Acta Cryst. (1962). **15**, 1311

Dynamical theory of diffraction applicable to crystals with any kind of small distortion.

By Satio Takagi, *H. H. Wills Physics Laboratory, University of Bristol, Bristol, England*

(*Received* 21 *September* 1961 *and in revised form* 28 *May* 1962)

Several developments of the dynamical theory which can be applied to a distorted crystal have been published (Cowley & Moodie, 1957; Kato, 1960, 1962; Howie & Whelan, 1960, 1961 and 1962) and some of them have been successfully applied to explain some features in the images of dislocations in electron micrographs or X-ray diffraction topographs. However, these theories are based on the 'lamellar' approach which in practice confines its application to a distortion which depends only on one coordinate, i.e. to a crystal which can be divided into a set of lamellae each of which has a perfect two-dimensionally periodic structure which may, however, differ from lamella to lamella. Howie & Whelan (1960, 1961) have avoided this restriction by introducing the 'column' approximation (Hirsch, Howie & Whelan, 1960), i.e. they divided the crystal into columns nearly perpendicular to the lamellae and applied the theory to each column individually. For electron waves where the Bragg angle is small and the crystal thin, this approximation is good enough for practical purposes, as will be seen below, but it could not be applied for X-rays except to some simple distortions. A new development extending the dynamical theory to include any small distortion inside the crystal is here outlined.

In the Ewald–Laue theory for a perfect crystal, a wave field in the crystal is expressed by a Bloch function as

$$\psi(\mathbf{r}) = \sum_h \psi_h \exp\left(-2\pi i \mathbf{k}_h . \mathbf{r}\right) , \tag{1}$$

where $\mathbf{h}$ is a reciprocal-lattice vector, $\mathbf{k}_h$'s are the wave vectors connected with each other by the relation

$$\mathbf{k}_h = \mathbf{k}_0 + \mathbf{h} , \tag{2}$$

and ψ_h is invariant with respect to the space coordinates. The wave actually excited in the crystal by the incident wave can be expressed by a sum of two or more of these wave fields with slightly different values of $\mathbf{k}_0$. As a result, the incident and diffracted waves show a kind of beat effect or amplitude (and phase) modulation ('Pendellösung' effect (Ewald, 1933; Kato & Lang, 1959)).

In the present theory, the wave in the crystal is expressed by a single sum (1), but now ψ_h is considered as a slowly varying function of position instead of being a constant. This allows a single ψ_h to represent all the possible modulations of the $\mathbf{h}$th diffracted wave inside the crystal. It also gives a slight ambiguity to the definition of $\mathbf{k}_0$ which is now left to an appropriate initial choice. A convenient choice is that $\mathbf{k}_0$ satisfies the tangential continuity condition with the incident wave vector at the entrance surface and its magnitude is

$$|\mathbf{k}_0| = k = nK , \tag{3}$$

where K is the wave number in vacuum and n is the mean refractive index. The crystal potential $\chi(\mathbf{r}) = V(\mathbf{r})/E$, $V(\mathbf{r})$ being the electrostatic potential in the crystal and E the accelerating voltage of the electron, can be expanded in a Fourier series based on the reciprocal-lattice vectors of the undistorted crystal, as long as the distortion is so slight that atoms within a single unit cell can be regarded as uniformly displaced. The coefficient χ_h, still given by

$$\chi_h = 1/v \int_{\text{cell}} \chi(\mathbf{r}) \exp\left(2\pi i \mathbf{h} . \mathbf{r}\right) d\mathbf{r} , \tag{4}$$

where v is the volume of a unit cell, has phase varying slowly from point to point in the crystal, its magnitude remaining constant.

We may substitute the wave function (1) with slowly varying $\psi_h(\mathbf{r})$ into the Schrödinger equation. If we then assume that (a), both $\chi_h(\mathbf{r})$ and $\psi_h(\mathbf{r})$ are constant within a unit cell, and that, (b), $\nabla^2\psi_h(\mathbf{r})$ is negligible compared with terms proportional to $\psi_h(\mathbf{r})$ or their first derivatives, owing to the slow variation of these functions, we obtain the following simultaneous differential equations

$$\partial\psi_h(\mathbf{r})/\partial s_h = i2\pi K \beta_h \psi_h(\mathbf{r}) - i\pi K \sum_{h' \neq h} \chi_{h-h'}(\mathbf{r}) \psi_{h'}(\mathbf{r}) ; \tag{5}$$

here $\partial/\partial s_h$ signifies differentiation with respect to the space coordinate parallel to the direction of k_h, and β_h the resonance error defined by

$$\beta_h = (1/2K^2)(\mathbf{k}_h^2 - k^2) \tag{6}$$

indicating the deviation from the exact fulfilment of the Bragg condition for the lattice plane $\mathbf{h}$ (half of that defined by Laue (1960)). A similar set of equations is obtained for X-rays with a slight complication on account of the vector character of the wave.

The validity of the assumption (a) is evident for a slightly distorted crystal. The exact proof of validity of (b) is not easy. However, for a perfect crystal with a plane wave incident, (b) corresponds to the assumption that the difference in the normal components of the wave vectors of corresponding waves in vacuum and in the crystal is negligible compared with the normal component itself. This assumption is very well satisfied in usual experimental conditions for both X-rays and electrons except when the wave vector is almost parallel to the surface. Hence this assumption would not be a serious obstacle to the application of the theory to slightly distorted crystals.

Equation (5) includes the result obtained by the lamellar theory as a special case. When $\chi_h(\mathbf{r})$ and therefore $\psi_h(\mathbf{r})$ depend only on one coordinate normal to the entrance surface, say z, (5) reduces to

$$d\psi_h(z)/dz = i2\pi(K/\gamma_h)\beta_h\psi_h(z) - i\pi(K/\gamma_h) \sum_{h' \neq h} \chi_{h-h}(z)\psi_{h'}(z) \tag{7}$$

where γ_h is the cosine of the angle between $\mathbf{k}_h$ and the z-axis. This equation is essentially the same as that given by the lamellar theory (Sturkey, 1960; Howie & Whelan, 1960, 1961).

The solution of (5) in this general form may be very difficult. However, in the case of two strong waves, which is the most important in the diffraction problem, two possible methods of solution are present. For two waves (5) reduces to

$$\left.\begin{aligned}\partial\psi_0(\mathbf{r})/\partial s_0 &= -i\pi K\chi_{\bar{h}}(\mathbf{r})\psi_h(\mathbf{r})\ ,\\ \partial\psi_h(\mathbf{r})/\partial s_h &= -i\pi K\chi_h(\mathbf{r})\psi_0(\mathbf{r})+i2\pi K\beta_h\psi_h(\mathbf{r})\end{aligned}\right\}\quad(8)$$

which hold also for X-rays, if $\chi_h(\mathbf{r})$ is read as the Fourier coefficient of 4π times the polarizability of the crystal with appropriate polarization factor. The boundary conditions at the entrance surface are expressed in similar form as in the ordinary theory, namely

$$\left.\begin{aligned}\psi_0(\mathbf{r}_e) &= \Psi_0(\mathbf{r}_e)\\ \psi_h(\mathbf{r}_e) &= 0\end{aligned}\right\}\quad(9)$$

where $\mathbf{r}_e$ is a position vector on the entrance surface, and $\Psi_0(\mathbf{r}_e)$ the amplitude of the incident wave in vacuum. The fact that both sides of (9) are slowly varying functions of position instead of constants is important; incident waves other than plane waves can be treated as well. One of the methods of solution of (8) is to convert it into second-order partial differential equations for ψ_0 and ψ_h, each of which have a hyperbolic form which is capable of solution by the method of Riemann functions. This method gives the solution at a point P inside or on the exit surface of the crystal by a surface integral over AB (Fig. 1) where A and B are points on the entrance surface such that AP and BP are, respectively, parallel to $\mathbf{k}_0$ and $\mathbf{k}_h$. The integral involves $\Psi_0(\mathbf{r}_e)$ and the Riemann function for this particular point P given by the values of χ_h, $\chi_{\bar{h}}$ and β_h inside the triangle PAB, and its derivatives. This result is of theoretical importance, since it shows that only values of the amplitude of the incident wave falling between A and B contribute to the wave function at P, providing a theoretical basis for the column approximation in the electron case where the triangle PAB reduces to a thin column owing to the small Bragg angle. Equation (8) is also capable of a numerical solution. It includes only the derivatives $\partial\psi_0/\partial s_0$ and $\partial\psi_h/\partial s_h$ out of four possible first-order ones. This shows that if we divide the triangle PAB by a fine mesh with axes parallel to $\mathbf{k}_0$ and $\mathbf{k}_h$, as shown in Fig. 1, the value of ψ_0 at P, say, is determined by the values of ψ_0 and ψ_h at Q, and that of ψ_h at P, by those of ψ_0 and ψ_h at R and so on. The repetition of this process from the top surface AB to the bottom will give the solution at P.

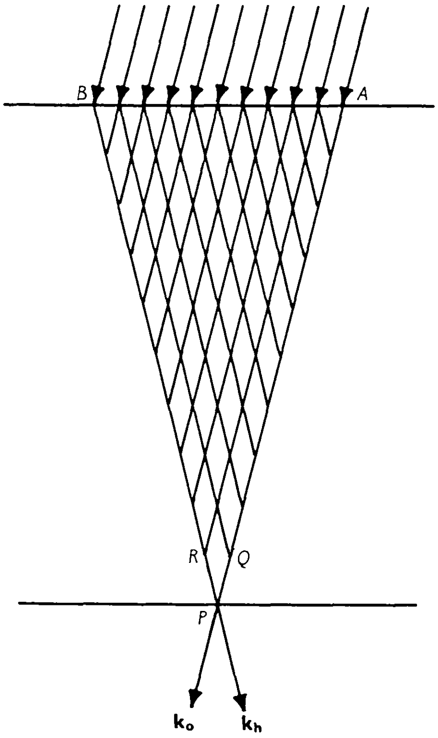

Fig. 1. Schematic drawing showing methods of solution of equation (8). The upper arrows and one of the lower ones are in the direction of the incident wave or of $\mathbf{k}_0$, and the other lower one in that of $\mathbf{k}_h$. The solutions at P on the exit surface are determined by the part of the incident wave falling between A and B, and can be calculated either by the method of Riemann functions or by successive numerical calculations at each mesh point.

The author would like to express his sincere thanks to Dr A. R. Lang for his encouragement and advice, and to Prof. M. H. L. Pryce, Prof. F. C. Frank and Dr M. E. Foglio for their suggestions and discussions. Financial support from the European Office, Office of Aerospace Research, USAF, is gratefully acknowledged.

References

Cowley, J. M. & Moodie, A. F. (1957). *Acta Cryst.* **10**, 609.

Ewald, P. P. (1933). *Handbuch der Physik*, **23**, 2, p. 290. Berlin: Springer.

Hirsch, P. B., Howie, A. & Whelan, M. J. (1960). *Phil. Trans. Roy. Soc.* A, **252**, 499.

Howie, A. & Whelan, M. J. (1960). *Proc. Eur. Reg. Conf. on Electron Microscopy, Delft*, Vol. 1, p. 194.

Howie, A. & Whelan, M. J. (1961). *Proc. Roy. Soc.* A, **263**, 217.

Howie, A. & Whelan, M. J. (1962). *Proc. Roy. Soc.* A, **267**, 206.

Kato, N. & Lang, A. R. (1959). *Acta Cryst.* **12**, 787.

Kato, N. (1960). *Acta Cryst.* **13**, 1091.

Kato, N. (1962). (To be published.)

Laue, M. von (1960). *Röntgenstrahlinterferenzen*, p. 337. Frankfurt am Main: Akademische Verlagsgesellschaft.

Sturkey, L. (1960). Private communication.

Acta Cryst. (1962). **15**, 1312

Epitaxial growth of rutile on oxidation of titanium carbide.

By K. H. G. Ashbee and W. T. Eeles,
Central Electricity Generating Board, Berkeley Nuclear Laboratories, Gloucestershire, England

(*Received* 19 *July* 1962)

Thin films of the rutile modification of titanium dioxide have been grown by Ashbee & Smallman (1962) on the (100) surfaces of TiC single crystals by oxidation in air at pressures ~ 10^{-3} cm. in the temperature range 800