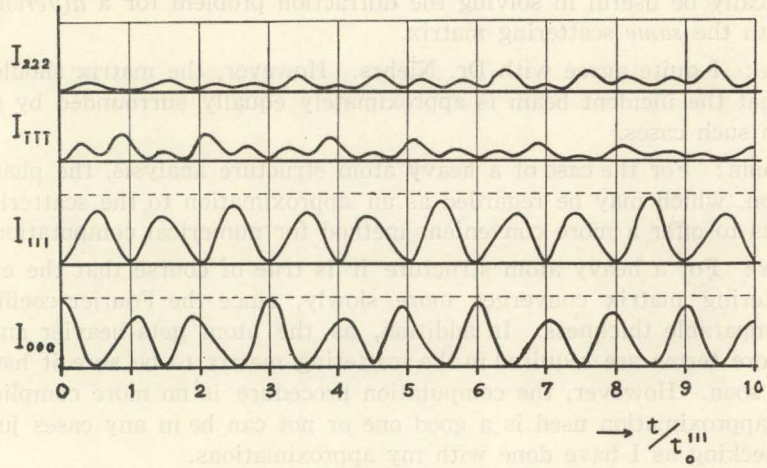

Fig. 2. Gold, 7-systematic reflections.

theory gives a poor description. The extinction distance $t_0^{(111)}$ (see above), which was calculated from the separation of the two main branches of the 7-beam dispersion surface at the 111 zone boundary, is lower than the 2-beam value as is expected from the Bethe dynamical potential argument. In gold, the weak beams show no tendency to decrease in thicker regions of the crystal.

S. MIYAKE (to M. J. WHELAN): What geometrical condition have you assumed in your calculation?

M. J. WHELAN: The calculations I have described were carried out for the exact Bragg condition for the 111 reflections. We have also studied the case where the beam is incident perpendicular to the reciprocal lattice row. We have also performed multiple-beam calculations for the absorbing case (complex potential).

H. RAETHER (to L. STURKEY): Do you think it possible to apply the two beam formula to describe the intensities of a powder diagram of a thick crystal by assuming some effective crystal size D_{dyn}, and can you give a relation between D_{dyn} and the real crystal size?

L. STURKEY: From the computed results it appears that for Bragg incidence the two-beam case holds to an accuracy of about 20%, but an entirely different "extinction distance" must be used from that computed using the two beam case. As to your second question, I should say that I have been unable to obtain yet this periodicity for a large number of crystal thicknesses.

G. HONJO (to L. STURKEY): Your calculation shows that the forbidden reflection of magnesium has an appreciable intensity, but could you observe it in experiment?

L. STURKEY: Yes. In single crystal patterns from Mg single crystals with the incident beam approximately normal to the (110) plane, both the (001) and the (003) reflections are fairly strong, as was shown in Montreal.

M. J. WHELAN: I would like to mention that the results Dr. Sturkey has described for a stacking fault were worked out in 1957 at Cambridge (Whelan, M. J. and Hirsch, P. B., 1957 Phil. Mag. **2**, 1121, 1303.). The case of absorption for a stacking fault was worked out by Dr. Hashimoto, Howie and myself (Hashimoto, H., Howie, A. and Whelan, M. J., 1960 Phil. Mag., **5** 967. 1961 Phil., Mag., (in press)), and the discussion of the symmetry of bright field and dark field images was made quite clearly in these papers.

L. STURKEY: I know your results of course. I gave the formulae only as an example of the application of my own method.