



# Neutron diffraction

## CHAPTER 14

### Neutron Diffraction

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Neutron diffraction is complementary to X-ray diffraction in determining crystal structures. Neutrons are chargeless (neutral) sub-atomic particles. The mass of a neutron is  $1.675 \times 10^{-27}$  kg. A beam of neutrons behaves like a wave. This beam can be scattered by atoms in a crystal like an X-ray or an electron beam. The neutron scattering by matter produces diffraction pattern similar to that obtained for X-ray diffraction and this is called *neutron diffraction*. From such diffraction pattern the positions of atoms and hence the crystal structure can be inferred.

#### Theory

Neutrons are produced by nuclear fission reactions in atomic piles and these neutrons have high energy. But the energy is lowered by the presence of moderators. Thus a neutron beam is formed from thermal (low energy) neutrons of a nuclear reactor. A velocity-selector device augmented by crystal diffraction produces a monochromatic neutron beam. The wavelength of neutron beam is related to the mass ( $m$ ) and velocity ( $v$ ) of the particle by the de Broglie equation

$$\lambda = h/mv$$

The kinetic energy and momentum of thermal neutron are given as.

$$\frac{1}{2} mv^2 = \frac{3}{2} kT \quad ; \quad mv = \sqrt{3mkT}$$

$$\therefore \lambda = h / \sqrt{3mkT}$$

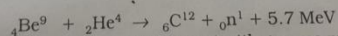
$T$  is absolute temperature

$k$  is Boltzmann constant

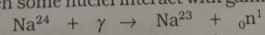
Substituting the constants and the absolute mass of a neutron, the wavelength  $\lambda$  of a neutron can be obtained:

$$\lambda = 1.46 \times 10^{-8} \text{ cm} = 1.46 \text{ \AA}$$

This value is of the order of bond lengths or spacings in crystals and therefore a beam of thermal neutrons is suitable for diffraction studies of crystals. Neutrons are produced in other nuclear reactions also; for example, when  $\text{Be}^9$  is bombarded with alpha particle, neutron is formed.



Neutrons can be obtained when some nuclei interact with gamma rays, e.g.,



By using  $\gamma$ -ray of a particular energy, monoenergetic (same wavelength) neutrons can be obtained.

### Detectors

Neutrons cannot be detected by photographic plate. These are detected by counters but these counters should be shielded against radiation. The detector in a neutron spectrometer is usually a boron trifluoride counter.  $\text{BF}_3$  is enriched with the heavier isotope of boron,  $^{10}\text{B}$ . The efficiency of the counter is low with  $^{10}\text{B}$ . The counter actually records the  $\alpha$ -particles emitted in the  $^{10}\text{B}(n, \alpha)^7\text{Li}$  nuclear reaction.

### Neutron Spectrometer

This spectrometer is used for recording neutron diffraction by a sample. A neutron beam from an atomic pile is directed on to a crystal (calcite or lithium fluoride). The resultant beam from the crystal is "monochromatic", i.e., has neutrons of same wavelength. The resultant beam from the crystal is "monochromatic", i.e., has neutrons of same wavelength. Then this beam is made to fall on the sample (powder). The beam gets diffracted by the sample. A  $\text{BF}_3$  counter, always pointing towards the sample, is rotated slowly about it. The plot of counter readings as a function of angle of rotation represents the neutron diffraction pattern of the sample. Fig. 14.1 represents such a pattern for metallic Mn powder. Each peak is due to reflection by a plane of the crystal. The peaks arise at angles for which Bragg's condition ( $n\lambda = 2d \sin \theta$ ) is valid for various planes.

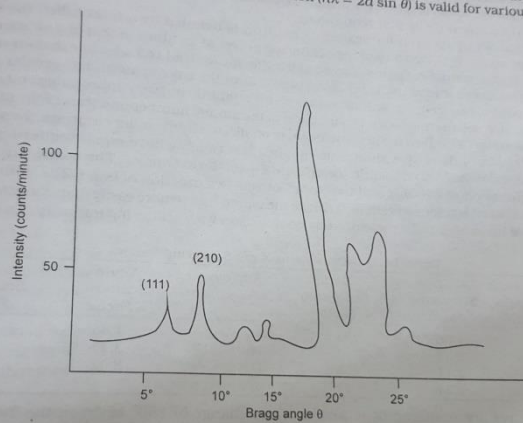


Fig. 14.1 Neutron Diffraction Pattern for Mn at 20° K

### Origin of Neutron Diffraction

The diffraction of X-rays is caused by the orbital electrons of the atoms in the substance through which the rays pass. The atomic nuclei do not contribute anything to the scattering of X-rays. The diffraction of neutrons is caused by: (a) nuclear scattering, and (b) magnetic scattering.

The nuclear scattering is brought about by interaction of neutrons with the protons or neutrons of the atomic nuclei and depends upon: (i) nuclear size, and (ii) nuclear structure. Even the small hydrogen atom scatters neutrons and this scattering is as good as that by potassium. Magnetic scattering arises from the interaction between magnetic moment of neutrons with the permanent magnetic moments of atoms or ions concerned. For example,  $\text{Fe}^{3+}$  has unpaired electrons and therefore it has permanent magnetic moment. When  $\text{Fe}^{3+}$  scatters a beam of neutrons, the scattering is due to both the nucleus and the electron cloud of iron atom. In neutron scattering, when the Bragg condition for scattering is satisfied, sharp maxima are obtained due to nuclear scattering and a diffuse background due to magnetic scattering. It is possible to distinguish between the two types of scattering by the fact that neutron waves are polarised by magnetic scattering and not by nuclear scattering.

#### Atomic Scattering

When an atom scatters X-radiation and electron waves, it is the outer electrons of the atom which are responsible for the scattering. But as the neutron beam is uncharged, it is unaffected by the outer electrons of the atom except for a very small magnetic coupling. Thus the penetrating power of neutron waves is greater than that of electron waves. The scattering centre for neutrons is mainly the nucleus of the diffracting atom.

The capacity of an atom for scattering neutron is denoted by a term called the *neutron scattering factor*. It is the ratio of the scattering power of an atom to that of a single electron (Table 14.1). For example, the neutron scattering factor for lead is 3.41 while that for oxygen is 2.11. This means that lead nucleus, being bigger than the oxygen atom, has greater neutron scattering power. However, the scattering factors for atoms do not vary appreciably and regularly with atomic size. Scattering factor is a function of the atomic number and thus of the number of electrons in the atom. But as the neutron beam is unaffected by the outer electrons, the scattering factors do not vary directly with atomic number but roughly have equal scattering factors. Scattering factors have no dependence on Bragg's scattering angle. The scattering factor of X-rays is a function of  $(\sin \theta)/\lambda$  and that for electrons is a function of  $(\sin \theta/2)/\lambda$ . Although the intensity of neutron scattering is small, it can be measured much more easily than X-ray scattering. The absolute intensity can be measured by comparison with scattering intensity of a standard substance.

Table 14.1 Neutron and X-ray Scattering Factors

Nucleus	Neutron Scattering Factor	X-ray Scattering Factor	Nucleus	Neutron Scattering Factor	X-ray Scattering Factor
$^1\text{H}$	-1.35	1	I	1.85	53
$^2\text{H}$	2.31	1	Pb	3.41	82
O	2.11	8	U	3.02	92
Na	1.24	11			

When X-rays are scattered by atoms, a phase change of  $180^\circ$  between the incident and scattered waves occurs. The same phase change happens when most nuclei scatter neutrons. However, with a few nuclei (e.g., hydrogen) there is no phase change. By convention, such nuclei are given negative scattering factors.

#### Location of Hydrogen

The neutron scattering factors for atoms do not vary appreciably unlike X-ray scattering factors. For example, the X-ray scattering factor for H is 1 whereas that for U is 92. Therefore, when

compound containing these two atoms scatter X-rays, the scattering capacity of H is overwhelmed by the scattering power of U. In this situation the location of hydrogen atom in the crystal cannot be ascertained from the X-ray diffraction pattern. On the other hand, this is possible with neutron diffraction, because hydrogen atom also scatters neutrons strongly. (The scattering factor for H is not far below that for U). Similarly, the X-ray diffraction of PbO does not give a clear picture about the positions of the oxygen atom in the crystal lattice. However, a complete picture of the crystal structure can be obtained from its neutron diffraction. Neutron diffraction is mainly used to study crystals whose structures are known except for the positions of the hydrogen atoms. Thus, in a compound such as  $\text{UH}_3$ , X-ray diffraction was utilized to determine the uranium coordinates and neutron diffraction the hydrogen coordinates. Since neutron shows the positions of hydrogen atoms precisely, better U-H bond lengths are obtained by this method.

By neutron diffraction the positions of atoms and the distribution of electron density in a molecule can be mapped. From such maps molecular and crystal structures can be inferred.

**Structure of Ice.** This has been established with X-ray and neutron diffraction data. The common form of ice has a structure related to that of Wurtzite; the oxygen atoms occupy the sites of both Zn and S atoms of Wurtzite; the H atoms are located just off the lines joining the oxygen atoms. In ice the non-bonded O-O distance is 2.24 Å and the O-H bond distance is 1.01 Å.

#### Magnetic Scattering

In magnetic scattering, the scattering centres are the electrons. Apart from the scattering of neutrons by atomic nuclei, there is an additional scattering if the specimen contains paramagnetic atoms or ion. This arises due to the interaction of the magnetic moments of neutrons with the permanent magnetic moments of the paramagnetic atoms.

An atom has a permanent magnetic moment when one of its inner shells is partially filled. Since the inner shells have a size comparable with the wavelength of the neutrons, magnetic scattering factor will fall off with increasing scattering angle unlike nuclear scattering factor. Magnetic moments of atoms in a paramagnetic crystal are arranged randomly. Magnetic scattering is thus incoherent and forms a diffuse background falling off with the angle. In ferromagnetic substances, the moments of neighbouring atoms are arranged parallel, and in anti-ferromagnetic substances, the magnetic moments of two neighbours are opposed. Examples of ferromagnetic substances are transition metals such as Fe, Co, and Ni and those of anti-ferromagnetic substances are ionic salts of transition metals such as  $\text{Fe}_2\text{O}_3$  and  $\text{MnF}_2$ .

Neutron diffraction can experimentally distinguish between ferromagnetic and anti-ferromagnetic crystal structures. The diffraction pattern can indicate the direction of alignment of spins within the crystal. For example, the crystal structure of manganous oxide  $\text{MnO}$  has been obtained by neutron diffraction. It is anti-ferromagnetic and has the rock-salt structure. Considering the  $\text{Mn}^{2+}$  ions in successive (111) planes in the crystal, the resultant spins are so oriented that they are directed positively and negatively along the (100) direction.

#### Magnetic Scattering in Transition Elements and Rare Earths

It is found that in certain transition elements, the observed magnetic moment is not in good agreement with the value calculated from the Lande splitting factor unless it is assumed that the magnetism is largely due to spin and not due to the orbital motion of the electrons of the scattering atoms. It is supposed that the orbital motion is quenched by the crystalline field. Since close shells do not have a resultant magnetic moment, it is the *d*-electrons in the transition element which are responsible for the magnetic effect. In rare earths, the resultant magnetism is due to the *f*-electrons which are not so much affected by the surrounding field, since they are further

inside the atom and protected by other electrons. With all cases of magnetic scattering there is a large incoherent effect due to spin interaction.

#### Neutron Diffraction and Intervalence Compounds

A compound containing an element in two different oxidation states is an intervalence compound. For example, in  $\text{Fe}_3\text{O}_4$ , one iron is divalent and the other two are trivalent ( $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ ). These two iron species  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  in  $\text{Fe}_3\text{O}_4$  cannot be distinguished by X-ray diffraction. However, this is possible with neutron diffraction because these two iron ions, having different numbers of unpaired electrons, scatter neutrons differently. Essentially, these two have different magnetic scattering capacities.

#### Comparison of X-ray and Neutron Diffraction

Neutron diffraction locates the nuclei of atoms and X-ray diffraction provides a clear picture of their electron clouds. Therefore, these two techniques can provide a fuller picture of molecular structures including the positions of bonds. A comparative account of the two techniques is given in Table 14.2.

Table 14.2 Comparison between X-ray Diffraction and Neutron Diffraction

Property	X-ray Diffraction	Neutron Diffraction
Atomic Scattering	Electronic Scattering factor depends on $(\sin \theta/\lambda)$  Regular increase of scattering power with atomic number, calculable from known electronic configuration  No difference among isotopes	Nuclear Isotropic i.e., equally in all directions. No angular dependence.  Irregular variation with atomic number, dependent on nuclear structure and only determined empirically  Different for different isotopes and is dependent also on nuclear spin.
Magnetic Scattering	No magnetic scattering	Additional scattering by atoms with magnetic moments; diffuse scattering by paramagnetic materials.
Absorption Coefficient	Very large. True absorption being much greater than scattering, increases with atomic number	Absorption usually very small.  Varies with isotopes.
Absolute Intensity Measurement	Difficult. Interpretation depends on precise knowledge of atomic scattering factors.	Straightforward, particularly by powder methods.

#### Neutron Diffraction by Gases and Liquids

Neutron scattering by a gas is of very low intensity and therefore this technique is difficult. However, certain useful information about the outer electrons in the scattering atom may be obtained. Neutron scattering is also possible with certain liquids like liquid argon and liquid nitrogen and amorphous solids.

**Applications**

1. Neutron diffraction may be used to study solids in the form of powders or single crystals to establish crystal structures.
2. It supplements and also complements the information derived from X-ray diffraction data.
3. It locates and characterises water molecules in hydrates.
4. It is useful in locating even small atoms like hydrogen atoms in crystals.
5. Neutron diffraction studies on ferromagnetic and anti-ferromagnetic materials are useful for the investigation of magnetic properties of alloys.
6. It is useful in the study of order-disorder transitions of alloys.

The chief drawback of neutron diffraction is that the neutron sources are expensive and not readily available in small laboratories.