5.1. Dynamical theory of X-ray diffraction

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5.1.1. Introduction

The first experiment on X-ray diffraction by a crystal was performed by W. Friedrich, P. Knipping and M. von Laue in 1912 and Bragg's law was derived in 1913 (Bragg, 1913). Geometrical and dynamical theories for the intensities of the diffracted X-rays were developed by Darwin (1914a,b). His dynamical theory took into account the interaction of X-rays with matter by solving recurrence equations that describe the balance of partially transmitted and partially reflected amplitudes at each lattice plane. This is the first form of the dynamical theory of X-ray diffraction. It gives correct expressions for the reflected intensities and was extended to the absorbing-crystal case by Prins (1930). A second form of dynamical theory was introduced by Ewald (1917) as a continuation of his previous work on the diffraction of optical waves by crystals. He took into account the interaction of X-rays with matter by considering the crystal to be a periodic distribution of dipoles which were excited by the incident wave. This theory also gives the correct expressions for the reflected and transmitted intensities, and it introduces the fundamental notion of a wavefield, which is necessary to understand the propagation of X-rays in perfect or deformed crystals. Ewald's theory was later modified by von Laue (1931), who showed that the interaction could be described by solving Maxwell's equations in a medium with a continuous, triply periodic distribution of dielectric susceptibility. It is this form which is most widely used today and which will be presented in this chapter.

The geometrical (or kinematical) theory, on the other hand, considers that each photon is scattered only once and that the interaction of X-rays with matter is so small it can be neglected. It can therefore be assumed that the amplitude incident on every diffraction centre inside the crystal is the same. The total diffracted amplitude is then simply obtained by adding the individual amplitudes diffracted by each diffracting centre, taking into account only the geometrical phase differences between them and neglecting the interaction of the radiation with matter. The result is that the distribution of diffracted amplitudes in reciprocal space is the Fourier transform of the distribution of diffracting centres in physical space. Following von Laue (1960), the expression *geometrical theory* will be used throughout this chapter when referring to these geometrical phase differences.

The first experimentally measured reflected intensities were not in agreement with the theoretical values obtained with the more rigorous dynamical theory, but rather with the simpler geometrical theory. The integrated reflected intensities calculated using geometrical theory are proportional to the square of the structure factor, while the corresponding expressions calculated using dynamical theory for an infinite perfect crystal are proportional to the modulus of the structure factor. The integrated intensity calculated by geometrical theory is also proportional to the volume of the crystal bathed in the incident beam. This is due to the fact that one neglects the decrease of the incident amplitude as it progresses through the crystal and a fraction of it is scattered away. According to geometrical theory, the diffracted intensity would therefore increase to infinity if the volume of the crystal was increased to infinity, which is of course absurd. The theory only works because the strength of the interaction is very weak and if it is applied to very small crystals. How small will be shown quantitatively in Sections 5.1.6.5 and 5.1.7.2. Darwin (1922) showed that it can also be applied to large imperfect crystals. This is done using the model of mosaic crystals (Bragg *et al.*, 1926). For perfect or nearly perfect crystals, dynamical theory should be used. Geometrical theory presents another drawback: it gives no indication as to the phase of the reflected wave. This is due to the fact that it is based on the Fourier transform of the electron density limited by the external shape of the crystal. This is not important when one is only interested in measuring the reflected intensities. For any problem where the phase is important, as is the case for multiple reflections, interference between coherent blocks, standing waves *etc.*, dynamical theory should be used, even for thin or imperfect crystals.

Until the 1940s, the applications of dynamical theory were essentially intensity measurements. From the 1950s to the 1970s, applications were related to the properties (absorption, interference, propagation) of wavefields in perfect or nearly perfect crystals: anomalous transmission, diffraction of spherical waves, interpretation of images on X-ray topographs, accurate measurement of form factors, lattice-parameter mapping. In recent years, they have been concerned mainly with crystal optics, focusing and the design of monochromators for synchrotron radiation [see, for instance, Batterman & Bilderback (1991)], the location of atoms at crystal surfaces and interfaces using the standing-waves method [see, for instance, the reviews by Authier (1989) and Zegenhagen (1993)], attempts to determine phases using multiple reflections [see, for instance, Chang (1987) and Hümmer & Weckert (1995)], characterization of the crystal perfection of epilayers and super-lattices by high-resolution diffractometry [see, for instance, Tanner (1990) and Fewster (1993)], *etc.*

For reviews of dynamical theory, see Zachariasen (1945), von Laue (1960), James (1963), Batterman & Cole (1964), Authier (1970), Kato (1974), Brümmer & Stephanik (1976), Pinsker (1978), Authier & Malgrange (1998), and Authier (2001). Topography is described in Chapter 2.7 of *IT* C (1999), in Tanner (1976) and in Tanner & Bowen (1992). For the use of Bragg-angle measurements for accurate lattice-parameter mapping, see Hart (1981).

A reminder of some basic concepts in electrodynamics is given in Section A5.1.1.1 of the Appendix.

5.1.2. Fundamentals of plane-wave dynamical theory

5.1.2.1. *Propagation equation*

The wavefunction Ψ associated with an electron or a neutron beam is *scalar* while an electromagnetic wave is a *vector* wave. When propagating in a medium, these waves are solutions of a *propagation equation*. For electrons and neutrons, this is Schrödinger's equation, which can be rewritten as

$$\Delta\Psi + 4\pi^2 k^2(1+\chi)\Psi = 0, \qquad (5.1.2.1)$$

where $k = 1/\lambda$ is the wavenumber in a vacuum, $\chi = \varphi/W$ (φ is the potential in the crystal and W is the accelerating voltage) in the case of electron diffraction and $\chi = -2mV(\mathbf{r})/h^2 k^2$ [$V(\mathbf{r})$ is the Fermi pseudo-potential and h is Planck's constant] in the case of neutron diffraction. The dynamical theory of electron diffraction is treated in Chapter 5.2 [note that a different convention is used in Chapter 5.2 for the scalar wavenumber: $k = 2\pi/\lambda$; compare, for example, equation (5.2.2.1) and its equivalent, equation (5.1.2.1)] and the dynamical theory of neutron diffraction is treated in Chapter 5.3.

In the case of X-rays, the propagation equation is deduced from Maxwell's equations after neglecting the interaction with protons. Following von Laue (1931, 1960), it is assumed that the positive charge of the nuclei is distributed in such a way that the medium is everywhere locally neutral and that there is no current. As a first approximation, magnetic interaction, which is very weak, is not taken into account in this review. The propagation equation is

534

derived in Section A5.1.1.2 of the Appendix. Expressed in terms of the local electric displacement, $\mathbf{D}(\mathbf{r})$, it is given for monochromatic waves by

$$\Delta\mathbf{D}(\mathbf{r}) + \text{ curl curl } \chi\mathbf{D}(\mathbf{r}) + 4\pi^2 k^2\mathbf{D}(\mathbf{r}) = 0. \qquad (5.1.2.2)$$

The interaction of X-rays with matter is characterized in equation (5.1.2.2) by the parameter χ, which is the dielectric susceptibility. It is classically related to the electron density $\rho(\mathbf{r})$ by

$$\chi(\mathbf{r}) = -R\lambda^2\rho(\mathbf{r})/\pi, \qquad (5.1.2.3)$$

where $R = 2.81794 \times 10^{-6}$ nm is the classical radius of the electron [see equation (A5.1.1.2) in Section A5.1.1.2 of the Appendix].

The dielectric susceptibility, being proportional to the electron density, is triply periodic in a crystal. It can therefore be expanded in Fourier series:

$$\chi = \sum_h \chi_h \exp(2\pi i\mathbf{h} \cdot \mathbf{r}), \qquad (5.1.2.4)$$

where $\mathbf{h}$ is a reciprocal-lattice vector and the summation is extended over all reciprocal-lattice vectors. The sign convention adopted here for Fourier expansions of periodic functions is the *standard crystallographic* sign convention defined in Section 2.5.2.3. The relative orientations of wavevectors and reciprocal-lattice vectors are defined in Fig. 5.1.2.1, which represents schematically a Bragg reflection in direct and reciprocal space (Figs. 5.1.2.1*a* and 5.1.2.1*b*, respectively).

The coefficients χ_h of the Fourier expansion of the dielectric susceptibility are related to the usual structure factor F_h by

$$\chi_h = -R\lambda^2 F_h/(\pi V), \qquad (5.1.2.5)$$

where V is the volume of the unit cell and the structure factor is given by

$$F_h = \sum_j (f_j + f_j' + if_j'')\exp(-M_j - 2\pi i\mathbf{h} \cdot \mathbf{r}_j)$$
$$= |F_h|\exp(i\varphi_h). \qquad (5.1.2.6)$$

f_j is the form factor of atom j, f_j' and f_j'' are the dispersion corrections [see, for instance, *IT* C, Section 4.2.6] and $\exp(-M_j)$ is the Debye–Waller factor. The summation is over all the atoms in the unit cell. The phase φ_h of the structure factor depends of course on the choice

of origin of the unit cell. The Fourier coefficients χ_h are dimensionless. Their order of magnitude varies from 10^{-5} to 10^{-7} depending on the wavelength and the structure factor. For example, χ_h is -9.24×10^{-6} for the 220 reflection of silicon for Cu $K\alpha$ radiation.

In an absorbing crystal, absorption is taken into account phenomenologically through the imaginary parts of the index of refraction and of the wavevectors. The dielectric susceptibility is written

$$\chi = \chi_r + i\chi_i. \qquad (5.1.2.7)$$

The real and imaginary parts of the susceptibility are triply periodic in a crystalline medium and can be expanded in a Fourier series,

$$\chi_r = \sum_h \chi_{rh}\exp(2\pi i\mathbf{h} \cdot \mathbf{r})$$
$$\chi_i = \sum_h \chi_{ih}\exp(2\pi i\mathbf{h} \cdot \mathbf{r}), \qquad (5.1.2.8)$$

where

$$\chi_{rh} = -R\lambda^2 F_{rh}/(\pi V),$$
$$\chi_{ih} = -R\lambda^2 F_{ih}/(\pi V) \qquad (5.1.2.9)$$

and

$$F_{rh} = \sum_j (f_j + f_j')\exp(-M_j - 2\pi i\mathbf{h} \cdot \mathbf{r}_j)$$
$$= |F_{rh}|\exp(i\varphi_{rh}), \qquad (5.1.2.10a)$$
$$F_{ih} = \sum_j (f_j'')\exp(-M_j - 2\pi i\mathbf{h} \cdot \mathbf{r}_j)$$
$$= |F_{ih}|\exp(i\varphi_{ih}). \qquad (5.1.2.10b)$$

It is important to note that

$$F_{rh}^* = F_{r\bar{h}} \text{ and } F_{ih}^* = F_{i\bar{h}} \text{ but that } F_h^* \neq F_{\bar{h}}, \qquad (5.1.2.11)$$

where f^* is the imaginary conjugate of f.

The *index of refraction* of the medium for X-rays is

$$n = 1 + \chi_{ro}/2 = 1 - R\lambda^2 F_o/(2\pi V), \qquad (5.1.2.12)$$

where F_o/V is the number of electrons per unit volume. This index is very slightly smaller than one. It is for this reason that specular reflection of X-rays takes place at grazing angles. From the value of the critical angle, $(-\chi_{ro})^{1/2}$, the electron density F_o/V of a material can be determined.

The linear absorption coefficient is

$$\mu_o = -2\pi k\chi_{io} = 2R\lambda F_{io}/V. \qquad (5.1.2.13)$$

For example, it is 143.2 cm^{-1} for silicon and Cu $K\alpha$ radiation.

5.1.2.2. *Wavefields*

The notion of a wavefield, introduced by Ewald (1917), is one of the most fundamental concepts in dynamical theory. It results from the fact that since the propagation equation (5.1.2.2) is a second-order partial differential equation with a periodic interaction coefficient, its solution has the same periodicity,

$$\mathbf{D} = \exp(-2\pi i\mathbf{K_o} \cdot \mathbf{r}) \sum_h \mathbf{D_h}\exp(2\pi i\mathbf{h} \cdot \mathbf{r}), \qquad (5.1.2.14)$$

where the summation is over all reciprocal-lattice vectors $\mathbf{h}$. Equation (5.1.2.14) can also be written

$$\mathbf{D} = \sum_h \mathbf{D_h}\exp(-2\pi i\mathbf{K_h} \cdot \mathbf{r}), \qquad (5.1.2.15)$$
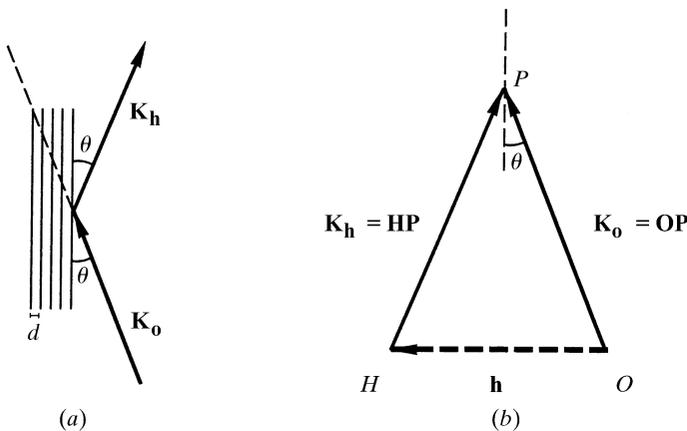
where

Fig. 5.1.2.1. Bragg reflection. (*a*) Direct space. Bragg reflection of a wave of wavevector $\mathbf{K_o}$ incident on a set of lattice planes of spacing d. The reflected wavevector is $\mathbf{K_h}$. Bragg's law $2d \sin\theta = n\lambda$ can also be written $2d_{hkl}\sin\theta = \lambda$, where $d_{hkl} = d/n = 1/OH = 1/h$ is the inverse of the length of the corresponding reciprocal-lattice vector $\mathbf{OH} = \mathbf{h}$ (see part *b*). (*b*) Reciprocal space. P is the tie point of the wavefield consisting of the incident wave $\mathbf{K_o} = \mathbf{OP}$ and the reflected wave $\mathbf{K_h} = \mathbf{HP}$. Note that the wavevectors are oriented *towards* the tie point.

references