4.1. Radiations used in crystallography

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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)]:

$$\nabla^2\psi + k^2\psi = 0. \qquad (4.1.2.1)$$

For electromagnetic waves,

$$k^2 = \varepsilon\mu\omega^2 = \omega^2/v^2, \qquad (4.1.2.2)$$

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

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

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

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

or the spherical wavefunctions

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

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

$$E = h\nu. \qquad (4.1.2.6)$$

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

$$\lambda = \frac{h}{mv} \qquad (4.1.2.7)$$

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

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

When relativistic effects are taken into account,

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

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,

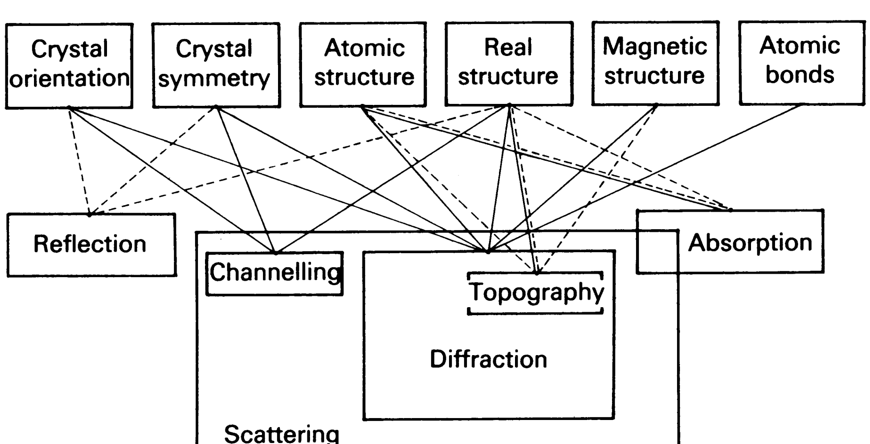

Fig. 4.1.1.1. Schematic diagram of the main types of radiation application in crystallography (dashed lines represent structure investigation on a larger than atomic scale).

$\lambda \approx 10^0$Å), protons or ions of elements with quite high atomic number and energy ($E_k \approx 10^3 - 10^6$ eV) are also used in scattering, channelling or shadowing experiments (see Section 4.1.5).

4.1.3. Most frequently used radiations

Average diffraction properties of X-rays, high-energy electrons, and neutrons are listed in Table 4.1.3.1. They can be varied with respect to the material analysed by changing the incident-beam operating conditions and they also greatly depend on the mutal interaction of radiation with the material. The values presented are typical rather than extreme ones and should be used as a guide for rough estimates and for general orientation in the subject. Details are given in the following sections. The properties of the radiations and the features of their interaction with crystals also impose limitations on the sample choice or preparation, on the recording of the diffraction data, and on the theoretical interpretation of these data. The different nature of the scattering of X-rays and electrons (interacting with the electron-density distribution or with the potential distribution) and neutrons (which are mainly scattered by nuclei) may be used in combined experiments to study details of thermal smearing of atomic positions and bonding characteristics of the electron-density distribution.

Notes to Table 4.1.3.1

(1) *Charge*. Charged electrons interact strongly with matter and must be used in vacuum whereas X-rays and neutrons can be used in air.

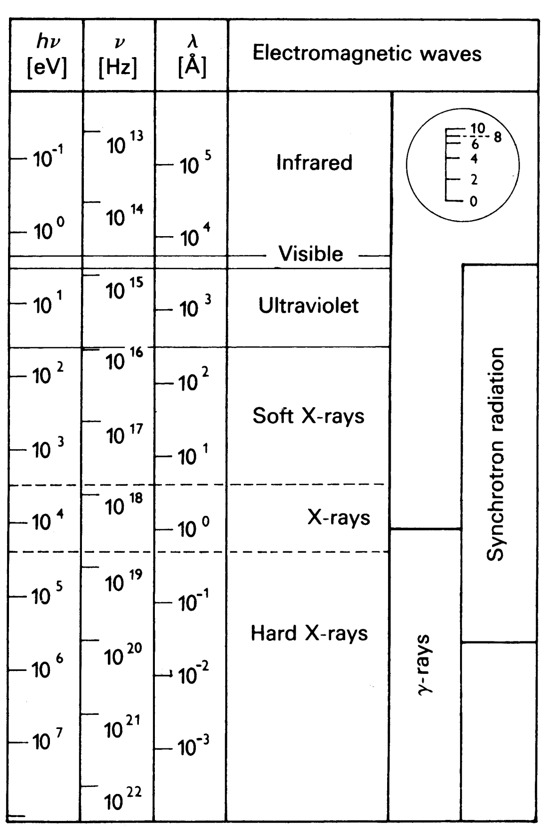

Fig. 4.1.2.1. Comparison of the energy, frequency, and wavelength of the electromagnetic waves used in crystallography (logarithmic scale).

Table 4.1.3.1. *Average diffraction properties of X-rays, electrons, and neutrons*

	X-rays	Electrons	Neutrons
(1) Charge	0	-1 e	0
(2) Rest mass	0	9.11×10^{-31} kg	1.67×10^{-27} kg
(3) Energy	10 keV	100 keV	0.03 eV
(4) Wavelength	1.5 Å	0.04 Å	1.2 Å
(5) Bragg angles	Large	1°	Large
(6) Extinction length	10 μm	0.03 μm	100 μm
(7) Absorption length	100 μm	1 μm	5 cm
(8) Width of rocking curve	5"	0.6°	0.5"
(9) Refractive index	$n < 1$	$n > 1$	$n \lesssim 1$
$n = 1 + \delta$	$\delta \approx -1 \times 10^{-5}$	$\delta \approx +1 \times 10^{-4}$	$\delta \approx \mp 1 \times 10^{-6}$
(10) Atomic scattering amplitudes f	10^{-3} Å	10 Å	10^{-4} Å
(11) Dependence of f on the atomic number Z	$\sim Z$	$\sim Z^{2/3}$	Nonmonotonic
(12) Anomalous dispersion	Common	–	Rare
(13) Spectral breadth	1 eV $\Delta\lambda/\lambda \approx 10^{-4}$	3 eV $\Delta\lambda/\lambda \approx 10^{-5}$	500 eV $\Delta\lambda/\lambda \approx 2$

(2) *Rest mass*. The wavelength of moving particles with the same energy is inversely proportional to the square root of their mass.

(3) *Energy*: Energies of X-rays generated in commonly used X-ray tubes range from 5 to 17 keV. High-energy electrons used in electron microscopes have energies from 40 to 300 keV, but energies of 1 MeV or more are achievable (for low-energy electrons, see Subsection 4.1.4.2). The extremely low energy of neutrons as compared with X-rays or electrons leads to their strong inelastic interaction with phonons (see Subsection 4.1.4.3).

(4) *Wavelength*. The radius of the Ewald sphere for electrons is much larger than that for X-rays or neutrons and thus part of the reciprocal-lattice plane image can be seen immediately if fixed-crystal electron diffraction is used. Wavelengths of electrons and neutrons are tunable by changing instrumental conditions (high voltage in the microscope and the temperature inside the reactor, respectively) whereas X-ray wavelengths are given by discrete lines of the characteristic spectra of the X-ray tube targets (for other X-ray sources, see Subsection 4.1.4.1).

(5) *Bragg angles*. The whole observable diffraction pattern obtained by electrons is contracted into small angles not exceeding 3–5° with the primary beam.

(6) *Extinction length*. The extinction length corresponds to the thickness of the crystal required for the whole incident beam to be scattered into the Bragg reflected beam and then to be scattered back into the direction of the incident beam. If the size of a nearly perfect crystal (or the size of the mosaic blocks) is comparable to or exceeds the extinction length for the given reflection then the dynamic diffraction theory (or the primary-extinction correction of applied kinematic theory in