

4.1. RADIATIONS USED IN CRYSTALLOGRAPHY

4.1.4. Special applications of X-rays, electrons, and neutrons

Special sources and/or special properties of these radiations are used in general crystallography.

4.1.4.1. X-rays, synchrotron radiation, and γ -rays

X-ray beams from *rotating-anode tubes* are approximately one hundred times more intensive than those from normal X-ray tubes. *Laser plasma X-ray sources* yield intensive nanosecond pulses of the line spectrum of nearly electron-free ions in the X-ray region with a spectral breadth of $\Delta\lambda/\lambda \approx 10^{-3}$. Several such pulses may be repeated per hour (Frankel & Forsyth, 1979). *Synchrotron radiation* is characterized by a continuous spectrum of wavelengths, high spectral flux, high intensity, high brightness, extreme collimation, sharp time structure (pulses with 30–200 ps length emitted in ns intervals), and nearly 100% polarization in the orbital plane (Kuntz, 1979; Bonse, 1980). Some of these properties are utilized in ordinary structure analysis: for example, fine tuning of the wavelength of synchrotron radiation for the solution of the phase problem by resonant scattering on chosen atomic species constituting the material under study. But these radiations also offer new advantages in other fields of crystallography, as, for example, in X-ray topography (Tanner & Bowen, 1980), in time-resolving studies (Bordas, 1980), in X-ray microscopy (Parsons, 1980), in studies of local atomic arrangements by extended X-ray absorption fine structure (XAFS) investigations (Lee, Citrin, Eisenberger & Kincaid, 1981) or studies of surface structures by X-ray photoemission spectroscopy (XPS) (Plummer & Eberhardt, 1982), *etc.* γ -rays emitted by radioactive sources such as ^{198}Au ($t_{1/2} = 2.7$ d), ^{153}Sm ($t_{1/2} = 46.8$ h), ^{192}Ir ($t_{1/2} = 74.2$ d) or ^{137}Cs ($t_{1/2} = 29.9$ a) are characterized by short wavelengths (typically hundreds of Å), by narrow spectral breadth ($\Delta E \approx 10^{-8}$ eV, $\Delta\lambda/\lambda \approx 10^{-6}$) and by relatively low beam intensity ($\sim 10^8 - 10^9$ m $^{-2}$ s $^{-1}$). They are mainly used for studies of the mosaic structure of single crystals (Schneider, 1983) or for the determination of charge density distribution (Hansen & Schneider, 1984). The typical absorption length of ~ 1 –4 cm and the increase of the extinction length by a factor of about 50 compared with ordinary X-rays are advantages utilized in these experiments. γ -rays also find applications in magnetic structure studies and in the determination of gradients of electric fields by Mössbauer diffraction and spectroscopy (Kuz'min, Kolpakov & Zhdanov, 1966).

For Compton scattering, see Sections 6.1.1 and 7.4.3.

4.1.4.2. Electrons

Low-energy electrons (10–200 eV) have wavelengths near 1 Å and a penetration of a few Å below the surface of a crystal. Low-energy electron diffraction (LEED) is thus used for the study of surface-layer structures (Ertl & Küppers, 1974). High-energy electrons are also currently used in electron microscopy in materials science. Under certain conditions, images of lattice planes with a resolution of 2 Å or better can be obtained. Transmission electron microscopy is also used for reconstruction of the three-dimensional structure of biological objects (such as viruses), alternatively in combination with X-ray diffraction (de Rossier & Klug, 1968).

4.1.4.3. Neutrons

The most important application of neutron diffraction is found in studies of magnetic structures (Marshall & Lovesey, 1971). The magnetic moment of neutrons is equal to $1.913 \mu_N$, where μ_N is the nuclear magneton, and neutrons have spin $I = 1/2$.

They can thus interact with the magnetic moments of nuclei or with the magnetic moments of the electron shells with uncompensated spins. Changes in wavelength from 1 to 30 Å enable one to study non-uniformities of different sizes and structures of polymers and biological objects by the small-angle method. Inelastic scattering of neutrons is used for determining phonon-dispersion curves. Neutron topography and neutron texture diffraction can be utilized for the relatively large samples used in technological applications. The *pulsed spallation neutron sources* are used for high-resolution time-of-flight powder diffraction (Windsor, 1981) or for time-resolved Laue diffraction.

4.1.5. Other radiations

4.1.5.1. Atomic and molecular beams

Fast charged particles like protons, deuterons or He^+ ions show preferential penetration through crystals when the direction of incidence is almost parallel to the prominent planes or axes of the lattice. The reverse effect of this *channelling* is *shadowing* when the centres of emission of the fast charged particles are the atoms of the crystal themselves. These methods are, for example, used in studies of surface structures, lattice defects, orientation, thermal vibrations, atomic displacements, and concentration profiles (Feldman, Mayer & Picraux, 1982). Ion beams are also applied in special analytical methods like Rutherford backscattering (RBS), inelastic scattering, proton-induced X-ray analysis (PIX), *etc.*

4.1.5.2. Positrons and muons

These elementary particles are used in crystallography mainly in studies of lattice defects (vacancies, interstitials, and impurity atoms) for the determination of their concentration, location, and diffusion by means of the techniques such as positron annihilation spectroscopy (PAS) and muon spin resonance (μSR) – see, for example, Siegel (1980) and Gyax, Kündig & Meier (1979). The positron implantation range in a solid is $\lesssim 100$ μm from the positron sources usually used (*e.g.* ^{22}Na , ^{64}Cu , ^{58}Co); these sources yield positrons with end-point energies of $\lesssim 1$ MeV. The PAS techniques are based on lifetime, Doppler broadening or angular correlation measurements of γ -rays emitted by the decaying nucleus of the radioactive source and those resulting from the positron–electron annihilation process. Muon sources require intense primary medium-energy proton beams. The positive muon μ^+ has charge $+e$, spin $1/2$, mass 105.659 MeV/ c^2 and a magnetic moment equal to 1.001 of the muon–magneton units. With a mean lifetime of 2.197 μs , the muon decays into a positron (e^+) and two neutrinos (ν_e and $\bar{\nu}_\mu$). The correlation between the direction of the emitted positron and the spin direction of the muon allows one to measure the spin precession frequency and/or the decay of the muon polarization of an ensemble of muons implanted in a solid.

4.1.5.3. Infrared, visible, and ultraviolet light

Visible light is one of the oldest tools used by crystallographers for macroscopic symmetry determination, for orientation of crystals, and in metallographic microscopes for phase analysis. Infrared and Raman spectroscopy are highly complementary methods in the infrared and visible range of wavelengths, respectively. The information content available with the two techniques is determined by molecular symmetry and polarity. This information is utilized for the identification of molecules or structural groups [symmetric

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vibrations and nonpolar groups are most easily studied by Raman scattering, antisymmetric vibrations and polar groups by infrared scattering (Grasselli, Snavely & Bulkin, 1980)]. The valence states or the bonds of surface atoms and the local structure in the immediate neighbourhood of the chosen atoms can be studied by ultraviolet radiation in the energy range 10–50 eV by means of angle-resolved photoelectron emission (Plummer & Eberhardt, 1982).

4.1.5.4. *Radiofrequency and microwaves*

Electromagnetic waves of frequencies 10^6 – 10^{10} Hz are used in nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR) experiments for studies of interatomic bonds, local atomic configurations, ordering, and relative population of atomic sites as well as for the determination of orientational features of magnetic structures (Kaufman & Shenoy, 1981).