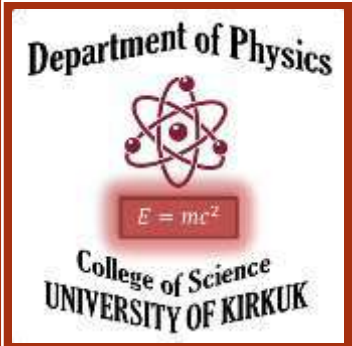

X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

Subject: Material Science - Lecture #9

مدرسة المادة : الدكتورة روژه برهان الدين عبدالرحمن

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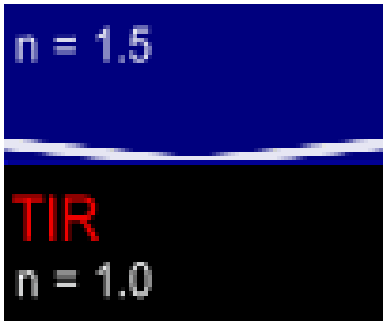
Physics Department – 3rd grade

X-RAY DIFFRACTION: DETERMINATION OF CRYSTAL STRUCTURES

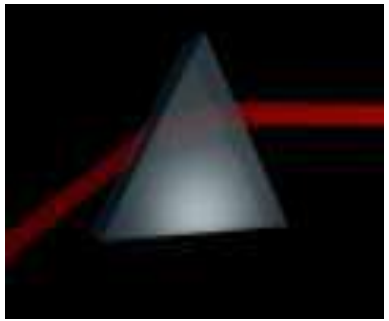
- The atomic and molecular arrangements in solids has resulted from x-ray diffraction investigations.
- X-rays are still very important in developing new materials.
- Understand a brief overview of the diffraction phenomenon and how, using x-rays, atomic interplanar distances and crystal structures are deduced.

The Diffraction Phenomenon

- Electromagnetic radiations (such as visible light) can interact among themselves and with matter, giving rise to a multitude of phenomena such as ***reflection***, ***refraction***, ***diffraction,*** ***scattering***, ***polarization***...

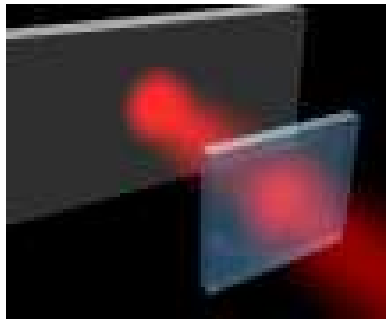


reflection



refraction

diffraction

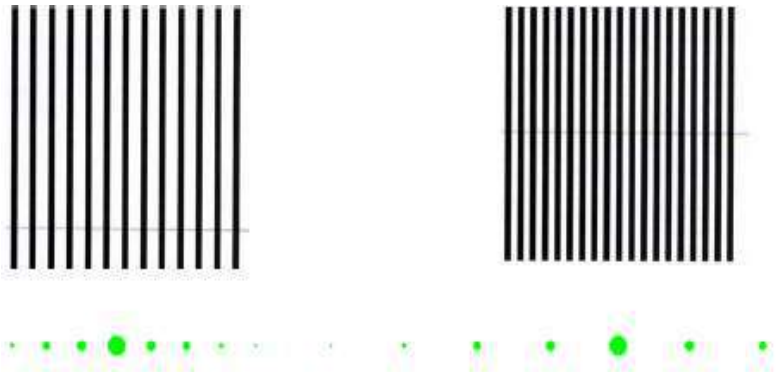


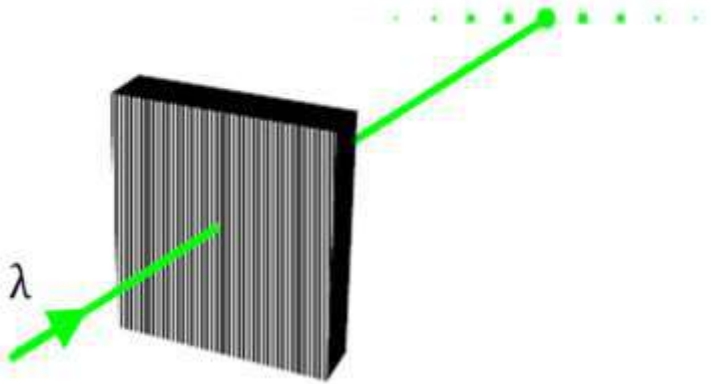
polarization

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

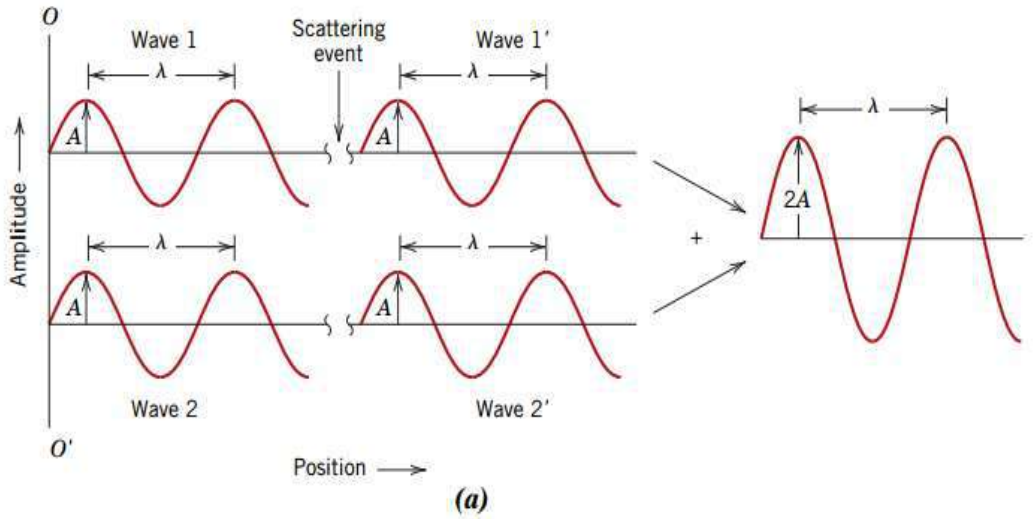
(1) are capable of scattering the wave, and (2) have spacing that are comparable in magnitude to the wavelength.

- diffraction is a consequence of specific phase relationships established between two or more waves that have been scattered by the obstacles.



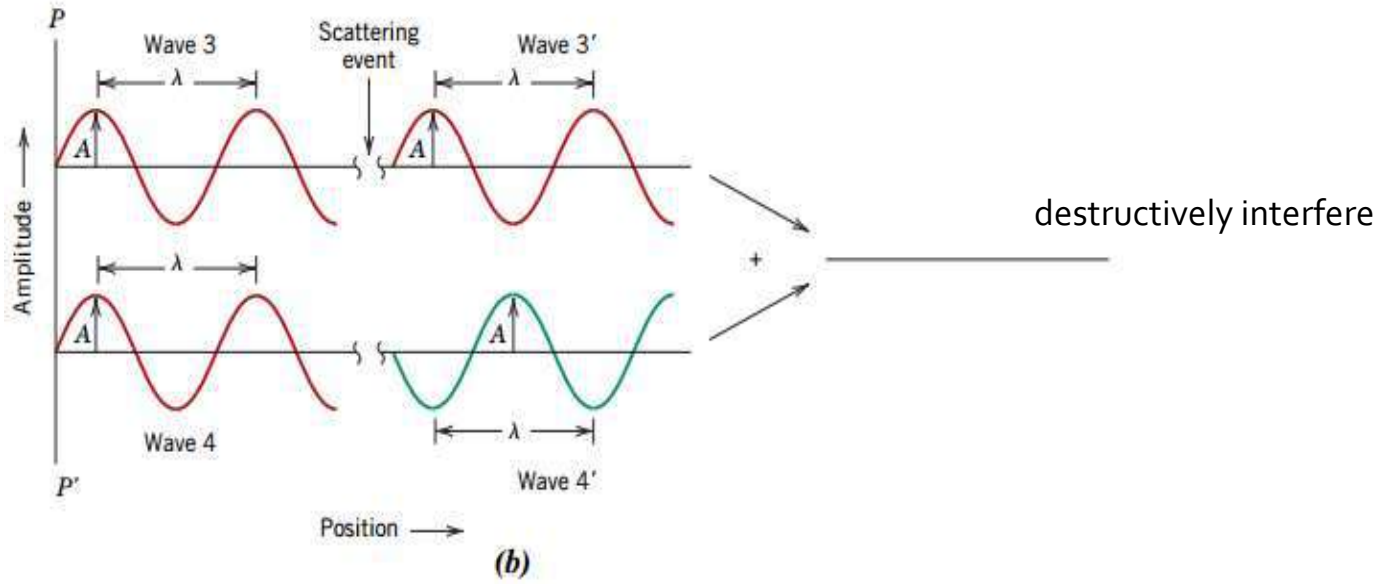


- Consider waves 1 and 2 in Figure *a*, which have the same wavelength (λ) and are in phase at point $O - O'$.
- Now let us suppose that both waves are scattered in such a way that they traverse (travel across or through) different paths.
- The path length difference is an integral number of wavelengths.



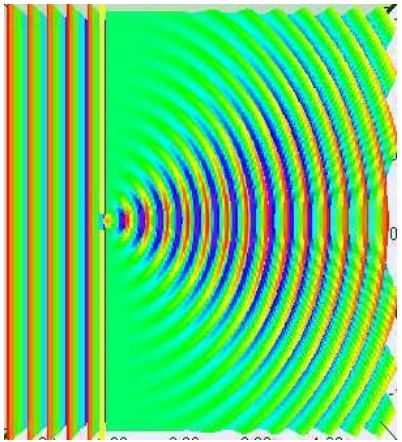
constructively interfere

- Other phase relationships are possible between scattered waves
- The path length difference after scattering is some integral number of *half*-wavelengths.

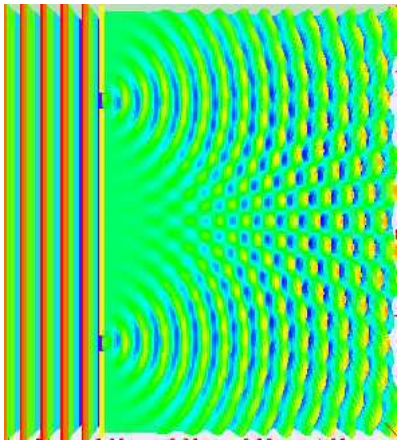


For example Diffraction of light wave

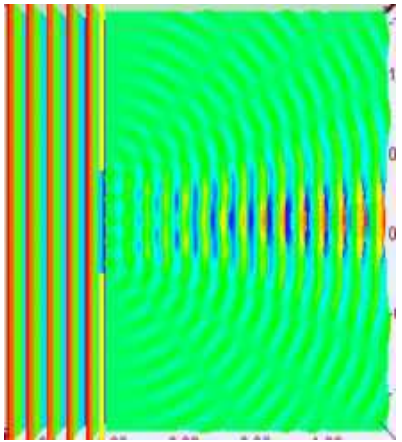
For electromagnetic radiation to be diffracted the spacing in the grating should be of the same order as the wavelength



Diffraction of a plane wave when the slit width equals the wavelength



Diffraction of a plane wave with two slit

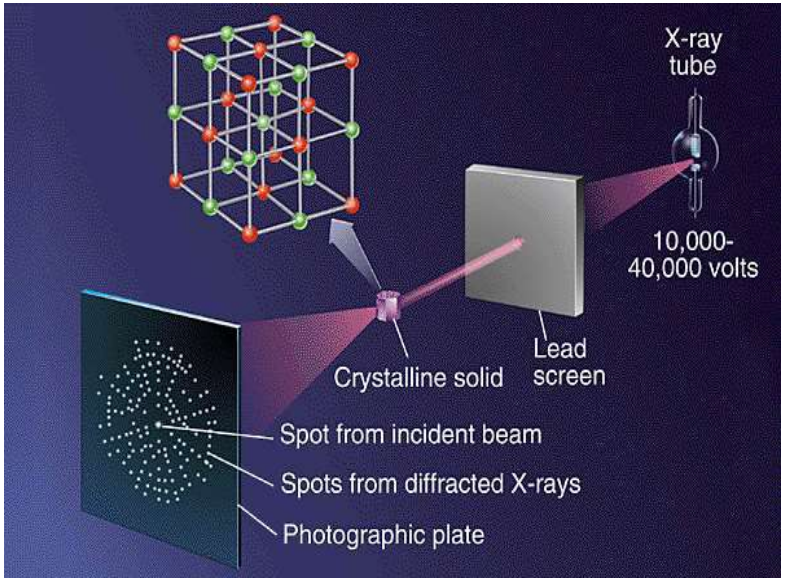


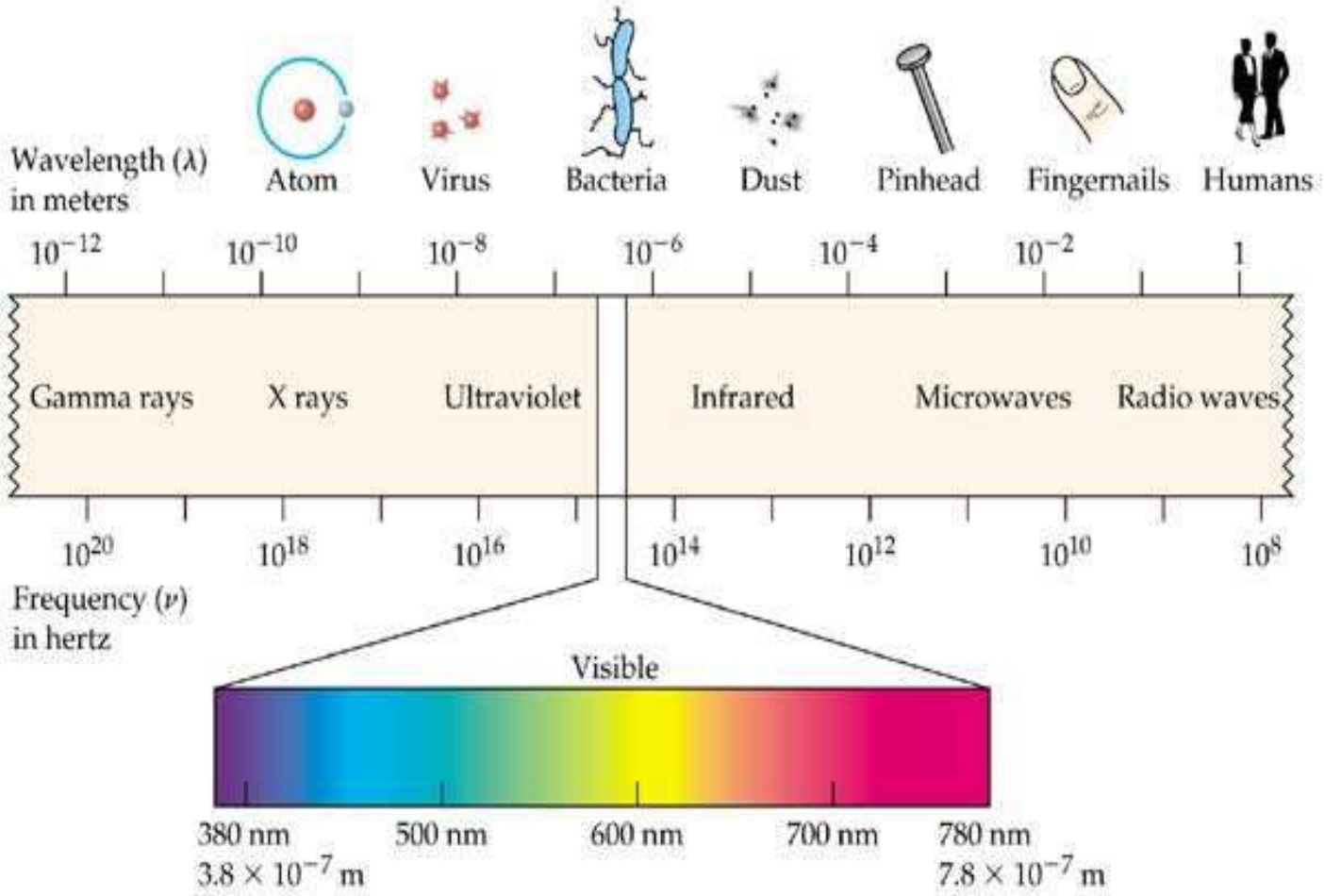
Diffraction of a plane wave at a slit whose width is several times the wavelength

X-Ray Diffraction and Bragg's Law

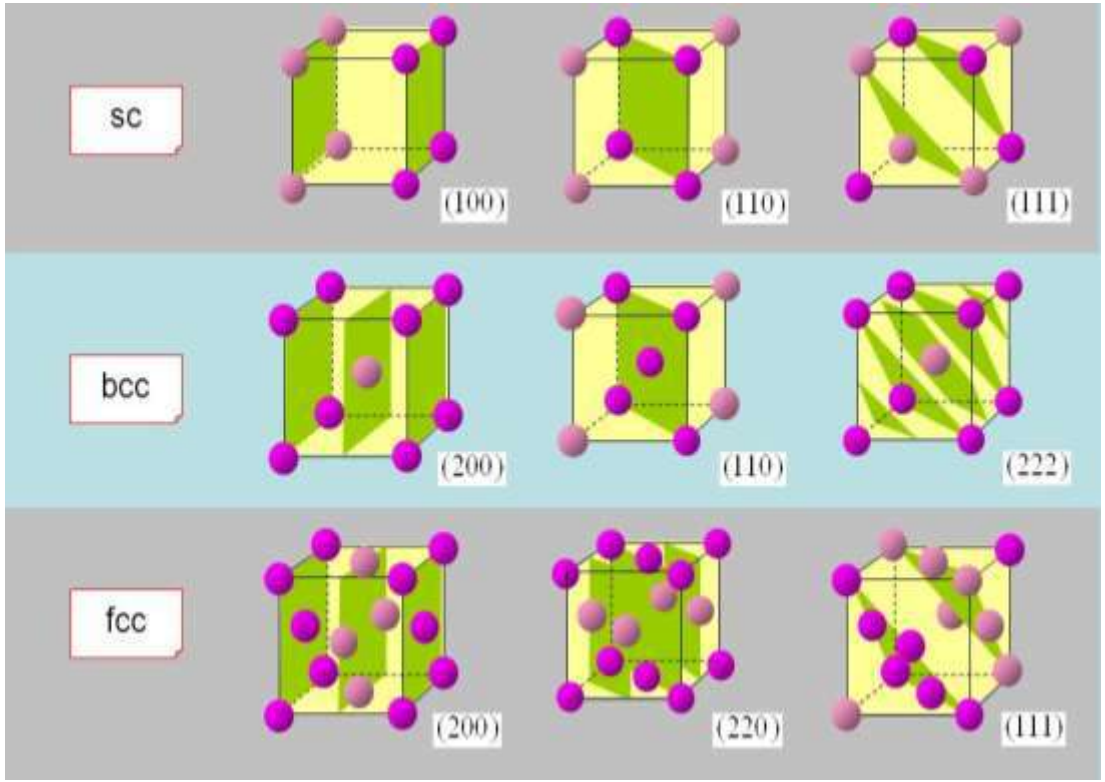
- X-rays are a form of electromagnetic radiation that have high energies and short wavelengths from (0.01-10 nm) (0.1 -100 Å) -wavelengths on the order of the atomic spacing for solids (In crystals the typical interatomic spacing ~ 2-3 Å).

- When a beam of x-rays impinges on a solid material, a portion of this beam is scattered in all directions by the electrons associated with each atom or ion that lies within the beam's path.

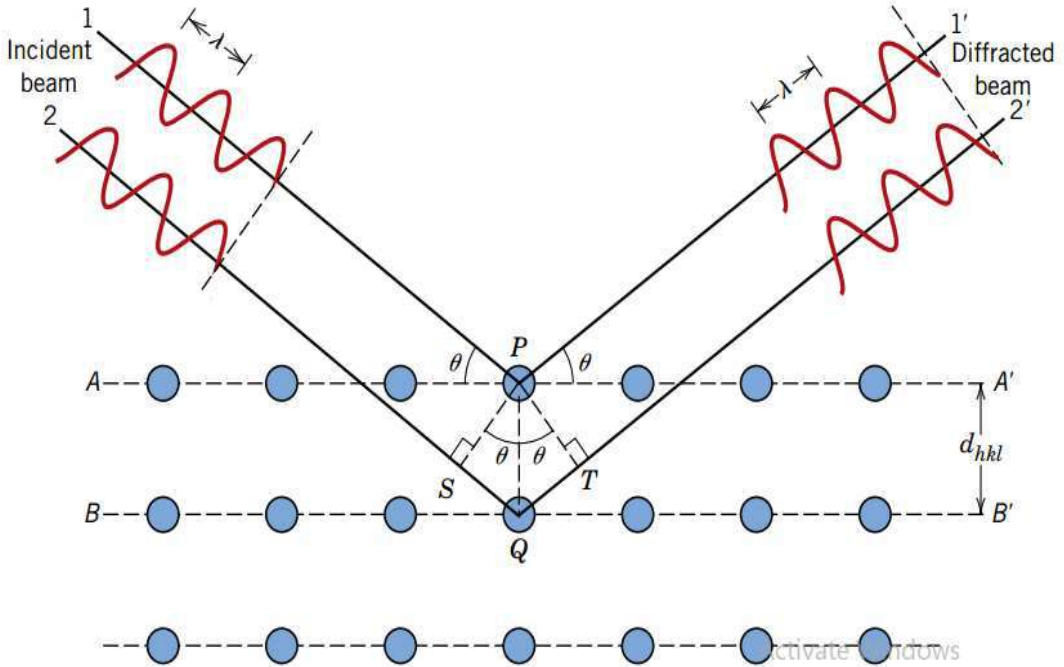



Wavelength (λ) in meters
Atom
Virus
Bacteria
Dust
Pinhead
Fingernails
Humans
10^{-12}
10^{-10}
10^{-8}
10^{-6}
10^{-4}
10^{-2}
1
Gamma rays
X rays
Ultraviolet
Infrared
Microwaves
Radio waves
10^{20}
10^{18}
10^{16}
10^{14}
10^{12}
10^{10}
10^{8}
Frequency (ν) in hertz
Visible
380 nm
3.8×10^{-7} m
500 nm
600 nm
700 nm
780 nm
7.8×10^{-7} m

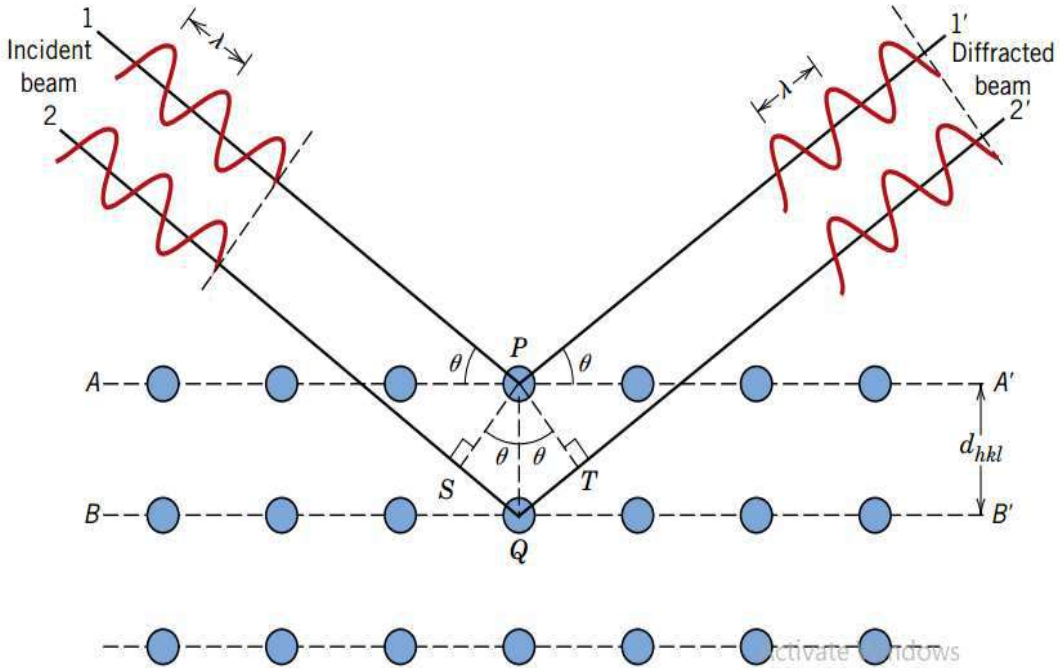
- Let us now examine the necessary conditions for diffraction of x-rays by a periodic arrangement of atoms.



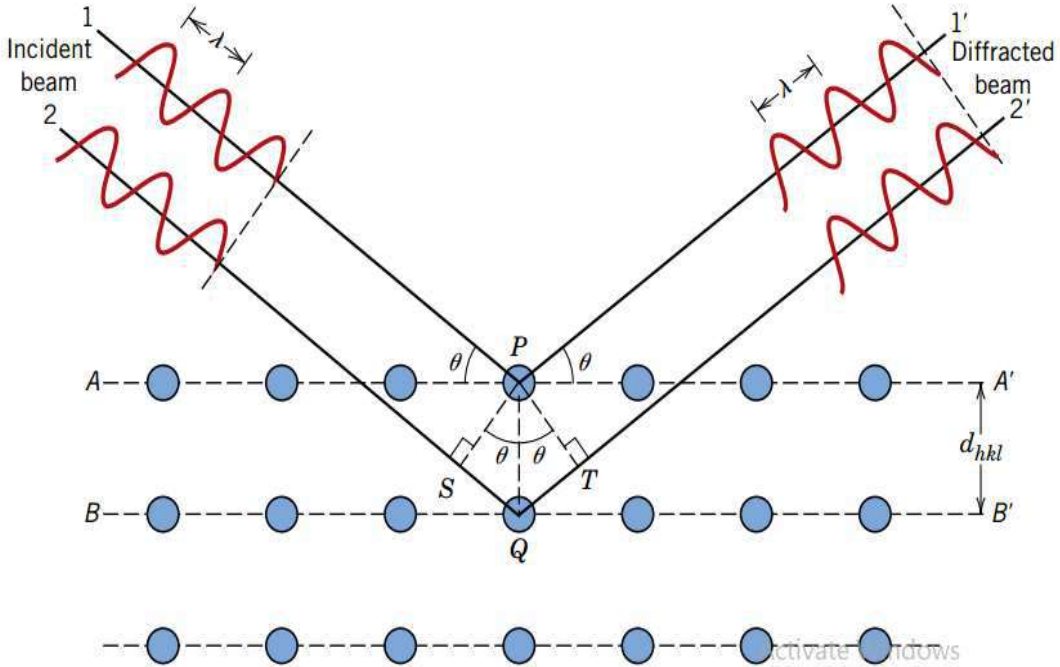
- Consider the two parallel planes of atoms $A - A'$ and $B - B'$ in Figure below which have the same $h, k, \text{and } l$ Miller indices and are separated by the interplanar spacing d_{hkl}



- 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.

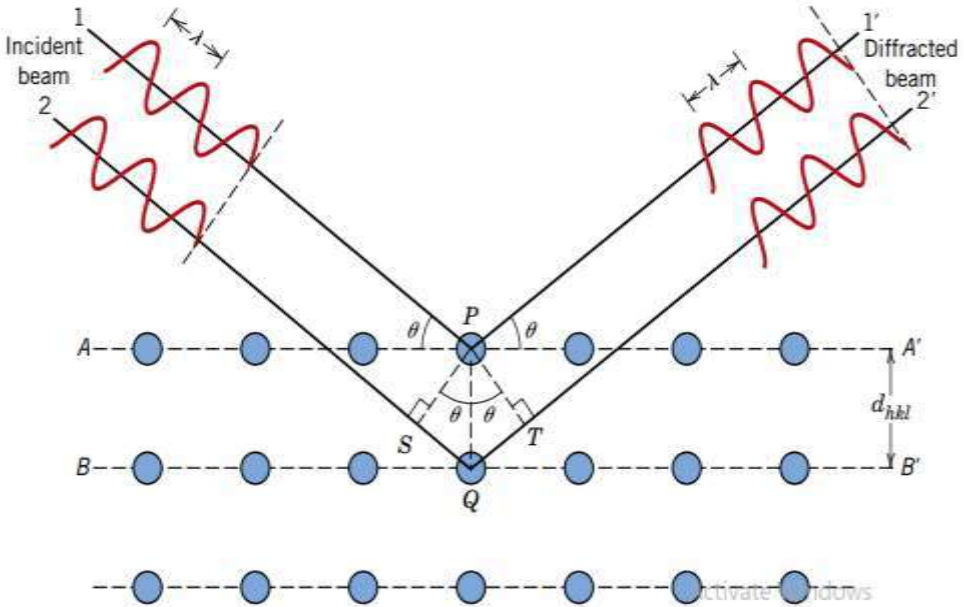


- Two rays in this beam, labeled 1 and 2, are scattered by atoms P and Q. Constructive interference of the scattered rays $1'$ and $2'$ occurs also at an angle θ to the planes



- if the path length difference between $1-P-1'$ and $2-Q-2'$ (i.e., $\overline{SQ}+\overline{QT}$) is equal to a whole number, n, of wavelengths that is, the condition for diffraction is:

$$n\lambda = \overline{SQ} + \overline{QT} \qquad \ldots\ldots\ldots (3.20)$$

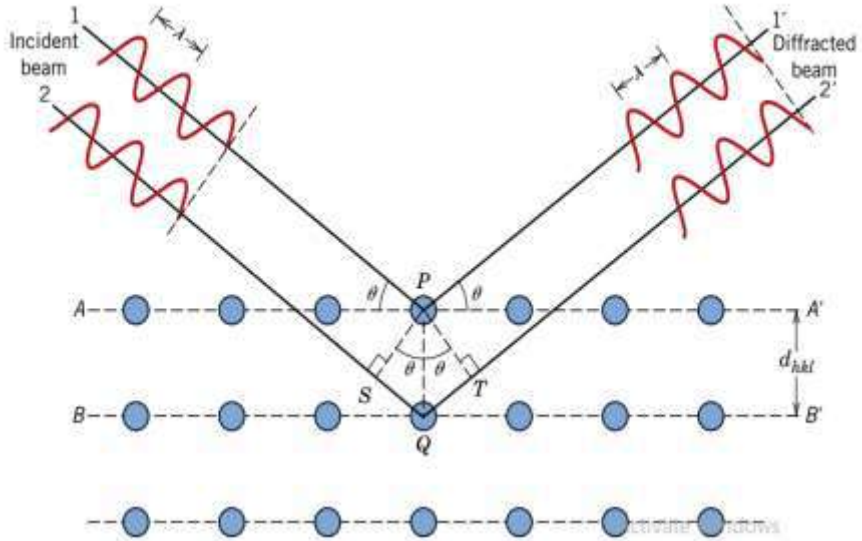


$$n\lambda = d_{hkl}\sin\theta + d_{hkl}\sin\theta$$

$$n\lambda = 2d_{hkl}\sin\theta \ldots\ldots\ldots (3.21)$$

Equation 3.21 is known as **Bragg's law**

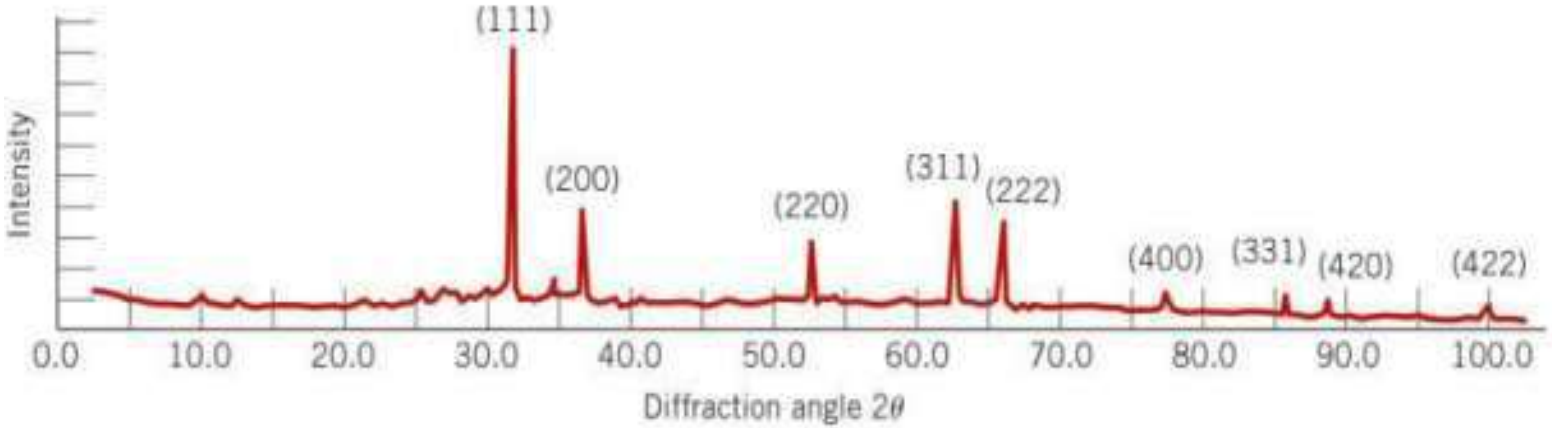
n is the order of reflection, which may be any integer (1, 2, 3, . . .) consistent with $\sin\theta$ not exceeding unity.



- Bragg's law expression relating the x-ray wavelength and interatomic spacing to the angle of the diffracted beam.

$$n\lambda = 2d_{hkl}\sin\theta \ldots\ldots\ldots (3.21)$$

- If Bragg's law is not satisfied, then the interference will be nonconstructive so as to yield a very low-intensity diffracted beam.



- The magnitude of the distance between two adjacent and parallel planes of atoms (i.e., the interplanar spacing d_{hkl}) is a function of the Miller indices ($h, k, \text{and } l$) as well as the lattice parameter(s).

For example, for crystal structures that have cubic symmetry,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \ldots\ldots\ldots (3.22)$$

a is the lattice parameter (unit cell edge length).

- Relationships similar to Equation 3.22, but more complex, exist for the other six crystal systems

Orthorhombic

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Tetragonal

$$\frac{1}{d_{hkl}^2} = \left[h^2 + k^2 + l^2\left(\frac{a}{c}\right)^2\right]\frac{1}{a^2}$$

Cubic

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

Monoclinic

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2 \sin^2\gamma} + \frac{k^2}{b^2 \sin^2\gamma} - \frac{2hk\cos\gamma}{ab\sin^2\gamma} + \frac{l^2}{c^2}$$

Hexagonal

$$\frac{1}{d_{hkl}^2} = \left[\frac{4}{3}(h^2 + k^2 + hk) + l^2\left(\frac{a}{c}\right)^2\right]\frac{1}{a^2}$$

Triclinic

$$\frac{1}{d_{hkl}^2} = \left[\frac{h}{a}\begin{vmatrix} \frac{h}{a} & \cos\gamma & \cos\beta \\ \frac{k}{b} & 1 & \cos\alpha \\ \frac{l}{c} & \cos\alpha & 1 \end{vmatrix} + \frac{k}{b}\begin{vmatrix} 1 & \frac{h}{a} & \cos\alpha \\ \cos\gamma & \frac{k}{b} & \cos\alpha \\ \cos\beta & \frac{l}{c} & 1 \end{vmatrix} + \frac{l}{c}\begin{vmatrix} 1 & \cos\gamma & \frac{h}{a} \\ \cos\gamma & 1 & \frac{k}{b} \\ \cos\beta & \cos\alpha & \frac{l}{c} \end{vmatrix}\right] \cdot \begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}^{-1}$$

Trigonal (rhombohedral)

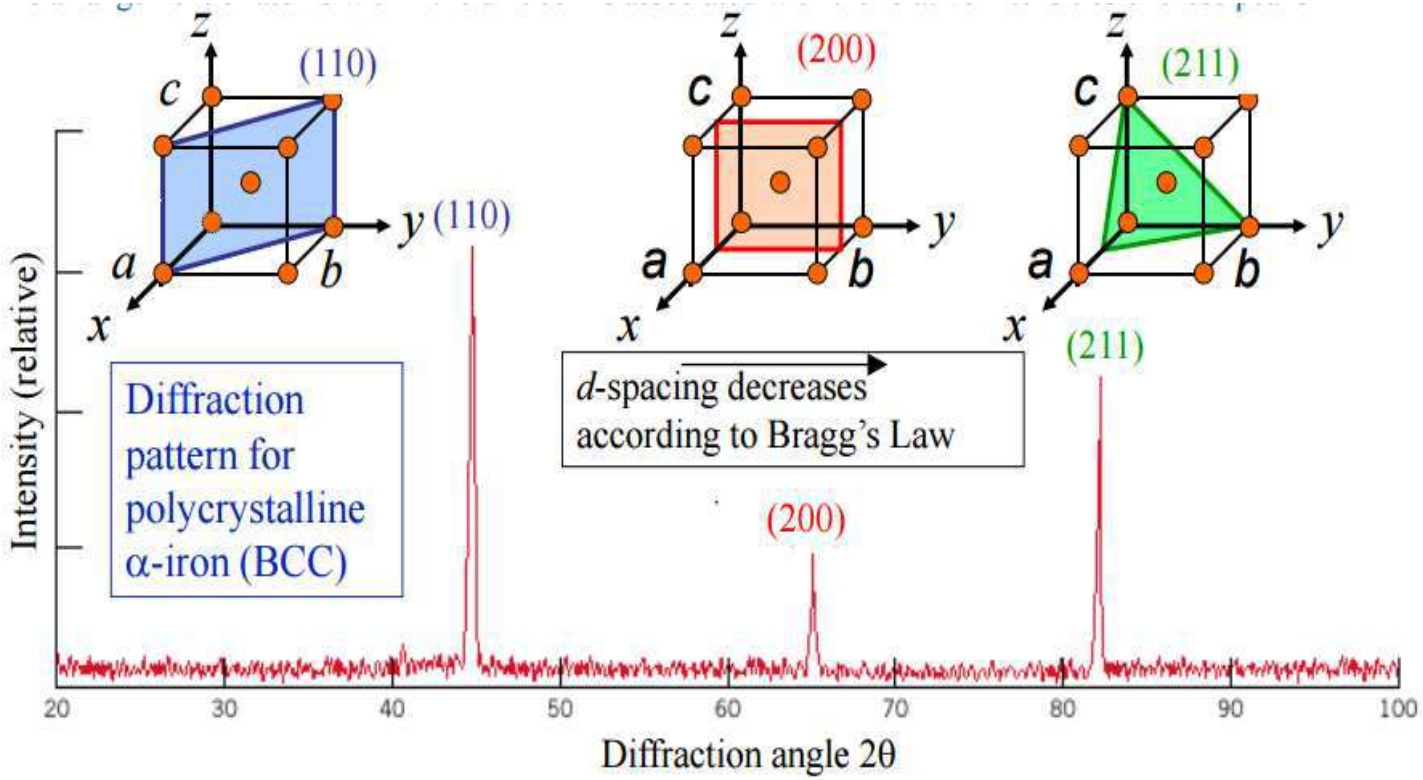
$$\frac{1}{d_{hkl}^2} = \frac{[(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + lh)(\cos^2\alpha - \cos\alpha)]}{A^2(1 + 2\cos^3\alpha - 3\cos^2\alpha)}$$

- Bragg's law, $n\lambda = 2d_{hkl}\sin\theta$ ... ... (3.21)

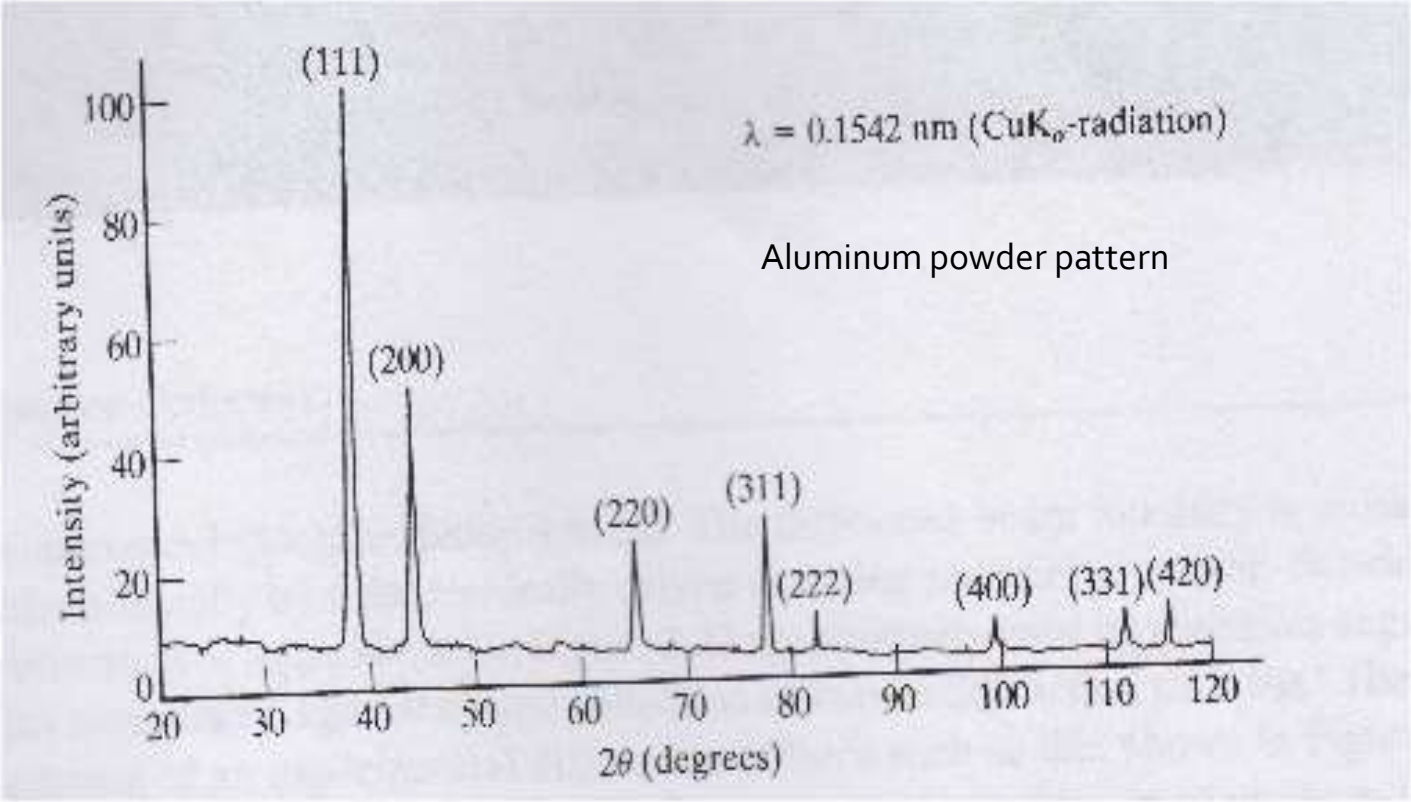
is a necessary but not sufficient condition for diffraction by real crystals.

- It specifies when diffraction will occur for unit cells having atoms positioned only at cell corners.
- However, atoms situated at other sites (e.g., face and interior unit cell positions as with FCC and BCC) act as extra scattering centers, which can produce out-of-phase scattering at certain Bragg angles.
- The net result is the absence of some diffracted beams that, according to Equation 3.21, should be present.

- For the BCC crystal structure, $h + k + l$ must be even if diffraction is to occur



- for FCC, $h, k, \text{and } l$ must all be either odd or even



- ***reflection rules***, are summarized in Table below
- Zero is considered to be an even integer

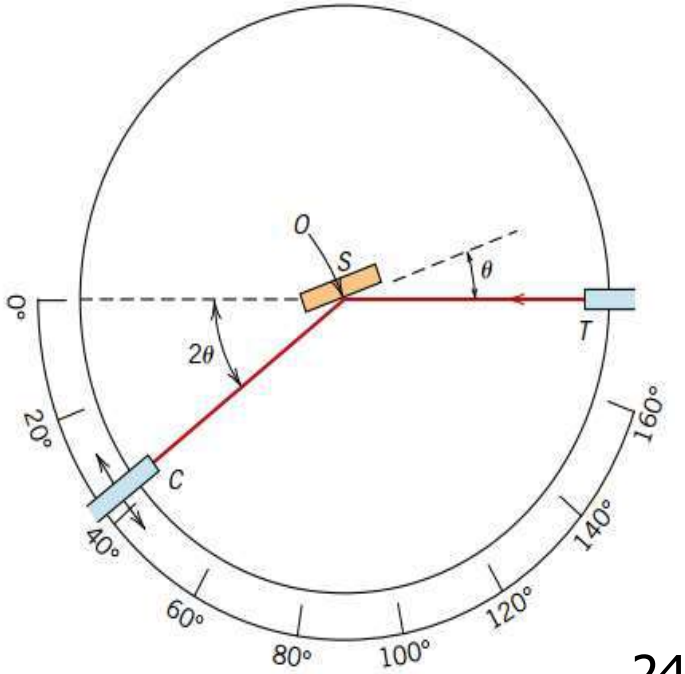
Crystal Structure	*Reflections Present*	*Reflection Indices for First Six Planes*
BCC	$(h + k + l)$ even	110, 200, 211, 220, 310, 222
FCC	h, k, and l either all odd or all even	111, 200, 220, 311, 222, 400
Simple cubic	All	100, 110, 111, 200, 210, 211

Diffraction Techniques

- One common diffraction technique employs a powdered or polycrystalline specimen consisting of many fine and randomly oriented particles that are exposed to monochromatic x-radiation.
- Each powder particle (or grain) is a crystal, and having a large number of them with random orientations ensures that some particles are properly oriented such that every possible set of crystallographic planes will be available for diffraction.

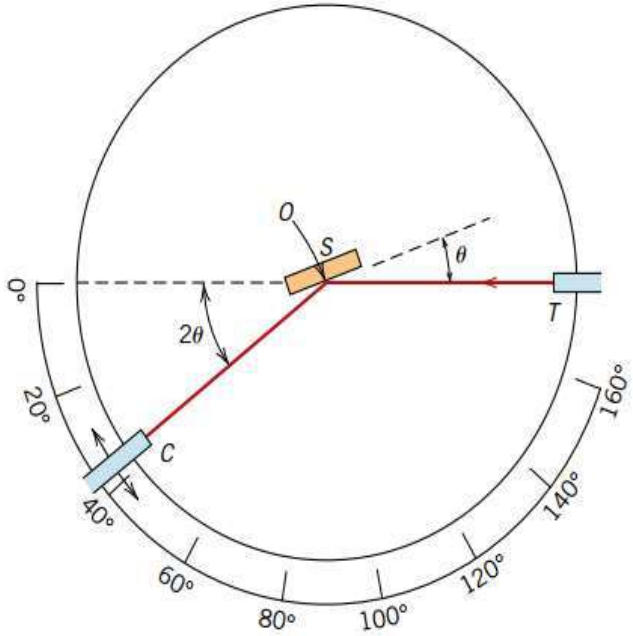
- The **diffractometer** is an instrument used to determine the angles at which diffraction occurs for powdered specimens; its features are represented schematically in Figure below:

T is the monochromatic x-ray source
S is the sample
C is the detector (the intensities of diffracted beams are detected with a counter labeled C)
O is the axis around which the sample and detector rotate (this axis is perpendicular to the plane of the page).

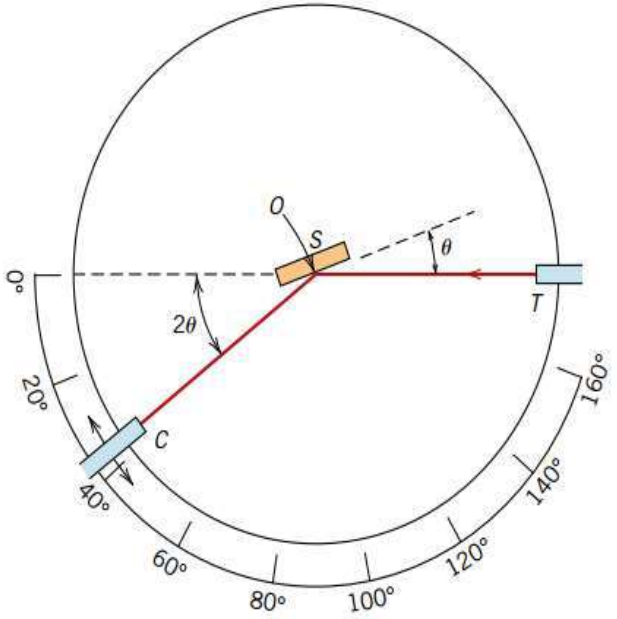


- The counter is mounted on a movable carriage that may also be rotated about the *O* axis; its angular position in terms of 2θ is marked on a graduated scale.

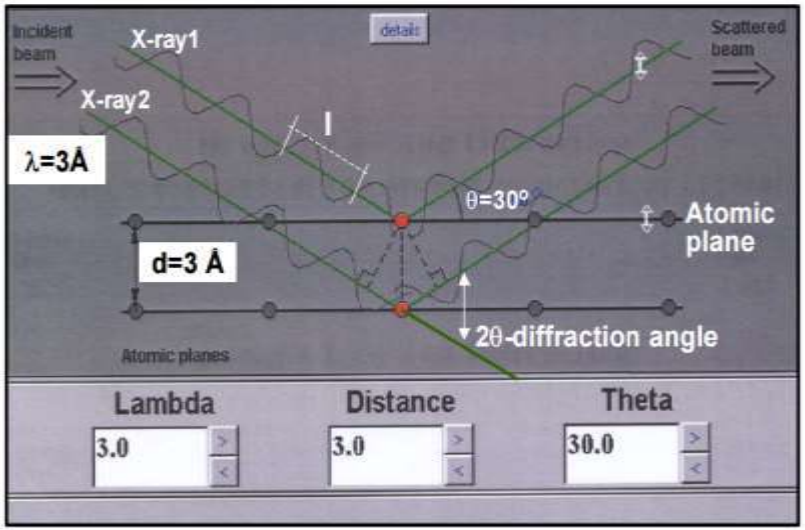
- Carriage and specimen are <u>mechanically coupled</u> such that a rotation of the specimen through θ is accompanied by a 2θ rotation of the counter; this <u>ensures</u> that the incident and reflection angles are maintained equal to one another



- Collimators (a device for producing a parallel beam of rays or radiation)are incorporated within the beam path to produce a well-defined and focused beam.
- Utilization of a filter provides a near-monochromatic beam.



- As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a function of 2θ
- 2θ is termed the *diffraction angle*, which is measured experimentally.

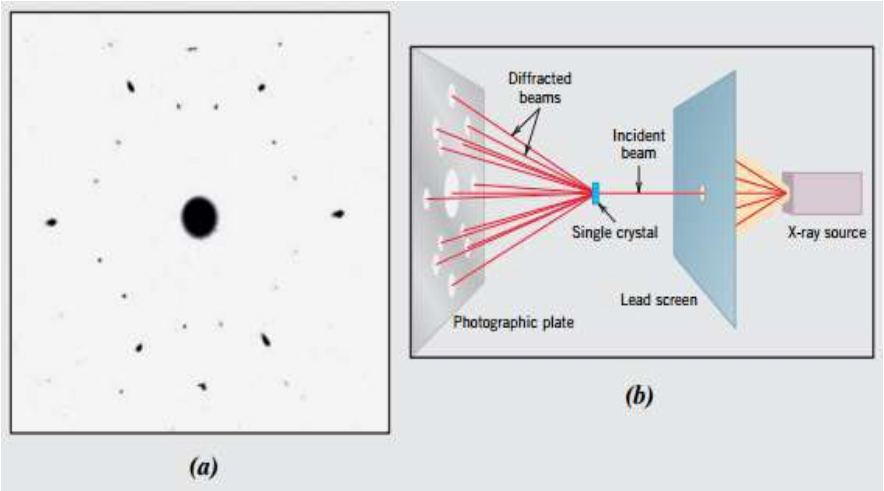


One of the primary uses of x-ray diffractometry is for the

- determination of crystal structure.
- The unit cell size and geometry
- the arrangement of atoms within the unit cell is associated with the relative intensities of these peaks.
- qualitative and quantitative chemical identifications
- determination of residual stresses and crystal size.

- X-rays, as well as electron and neutron beams, are also used in other types of material investigations.

For example, crystallographic orientations of single crystals are possible using x-ray diffraction (or Laue) photographs.



(*a*) X-ray diffraction photograph [or Laue photograph for a single crystal of magnesium. (*b*) Schematic diagram illustrating how the spots (i.e., the diffraction pattern) in (*a*) are

EXAMPLE PROBLEM
Interplanar Spacing and Diffraction Angle Computations

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. Assume that monochromatic radiation having a wavelength of 0.1790 nm is used, and the order of reflection is 1.

Solution

(a)

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad \ldots\ldots\ldots (3.22)$$

$$d_{hkl} = \frac{0.2866\ nm}{\sqrt{2^2 + 2^2 + 0^2}} = 0.1013\ m$$

(b)

$$n\lambda = 2d_{hkl}\sin\theta \ldots\ldots\ldots (3.21)$$

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

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

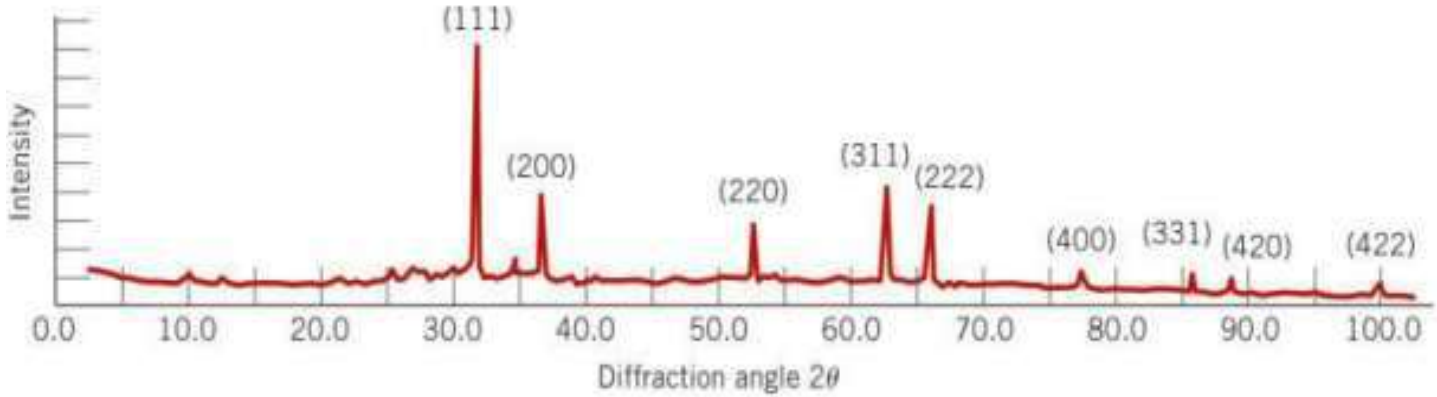
The diffraction angle is 2θ, or

$$2\theta = 2 \times 62.13^{\circ} = 124.26^{\circ}$$

EXAMPLE PROBLEM

Interplanar Spacing and Lattice Parameter Computations for Lead

Figure 3.24 shows an x-ray diffraction pattern for lead taken using a diffractometer and monochromatic x-radiation having a wavelength of 0.1542 nm; each diffraction peak on the pattern has been indexed. Compute the interplanar spacing for each set of planes indexed; also, determine the lattice parameter of Pb for each of the peaks. For all peaks, assume the order of diffraction is 1



Solution

For each peak, in order to compute the interplanar spacing and the lattice parameter we must employ Equations 3.21 and 3.22, respectively. The first peak of Figure 3.24, which results from diffraction by the (111) set of planes, occurs at $2\theta = 31.3°$; the corresponding interplanar spacing for this set of planes, using Equation 3.21, is equal to

$$d_{111} = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.1542\text{ nm})}{(2)\left[\sin\left(\frac{31.3°}{2}\right)\right]} = 0.2858\text{ nm}$$

And, from Equation 3.22, the lattice parameter a is determined as

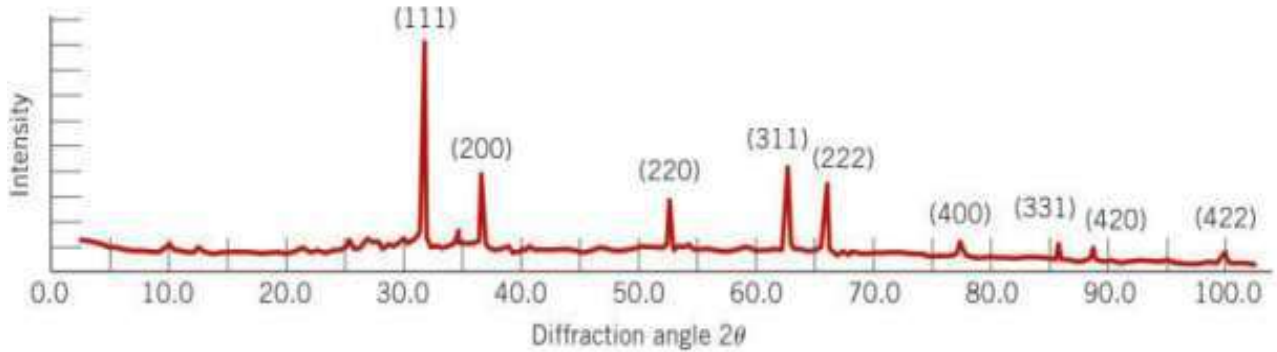
$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2}$$

$$= d_{111}\sqrt{(1)^2 + (1)^2 + (1)^2}$$

$$= (0.2858\text{ nm})\sqrt{3} = 0.4950\text{ nm}$$

Similar computations are made for the next four peaks; the results are tabulated below:

Peak Index	*2θ*	d_{hkl}*(nm)*	*a(nm)*
200	36.6	0.2455	0.4910
220	52.6	0.1740	0.4921
311	62.5	0.1486	0.4929
222	65.5	0.1425	0.4936



RECIPROCAL SPACE

- Reciprocal Lattice: Reciprocal vectors are defined to be perpendicular to two of the three lattice vectors and with length equal to 1/length of the third vector.

We construct the axis vectors a^*, b^*, c^* of the **reciprocal lattice**:

$$a^* = 2\pi \frac{b \times c}{a \cdot b \times c} \quad ; \quad b^* = 2\pi \frac{c \times a}{a \cdot b \times c} \quad ; \quad c^* = 2\pi \frac{a \times b}{a \cdot b \times c} \ldots\ldots (3.23)$$

- The factors 2π are not used by crystallographers but are convenient in solid state physics.
- The reciprocal lattice is a lattice in the Fourier space associated with the crystal

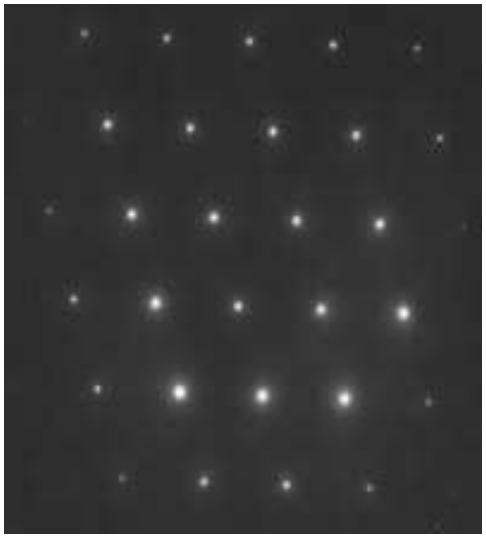
Points in the reciprocal lattice are mapped by the set of vectors

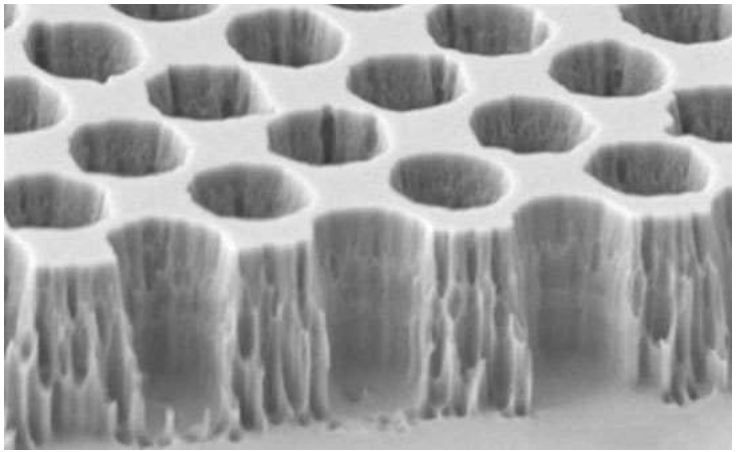
$\mathbf{G} = v_1 a^* + v_2 b^* + v_3 c^*$ ... ...(15)

where v_1, v_2, v_3 are integers.

A vector $\mathbf{G}$ of this form is a **reciprocal lattice vector**.

- A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal.
- A microscope image, if it could be resolved on a fine enough scale, is a map of the crystal structure in real space.

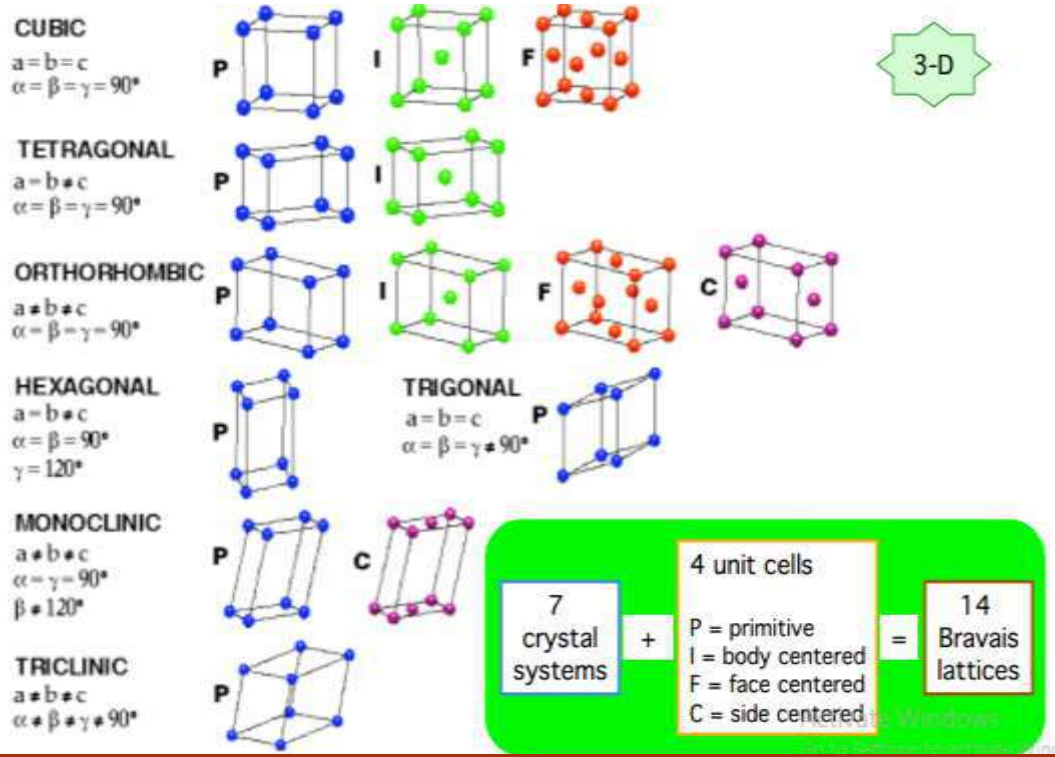




Brillouin zone

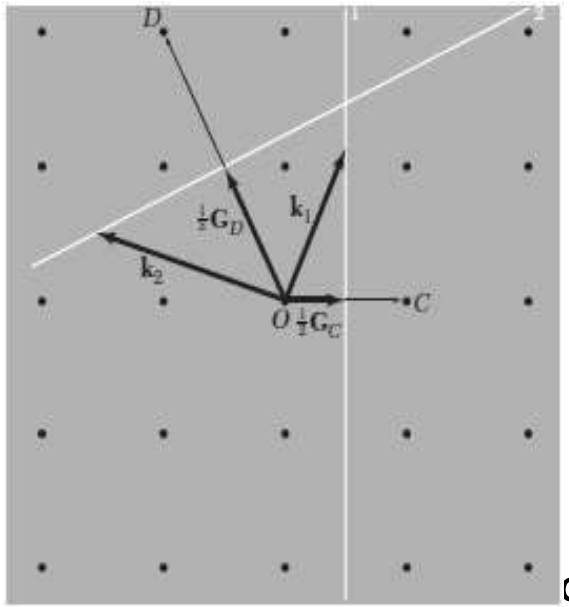
A **Brillouin zone** is defined as a Wigner-Seitz primitive cell in the reciprocal lattice.

- primitive cell is a minimum volume cell (a unit cell) corresponding to a single lattice point of a structure

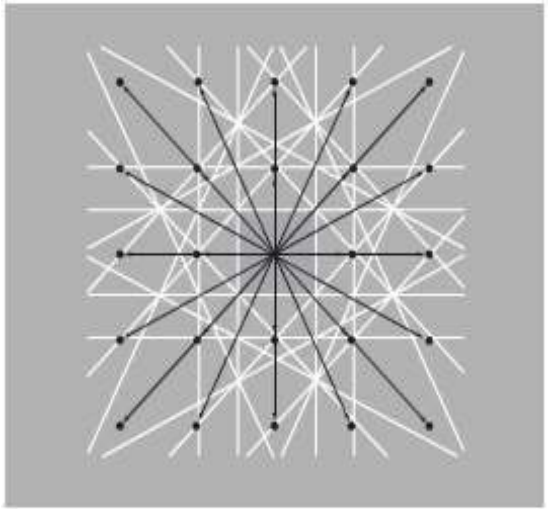


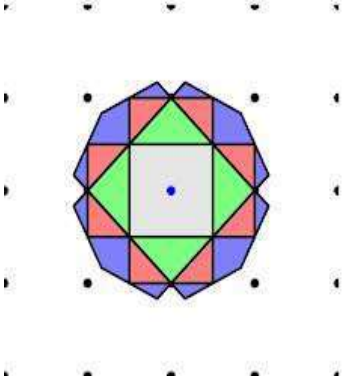
We now work in reciprocal space, the space of the **k**'s and **G**'s. Select a vector **G** from the origin to a reciprocal lattice point.

- Reciprocal lattice points near the point O at the origin of the reciprocal lattice.
- The reciprocal lattice vector $\mathbf{G}_C$ connects points OC; and $\mathbf{G}_D$ connects OD.
- Two planes 1 and 2 are drawn which are the perpendicular bisectors of $\mathbf{G}_C$ and $\mathbf{G}_D$, respectively.

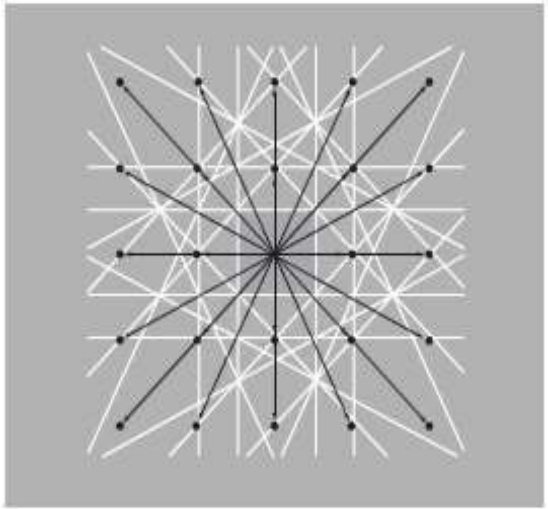


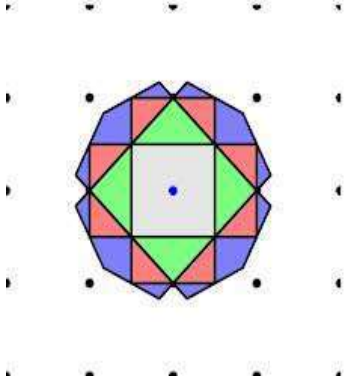
- These planes divide the Fourier space of the crystal into fragments, as shown in Figure below for a square lattice. The central square is a primitive cell of the reciprocal lattice. It is a Wigner-Seitz cell of the reciprocal lattice it call the **first Brillouin zone**.





The **first Brillouin zone** is the smallest volume entirely enclosed by planes that are the perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.

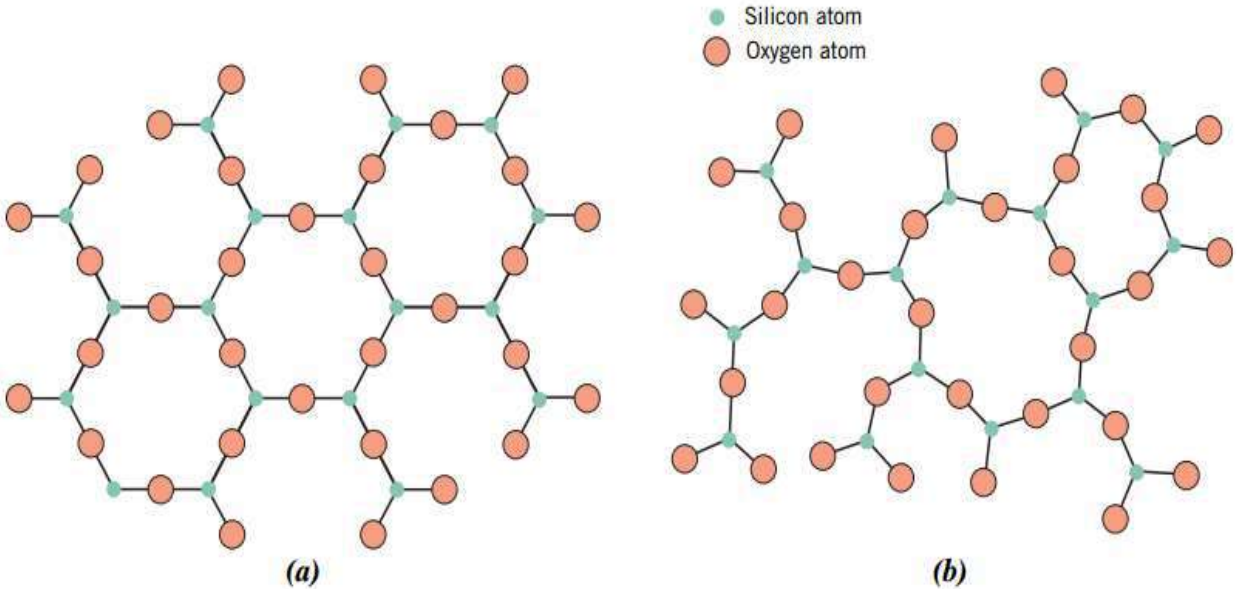




NONCRYSTALLINE SOLIDS

- A **noncrystalline** solids lack a systematic and regular arrangement of atoms over relatively large atomic distances.

Sometimes such materials are also called **amorphous** (meaning literally “without form”).



Two-dimensional schemes of the structure of
(a) crystalline silicon dioxide and
(b) (*b*) noncrystalline silicon dioxide.

- Metals normally form crystalline solids.
- Some ceramic materials are crystalline, whereas others (the inorganic glasses) are amorphous.
- Polymers may be completely noncrystalline or semicrystalline consisting of varying degrees of crystallinity.

Thank you for your attention

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