CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 53: Analysis of Diffraction Pattern for a Cubic Crystal - II

In the previous lecture, actual data obtained from an X-ray diffractometer were used to analyze the crystal structure of a material, and that same data have been reproduced here. The measured quantities were the 2θ values, that is, the scattering angles obtained from the X-ray diffractometer. Using these values, the structure was analyzed and identified as that of a face-centered cubic material. The diffraction peaks corresponding to these 2θ values were indexed, and the appropriate (hkl) indices were determined for each peak.

Now, suppose that using this data we wish to determine the lattice parameter of the material. Since the structure is cubic, there is only one lattice parameter, which is conventionally denoted as a and corresponds to the edge length of the cube. To determine the lattice parameter, we return to Bragg's equation,

$$\lambda = 2d sin\theta,$$

from which the interplanar spacing can be written as

$$d = \frac{\lambda}{2sin\theta}.$$

Using this relation, a value of d can be obtained from each diffraction peak. The first peak, indexed as (111), gives the interplanar spacing corresponding to the (111) planes; the second peak, indexed as (200), gives the interplanar spacing for the (200) planes, and so on. In total, there are six peaks, and hence six different values of d can be obtained.

Once the interplanar spacings are known, the lattice parameter can be related to d for a cubic structure using

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

Thus, the lattice parameter can be written as

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

From each diffraction peak, a value of the lattice parameter can be calculated. Ideally, all of these values should be identical; however, because the data are experimental, small differences will arise among the calculated values of a.

If one wishes to determine an accurate value of the lattice parameter, one might consider simply averaging all the calculated a values, as is often done when multiple measurements of the same quantity are available. However, in this case, taking a simple average may not be the best approach. To understand why, it is useful to examine how errors propagate from the X-ray diffractometer data, where the angle θ is measured, through to the final value of the lattice parameter.

An error in the measured angle θ for a given peak will affect the calculated value of d. This, in turn, will produce an error in the lattice parameter a, since a is directly related to d. Thus, the error propagates from $\Delta\theta$ to Δd, and then to Δa. This can be expressed in terms of fractional error as $\frac{\Delta a}{a}$.

For a given peak, since

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

the differential form gives

$$\frac{\Delta a}{a} = \frac{\Delta d}{d}.$$

Now, considering the expression

$$d = \frac{\lambda}{2sin\theta},$$

and differentiating with respect to θ, one obtains

$$\frac{\Delta d}{d} = -\, cot\theta\, \Delta\theta.$$

Hence,

$$\frac{\Delta a}{a} = -\, cot\theta\, \Delta\theta.$$

From this expression, it is evident that as θ decreases, the value of $cot\theta$ increases, and therefore the magnitude of the fractional error in the lattice parameter increases. Conversely, as θ increases, $cot\theta$ decreases, and the error in the lattice parameter becomes smaller. In the limiting case where $\theta \rightarrow \pi/2$, $cot\theta \rightarrow 0$, and the fractional error in a tends to zero.

This analysis shows that there is a systematic dependence of the error in the lattice parameter on the Bragg angle. Peaks at lower θ values yield larger errors in the calculated lattice parameter, whereas peaks at higher θ values yield smaller errors. In principle, the most accurate value would be obtained from a peak at $\theta = 90^{\circ}$, although such a peak is not experimentally accessible. Nevertheless, one conclusion is that peaks at higher Bragg angles provide better estimates of the lattice parameter.

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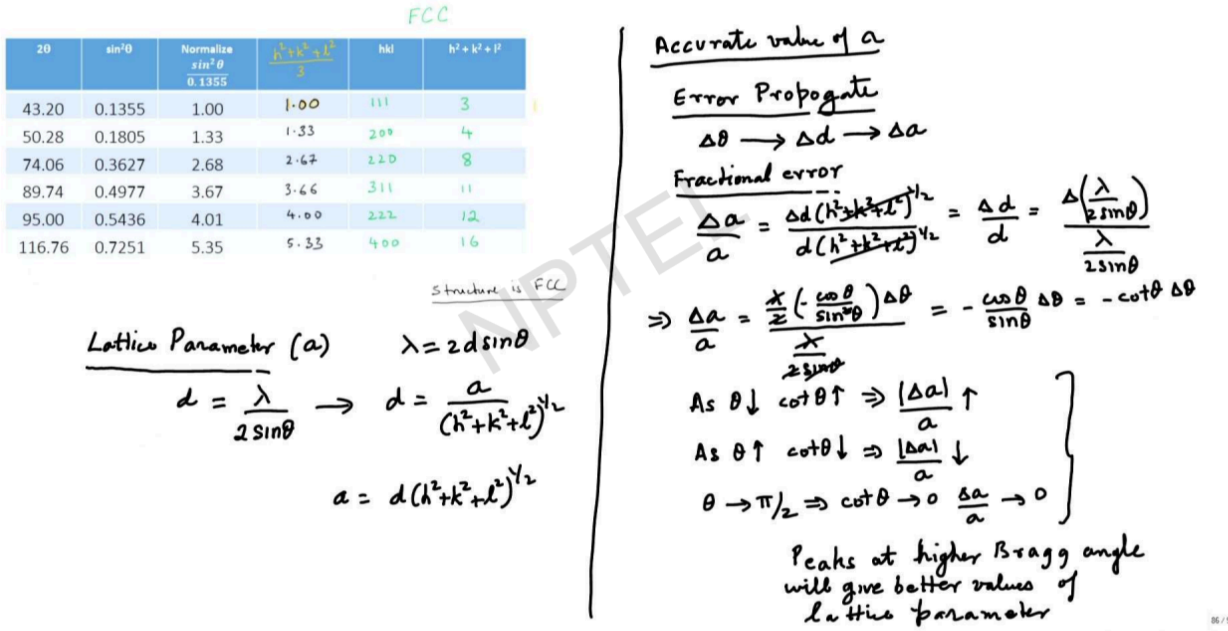

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2θ	$\sin^2\theta$	Normalize $\frac{\sin^2\theta}{0.1355}$	$\frac{h^2+k^2+l^2}{3}$	hkl	$h^2+k^2+l^2$
43.20	0.1355	1.00	1.00	111	3
50.28	0.1805	1.33	1.33	200	4
74.06	0.3627	2.68	2.67	220	8
89.74	0.4977	3.67	3.66	311	11
95.00	0.5436	4.01	4.00	222	12
116.76	0.7251	5.35	5.33	400	16

One simple approach would be to take the lattice parameter calculated from the highest-angle peak. However, this uses only a single data point. A more effective approach is to use all the calculated lattice parameter values and extrapolate them to $\theta = 90^\circ$ using an appropriate function.

One such extrapolation function is the Bradley–Jay function, which is simply $cos^2\theta$. In this method, $cos^2\theta$ is plotted on the horizontal axis, and the corresponding lattice parameter values are plotted on the vertical axis. A straight line is then fitted to the data points using a least-squares method. The intercept of this line at $cos^2\theta = 0$ corresponds to $\theta = \pi/2$, and the lattice parameter obtained at this intercept, denoted as a_0, is taken as an improved estimate of the lattice parameter.

A second, and generally more reliable, extrapolation function is the Nelson–Riley function, given by

$$f(\theta) = \frac{cos^2\theta}{sin\theta} + \frac{cos\theta}{\theta}.$$

In this case, the lattice parameter values are plotted against the Nelson–Riley function. A least-squares fit is again performed, and the intercept at the appropriate limit gives the extrapolated lattice parameter a_0. This value is often referred to as the precision lattice parameter. In practice, the Nelson–Riley function is usually preferred over the $cos^2\theta$ function.

Using the X-ray diffraction data, one can calculate the lattice parameter for each peak, apply one of these extrapolation methods, and obtain a precision value for the lattice parameter. This can be done conveniently using a spreadsheet program such as Microsoft Excel by plotting the data, fitting a trend line, and determining the intercept on the vertical axis.

As an assignment, the data presented here can be used to determine the precision lattice parameter using the Nelson–Riley function. The material analyzed is an elemental solid. By comparing the obtained lattice parameter with known values for face-centered cubic elements, the identity of the material that produced the diffraction pattern can be determined.

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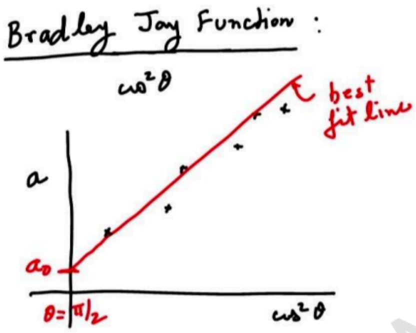

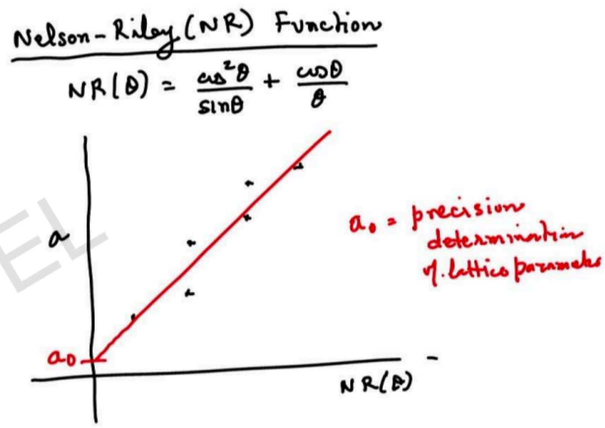

Up to this point, the discussion has focused on indexing cubic crystals. If the crystal is non-cubic, such as in a tetragonal system, the situation becomes more complex. For a tetragonal crystal, the interplanar spacing is given by

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2},$$

where $a = b \neq c$, and all interaxial angles are 90°. Starting from Bragg's law,

$$\lambda = 2d sin\theta,$$

one can write

$$sin^2\theta = \frac{\lambda^2}{4d^2} = \frac{\lambda^2}{4a^2}(h^2 + k^2) + \frac{\lambda^2}{4c^2}l^2.$$

Although a full analysis is not carried out here, some general comments can be made. A series of diffraction peaks will again be observed at different Bragg angles, and the task is to index them. One strategy is to identify groups of peaks corresponding to specific types of indices, such as $(hk0)$. For these planes, $l = 0$, and $sin^2\theta$ is proportional to $h^2 + k^2$. One can list possible values of $h^2 + k^2$ in order of decreasing interplanar spacing, such as

(100) with $h^2 + k^2 = 1$, (110) with 2, (200) with 4, (210) with 5, and (220) with 8, and then look for peaks that satisfy this proportionality.

If the lattice is primitive tetragonal, all such reflections are allowed. If the lattice is body-centered tetragonal, certain reflections will be systematically absent; for example, reflections for which $h + k + l$ is odd will not appear, so the (100) reflection would be absent, whereas others may be present.

A similar approach can be used for $(00l)$ reflections, for which $sin^2\theta$ is proportional to l^2. By identifying reflections such as (001), (002), (003), and so on, the lattice parameter c can be determined. Once a and c are known, the remaining general (hkl) reflections can be indexed.

This approach is practical for crystals with two lattice parameters. However, for structures with more than two lattice parameters and non-orthogonal angles, such methods become impractical. In modern practice, much of this work is performed using computer-based analysis, which can also assist in determining space groups from diffraction patterns.

Finally, it is worth noting some additional applications of X-ray diffraction. These include phase identification, particularly when more than one phase is present in a material, leading to diffraction peaks from multiple crystal structures. Phase quantification can also be performed by analyzing peak intensities, specifically the integrated intensity, which corresponds to the area under a peak. X-ray diffraction can also be used to determine crystallite size, as well as residual stresses, through analysis of peak broadening. There is a wide range of applications of X-ray diffraction, making it an extremely important tool for determining many structural aspects of materials.

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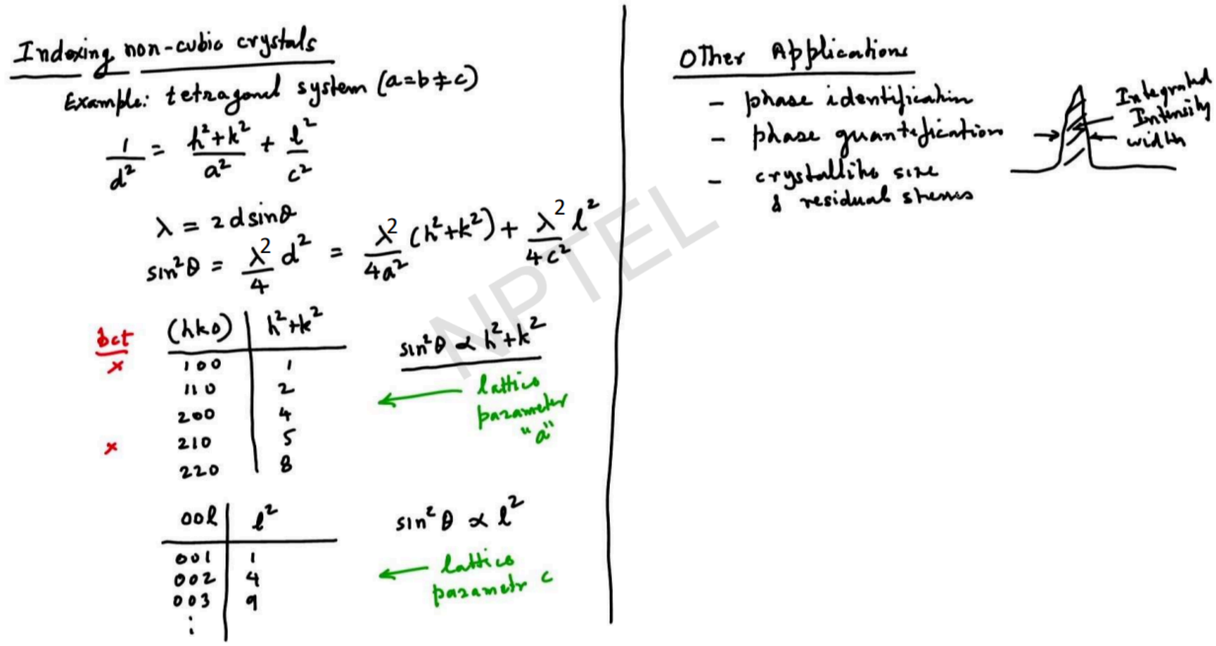
Indexing non-cubic crystals
Example: tetragonal system (a=b≠c)
1/d² = (h²+k²)/a² + l²/c²
λ = 2d sinθ
sin²θ = λ²/4 d² = λ²/4a² (h²+k²) + λ²/4c² l²
bct
(hk0) | h²+k²
100 | 1
110 | 2
200 | 4
210 | 5
220 | 8
sin²θ ∝ h²+k²
lattice parameter "a"
00l | l²
001 | 1
002 | 4
003 | 9
sin²θ ∝ l²
lattice parameter c
Other Applications
- phase identification
- phase quantification
- crystallite size & residual stress
Integrated Intensity
width
NPTEL

Thank you.