



CHAPTER II

NEUTRON DIFFRACTION

II.1 Neutron Source and Neutron Beam

In 1924 Louis de Broglie⁽⁴⁾ postulated that a particle of mass m travelling with a velocity v has associated with it a wavelength given by the relation

$$\lambda = \frac{h}{mv} \quad (1)$$

where h is Planck's constant. This relationship was latter verified by Elsasser⁽⁵⁾ for neutrons. In case of neutrons travelling with a velocity of 3 km/sec, the associated wavelength is 1.32 Å and the corresponding energy is 0.047 eV. This wavelength happens to be just the magnitude desired for the investigation of atomic arrangements of the atoms making up a crystal. The only other requirement necessary for the atomic structure determination is an intense source of these particles. Fortunately, in a nuclear reactor, the neutrons emitted from nuclear fissions and come into equilibrium with the moderator are of sufficient intensity for diffraction work. The neutrons available from a swimming pool type reactor may be broadly divided into two groups: (a) thermal neutrons which have come into equilibrium with the moderator, and (b) fast neutrons which have not been sufficiently slowed down by the interaction with the moderator. In a reactor,

the neutron flux distribution is approximately Maxwellian with a peak in the range of $1 - 2 \text{ \AA}$. This range is of the same order of magnitude as the interatomic distance in a solid. Thus thermal neutrons can be utilized to study the positions of atoms in a solid.

Neutrons for use in diffraction studies must be monochromatic neutrons, i.e. neutrons having one wavelength or one energy. These neutrons are obtained by having a well collimated beam from the reactor impinge on a suitable plane of a single crystal. The wavelength of the neutrons reflected from the crystal is determined by the well known Bragg equation

$$\lambda = 2 d_{hkl} \sin \theta \quad (2)$$

where θ is the Bragg angle, d is the lattice spacing of the crystal planes used for reflection, and hkl are the Miller indices of the reflection planes. By suitable choice of the angle θ , a beam of neutrons of any desired wavelength can be separated out by the crystal and is then available for diffraction experiments. In general, the "monochromatic" neutron beam will also contain a small amount of second order contaminating neutrons with a wavelength half of the wavelength of the desired monochromatic beam. In practice, this second order component should be kept as small as possible. Removal of second order neutrons by oriented single crystal filters has been studied by Iyengar et.al.⁽⁶⁾.

II.2 Nuclear Scattering by Neutrons

The fundamental scattering body of neutrons in most atoms is the nucleus and not electrons as in X - ray scattering. The scattering cross-section of the nucleus is dependent on the scattering amplitude or scattering length which is defined as b of the nucleus. In neutron scattering, the scattering amplitude b is constant for each isotope which is in contrast to the case of X - ray scattering where the scattering amplitude is dependent on the atomic form factor of each atom. The atomic form factor in case of X -ray scattering falls off quite rapidly with $\sin \theta / \lambda$. The neutron scattering amplitude can be positive, negative or complex value and does not increase with atomic number. The value of b can not be directly calculated at present, but can be determined by experiment. The scattering amplitude of some atoms are listed in Table 1 (from Bacon⁽⁷⁾). Since the scattering amplitude of atom is independent of atomic number, neutron diffraction technique can be used for determination of the atomic position of light elements, and for structural investigations involving distinction between atoms of neighboring atomic number.

Table I The scattering amplitude of some atoms

Element	Specific nucleus	Scattering amplitude b (10^{-12} cm)
H	H^1	- 0.378
	H^2	0.65
Al	Al^{27}	0.35
Mn	Mn^{55}	- 0.36
Fe		0.96
Ni		1.03
	Ni^{58}	1.44
	Ni^{60}	0.30
	Ni^{62}	- 0.87
Ge		0.84
Cd		$0.38 + 80.12 i$
Pb		0.86
U		0.85



II.3 Diffraction of Neutron by Materials

When neutrons are incident on a crystal, the intensities of diffracted neutrons will depend on the square of the structure factor of the unit cell. The structure factor of a unit cell of the crystal is expressed in the form of

$$F_{hkl}^2 = \left| \sum b \exp 2 \pi i (hx + ky + lz) \right|^2 \quad (3)$$

where F_{hkl} = the structure factor of the diffracted neutron beam for the (hkl) reflection,

hkl = the Miller's indices of the reflected plane,

b = the scattering amplitude of atoms in the unit cell,

x, y, z = the positions of atoms in the unit cell.

The summation in expression (3) is taken over all the atoms in the unit cell. In the case of compounds the value of b taken for each atomic position is, of course, that appropriate to the particular atom situated there.

In general, neutron diffraction studies will be made on powdered crystalline samples when single crystal is not available. This method is similar to the Debye - Scherrer method of X-ray analysis. Important information is obtained because most of the materials studied are of high crystallographic symmetry and give simple diffraction patterns. With a polycrystalline sample there are two geometrical arrangements which permit a ready comparison of the experimentally measured intensity with the results of predicted intensities. The two different types of containers for powdered sample are the

flat cassette and the vertical cylindrical tube. The materials used for container are usually made of metals with low scattering amplitude and negligible absorption such as aluminum or vanadium. In the case of flat cassette the intensity of the diffracted neutrons is given by the relation

$$I \propto j \frac{e^{-\mu t \sec \theta}}{\sin 2 \theta} F^2 e^{-2w} \quad (4)$$

where j = number of co - operating planes for the particular reflection being measures,

μ = linear absorption coefficient of the sample,

t = thickness of specimen,

F = the structure factor,

e^{-2w} = the Debye temperature correction factor.

For vertical cylindrical container case, the intensity of diffracted neutron beam is given by the relation

$$I \propto \frac{j F^2 e^{-2w}}{\sin \theta \sin 2 \theta} A_{hkl} \quad (5)$$

where A_{hkl} is the absorption factor and other terms in equation(5) are the same as those in equation (4).

The vertical cylindrical container is more convenient than the flat cassette. It is more economical in use of material, which is of importance considering the relatively large samples needed for neutron diffraction. With a cylindrical sample it may be possible sometimes to

reduce effects due to preferred orientation by rotating the cylinder about its vertical axis. The absorption factor for the latter form will vary very slowly with diffraction angle, and for most materials can be ignored.

II.4 Temperature Dependence of the Elastic Scattering

Using the Debye approximation, (which has been successful for explaining the specific heats as discussed, by Roberts⁽⁸⁾ to describe the lattice vibrations), Weinstock⁽⁹⁾ showed that the coherent scattering amplitude is reduced by the factor e^{-w} , where

$$w = \frac{6h^2 \sin^2 \theta}{m_A k \theta \lambda^2} \left[\frac{\phi(x)}{x} + \frac{1}{4} \right]. \quad (6)$$

Here h is Planck's constant, M_A is the nuclear mass, k is Boltzmann's constant, θ is the Debye temperature of the crystal, x is equal to $\frac{\theta}{T}$, T is the absolute temperature of measurement, and ϕ is a function of x defined by

$$\phi(x) = \frac{1}{x} \int_0^x \frac{\zeta d\zeta}{\exp(\zeta) - 1}. \quad (7)$$

The above expression for temperature factor applies strictly to monatomic cubic crystals, but reasonable agreement can usually be obtained for polyatomic crystals by using a mean value for θ . Values of θ for the elements are tabulated in the International Table for X-Ray Crystallography, Volume 3⁽¹⁰⁾, and the function $\exp(-w)$, and $\phi(x)/x + \frac{1}{4}$ are tabulated in the International Table for X-Ray Crystallography, Volume 2⁽¹¹⁾.

II.5 Principles of Magnetic Scattering

In addition to its mass, a neutron possesses a spin $\frac{1}{2}$, and a magnetic moment of 1.9 nuclear magneton. In general the scattering of neutrons by atoms is a nuclear process, but in case of magnetic atoms there is an additional scattering which occurs from an interaction between the neutron magnetic moment and the magnetic moment of the atom. The magnetic moment of atoms occurred in atoms whenever there are unpaired electrons, such as, transition metals and rare-earth metals.

For true paramagnetic substance the magnetic moments of the atoms are completely uncoupled to each other and are randomly oriented in direction. Halpern and Johnson⁽¹²⁾ have shown that for randomly oriented paramagnetic ions there will be a differential magnetic scattering cross-section, and the cross section per atom per unit solid angle is given by

$$d\sigma_p = \frac{2}{3} S(S+1) \left(\frac{e^2 \gamma}{mc^2} \right)^2 f^2 \quad (8)$$

Here S is the spin quantum number of the scattering atom

γ is the magnetic moment of the neutron expressed in nuclear magnetons,

e and m are the electronic charge and mass respectively,

c is the velocity of light, and

f is the magnetic form factor.

Since only a few of electrons in orbit in an outer shell of the atom contribute to the magnetic moment, the magnetic form factor will

fall off more rapidly with angle than does the form factor for X - ray scattering. For paramagnetic solids where the atomic ions are randomly oriented, the magnetic scattering is entirely incoherent and adds to the background of the powder diffraction pattern.

II.6 Scattering by Antiferromagnetic and Ferromagnetic Materials

In the case of ordered magnetic materials, e.g. antiferromagnetic and ferromagnetic materials, the magnetic moments of the individual ions are oriented in a regular manner. In a ferromagnetic substance all the moments are aligned parallel and point in the same direction. In an antiferromagnetic the atoms can be considered to lie on two sublattices whose spins are oppositely directed. All the atoms lying on one sublattice have their magnetic moments parallel to a given direction and those on another sublattice are antiparallel, and magnetic moments on both sublattices are equal. For ferrimagnetic material the magnetic moments on the two sublattices are not equal which results in a net magnetic moment. The differential magnetic scattering cross-section per ordered atom is given by

$$d\sigma_m = q^2 s^2 \left(\frac{e^2 \gamma}{m c^2} \right)^2 f^2 \quad (9)$$

where \underline{q} is the magnetic interaction vector defined by

$$\underline{q} = \underline{\epsilon} (\underline{\epsilon} \cdot \underline{K}) - \underline{K} \quad (10)$$

$\underline{\epsilon}$ is a unit scattering vector normal to the effective reflecting plane, and \underline{K} is a unit vector in the direction of the atomic moment.

The atoms may be regarded as having a magnetic scattering amplitude which we denote by p , where

$$p = \left(\frac{e^2 \delta}{mc^2} \right) s f . \quad (11)$$

Then equation (9) may be rewritten as

$$d\sigma_m = q^2 p^2 . \quad (12)$$

In term of the Bohr magneton number of the atomic magnetic moment, the magnetic scattering amplitude can be expressed as

$$p = 0.269 \mu_B f \times 10^{-12} \text{ cm} \quad (13)$$

where μ_B is the magnitude of the atomic magnetic moment in Bohr magneton.

For unpolarised neutrons, the magnetic and nuclear scattering are not coherent and the total scattering cross-section $d\sigma$ is

$$d\sigma = b^2 + q^2 p^2 \quad (14)$$

which means that the intensities of nuclear and magnetic scattering are additive.

The total scattered intensity for any reflection plane is obtained by calculating the total structure factor F for the unit cell.

The nuclear structure factor F_n is given by

$$F_n = \sum_r b_r \exp 2 \pi i (hx_r + ky_r + lz_r) \quad (14)$$

and the magnetic structure factor F_m is given by

$$F_m = \sum_r p_r \exp 2\pi i (hx_r + ky_r + lz_r) \quad (15)$$

The value of p will be positive or negative for ions of parallel or antiparallel spin respectively in an antiferromagnetic material.

For the ordinary non-magnetic atoms in the unit cell p will be zero.

The resultant intensity is proportional to F^2 which is given by

$$F^2 = F_n^2 + q^2 F_m^2 \quad (16)$$

From equation (10)

$$q^2 = 1 - (\underline{\epsilon} \cdot \underline{K})^2 = \sin^2 \alpha \quad (17)$$

where α is the angle between the scattering and magnetisation vectors.

Therefore if q^2 is known for a particular reflection, the orientation of the magnetic moment may in principle be determined. For polycrystalline materials only a mean value of q^2 from all reflection plane of the same form is obtained. Therefore the most that can be calculated is the orientation of the moments with respect to the unique axis. If the magnetic moments are directed randomly with respect to the crystallographic axis, and all the atoms in an individual domain having parallel moments, the effective value of q^2 would be $\frac{2}{3}$. Thus it would be impossible to determine the moment orientations from measurements on polycrystalline samples using unpolarised neutrons.

For antiferromagnetic materials if the magnetic unit cell is the same size as the chemical unit cell, the magnetic diffraction

peaks will be superimposed on nuclear diffraction peaks, but usually the magnetic unit cell will be larger than the chemical unit cell and the magnetic and nuclear diffraction peaks would not be superimposed. A common practice is to index nuclear and magnetic reflection according to their own different unit cells. Then the nuclear and magnetic reflection occurring at the same angle θ will have different indices. For calculating F_n and F_m , it is usually convenient to evaluate the two terms by using the number of molecules in the magnetic unit cell. The magnetic and nuclear contributions to the diffraction peaks may be determined by measuring the intensities of diffraction patterns at above and below the Neel temperature, or compares the intensities of diffraction lines at low and high angles. At low angles the magnetic contribution may be large, but there would be rapid fall off in magnetic contribution with increasing angle due to the magnetic form factor. The high-angle lines have virtually no magnetic component.

In ferromagnetic materials the magnetic and nuclear unit cells are usually of the same size so that the magnetic and nuclear peaks are superimposed at the same Bragg angles. The magnetic and nuclear contributions to the diffraction peaks can be measured by three methods. The best method is to vary q^2 . This may be done by applying a magnetic field sufficiently large to saturate the samples, along or perpendicular to the scattering vector. In the former case $q^2 = 0$, while in the latter case $q^2 = 1$. The difference between the two diffraction patterns would therefore be the magnetic scattering.

If suitable magnetic fields are not available, measurements may be made above and below the Curie temperature, but this method suffers from the disadvantage that other parameters may change with temperature, and corrections have to be applied. The third method is to compare the intensities of diffraction peaks at low and high angles. The disadvantage of this method is that intensities cannot be measured as accurately at high angle as at low angle.

II.7 Nuclear Structure Factor of Cubic Laves Phase Compounds.

Laves phase compounds can be divided into two types, i.e. cubic and hexagonal Laves phase compounds. The hexagonal Laves phase has the $MgZn_2$ (C 14 type) structure with twelve atoms per unit cell. The cubic Laves phase compounds have structure of $MgCu_2$ type. The $MgCu_2$ structure determined by Friauf⁽¹³⁾ has been described by Laves^(14,15), and by Schulze⁽¹⁶⁾. This structure belongs to the space group $O_h^7 - Fd 3m$ and the unit cell contains twenty-four atoms. The formula is AB_2 in which the 8 A atoms occupy position (a): $0,0,0; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}; f.c.$ and the 16 B atoms are in position (d): $\frac{5}{8}, \frac{5}{8}, \frac{5}{8}; \frac{5}{8}, \frac{7}{8}, \frac{7}{8}; \frac{7}{8}, \frac{5}{8}, \frac{7}{8}; \frac{7}{8}, \frac{7}{8}, \frac{5}{8}; f.c.$ Each A atom is coordinated to four A atoms at distance of $0.4330 a_0$ and to twelve B atoms at distance of $0.4146 a_0$. Each B atom is coordinated to six B atoms at $0.3535 a_0$ and to six A atoms at $0.4146 a_0$.

The investigation of magnetic properties of Laves phase compounds had been done by Matthias and Corenzwit⁽¹⁷⁾, Matthias and Bozorth⁽¹⁸⁾, Matthias et.al.⁽¹⁹⁾ They studied the superconductivity and ferromagnetism of a number of rare earth compounds. The investigation of these compounds were done by X - ray diffraction and magnetic

measurement techniques.

For neutron diffraction studies, the square of the structure factor of cubic Laves phase compounds can be calculated by substituting the positions of A and B atoms in equation (3). The results for various planes are shown in Table II.

Table II The square of nuclear structure factor of cubic Laves phase compound.

hkl	F_n^2
111	$2(4b_A - 5.656 b_B)^2$
220	$(8 b_A)^2$
311	$2(4b_A + 5.656 b_B)^2$
222	$(16 b_B)^2$
400	$(8b_A - 16b_B)^2$
331	$2(4b_A - 5.656 b_B)^2$
422	$(8 b_A)^2$
511, 333	$2(4b_A + 5.656 b_B)^2$
440	$(8b_A + 16 b_B)^2$
531	$2(4b_A - 5.656 b_B)^2$

Here b_A and b_B are the nuclear scattering amplitude of atom A and atom B respectively.