4.1. Radiations used in crystallography

By V. Valvoda

4.1.1. Introduction

The radiations used in crystallography are either electromagnetic waves or beams of particles. The choice of radiation depends on the type of crystallographic information needed. The most general tool for obtaining any crystallographic information is diffraction but other types of scattering or reflection and absorption phenomena are also used in *general* crystallography (see Fig. 4.1.1.1).

4.1.2. Electromagnetic waves and particles

Both electromagnetic waves and particles can be described by the wavefunction $\psi(\mathbf{r})$, as a complex function of spatial coordinates, by the wavelength λ, the wavevector $\mathbf{k}$, which indicates the direction of propagation and is of magnitude $2\pi/\lambda$, the frequency ν or angular frequency ω in rad s^{-1}, and the phase velocity v (and the group velocity). Intensity in $\mathbf{r}$ is given by $|\psi(\mathbf{r})|^2$. These wavefunctions are solutions of the same type of differential equation [see, for example, Cowley (1975)]:

$$\nabla^2\psi + k^2\psi = 0. \tag{4.1.2.1}$$

For electromagnetic waves,

$$k^2 = \varepsilon\mu\omega^2 = \omega^2/v^2, \tag{4.1.2.2}$$

where k is the wavenumber, ε is the permittivity or dielectric constant and μ is the magnetic permeability of the medium; $\mu \approx 1$ for most cases. The velocity of the waves in free space is $c = 1/(\varepsilon_0\mu_0)^{1/2}$; otherwise $v = c/n$, where $n = (\varepsilon/\varepsilon_0)^{1/2}$ is the refraction index.

For particles of mass m and charge q with kinetic energy E_k in field-free space, the wave equation (4.1.2.1) is the time-independent Schrödinger equation and

$$k^2 = \frac{8\pi^2 m}{h^2}\{E_k + q\mathscr{S}(\mathbf{r})\}, \tag{4.1.2.3}$$

where $\mathscr{S}(\mathbf{r})$ is the electrostatic potential function and the bracket gives the sum of the kinetic and potential energies of the particles.

Important nontrivial solutions of (4.1.2.1) are (after adding the time dependence) the plane wavefunctions

$$\psi = \psi_0 \exp\{i(\omega t - \mathbf{k}\cdot\mathbf{r})\} \tag{4.1.2.4}$$

or the spherical wavefunctions

$$\psi = \psi_0 \frac{\exp\{i(\omega t - kr)\}}{r}. \tag{4.1.2.5}$$

Thus, relatively simple semi-classical wave mechanics, rather than full quantum mechanics, is needed for interactions with no appreciable loss of energy. The interaction of the waves with matter depends on the spatial variation of the refractive index given by the spatial variations of the electron density or the electrostatic potential functions.

Electromagnetic waves can also be described in terms of energy quanta, photons, with energy given by Planck's law

$$E = h\nu. \tag{4.1.2.6}$$

The values of E, ν, and λ of the electromagnetic waves used in general crystallography are scaled in Fig. 4.1.2.1. It should be noted that there are several types of electromagnetic waves in the most important wavelength range near 1 Å, which are called X-rays (when generated in X-ray tubes), γ-rays (when emitted by radioactive isotopes) or synchrotron radiation (emitted by electrons moving in a circular orbit).

On the other hand, the beam of particles of mass m, moving with velocity v, behaves like waves with wavelength given by de Broglie's law

$$\lambda = \frac{h}{mv} \tag{4.1.2.7}$$

or using $E_k = \frac{1}{2}mv^2$ for the kinetic energy of particles

$$\lambda = \frac{h}{(2mE_k)^{1/2}}. \tag{4.1.2.8}$$

When relativistic effects are taken into account,

$$\lambda = \lambda_0\left\{1 + \frac{E_k}{2m_0c^2}\right\}^{-1/2}, \tag{4.1.2.9}$$

where m_0 is the rest mass and λ_0 the non-relativistic wavelength. High-energy electrons ($E_k \approx 10^5$ eV, $\lambda \approx 10^{-2}$ Å) and neutrons ($E_k \approx 10^{-2}$ eV, $\lambda \approx 10^0$ Å) belong to the most prominent particles used in diffraction crystallography (see Table 4.1.3.1). However, low-energy electrons ($E_k \approx 10^2$ eV,

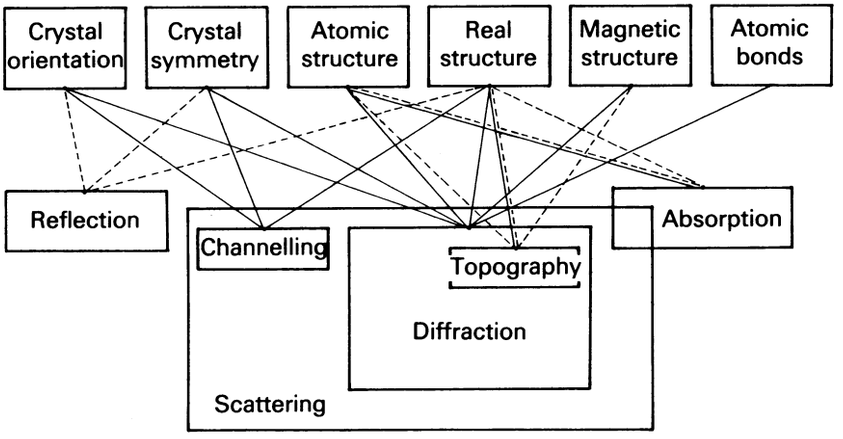

Fig. 4.1.1.1. Schematic diagram of the main types of radiation application in crystallography (dashed lines represent structure investigation on a larger than atomic scale).

references