# 2.3. Neutron powder diffraction

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### 2.3.1. Introduction to the diffraction of thermal neutrons

Diffraction of neutrons occurs by virtue of their wave character, the de Broglie wavelength λ being

$$\lambda = \frac{h}{mv} = \frac{h}{(2mE)^{1/2}}, \tag{2.3.1}$$

where $m$, $v$ and $E$ are the mass, speed and energy of the neutron, respectively, and $h$ is Planck's constant. It may be convenient to express the neutron energy in meV, in which case the wavelength in ångströms is given by

$$\lambda\ (\text{Å}) = 9.045/(E)^{1/2}\ (\text{meV}). \tag{2.3.2}$$

Thermal neutrons produced by a fission reactor have a representative energy of 25 meV, and accordingly a wavelength of 1.809 Å, which is well suited to the study of condensed matter since it is of the order of the interatomic spacings therein.

Neutrons have a number of distinctive properties making neutron diffraction uniquely powerful in several applications. They may be scattered by nuclei or by magnetic entities in the sample under study.

(*a*) *Scattering by nuclei*: The atomic nucleus is tiny compared with the atomic electron cloud, which is the entity that scatters X-rays and electrons. The scattering cross section for a particular nucleus is written as

$$\sigma = 4\pi b^2, \tag{2.3.3}$$

where $\sigma$ is typically of the order of $10^{-28}$ m$^2$ ($1 \times 10^{-28}$ m$^2$ = 1 barn) and $b$, which is termed the *scattering length*, is of the order of femtometres. The small size of the nucleus relative to the wavelength of interest means that the scattering is isotropic – there is no angle-dependent form factor, as occurs in the X-ray case (*cf.* Section 1.1.3.1). This confers advantages in studies aimed at determining atomic displacement parameters (ADPs),[1] and indeed for the total-scattering studies requiring data over a large $Q$ range ($Q = 4\pi \sin\theta/\lambda$) that are described in Chapter 5.7. Importantly, scattering lengths vary somewhat erratically with atomic number $Z$; this is in marked contrast to the X-ray case in which the form factor increases monotonically with $Z$ (see Figs. 2.3.1 and 2.3.2). This can make it much easier to detect the scattering from light (low-$Z$) elements in the presence of much heavier ones; it also makes it easier to distinguish scattering from elements adjacent in the periodic table, *e.g.* Cu with $Z$ = 29, $b$ = 7.718 fm and Zn with $Z$ = 30, $b$ = 5.680 fm. The scattering length is also different for different isotopes of the same element,[2] *e.g.* for $^1$H $b$ = −3.741 fm, whereas for $^2$H $b$ = 6.671 fm, so that sometimes isotopic substitution can be employed to obtain contrast as desired.

(*b*) *Scattering by magnetic entities*: The neutron carries a magnetic moment of $-1.913\ \mu_N$ (where $\mu_N$ is the nuclear magneton) and accordingly it interacts with magnetic entities in the sample. These may be nuclei, with magnetic moments of the order of the nuclear magneton, or atoms with much larger magnetic moments, of the order of the Bohr magneton ($\mu_B$). If the magnetic entities are disordered, then the result is magnetic diffuse scattering, but if they are in some way ordered then the magnetic structure can be studied *via* the magnetic Bragg reflections that arise. (These may not be so obvious if they coincide with the nuclear Bragg reflections.) The magnetic moment of the neutron interacts with atomic magnetic moments, attributable to unpaired electrons in the atoms. These electrons tend to be the outer electrons, spread over dimensions comparable with atomic spacings and hence with the wavelengths used for diffraction; a consequence is that magnetic scattering is characterized by a magnetic form factor which falls off with $Q$ more rapidly than does the form factor for the X-ray case (Fig. 2.3.3). The confirmation of the antiferromagnetic ordering in MnO below its ordering (Néel) temperature of 120 K (Fig. 2.3.4; Shull *et al.*, 1951) was the first of numerous studies of magnetic structure by neutron powder diffraction that have continued to the present day (Izyumov & Ozerov, 1970; Chatterji, 2006; Chapter 7 in Kisi & Howard, 2008). Investigations of nuclear moments are more challenging largely because the smaller moments mean extremely low ordering temperatures; nevertheless neutron diffraction has been used, for example, to study the ordering

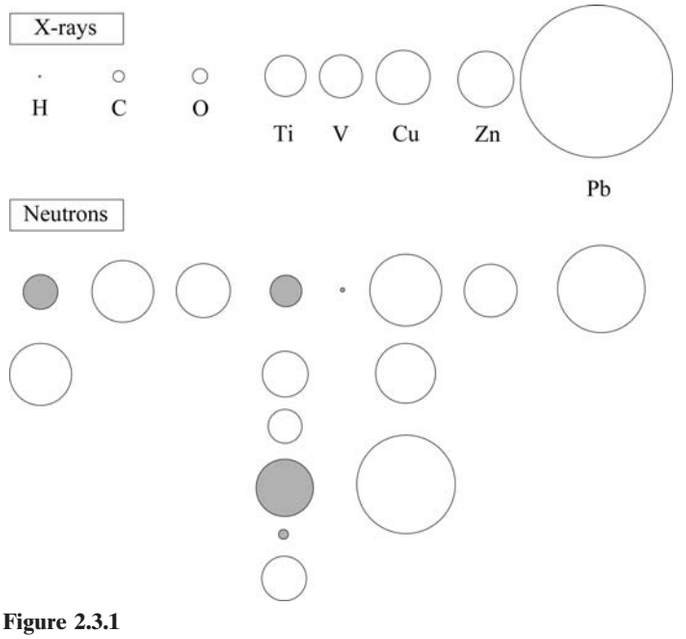


**Figure 2.3.1**
Representations of the scattering of X-rays and neutrons by selected elements. The scattering cross sections are proportional to the areas of the circles shown. For the neutron case, separate entries appear for the different isotopes and negative scattering lengths are indicated by shading. The figure is not intended to imply a relationship between the X-ray and neutron cross sections.

[1] The atomic displacements (*e.g.* thermal vibrations) smear the scattering sites to an extent that is likely to be considerably smaller than the atom itself, but very much larger than the nucleus.

[2] If the nucleus in question carries spin, the scattering length also depends on the relative orientation of the neutron and nuclear spins.

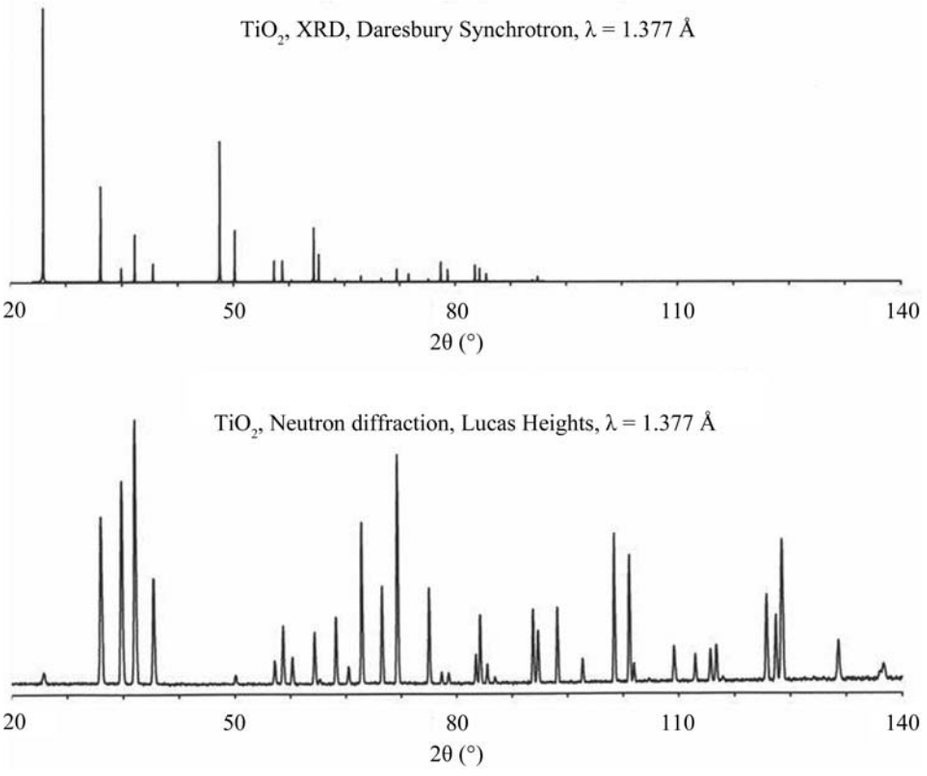


**Figure 2.3.2**
Comparison of X-ray and neutron powder-diffraction patterns from rutile, $TiO_2$. The patterns were recorded at the same wavelength, 1.377 Å. The differences between form factors and scattering lengths give rise to large differences in the relative intensities of the different peaks; note also that the fall off in the form factor evident in the X-ray case does not occur for neutrons.

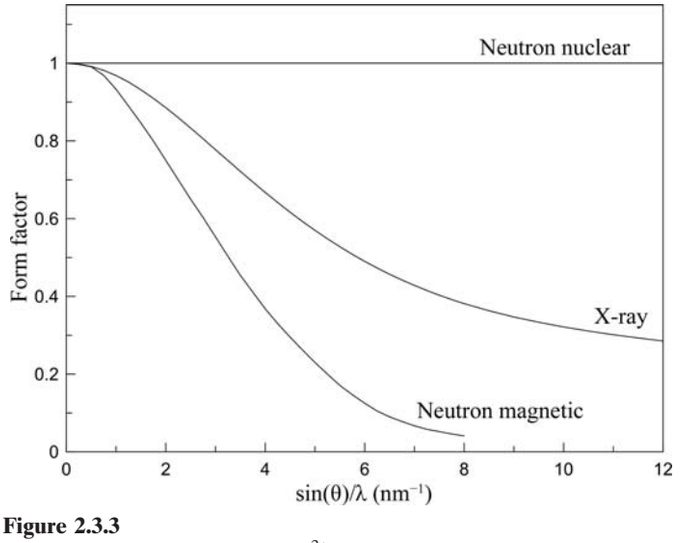


**Figure 2.3.3**
The magnetic form factor for $Mn^{2+}$ compared with the normalized X-ray form factor and the normalized neutron nuclear scattering length.

of nuclear moments in metallic copper ($^{65}Cu$) at temperatures below 60 nK (Hakonen *et al.*, 1991).[3]

(*c*) *Low attenuation*: The combination of the small scattering cross sections and generally low cross sections for absorption (notable exceptions are B, Cd and Gd) gives thermal neutrons the ability to penetrate quite deeply into most materials. Indeed, the linear attenuation coefficient for thermal (25 meV) neutrons in Fe is 110 $m^{-1}$, and for neutrons in Al it is only about 9.8 $m^{-1}$; the implication is that it takes about 10 cm of Al to reduce the intensity by a factor 1/*e*. The fact that neutrons are so little attenuated by these materials makes it easier to design large and complex sample-environment chambers which may be used for *in situ* studies at high temperature, under pressure or stress, in magnetic fields, and in reaction cells (Chapters 2.6–2.9; Chapter 3 in Kisi & Howard, 2008). Neutron powder diffraction is well suited to quantitative phase analysis (QPA, see Chapter 3.9 and Chapter 8 in Kisi & Howard, 2008); as pointed out in Chapter 8, Section 8 of Kisi & Howard (2008), neutron QPA provides a better sampling ability and is less prone to micro-absorption errors than the X-ray technique; indeed, neutron diffraction was the method employed in one of the earliest and most convincing demonstrations of the Rietveld method in QPA (Hill & Howard, 1987). Another advantage conferred by the deep penetration of neutrons is the ability to probe below the surface of samples to measure such aspects as structure, phase composition and stress; a particular example is the application to the analysis of zirconia ceramics (Kisi *et al.*, 1989) where the surface composition (as would be measured by X-rays) is unrepresentative of the bulk. A downside of the small scattering cross sections (along with neutron sources of limited 'brightness') is that relatively large samples may be required.

(*d*) *Low energy*: We note from equation (2.3.1) that, for a specified wavelength, the energy of the neutron is much less than that for lighter probes, such as electrons or photons. This is critically important for studying inelastic processes (*e.g.* measurement of phonon dispersion curves), but is usually not a factor in neutron powder diffraction.[4]

Neutron sources, in common with synchrotrons, are large national or international facilities, set up to cater for scientists from external laboratories. There are usually well defined access procedures, involving the submission and peer review of research proposals. Visiting users are usually assisted in their experiments by in-house staff. In some cases external users can mail in their samples for collection of diffraction data by the resident staff.

### 2.3.2. Neutrons and neutron diffraction – pertinent details

#### 2.3.2.1. *Properties of the neutron*

The basic properties of the neutron are summarized in Table 2.3.1.

[3] This study depends on the spin-dependent scattering lengths rather than magnetic scattering *per se*.

[4] However, if the incident beam is monochromatic, a crystal monochromator placed in the diffracted beam can be used to exclude inelastic scattering from the 'background'.



references