$\lambda \approx 10^0$ 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.

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 | $9.11 \times 10^{-31}$ kg | $1.67 \times 10^{-27}$ 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 | $n < 1$ | $n > 1$ | $n \lesseqgtr 1$ |
| $n = 1 + \delta$ | $\delta \approx -1 \times 10^{-5}$ | $\delta \approx +1 \times 10^{-4}$ | $\delta \approx \mp 1 \times 10^{-6}$ |
| (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 $\Delta\lambda/\lambda \approx 2$ |

*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.

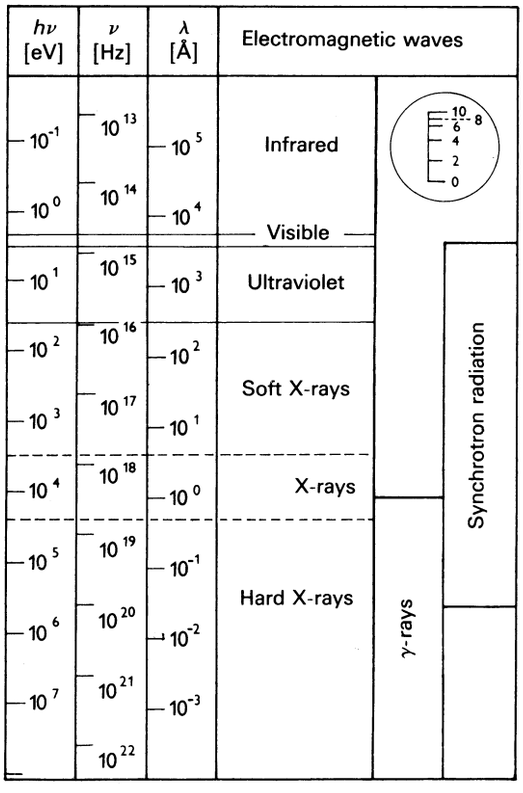


Fig. 4.1.2.1. Comparison of the energy, frequency, and wavelength of the electromagnetic waves used in crystallography (logarithmic scale).

(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

the case of the mosaic crystal) must be used. The dynamical effects thus decrease when passing from electrons to X-rays and neutrons for a given crystal thickness.

(7) *Absorption length*. Absorption length is here estimated by the reciprocal values of the linear absorption coefficients. The value of the absorption length determines the size of the sample or the surface layer thickness accessible for diffraction analysis. The penetration of the electron beam into the crystal is severely limited by absorption or by diffraction when a strong reflection is excited and thus only 10–1000 Å surface layers contribute to the electron diffraction. Owing to the Borrmann effect, there occurs a substantial decrease of X-ray absorption for nearly perfect crystals in diffraction position. The relatively large crystals used for neutron diffraction in order to obtain useful diffraction intensities have been found to cause particularly important secondary-extinction effects due to disorientation of the mosaic blocks.

(8) *Width of rocking curve*. The range of angles between a crystal plane and the diffracted beam over which there is significant Bragg reflection is much larger for electrons than for X-rays or neutrons.

(9) *Refractive index*. The refractive index deviates slightly from unity for the radiations compared and the angle of refraction thus makes only a few angular minutes and increases with increasing wavelength. Negative values of $\delta$ for neutrons correspond to positive values of atomic scattering amplitudes and *vice versa*. The refraction effects will be considerable for the small angles of incidence of electrons needed in the Bragg case of diffraction (see *Bragg angles*) and the waves diffracted from planes parallel to the surface having spacings as small as 2 or 3 Å may suffer total internal reflection and be unable to leave the crystal.

(10) *Atomic scattering amplitudes*. The example given corresponds to the scattering of the atoms of lead at $(\sin\theta)/\lambda = 0.4\,\text{Å}^{-1}$. The absolute values of the atomic scattering amplitudes for electrons are considerably greater than for X-rays or neutrons; this is also reflected in the structure-amplitude values and in the corresponding intensities of the Bragg reflections. For the angular dependence of the atomic scattering amplitudes, see Fig. 4.1.3.1. The constant value of the atomic scattering amplitudes for neutrons (also often called the scattering length) makes neutron diffraction suitable for precise measurement of thermal parameters.

(11) *Dependence of atomic scattering amplitudes on the atomic number Z*. This kind of dependence is illustrated for neutral atoms in Fig. 4.1.3.2. Because of the relatively weaker dependence on the atomic number, the peaks of light atoms in the presence of heavy atoms are revealed more clearly in the Fourier synthesis of electron-density maps obtained by the electron-diffraction method than by X-ray diffraction. The same is generally true for neutron diffraction, which also enables atoms of elements with similar atomic numbers to be distinguished in certain cases (based on the irregular change of atomic scattering amplitudes with $Z$); different isotopes of the same element may also be distinguished.

(12) *Anomalous dispersion*. This effect is utilized for the solution of the phase problem in crystal structure analysis by X-ray diffraction. In the case of neutron diffraction, there are only a few stable isotopes convenient for this purpose (mainly $^{149}$Sm, $^{157}$Gd, and $^{113}$Cd). The wavelength of the high-energy electrons is too short compared with the $K$-absorption edges of atoms and the resonance scattering of electrons is thus negligible.

(13) *Spectral breadth*. The value for X-rays corresponds to the characteristic lines of X-ray spectra. The spread of energies or wavelengths in the beam of neutrons obtained from a reactor is quite broad and for diffraction experiments a narrow range of wavelengths is usually selected by the use of a crystal monochromator or, especially for long wavelengths, by a time-of-flight chopper device that selects a range of neutron velocities.

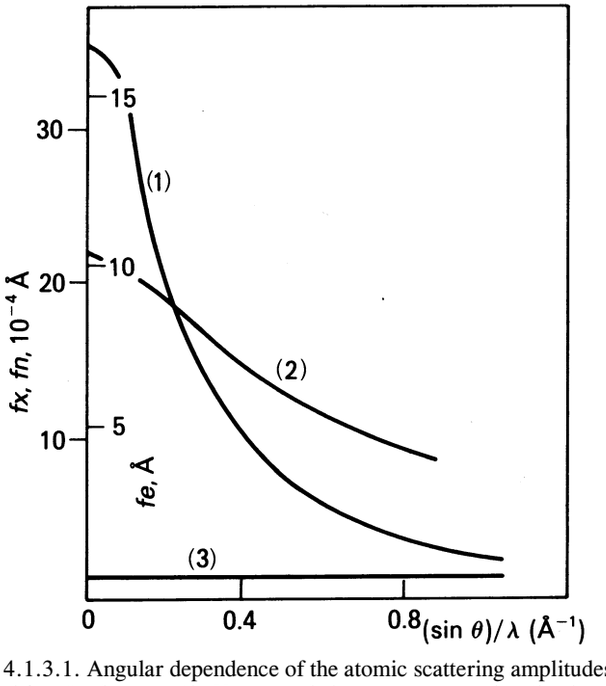


Fig. 4.1.3.1. Angular dependence of the atomic scattering amplitudes of lead for (1) electron, (2) X-ray, and (3) neutron scattering (in absolute values).

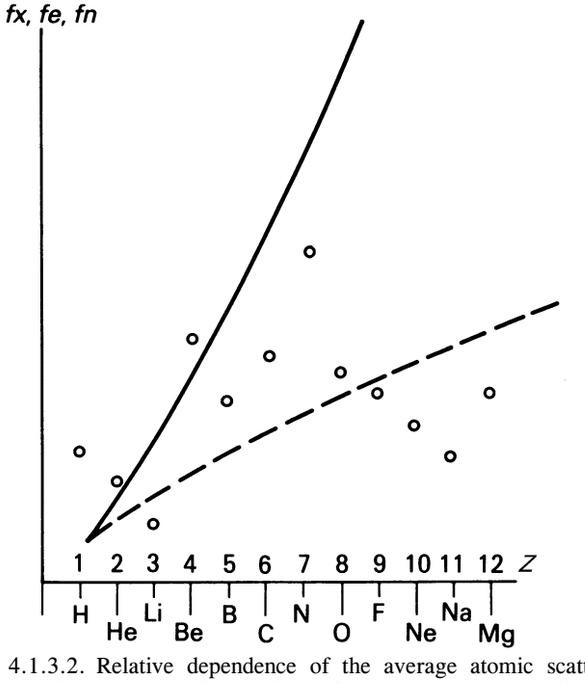


Fig. 4.1.3.2. Relative dependence of the average atomic scattering amplitudes on the atomic number $Z$ for X-rays (———), electrons (— — —), and neutrons (○). The values plotted are averages over $(\sin\theta)/\lambda$.



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