

2.1. Classification of experimental techniques

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The diffraction of a wave of characteristic length, λ , by a crystal sample requires that λ is of the same order in size as the interatomic separation. Beams of X-rays, neutrons, and electrons can easily satisfy this requirement; for the latter two, the wavelength is determined by the de Broglie relationship $\lambda = h/p$, where h is Planck's constant and p is the momentum.

We can define 'diffraction geometry' as the description of the relationship between the beam and the sample orientation and the subsequent interception of the diffracted rays by a detector of given geometry and imaging properties. Each diffracted ray represents successful, constructive interference. The full stimulation of a reflection is achieved either by using a continuum of values of λ incident on the crystal, as used originally by Friedrich, Knipping & von Laue (1912) (the Laue method) or alternatively by using a monochromatic beam and rotation or precession of a crystal (moving-crystal methods) or a set of randomly oriented crystallites (the powder method).

The analysis of single-crystal reflection intensities allows the three-dimensional architecture of molecules to be determined. However, a single crystal cannot always be obtained. Diffraction from noncrystalline samples, *i.e.* fibres, amorphous materials or solutions, yields less detailed, but often very valuable, molecular information. Another method, surface diffraction, involves the determination of the organization of atoms deposited on the surface of a crystal substrate; a surface of perfectly repeating identical units, in identical environments, on such a substrate is sometimes referred to as a two-dimensional crystal. Ordered two-dimensional arrangements of proteins in membranes are studied by electron diffraction and, more recently, by undulator X-radiation. Another experimental probe of the structure of matter is EXAFS (extended X-ray absorption fine structure). This technique yields details of the *local* environment of a

specific atom whose X-ray absorption edge is stimulated; the atom absorbs an X-ray photon and yields up a photoelectron, which can be scattered by neighbouring atoms. Interpretation of EXAFS therefore closely follows low-energy electron-diffraction (LEED) theory. All these methods (Table 2.1.1) can be called methods of structure analysis. Techniques for examining the perfection of crystals are also very important. Defects in crystals represent irregularities in the growth of a perfect crystalline array. There are many types of defect. The experimental technique of X-ray topography (Chapter 2.7) is used to image irregularities in a crystal lattice.

X-ray techniques have expanded in the 1970's and 1980's with the utilization of synchrotron radiation. The methods based on the use of neutrons and electrons have developed. Broadly speaking, the diffraction geometry is independent of the nature of the wave and depends only on its state, namely, the wavelength, λ , the spectral bandpass, $\delta\lambda/\lambda$, the convergence/divergence angles, and the beam direction. In what follows, the term monochromatic refers to the case where there is, practically speaking, a very small but finite wavelength spread. Similarly, the term polychromatic refers to the situation where the wavelength spread is of the same order as the mean wavelength. The technical means by which a given beam (of X-rays, neutrons or electrons) is conditioned vary, as do the means of detection. These methods are dealt with in the following pages as far as they relate to the geometry of diffraction.

In the previous version of *International Tables* (IT II, 1959, Part 4), various diffraction geometries were detailed and a variety of numerical tables were given. The numerical tables have mainly been dispensed with since the use of hand-held calculators and computers has rendered them obsolete.

2.1 CLASSIFICATION OF EXPERIMENTAL TECHNIQUES

Table 2.1.1. Summary of main experimental techniques for structure analysis

Name of technique	Beam		Sample	Usual detectors
	Usual type	Spectrum		
<i>(A) Single crystal</i>				
Laue	X-ray or neutron	Polychromatic	Stationary single crystal	Film; image plate or storage phosphor; electronic area detector (e.g. CCD); for neutron case, detector sensitive to time-of-flight
Still	X-ray or neutron or electron	Monochromatic	Stationary single crystal	Film; image plate or storage phosphor; electronic area detector (e.g. MWPC, TV, CCD)
Rotation/oscillation	X-ray	Monochromatic	Single crystal rotating about a single axis (typical angular range per exposure 5–15° for small molecule; 1–2° for protein; 0.25–0.5° for virus)	Film; image plate or storage phosphor; electronic area detector (e.g. MWPC, TV, CCD)
Weissenberg	X-ray	Monochromatic	Single crystal rotating about a single axis (angular range $\geq 15^\circ$), coupled with detector translation	Film; image plate or storage phosphor
Precession	X-ray	Monochromatic	Single crystal (the normal to a reciprocal-lattice plane precesses about X-ray beam)	Flat film moving behind a screen coupled with crystal so as to be held parallel to a reciprocal-lattice plane
Diffraction	X-ray or neutron	Monochromatic	Single crystal rotated over a small angular range	Single counter, linear detector or area detector
<i>(B) Polycrystalline powders</i>				
Monochromatic powder method	X-ray or neutron or electron	Monochromatic	Powder sample rotated to increase range of orientations presented to beam	Film or image plate; counter; 1D position-sensitive detector (linear or curved)
Energy-dispersive powder method	X-ray or neutron	Polychromatic	Powder sample	Energy-dispersive counter (for neutron case, detector sensitive to time-of-flight)
<i>(C) Fibres, solutions, surfaces, and membranes</i>				
Fibre method	X-ray or neutron	Monochromatic	Single fibre or a bundle of fibres; preferred orientation in a sample	Film or image plate; electronic area detector (e.g. MWPC or TV); records high-angle or low-angle diffraction data
Solution or 'small-angle method'	X-ray or neutron	Monochromatic	Dilute solutions of particles; crystalline defects	Counter or MWPC
Surface diffraction	Electron or X-ray	Monochromatic	Atoms deposited or adsorbed onto a substrate	Phosphor or counter
Membranes	Electron or X-ray	Monochromatic	Naturally occurring 2D ordered membrane protein	Film or image plate; CCD

Notes

(1) Monochromatic. Typical value of spectral spread, $\delta\lambda/\lambda$, on a conventional X-ray source; $K\alpha_1 - K\alpha_2$ line separation $\sim 2.5 \times 10^{-3}$, $K\alpha_1$ line width $\sim 10^{-4}$. On a synchrotron source a variable quantity dependent on type of monochromator; typical values $\sim 10^{-3}$ or $\sim 10^{-4}$ for the two common monochromator types (see Figs. 2.2.7.2 and 2.2.7.3, respectively).

(2) CCD = charge-coupled device; MWPC = multiwire proportional chamber detector; TV = television detector.

(3) Image plate is a trade name of Fuji. Storage phosphor is a trade name of Kodak.

(4) EXAFS can be performed on all types of sample whether crystalline or noncrystalline. It uses an X-ray beam that is tuned around an absorption edge and the transmitted intensity or the fluorescence emission is measured.

2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

has been annealed. Then a model for the diffusion is assumed, and the coefficients are calculated. Using standard techniques, researchers are unable to detect the movement of an atom through a sample of like atoms. However, using single bilayers of amorphous ^{10}B and ^{11}B , it was shown (Smith, Hamilton, Fitzsimmons, Baker, Hubbard, Nastasi, Hirvonen & Zocco, 1992) through neutron-reflectivity measurements that the diffusion of boron in boron could be measured by studying the density profile (see Figs. 2.9.7.1 and 2.9.7.2) of one isotope in the other as a function of annealing time. Also, because of the sensitivity of the technique to the interfacial density profile, it was found that standard Fickian diffusion models could not explain the measured density profiles.

2.9.7.2. Magnetic multilayers

In order to understand interlayer coupling mechanisms, it is necessary to know what the magnetic superstructure is for a given nonmagnetic spacer layer thickness and/or applied field strength. Fig. 2.9.7.3 shows the spin-dependent reflectivities for a Co/Cu (111) multilayer along with the nuclear (Nb) and magnetic (Np) scattering-density profiles deduced from the data of Schreyer, Zeidler, Morawe, Metoki, Zabel, Ankner & Majkrzak (1993). In this specific case, the in-plane ferromag-

netic Co layers are themselves coupled ferromagnetically across the nonmagnetic Cu, all at a constant angle.

2.9.7.3. Hydrogenous materials

There are a substantial number of applications of neutron reflectometry in the study of hydrogenous films and multilayers, including diblock copolymer, surfactant, Langmuir–Blodgett, self-assembled monolayer, and lipid bilayer films. Reviews of the extensive research that has already been done have been written by Russell (1990) and Penfold & Thomas (1990). Only one specific example will be given here.

Fig. 2.9.7.4 shows neutron reflectivity data and the corresponding density profile for a Langmuir–Blodgett film composed of alternating bilayers of deuterated and hydrogenated stearic acid [after Wiesler, Feigin, Majkrzak, Ankner, Berzina & Troitsky (1995)]. Also shown in Fig. 2.9.7.4 is the scattering-density profile for the same sample as seen by X-rays. It is obvious that the X-rays are more sensitive to the high-Z barium in the head group, whereas the neutrons are especially good at distinguishing the degree of mixing between adjacent hydrogenated and deuterated hydrocarbon tails. This is a good example of the complementary nature of neutron and X-ray reflectivities.

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2.1–2.2

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