

5.1. Dynamical theory of X-ray diffraction

BY A. AUTHIER

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 (1914*a,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, determination of phases using multiple reflections [for reviews of *n*-beam diffraction, see Weckert & Hümmel (1997) and Chang (2004); for recent determinations of phases, see Chang *et al.* (2002), Mo *et al.* (2002), Weckert *et al.* (2002), Shen & Wang (2003)], characterization of the crystal perfection of epilayers and superlattices by high-resolution diffractometry [see, for instance, Tanner (1990) and Fewster (1993)], *etc.*

Modern developments include the extension of dynamical theory to time-dependent phenomena (Chukhovskii & Förster, 1995; Shastri *et al.*, 2001; Graeff, 2002*a,b*, 2004; Malgrange & Graeff, 2003; Sondhauss & Wark, 2003; Adams, 2004) and the study of the influence of the coherence of the source (Yamazaki & Ishikawa, 2002, 2004).

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 *et al.* (1996), Authier & Malgrange (1998), and Authier (2005). Topography is described in Chapter 2.7 of *IT C* (2004), in Tanner (1976) and in Tanner & Bowen (1992). For the use of Bragg-angle measurements for accurate lattice-parameter mapping, see Hart (1981). For online calculations in the case of multiple diffraction, grazing incidence or for strained crystals, see <http://sergey.gmca.aps.anl.gov>.

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

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