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, $\mathbf{D(r)}$, it is given for monochromatic waves by

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

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

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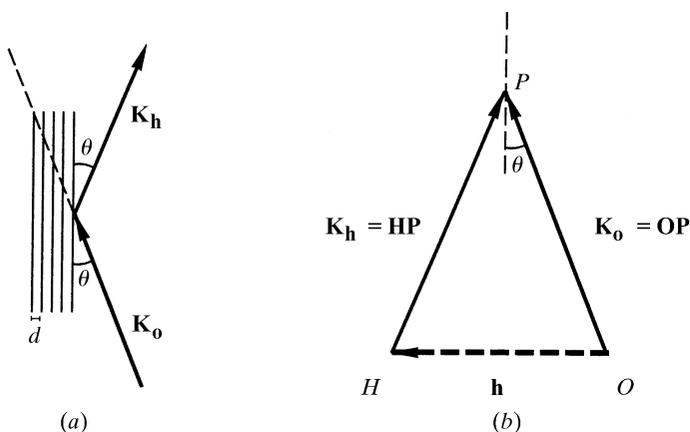
where

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.

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