5.1. DYNAMICAL THEORY OF X-RAY DIFFRACTION

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

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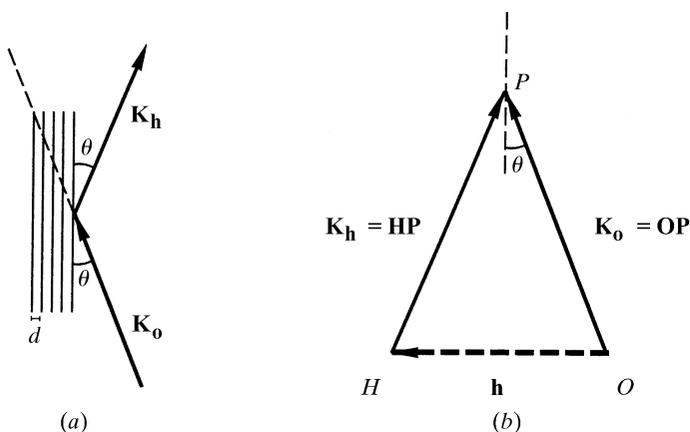
where

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.

$$\mathbf{K_h} = \mathbf{K_o} - \mathbf{h}. \qquad (5.1.2.16)$$

Expression (5.1.2.15) shows that the solution of the propagation equation can be interpreted as an infinite sum of plane waves with amplitudes $\mathbf{D_h}$ and wavevectors $\mathbf{K_h}$. This sum is a *wavefield*, or *Ewald wave*. The same expression is used to describe the propagation of any wave in a periodic medium, such as phonons or electrons in a solid. Expression (5.1.2.14) was later called a *Bloch wave* by solid-state physicists.

The wavevectors in a wavefield are deduced from one another by translations of the reciprocal lattice [expression (5.1.2.16)]. They can be represented geometrically as shown in Fig. 5.1.2.1(*b*). The wavevectors $\mathbf{K_o} = \mathbf{OP}$; $\mathbf{K_h} = \mathbf{HP}$ are drawn *away* from reciprocal-lattice points. Their common extremity, *P*, called the *tie point* by Ewald, characterizes the wavefield.

In an absorbing crystal, wavevectors have an imaginary part,

$$\mathbf{K_o} = \mathbf{K_{or}} + i\mathbf{K_{oi}}; \ \ \mathbf{K_h} = \mathbf{K_{hr}} + i\mathbf{K_{hi}},$$

and (5.1.2.16) shows that all wavevectors have the same imaginary part,

$$\mathbf{K_{oi}} = \mathbf{K_{hi}}, \qquad (5.1.2.17)$$

and therefore undergo the same absorption. This is one of the most important properties of wavefields.

5.1.2.3. *Boundary conditions at the entrance surface*

The choice of the '**o**' component of expansion (5.1.2.15) is arbitrary in an infinite medium. In a semi-infinite medium where the waves are created at the interface with a vacuum or air by an incident plane wave with wavevector $\mathbf{K_o^{(a)}}$ (using von Laue's notation), the choice of $\mathbf{K_o}$ is determined by the boundary conditions.

This condition for wavevectors at an interface demands that their tangential components should be continuous across the boundary, in agreement with Descartes–Snell's law. This condition is satisfied when the difference between the wavevectors on each side of the interface is parallel to the normal to the interface. This is shown geometrically in Fig. 5.1.2.2 and formally in (5.1.2.18):

$$\mathbf{K_o} - \mathbf{K_o^{(a)}} = \mathbf{OP} - \mathbf{OM} = \overline{MP} \cdot \mathbf{n}, \qquad (5.1.2.18)$$

where $\mathbf{n}$ is a unit vector normal to the crystal surface, oriented towards the inside of the crystal.

There is no absorption in a vacuum and the incident wavevector $\mathbf{K_o^{(a)}}$ is real. Equation (5.1.2.18) shows that it is the component normal to the interface of wavevector $\mathbf{K_o}$ which has an imaginary
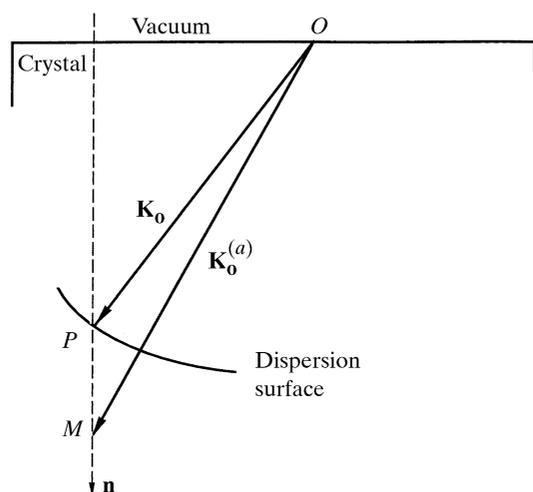

Fig. 5.1.2.2. Boundary condition for wavevectors at the entrance surface of the crystal.

part,

$$\mathbf{K_{oi}} = \mathcal{I}(\overline{MP}) \cdot \mathbf{n} = -\mu\mathbf{n}/(4\pi\gamma_o), \qquad (5.1.2.19)$$

where $\mathcal{I}(f)$ is the imaginary part of f, $\gamma_o = \cos(\mathbf{n} \cdot \mathbf{s_o})$ and $\mathbf{s_o}$ is a unit vector in the incident direction. When there is more than one wave in the wavefield, the effective absorption coefficient μ can differ significantly from the normal value, μ_o, given by (5.1.2.13) – see Section 5.1.5.

5.1.2.4. *Fundamental equations of dynamical theory*

In order to obtain the solution of dynamical theory, one inserts expansions (5.1.2.15) and (5.1.2.4) into the propagation equation (5.1.2.2). This leads to an equation with an infinite sum of terms. It is shown to be equivalent to an infinite system of linear equations which are the *fundamental equations* of dynamical theory. Only those terms in (5.1.2.15) whose wavevector magnitudes K_h are very close to the vacuum value, k, have a non-negligible amplitude. These wavevectors are associated with reciprocal-lattice points that lie very close to the Ewald sphere. Far from any Bragg reflection, their number is equal to 1 and a single plane wave propagates through the medium. In general, for X-rays, there are only two reciprocal-lattice points on the Ewald sphere. This is the so-called *two-beam* case to which this treatment is limited. There are, however, many instances where several reciprocal-lattice points lie simultaneously on the Ewald sphere. This corresponds to the *many-beam* case which has interesting applications for the determination of phases of reflections [see, for instance, Chang (1987) and Hümmer & Weckert (1995)]. On the other hand, for electrons, there are in general many reciprocal-lattice points close to the Ewald sphere and many wavefields are excited simultaneously (see Chapter 5.2).

In the two-beam case, for reflections that are not highly asymmetric and for Bragg angles that are not close to $\pi/2$, the fundamental equations of dynamical theory reduce to

$$\begin{aligned} 2X_o D_o - kC\chi_{\bar{h}}D_h &= 0 \\ -kC\chi_h D_o + 2X_h D_h &= 0, \end{aligned} \qquad (5.1.2.20)$$

where $C = 1$ if $\mathbf{D_h}$ is normal to the $\mathbf{K_o}, \mathbf{K_h}$ plane and $C = \cos 2\theta$ if $\mathbf{D_h}$ lies in the plane; this is due to the fact that the amplitude with which electromagnetic radiation is scattered is proportional to the sine of the angle between the direction of the electric vector of the incident radiation and the direction of scattering (see, for instance, *IT* C, Section 6.2.2). The polarization of an electromagnetic wave is classically related to the orientation of the electric vector; in dynamical theory it is that of the electric displacement which is considered (see Section A5.1.1.3 of the Appendix).

The system (5.1.2.20) is therefore a system of four equations which admits four solutions, two for each direction of polarization. In the *non-absorbing* case, to a very good approximation,

$$\begin{aligned} X_o &= K_o - nk, \\ X_h &= K_h - nk. \end{aligned} \qquad (5.1.2.21)$$

In the case of an *absorbing crystal*, X_o and K_h are complex. Equation (5.1.5.2) gives the full expression for X_o.

5.1.2.5. *Dispersion surface*

The fundamental equations (5.1.2.20) of dynamical theory are a set of linear homogeneous equations whose unknowns are the amplitudes of the various waves which make up a wavefield. For the solution to be non-trivial, the determinant of the set must be set equal to zero. This provides a secular equation relating the magnitudes of the wavevectors of a given wavefield. This equation is that of the locus of the tie points of all the wavefields that may