CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 52: Analysis of Diffraction Pattern for a Cubic Crystal - I

In the previous lecture, some X-ray diffraction techniques were described, with particular emphasis on the X-ray diffractometer technique. In the present discussion, an analysis of a crystal structure using this technique is carried out. The material considered is deliberately chosen to be simple. It is assumed to have a cubic structure, but it is not known a priori whether the structure is simple cubic, body-centered cubic, or face-centered cubic. The sample is polycrystalline, which is required for the X-ray diffractometer technique. A powder sample may also be used instead of a polycrystalline sample, since each powder particle behaves as a single crystal and the particles are randomly oriented.

A brief review of the structure factor is useful at this point. If there are m atoms in the unit cell, the structure factor is given by

$$F = \sum_{j=1}^{m} exp\left[2\pi i(hu_j + kv_j + lw_j)\right],$$

where h, k, and l are the Miller indices of the reflecting plane, and u_j, v_j, and w_j are the fractional coordinates of the jth atom in the unit cell. The structure factor must be calculated because, even if Bragg's law is satisfied, a reflection may have zero intensity if the structure factor is zero, leading to extinction. The intensity of a reflection is proportional to the structure factor multiplied by its complex conjugate. The detailed derivation of extinction conditions was discussed in an earlier lecture, and those results are used here without repeating the derivation.

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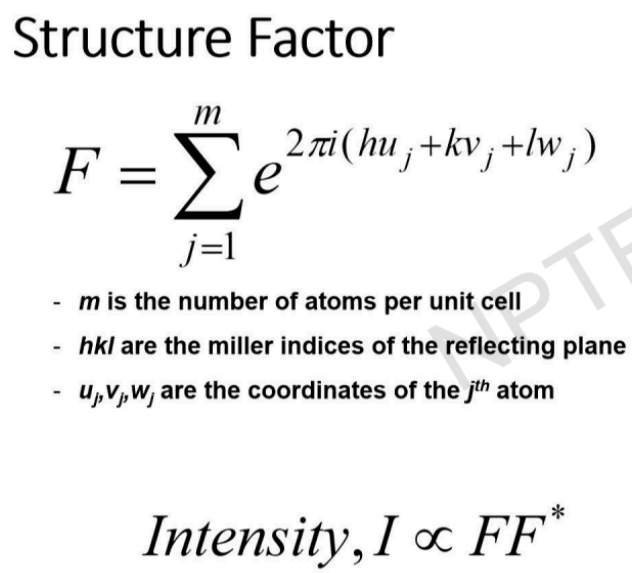

Only cubic crystals with a monoatomic basis are considered. In this case, there is only one atom in the basis, and that atom occupies every lattice point of the cubic crystal. For a simple cubic structure, atoms are located only at the corners of the unit cell. For a body-centered cubic structure, atoms are located at the corners and at the body center. For a face-centered cubic structure, atoms are located at the corners and at the centers of all six faces. These structures are denoted as SC for simple cubic, BCC for body-centered cubic, and FCC for face-centered cubic.

The extinction rules for these structures are now summarized. Consider first the reflecting plane (100). For this plane, $h^2 + k^2 + l^2 = 1$, a quantity that will be used later. For the simple cubic structure, there is no extinction and the (100) reflection is allowed. For both the body-centered cubic and face-centered cubic structures, the (100) reflection is extinct, and no diffraction peak is observed. In the simple cubic structure, all hkl planes are allowed. In the body-centered cubic structure, reflections occur only when $h + k + l$ is an even number. In the face-centered cubic structure, reflections occur only when h, k,

and l are unmixed, meaning that they are either all even or all odd. For the (100) plane, the indices are mixed, since 1 is odd and 0 is even. The sum $h + k + l = 1$ is odd, so both BCC and FCC structures show extinction for this plane.

Next, consider the (110) plane. For the simple cubic structure, this reflection is allowed. For the body-centered cubic structure, the sum $h + k + l = 1 + 1 + 0 = 2$, which is even, so the reflection is allowed. However, the indices are mixed, since 0 is even and the other two are odd, so the (110) reflection is extinct for the face-centered cubic structure.

The planes are considered in order of increasing values of $h^2 + k^2 + l^2$. This ordering is important because, for a cubic crystal, the interplanar spacing is given by

$$d = \frac{a}{\sqrt{h^2+k^2+l^2}},$$

where a is the lattice parameter. As $h^2 + k^2 + l^2$ increases, the interplanar spacing d decreases. Thus, the planes are ordered in decreasing interplanar spacing.

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Reflection / Extinction Conditions - Cubic Crystals (mono-atomic basis)

$d = \frac{a}{(h^2+k^2+l^2)^{1/2}}$

$h^2+k^2+l^2 \uparrow \Rightarrow d \downarrow$

hkl	$h^2 + k^2 + l^2$	SC	BCC	FCC
100	1	√	×	×
110	2	√	√	×
111	3	√	×	√
200	4	√	√	√
210	5	√	×	×
211	6	√	√	×
220	8	√	√	√
221	9	√	×	×
300	9	√	×	×
310	10	√	√	×
311	11	√	×	√
222	12	√	√	√
320	13	√	×	×
321	14	√	√	×
400	16	√	√	√

SC → all hkl planes allowed

BCC → h+k+l = even for reflection

FCC → hkl unmixed for reflection

Now consider the (111) plane. For the simple cubic structure, this reflection is allowed. For the body-centered cubic structure, the sum $h + k + l = 3$, which is odd, so the reflection is not allowed. For the face-centered cubic structure, the indices are all odd, so the reflection is allowed. Therefore, if the material is face-centered cubic, the first peak in the diffraction pattern corresponds to the (111) plane. If the material is body-centered cubic, the first peak corresponds to the (110) plane. If the material is simple cubic, the first peak corresponds to the (100) plane. By examining which reflections appear first, one can distinguish between these structures.

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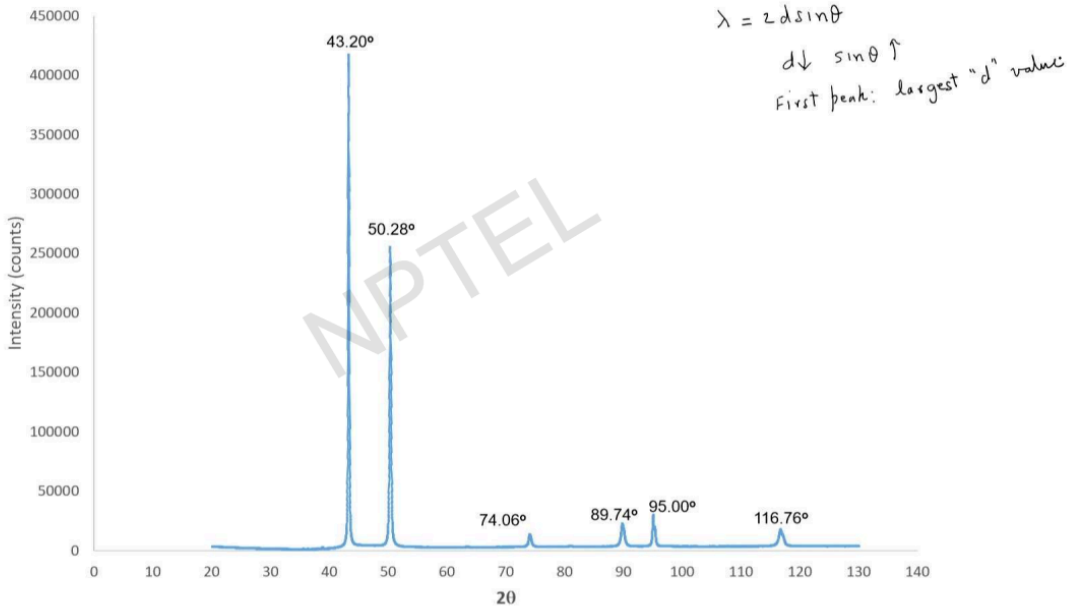

With these rules in mind, attention is now turned to the diffraction pattern. The diffraction pattern shown earlier is considered again, now with the 2θ values indicated for each peak. These peaks are listed in a table in order of increasing $h^2 + k^2 + l^2$, or equivalently, decreasing interplanar spacing.

Bragg's law is written as

$$\lambda = 2dsin\theta.$$

For a cubic crystal, substituting the expression for d gives

$$\lambda = \frac{2asin\theta}{\sqrt{h^2+k^2+l^2}}.$$

Rearranging and squaring both sides yields

$$\frac{sin^2\theta}{h^2+k^2+l^2} = \left(\frac{\lambda}{2a}\right)^2.$$

For a given experiment, the wavelength λ is fixed, for example in the case of Cu Kα radiation, and the lattice parameter a of the material is also fixed. Therefore, the right-hand side of the equation is a constant. This implies that $sin^2\theta$ is proportional to $h^2 + k^2 + l^2$, and the ratios of $sin^2\theta$ values for different peaks must match the ratios of $h^2 + k^2 + l^2$ for the corresponding planes.

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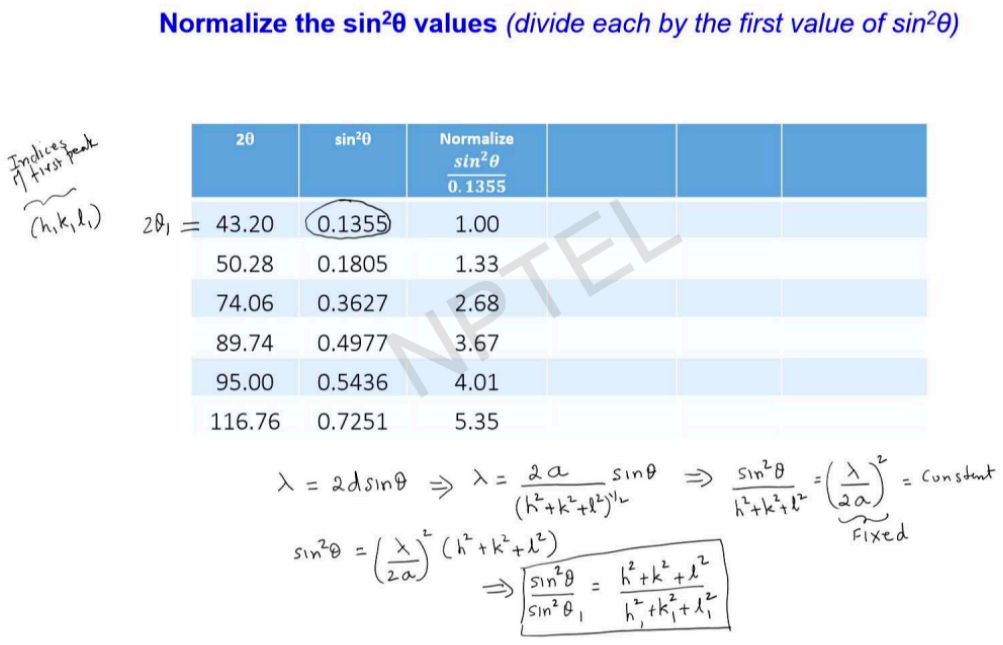

This can be expressed as

$$\frac{sin^2\theta}{sin^2\theta_1} = \frac{h^2+k^2+l^2}{h_1^2+k_1^2+l_1^2},$$

where θ_1 corresponds to the first peak, and $(h_1 k_1 l_1)$ are the indices assigned to that peak.

The analysis now proceeds by trial. First, the possibility that the structure is body-centered cubic is examined. For a BCC structure, the allowed reflections satisfy the condition that $h + k + l$ is even. The first few allowed planes are (110), (200), (211), (220), (310), and (222). The corresponding values of $h^2 + k^2 + l^2$ are 2, 4, 6, 8, 10, and 12. Taking (110) as the first peak, all values are divided by 2, giving ratios of 1.00, 2.00, 3.00, 4.00, 5.00, and 6.00. These ratios are compared with the experimentally obtained ratios of $sin^2\theta/sin^2\theta_1$. The values do not match closely, indicating that the structure is not body-centered cubic.

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Try hkl indices for different cubic structures *(hit and trial)*

BCC

2θ	sin²θ	Normalize $\frac{sin^2\theta}{0.1355}$	$\frac{h^2+k^2+l^2}{2}$	hkl	$h^2+k^2+l^2$
43.20	0.1355	1.00	1.00	110	2
50.28	0.1805	1.33	2.00	200	4
74.06	0.3627	2.68	3.00	211	6
89.74	0.4977	3.67	4.00	220	8
95.00	0.5436	4.01	5.00	310	10
116.76	0.7251	5.35	6.00	222	12

← $(h_1 k_1 l_1)$

Do Not Match

Next, the face-centered cubic structure is considered. For FCC, the allowed reflections have unmixed indices. The first few allowed planes are (111), (200), (220), (311),

(222), and (400). The corresponding values of $h^2 + k^2 + l^2$ are 3, 4, 8, 11, 12, and 16. Dividing each by 3, which corresponds to the first peak (111), gives ratios of 1.00, 1.33, 2.67, 3.66, 4.00, and 5.33. These ratios match closely with the experimentally obtained ratios of $sin^2\theta/sin^2\theta_1$. Therefore, it can be concluded with confidence that the structure is face-centered cubic.

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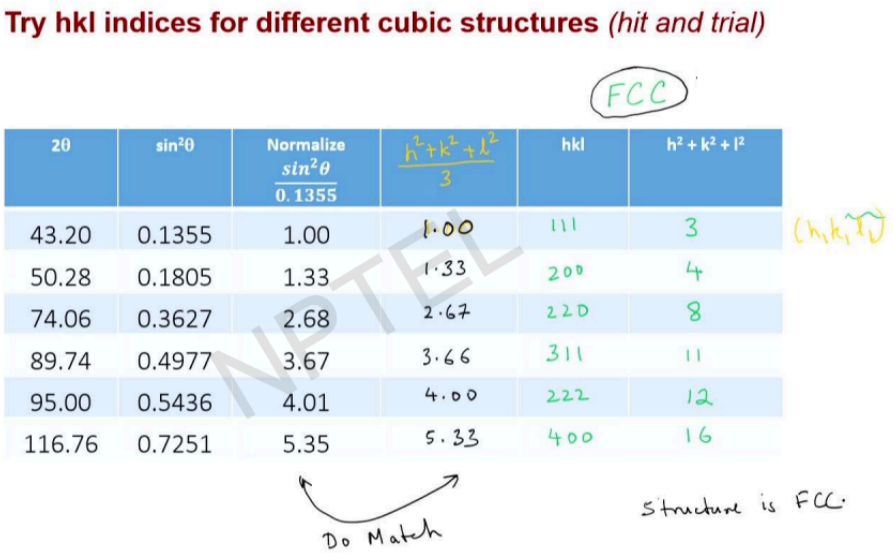

Returning to the diffraction pattern, indices can now be assigned to the individual peaks. The first peak corresponds to (111), the second to (200), the third to (220), the fourth to (311), the fifth to (222), and the last to (400). With this, the indexing of the diffraction peaks is complete, and the crystal structure has been identified as face-centered cubic.

Further analysis, including the determination of the lattice parameter and additional details, will be carried out in the next lecture. Thank you.