Module 4 : Solid State Chemistry

Lecture 19 : Indexing Diffraction Patterns

Objectives

In this Lecture you will learn the following

- Systematic absences in the diffraction patterns

- Electron densities from Fourier synthesis

- Strategies to resolve the phase problem.

- Other diffraction methods.

19.1 Introduction

The central problem in diffraction methods is to interpret the data obtained from diffraction experiments and identify uniquely the nature of the crystal responsible for the diffraction pattern. Nowadays, there are standard softwares built into the diffractometers which just about give a printout of the three dimensional structure. In this lecture we will illustrate some important features and concepts involved in this process.

We know from Bragg's law that n λ = 2d $_{h\ k\ l}$ sin θ and d$_{h\ k\ l}$ = a [h^2 + k^2 + l^2] $^{-1/2}$ where d$_{h\ k\ l}$ is the perpendicular distance between two adjacent Miller planes and a is the edge length of the unit cell of a cubic lattice. These two equations can be combined to give

$$\sin \theta = (h^2 + k^2 + l^2)^{1/2} \lambda / 2a \qquad\qquad (19.1)$$

For each hkl plane present in the crystal, there will be a maximum intensity corresponding to θ in Eq (19.1).

19.2 Rationalizing Systematic Absences in Diffraction patterns.

Let us see how Eq (19.1) works in detail. The short table below (Table 19.1) gives the values of h^2 + k^2 + l^2 for different Miller planes.

h k l	100	110	111	200	210	211	220	300	221	310
h^2 + k^2 + l^2	1	2	3	4	5	6	7	8	9	10

Table (19.1) h^2 + k^2 + l^2 for Miller planes of a simple cubic lattice

Continuing the table for higher values of h k l we will see that the integers 7 and 15 are absent for h^2 + k^2 + l^2 because the sums of squares of three integers can not be 7 or 15. Of course, there are other higher missing integers for the sums too!

We conclude from the above discussion that if θ values corresponding to integer square sums of 7 and 15 are absent, but all other integers are present between 1 to 15, then the unit cell must correspond to a simple cubic (sc) lattice.

In Fig 19.1 the Schematic diffraction patterns for the three cubic lattices (SC, BCC and FCC) are shown. It is

seen that in the case of BCC, all reflections with $h + k + l$ = odd are absent and that in the case of FCC, only the reflections with all h, k, l even or all h k l odd are present.

Figure 19.1 Diffraction patterns for SC, BCC and FCC lattices.

We readily note that systematic absences can be used to identify the nature of the unit cell.

To understand the absences, we need to consider the phase differences between reflections from adjacent layers when the atoms in the layers are of different type. The case where layer 1 is A, layer 2 is B and layer 3 is A again is shown in Fig 19.2

Figure 19.2 Diffraction patterns from three layers A , B and A showing the phase differences in

reflections from different layers.

The distance between the two A layers is *a* and the distance between the A and B layers is x*a*. When there is a constructive interference from two adjacent A layers, the phase difference between the layers is 2π. For an analogous reflection from the B layer, the phase difference is 2π x as the distance a is reduced by a factor of x. Considering all the indices h k *l*, the phase difference θ_{hkl} between adjacent h k *l* planes when the distances between the planes are x*a*, yb and xc is given by

$$\theta_{hkl} = 2\pi(hx + ky + lz) \qquad\qquad (19.2)$$

Note that when x, y, z are 1, the phase difference corresponding to a, b and c gives the maximum intensity because 2π a, 2π b and 2π c together correspond to $2d\sin\theta = n\lambda$). These phase differences correspond to 100 or 010 or 001 type reflections. If the reflection is from 200 planes, then the phase difference will be 4π x and not 2π x.

We should now be able to see the rationale for the additional absences in BCC and FCC lattices (relative to an SC lattice).
For a BCC lattice, x = y = z = 1/2 since an atom is present at x = y = z = 1/2 a where a = edge length. In such a situation, the phase difference between the A and B layers is $(h + k + l)\pi$. This means that when the value of h + k + *l* = odd, there is destructive interference and all reflections with h + k + *l* = odd are absent in a BCC lattice. Our analysis so far has assumed identical atoms in the A and B layers.

Even if the atoms in the adjacent layers have very similar scattering powers, the same absences would occur. In general, the scattering power of an atom or an ion depends on its electron density distribution ρ (r) where ρ (r) is given by ρ (r) = ψ^{*} (r) ψ (r)) (see Module 1).

The scattering power of an atom A, f_A is related to ρ_A (r) by

$$f_A \; 4\pi \int_0^\infty \rho_A \; (r) \; \frac{\sin kr}{kr} \; r^2 dr$$

$$\qquad\qquad (19.3)$$

$$k = \frac{4\pi\sin\theta}{\lambda}$$

$$\qquad\qquad (19.4)$$

19.3 Structure Factors and Electron Densities

We have seen that Eq (19.3) gives the scattering factor of an atom or an ion in terms of its electron density. This scattering factor is a function of the wave - vector $\vec{k}$, which gives the vector in the direction of the propagation of the wave. The magnitude of this vector is k. From an analysis of Eq (19.3) we find that f_A is greatest in the forward direction and smaller in other directions. A sketch of f_A as a function of k is given in Fig 19.3.

Figure 19.3 Scattering factors of atoms as a function of angle (k).

As k $\rightarrow$ 0, sin (kr) / kr $\rightarrow$ 1 (as the $\lim_{x \to 0} \frac{\sin x}{x} \to 1$) and f_A is equal to the number of electrons in the atom /ion (N_e)

As k $\rightarrow$ 0, $f_A = 4 \pi \int_0^\infty \rho_A(r) \, r^2 d\,r = N_e$ (19.5)

From the above discussion, we conclude that very good results for diffraction can be obtained for smaller values of θ (as scattering factors are large). Also since the scattering factor of hydrogen is very small for all values of k, it is very difficult to infer about the location of hydrogen atoms through X - ray diffraction.

Continuing our discussion from Fig 19.2, the total amplitude at the detector from layers of atoms A and layers of atom B is

$F_{hkl} = f_A + f_B e^{i \phi_{hkl}}$ (19.6)

where ϕ is the phase difference between the h k l reflections from A atoms and B atoms.
The intensity (I) of X-rays is proportional to the square modulus of the amplitude given by Eq (19.6). We get

$I \propto F^*_{hkl} F_{hkl} = (f_A + f_B e^{-i \phi_{hkl}})(f_A + f_B e^{i \phi_{hkl}})$

$= f_A{}^2 + f_B{}^2 + 2 f_A f_B \cos \phi_{hkl}$ (19.7)

We thus observe that depending on ϕ_{hkl} (ie the phase difference between the h, k, l planes expressed in terms of the distance between layers A and B and fractions x, y and z) the intensities of two lattices containing different sets of atoms is different. If the unit cell contains several types of atoms labeled by j with scattering factors f_j and coordinates (x_j a, y_j b, z_j c) then the total amplitude of the wave scattered by the h k l planes is

$F_{hkl} = \sum_j f_j e^{i \phi_{hkl}(j)}$ (19.8)

where $\phi_{hkl}(j) = 2 \pi (h x_j + k y_j + l z_j)$ and

the summation is over all the atoms in the unit cell. F_{hkl} is known as the structure factor and the intensity of reflection from the h k l plane is proportional to $| F_{hkl} |^2$

Let us use Eq (19.8) to analyze the structure factor of NaCl, whose structure is shown in fig 19.4. The coordinates of the atoms are also shown as (0, 0, 0), (1 1 1), (1/2, 1/2, 0) and so on.

Figure 19.4 NaCl structure with coordinates.

Let f^+ and f^- be the scattering factors of Na^+ and Cl^- respectively. Just as the atom inside a BCC unit cell contributes one atom to the unit cell, an atom inside the unit cell contributes a strength of f to the scattered intensity. An atom shared between faces contributes f / 2, an atom at a corner contributes f / 8 and an atom on the edge of a side contributes f / 4 . We will also need the two useful relations given below

$$e^0 = e^{2\pi i n} = 1, \; e^{i\pi} = -1, \; (e^{i\phi} + e^{-i\phi})/2 = \cos\phi \qquad\qquad (19.9)$$

where n is an integer

There are 27 atoms in the unit cell of fig 19.4. Summing over all ions,

$$F_{hkl} = f^+[\, 1/8 + 1/8 \, e^{2\pi i l} + \ldots\ldots 1/2 \, e^{2\pi i (1/2 h + 1/2 k + l)}\,] + f^-[\, e^{2\pi i (1/2 h + 1/2 k + 1/2 l)} + 1/4$$

$$e^{2\pi i (h/2)} \ldots\ldots \ldots\ldots\ldots\ldots\ldots + 1/4 \, e^{2\pi i (1/2 h + 1)}\,] \qquad\qquad (19.10)$$

Using Eq (19.9), Eq (19.10) can be simplified to

$$F_{hkl} = f^+ [\, 1 + \cos(h+k)\pi + \cos(h+l)\pi + \cos(k+l)\pi \,] + f^- [\, (-1)^{h+k+l} + \cos k\pi + \cos l\pi + \cos h$$

$$\pi\,] \qquad\qquad (19.11)$$

since $\cos n\pi = (-1)^n$, we get

$$F_{hkl} = f^+ [\, 1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{l+k} \,] + f^- [\, (-1)^{h+k+l} + (-1)^h + (-1)^k + (-1)^l \,] \qquad\qquad (19.12)$$

We can easily deduce from Eq (19.12) that

$$F_{hkl} = f^+ (1+1+1+1) + f^- (1+1+1+1) = 4f^+ + 4f^- \qquad\qquad (19.13)$$

if all h, k and l are even

$$F_{h\,k\,l} = 4\,(\,f^{\,+} - f^{\,-}\,) \text{ if each of h, k and l is odd} \tag{19.14}$$

and

$$F_{h\,k\,l} = 0 \text{ if one is odd and two are even or two are odd and one is even} \tag{19.15}$$

This analysis now justifies our assertion made in Fig 19.12. This also brings out the fact that even if two unit cells are the same (e.g., FCC or BCC), their diffraction patterns can be very different if $f^{\,+}$ and $f^{\,-}$ in Eqs (19.13) to (19.15) are different. This is illustrated in Fig 19.5.

Figure (19.5) Reflections from NaCl and kcl crystals (Powder diffractions)

In KCl, K^{+} and Cl^{-} have similar scattering factors and hence there are greater number of absences in KCl.

From X - ray diffraction, we get $F_{h\,k\,l}$ for different hkl planes. Since the origin of $F_{h\,k\,l}$ is the electron density ρ (r) of different atoms [Eq (19.3) and Eq (19.8)] it is possible to obtain ρ (r) from all the $F_{h\,k\,l}$ values through

$$V \rho\ (r) = \sum_{hkl} F_{h\,k\,l}\,e^{-\,2\pi\,i\,(\,h\,x\,+\,k\,y\,+\,l\,z\,)} \tag{19.16}$$

where V is the volume of the unit cell and the summation is over all h k l values. This is a very crucial result, since the location of all the atoms in the unit cell (through the values of ρ (r) corresponding to these atoms) can be obtained by using the above equation.

19.4 The Phase Problem

Everything seemed to be working rather well so far but it would be good to be aware of a major difficulty encountered in the diffraction method and the ways and means of nearly overcoming them. We know that the measured intensity $I_{h\,k\,l}$ of diffracted light is proportional to $|\,F_{h\,k\,l}\,|^{\,2}$. We need $F_{h\,k\,l}$ in Eq (19.16). How do we know whether to use $F_{h\,k\,l}$ or $-F_{h\,k\,l}$ or even more generally $|F_{h\,k\,l}|\,e^{\,i\,\alpha}$ where α is the phase of

$F_{h\,k\,l}$. While there are no methods to fully eliminate the problem, a common approach is to use $(F_{h\,k\,l})^2$ in place of $F_{h\,k\,l}$ in Eq (19.16). This is called Patterson synthesis.

$$\rho_{approximate}\,(r) = (1/V)\sum_{hkl}|F_{h\,k\,l}|^2\,e^{-2\pi\,i\,(h\,x\,+\,k\,y\,+\,l\,z)} \qquad (19.17)$$

The use of Eq (19.17) results in multiple locations of some atoms which have to be corrected by trial and error. Another useful approach is to neglect the scattering functions of light atoms relative to those of the heavy atoms.

$$F = (\pm)\,f_{heavy}\,(\pm)\,f_{light} \qquad\qquad (19.20)$$

Since f_{light} values are much smaller than f_{heavy}, the former may be neglected in the first approximation. Other convenient relations like relating the signs of $F_{a\,b\,c}$ and $F_{d\,e\,f}$ to the sign of $F_{a\,+\,d,\,b\,+\,c,\,c\,+\,f}$ are also used in finding partial solutions to the phase problem. Finally, the actual structure of the crystal is obtained by repeatedly refining the results obtained from the diffraction pattern and getting back the diffraction pattern from the estimated electron densities.

19.5 Other Diffraction Methods :

In addition to X - rays, neutrons and electrons can also be used in diffraction techniques by carefully choosing their wavelengths to lie between 10 pm to 200 pm. The wavelength λ of any object may be obtained from the de Broglie relation $\lambda = h\,/\,p$ where h is Planck's constant and p, the momentum of the particle.

The wavelength of thermal neutrons can be obtained by using the thermal value of $p = (m\,k\,T)^{1/2}$. Neutrons interact with the atomic nuclei and can sensitively detect the presence of hydrogen atoms as well as distinguish atoms of similar electron densities such as Co and Ni. The bond lengths of C - H (109 pm) and O - H (97 pm) estimated by neutrons are more accurate than the X - ray results. Furthermore, since neutrons have a spin (spin angular momentum of $\hbar\,/\,2$), they can distinguish magnetically different atoms of the same substance and are very useful in the study of lattices wherein there is magnetic (spin) ordering

Electron diffraction is useful when the number of scattering centers are fewer, as in the case of molecules in the gas phase as well as the surfaces of solids. Electron diffraction has been used to estimate interparticle separations in molecules as well as the structures of the surfaces of solids.

19.6 Problems

19.1) Associate the contribution of the scattering factor of each ion to each term of Eq (19.10)

19.2) In an FCC lattice, what can you say about the reflections from all h k l even vis-a-vis all h k l odd?

19.3) For a body-centered lattice, deduce the rules for systematic absences using analogies from the details worked out for the FCC lattice.

19.4) Determine the coordinates of each atom of a hexagonal lattice and a monoclinic lattice.

19.5) The von Laue method is different from Bragg's derivation of Bragg's law. But both the results agree at the end. Look up the derivation based on von Laue method.

19.6) Using $\lambda = h\,/\,\sqrt{m\,k\,T}$ estimate the temperature at which thermal neutrons have a wavelength of 10 pm . Through what potential difference (V) should electrons be accelerated so that they attain a value of $\lambda = 10$ pm ? Use $\lambda = h\,/\,\sqrt{2m_e eV}$

Recap
In this Lecture you have learnt the following

Summary

In this lecture we have studied how systematic absences are brought about in the diffraction patterns of different lattices. The emphasis was on cubic lattices. The scattering function is derived from the electron density and the resultant of the scattering functions of all the atoms in the unit cells (weighted by their phases and their effective number in the unit cell) gives the structure factor $F_{h\,k\,l}$ whose square is proportional to the diffracted intensity $I_{h\,k\,l}$.

Since only the square of $F_{h\,k\,l}$ is measurable, the square root of $I_{h\,k\,l}$ can be determined except for a phase factor $e^{i\,\alpha}$. Methods to circumvent the phase problem were listed. The difference between the diffraction patterns of SC, BCC and FCC lattices was illustrated in Fig (19.2) and rationalized in section 19.3. Diffraction techniques using neutrons and electrons were mentioned in section 19.4 and the special advantages of these methods were indicated.