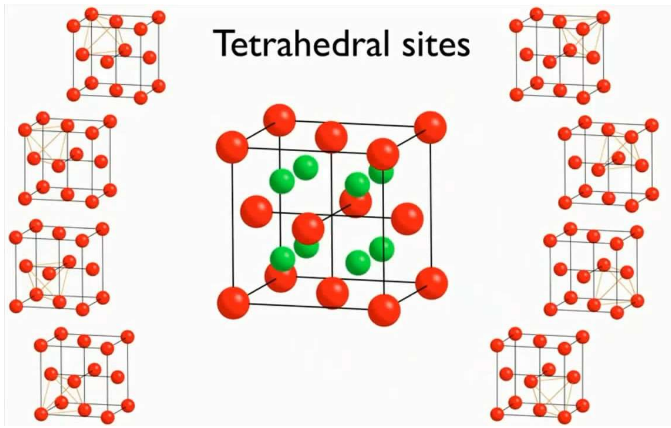

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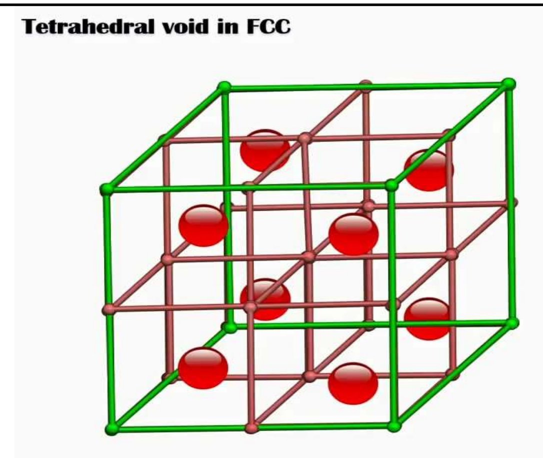

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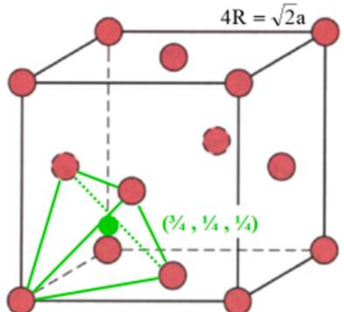
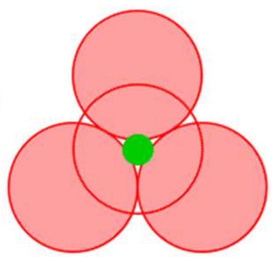
Tetrahedral sites in FCC



$$\boxed{r = 0.225R}$$



$$r + R = \sqrt{\left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2 + \left(\frac{a}{4}\right)^2}$$
$$= \left(\frac{\sqrt{3}}{4}\right)a$$
$$= \left(\frac{\sqrt{3}}{\sqrt{2}}\right)R$$

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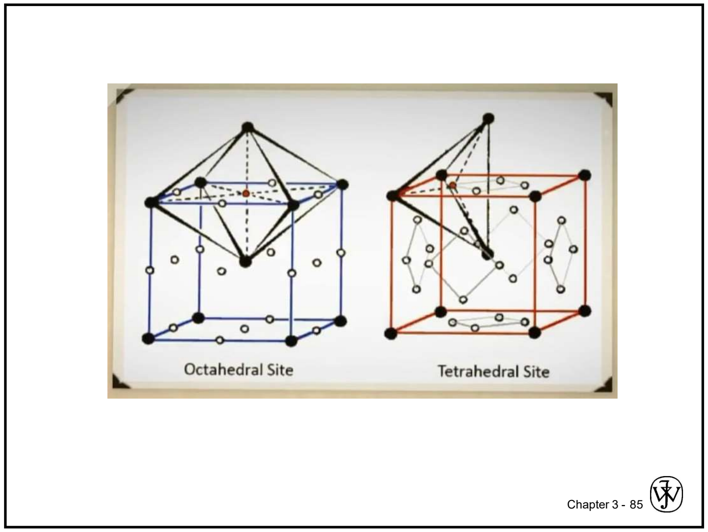
Octahedral Site
Tetrahedral Site
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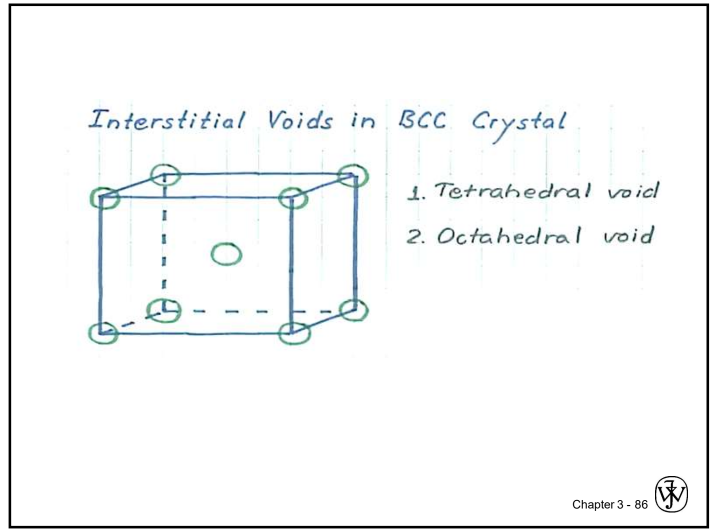
Interstitial Voids in BCC Crystal
1. Tetrahedral void
2. Octahedral void
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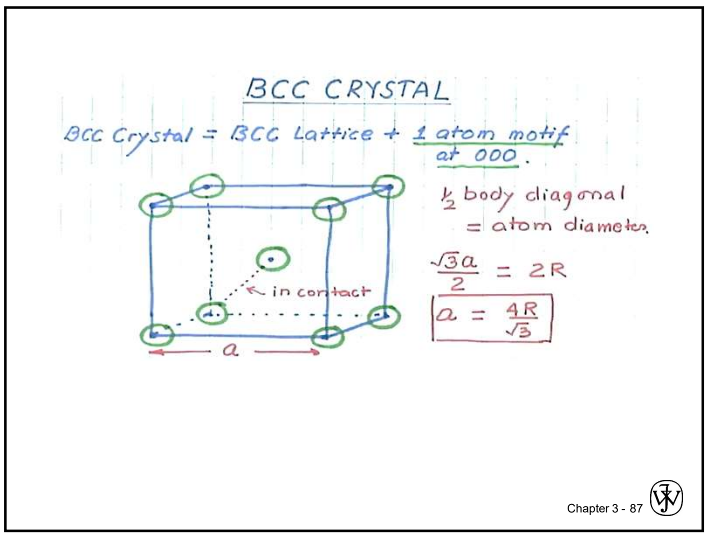
BCC CRYSTAL
BCC Crystal = BCC Lattice + 1 atom motif at 000.
½ body diagonal = atom diameter
$\frac{\sqrt{3}a}{2} = 2R$
$a = \frac{4R}{\sqrt{3}}$
in contact
a
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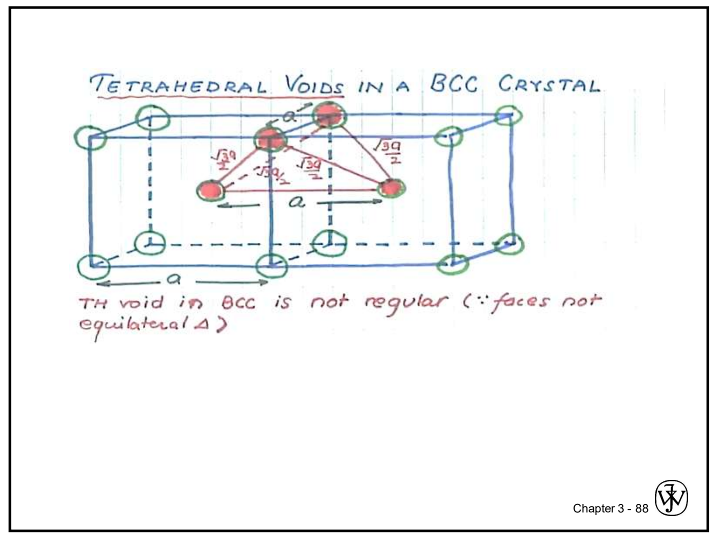
TETRAHEDRAL VOIDS IN A BCC CRYSTAL
a
a
TH void in BCC is not regular (∵ faces not equilateral Δ)
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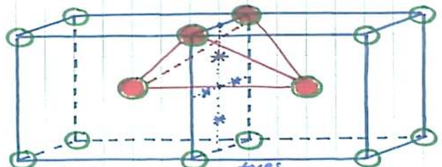
Geometry of Tetrahedral Voids in a BCC Crystal



No. of TH voids / cell = $\frac{6 \times 4}{2}$ = 12 THV/cell

faces; shared by 2 cubes

$\Rightarrow$ 6 THV/atom

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Geometry of Tetrahedral Voids in a BCC Crystal

CB = dist. from centroid of THV to a corner = d = $(CP^2 + BP^2)^{1/2}$

No. of TH voids / cell = $\frac{6 \times 4}{2}$ = 12 THV/cell

faces; shared by 2 cubes

$\Rightarrow$ 6 THV/atom

$d = \left[\left(\frac{a}{4}\right)^2 + \left(\frac{a}{2}\right)^2\right]^{1/2} = \left(\frac{a^2}{16} + \frac{a^2}{4}\right)^{1/2} = \frac{\sqrt{5}}{4} a = \frac{\sqrt{5}}{4} \cdot \frac{4R}{\sqrt{3}}$

$= 4\sqrt{5}/\sqrt{3}\, R.$

ETSC, IIT DELHI

$d = \frac{\sqrt{5}}{\sqrt{3}} R = r_T + R$

$\Rightarrow r_T = \left(\frac{\sqrt{5}}{\sqrt{3}} - 1\right) R \approx 0.29 R.$

~~Clospe~~ close-packed $r_T = 0.225$

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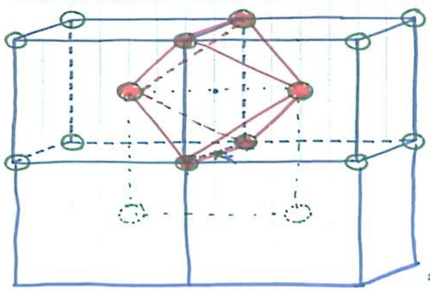
Octahedral Voids in a BCC Crystal



Centroids of OHV located at face-centres and edge-centres.

No. of voids per cell

$= \frac{6}{2} + \frac{12}{4}$

faces, edges

= 6 OHV/cell.

= 3 OHV/atoms!

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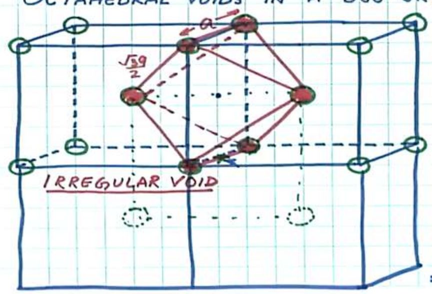
Octahedral Voids in a BCC Crystal



Centroids of OHV located at face-centres and edge-centres.

No. of voids per cell

$= \frac{6}{2} + \frac{12}{4}$

faces, edges

= 6 OHV/cell.

= 3 OHV/atoms!

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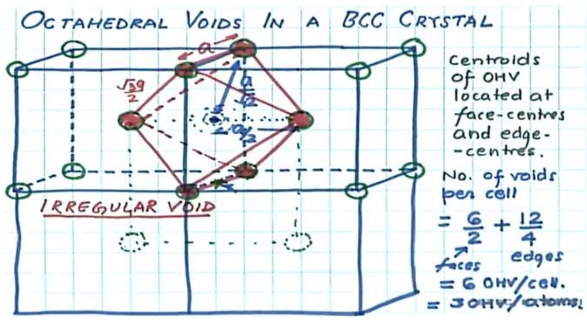

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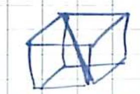
$$d = a = \frac{4R}{\sqrt{3}} = 2R + 2r_o$$

$$\Rightarrow r_o + R = \frac{2R}{\sqrt{3}}$$

$$\Rightarrow r_o = \left(\frac{2}{\sqrt{3}} - 1\right) R$$

$$\approx 0.15\, R \quad !$$

$$r_T \approx 0.29\, R$$



$\sqrt{3}a = 4R$

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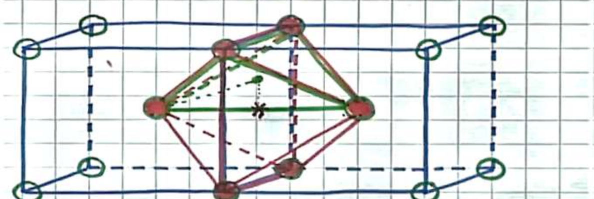

$OHV = 4\,THV \qquad r_o \approx \frac{1}{2} r_{TH}$

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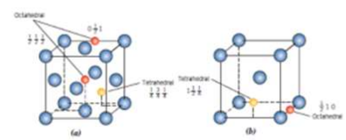

Computation of Radius of BCC Interstitial Site

Compute the radius r of an impurity atom that just fits into a BCC octahedral site in terms of the atomic radius R of the host atom (without introducing lattice strains).

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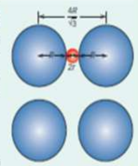
As Figure 4.3*b* notes, for BCC, the octahedral interstitial site is situated at the center of a unit cell edge. In order for an interstitial atom to be positioned in this site without introducing lattice strains, the atom just touches the two adjacent host atoms, which are corner atoms of the unit cell. The drawing shows atoms on the (100) face of a BCC unit cell; the large circles represent the host atoms—the small circle represents an interstitial atom that is positioned in an octahedral site on the cube edge.

On this drawing is noted the unit cell edge length—the distance between the centers of the corner atoms—which, from Equation 3.4, is equal to



$$\text{Unit cell edge length} = \frac{4R}{\sqrt{3}}$$

Also shown is that the unit cell edge length is equal to two times the sum of host atomic radius $2R$ plus twice the radius of the interstitial atom $2r$; i.e.,

$$\text{Unit cell edge length} = 2R + 2r$$

Now, equating these two unit cell edge length expressions, we get

$$2R + 2r = \frac{4R}{\sqrt{3}}$$

and solving for r in terms of R

$$2r = \frac{4R}{\sqrt{3}} - 2R = \left(\frac{2}{\sqrt{3}} - 1\right)(2R)$$

or

$$r = \left(\frac{2}{\sqrt{3}} - 1\right)R = 0.155R$$

X-Ray Diffraction

Historically much of our understanding regarding the atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations; furthermore, x-rays are still very important in developing new materials.

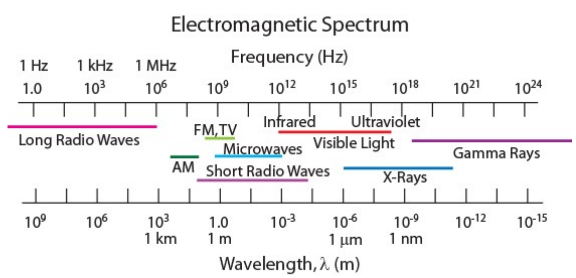
THE DIFFRACTION PHENOMENON

Diffraction occurs when a wave encounters a series of regularly spaced obstacles that

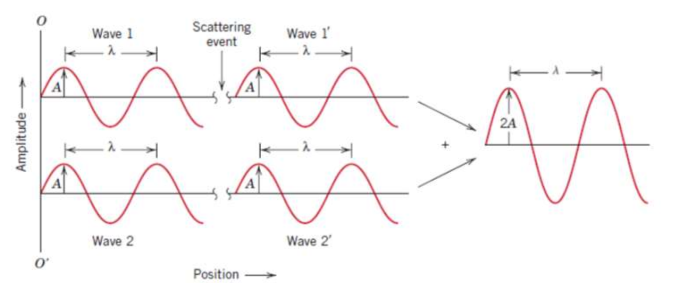
(1) are capable of scattering the wave, and
(2) have spacing's that are comparable in magnitude to the wavelength. Furthermore, diffraction is a consequence of specific phase relationships that are established between two or more waves that have been scattered by the obstacles.

X-RAY DIFFRACTION AND BRAGG'S LAW

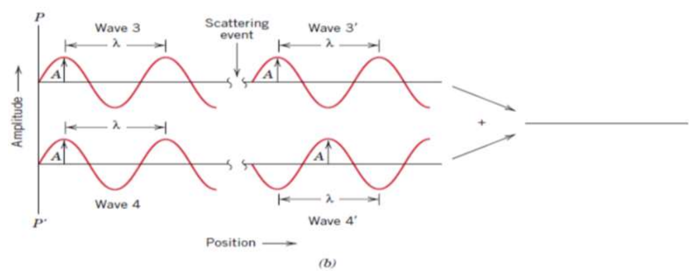
X-rays are a form of electromagnetic radiation that have high energies and short wavelengths—wavelengths on the order of the atomic spacing's for solids.



When a beam of x-rays impinges on a solid material, a portion of this beam will be scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path. Let us now examine the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.



Consider waves 1 and 2 in fig, which have the same wavelength λ and are in phase at point O-O'. Now let us suppose that both waves are scattered in such a way that they traverse different paths. The phase relationship between the scattered waves, which will depend upon the difference in path length, is important. One possibility results when this path length difference is an integral number of wavelengths. As noted in fig, these scattered waves (now labeled 1'and 2') are still in phase. They are said to mutually reinforce (or constructively interfere with) one another; and, when amplitudes are added, the wave shown on the right side of the figure results. This is a manifestation of **diffraction,** and we refer to a diffracted beam as one composed of a large number of scattered waves that mutually reinforce one another.



Other phase relationships are possible between scattered waves that will not lead to this mutual reinforcement. The other extreme is that demonstrated in Fig, wherein the path length difference after scattering is some integral number of *half* wavelengths. The scattered waves are out of phase—that is, corresponding amplitudes cancel one another, or destructively interfere (i.e., the resultant wave has zero amplitude), as indicated on the extreme right side of the figure.

Of course, phase relationships intermediate between these two extremes exist, resulting in only partial reinforcement.

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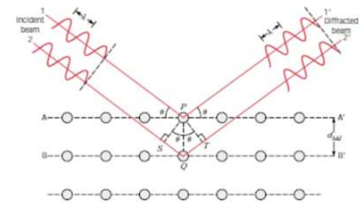

Consider the two parallel planes of atoms A–A and B–B in Fig, which have the same *h*, *k*, and *l* Miller indices and are separated by the interplanar spacing *dhkl* . Now assume that a parallel, monochromatic, and coherent (in-phase) beam of x-rays of wavelength λ is incident on these two planes at an angle θ. Two rays in this beam, labeled 1 and 2, are scattered by atoms *P* and *Q*. Constructive interference of the scattered rays 1' and 2' occurs also at an angle θ to the planes, if the path length difference between 1–*P*–1' and 2–*Q*–2' (i.e., *SQ* *QT*) is equal to a whole number, *n*, of wavelengths. That is, the condition for diffraction is

$$n\lambda = \overline{SQ} + \overline{QT}$$

$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta = 2\,d_{hkl}\sin\theta$$

Equation is known as **Bragg's law**

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The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing *dhkl*) is a function of the Miller indices (*h*, *k*, and *l*) as well as the lattice parameter(s).
For example, for crystal structures having cubic symmetry,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

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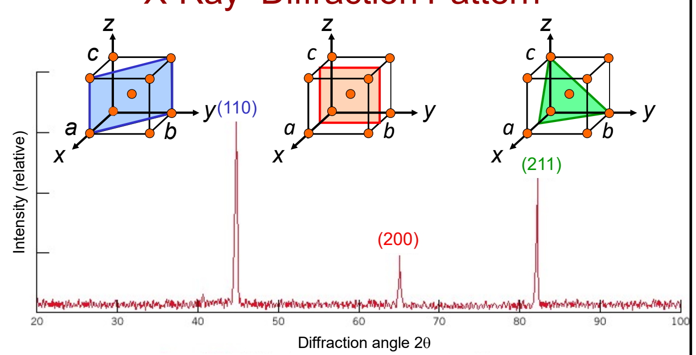
X-Ray Diffraction Pattern



Diffraction pattern for polycrystalline α-iron (BCC)

Adapted from Fig. 3.20, *Callister 5e.*

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For BCC iron, compute (a) the interplanar spacing, and (b) the diffraction angle for the (220) set of planes. The lattice parameter for Fe is 0.2866 nm (2.866A°). Also, assume that monochromatic radiation having a wavelength of 0.1790 nm (1.790 A°) is used, and the order of reflection is 1.

SOLUTION

(a) The value of the interplanar spacing d_{hkl} is determined using Equation 3.11, with $a = 0.2866$ nm, and $h = 2$, $k = 2$, and $l = 0$, since we are considering the (220) planes. Therefore,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$= \frac{0.2866 \text{ nm}}{\sqrt{(2)^2 + (2)^2 + (0)^2}} = 0.1013 \text{ nm } (1.013 \text{ Å})$$

(b) The value of θ may now be computed using Equation 3.10, with $n = 1$, since this is a first-order reflection:

$$\sin\theta = \frac{n\lambda}{2d_{hkl}} = \frac{(1)(0.1790 \text{ nm})}{(2)(0.1013 \text{ nm})} = 0.884$$

$$\theta = \sin^{-1}(0.884) = 62.13°$$

The diffraction angle is 2θ, or

$$2\theta = (2)(62.13°) = 124.26°$$

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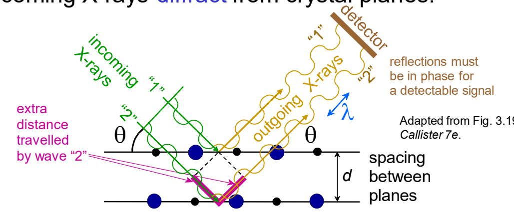
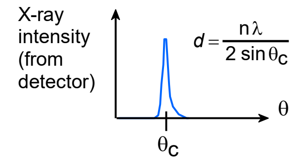
X-Rays to Determine Crystal Structure

- Incoming X-rays diffract from crystal planes.



Adapted from Fig. 3.19, *Callister 7e.*

Measurement of critical angle, θ_c, allows computation of planar spacing, *d*.



$$d = \frac{n\lambda}{2\sin\theta_c}$$

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The results of a x-ray diffraction experiment using x-rays with $\lambda = 0.7107$ Å (a radiation obtained from a molybdenum (Mo) target) show that diffracted peaks occur at the following 2θ angles:

Peak	2θ	Peak	2θ
1	20.20	5	46.19
2	28.72	6	50.90
3	35.36	7	55.28
4	41.07	8	59.42

Determine the crystal structure, the indices of the plane producing each peak, and the lattice parameter of the material.

We can first determine the $\sin^2\theta$ value for each peak, then divide through by the lowest denominator, 0.0308.

Peak	2θ	$\sin^2\theta$	$\sin^2\theta/0.0308$	$h^2+k^2+l^2$	(hkl)
1	20.20	0.0308	1	2	(110)
2	28.72	0.0615	2	4	(200)
3	35.36	0.0922	3	6	(211)
4	41.07	0.1230	4	8	(220)
5	46.19	0.1539	5	10	(310)
6	50.90	0.1847	6	12	(222)
7	55.28	0.2152	7	14	(321)
8	59.42	0.2456	8	16	(400)

When we do this, we find a pattern of $\sin^2\theta/0.0308$ values of 1, 2, 3, 4, 5, 6, 7, and 8. If the material were simple cubic, the 7 would not be present, because

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PROCEDURE FOR INDEXING CUBIC XRD PATTERNS

When you index a diffraction pattern, you assign the correct Miller indices to each peak (reflection) in the diffraction pattern. An XRD pattern is properly indexed when ALL of the peaks in the diffraction pattern are labeled and no peaks expected for the particular structure are missing.

How to we correctly index a pattern?

The correct procedures follow.

Interplanar spacings in cubic crystals can be written in terms of lattice parameters using the plane spacing equation:

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

You should recall Bragg's law ($\lambda = 2d\sin\theta$), which can be re-written either as:

$$\lambda^2 = 4d^2\sin^2\theta \text{ OR } \sin^2\theta = \frac{\lambda^2}{4d^2}$$

Combining this relationship with the plane spacing equation gives us a new relationship:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{4\sin^2\theta}{\lambda^2},$$

which can be rearranged to:

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2 + k^2 + l^2)$$

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$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2+k^2+l^2)$$

The term in parentheses $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any one pattern (because the X-ray wavelength λ and the lattice parameters a do not change). Thus $\sin^2\theta$ is proportional to $h^2+k^2+l^2$. This proportionality shows that planes with higher Miller indices will diffract at higher values of θ.

Since $\left(\frac{\lambda^2}{4a^2}\right)$ is constant for any pattern, we can write the following relationship for any two different planes:

$$\frac{\sin^2\theta_1}{\sin^2\theta_2} = \frac{\left(\frac{\lambda^2}{4a^2}\right)(h_1^2+k_1^2+l_1^2)}{\left(\frac{\lambda^2}{4a^2}\right)(h_2^2+k_2^2+l_2^2)} \quad \text{or} \quad \frac{\sin^2\theta_1}{\sin^2\theta_2} = \frac{(h_1^2+k_1^2+l_1^2)}{(h_2^2+k_2^2+l_2^2)}$$

The ratio of $\sin^2\theta$ values scales with the ratio of $h^2+k^2+l^2$ values.

In cubic systems, the first XRD peak in the XRD pattern will be due to diffraction from planes with the lowest Miller indices, which interestingly enough are the close packed planes (*i.e.*: simple cubic, (100), $h^2+k^2+l^2$=1; body-centered cubic, (110) $h^2+k^2+l^2$=2; and face-centered cubic, (111) $h^2+k^2+l^2$=3).

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Since h, k, and l are always integers, we can obtain $h^2+k^2+l^2$ values by dividing the $\sin^2\theta$ values for the different XRD peaks with the minimum one in the pattern (*i.e.*, the $\sin^2\theta$ value from the first XRD peak) and multiplying that ratio by the proper integer (either 1, 2 or 3). This should yield a list of integers that represent the various $h^2+k^2+l^2$ values. You can identify the correct Bravais lattice by recognizing the sequence of allowed reflections for cubic lattices (*i.e.*, the sequence of allowed peaks written in terms of the quadratic form of the Miller indices).

Primitive	$h^2+k^2+l^2$ = 1,2,3,4,5,6,8,9,10,11,12,13,14,16…
Body-centered	$h^2+k^2+l^2$ = 2,4,6,8,10,12,14,16…
Face-centered	$h^2+k^2+l^2$ = 3,4,8,11,12,16,19,20,24,27,32…
Diamond cubic	$h^2+k^2+l^2$ = 3,8,11,16,19,24,27,32…

The lattice parameters can be calculated from:

$$\sin^2\theta = \left(\frac{\lambda^2}{4a^2}\right)(h^2+k^2+l^2)$$

which can be re-written as:

$$a^2 = \frac{\lambda^2}{4\sin^2\theta}(h^2+k^2+l^2) \quad \text{OR} \quad a = \frac{\lambda}{2\sin\theta}\sqrt{h^2+k^2+l^2}$$

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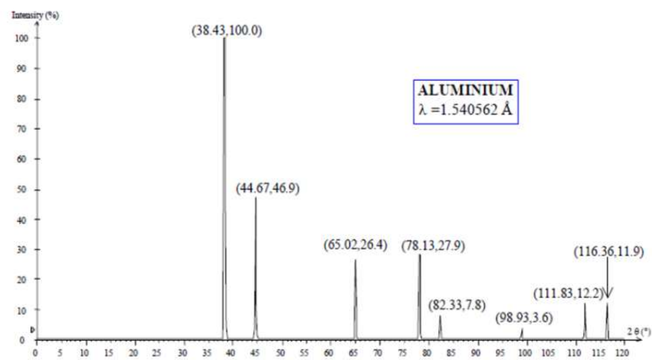
Consider the following XRD pattern for Aluminum, which was collected using CuKα radiation.



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Index this pattern and determine the lattice parameters.

Steps:
(1) Identify the peaks.
(2) Determine $\sin^2\theta$.
(3) Calculate the ratio $\sin^2\theta / \sin^2\theta_{min}$ and multiply by the appropriate integers.
(4) Select the result from (3) that yields $h^2+k^2+l^2$ as an integer.
(5) Compare results with the sequences of $h^2+k^2+l^2$ values to identify the Bravais lattice.
(6) Calculate lattice parameters.

Here we go!

(1) Identify the peaks and their proper 2θ values. Eight peaks for this pattern. Note: most patterns will contain α_1 and α_2 peaks at higher angles. It is common to neglect α_2 peaks.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43							
2	44.67							
3	65.02							
4	78.13							
5	82.33							
6	98.93							
7	111.83							
8	116.36							

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(2) Determine $\sin^2\theta$.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083						
2	44.67	0.1444						
3	65.02	0.2888						
4	78.13	0.3972						
5	82.33	0.4333						
6	98.93	0.5776						
7	111.83	0.6859						
8	116.36	0.7220						

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(3) Calculate the ratio $\sin^2\theta / \sin^2\theta_{min}$ and multiply by the appropriate integers.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

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(4) Select the result from (3) that most closely yields $h^2+k^2+l^2$ as a series of integers.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000			
2	44.67	0.1444	1.333	2.667	4.000			
3	65.02	0.2888	2.667	5.333	8.000			
4	78.13	0.3972	3.667	7.333	11.000			
5	82.33	0.4333	4.000	8.000	12.000			
6	98.93	0.5776	5.333	10.665	15.998			
7	111.83	0.6859	6.333	12.665	18.998			
8	116.36	0.7220	6.666	13.331	19.997			

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(5) Compare results with the sequences of $h^2+k^2+l^2$ values to identify the miller indices for the appropriate peaks and the Bravais lattice.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Bravais lattice is Face-Centered Cubic

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(6) Calculate lattice parameters.

Peak No.	2θ	$\sin^2\theta$	$1\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$2\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$3\times\frac{\sin^2\theta}{\sin^2\theta_{min}}$	$h^2+k^2+l^2$	hkl	a (Å)
1	38.43	0.1083	1.000	2.000	3.000	3	111	4.0538
2	44.67	0.1444	1.333	2.667	4.000	4	200	4.0539
3	65.02	0.2888	2.667	5.333	8.000	8	220	4.0538
4	78.13	0.3972	3.667	7.333	11.000	11	311	4.0538
5	82.33	0.4333	4.000	8.000	12.000	12	222	4.0538
6	98.93	0.5776	5.333	10.665	15.998	16	400	4.0541
7	111.83	0.6859	6.333	12.665	18.998	19	331	4.0540
8	116.36	0.7220	6.666	13.331	19.997	20	420	4.0541

Average lattice parameter is 4.0539 Å

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SUMMARY

- Atoms may assemble into crystalline or amorphous structures.
- Common metallic crystal structures are FCC, BCC, and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Crystallographic points, directions and planes are specified in terms of indexing schemes. Crystallographic directions and planes are related to atomic linear densities and planar densities.

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SUMMARY

- Materials can be single crystals or polycrystalline. Material properties generally vary with single crystal orientation (i.e., they are anisotropic), but are generally non-directional (i.e., they are isotropic) in polycrystals with randomly oriented grains.
- Some materials can have more than one crystal structure. This is referred to as polymorphism (or allotropy).
- X-ray diffraction is used for crystal structure and interplanar spacing determinations.

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ANNOUNCEMENTS

Reading:

Core Problems:

Self-help Problems:

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