CHAPTER IV

X-RAY DIFFRACTION STUDIES

4. X-ray diffraction studies

4.1. General

A powder pattern is produced when X-rays are diffracted by a sample consisting of a large number of randomly oriented crystalline particles. At first the powder patterns are chiefly used as a rapid means of identification of lattice parameters\textsuperscript{214} when the single crystal study is not possible. Later on other uses were developed, and today the method is applied, not only to structure determination, but to such diverse problems as chemical analysis and stress measurement, to the study of phase equilibria and the measurement of particle size, to the determination of the orientation of one crystal or the ensemble of orientations in a polycrystalline aggregate. The two essentials for diffraction are a wave motion capable of interference (X-rays) and a set of periodically arranged scattering centers (the atoms of a crystal).
4.2. Diffraction Methods

Diffraction can occur whenever the Bragg law, \( \lambda = 2d \sin \theta \) is satisfied. This equation puts very stringent conditions on \( \lambda \) and \( \theta \) for any given crystal. With monochromatic radiation, an arbitrary setting of a single crystal in a beam of X-rays will not in general produce any diffracted beams. Some way of satisfying Bragg law must be devised, and this can be done by continuously varying either \( \lambda \) and \( \theta \) during the experiment. The ways in which these quantities are varied distinguish the three main diffraction methods.

\[
\begin{array}{ccc}
\lambda & \theta \\
(1) & \text{Laue method} & \text{Variable} & \text{Fixed} \\
(2) & \text{Rotating crystal method} & \text{Fixed} & \text{Variable (in part)} \\
(3) & \text{Powder method} & \text{Fixed} & \text{Variable} \\
\end{array}
\]

4.2.1. Powder method

The crystal to be examined is reduced to a very fine powder and placed in a beam of monochromatic X-rays. Each particle of the powder is a tiny crystal oriented at random with respect to the incident beam. Just by chance, some of the particles will be correctly oriented, so that their (100) planes, for example, can reflect the incident beam. Other particles will be correctly oriented for (110) reflections and so on. The result is that every set of lattice
planes will be capable of reflection. The mass of powder is equivalent, in fact, to a single crystal rotated, not about one axis, but about all possible axes.

The most important use of the powder method is in the qualitative identification of crystalline phases or compounds. The technique is unique in that it tells which crystalline compounds or phases are present but gives no direct information about their chemical constitution. The three different powder methods employed are given below.

4.2.1. Debye-Scherrer method

The original powder method, the Debye-Scherrer method is little used now a days. In a finely powdered sample, crystals are present at every possible angular position about the incident beam and the diffracted beams that result, appears to be emitted from the sample as cones of radiation. If the Bragg angle is $\theta$, then the angle between diffracted and undiffracted beam is $2\theta$ and the angle of the cone is $4\theta$. A thin strip of film wrapped around the sample detects the cones; each cone intersects the film as two short arcs. In a well-powdered sample, each arc appears as a continuous line, but in coarser samples the arcs may be spotty due to the relatively small number of crystals present. To obtain d-spacing from the Debye-Scherrer film, the separation, $S$, between pairs of corresponding arcs is measured. If the camera (film) radius $R$, is known, then

$$\frac{S}{2\pi R} = \frac{4\theta}{360}$$

from which $2\theta$ and therefore ‘d’ may be obtained for each pair of
arcs. The disadvantages of this method are that exposure times are long and that closely spaced arcs are not well resolved.

4.2.1.2. Guinier focusing method

In this method, a convergent intense incident beam is used with the result that excellent resolution of lines is obtained and exposure times are much reduced. A convergent beam is obtained by placing a bent single crystal of quartz or graphite between X-ray source and the sample. The orientation of this bent crystal is adjusted so that it diffracts the incident beam and converts it from a divergent beam into a convergent cone. The beam then strikes the sample and the diffracted beams are arranged to focus at the surface of the film.

4.2.1.3. Diffractometry

In this modern technique a series of peaks is obtained on a chart paper. A convergent incident beam is used to give fairly good resolution of peaks. Both peak positions and intensities are readily obtained from the chart to make this a very useful and rapid method of phase analysis.

4.2.2. Single crystal methods

The main use of single crystal methods is to determine unit cells and space groups and crystal structure determination. Monochromatic X-rays are generally used, an optimum crystal size ~0.2 mm diameter and the detector may be either film or counter. There are three main film techniques.
4.2.2.1. Rotation or oscillation method

In this method, the crystal is mounted by sticking it onto a glass fibre. The crystal is set so that one of its unit cell axes is vertical and is made to oscillate or rotate about this axis. A horizontal beam of X-rays strikes the crystal and the diffracted beams are detected by a piece of film bent round the crystal in the form of a cylinder. On developing the film, parallel rows of spots are seen, each spot corresponding to diffraction from one particular set of planes in the crystal. From this photograph the presence of symmetry and the magnitude of unit cell dimension can be determined.

4.2.2.2. Weissenberg method

In this method also the crystal is surrounded cylindrically by film but metal screens are placed between the crystal and the film such that only one row of spots or layer line is allowed through. During exposure, the crystal undergoes a slow oscillation and at the same time translates up and down. The coupling of the film and crystal motions is rather complicated and the pattern of spots is distorted. The separation of spots along any two axes is related inversely to the value of the cell parameter of those axes and the distance between two axial rows of spots is related to the angle between these two axes in the unit cell.

4.2.2.3. Precession method

This method gives photographs that are much easier to interpret and measure. Each layer line of a rotation photograph is converted, in a precession
photograph, into a two dimensional network of spots. A fundamental feature
of precession photographs is that distances between pairs of spots are
inversely proportional to the corresponding distances in the actual crystal. In
precession method, photographs give an undistorted picture of the reciprocal
lattice. This makes their interpretation very easy and logical. A slight
disadvantage is that the theory behind the operation of the camera is rather
complicated.

4.3. A Powder Pattern is a Crystal’s ‘Fingerprint’

The powder X-ray diffraction method is very important and useful in
qualitative phase analysis because every crystalline material has its own
characteristic powder pattern. There are two main factors, which determine
powder patterns (a) the size and shape of the unit cell and (b) the atomic
number and position of the various atoms in the cell. Thus two materials may
have the same crystal structure, but almost certainly they have quite distinct
powder patterns.

The powder pattern has two characteristic features. The d-spacing of
the lines and their intensity. Of the two, the d-spacing is far more useful and
capable of precise measurement. The d-spacing should be reproducible from
sample to sample unless impurities are present to form solid solution or the
material is in some stressed, disordered or metastable condition. On the other
hand intensities are more difficult to measure quantitatively and often vary
from sample to sample. Intensities can usually be measured only semi-
quantitatively and may show variation of, say, 20 percent from sample to
sample.

4.4. Diffraction Directions

The directions in which a beam of given wavelength is diffracted by a
given set of lattice planes is determined by the crystal system to which the
crystal belongs and its lattice parameters. In short, diffraction directions are
determined solely by the shape and size of the unit cell. For many crystals,
there are particular atomic arrangements which reduce the intensities of some
diffracted beams to zero. In such a case there is simply no diffracted beam at
the angle predicted by the general equation. A general relation which will
predict the diffraction angle for any set of planes can be obtained by
combining the Bragg law and the plane-spacing equation applicable to the
particular crystal involved. If the crystal is cubic, the general equation is
\[ \sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2). \]
This equation predicts, for a particular incident wavelength and a particular cubic crystal of unit cell size ‘a’, all the possible
Bragg angles at which diffraction can occur from the planes (hkl). If the
crystal is tetragonal, with axes a and c, then the corresponding general
equation is \[ \sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right). \] Similar equations can readily be
obtained for the other crystal systems.
If a cubic cell is expanded or contracted uniformly but still remains cubic, the diffraction lines merely shift their positions, but do not increase in number, since no change in cell symmetry is involved. If a cubic cell is distorted along only one axis, then it becomes tetragonal, its symmetry decreases, and more diffraction lines are formed. If the tetragonal cell is distorted, it becomes orthorhombic. The result of this distortion is to add still more lines to the pattern. The increase in the number of lines is due essentially to the introduction of new plane spacings, caused by non-uniform distortion.

4.5. Intensities of Diffracted Beams.

The positions of the atoms in the unit cell affect the intensities but not the directions of the diffracted beams. Any calculation of the intensity of a diffracted beam begins with the structure factor. There are six factors affecting the relative intensity of the diffraction lines on a powder pattern. They are (1) polarisation factor (2) structure factor (3) multiplicity factor (4) Lorentz factor (5) absorption factor and (6) temperature factor. The relative intensity of powder pattern lines is given by the equation, 

\[ I = \frac{|F|^2 P}{\sin^2 \theta \cos \theta} \]

where I = relative integrated intensity, F = structure factor, P = multiplicity factor and \( \theta \) = Bragg angle.

Variation of intensity of the diffracted X-ray beam for different sets of \( hkl \) planes is presumably due to the variation of density of atoms in these planes. The planes having high atomic density give rise to a better X-ray
diffraction thereby producing a more intense diffracted beam. If the crystal contains more than one kind of atom, the atom containing greater number of electrons scatters the X-rays to a greater extent. It is found that scattering power of an atom is directly proportional to the number of electrons in the atom.

4.6. Effect of Stress on a Powder Pattern

Crystals that are under stress may exhibit anomalous powder patterns. The whole powder pattern may be shifted to lower d-spacings if the crystals are under a uniform compressive stress such that a contraction of the unit cell occurs. If the stress is non-uniform, different crystals or different parts of the same crystal may be deformed to differing degrees and the powder lines become broadened. Commonly both effects occur and lines may be both displaced and broadened.

There are many more lines on the pattern of a substance of low symmetry, than on the pattern of a substance of high symmetry. Any distortion of the unit cell, which decreases its symmetry, in the sense of introducing additional variable parameters, will increase the number of lines on the powder pattern. The changes produced in a powder pattern by cell distortion depend on the extent of distortion. If the latter is small, the pattern retains the main features of the pattern of the original undistorted cell.
4.7. Effect of Crystal Size on the Powder Pattern

If the average crystal size in a powder is below a certain limit (~2000 Å diameter) additional broadening of diffracted X-ray beam occurs. From measurement of this extra broadening an average particle size may be obtained. In the absence of extra broadening due to small particle size, powder lines or peaks have a finite breadth for several reasons: the radiation is not absolutely monochromatic, the K line has an intrinsic breadth due to the Heisenberg uncertainty principle and the focusing geometry of the instrument may not be perfect for a variety of reasons.

The commonly accepted formula for particle size broadening is the Scherrer formula:

$$ t = \frac{0.9 \lambda}{B \cos \theta_B} $$

Where $t$ is the thickness of the crystal (in angstroms), $\lambda$ the X-ray wavelength and $\theta_B$ the Bragg angle. The line broadening $B$ is measured from the extra peak width at half the peak height and is obtained from the Warren\textsuperscript{215} formula:

$$ B^2 = B_M^2 - B_S^2 $$

Where $B_M$ is the measured peak width in radians at half peak height, $B_S$ is the corresponding width of a peak of a standard material, mixed in with
the sample, whose particle size is considerably greater than 2000\(\text{Å}\) and which has a diffraction peak near to the relevant peak of the sample.

With good experimental techniques, broadening of high angle lines may be detected for crystal thickness up to \(~2000\) \(\text{Å}\). For a thickness of 50 to 500\(\text{Å}\) the broadening is very easy to detect and measure. The lower limit of detection occurs when the peaks become so broad that they disappear into the background radiation. For very small particle size, it is best to use low angle peaks if possible because, for a given crystal thickness, the broadening increases with Bragg angle.

4.8. Results

The X-ray powder pattern of the complexes was recorded before and after gamma irradiation to see whether the complexes are crystalline and if so to determine the nature of unit cell. X-ray powder patterns of irradiated and unirradiated \([\text{Ni(dien)}_2](\text{NO}_3)_2\), \([\text{Zn(dien)}_2](\text{NO}_3)_2\), \([\text{Cd(dien)}_2](\text{NO}_3)_2\), \([\text{Ni(pyh)}_2(\text{NO}_3)_2]\) and \([\text{Zn(pyh)}_2(\text{NO}_3)_2]\) are given in figures (34-38). The diffraction pattern was indexed using the method developed by R. Hesse and H. Lipson. The cell parameters have been calculated for orthorhombic system using the equation \(S\sin^2\theta(hkl) = Ah^2 + Bk^2 + Cl^2\) where \(A = \frac{\lambda^2}{4a^2}\), \(B = \frac{\lambda^2}{4b^2}\) and \(C = \frac{\lambda^2}{4c^2}\). Cell constants and cell parameters of
diethylenetriamine and pyridine complexes are listed in Tables 26 and 27 respectively.

4.8.1. Nickel(II), zinc(II) and cadmium(II) complexes of diethylenetriamine

4.8.1.1. Bis(diethylenetriamine) nickel(II) nitrate

The lattice constants for \([\text{Ni} (\text{dien})_2,] (\text{NO}_3)_2\) are \(A = 0.008, B = 0.006\) and \(C = 0.004\) and hence \(a = 8.612, b = 9.945\) and \(c = 12.179\) Å respectively (Table 26). Upon irradiation \(A\) and \(B\) changed to 0.033, and 0.040 and ‘\(a\)’ and ‘\(b\)’ changed to 4.240 and 3.851. Lattice constant \(C\) and lattice parameter ‘\(c\)’ remained the same. Both irradiated and unirradiated complexes are found to have orthorhombic lattice. Lattice parameter ‘\(a\)’ and ‘\(b\)’ decreased while ‘\(c\)’ remained the same. Intensities of the diffracted lines also changed (Fig 34). The powder lines corresponding to higher 2θ values are not observed in the irradiated sample.

4.8.1.2. Bis(diethylene triamine) zinc(II) nitrate

For unirradiated \([\text{Zn} (\text{dien})_2,] (\text{NO}_3)_2\) the lattice constants \(A\), \(B\) and \(C\) are 0.009, 0.016 and 0.008 respectively. Hence \(a, b\) and \(c\) are 8.119, 6.089 and 8.612. In the irradiated sample, \(A\), \(B\) and \(C\) are 0.002, 0.009 and 0.005 respectively and \(a, b\) and \(c\) are 17.224, 8.119 and 10.893 Å respectively. Upon irradiation, until cell parameters \(a, b\) and \(c\) were increased (Table 26).
The intensities of the diffracted lines decreased in the irradiated sample. (Fig. 35). Both irradiated and unirradiated samples have orthorhombic lattice.

**4.8.1.3. Bis(diethylene triamine) cadmium(II) nitrate**

In [Cd(dien)$_2$(NO$_3$)$_2$], upon irradiation lattice constants A, B and C changed from 0.019, 0.009 and 0.007 to 0.025, 0.007 and 0.006 respectively. Lattice parameters a, b and c changed from 5.588, 8.119 and 9.207 to 4.872, 9.207 and 9.945 respectively. Unit cell parameter ‘a’ decreased while ‘b’ and ‘c’ shows nominal increase (Table 26). The intensities of the diffracted lines changed in the irradiated sample (Fig. 36). Unirradiated and irradiated samples have orthorhombic lattice.

**4.8.2. Nickel(II) and zinc(II) complexes of pyridine**

**4.8.2.1. Dinitrato bis(pyridine) nickel(II)**

X-ray studies showed that the unirradiated complex have orthorhombic lattice. The irradiated sample retained the orthorhombic lattice, but the unit cell parameter ‘a’ and ‘b’ increased and ‘c’ remained almost same. For unirradiated [Ni(py)$_2$(NO$_3$)$_2$] lattice parameters a, b and c are 4.177, 3.901 and 4.375 Å and for irradiated sample the values are 9.206, 5.741 and 4.523 respectively. (Table 27). Broadening of lines is observed in the powder pattern of irradiated sample (Fig. 37).
4.8.2.2. Dinitrato bis(pyridine) zinc(II)

The lattice constants for unirradiated \([\text{Zn(py)}_2(\text{NO}_3)_2]\) are \(A = 0.003\), \(B = 0.007\) and \(C = 0.017\) and hence \(a = 14.064\), \(b = 9.207\) and \(c = 5.908\) Å respectively. For irradiated \([\text{Zn(py)}_2(\text{NO}_3)_2]\), \(A = 0.019\), \(B = 0.009\) and \(C = 0.016\) and hence \(a = 5.588\), \(b = 8.119\) and \(c = 6.089\) Å respectively (Table 27). Lattice parameters \(a\) and \(b\) decreased whereas nominal change is observed in \(c\), upon irradiation. In the irradiated sample, broadening of lines is observed in the XRD pattern (Fig. 38).

4.9. Discussion

X-ray diffraction techniques are usually thought of as means of investigating the structure and lattice parameters of solids as well as the composition, orientation and degree of perfection. Any imperfection gives rise to local changes in diffracted or transmitted X-ray intensities. In the neighbourhood of lattice defects, the lattice planes are slightly bend and local diffraction conditions differ from those in the perfect crystal. When the distorted regions of the lattice are in a diffraction position, they change the path of the diffracted beam so that it interferes with the main transmitted beam changing the transmitted intensity. Upon irradiation a large super saturation of point defects may exist. The presence of defects in a crystalline lattice may change both the unit cell and the physical size of the crystal. For a crystal containing substantial concentration of point defects, the effect of defect on
diffraction pattern is to produce diffuse scattering around and between Bragg reflections.

It is observed that intensities of powder lines and unit cell parameters of complexes changed upon irradiation. Intensities of powder pattern depend on several factors and one of them is the structure factor, which is related to the position of atoms in the unit cell and their scattering power. In all crystals, the atoms are not in fixed positions but vibrate about a mean position. When exposed to radiation, the atoms may be disturbed from the equilibrium position. Consequently the scattering power changes so that the structure factor is now different. Hence the Bragg angle for constructive diffraction from a set of plane will change and the interplanar distance will be different. Irradiation can cause stress on the crystal and therefore the size of the crystal may change. If the stress is significant a contraction of the unit cell occurs. If the average crystal size is below a certain limit broadening of powder pattern results.

4.9.1. Nickel(II), zinc(II) and cadmium(II) complexes of diethylenetriamine

4.9.1.1. Bis(diethylenetriamine) nickel(II) nitrate

In the case of [Ni (dien)₂] (NO₃)₂ the parameters ‘a’ and ‘b’ decreased by more than 50% whereas ‘c’ remained almost the same. The intensities also changed. The powder lines corresponding to higher 2θ values are not observed
in the irradiated sample. This may be due to contraction of the unit cell caused by irradiation.

4.9.1.2. Bis (diethylenetriamine) zinc(II) nitrate

In \([\text{Zn (dien)}]_2 (\text{NO}_3)_2\) the parameters ‘a’ and ‘b’ decreased by more than 25% while parameter ‘a’ showed a twofold increase. The powder lines also decreased in intensities, showing lesser degree of crystallinity.

4.9.1.3. Bis (diethylene triamine) cadmium(II) nitrate

In \([\text{Cd(dien)}]_2(\text{NO}_3)_2\), upon irradiation the change in lattice parameters is not as significant as in \([\text{Ni(dien)}]_2(\text{NO}_3)_2\) and \([\text{Zn(dien)}]_2(\text{NO}_3)_2\). Lattice parameter ‘a’ decreased while ‘b’ and ‘c’ increased by 12.8%, 13.4% and 8% respectively.

4.9.2. Nickel(II) and zinc(II) complexes of pyridine

4.9.2.1. Dinitrato bis(pyridine) nickel(II)

Decrease in intensity of powder lines and increase in unit cell parameters are observed in \([\text{Ni(py)}]_2(\text{NO}_3)_2\) upon irradiation. Irradiation causes no significant change in parameter ‘c’, but ‘a’ and ‘b’ are increased by more than 50% and 32% respectively.

4.9.2.2. Dinitrato bis(pyridine) zinc(II)

Upon irradiation, the intensities of diffracted lines and unit cell parameters ‘a’ ‘b’ and ‘c’ changed. Broadening of lines is observed in the diffractogram of irradiated sample indicating significant stress on the crystal.
In [Zn (py)$_2$(NO$_3$)$_2$], the parameter ‘a’ and ‘b’ decreased by about 60% and 11% respectively whereas ‘c’ remained almost same.

Upon irradiation, the intensities of the diffracted lines decreased indicating lesser degree of crystallinity in the irradiated samples. The effect of irradiation is found to be greater in [Ni(dien)$_2$(NO$_3$)$_2$] and [Zn(dien)$_2$](NO$_3$)$_2$ than in [Ni(py)$_2$(NO$_3$)$_2$] and [Zn(py)$_2$(NO$_3$)$_2$]. More broadening of lines is seen in zinc(II) and nickel(II) complexes of pyridine than in zinc(II) and nickel(II) and cadmium(II) complexes of diethylenetriamine. The powder lines corresponding to higher 2θ values are not observed in the X-ray diffraction patterns of irradiated samples of [Ni(dien)$_2$(NO$_3$)$_2$]. This may be due to contraction of the unit cell caused by irradiation. It may be concluded that stress factor and structure factor are responsible for the overall change in powder pattern in all cases.

Summary

Lattice imperfections caused by irradiation influence the X-ray diffraction pattern of a crystal. In the present study, X-ray powder pattern of nickel(II), zinc(II) and cadmium(II) complexes of diethylenetriamine and nickel(II) and zinc(II) complexes of pyridine were studied to see the effect of gamma radiation. The powder diffraction patterns were recorded using nickel filtered Cu- Kα radiation. The diffraction patterns were indexed using analytical method developed by R.Hesse and H.Lipson. All the complexes
under investigation were found to be orthorhombic. Upon irradiation all the samples retained the orthorhombic lattice. Lattice constants and lattice parameters changed upon irradiation. Peak intensities are decreased in the X-ray diffractograms of irradiated samples. In nickel(II) complex of diethylenetriamine, the powder lines corresponding to higher 2θ values are not observed in the irradiated sample. Broadening of diffracted lines is observed in the X-ray diffraction pattern of irradiated zinc(II) and nickel(II) complexes of pyridine.
Fig. 34. X-ray diffractograms of $[\text{Ni (dien)}_2](\text{NO}_3)_2$

[a] unirradiated  [b] irradiated
Fig. 35. X-ray diffractograms of [Zn (dien)$_2$](NO$_3$)$_2$

[a] irradiated    [b] unirradiated
Fig. 36. X-ray diffractograms of [Cd (dien)$_2$](NO$_3$)$_2$

[a] irradiated  [b] unirradiated
Fig. 37. X-ray diffractograms of [Ni (py)$_2$(NO$_3$)$_3$]
[a] unirradiated  [b] Irradiated
Fig. 38. X-ray diffractograms of [Zn (py)$_2$(NO$_3$)$_3$]

[a] irradiated  [b] unirradiated
Table 26
Lattice constants and parameters of [Ni(dien)$_2$](NO$_3$)$_2$, [Zn(dien)$_2$](NO$_3$)$_2$ and [Cd(dien)$_2$](NO$_3$)$_2$

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<td></td>
<td>A</td>
<td>B</td>
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Table 27

Lattice constants and parameters of \([\text{Ni(py)}_2(\text{NO}_3)_2]\) and \([\text{Zn(py)}_2(\text{NO}_3)_2]\)

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