Für die Madelung'schen Zahlen wurde ein Programm von Herrn Dr K. Sahl benutzt, für die anderen Aufgaben (interatomare Abstände, Deformation der Struktur) Programme eines der Autoren (H.-E. v. Mertens).

Literatur

BERTAUT, F. (1952). *J. Phys.* **13**, 499.
BETZL, M., HASE, W., KLEINSTÜCK, K. & TOBISCH, J. (1963). *Z. Kristallogr.* **118**, 473.
BORN, L. (1964). *N. Jb. Miner. Mh.* p. 81.
BORN, L. & ZEMANN, J. (1964). *Beitr. z. Mineralogie Petrogr.* **10**, 2.
EWALD, P. P. (1921). *Ann. Phys. Lpz.* **64**, 253.
NEWNHAM, R. E. & DE HAAN, Y. M. (1962). *Z. Kristallogr.* **117**, 235.
PATON, M. G. & MASLEN, E. N. (1965). *Acta Cryst.* **19**, 307.
SAHL, K. (1965). *Acta Cryst.* **19**, 1027.
SAHL, K. & ZEMANN, J. (1965). *Tschermaks min. u. petr. Mitt.* **10**, 97.
SCHMAELING, V. (1928). *Z. Kristallogr.* **67**, 1.
WYCKOFF, R. W. G. (1964). *Crystal Structures.* 2. Ed. Vol. 2. New York: Interscience.
ZACHARIASEN, W. (1928). *Z. Kristallogr.* **67**, 455.

Acta Cryst. (1966). **21**, 470

The Theory of the Borrmann Effect in Terms of Difference Equations*

BY BERNARD BORIE

Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, *U.S.A.*

(*Received* 18 *January* 1966)

The Borrmann effect must be described theoretically in terms of the dynamical theory of X-ray diffraction. This is conventionally done with the Ewald–von Laue formulation of that theory. It is shown that the effect may be equally well described with the simpler Darwin theory. A system of difference equations similar to those of Darwin is solved, yielding two systems of waves in the crystal with different refractive indices and different absorption coefficients. As in the Ewald–von Laue treatment, for one state of polarization the linear absorption coefficient essentially vanishes for one set of waves, giving rise to the phenomenon of anomalous transmission.

Introduction

Possibly the most significant new development in X-ray diffraction physics in the last few years has been the emergence of the Borrmann effect, or anomalous transmission, as an important new tool for studying the crystalline nature of solids. The phenomenon observed is that, given a perfect crystal oriented to diffract with the diffracting planes normal to its irradiated surface (Laue geometry), for one of the states of polarization of the incident X-radiation the linear absorption coefficient essentially disappears. The energy of the radiation is thus interchanged between two electromagnetic waves, one in the primary beam direction and one in the diffracted beam direction, throughout the thickness of the crystal, corresponding to a net energy flow along the diffracting planes. Since there is very little attenuation due to photoelectric absorption, very intense, parallel, plane polarized beams of X-rays may be transmitted through nearly perfect crystals large enough completely to absorb the incident radiation under normal circumstances.

Anomalous transmission may be accounted for theoretically only in terms of the dynamical theory of X-ray diffraction. Two formulations of that theory exist: that due to Darwin, later modified by Prins, and that due to Ewald and extended by von Laue. The Darwin theory is the simpler of the two, but has been reserved for diffraction in the Bragg geometry, *i.e.* the case in which the diffracting planes are parallel to the irradiated surface so that the incident and diffracted beams make equal angles with the surface. The unusual diffraction phenomena associated with the Borrmann effect have been treated only in terms of the more elegant (and more difficult) Ewald theory.

We show here that the Borrmann effect may equally well be described in terms of the simple Darwin theory.

Theory

The notation used and the formulation of the problem follows closely James's (1950) treatment of the Darwin theory in Bragg geometry. Fig. 1 is analogous to James's Fig. 24 (James, 1950, page 55). It represents a family of planes of atoms parallel to the crystal surface. The planes are numbered, beginning with the zero plane at the surface. Incident onto the crystal is a beam

---

* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

of X-radiation in the T_0 direction. T_0 is the displacement due to that wave just before its encounter with the crystal. The atoms populating the zero (and subsequent) planes are assumed to be distributed so that they scatter in phase to form a plane wave in the S_0 direction. S_0 is the displacement of the scattered wave just after the zero plane of atoms. The directions of S_0 and T_0 are taken to make equal angles with the family of planes.

Define q, the single plane reflection coefficient, to be

$$S_0 = -iqT_0 \, .$$

It may be shown that q is given by

$$q = -\frac{n\lambda}{\sin\alpha} f e^2/mc^2 \tag{1}$$

where n is the number of atoms per unit area in the plane, α is the angle between T_0 and the plane (in this case the complement of the Bragg angle), and the other symbols have their usual significance. The derivation of this expression is similar to that given by James (1950, page 35). Though the treatment in James is in terms of Bragg geometry, so that the scattering atomic planes are the 'reflecting' planes in the sense of Bragg's law, it may be shown that a similar result obtains for Laue geometry under consideration here. It is important to note that the atomic planes of Fig. 1 are not the Bragg planes but are perpendicular to them.

In addition to the S_0 wave, the zero plane of atoms will also scatter in phase in the T direction. Hence the net wave in the T direction just after the zero plane is $(1-iq_0)T_0$. The reflection coefficient at zero scattering angle, q_0, is identical with q except that f must be replaced by its value at $\theta=0$. Let φ be the phase change associated with an advance of the wave front of either T or S from the zero plane to the first plane. Then T_1, the displacement of the transmitted wave just before the first plane, is given by

$$T_1 = (1-iq_0)e^{-i\varphi}T_0 \, . \tag{2}$$

In general T_r is the displacement of the transmitted wave between the $(r-1)$th and rth planes, just before its encounter with the rth plane; S_r is that of the scattered wave between the rth and $(r+1)$th planes, just after the rth plane.

We may write difference equations relating these quantities. S_r is composed of that part of T_r which is scattered in the S direction by the rth plane, plus that part of S_{r-1} which is transmitted by the rth plane. Hence

$$S_r = -iqT_r + (1-iq_0)e^{-i\varphi}S_{r-1} \, . \tag{3}$$

T_{r+1} is made up of that part of T_r which is transmitted by the rth plane, plus that part of S_{r-1} which is scattered in the T direction by the rth plane:

$$T_{r+1} = (1-iq_0)e^{-i\varphi}T_r - iqe^{-2i\varphi}S_{r-1} \, . \tag{4}$$

Equations (3) and (4) may be combined to obtain an expression in T with the S's eliminated:

$$2(1-iq_0)T_r = T_{r+1}e^{i\varphi} + T_{r-1}[q^2e^{-i\varphi} + (1-iq_0)^2e^{-i\varphi}] \, . \tag{5}$$

This equation is the Laue analog to James's equation (2.69), which was developed for the Darwin theory in Bragg geometry.

The general solution to a difference equation such as (5) is of the form $T_r = C\beta^r$ where C and β are constants independent of r. If we substitute this into equation (5), there results

$$2(1-iq_0)\beta = \beta^2e^{i\varphi} + [q^2e^{-i\varphi} + (1-iq_0)^2e^{-i\varphi}] \, ,$$

and if we solve this for β we obtain

$$\beta = e^{-i\varphi}[(1-iq_0) \pm iq] \, .$$

Thus the solution to equation (5) is

$$T_r = C_1e^{-ir\varphi}[1-iq_0-iq]^r + C_2e^{-ir\varphi}[1-iq_0+iq]^r \tag{6}$$

with C_1 and C_2 to be determined by boundary conditions. They are given by equation (2) and by a choice of $T_0=1$. The substitution of the boundary conditions into equation (6) gives $C_1=C_2=\frac{1}{2}$, so

$$T_r = \tfrac{1}{2}e^{-ir\varphi}[(1-iq_0-iq)^r + (1-iq_0+iq)^r] \, . \tag{7}$$

With the aid of equation (4) we obtain

$$S_r = \tfrac{1}{2}e^{-ir\varphi}[(1-iq_0-iq)^{r+1} - (1-iq_0+iq)^{r+1}] \, . \tag{8}$$

We may interpret the refractive index of the crystal in terms of q_0, as does James (1950, page 53). What we have shown is that it is related to q_0 only if the crystal is not oriented to diffract. When the conditions for diffraction described here are realized, we see that T and S are each composed of two waves, each with a slightly different index of refraction. One is greater and the other less than that given by q_0. If we let the displacements associated with these two waves be

$$V_r = \tfrac{1}{2}e^{-ir\varphi}(1-iq_0-iq)^r \tag{9}$$

and

$$W_r = \tfrac{1}{2}e^{-ir\varphi}(1-iq_0+iq)^r \, , \tag{10}$$

we have that

$$T_r = V_r + W_r \tag{11}$$

and

$$e^{-i\varphi}S_{r-1} = V_r - W_r \, . \tag{12}$$

The displacement due to S just before its encounter with the rth plane, $e^{-i\varphi}S_{r-1}$, is the proper quantity to be compared with T_r.

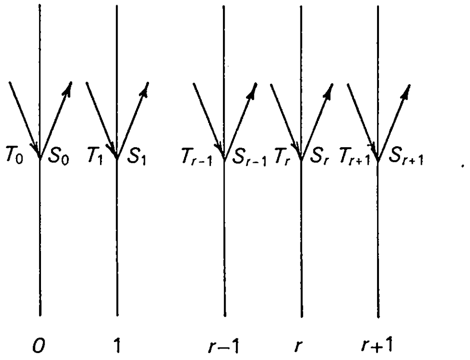

Fig. 1. Schematic illustration of the diffraction geometry.

Discussion

At the surface of the crystal, V_r and W_r are in phase, but since their refractive indices are different, their phase difference increases as they penetrate the crystal Hence for small r, T_r is only slightly less than unity and S_r is very small. At some distance $r=R$ (the extinction distance) into the crystal, V_r and W_r are exactly out of phase, and $T_R=0$ and $e^{-i\varphi}S_{R-1}=1$. The extinction distance is given by

$$(1-iq_0-iq)^R+(1-iq_0+iq)^R=0\ .$$

Thus for a non-absorbing crystal (hence one for which f, q, and q_0 are real), the energy is interchanged between T and S throughout the thickness of the crystal at intervals determined by the extinction distance.

Since we have made no assumptions about the nature of f and q, equations (7), (8), (9), (10), (11), and (12) may also be used to describe the case of an absorbing crystal. In this case f, q, and q_0 are complex and we may associate the linear absorption coefficient with their imaginary components as does James (1950, page 63). Thus, when the crystal is oriented to diffract, not only are the indices of refraction of the waves V and W anomalous, but their absorption coefficients as well.

Suppose that we take the imaginary part of f to be independent of 2θ and we ignore the effect of thermal motion. Then if T_0 is polarized so that its electric vector is in the plane of Fig. 1 (case I),

$$q_0'' \cos 2\theta=q''$$

where q'' and q_0'' are the imaginary parts of q and q_0. If the electric vector of T_0 is normal to the plane of Fig. 1 (case II),

$$q_0''=q''\ .$$

From equation (9) we see that the effective value of μ for the V wave is greater than the normal value of μ, and the wave is very quickly attenuated by photoelectric absorption. However, for case I, the W wave [equation (10)] has an anomalously small value of μ, and in fact for case II the effective value of μ for the W wave is identically zero.

Thus for a thick absorbing crystal, sufficiently far from the surface so that the V waves in both cases and the W wave in case I have been dissipated by absorption, the wave field inside the crystal consists only of W waves in the directions of the incident and diffracted beams, polarized in the sense of case II. If the incident beam is unpolarized, exactly one-fourth of its intensity is associated with these waves which are transmitted through the crystal without absorption. At the exit interface, half of this intensity goes into the transmitted-diffracted beam and half into the transmitted-direct beam. Hence for an unpolarized incident beam, each of the anomalously transmitted Borrmann beams has an intensity of one-eighth the incident intensity. In a real crystal, the effect of thermal motion is to cause the transmitted intensity to be somewhat less.

The magnitudes of the propagation vectors of the W waves in the T and S directions are equal. If the x direction is taken normal to the crystal surface, and if the components of the propagation vector for the W wave in the T direction are k_x, k_y, then the components of the vector for the wave in the S direction are k_x, $-k_y$.

Let the components of a position vector in the crystal be r_x, r_y. Then far from the crystal surface, after the V waves have been dissipated by absorption, equations (10) and (11) reduce to $T_r=W_r$ and $e^{-i\varphi}S_{r-1}=-W_r$. The phase factors for these two waves may be written

$$T=\tfrac{1}{2}\exp\{i(k_xr_x+k_yr_y)\}$$

and

$$S=-\tfrac{1}{2}\exp\{i(k_xr_x-k_yr_y)\}\ .$$

The resultant electromagnetic displacement is

$$T+S=\exp\,(i\pi/2)\,\exp\,(ik_xr_x)\,\sin k_yr_y\ .$$

Thus the net effective wave field in the crystal is a plane wave moving in a direction normal to the surface, but with nodes and antinodes across its wave front given by $\sin k_yr_y$. Since $k_y=|k|\sin\theta$ and $|k|=2\pi/\lambda$,

$$k_y=\frac{2\pi}{\lambda}\sin\theta=\frac{\pi}{d}\ .$$

Hence the nodes occur at $r_y=nd$, where n is any integer. The occurrence of nodes in the net wavefield just at the atomic planes may be interpreted qualitatively to account for the vanishing of μ for the Borrmann beams.

Reference

James, R. W. (1950). *The Optical Principles of the Diffraction of X-rays*. London: Bell.