25 Neutron Diffraction

INTRODUCTION

Neutrons like *X*-rays exhibit diffraction pattern when scattered from the regular array of atoms in a crystal. Whereas *X*-rays are scattered by the orbital electron, the neutrons are scattered by atomic nuclei. Neutron diffraction is caused by two additional factors, *viz., nuclear scattering due to interaction of neutrons with the atomic nuclei and magnetic scattering due to the interaction of the magnetic moments of neutrons with permanent magnetic moments of atoms or ions.* The de-Broglie wavelength associated with a beam of particles of mass m, speed v and energy E is given by

$$\lambda = h/mv = h/(2mE)^{1/2} \quad \text{...(1)}$$

Diffraction effects may be expected if we allow thermal neutrons to fall on crystals. **Bragg's** law will hold good for neutron diffraction like *X*-rays. Hence condition for scattering follows

$$n\lambda = 2d \sin \theta \quad \text{...(2)}$$

where n = order of interference, d = spacing of lattice planes, θ = glancing angle for the incident and diffracted beams with reference to lattice planes. Combining equations (1) and (2), we get

$$E = n^2h^2/8md^2 \sin^2 \theta \quad \text{...(3)}$$

Highly monochromatic beams of neutrons after diffraction from a crystal at various angles can be obtained, if a collimated beam containing a spread of energies falls on a crystal so that the equation (3) is satisfied.

Production of Monochromatic Neutron Beam. Intense beam of monochromatic neutrons can be produced by two methods.

(i) By reflection from crystals (calcite or LiF) according to **Bragg's law.** This technique sorts out the higher energy neutrons whose de-Broglie wavelengths are within the Bragg's reflection limit.

(ii) By total reflection from highly polished surfaces like *X*-rays. In this method low energy neutrons of longer wavelengths are totally reflected. Mirrors of Al, Be, Cu, Ni or graphite etc., produce intense reflected beams at glancing angles upto 10 mins of arc.

THEORY OF NEUTRON DIFFRACTION

A monochromatic beam of neutron scattered by a crystal is allowed to fall on a photographic film for studying crystal structure. Since neutrons do not affect a photographic film, so indium coated film is used which is capable of capturing the neutrons. The unstable nuclei so formed emit β-particles which register dark spots on the film. This pattern is called **Laue pattern.** In these experiments, thermal neutrons from a reactor are collimated by cadmium slits and then diffracted by a large size calcite or lithium fluoride crystal. The

neutron intensities are recorded by BF_3 counters. Since diffracting properties of the nuclei depend upon specific nuclear differences so neutron diffraction technique is employed to identify light as well as heavy atoms. This technique is better than X-ray diffraction method.

In case of perfect crystals, the scattering is all coherent and the measured total cross section will be just σ_{coh}. The amplitude of the peaks depends upon σ_{coh} for the crystal. Scattering between the peaks can be measured by σ_d. These quantities can be deduced from the diffraction patterns.

SCATTERING OF NEUTRONS BY SOLIDS AND LIQUIDS

Since neutrons are neutral, they cannot interact with the peripheral electrons or with positively charged atomic nuclei according to the law of inverse squares. Hence their absorption in matter is due exclusively to their short range interactions with nuclei. Their interaction may be regarded as a collision which may be elastic or inelastic collision. According to the law of conservation of energy and momentum, elastic collision will give rise to scattering of neutrons. A portion of the energy of striking neutron will be transferred to the struckked nucleus. The loss in energy will be very small if the nucleus is very heavy. Light nuclei will appreciably reduce the energy of fast neutrons at each collision. This explains the slowing down action of hydrogeneous materials. A beam of fast neutrons is reduced to half its intensity by 5 g cm^{-2} of water or paraffin. The scattering cross-section for fast neutrons increases with the increase in atomic number of the nucleus. Its value is of the order of 10^{-24} cm^2 for all nuclei varying from $1{\cdot}4 \times 10^{-24}$ to $5{\cdot}5 \times 10^{-24}$ cm^2.

The inelastic collision may be partial or total. In partial collisions, nucleus is scattered anomalously and the struck nucleus undergoes internal changes and is raised to an excited state of higher energy. In total collisions, the neutron is captured by the nucleus leading to real transformation.

Inelastic scattering has been observed in Mg with fast neutrons. In this case, the cross-section for inelastic scattering was roughly one-third that for elastic scattering. Similar anomalous scattering of thermal neutrons is observed in iron, where it was found that magnetization of iron decreased the scattering by about 10% almost to saturation. It shows the existence of magnetic moment of the neutron inspite of the fact that neutron carries no charge.

Neutrons which possess magnetic moment by virtue of having a spin of 1/2, interact with nuclei which have magnetic moments to produce further background scattering for substances for which the nuclear spins are randomly oriented. The spin-disorder scattering is so great for hydrogen in comparison with the ordered scattering that deuterated compounds are often used for neutron diffraction studies. Paramagnetic substances also contribute to the general background scattering because of the interaction of the magnetic moments of neutrons with the randomly oriented orbital magnetic moments of the electrons. *The magnetic moments of neighbouring atoms are oriented in the same direction in ferromagnetic substances* whereas the magnetic moments of the neighbouring atoms are oriented in opposite directions in antiferromagnetic substances.

The motion of molecules in liquids can be studied experimentally by inelastic neutron scattering, *in which the energetic neutrons collect or discard as they pass through a sample*. The technique is also used to examine the internal dynamics of macro molecules.

MAGNETIC SCATTERING

Since neutrons possess a spin and associated magnetic moment, magnetic interaction between neutrons and atomic electrons, which is responsible for magnetic properties of materials may be expected. Thus a neutron can be scattered by interaction of its magnetic moment with the atomic or ionic magnetic moments of the sample atoms. This type of scattering is generally referred to as **magnetic scattering.** Whereas diffraction of *X*-rays is caused by the orbital electrons of the atoms in the material through which they pass and atomic nuclei contribute practically nothing to scattering, diffraction of neutrons is caused by two effects.

(i) *Nuclear scattering due to interaction of neutrons with atomic nuclei and*

(ii) *Magnetic scattering due to interaction of the magnetic moments of neutrons with permanent magnetic moments of atoms or ions.*

The magnetic moments of atoms in a paramagnetic crystal are arranged at random in the absence of external magnetic field hence **magnetic scattering of neutrons by such a** crystal is also random. In ferromagnetic substances, the magnetic moments are regularly aligned, so that the resultant spins of adjacent atoms are parallel, even in the absence of an external field. In antiferromagnetic materials, the magnetic moments are also regularly aligned but in such a way that adjacent spins along certain directions are opposed.

Neutron diffraction is used to make distinction between ferromagnetic and anti-ferromagnetic materials. The former are usually transition metals such as Fe, Co or Cr while the latter are mainly ionic salts of transition metals like Fe_2O_3 or MnF_2. Neutrons suffer a **magnetic scattering** when the diffracting material is paramagnetic, ferromagnetic or anti-ferromagnetic and the magnetic moments have some kind of ordered arrangement internally, because they themselves possess a small magnetic moment which interacts with the moment of the lattice atoms.

Studies of scattering and neutron diffraction by paramagnetic and anti-ferromagnetic crystals revealed that for completely uncoupled moments, magnetic scattering effects show **diffuse scattering** in the pattern with a form factor decrease in intensity. This **form factor** permits the determination of the radial distribution function for the specific electrons in the atom, which are responsible for the atomic moment. *When the atomic moments in a crystal are coupled together, coherence in the magnetic scattering* is introduced and the scattering is concentrated in the **Bragg reflections** from the crystals, which manifests itself in a sharp and well defined diffraction pattern. This shows that in ferromagnetic and antiferromagnetic substances all the moments are rigidly aligned.

MEASUREMENT TECHNIQUE

Neutron spectrometers (**Fig. 1**) used along with the absorber material in the path of monochromatic diffracted beam gives accurate measurements of neutron induced reactions in the low energy region (*i.e.*, neutron energies from 0·025 eV to 70 eV).

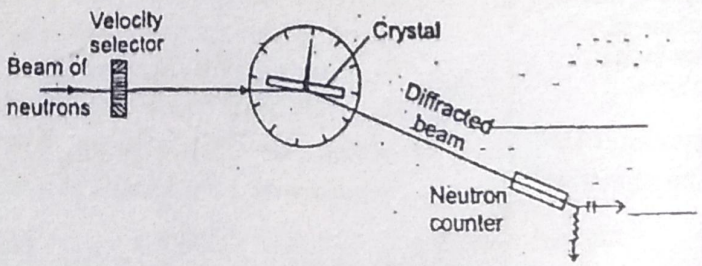

Fig. 1. Neutron spectrometer for crystals.

Method. The Debye-Scherrer Hull *X*-ray technique for powdered samples can be used for neutron diffraction. The neutron beam from the atomic pile falls on a crystal which is oriented to yield a diffracted beam of certain wavelength. This

oenergetic beam falls on sample. A BF_3 counter, ays pointing towards the ple, is rotated slowly ut it. The counter dings, corrected for kground, as a function of le of rotation gives the raction patterns (Fig. 2).

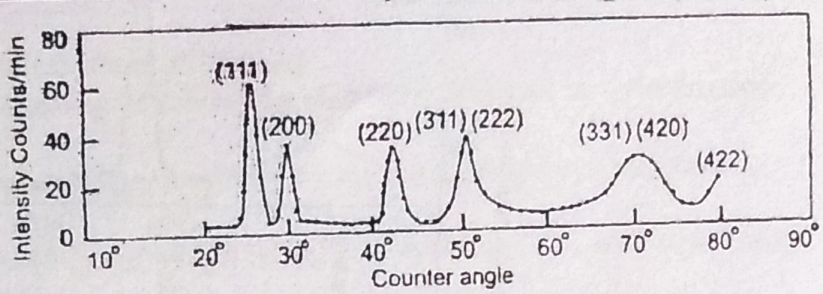

Fig. 2. A neutron diffraction pattern of a powdered aluminium sample. The numbers over the peaks are the Miller indices.

The peaks occur at angles for which Bragg's condition holds good for various planes. The utron diffraction is due to a coherent scattering by atomic nuclei in the crystal. For a stalline sample, the equation $n\lambda = 2d \sin\theta$ will be satisfied for just a few directions. Here scattering is maximum. In other directions there will be destructive interference and no ttering. Scattering associated with these Bragg's reflections is called coherent scattering. e rate at which neutrons are scattered in these allowed directions is determined by a herent scattering cross section σ_{coh}.

ELUCIDATION OF STRUCTURE OF MAGNETICALLY ORDERED UNIT CELL

Scattering of neutrons is a nuclear phenomenon. Neutrons pass through the extra nuclear electrons of atoms and interact with the nuclei through the strong force that is responsible for binding of nucleons together. As a result, the intensity with which neutrons are scattered is independent of the number of electrons, and neighbouring elements in the periodic table may scatter neutrons with markedly different intensities.

Neutron diffraction can be used to distinguish atoms of elements such as Ni and Co that are present in the same compound and to study order-disorder phase transitions in $Fe(CO)_5$.

Neutron diffraction is well suited to the investigation of magnetically ordered lattices in which neighbouring atoms may be of the same element but have different orientations of their electronic spin.

If the spins of atoms at lattice points are orderly as in antiferromagnetic material (where the spins of one set of atoms are aligned antiparallel to those of the other set), neutron diffraction detects two interpenetrating simple cubic lattices on account of the magnetic interaction of the neutrons with the atoms (Note that *X*-ray diffraction would detect only a single bcc lattice).

Fig. 3 shows neutron diffraction pattern for MnO below and above its curie temperature 120 K). At curie temperature, thermal agitation is so great that purely paramagnetic ehaviour prevails. When MnO crystal is above the curie point, there are no magnetic nterference effects but below the curie point, additional diffraction peaks appear orresponding to double the spacing of unit cell as determined by *X*-rays. That is, below 120 K, extra reflections were found which shows a magnetic unit cell whose edge is twice that f chemical unit cell (442·6 pm). However, these additional reflections disappeared at emperatures above 120 K. Thus the intensity of magnetic lines can be explained by ssuming that below 120 K the nearest neighbour manganous ions had their magnetic oments antiparallel, in which only the manganous ions are included.

In MnO crystal, which is antiferromagnetic, below the curie point there are strong lignments of spin of atoms that are alternately up and down as indicated in Fig. 4. Also the inimum magnetic repeat distance is two atoms in the antiferromagnetic state.

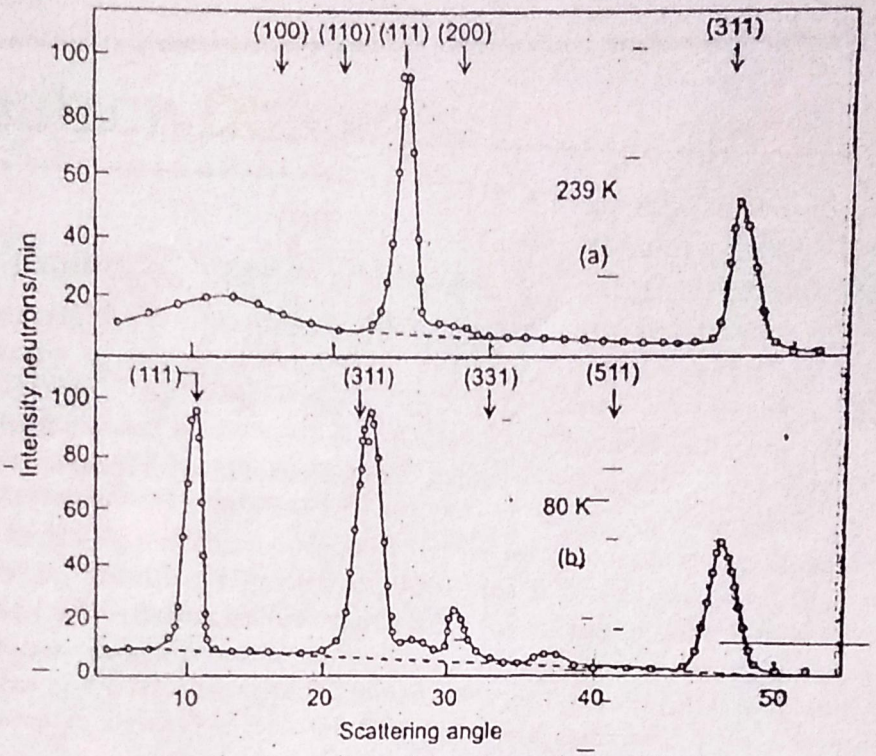

Fig. 3. The neutron diffraction pattern of MnO.
(a) Above and (b) Below the antiferromagnetic Curie point, which is at 120 K.

In MnO, the coupling between spins of Mn ions is through excited states, where the O ion acts as intermediate ion. When the atoms Mn—O—Mn are colinear, the coupling between two Mn ions (next to nearest neighbours) is very strong. Thus in such structures, the magnetic vectors of adjacent Mn ions, when separated by intervening ions, point in opposite direction and give rise to antiferromagnetism. In case of crystalline substances such as FeO, $FeCl_2$, CoO, NiO, MnO, Mn, Cr etc., the magnetic vectors of adjacent atoms are oppositely directed through out the lattice, which cause the interaction of next to nearest spins to become more important than that between those which are immediate neighbours.

X-ray diffraction of MnO showed that it has the same crystal structure as NaCl. In this structure both the Mn and O ions lie in a **face centred** array with two arrays displaced in the same manner as in NaCl. The length of unit cell side is 442·6 pm. The neutron diffraction pattern of MnO showed that the spins are oriented along (100) crystal axes whereas in FeO, they are aligned along the (111) axes.

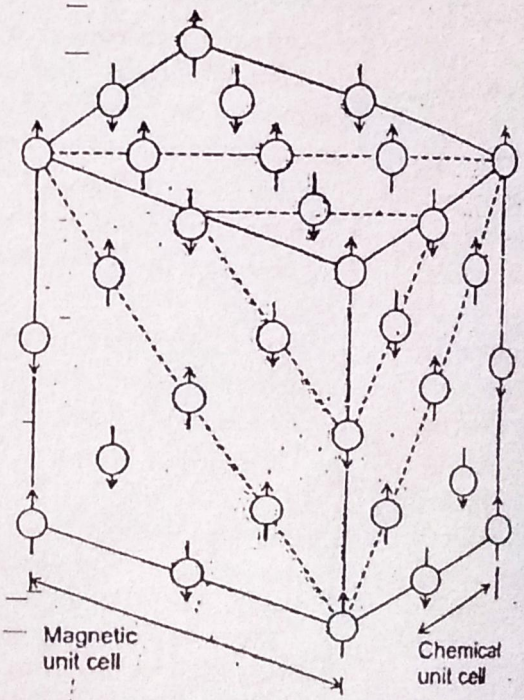

Fig. 4. Chemical and magnetic unit cell in MnO. The arrows show spin orientations and circles indicate positions of Mn atoms.

The magnetic moment of Mn^{2+} is 5·92 BM. If we consider Mn^{2+} ions in successive (111) planes in the crystal, the resultant spins are oriented so that they are directed positively and

egatively along the (100) direction. The appearance of diffraction peaks at double the pacing of the unit cell is due to the fact that in antiferromagnetic crystals the parallel spins ave twice period of the lattice spacing.

APPLICATIONS OF NEUTRON DIFFRACTION

Neutron diffraction is mainly used to ascertain the location of light atoms (mainly H toms) in presence of heavier ones. Neutron diffraction can supplement *X*-ray diffraction here the sample contains elements which are either very close in atomic number or very ar apart.

Structure of Uranyl Nitrate Hexahydrate. Neutron diffraction studies confirmed the configuration of $UO_2(NO_3)_2 . 6H_2O$ in which uranyl group is perpendicular to the plane of paper and is surrounded equatorially by an irregular hexagon of six O atoms, four from bidentate nitrate group and two from water. The U—O distances being 177 ± 0·7 pm and 174 ± 0·7 pm. The uranyl group is linear with O-U-O angle 179·1 ± 0·5° and $\angle O_5UO_6 = 179·1°$.

- **Structure of Deutero ammonia.** The parameters obtained from neutron diffraction give a value of 100·5 ± 2·3 pm for the length of N—D bond and a value of 11040 ± 200 pm for the DND angle. These values are in agreement with the values 100·8 ± 0·4 pm and 10700 pm obtained for free NH_3 by microwave spectroscopy.
- Neutron diffraction studies have been used for the first time for determining the crystal structure of ice and the location of H atoms.
- Neutrons, having no charge can be scattered only by the atomic nuclei and are not affected by the peripheral electrons of atoms. The *X*-ray scattering cross section vary regularly with increasing electron content of heavier atoms but there is no such variation for the neutron scattering cross section. For example, in the study of ice crystals, the effects with *X*-rays are almost entirely produced by the oxygen atoms in the crystal. Scattering effects due to hydrogen are not detectable because of its extremely small *X*-ray scattering cross-section. But with neutrons, if heavy ice containing D_2 is used, the scattering cross sections of D_2 and *O*-atoms are very close and constitute a direct measure of its positional arrangement of these atoms in the crystal.
- The ***X*-ray diffraction peaks** that have **odd Miller indices** (111), (113) etc., are **weak** (*e.g.*, in NaCl type structure) and strong in those with **even Miller indices** (200), (220) etc. In neutron diffraction, same conclusion is true if the two nuclei involved have the same sign of scattering amplitude. If the signs differ, the above statement must be reversed.
- In *X*-ray diffraction, the scattering lengths are always negative. Neutron diffraction provides informations regarding the sign of two scattering amplitudes, it cannot tel us for any given nucleus whether scattering length is positive or negative. However reflection of neutron beams from mirrors can provide this information. That is, substance with positive scattering length should reflect neutrons at small glancin angles, from mirror. This **total external reflection** is due to the fact that refractiv index of the mirror substance (if it has a positive scattering length) is slightly les than unity. The limiting glancing angle, above which there is no reflection is given b $\theta_C = \lambda(N \cdot a/\pi)^{1/2}$ ($a > 0$ only) where λ is the neutron's wavelength, N is the number atoms per unit volume. **Fermi and Marshall** have found that θ_C for berylliu mirror was 12 minutes of arc. The totally reflected beam shows that Be has a positi

scattering length of 0.89×10^{-12} cm. Scattering amplitudes for most nuclei are positive.

- An application of neutron diffraction is the use of a long graphite rod to provide a source of **cold neutrons** which have quite low effective temperatures. Neutrons may be classified according to their energy : **slow neutrons** (0 to 100 eV), **cold** neutrons (0·001 eV), **thermal** neutrons (0·25 eV at 293K), **resonance** neutrons (100 eV), **intermediate** neutrons (1000 eV to 0·5 MeV), high energy and **ultra high energy** neutrons with 0·5–10 MeV and 1 to 5 BeV energy.
- Neutrons produce intense biological effects, even more than *X*-rays and γ-rays on tumour tissues. Neutrons are rapidly absorbed in the fleshy tissues, probably because of greater concentration of hydrogen nuclei there.

SHORT ANSWER QUESTIONS

1. *Name the factors causing neutron diffraction.*
Ans. Neutron diffraction is caused by nuclear scattering and magnetic scattering.
2. *List the major advantage of neutron diffraction technique.*
Ans. The major advantage is that light elements (H or D), which cannot be located by *X*-ray diffraction, can be located by neutron diffraction because they are comparable in neutron scattering power to heavy elements.

MULTIPLE CHOICE QUESTIONS

1. If we consider crystals made of several isotopes of one element, recognise spin dependence of the scattering and allow the crystal temperature to be different, then some neutrons are scattered in all directions and a few are scattered in allowed Bragg's directions. This is termed as
(a) Diffuse scattering (b) Coherent scattering
(c) Incoherent scattering (d) Elastic scattering
2. The typical wavelength of neutrons that have reached thermal equilibrium with their surroundings at 373 K is
(a) 125 pm (b) 226 pm (c) 300 pm (d) 356 pm
[**Hint.** $\lambda = h/(mkT)^{1/2} = \dfrac{6.626 \times 10^{-34}\ \text{Js}}{1.675 \times 10^{-27}\ \text{kg} \times 1.38 \times 10^{-23}\ \text{JK}^{-1} \times (373\ \text{K})^{1/2}}$
$= 226$ pm].
3. The temperature needed for the average wavelength of neutrons to be 100 pm is
(a) 1.90×10 K (b) 1.90×10^2 K (c) 1.90×10^3 K (d) 1.50×10^2 K
4. H_2 and D_2 can be easily distinguished by neutron diffraction method because
(a) H_2 has a negative scattering factor for neutrons.
(b) D_2 has a positive scattering factor
(c) Both (a) and (b)
(d) H-atoms can be located with high accuracy.
5. Anisotropic crystals show
(a) Double refraction (b) Diffraction (c) Reflection (d) Interference
6. The wavelength of neutron beam is related to the neutron mass and velocity by
(a) Bragg's equation (b) de Broglie relation
(c) Born equation (d) Lande equation

Select the correct statement (s) about diffraction

(a) In *X*-ray diffraction, scattering is mainly by electrons, followed by interference (λ = 0·01 to 1 nm)

(b) In neutron diffraction, scattering is mainly by nuclei, followed by interference (λ = 0·1 nm)

(c) Electron diffraction is mainly by nuclei but also by electrons (λ = 0·01 to 0·1 nm)

(d) All statements are correct

The limitation(s) of neutron diffraction is (are)

(a) One must have a source of neutrons so the method is expensive

(b) Rigorous monochromatization leads to a great loss of intensity

(c) Loss of precision in intensity measurements and poor resolution

(d) All are correct

9. A neutron with a speed of $3{\cdot}9 \times 10^5$ cm s^{-1} with a KE of 0·08 eV has wavelength

(a) 0·1 nm (b) 0·2 nm (c) 1 nm (d) 2 nm

10. Neutron diffraction technique was developed in 1994 by Nobel prize winner

(a) C. G. Shull (b) B. N. Brockhouse

(c) Both (a) and (b) (d) J.Karle

ANSWERS

1. (a) 2. (b) 3. (c) 4. (c) 5. (a) 6. (b) 7. (d) 8. (d) 9. (a) 10. (c)