Lecture C4b
Microscopic to Macroscopic, Part 4:
X-Ray Diffraction and Crystal Packing

X-ray Diffraction

Max von Laue won the 1914 Nobel Prize "for his discovery of the diffraction of x-rays by crystals."

His measurements showed that x-rays were photons, and additional value of his work came in the relation of the x-ray diffraction patterns to crystal structure.

He later went on to direct the *Fritz Haber Institute* in Berlin in 1951.

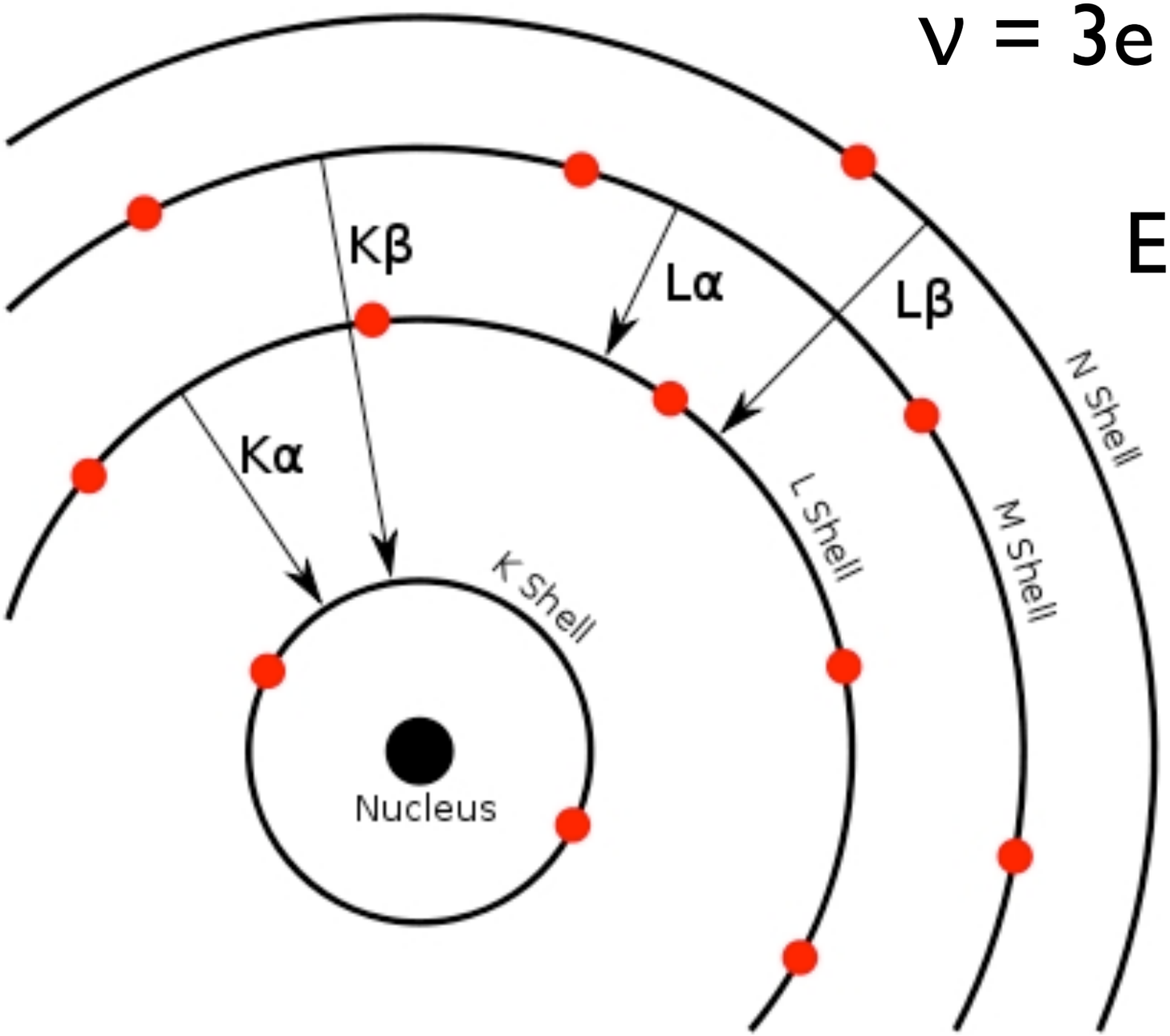
Max von Laue (1879-1960)

X-Rays are photons:

λ = 10 nm to 10 pm

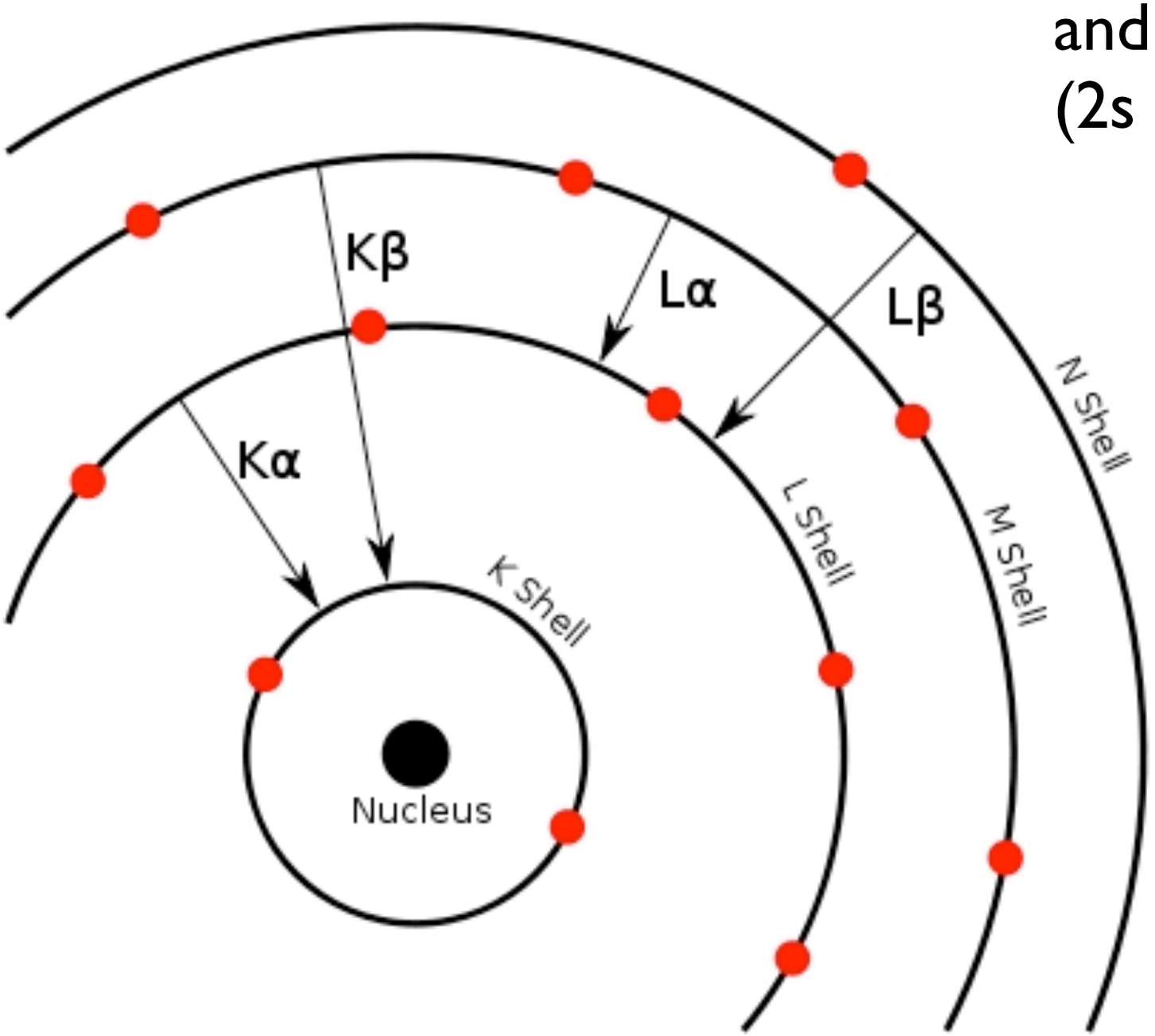
ν = 3e16 to 3e19 Hz.

E = 124 ev to 124 keV



X-Rays are created by ejection of a 1s electron followed by filling from a higher shell.

X-Rays are photons:



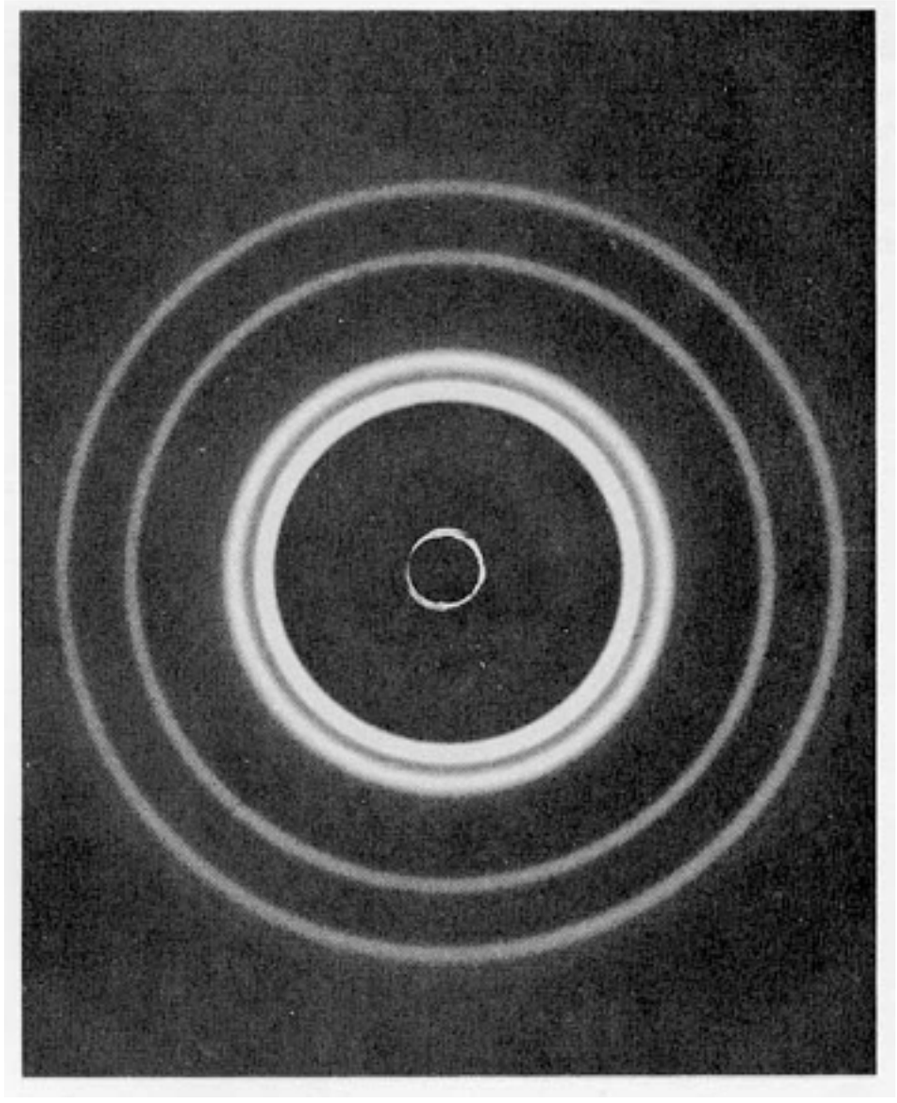
The transitions are labelled K if the final state is n=1 (1s), and L if the final state is n=2 (2s or 2p).

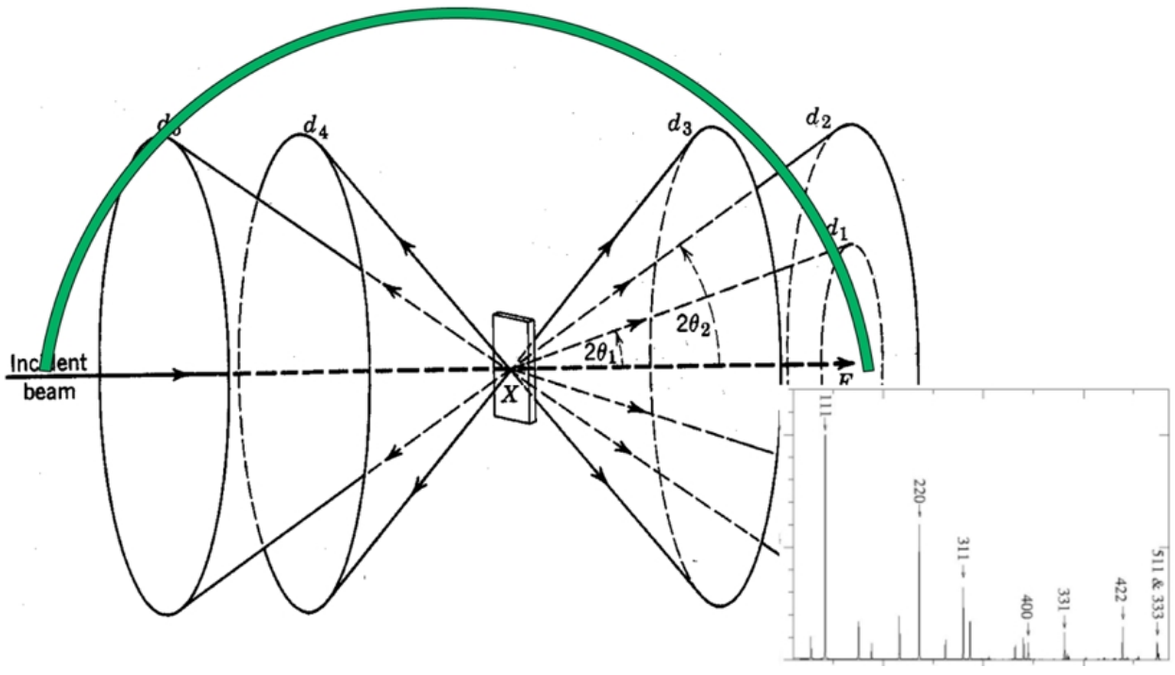
The transitions are sub-labelled α β γ... based on the initial state of the electron that is filling the hole.

X-ray Diffraction

A monochromatic x-ray beam passing through an Al foil creates a pattern of rings on a photographic plate.

These diffraction rings are observed at specific angles relative to the crystal surface.

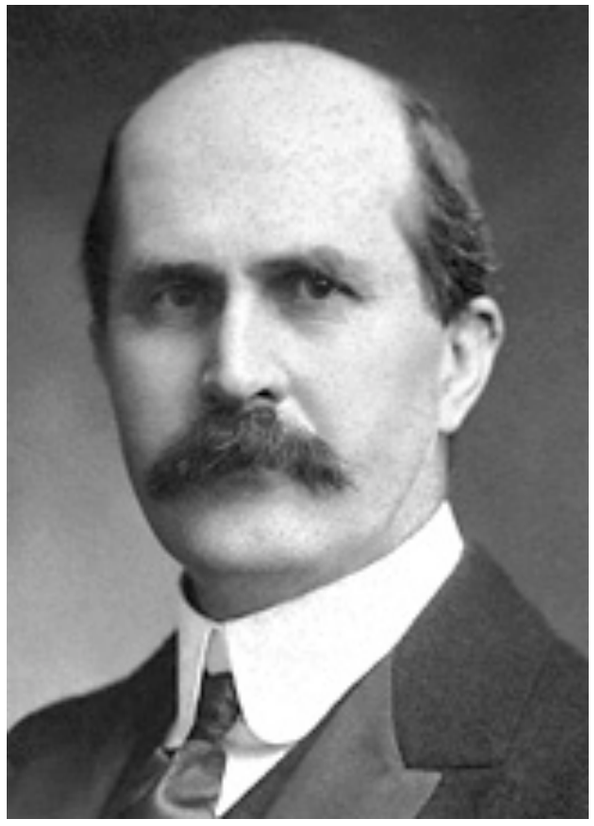




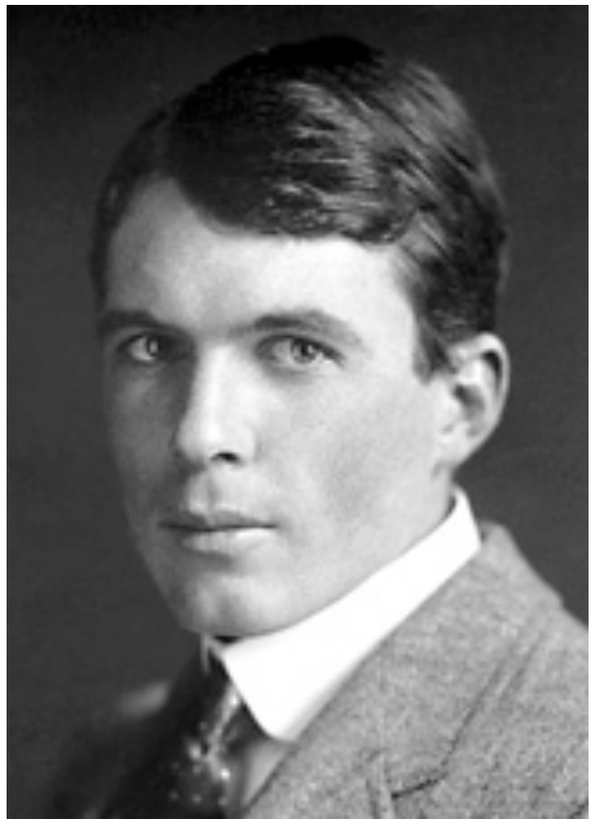
The W. H. Bragg/W L. Bragg father and son team won the 1915 Nobel Prize (the very next year) for providing a quantitative understanding of these diffraction patterns.

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

where
n = integer order of diffraction.
λ= wavelength,
d = crystal spacing,
θ = angle of x-rays relative to surface.

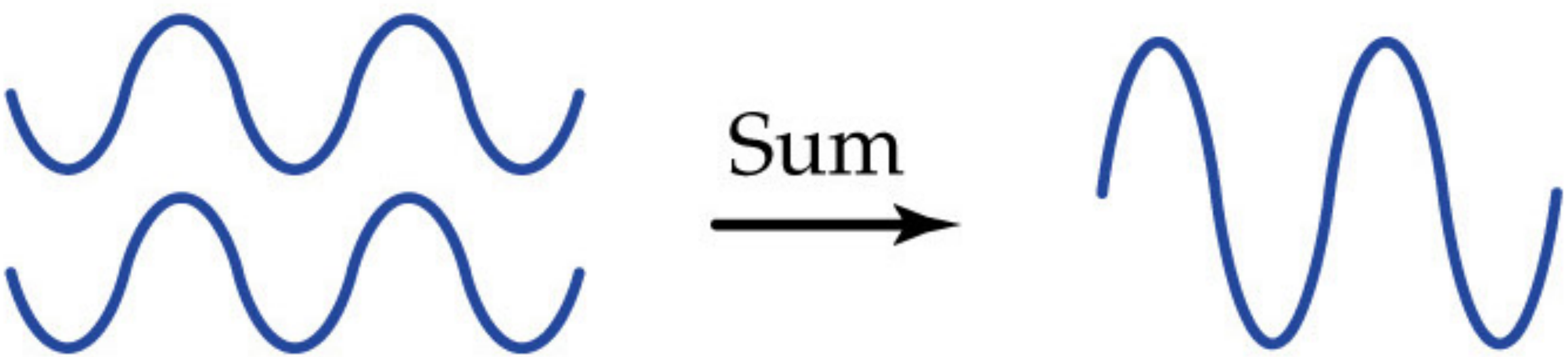


William H. Bragg
(1862 – 1942)

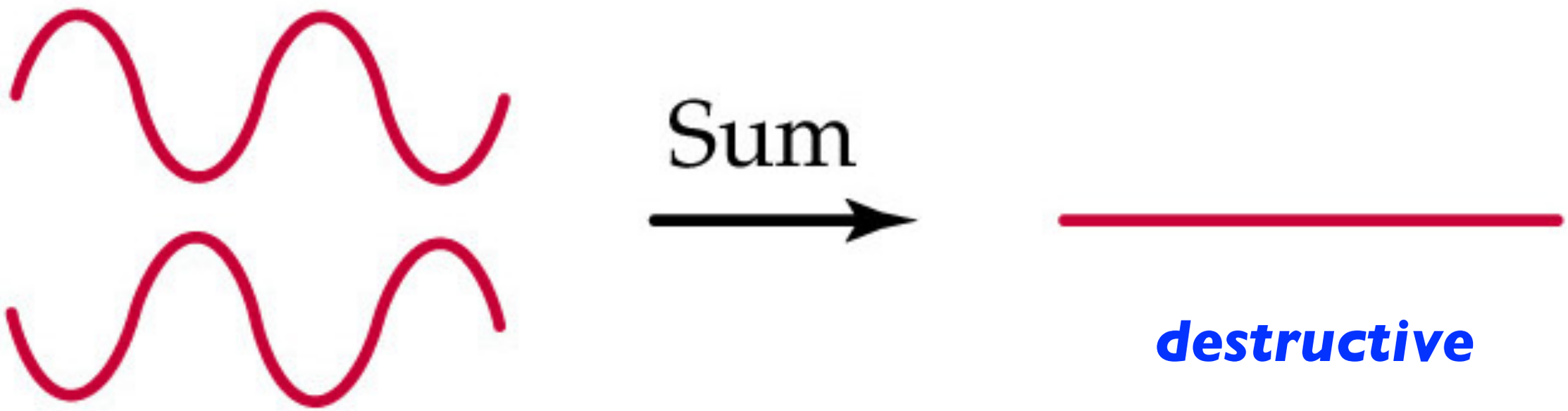


William L. Bragg
(1890 – 1971)

To understand the Bragg equation, let's first remember the concepts of ***constructive*** *and* ***destructive*** *interference:*

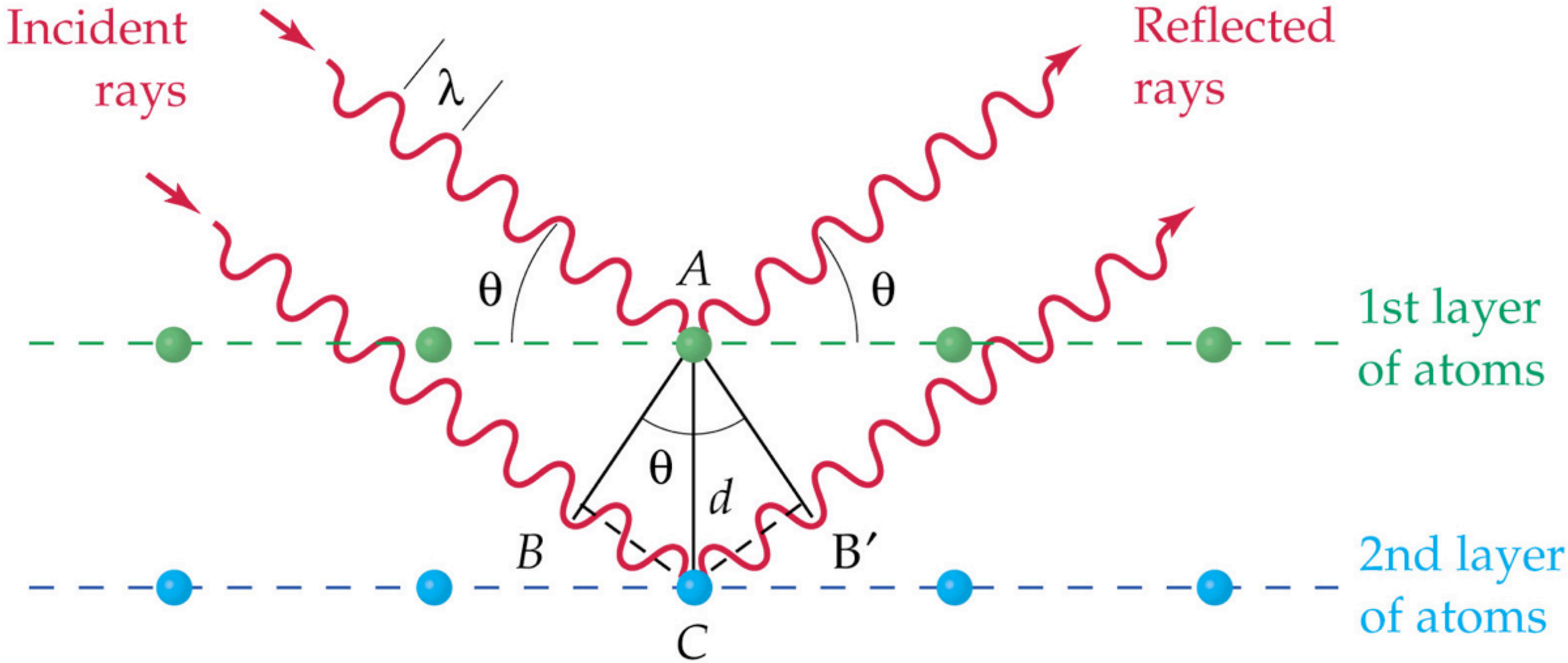


constructive



destructive

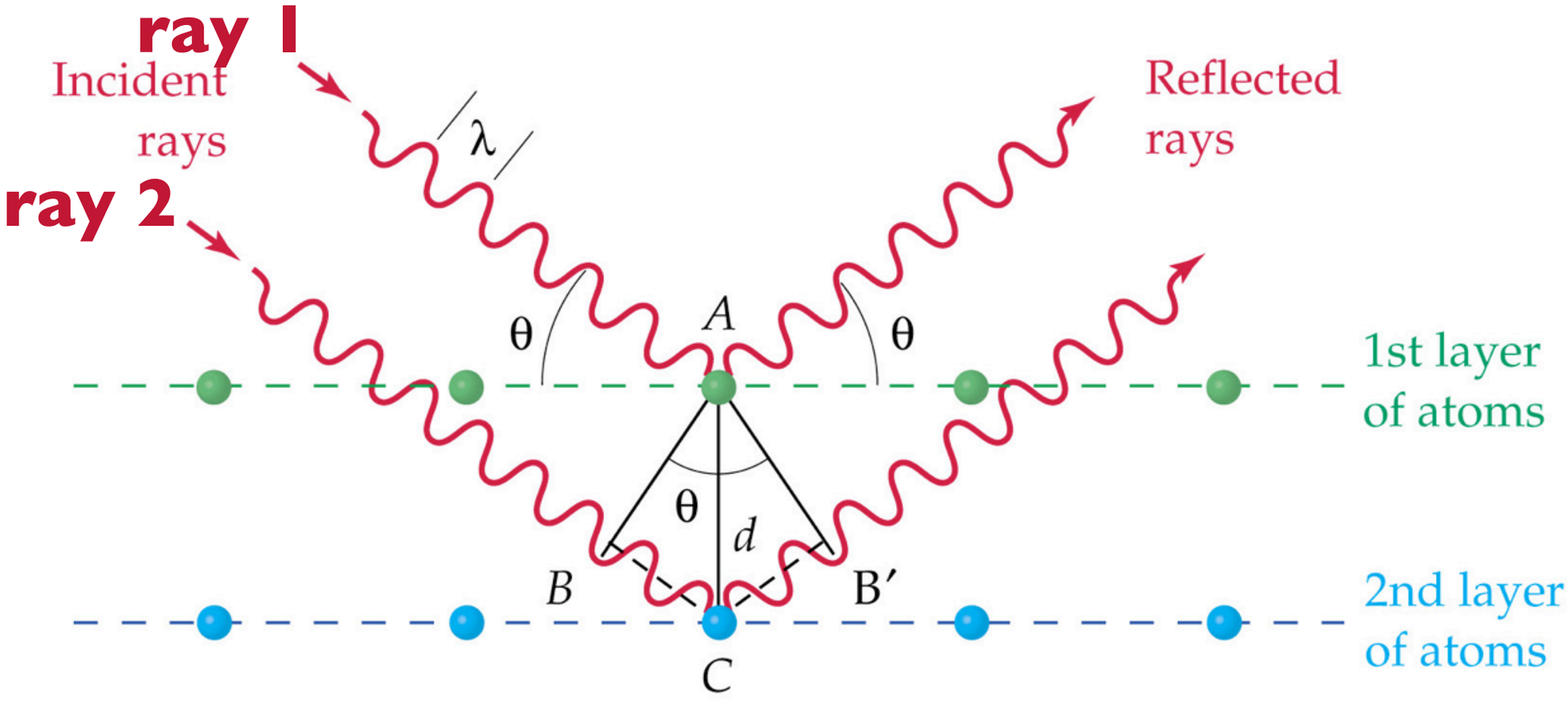
Bragg Diffraction



Constructive interference between x-rays reflected from two adjacent atomic layers leads to angle dependent diffraction.

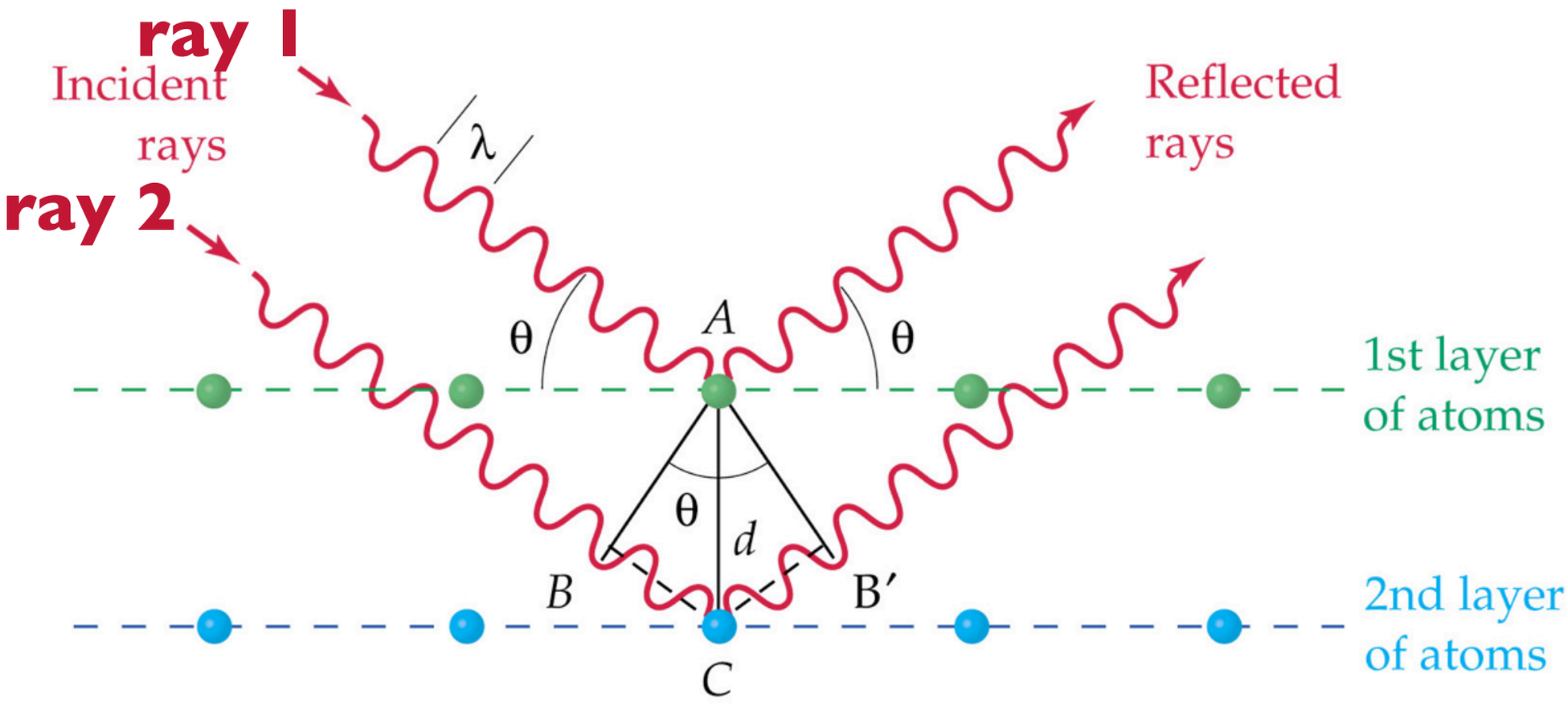
Let's derive the Bragg Eq.:

1. Compared to ray 1, ray 2 travels an extra distance BC + CB' = 2BC.



Let's derive the Bragg Eq.:

1. Compared to ray 1, ray 2 travels an extra distance BC + CB' = 2BC.
2. This extra distance must equal a multiple of λ in order for the interference with ray 1 to be constructive: $n\lambda = 2BC$.



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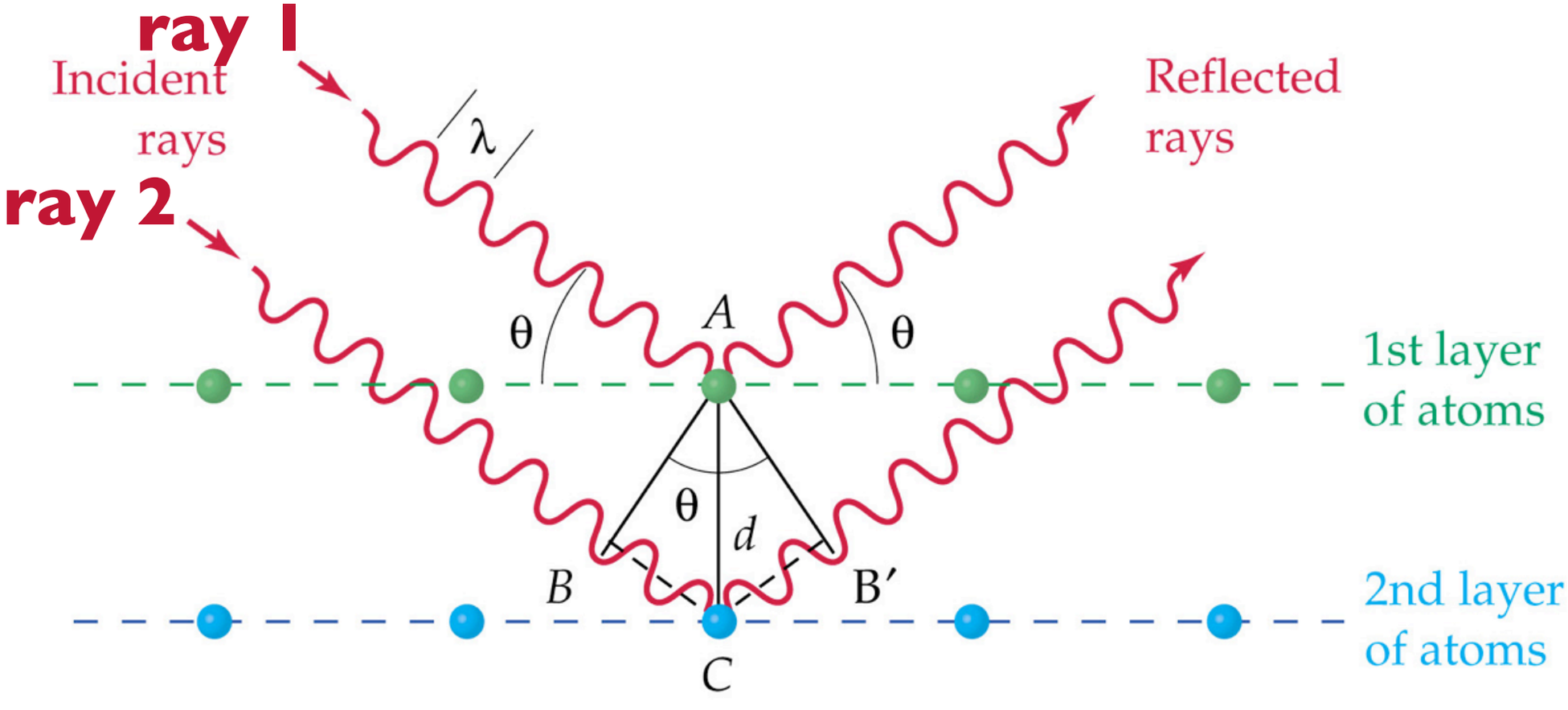
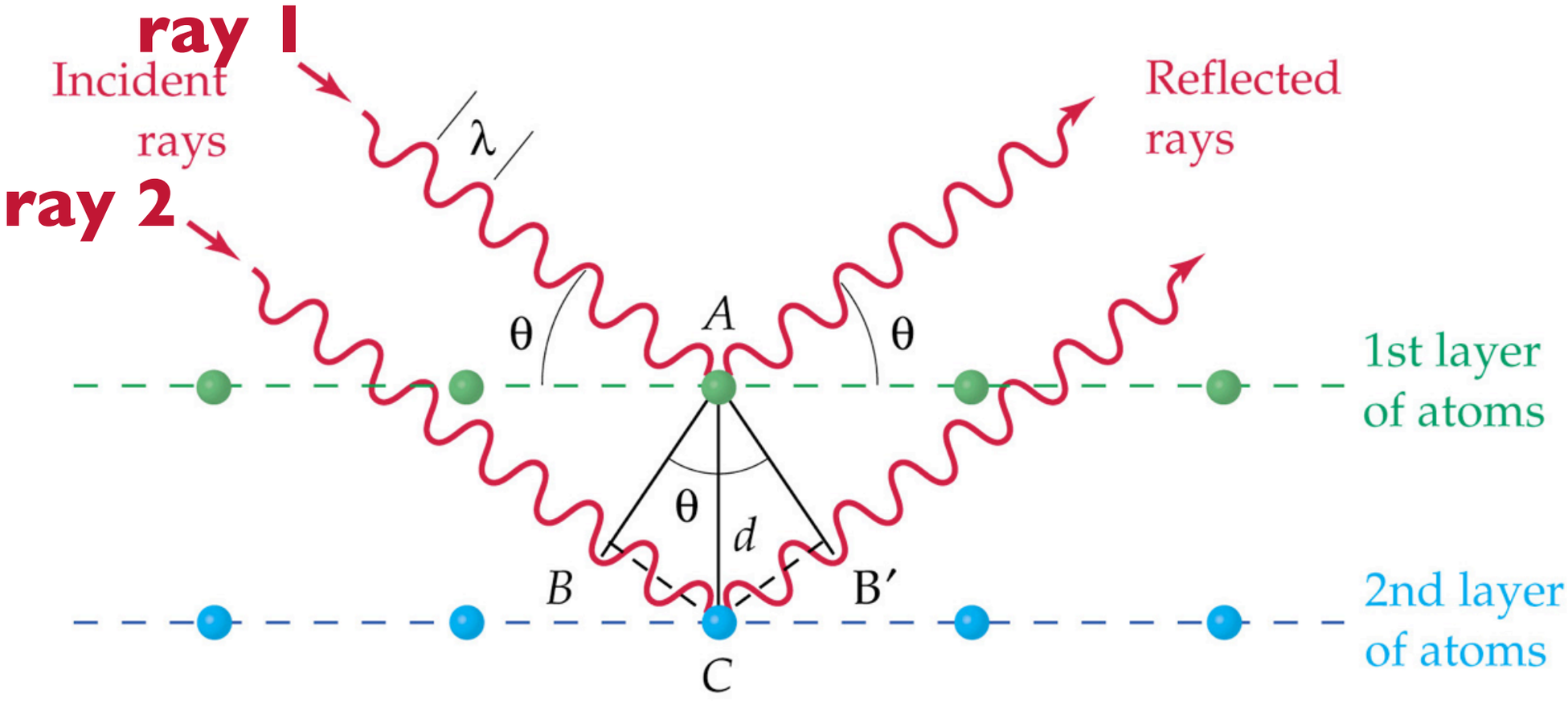
3. Since AC is the hypothenuse of a right triangle ABC, $BC = d\sin\theta$.

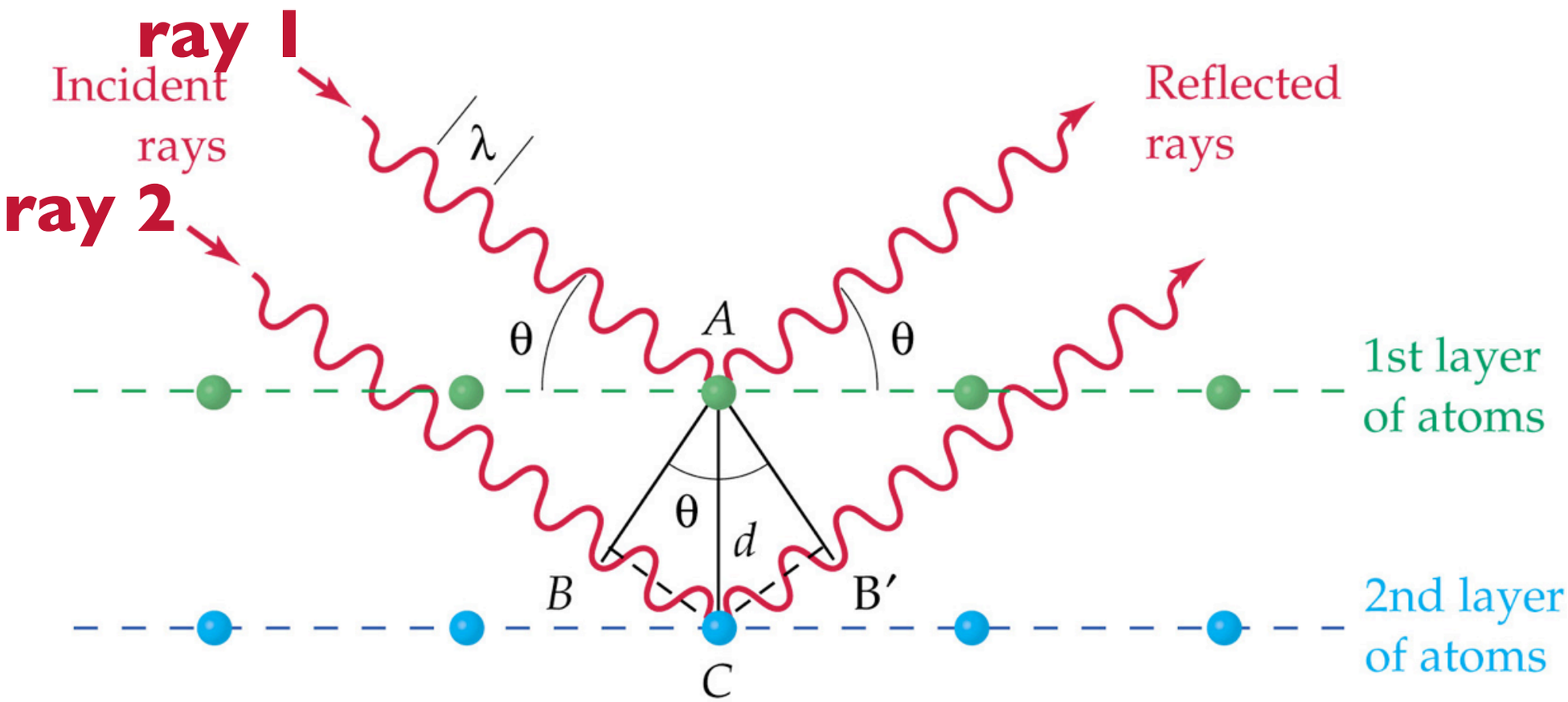


Let's derive the Bragg Eq.:

1. Compared to ray 1, ray 2 travels an extra distance BC + CB' = 2BC.
2. This extra distance must equal a multiple of λ in order for the interference with ray 1 to be constructive: $n\lambda = 2BC$
3. Since AC is the hypothenuse of a right triangle ABC, $BC = d\sin\theta$.
4. So, $\mathbf{n\lambda} = 2BC = \mathbf{2d\sin\theta}$ Q.E.D.



Thus, when $2d\sin\theta = n\lambda$, there is **constructive** interference.



Let's do an example:

A polycrystalline sample scatters a beam of x-rays of wavelength 0.7093Å at an angle of 2Θ of 14.66°. If this is a second-order Bragg reflection (n=2), compute the distance between the parallel planes of atoms from which the scattered beam appears to have been reflected.

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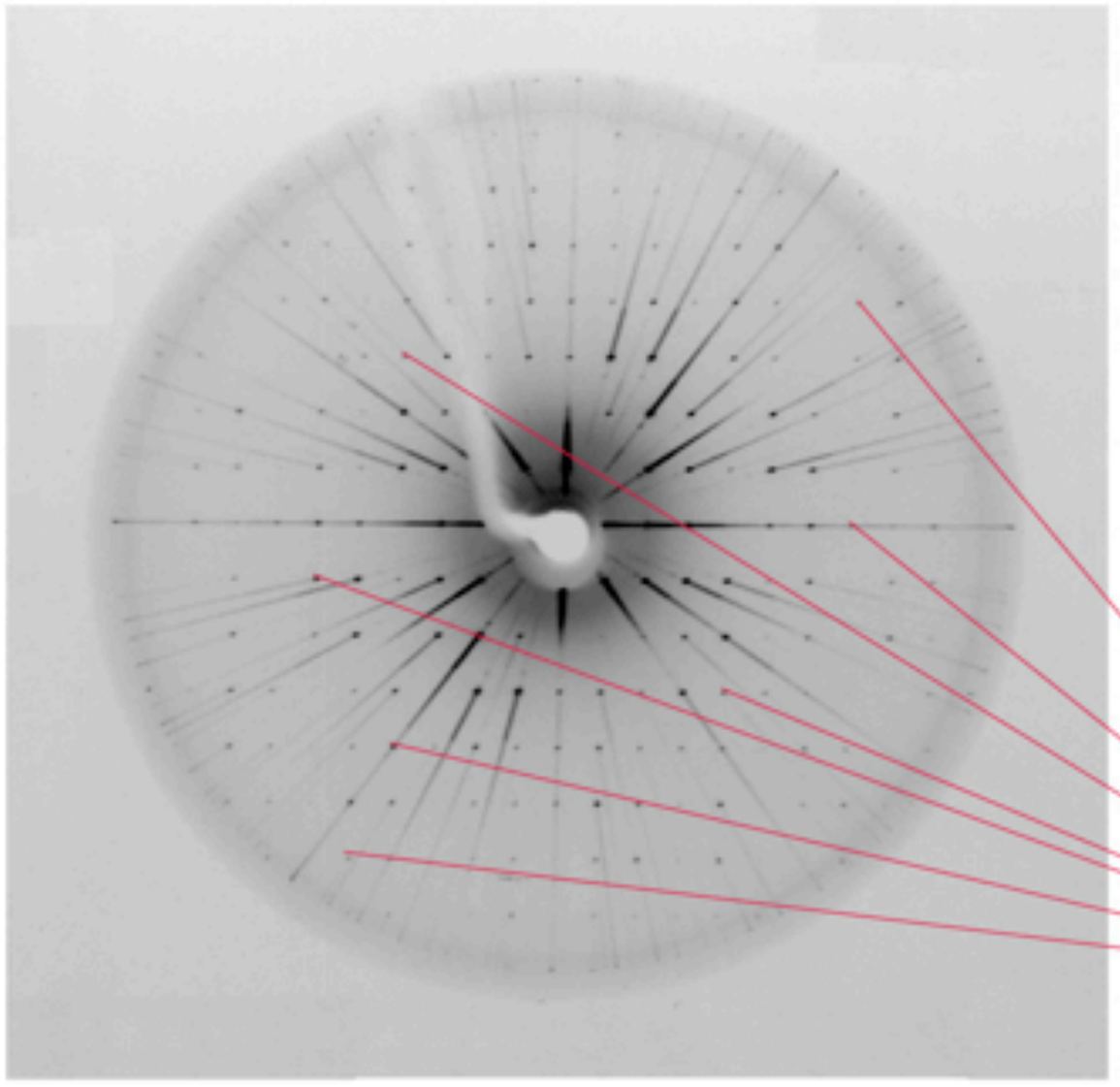
solution: 1) Solve the Bragg's Law for *d*:

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

2) Substitute:

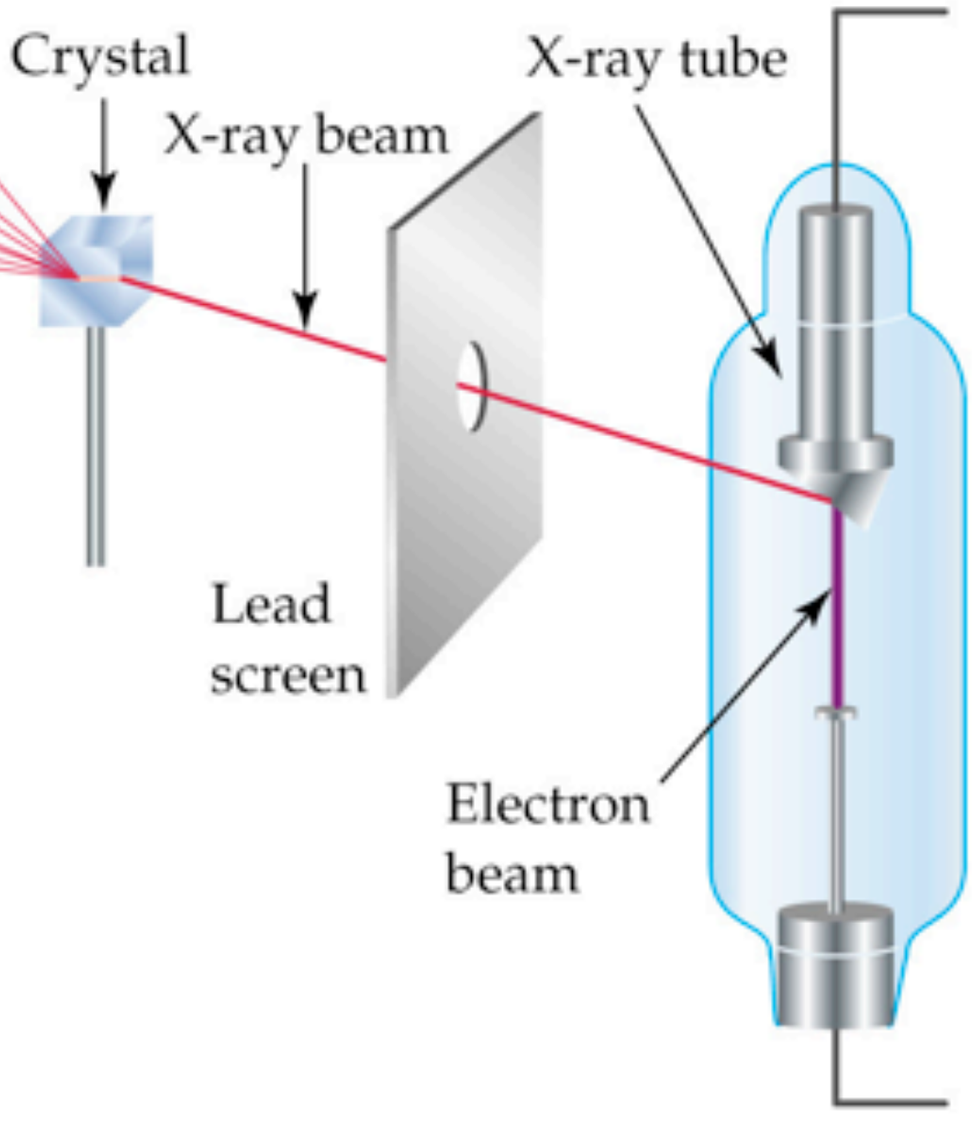
$$d = \frac{n\lambda}{2\sin\theta} = \frac{2(0.7093\text{Å})}{2\sin(14.66/2)} = 5.559\text{Å}$$

Voilà!



Photographic film

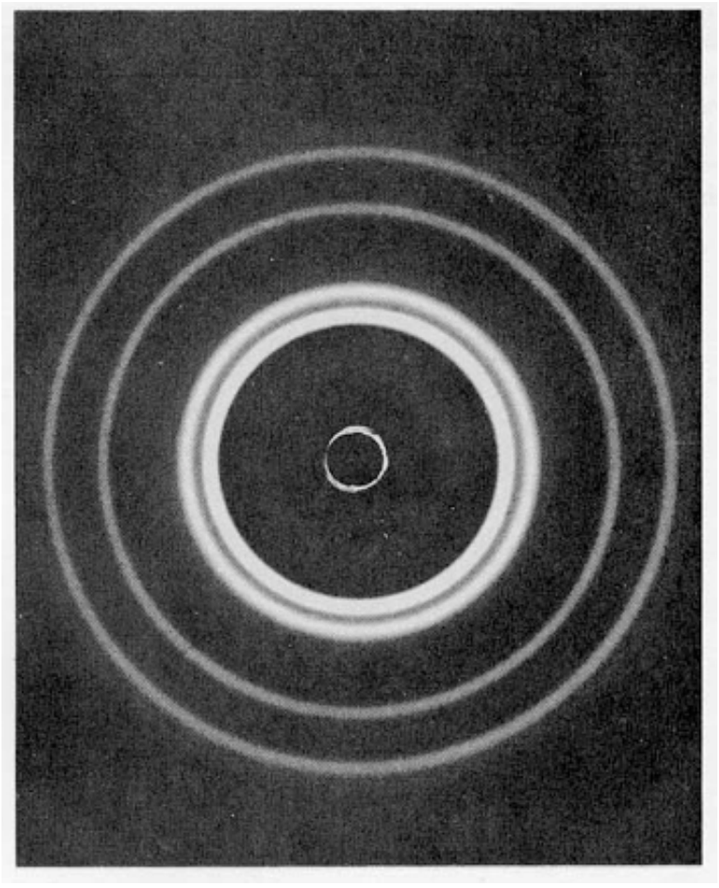
X-Ray Diffraction yields lattice parameters & atomic positions



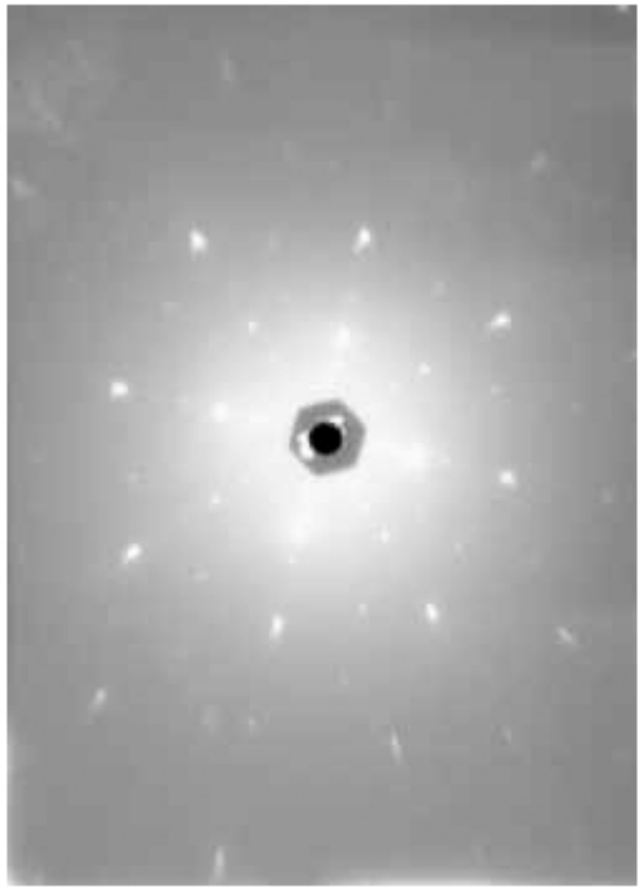
Bragg Equation:

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

Why Rings?



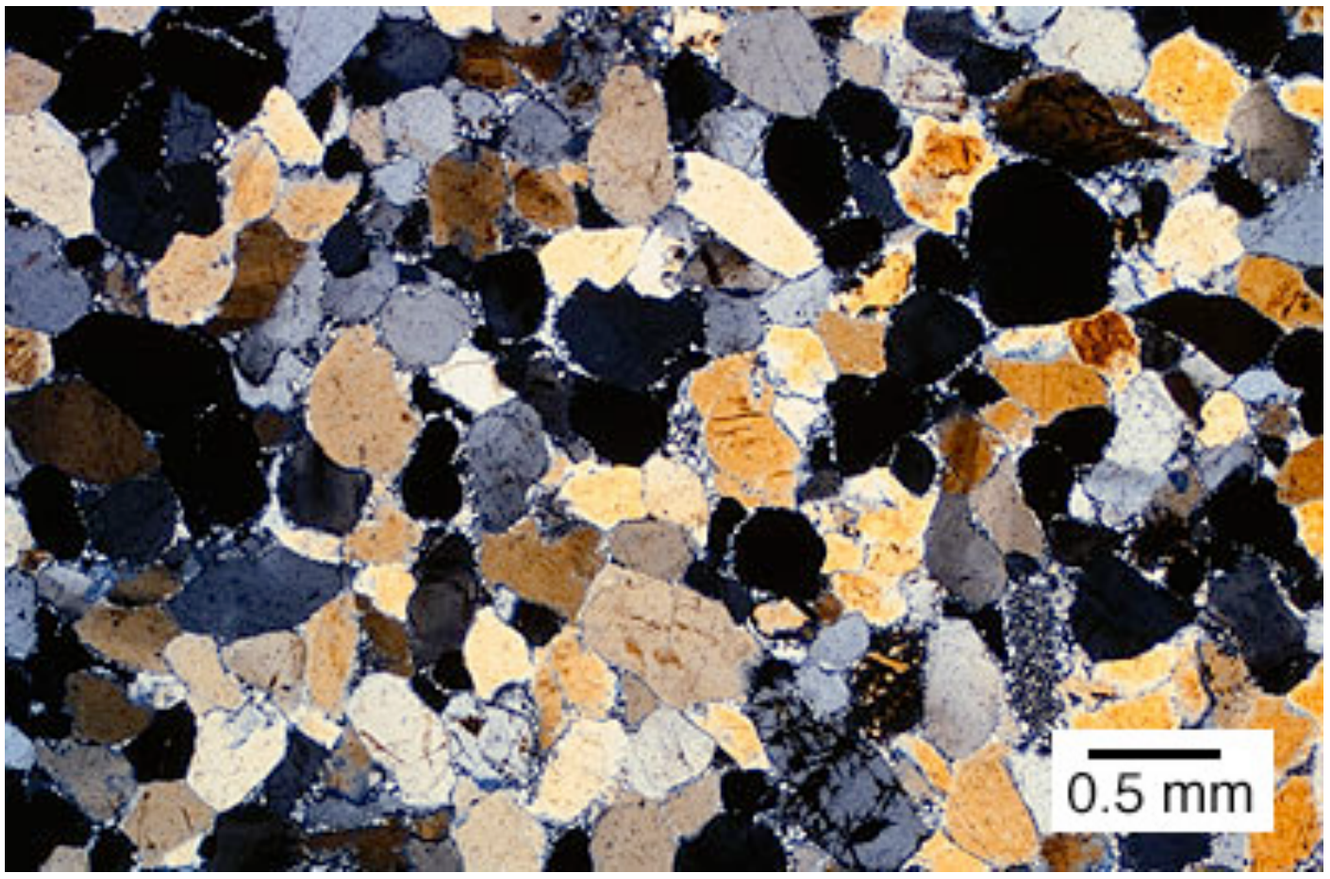
Thin foil

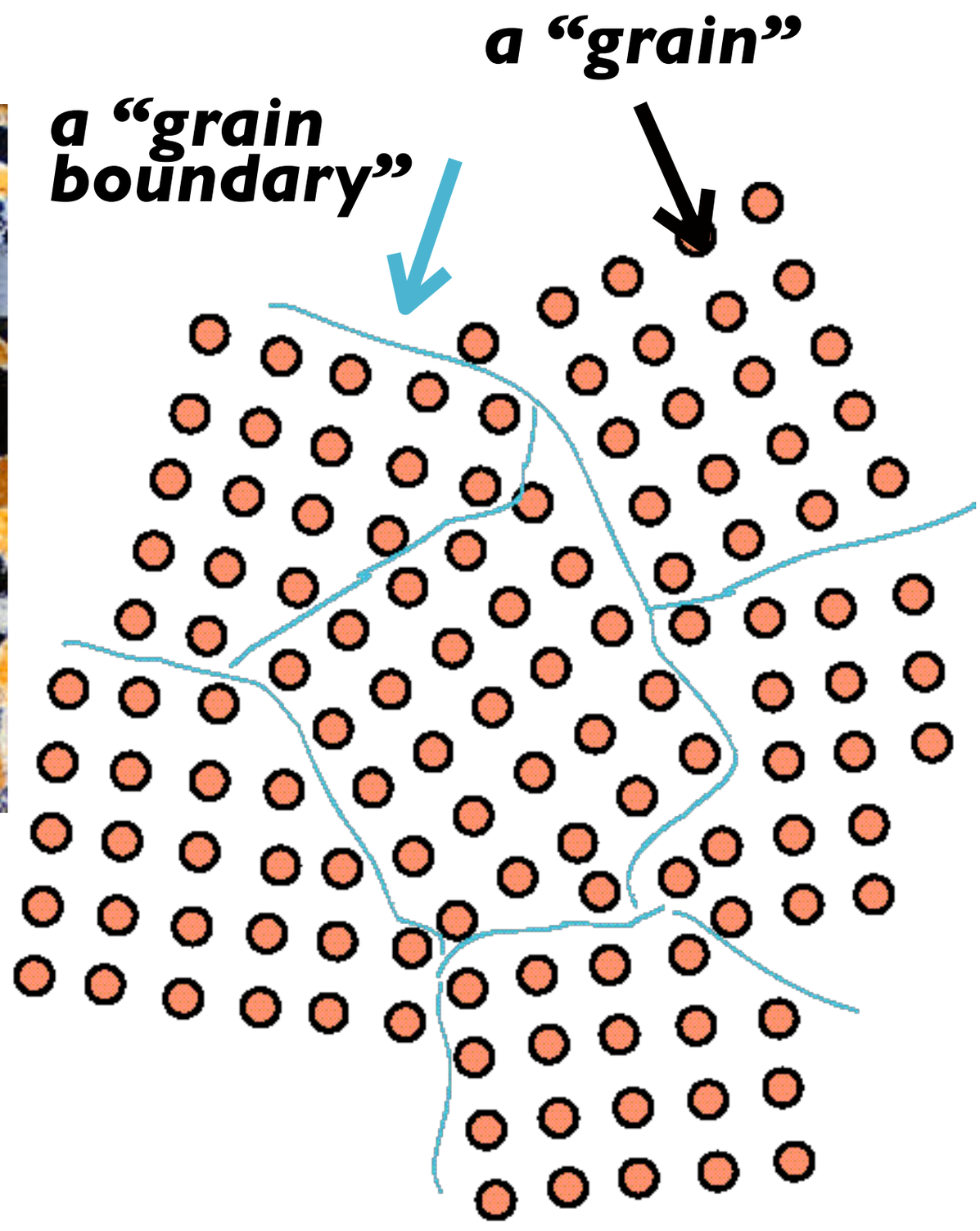


Single Crystal

Polycrystalline Samples give ring patterns. Single crystal samples yield two dimensional arrays of spots.

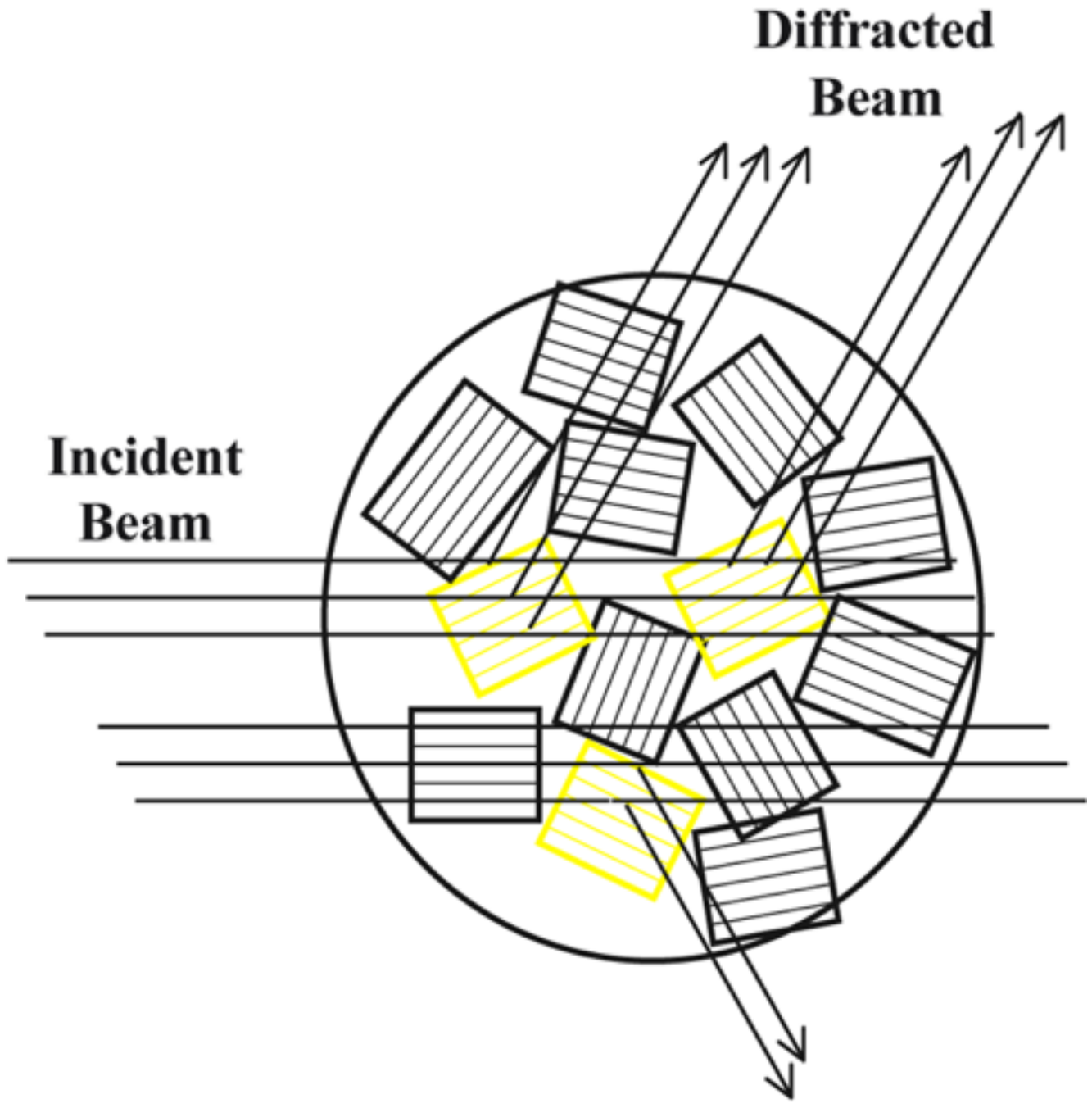
Polycrystalline samples average over all orientations.





In a sufficiently large, randomly oriented polycrystalline sample (e.g. a powder), there are a large number of small crystallites.

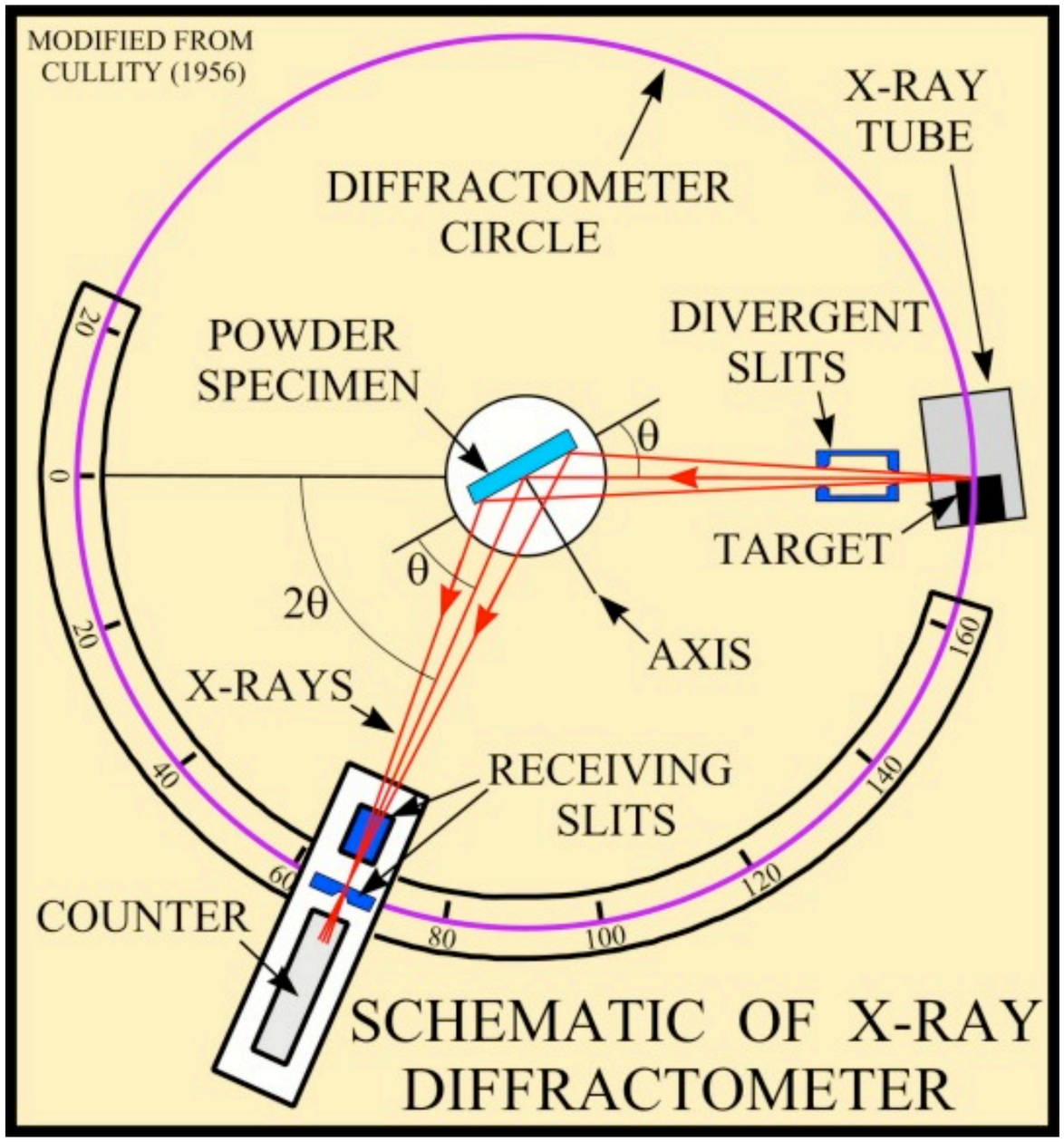
A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction



Powder XRD Measurements

The XRD powder pattern can be used to determine the lattice parameters of the crystal.

As the sample is rotated through an angle θ, the detector needs to be rotated through an angle 2θ



Source: X-Ray tube Detector: Si-Li

A typical XRD powder pattern. The data is usually plotted as a function of 2θ (detector travel).

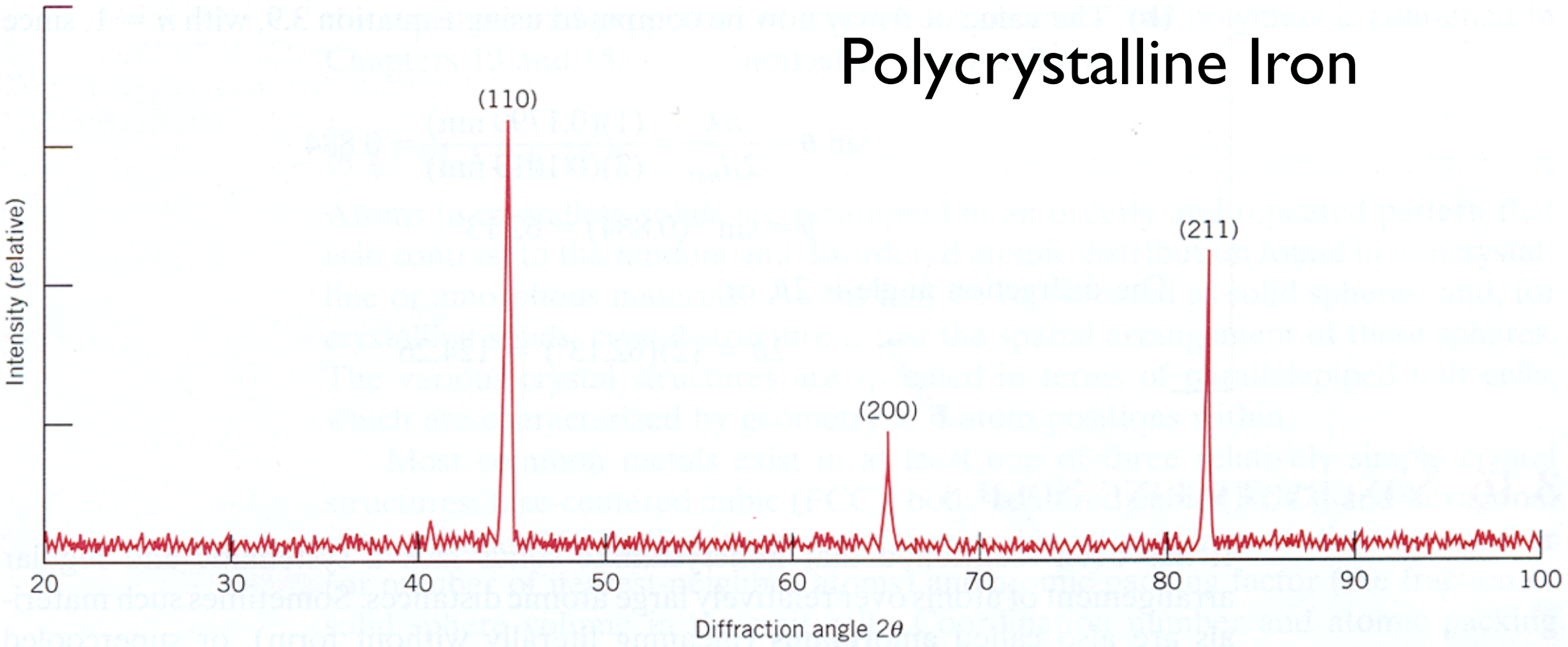
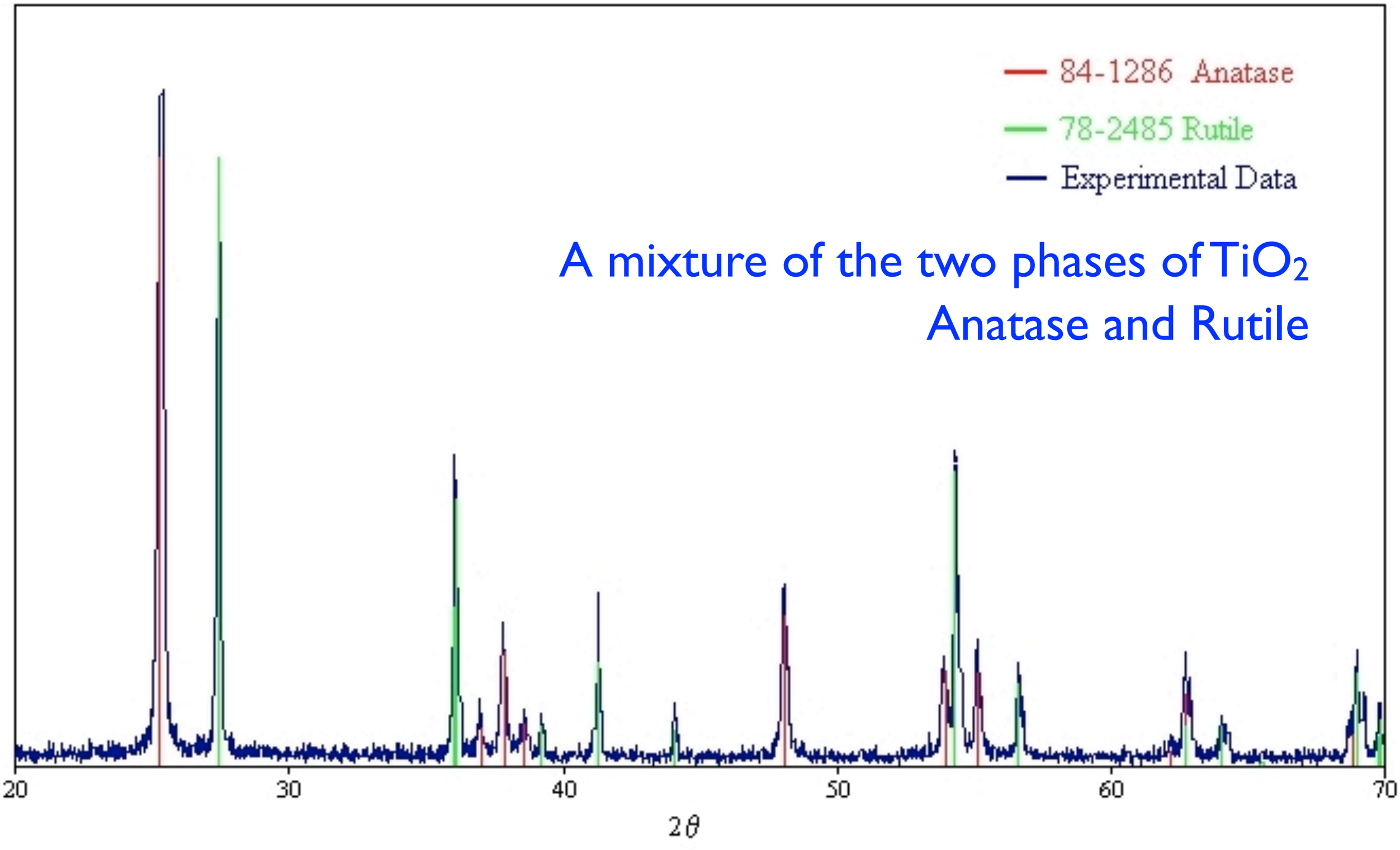
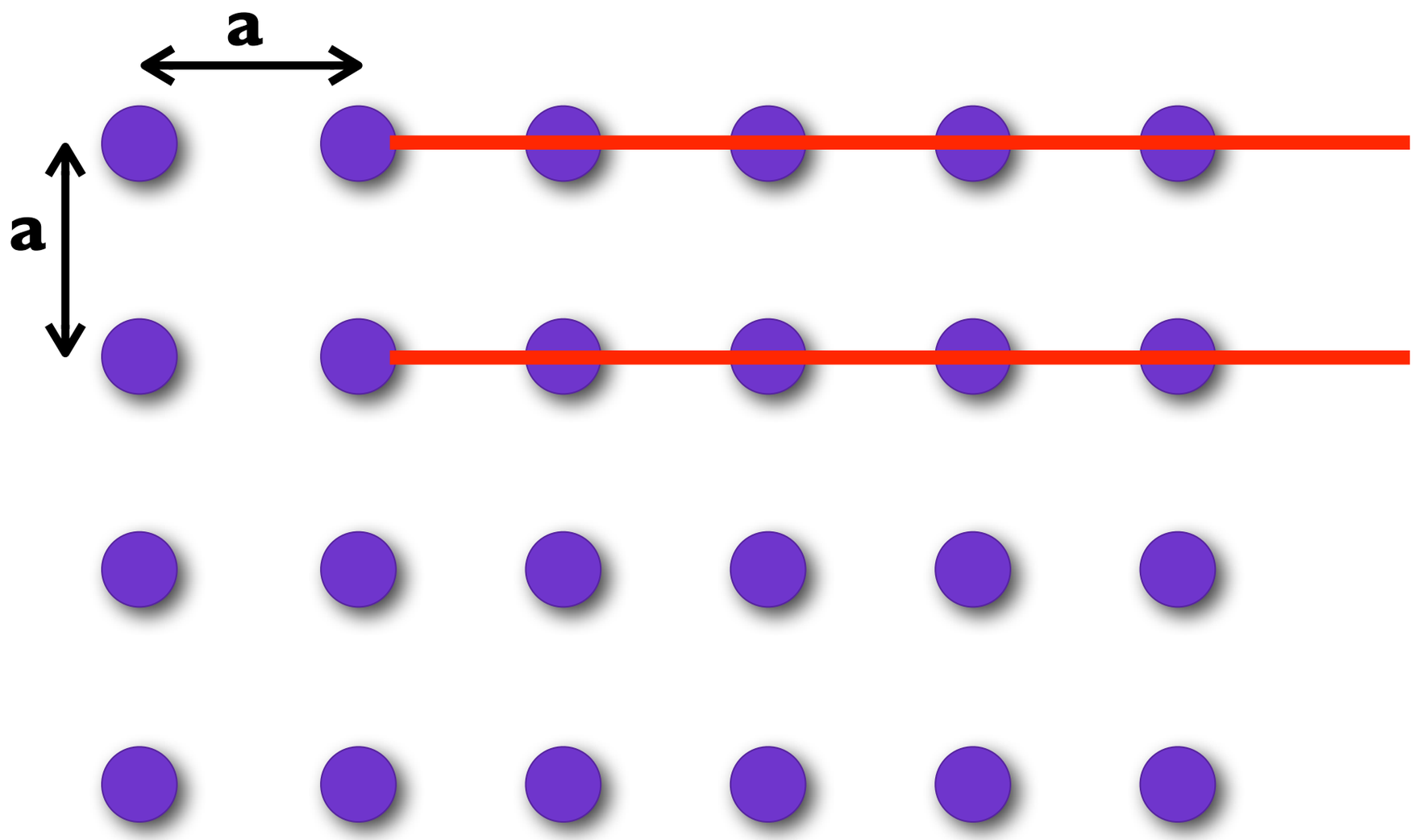


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

A typical XRD powder pattern. The data is usually plotted as a function of 2θ (detector travel).

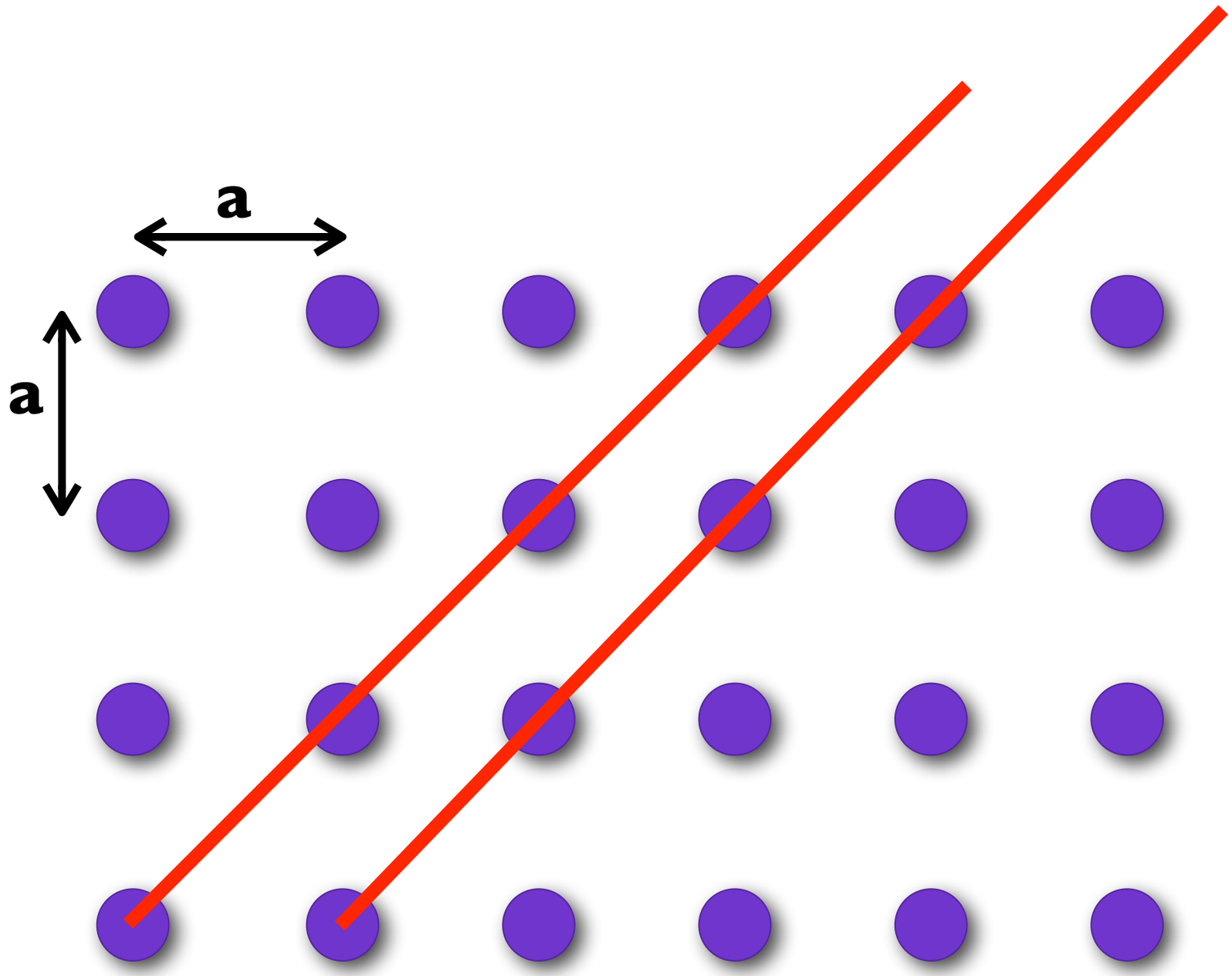


Let's take a look at the possible diffraction patterns for this 2-D crystal.



d = a for this diffraction ring.

Let's take a look at the possible diffraction patterns for this 2-D crystal.



d ≠ a, diffraction occurs at a different angle

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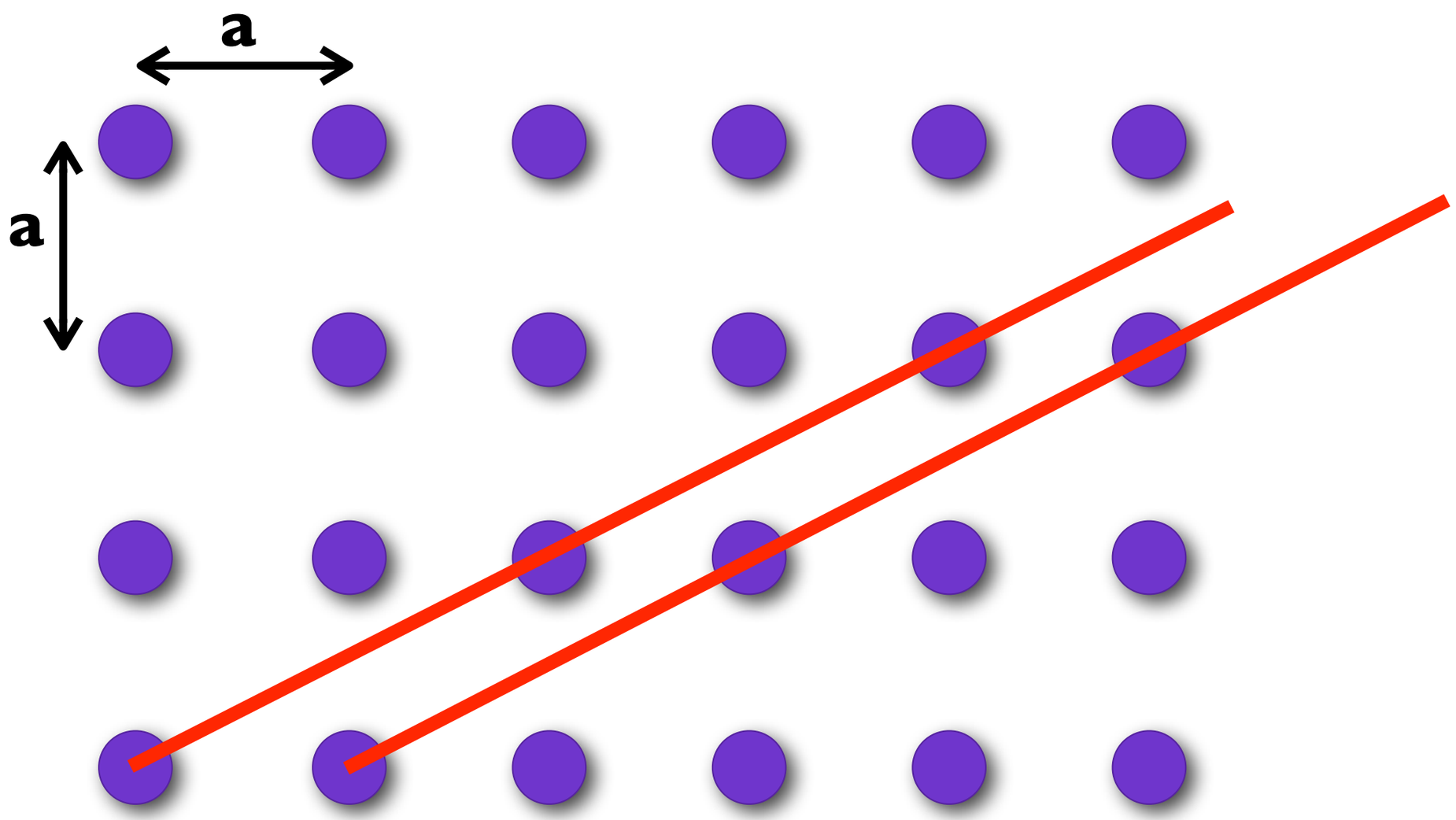
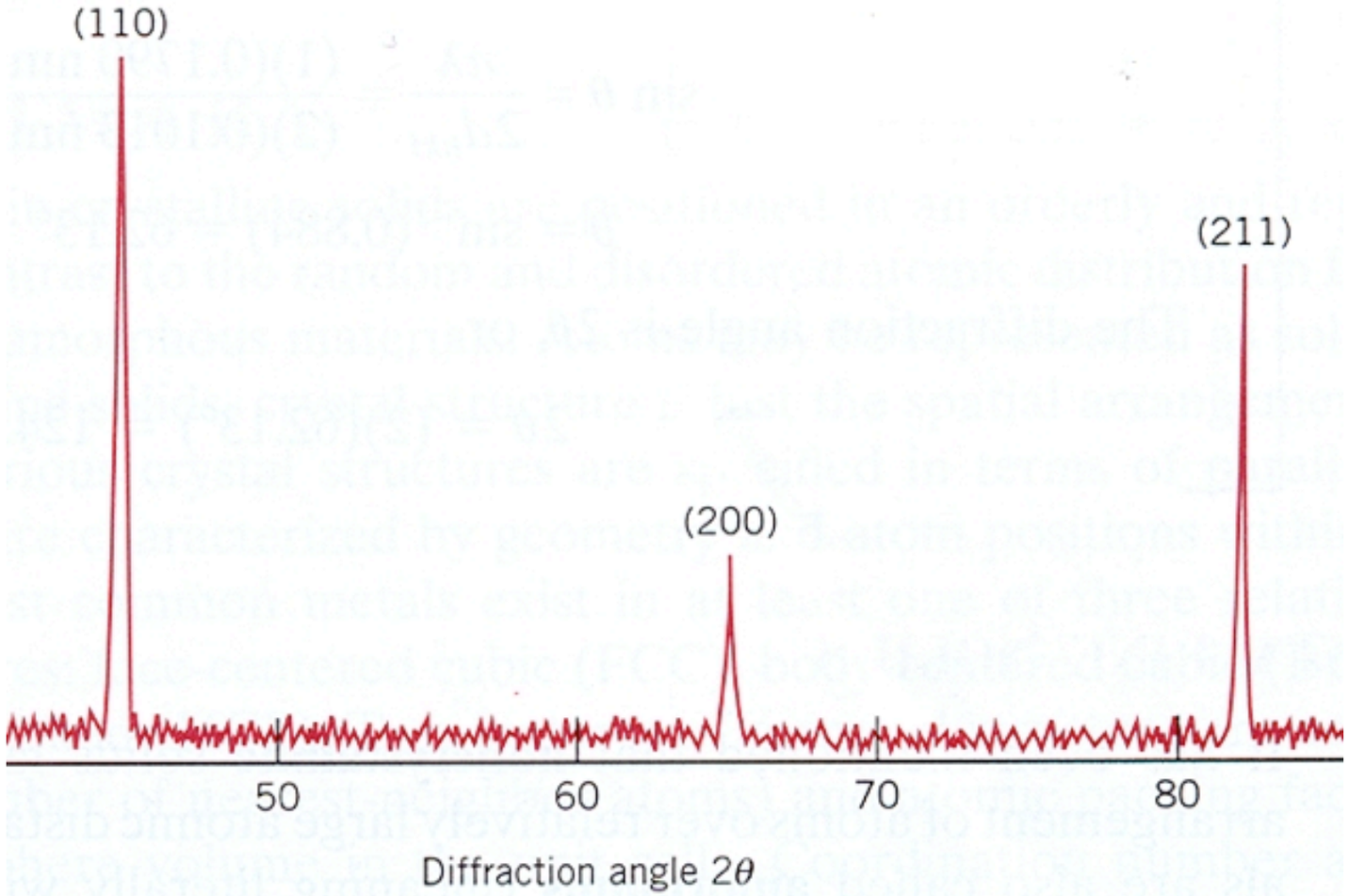
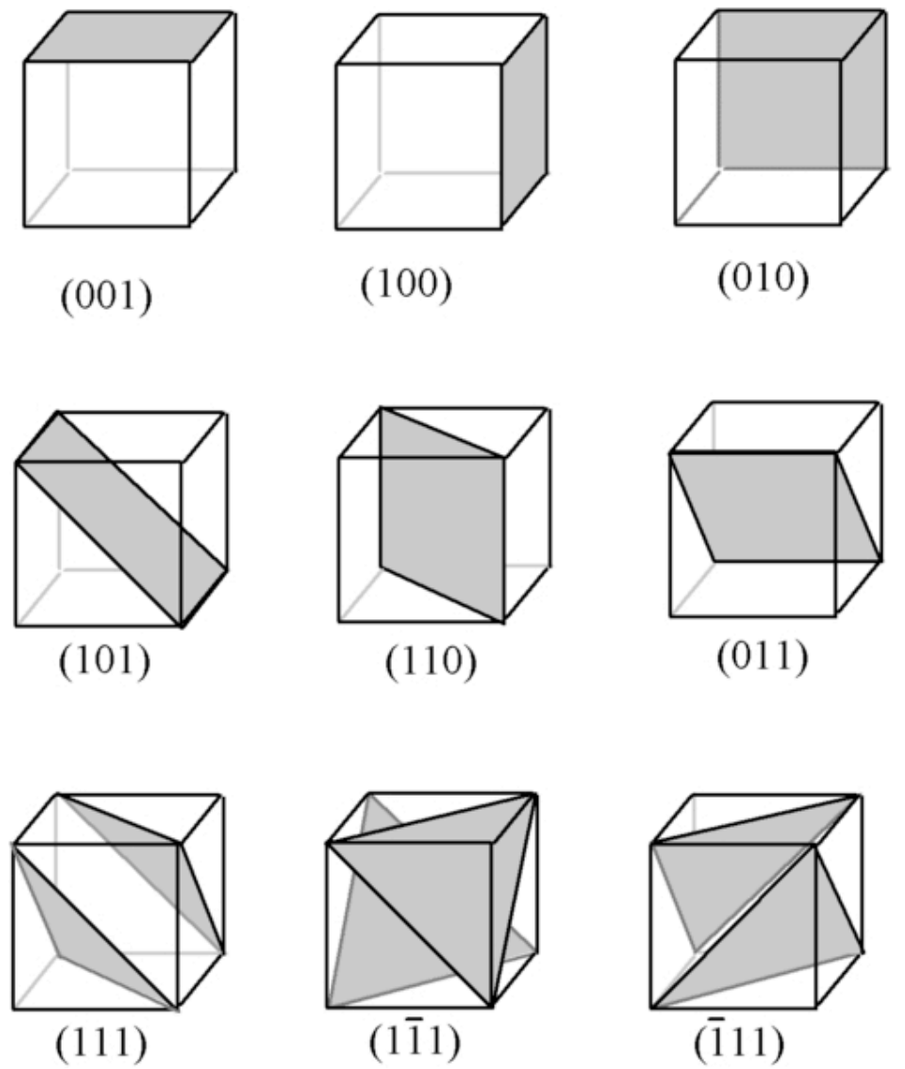


d ≠ a, diffraction occurs at yet another different angle

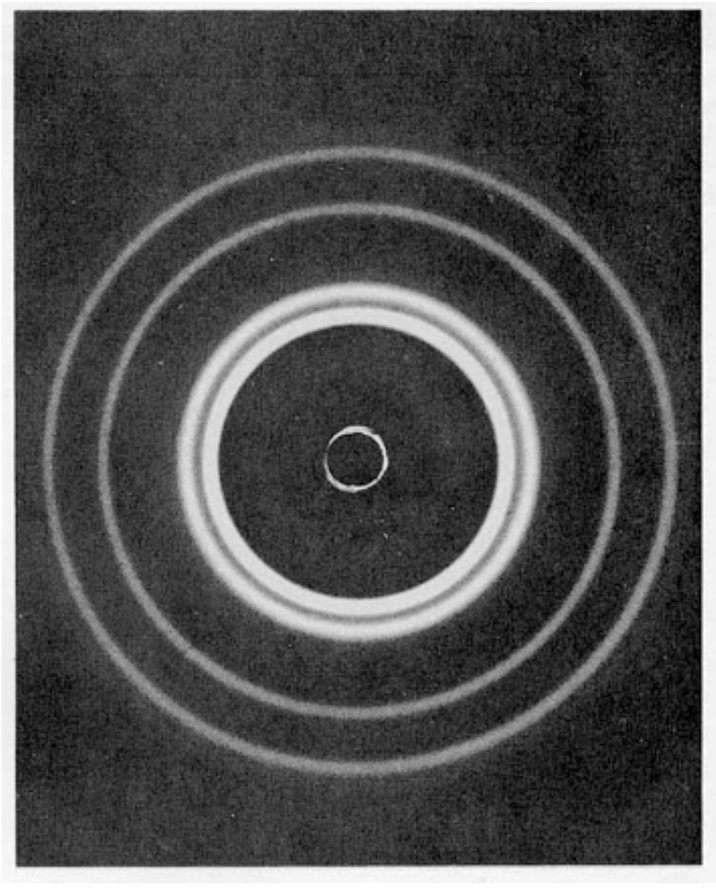
The various diffraction peaks are identified with Miller indices. (We won't go into how to get these, but it's not hard.).



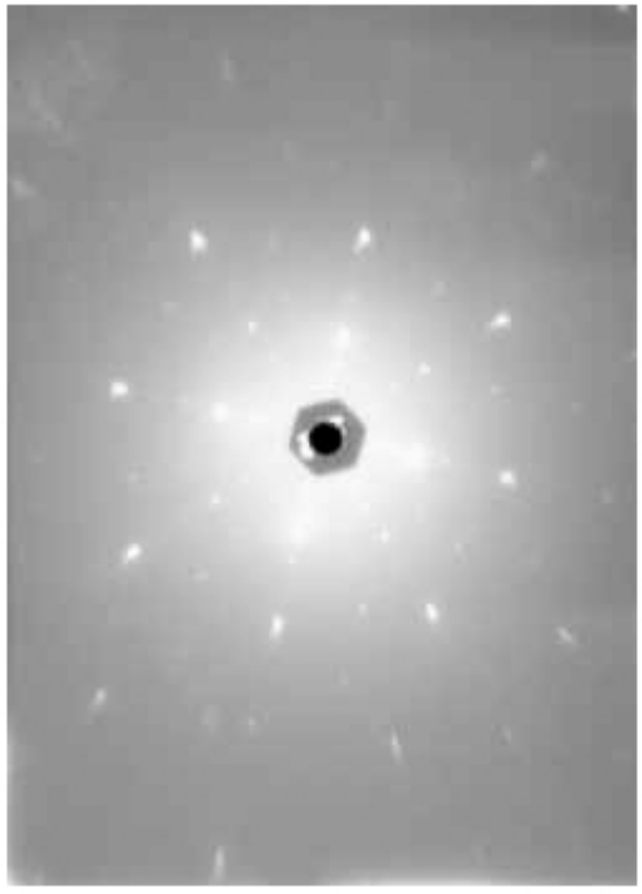


Diffraction peaks at (110), (200) and (211)

Single Crystal X-Ray Measurements



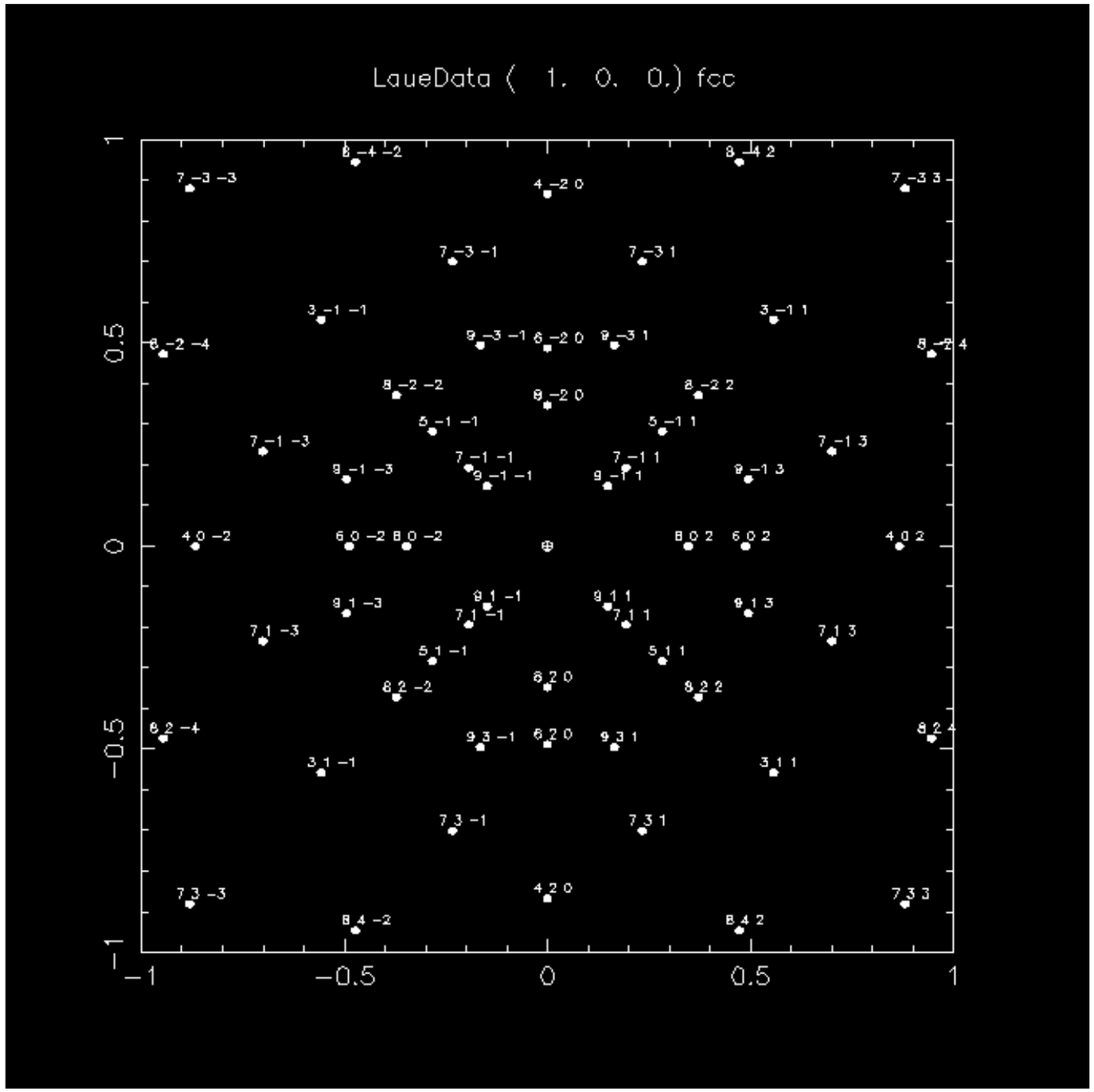
Thin foil



Single Crystal

Polycrystalline samples give ring patterns. Single crystal samples yield two dimensional arrays of spots, and can be used to determine the atomic positions in the unit cell.

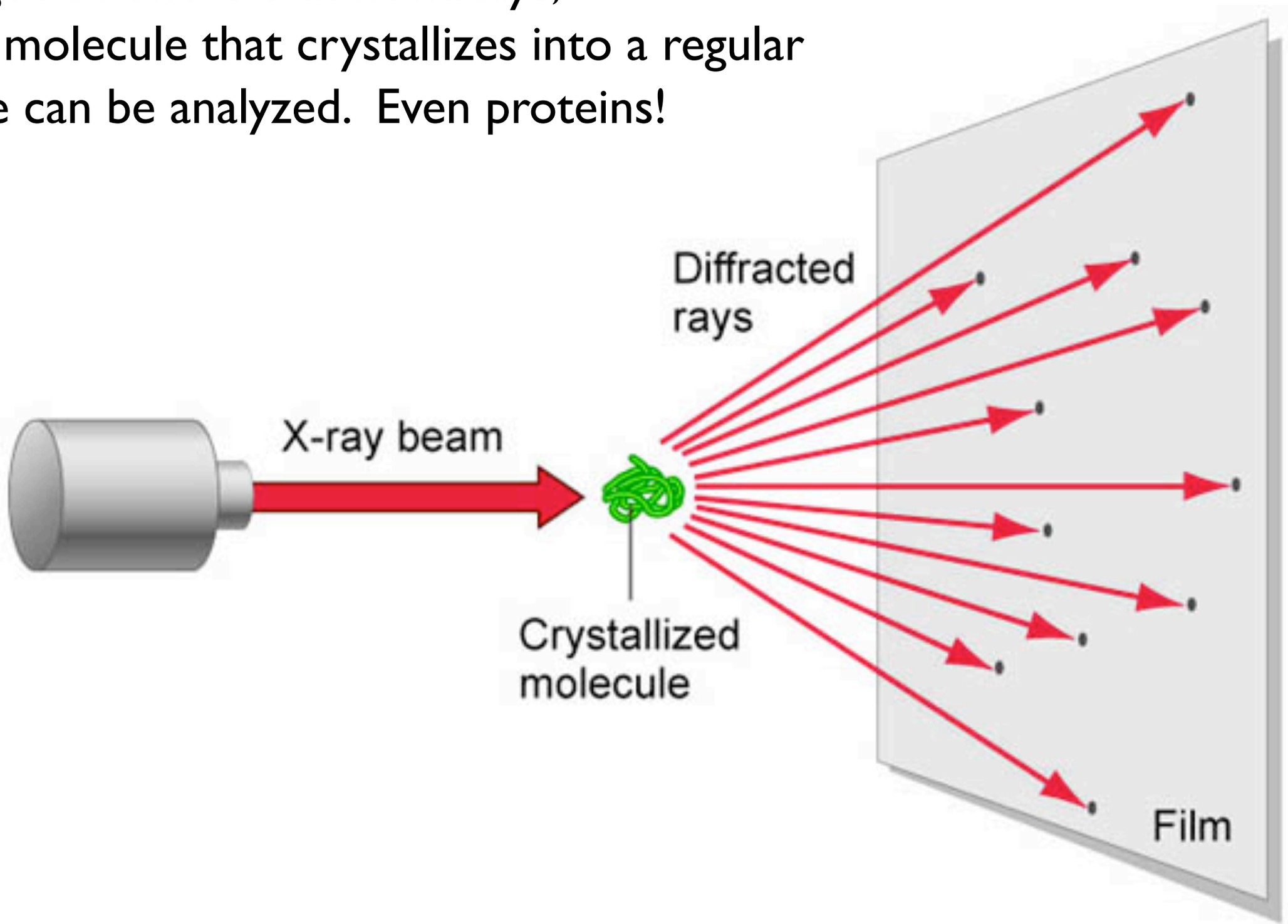
Single Crystal X-Ray Measurements



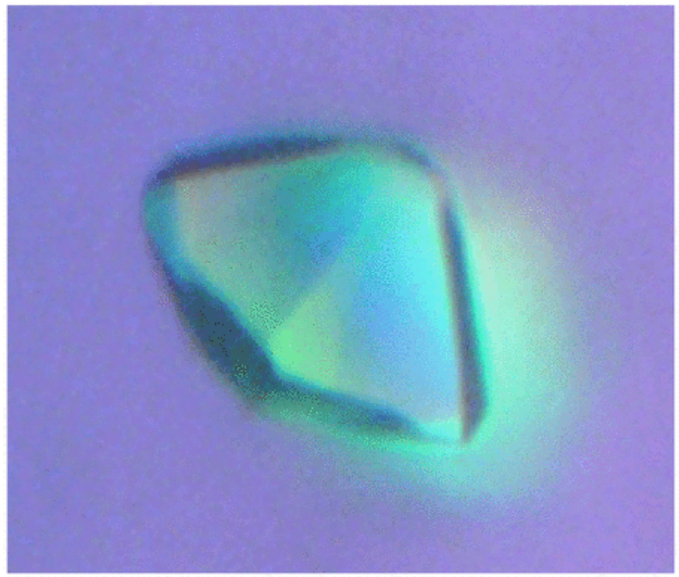
XRD pattern for diffraction from the (1,0,0) face of an fcc crystal

Simple lattice types are easy to characterize, but more complex crystals require more sophisticated data analysis.

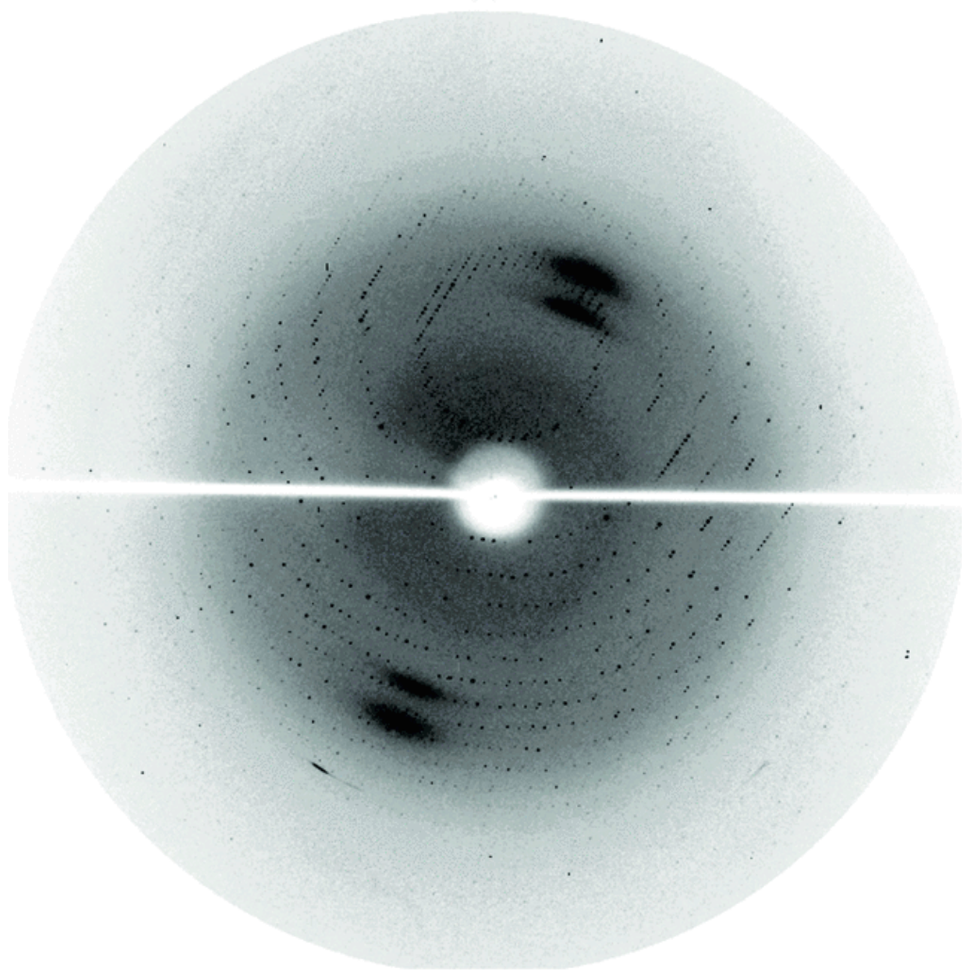
The good news is that nowadays,
ANY molecule that crystallizes into a regular lattice can be analyzed. Even proteins!



X-ray diffraction-quality crystals. (*a*) A typical crystal of *Y. pestis* SspA with dimensions of 0.1 × 0.1 × 0.1 mm. (*b*) X-ray diffraction at 2.0 Å of the crystal at the National Synchrotron Light Source.

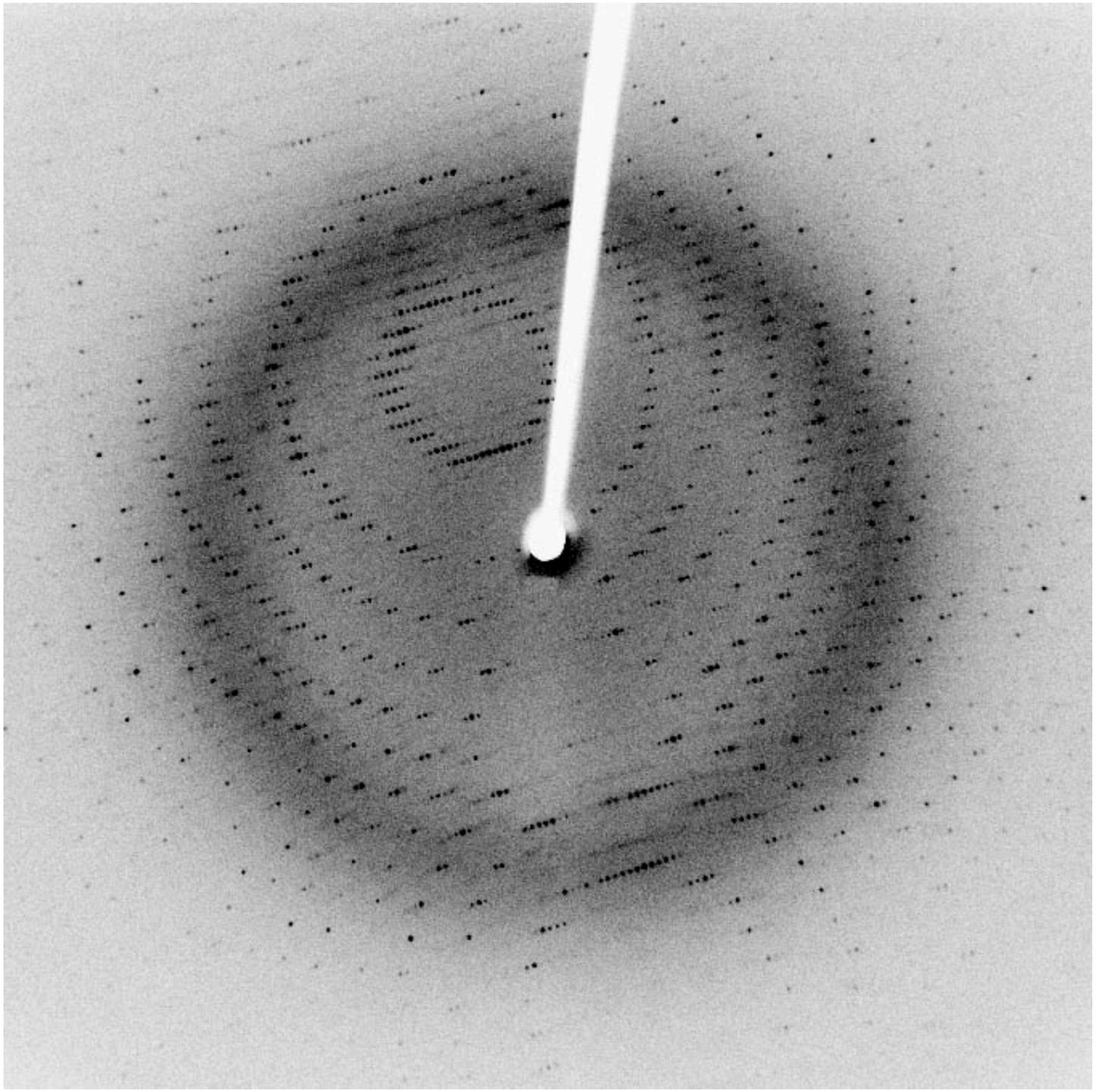


(*a*)

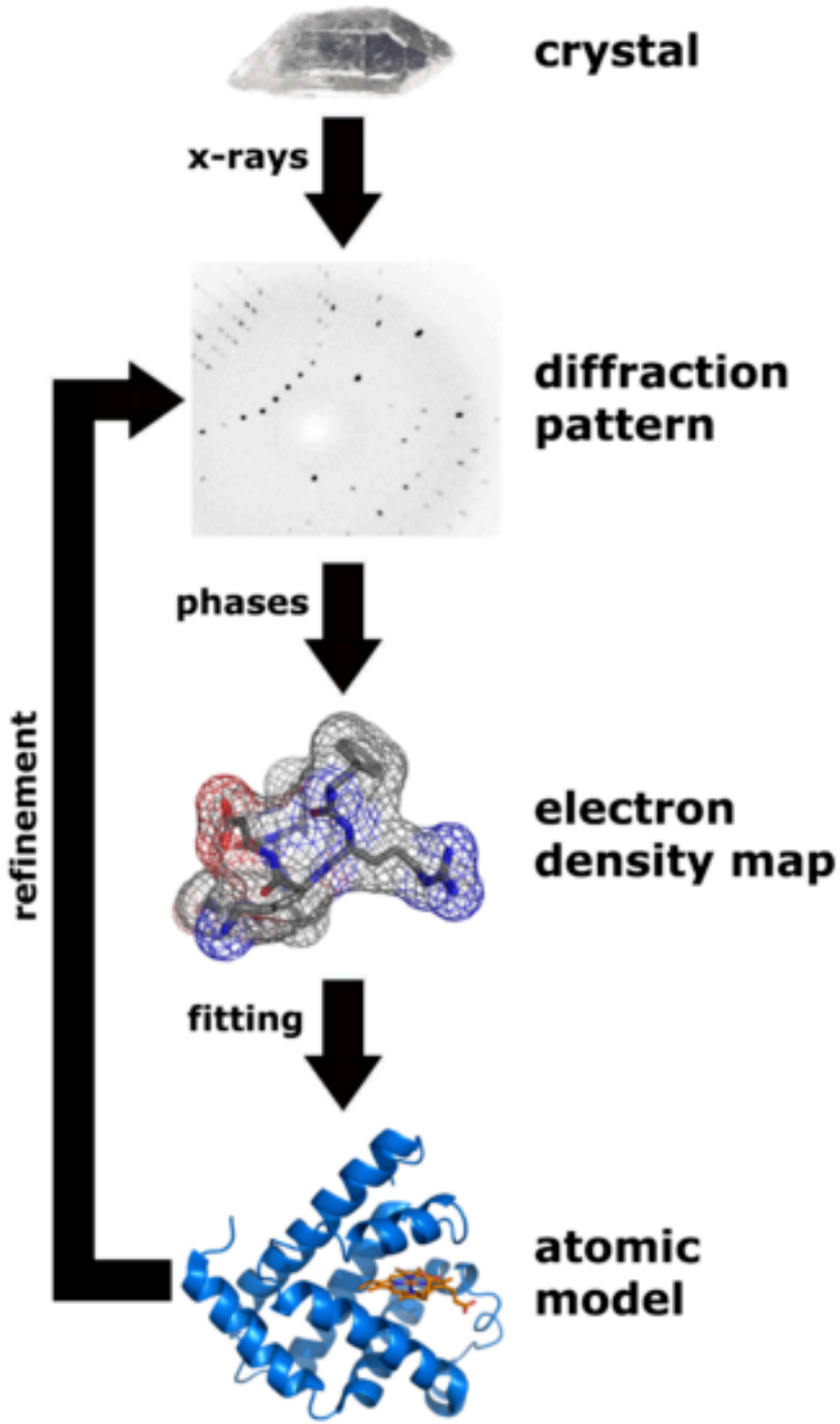


(*b*)

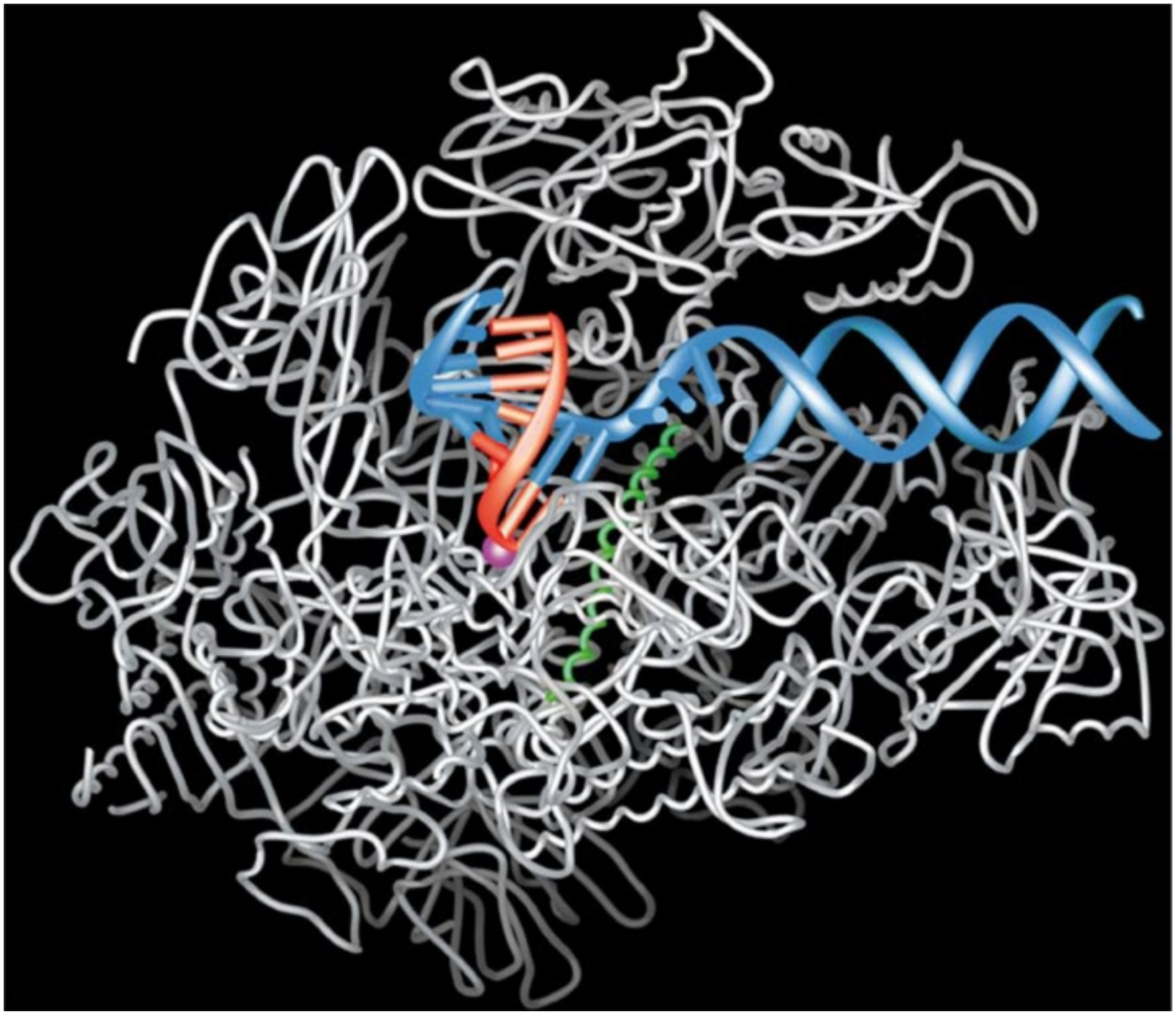
Lots of diffraction spots are obtained from many different incident angles on the crystal.



In the case of complex molecules, we use the x-ray diffraction data to produce a model, back calculate the pattern again, and adjust the model until it fits the pattern.



RNA polymerase - MW≈400 kDa or 400,000 g/mol



Structure obtained from the X-ray diffraction data!

RNA Ribosome 50S subunit

The Nobel Prize in Chemistry 2009

Venkatraman Ramakrishnan, Thomas A. Steitz, Ada E. Yonath

Photo: U. Montan

Venkatraman Ramakrishnan

Photo: U. Montan

Thomas A. Steitz

Photo: U. Montan

Ada E. Yonath

The Nobel Prize in Chemistry 2009 was awarded jointly to Venkatraman Ramakrishnan, Thomas A. Steitz and Ada E. Yonath *"for studies of the structure and function of the ribosome"*.

Structure obtained from the X-ray diffraction data!

50S Subunit of the Ribsome

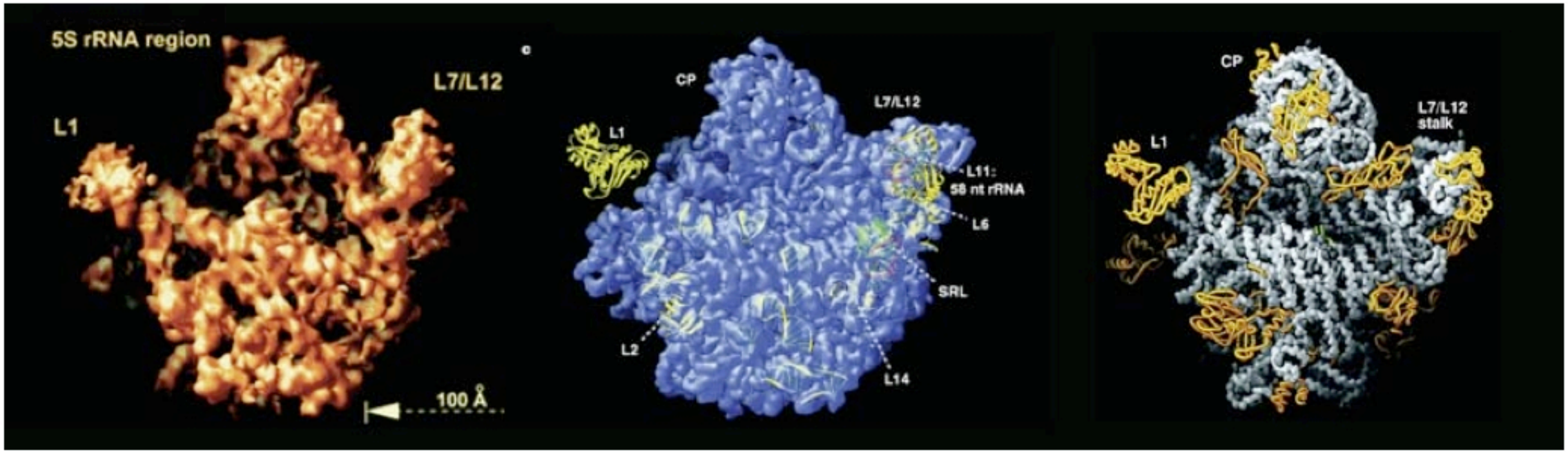
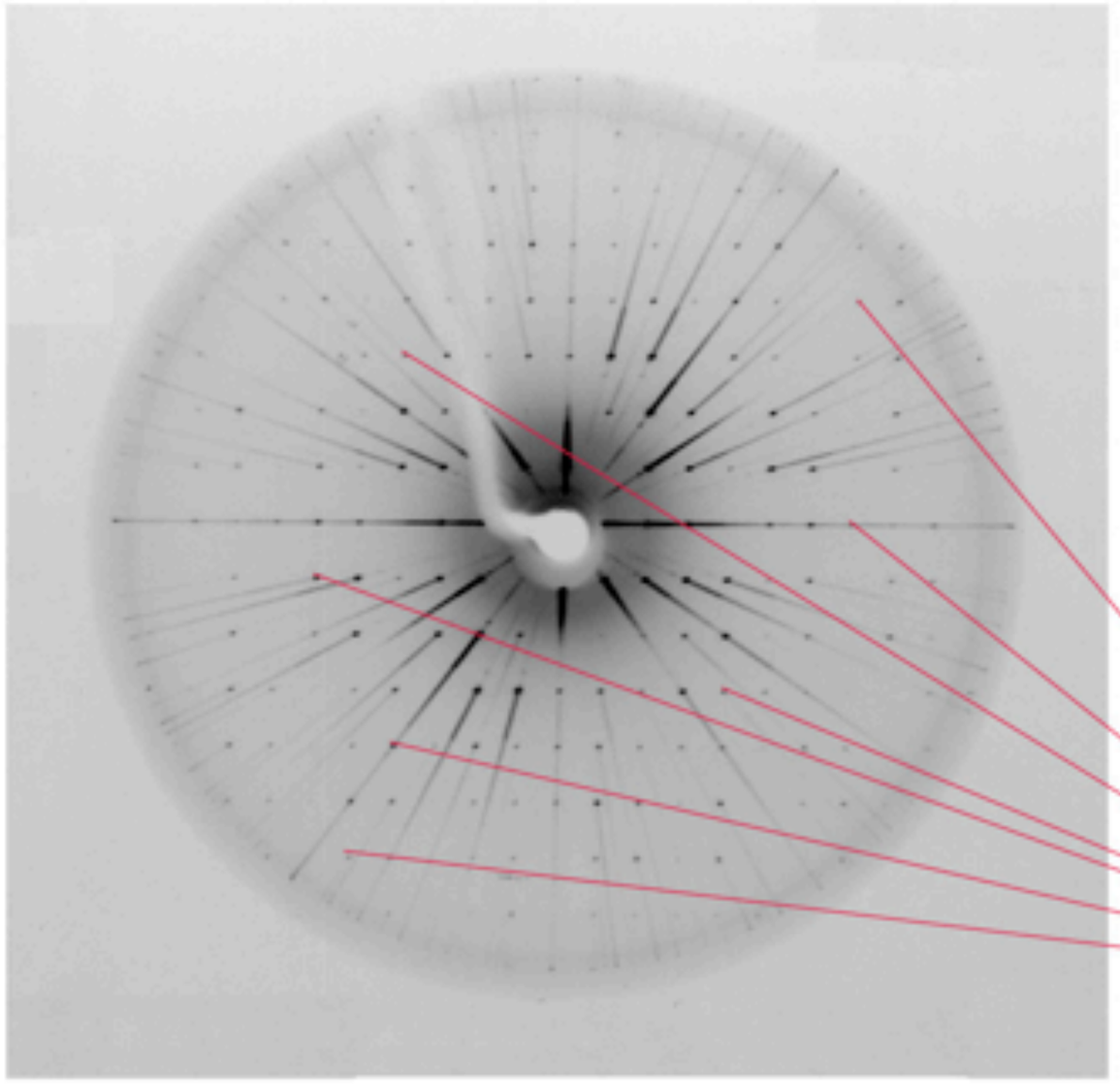


Figure 4. The path to the 50S subunit structure at high resolution. The 50S subunit structure at 9Å resolution (left, 1998), 5Å resolution (middle, 1999) and 2.4Å resolution (right, 2000) (From Ban et al., 1998; 1999; 2000).

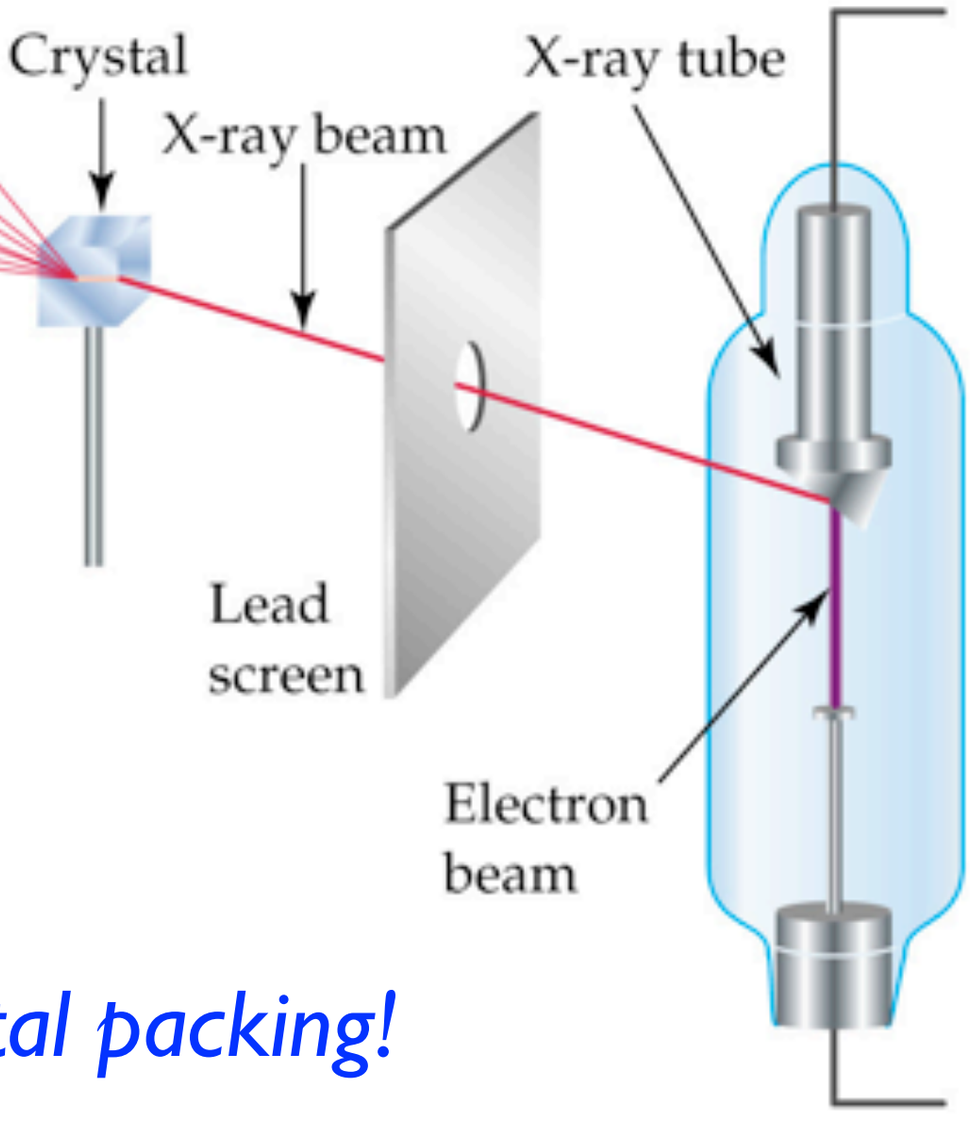
The model of 50S determined in 2000 by the Steitz lab includes 2711 of the 2923 nucleotides of 23S rRNA, all 122 nucleotides of its 5S rRNA, and structure of 27 of its 31 proteins.

Structure obtained from the X-ray diffraction data!

X-Ray Diffraction yields lattice parameters & atomic positions



Photographic film

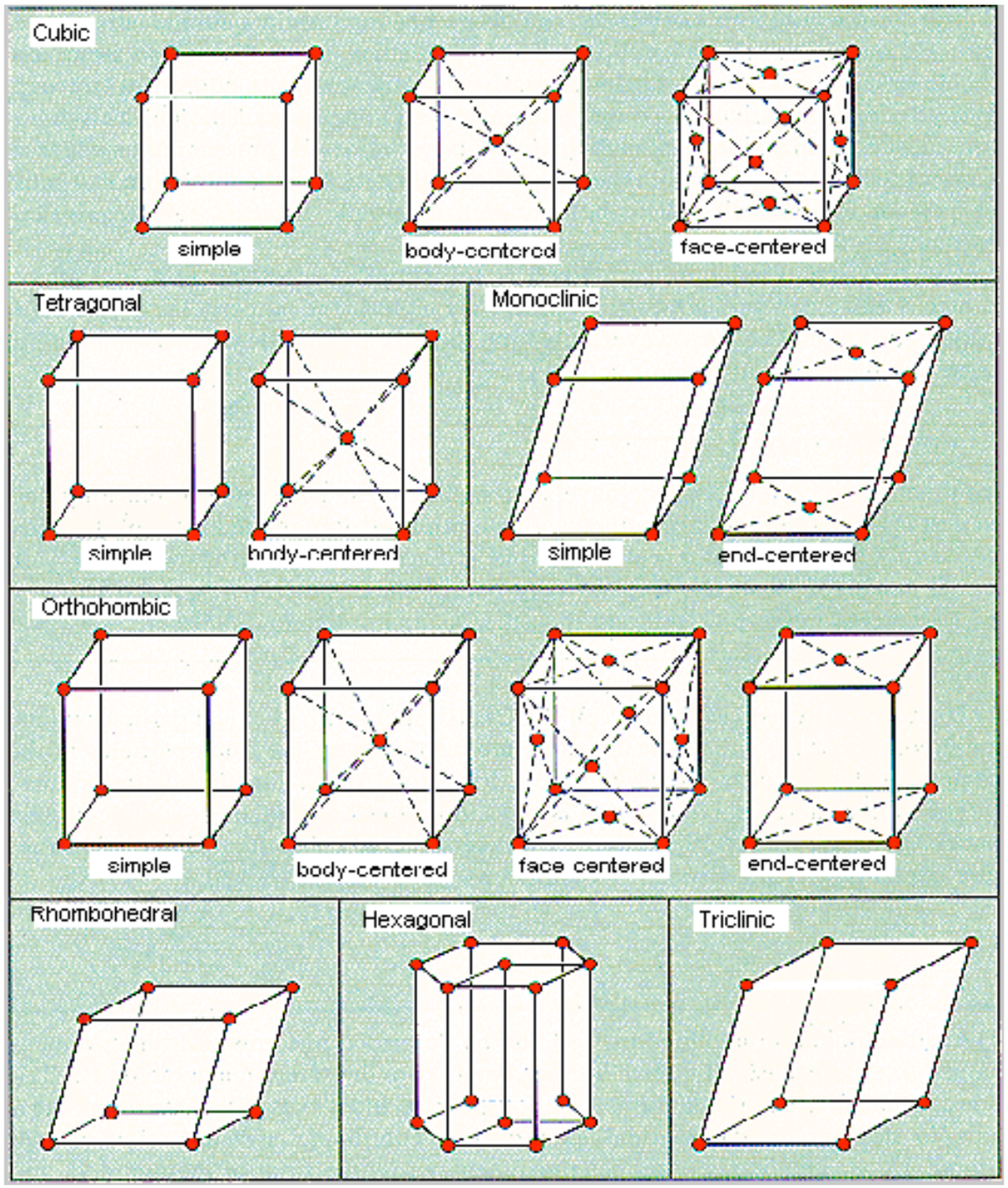


Bragg Equation:

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

Let's use this data to understand crystal packing!

Back to the Future: Crystal Packing (again!)

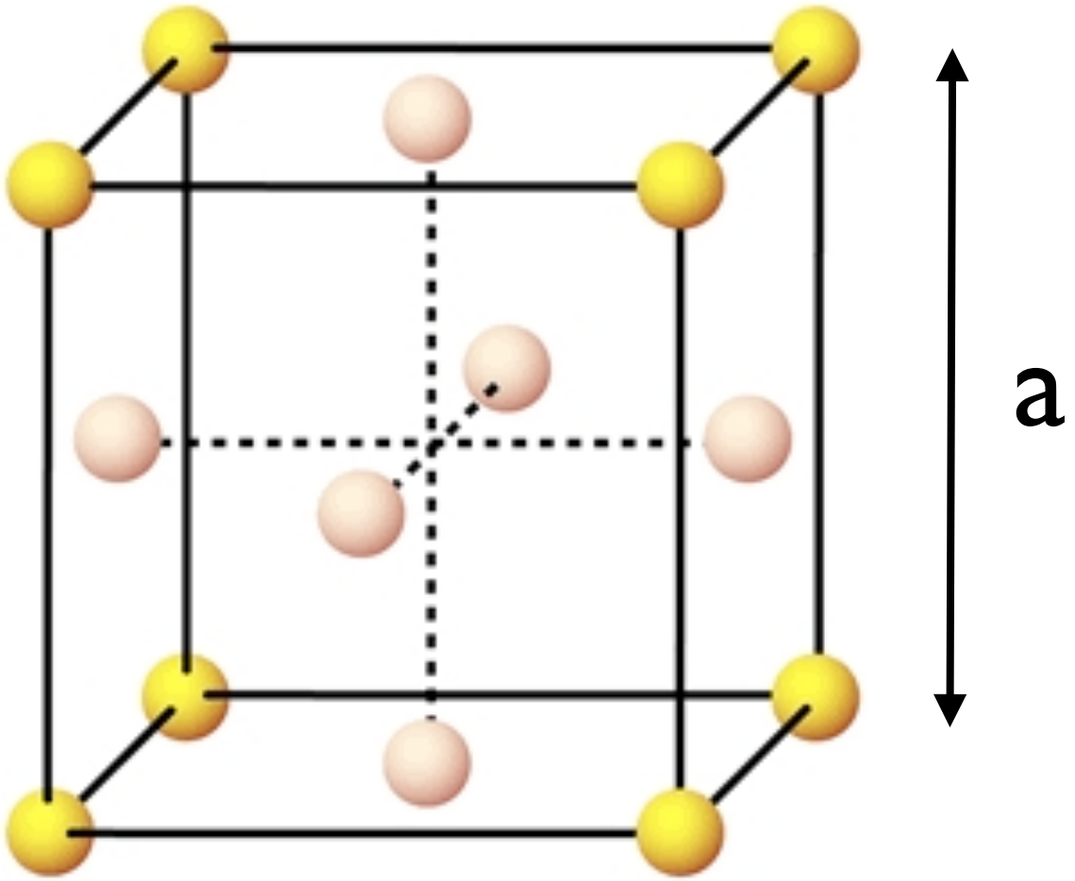


For crystals of elemental solids, there are some fundamental packing structures:

fcc (Face Centered Cubic)
bcc (Body Centered Cubic)
hcp (Hexagonally Close Packed)
Diamond Structure

We have looked at the fcc and bcc crystal lattices previously.

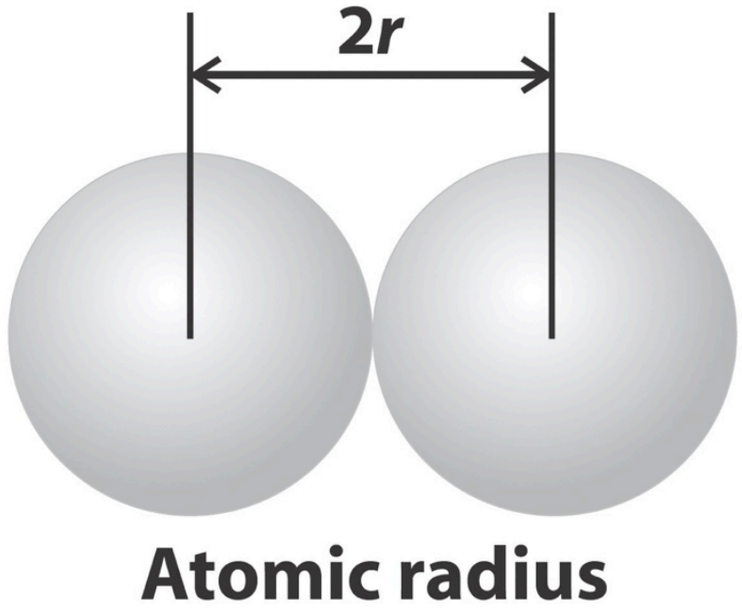
Face-Centered Cubic (fcc) Crystal Lattice



fcc Argon
a = 526.0 pm

r = 186.0 pm

$r = (\sqrt{2}/4)a$

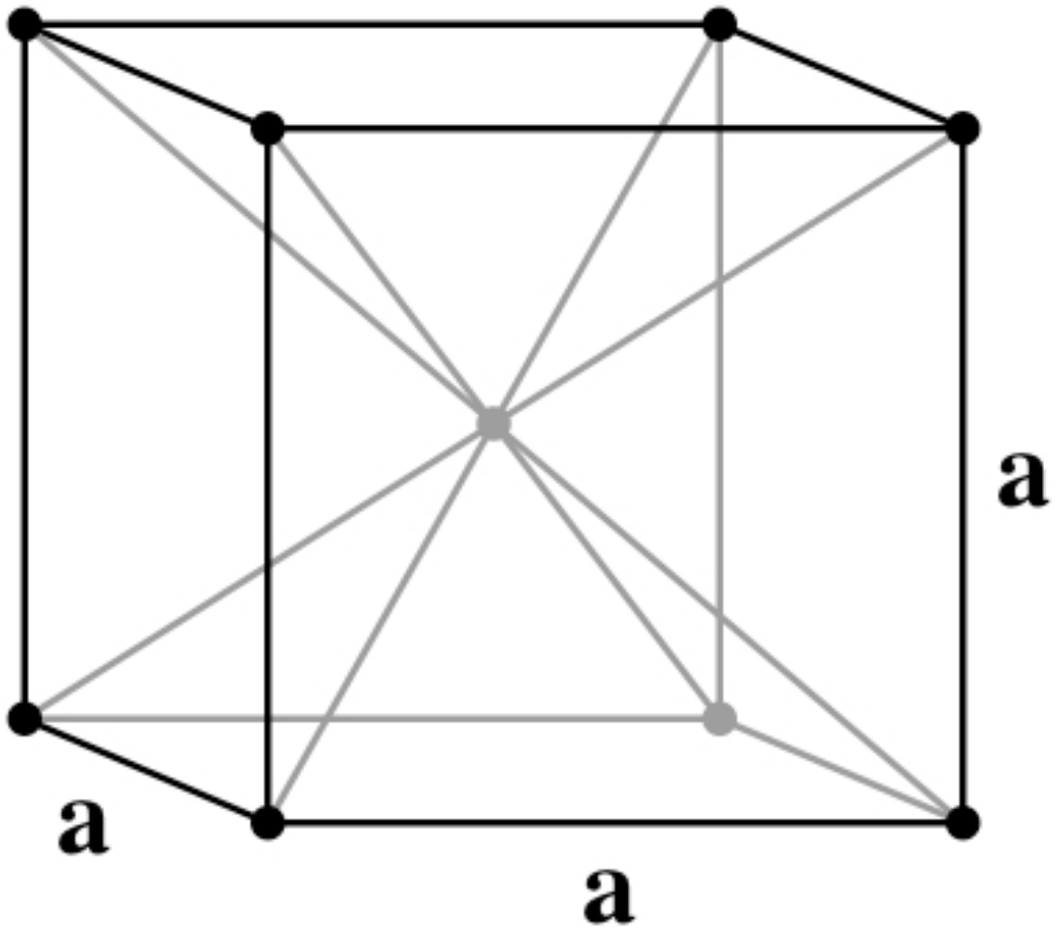


4 atoms/unit cell

74% packing efficiency

Also called cubic close packed (ccp)

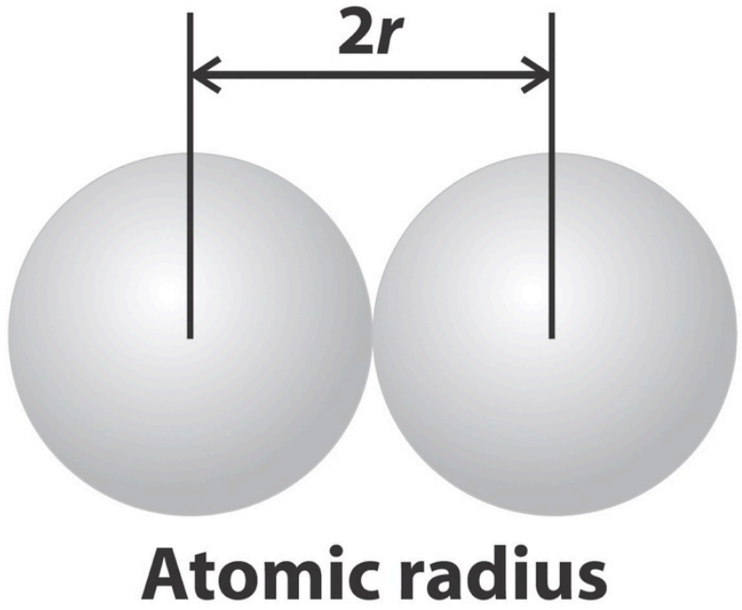
Body-Centered Cubic (bcc) Crystal Lattice



bcc Lithium
a = 349.0 pm

r = 151.1 pm

$r = (\sqrt{3}/4)a$

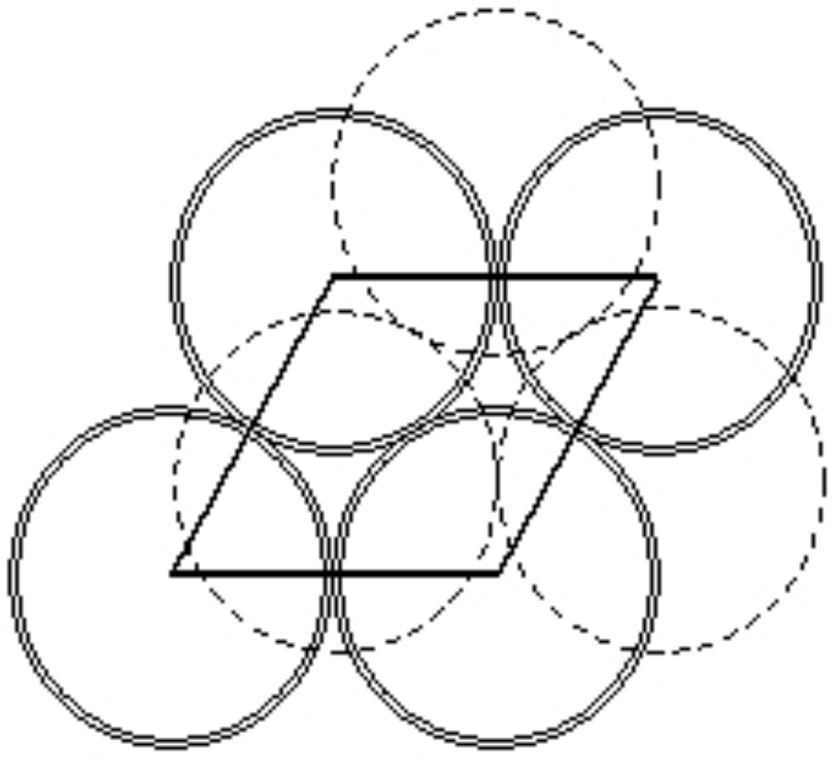


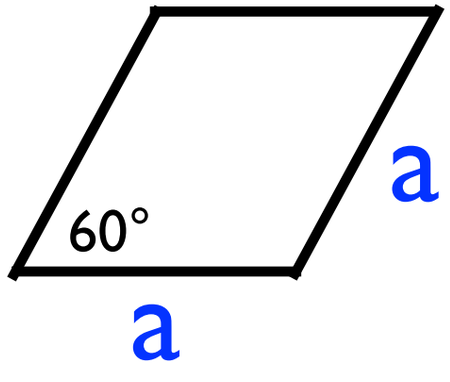
2 atoms/unit cell

68% packing efficiency

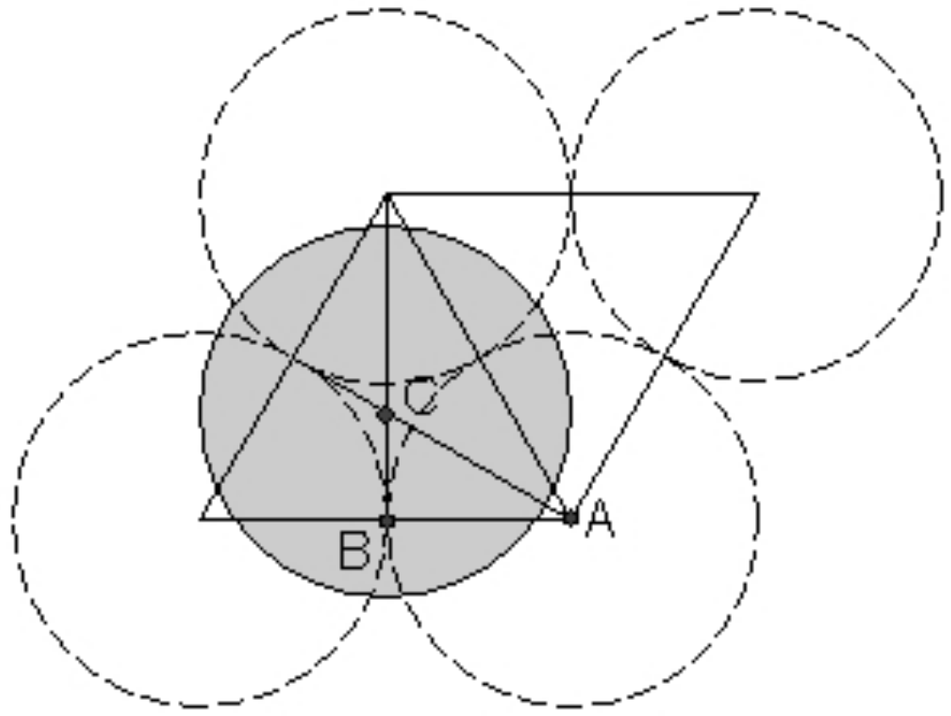
Hexagonal Close Packed (hcp) Crystal Lattice

Rhombohedral unit cell (60° angle)





r = a/2



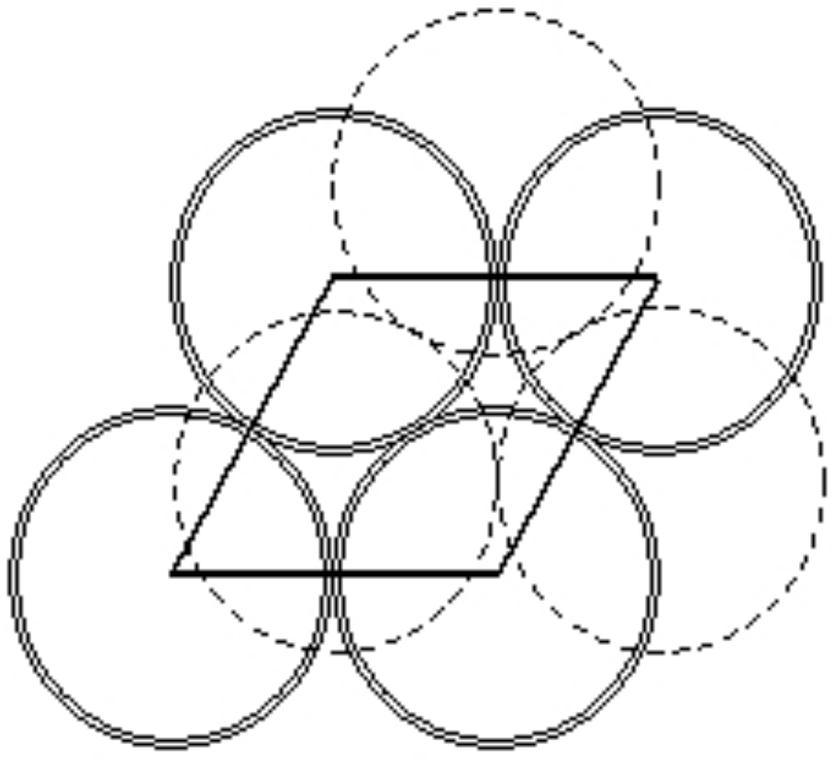
AB = r

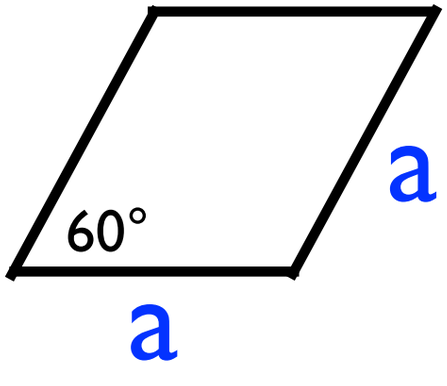
BC = $(\sqrt{3}/3)r$

AC = $(2\sqrt{3}/3)r$

Hexagonal Close Packed (hcp) Crystal Lattice

Rhombohedral unit cell
(60° angle)





$r = a/2$

2 atoms/unit cell

74% packing efficiency

Examples: Co, Ti, Ru

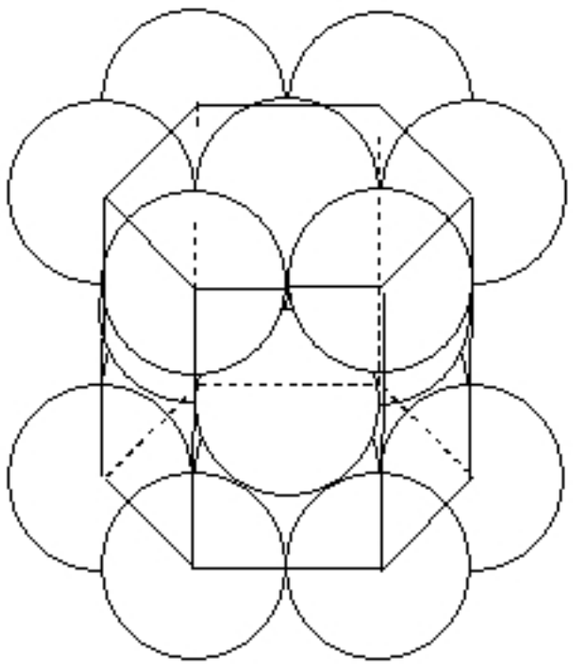
Co: r =125 pm

Ru: r =134 pm

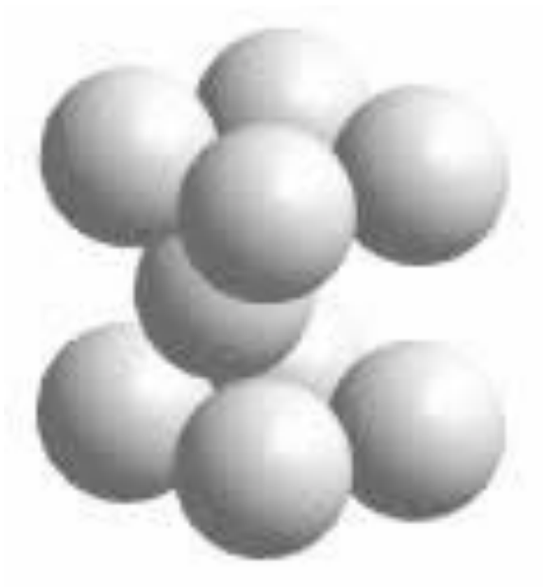
Ti: r =147 pm

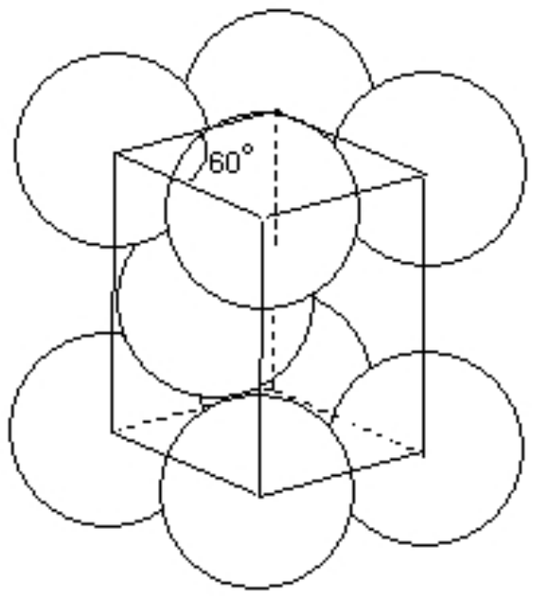
Hexagonal Close Packed (hcp) Crystal Lattice

Hexagonal unit cell



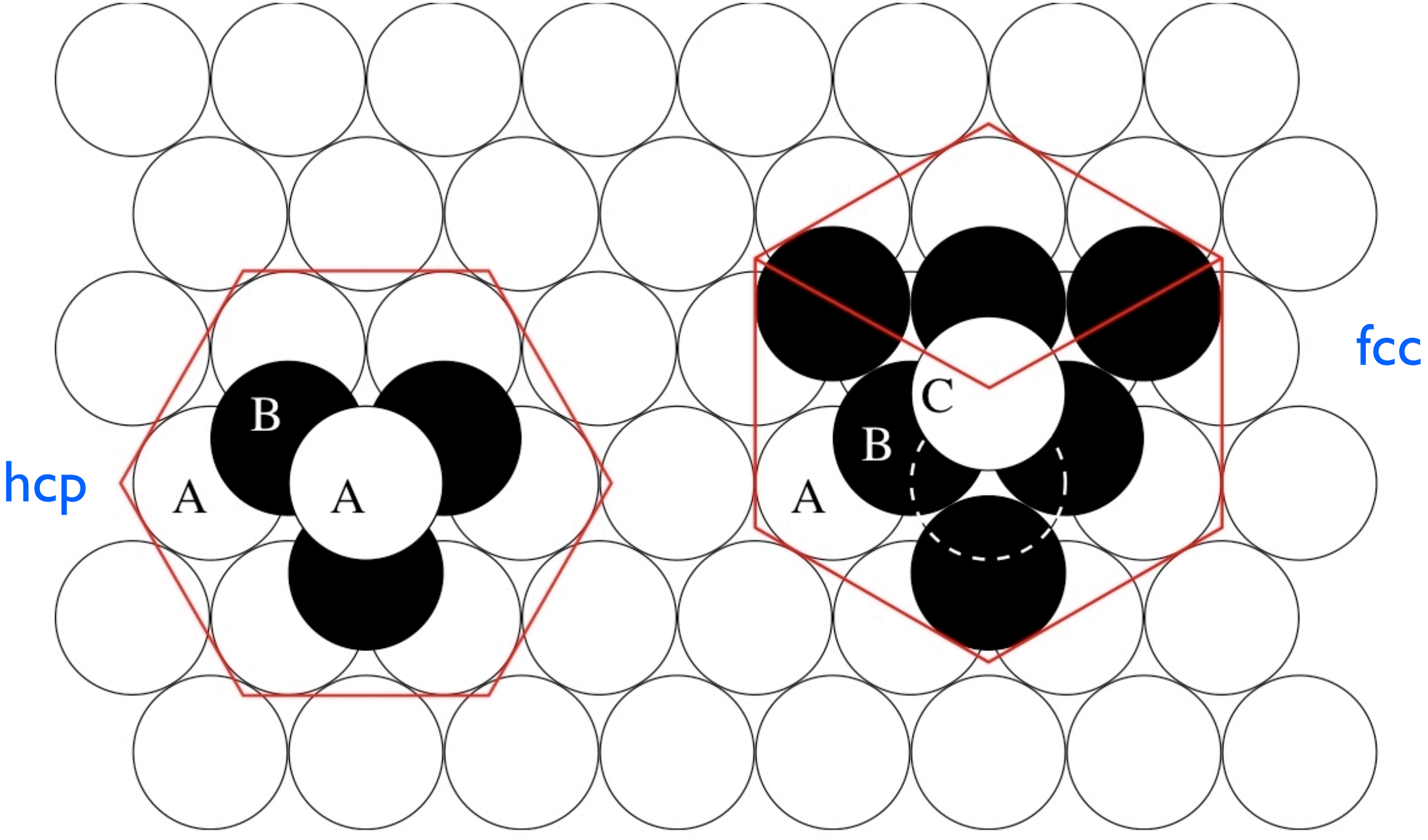
Rhombohedral unit cell



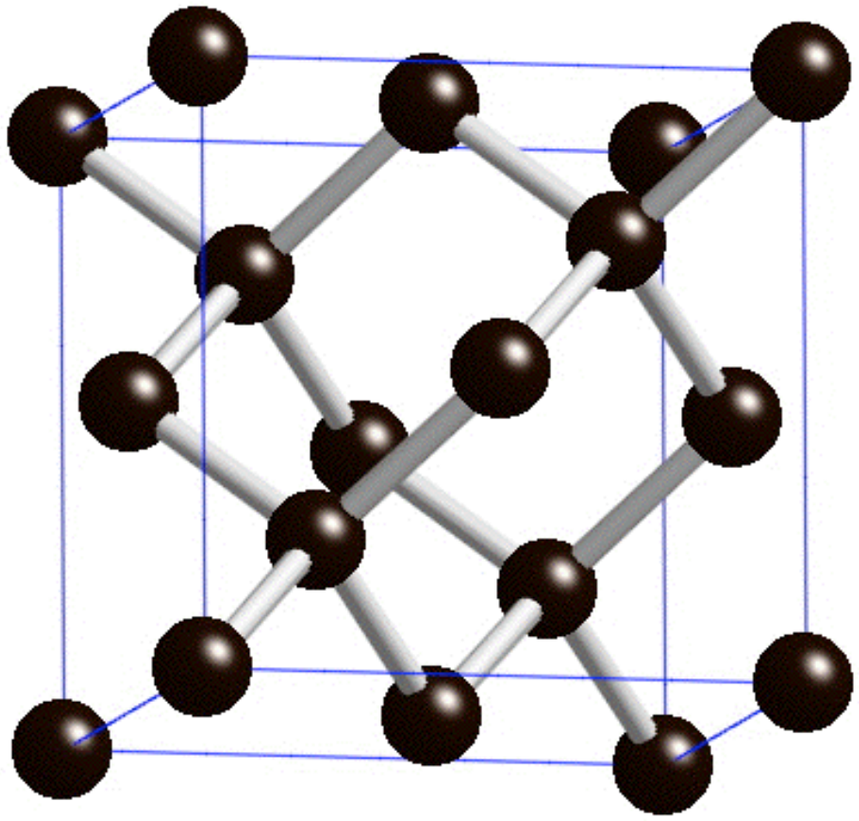


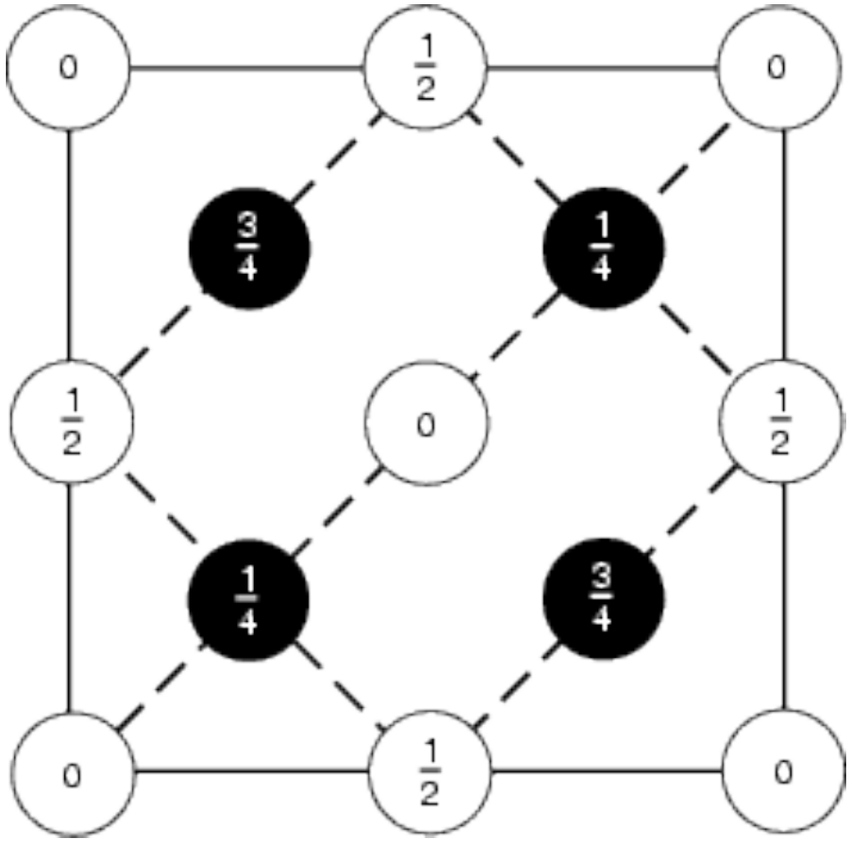
Hexagonal Close Packed (hcp) Crystal Lattice

hcp versus fcc packing:



In addition to fcc, bcc and hcp, there is the Diamond Lattice:

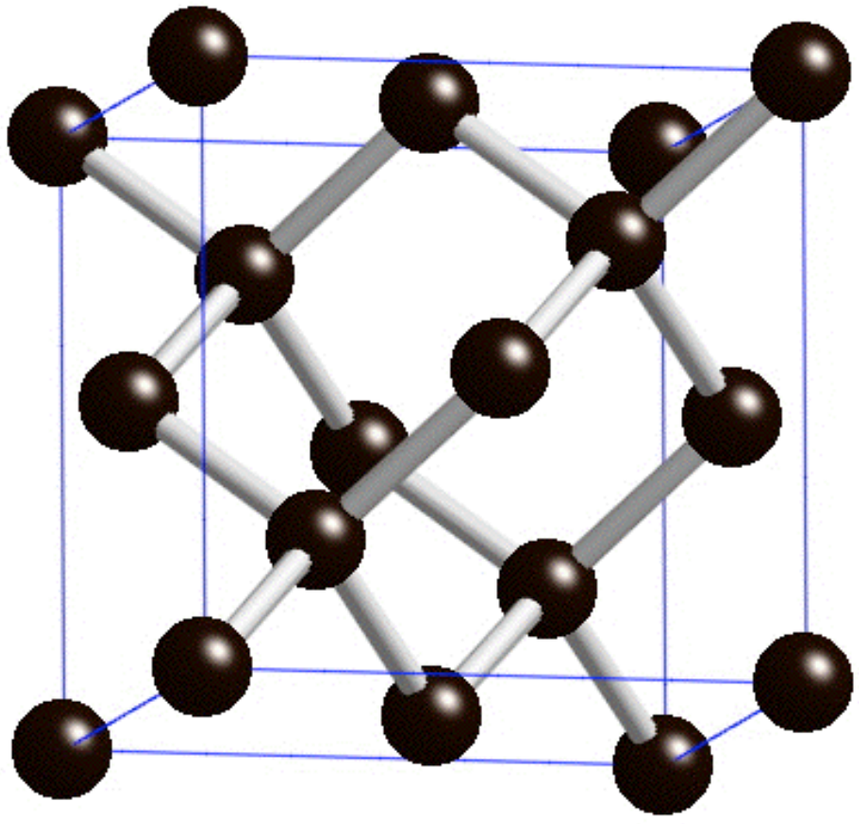




The diamond lattice is a is a face-centered lattice, with 4 additional atoms also occupying half of the tetrahedral interstices.

Examples: Carbon, Silicon and Germanium.

In addition to fcc, bcc and hcp, there is the Diamond Lattice:



$r = (\sqrt{3}/8)a$

8 atoms/unit cell

34% packing efficiency

The diamond lattice is a is a face-centered lattice, with 4 additional atoms also occupying half of the tetrahedral interstices.

Examples: Carbon, Silicon and Germanium.

Question: The density of silicon is 2.33 g/cm^3. Calculate the lattice constant and Si-Si distance in a Si crystal.

$$density = \frac{mass}{volume} = \frac{mass}{a^3}$$

$$a = \sqrt[3]{\frac{mass}{density}}$$

$$mass = \frac{(8 atoms)}{dia.unitcell} \frac{28.09 g/mol}{6.022 x 10^{23} atoms/mol} = 3.7317 x 10^{-22} g$$

Question: The density of silicon is 2.33 g/cm^3. Calculate the lattice constant and Si-Si distance in the crystal.

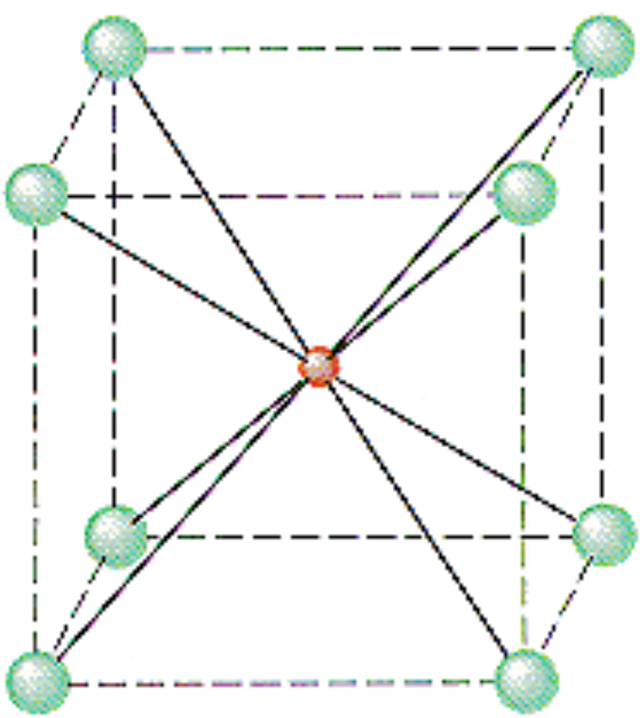
$$mass = 3.7317x10^{-22}g$$

$$a = \sqrt[3]{\frac{mass}{density}} = \sqrt[3]{\frac{3.7317x10^{-22}g}{2.33g/cm^3}} = 5.4306x10^{-8}cm = 5.43\text{Å}$$

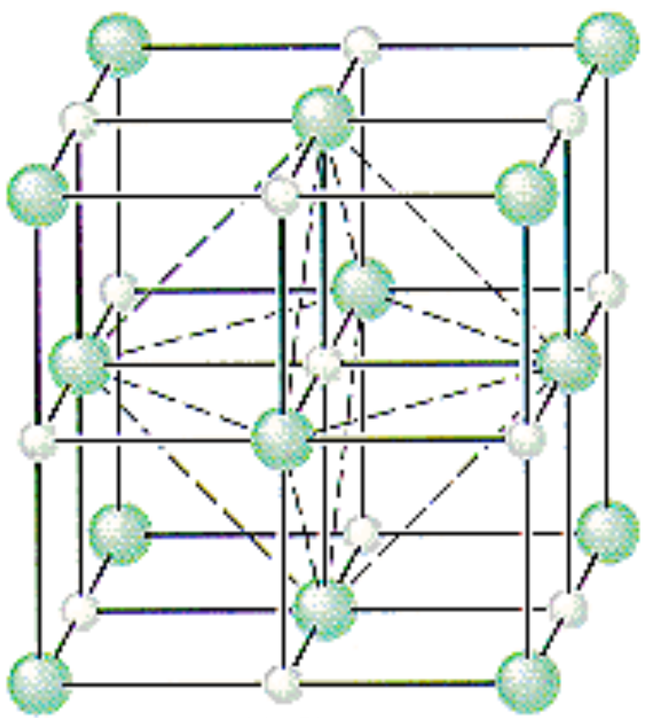
a = 543 pm

Si-Si distance =2r = 2($\sqrt{3}$/8)a = 235 pm

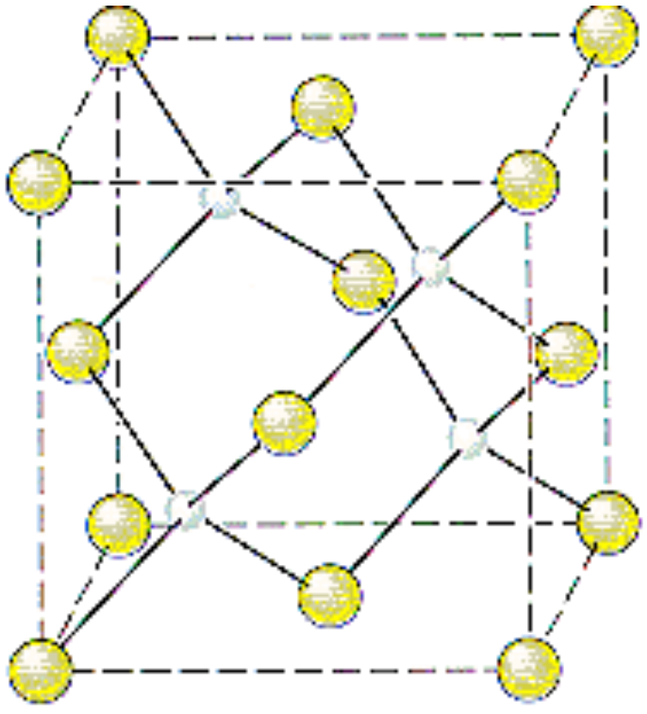
Compound Lattices:



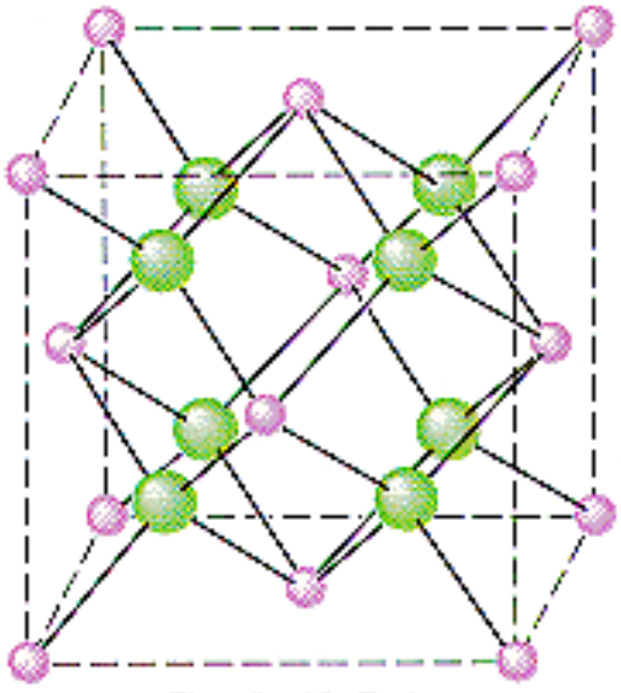
CsCl



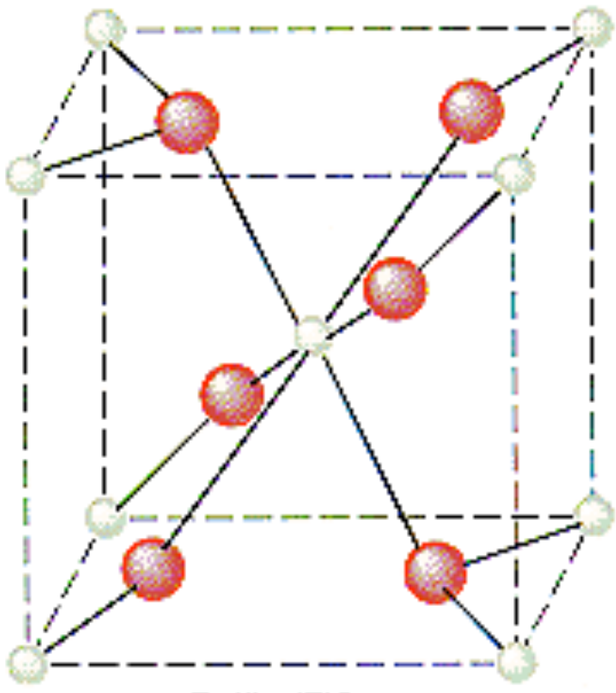
NaCl



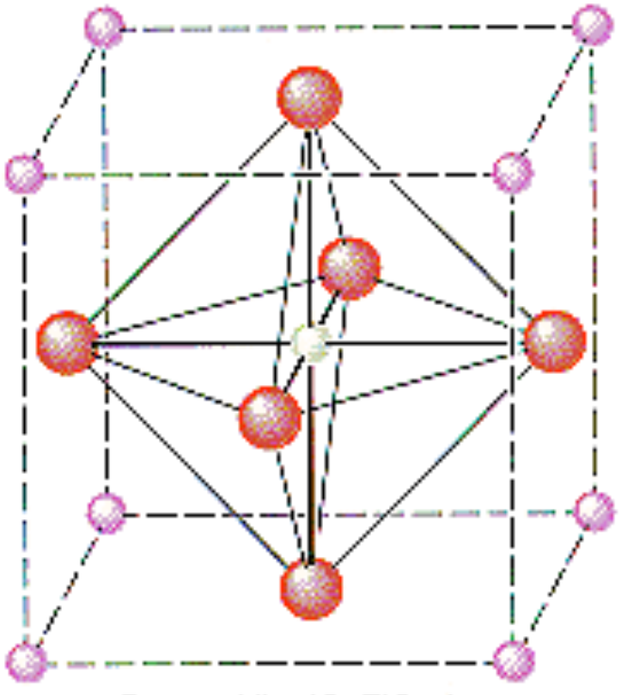
Zinc blende (cubic ZnS)



Flourite (CaF_2)



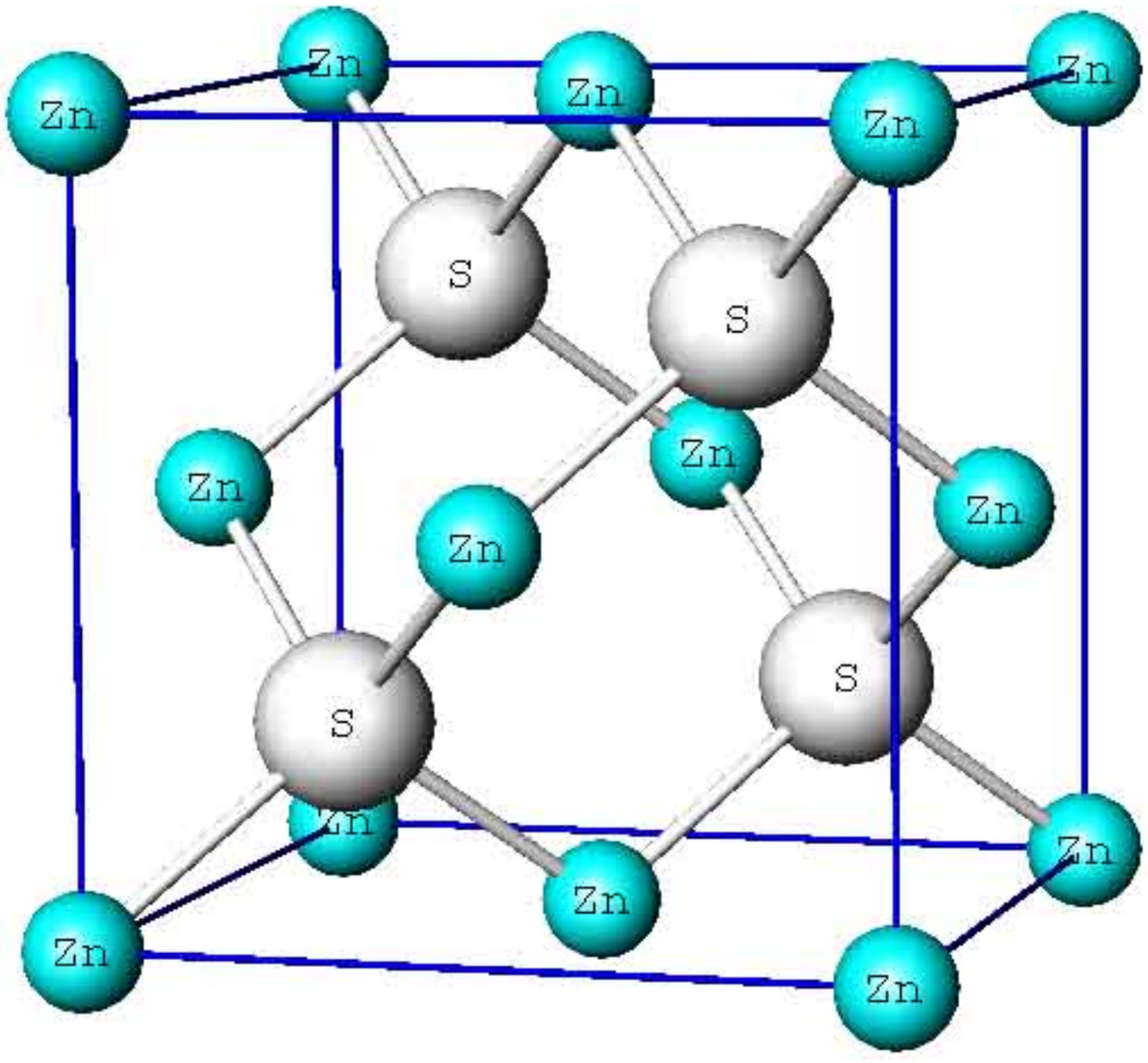
Rutile (TiO_2)



Perovskite ($CaTiO_3$)

= Ca^{2+} = Ti^{iv} = Ca^{2+} = O^{2-}

An example: zinc blende (ZnS) structure



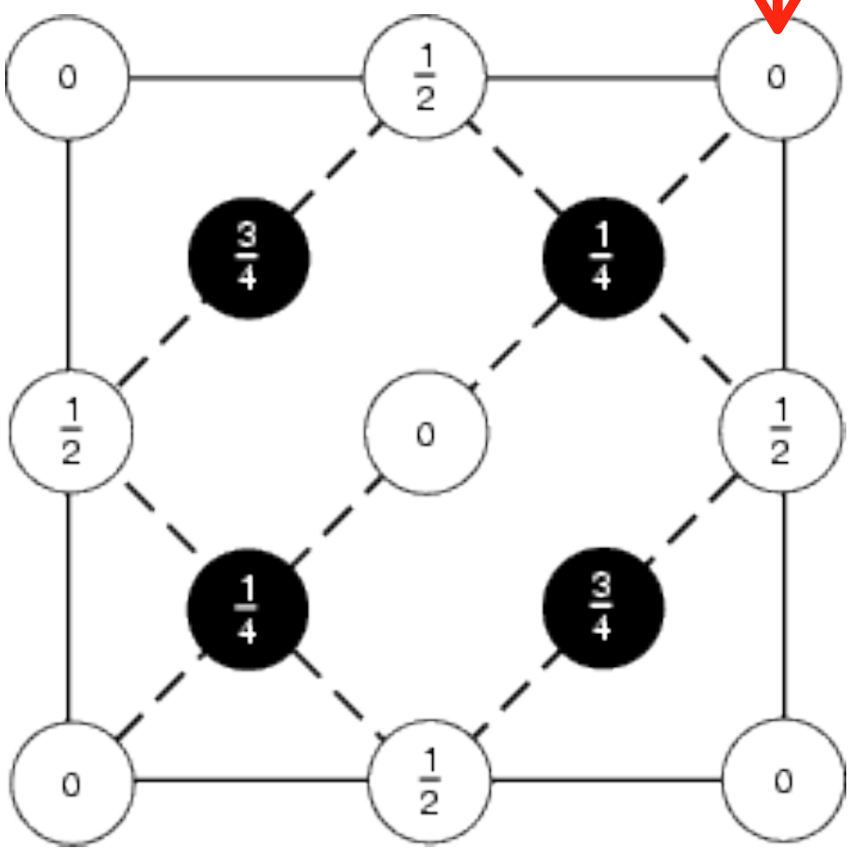
3D view!

ionic bonding or covalent bonding?

An example: zinc blende (ZnS) structure

Atoms of one type occupy FCC lattice positions

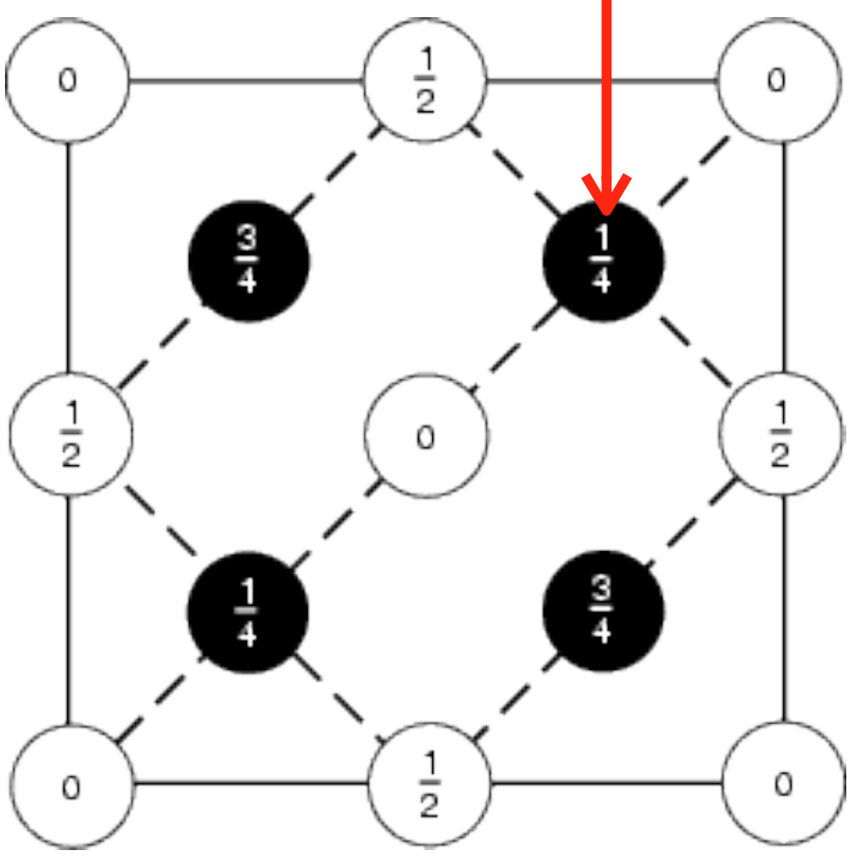
Top view:



An example: zinc blende (ZnS) structure

Atoms of second type fill **half** of the tetrahedral holes (diamond lattice).

Top view:



Let's calculate the packing efficiency for a fcc crystal:

the packing efficiency, f, is the ratio between the volume of the atoms in the unit cell, V_{atoms}, and the total unit cell volume, V_{cell}:

$$f = \frac{V_{atoms}}{V_{cell}}$$

since it contains four atoms, the fcc unit cell is characterized by:

$$V_{atoms} = 4\left(\frac{4}{3}\pi r^3\right) = \frac{16\pi r^3}{3}$$

Let's calculate the packing efficiency for a fcc crystal:

using $4r = \sqrt{2}a$, the total volume of the fcc unit cell is just:

$$V_{cell} = a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3 = \frac{64r^3}{2\sqrt{2}}$$

taking the ratio between V_{atoms} and V_{cell}, we get:

$$f = \frac{V_{atoms}}{V_{cell}} = \frac{\frac{16\pi r^3}{3}}{\frac{64r^3}{2\sqrt{2}}} = \frac{\frac{16\pi}{3}}{\frac{64}{2\sqrt{2}}} = \frac{32\pi\sqrt{2}}{3(64)} = 0.74$$