Lecture C3
Microscopic to Macroscopic, Part 3:
Hydrogen Bonding and X-ray Diffraction

Last time we examined various types of noncovalent intermolecular interactions:

a. ion-ion
b. ion-dipole
c. electric dipole-electric dipole
d. magnetic dipole-magnetic dipole
e. dispersion forces
f. hydrogen bonding
g. metal-ligand bonding

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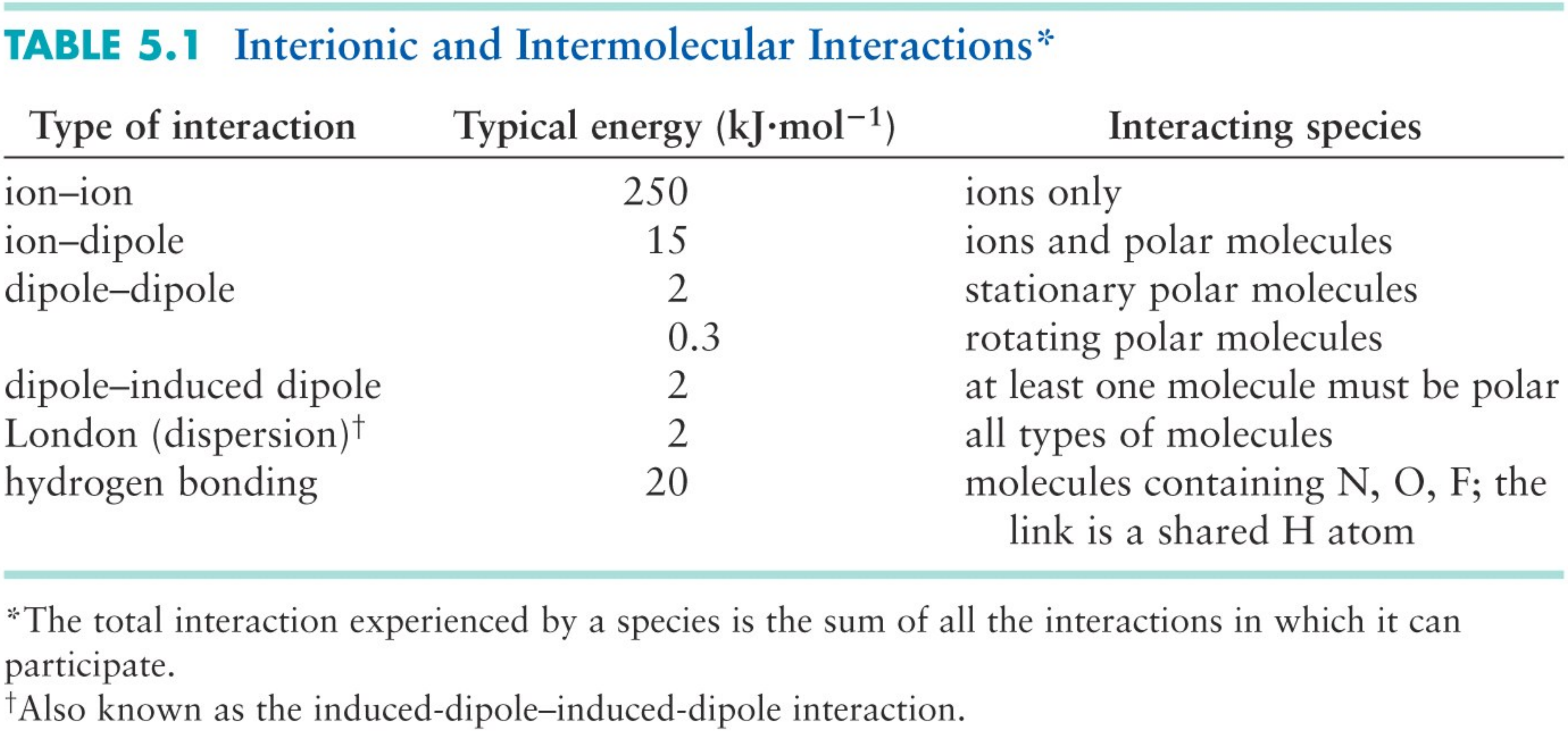

TABLE 5.1 Interionic and Intermolecular Interactions*

Type of interaction	Typical energy ($kJ \cdot mol^{-1}$)	Interacting species
ion–ion	250	ions only
ion–dipole	15	ions and polar molecules
dipole–dipole	2	stationary polar molecules
	0.3	rotating polar molecules
dipole–induced dipole	2	at least one molecule must be polar
London (dispersion)†	2	all types of molecules
hydrogen bonding	20	molecules containing N, O, F; the link is a shared H atom

*The total interaction experienced by a species is the sum of all the interactions in which it can participate.

†Also known as the induced-dipole–induced-dipole interaction.

C-H covalent bond in CH_4 = 440 kJ mol^{-1}

Noncovalent Intermolecular Interactions

a. ion-ion
b. ion-dipole
c. electric dipole-electric dipole
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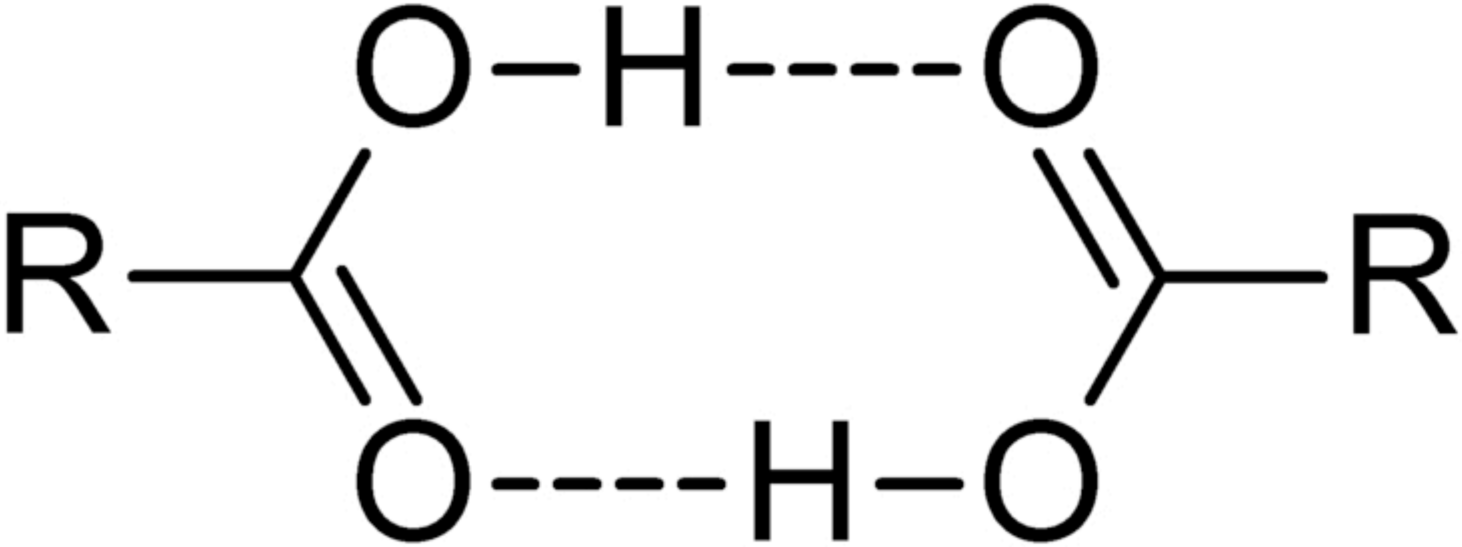
e. dispersion forces
f. hydrogen bonding
g. metal-ligand bonding

Let's look at hydrogen bonding next!

Noncovalent Intermolecular Interactions

f. hydrogen bonding

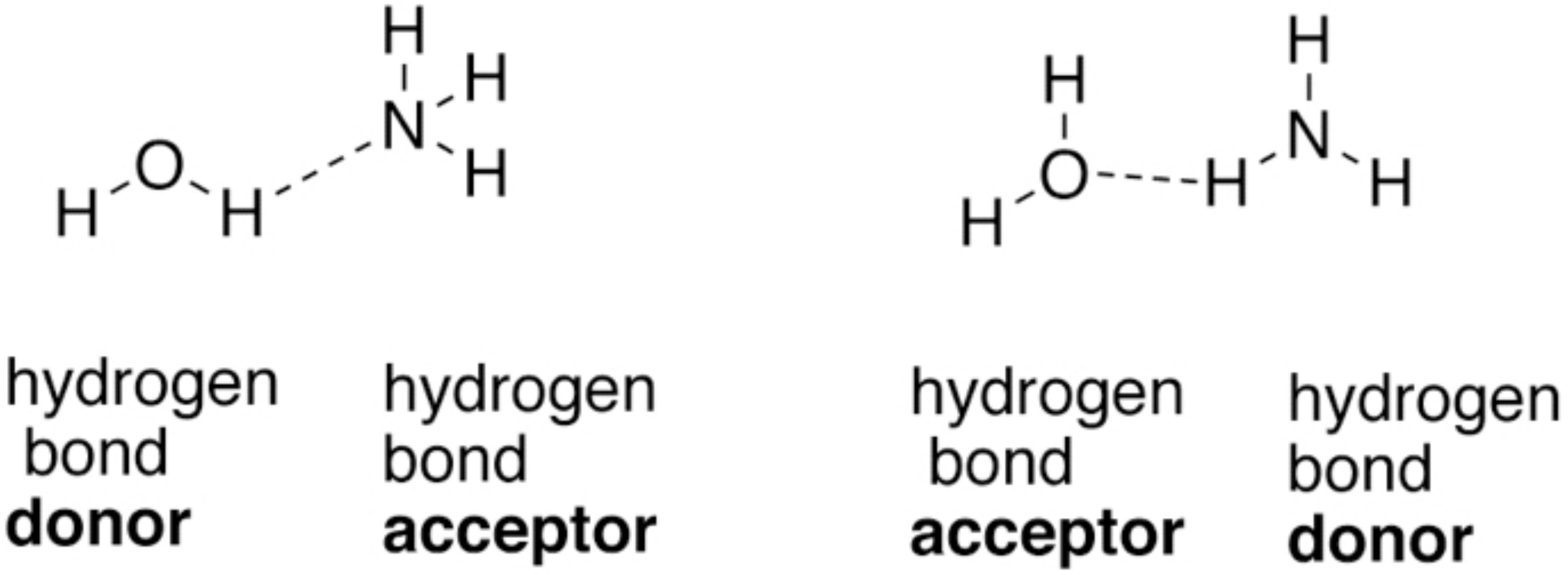


carboxylic acid dimer

Hydrogen bonds are formed by electronegative atoms (e.g., O, N, F) sharing their lone pair electrons with hydrogen atoms.

Noncovalent Intermolecular Interactions

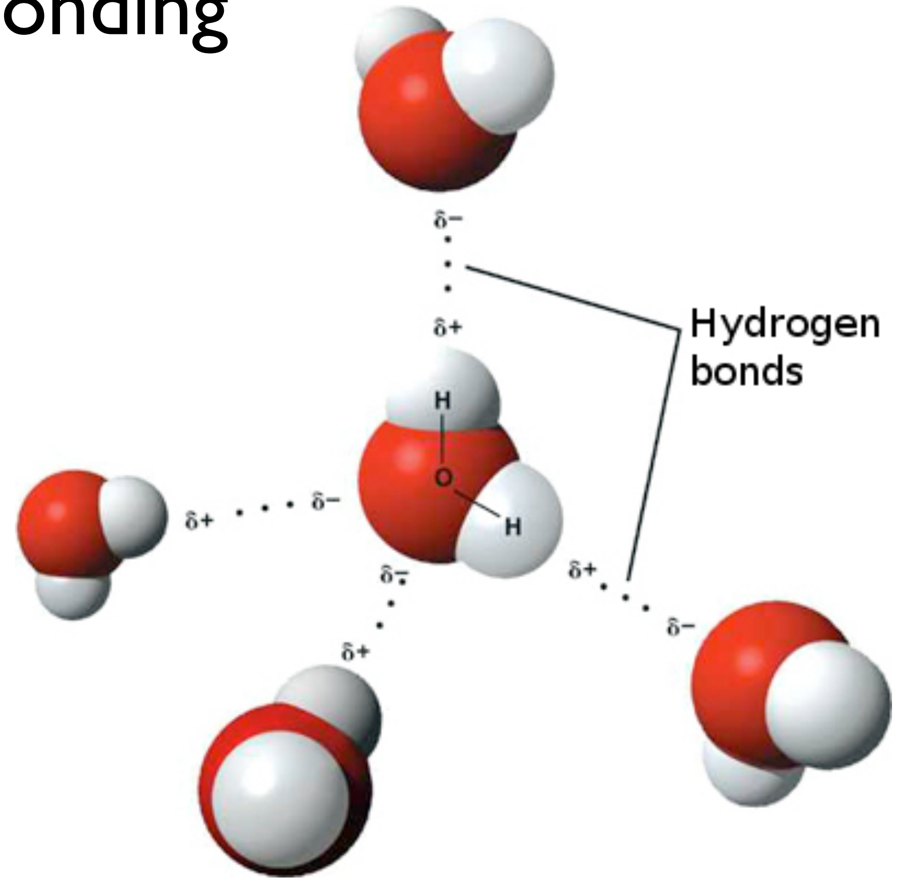
f. hydrogen bonding



The H-bond donor shares the Hydrogen atom;
the acceptor shares the lone pair.

Noncovalent Intermolecular Interactions

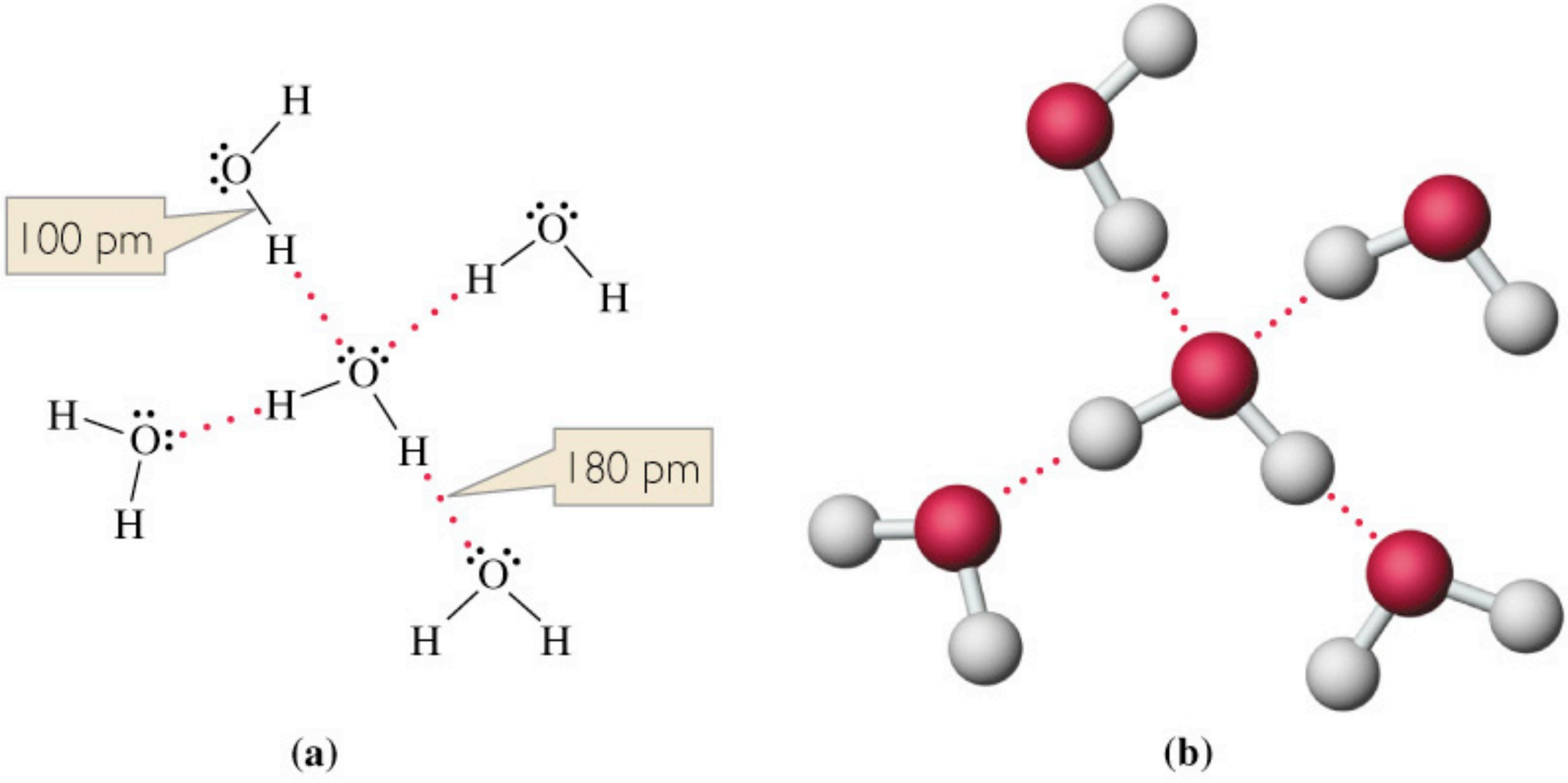
f. hydrogen bonding



Water is highly hydrogen bonded

Noncovalent Intermolecular Interactions

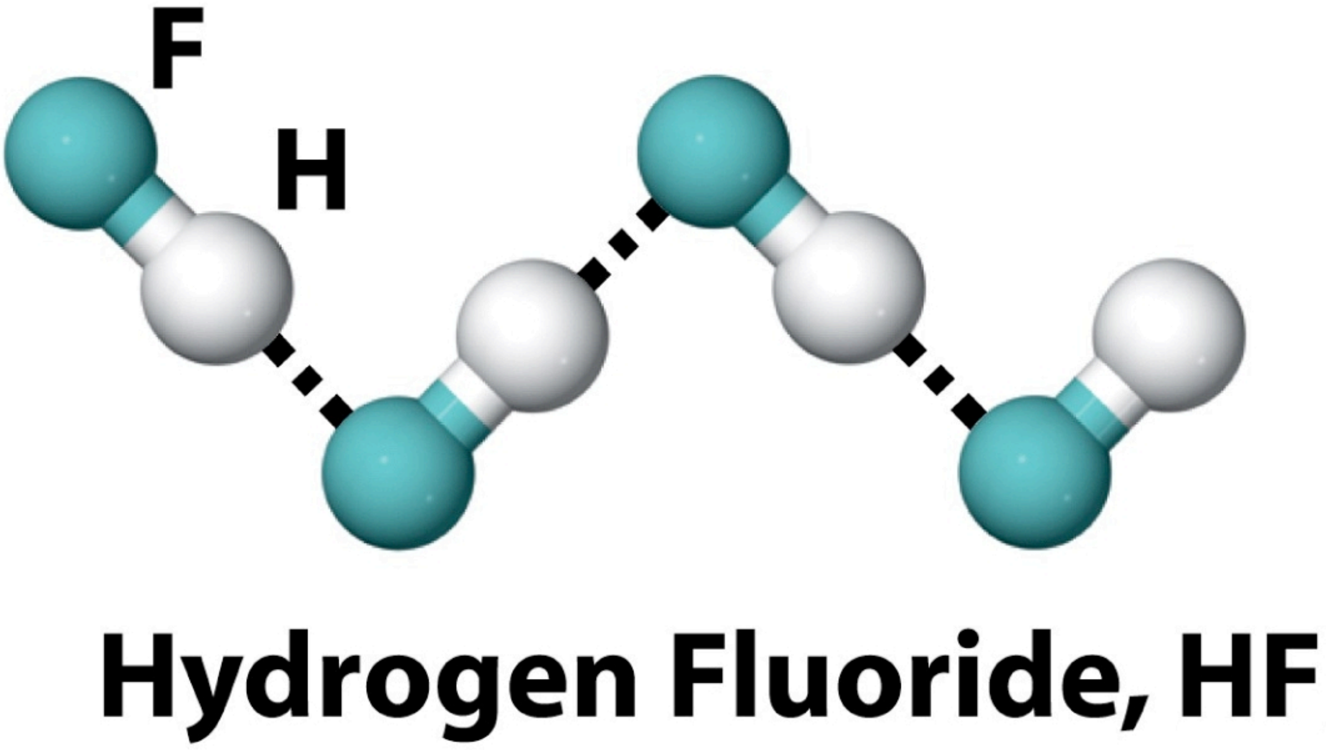
f. hydrogen bonding



a typical hydrogen bond energy is 20 kJ mol^{-1}

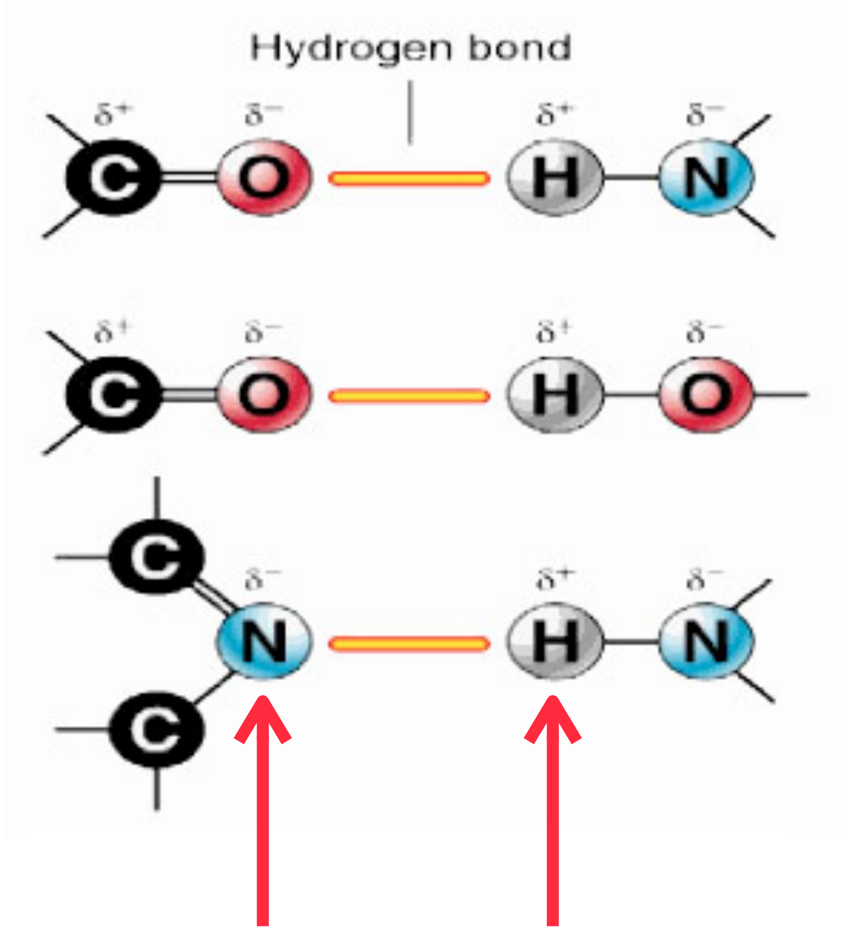
Noncovalent Intermolecular Interactions

f. hydrogen bonding



HF hydrogen bond energy - a whopping 40 kJ mol^{-1}

Some more hydrogen bonds...



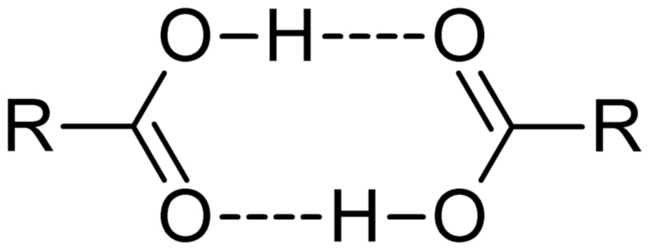
NH-carbonyl O

OH-carbonyl O

NH-amine N

H-bond: acceptor donor

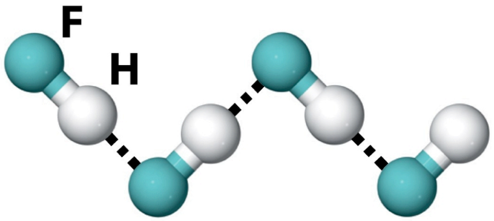
OH stretching frequencies in Hydrogen Bonds



carboxylic acid dimer

Formic Acid (R=H):
OH 3570 cm-1 monomer
OH 3080 cm-1 dimer

$\Delta\nu = 490\ \text{cm}^{-1}$



Hydrogen Fluoride, HF

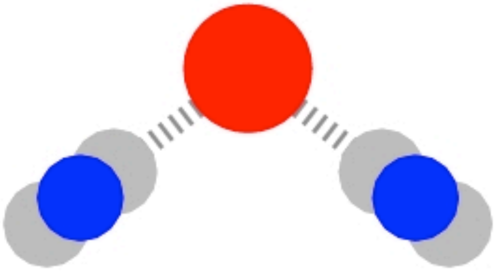
HF
HF 3960 cm-1 monomer
HF 3450 cm-1 hydrogen bonded

$\Delta\nu = 510\ \text{cm}^{-1}$

Frequency decreases (smaller k), but the Intensity increases : $\Delta\mu/\Delta x$ is substantially larger when H-bonding occurs

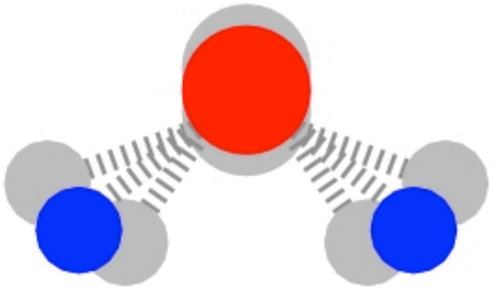
OH stretching frequencies in Hydrogen Bonds

Water: gas phase
3756 cm^{-1} ν_3 OH asymmetric stretch
3651 cm^{-1} ν_1 OH symmetric stretch
1595 cm^{-1} ν_2 HOH bend



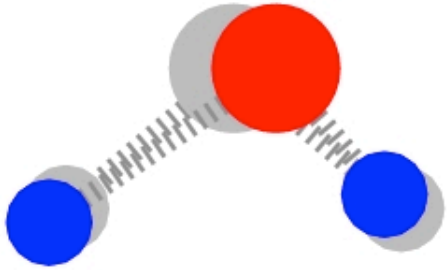
ν_1

sym stretch



ν_2

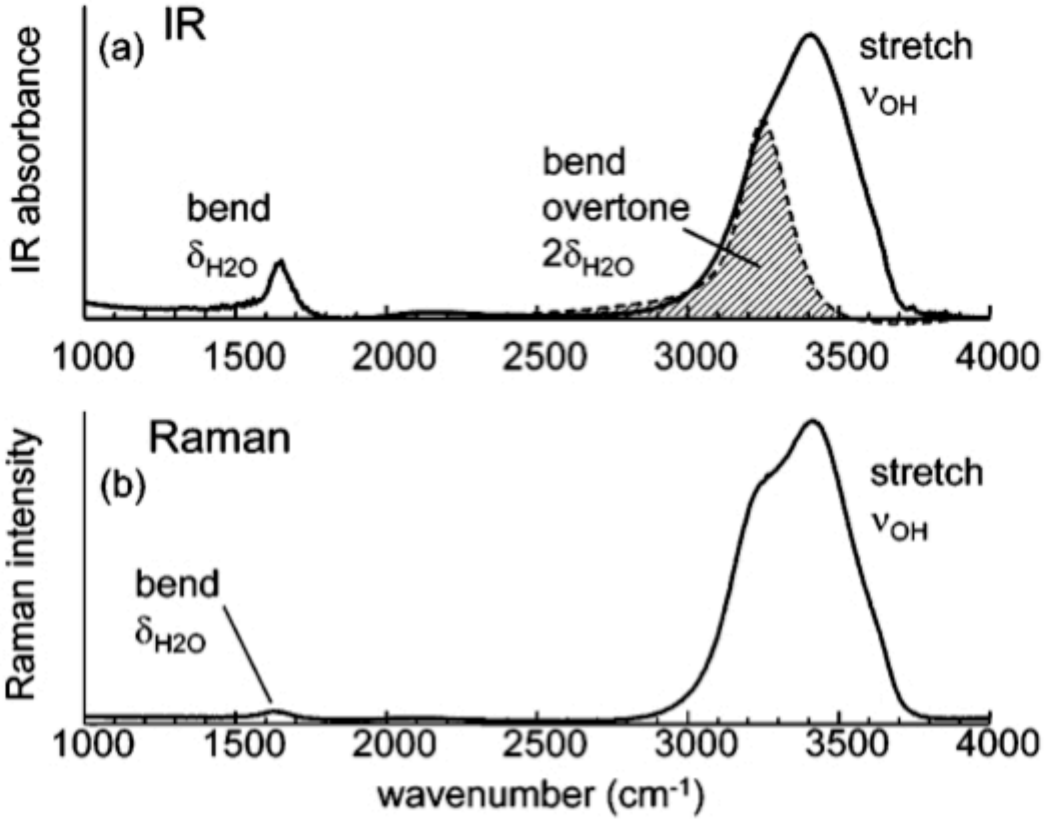
bend

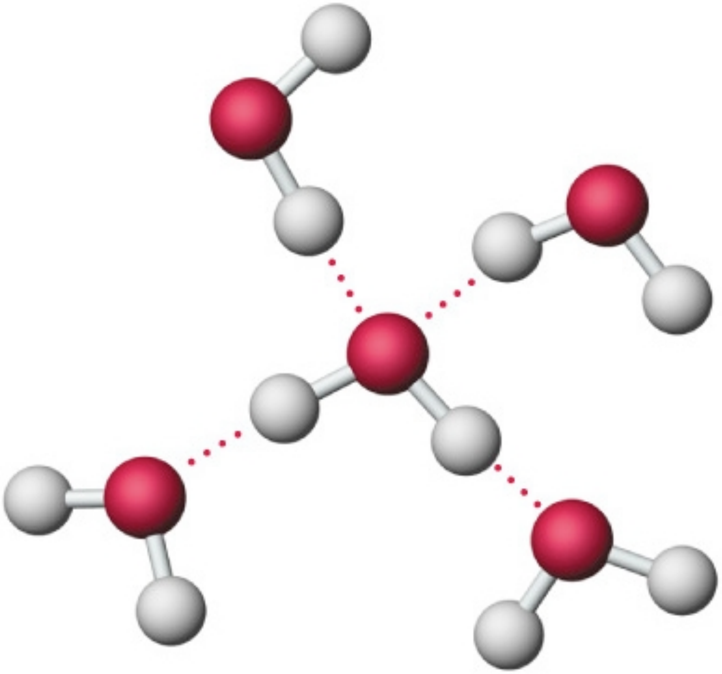


ν_3

asym stretch

IR and Raman OH stretching bands in liquid water:





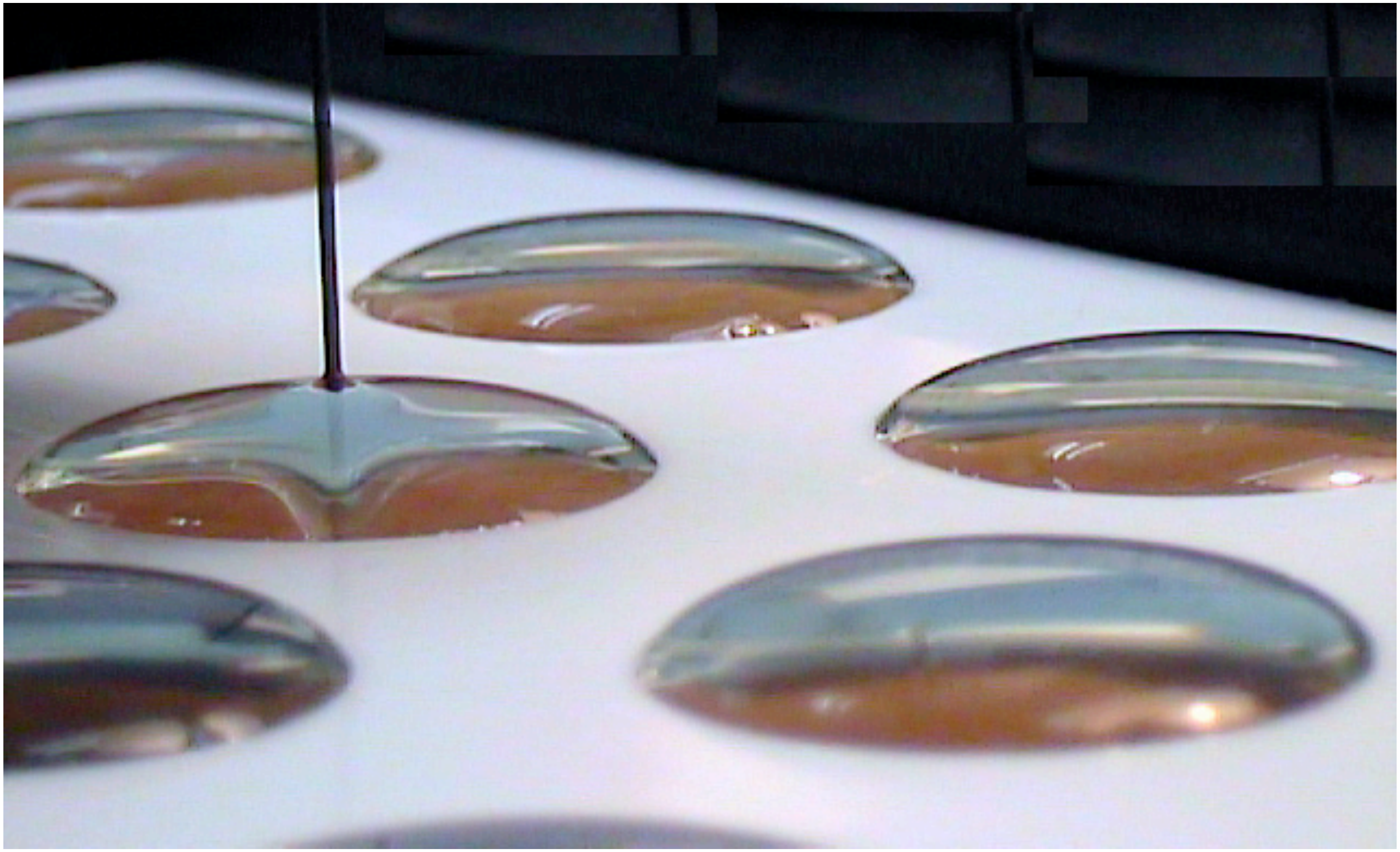
Water: liquid
OH 3400 cm^{-1} sym stretch (Raman)
OH 3400 cm^{-1} asym stretch (IR)

$\Delta\nu$ = 356 cm^{-1}

Intense, broad bands

ice: 3200 cm^{-1}

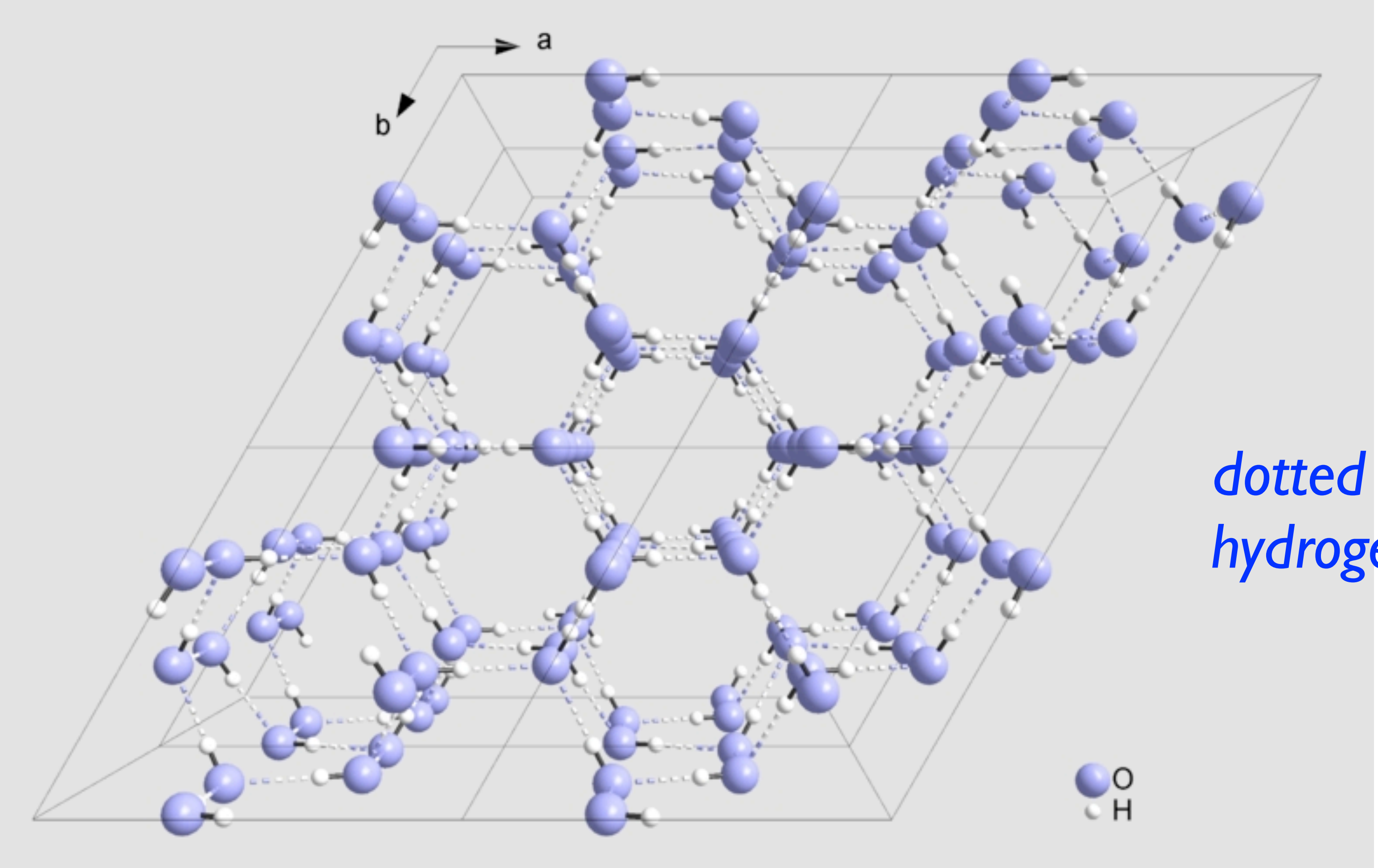
*Water also has a very high **surface tension** that is due to H-bonding*



H_2O: 72.8 dynes/cm

Octane: 21.62 dynes/cm

There are 15 known phases of ice. Here is the crystal structure for the most familiar to us, Ice I_h (hexagonal ice).



dotted lines are hydrogen bonds

This structure was obtained from a combination of x-ray diffraction (for the oxygen atoms) and neutron diffraction (for the hydrogen atoms).

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, but the real value of his work lies in the relation of the x-ray diffraction patterns to crystal structure.

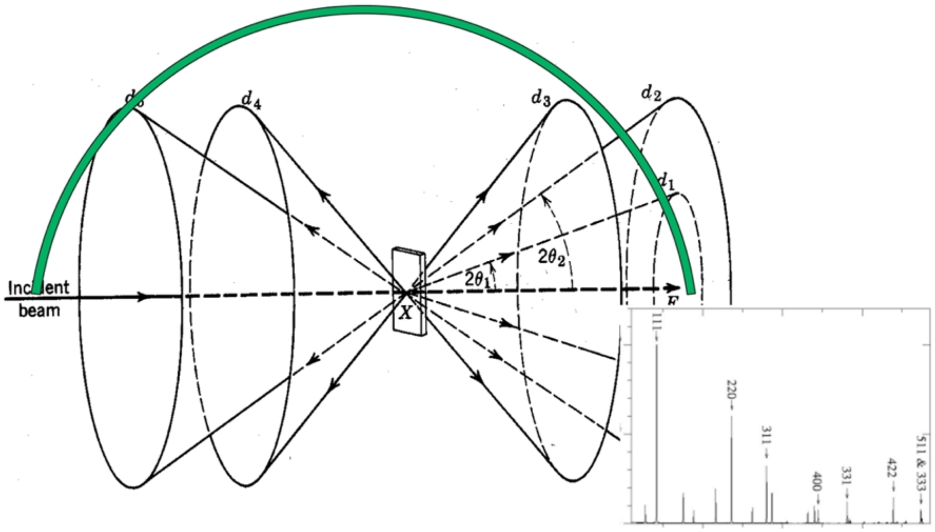
He later went on to direct the *Fritz Haber Institute* in Berlin in 1951.

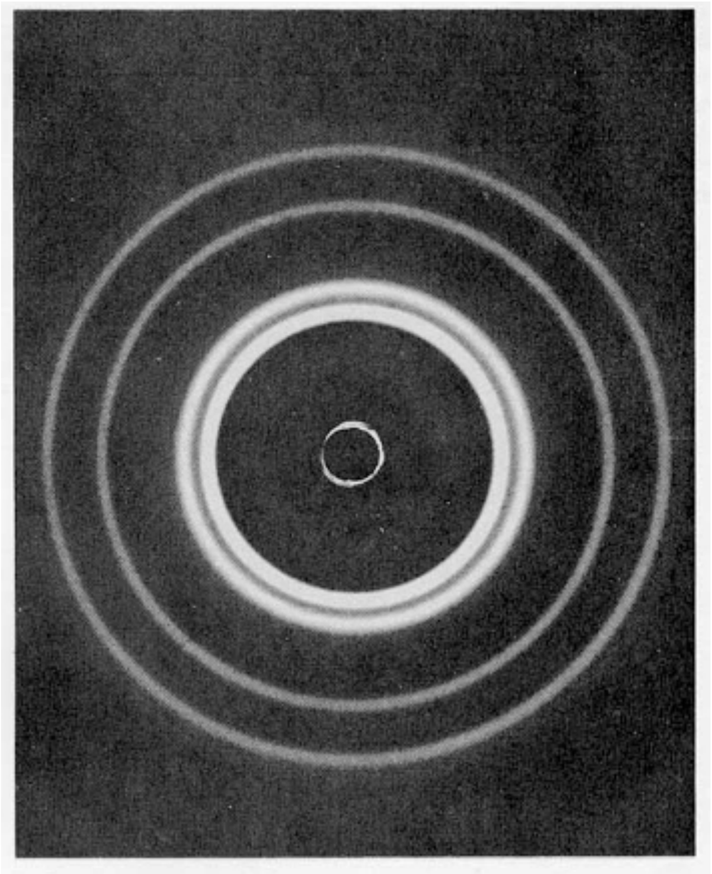
Max von Laue (1879-1960)

X-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.

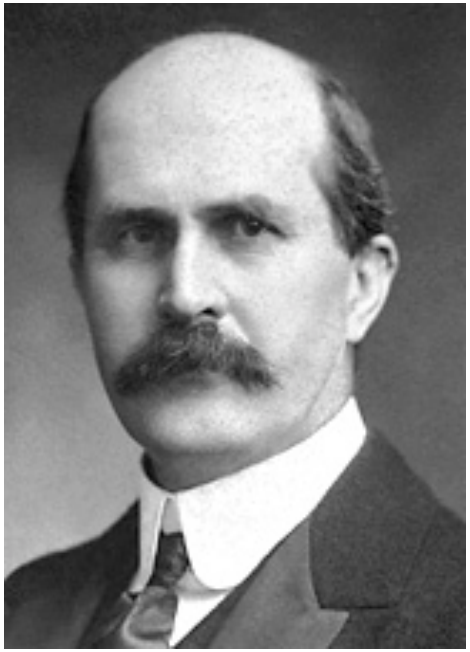




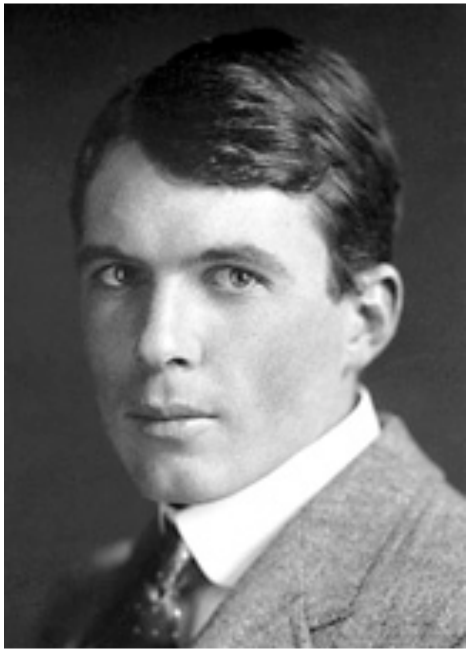
The W. H. Bragg/W L. Bragg father and son team won the 1915 Nobel Prize (the very next year) for providing a quantitative understanding of these diffraction patterns.

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

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

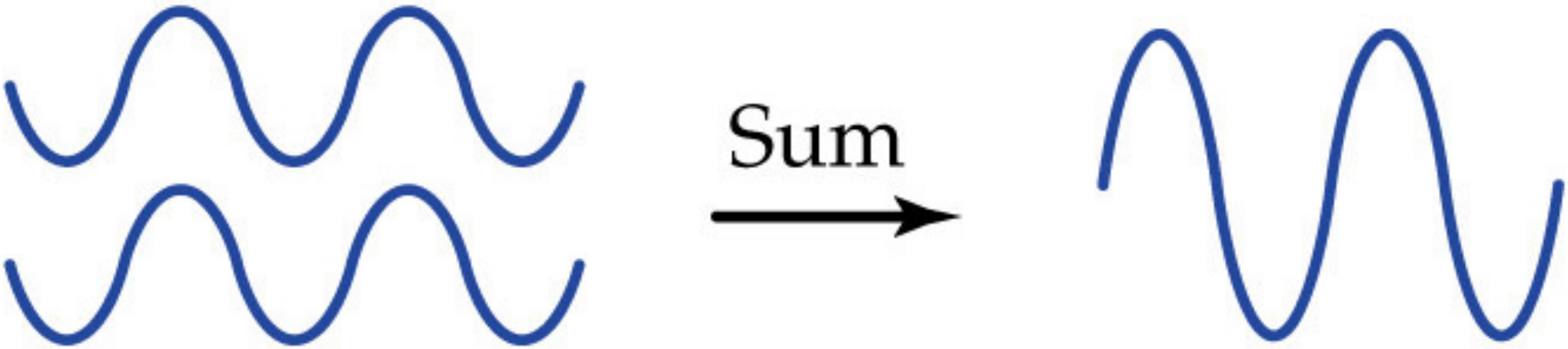


William H. Bragg
(1862 – 1942)

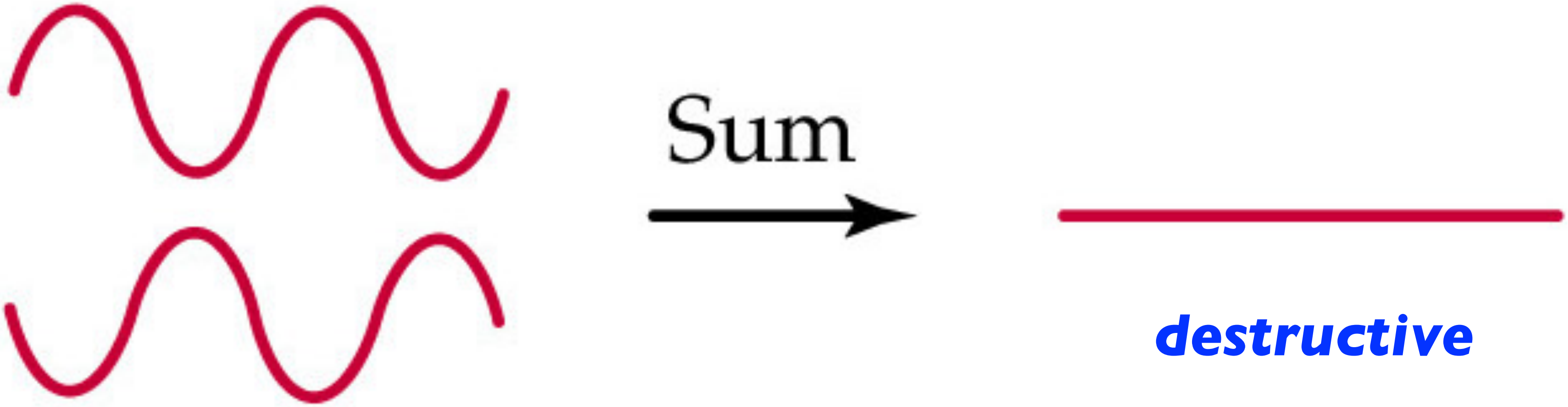


William L. Bragg
(1890 – 1971)

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

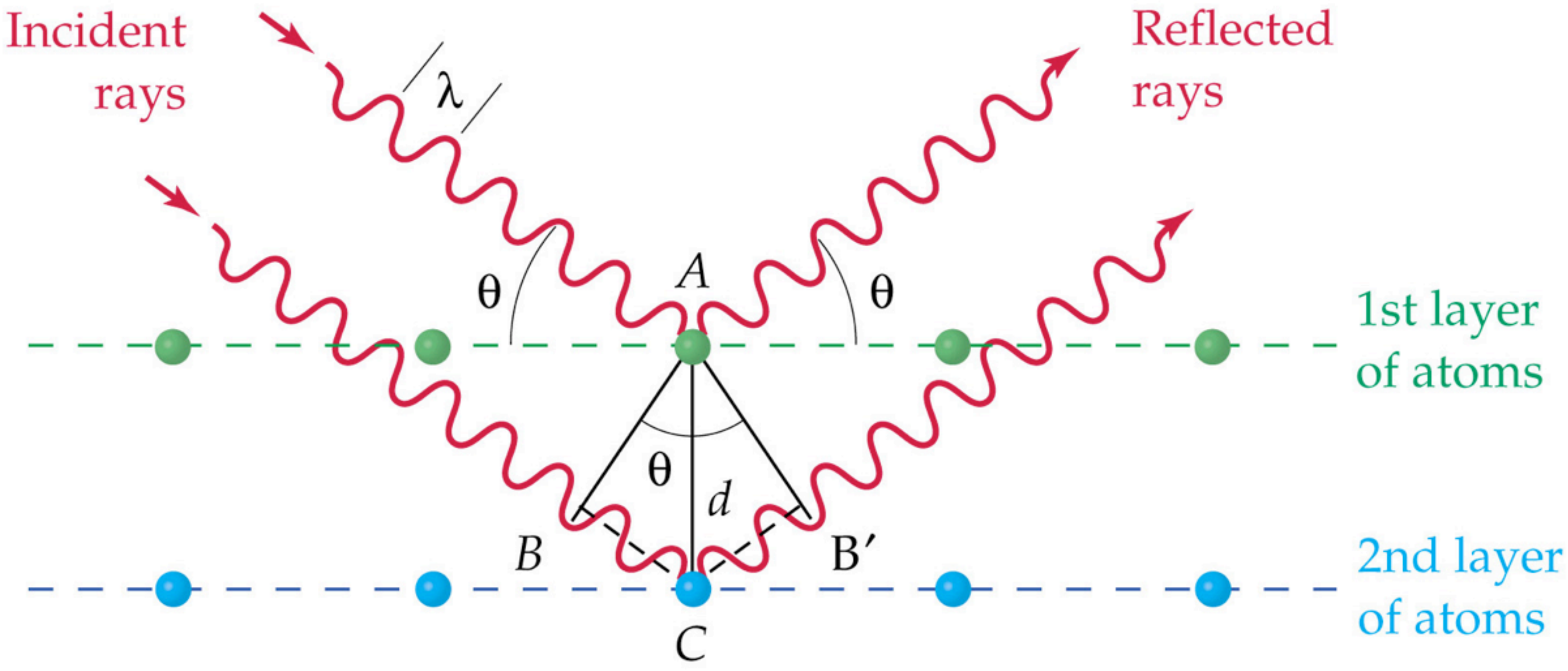


constructive



destructive

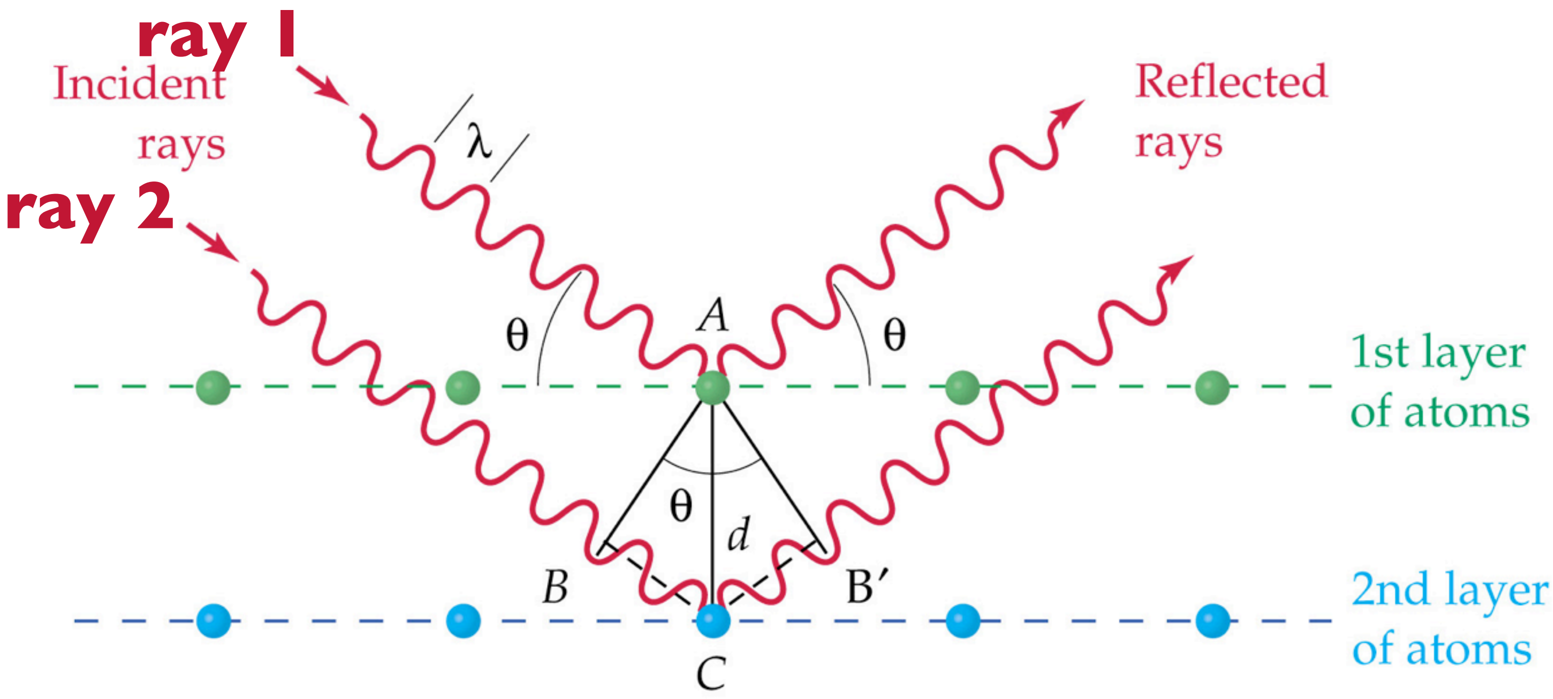
Bragg Diffraction



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

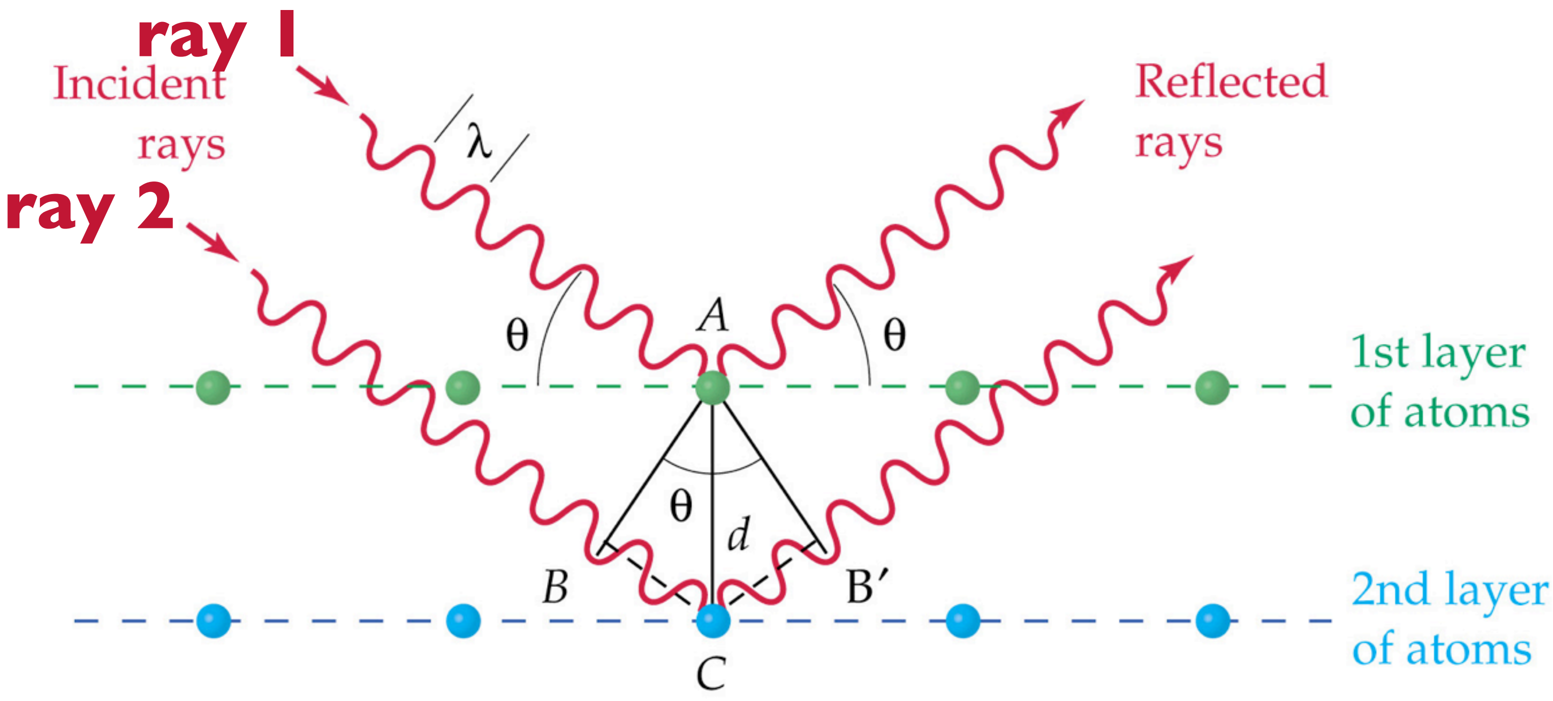
Let's derive the Bragg Eq.:

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: nλ = 2BC.



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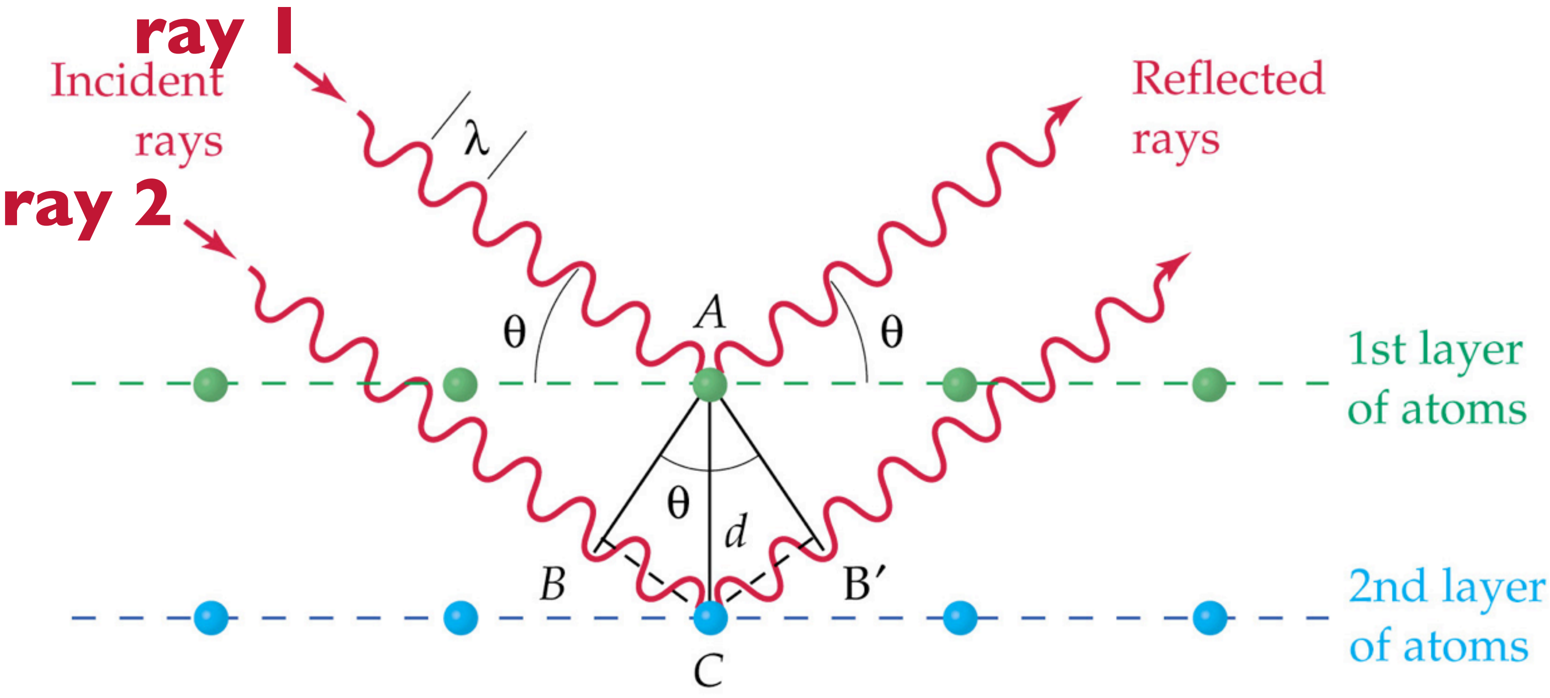
3. Since AC is the hypothenuse of a right triangle ABC, BC = dsinθ.



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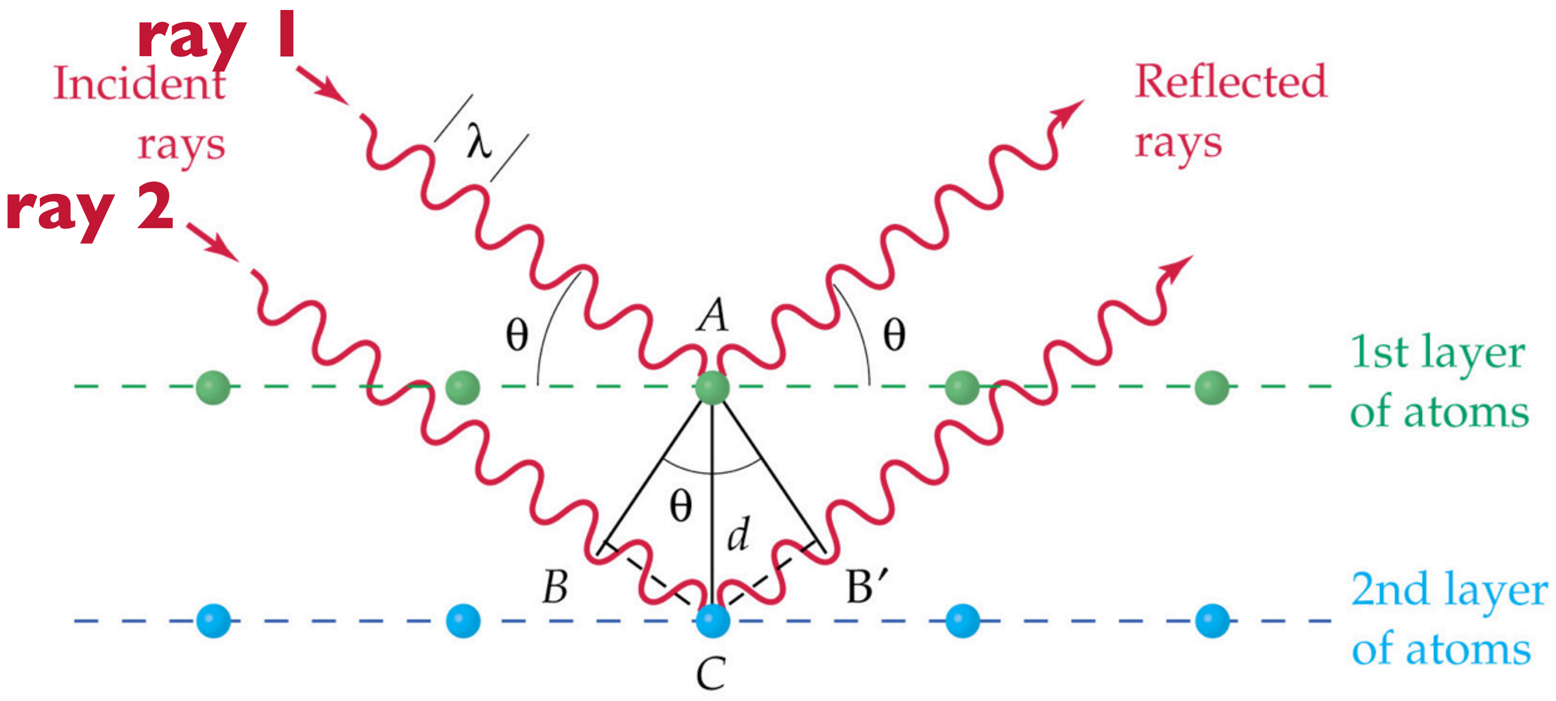
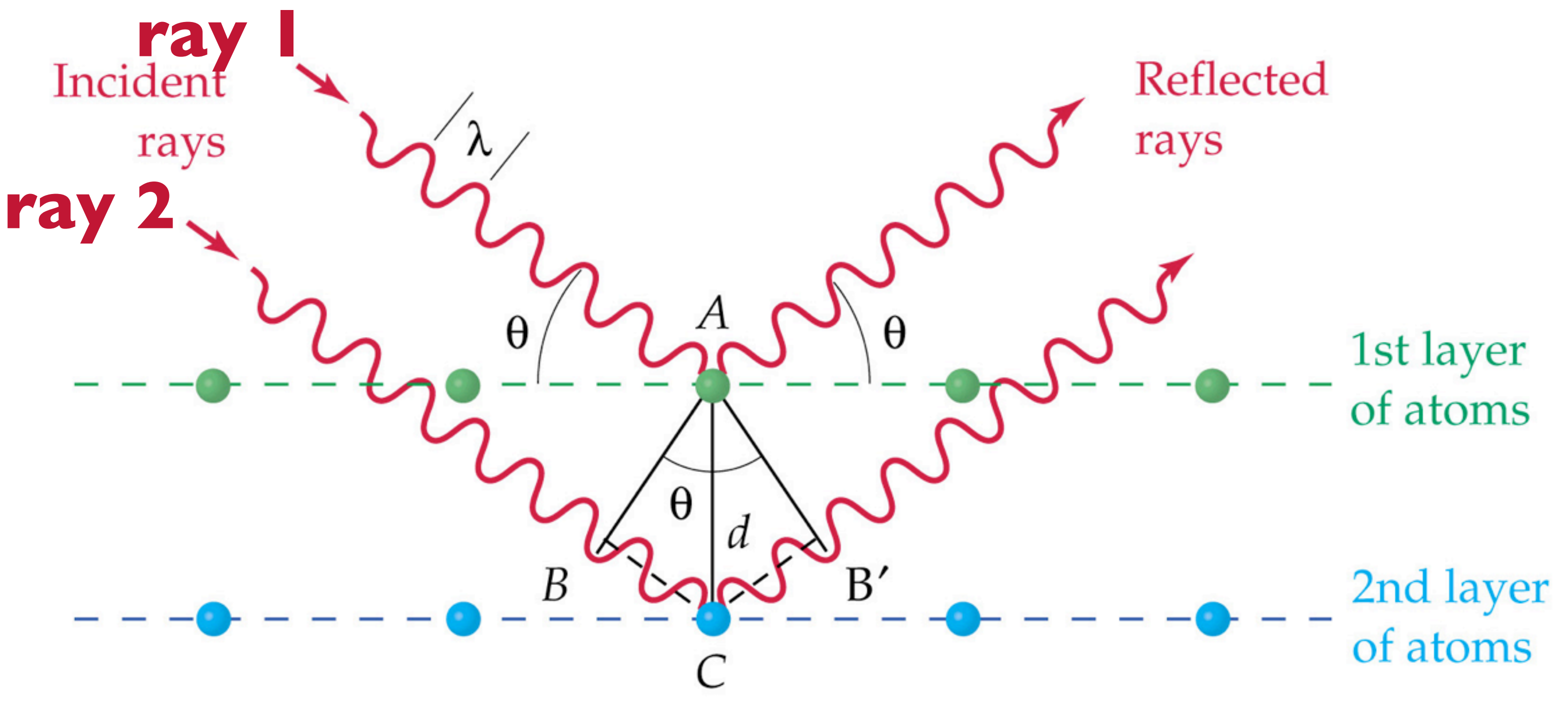
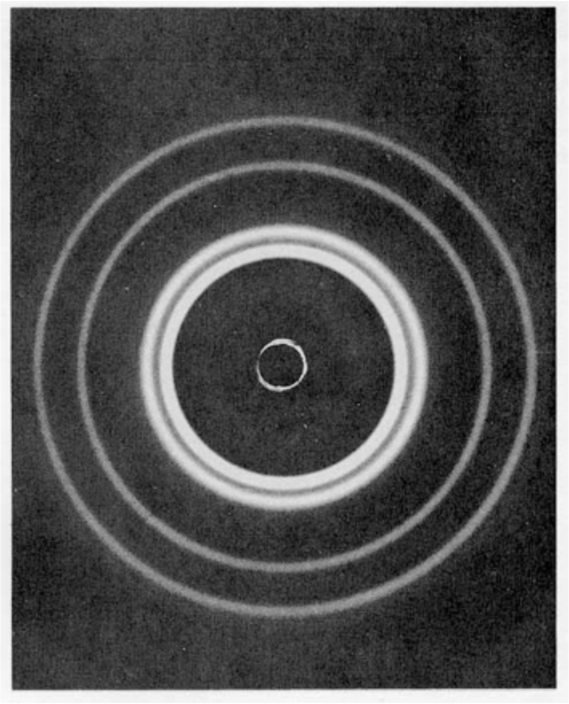
2. This extra distance must equal a multiple of λ in order for the interference with ray 1 to be constructive: $n\lambda = 2BC$
3. Since AC is the hypothenuse of a right triangle ABC, $BC = d\sin\theta$.
4. So, $\mathbf{n\lambda} = 2BC = \mathbf{2d\sin\theta}$ Q.E.D.



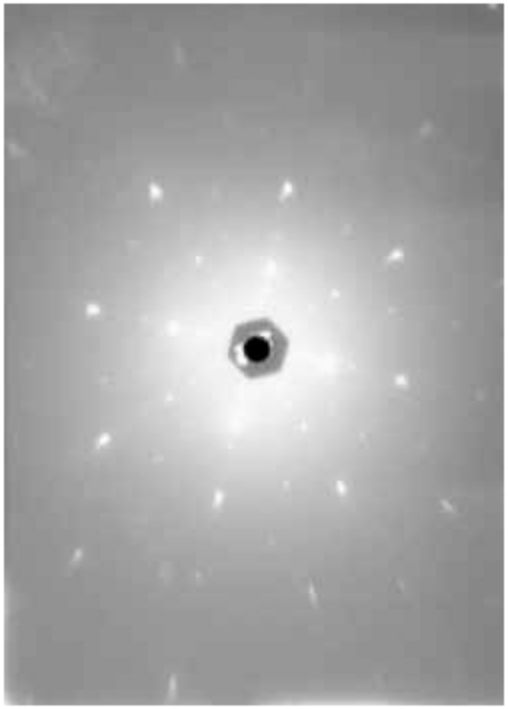
Thus, when 2dsinθ = nλ, there is **constructive** interference.



Why Rings?



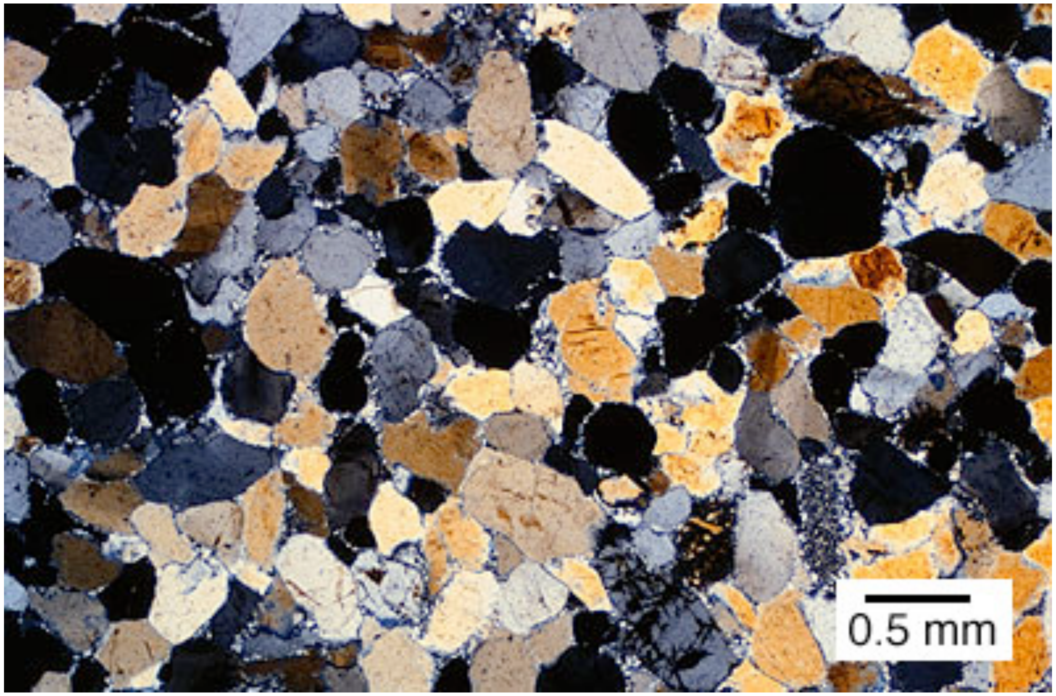
Thin foil

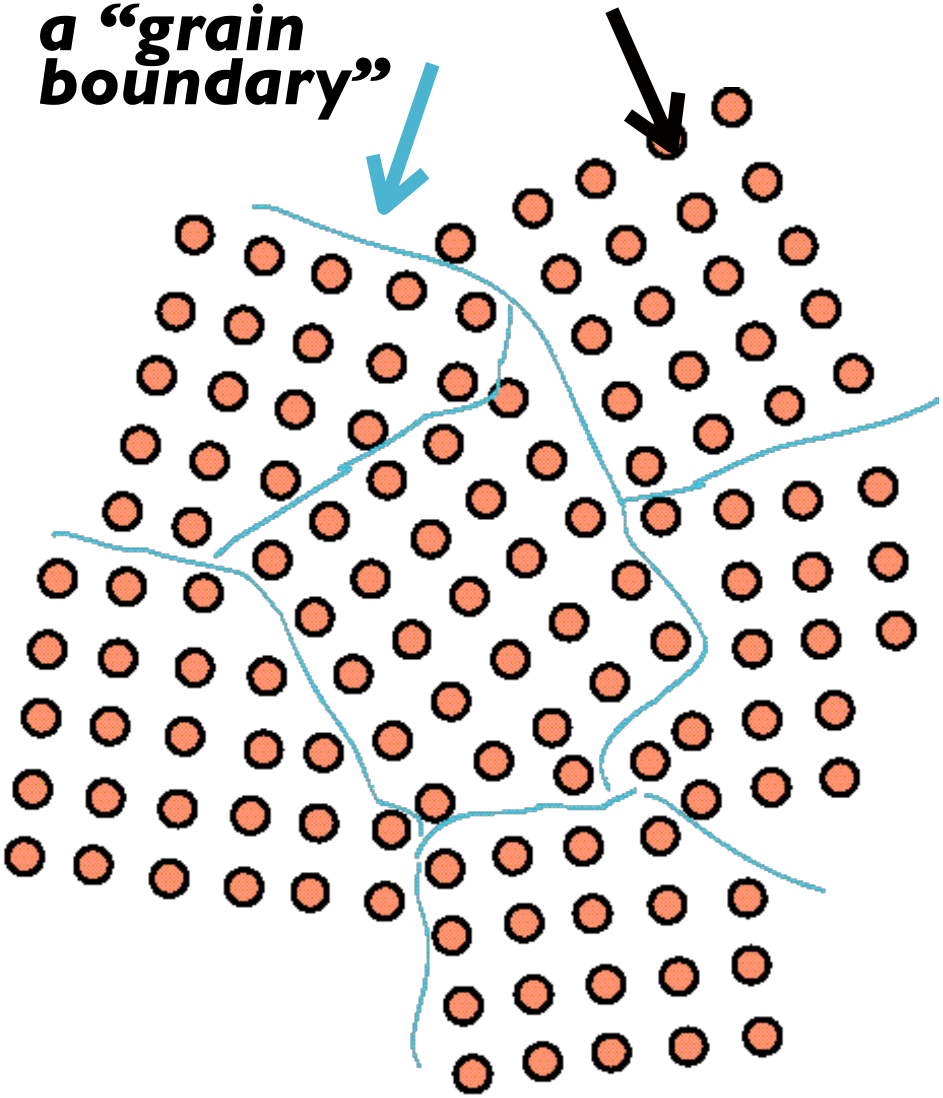


Single Crystal

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

Polycrystalline samples average over all orientations.



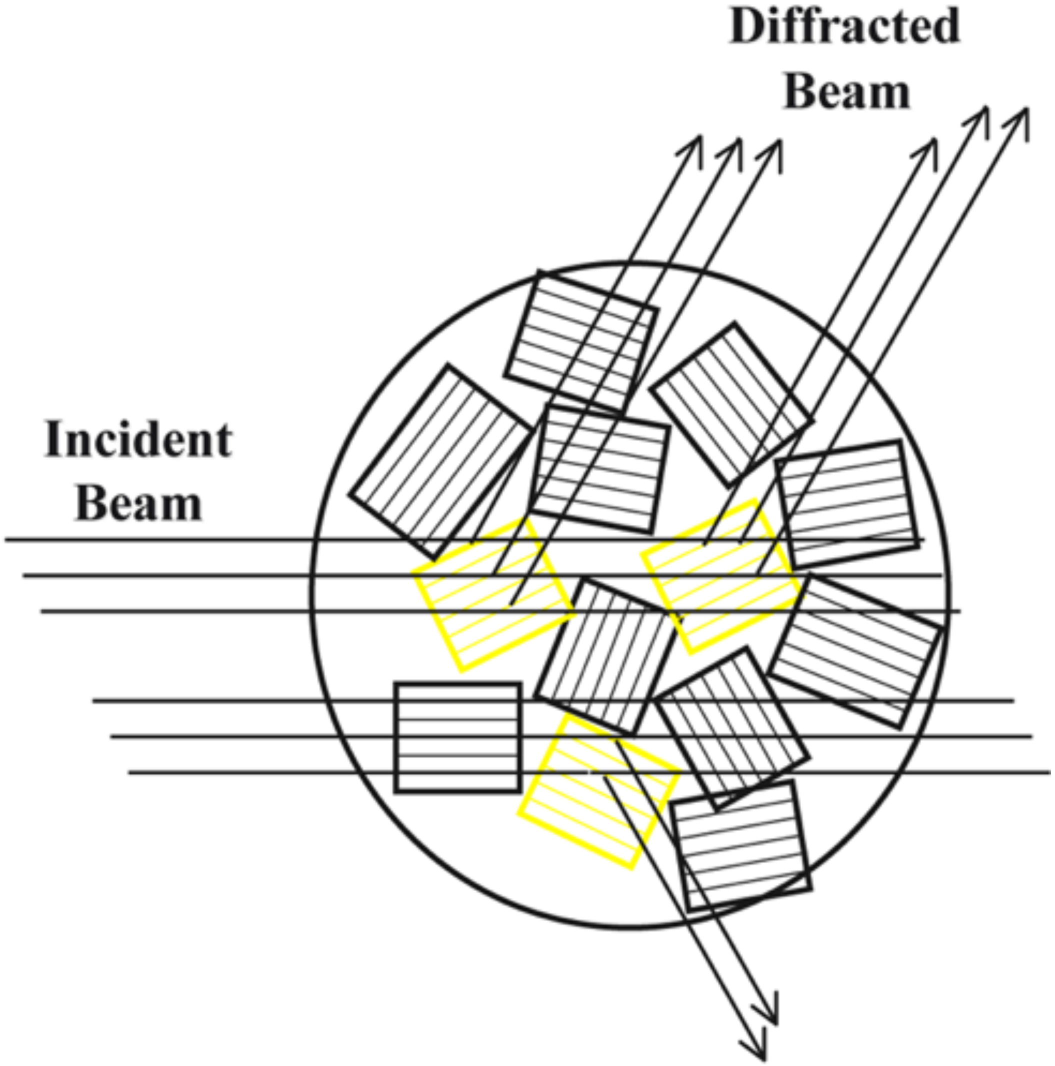


a “grain boundary”

a “grain”

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

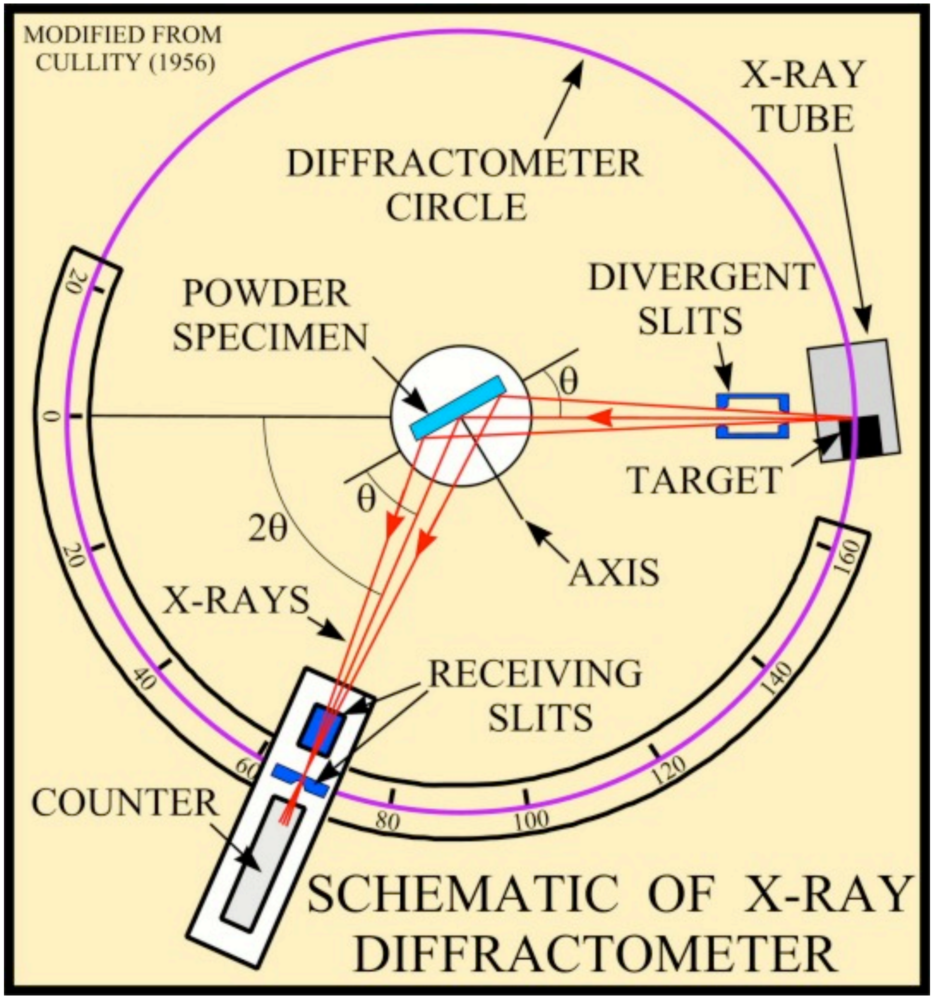
A beam impinging on the sample will find a representative number of crystallites in the right orientation for diffraction



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).

Polycrystalline Iron

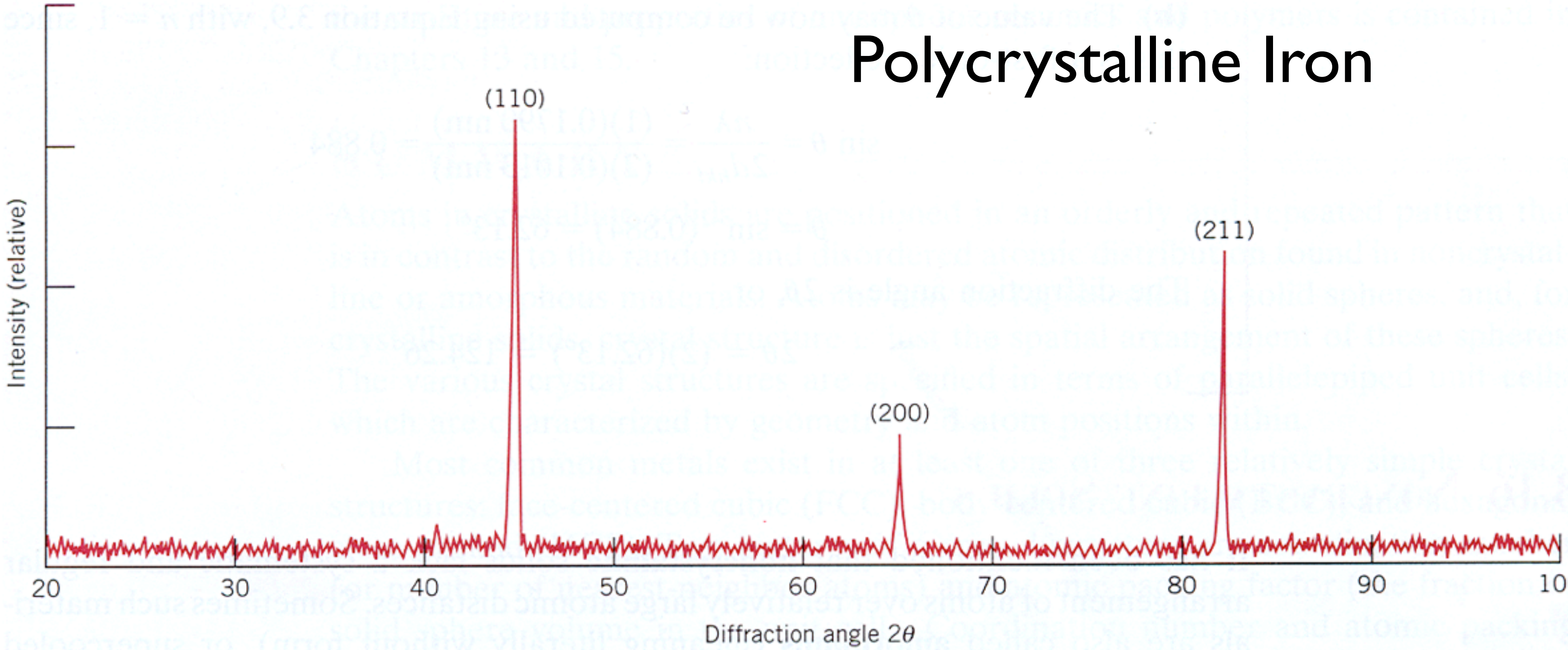
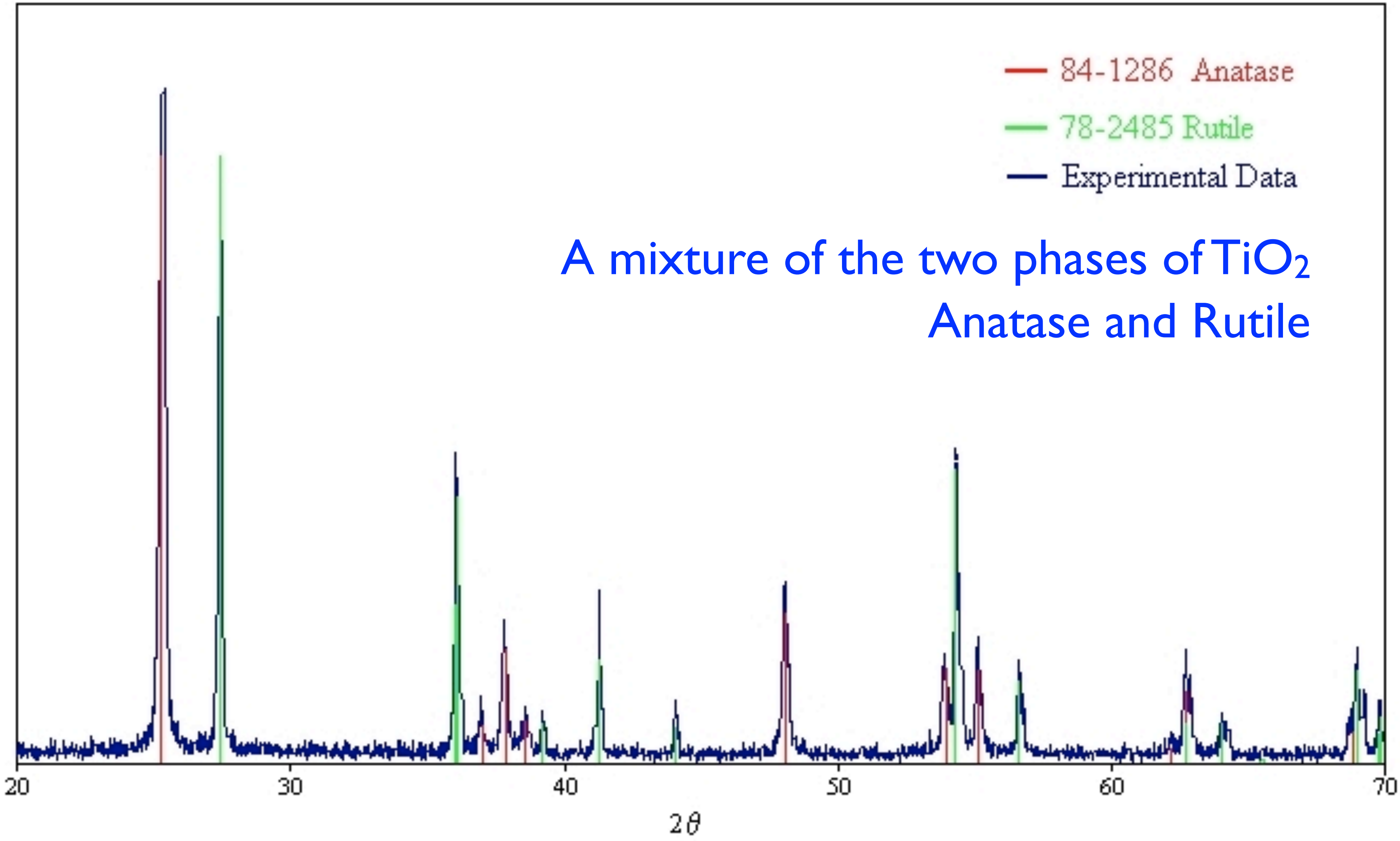


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

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



A mixture of the two phases of TiO_2
Anatase and Rutile

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!

Another example:

In a crystal of silver, planes of silver atoms are separated by a distance of 1.446Å. Compute the Θ's for all possible Bragg reflections for these planes if the wavelength of the incident x-radiation is 0.7093 Å.

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

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solution: 1) Solve the Bragg's Law for Θ:

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

2) Substitute:

$$\sin\theta = \frac{n\lambda}{2d} = \frac{n(0.7093\text{Å})}{2(1.446\text{Å})} = n \times 0.2455$$

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3) Decide which values of n yield a rational value for sinΘ.

For n=1, $\sin\Theta = 0.2455$ and $\Theta = \sin^{-1}(0.2455) = 14.21°$

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$n=3$, $\sin\Theta = 0.7335$ and $\Theta = \sin^{-1}(0.7335) = 47.43°$

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n=2, $\sin\Theta = 0.4910$ and $\Theta = \sin^{-1}(0.4910) = 29.41°$
n=3, $\sin\Theta = 0.7335$ and $\Theta = \sin^{-1}(0.7335) = 47.43°$
n=4, $\sin\Theta = 0.9820$ and $\Theta = \sin^{-1}(0.9820) = 79.11°$

Higher n values give $\sin\Theta > 1.0$ which can not happen.

Higher order diffractions, corresponding to n=2,3,4 etc. are often too weak to be observed (this is the case here for an Fe sample).

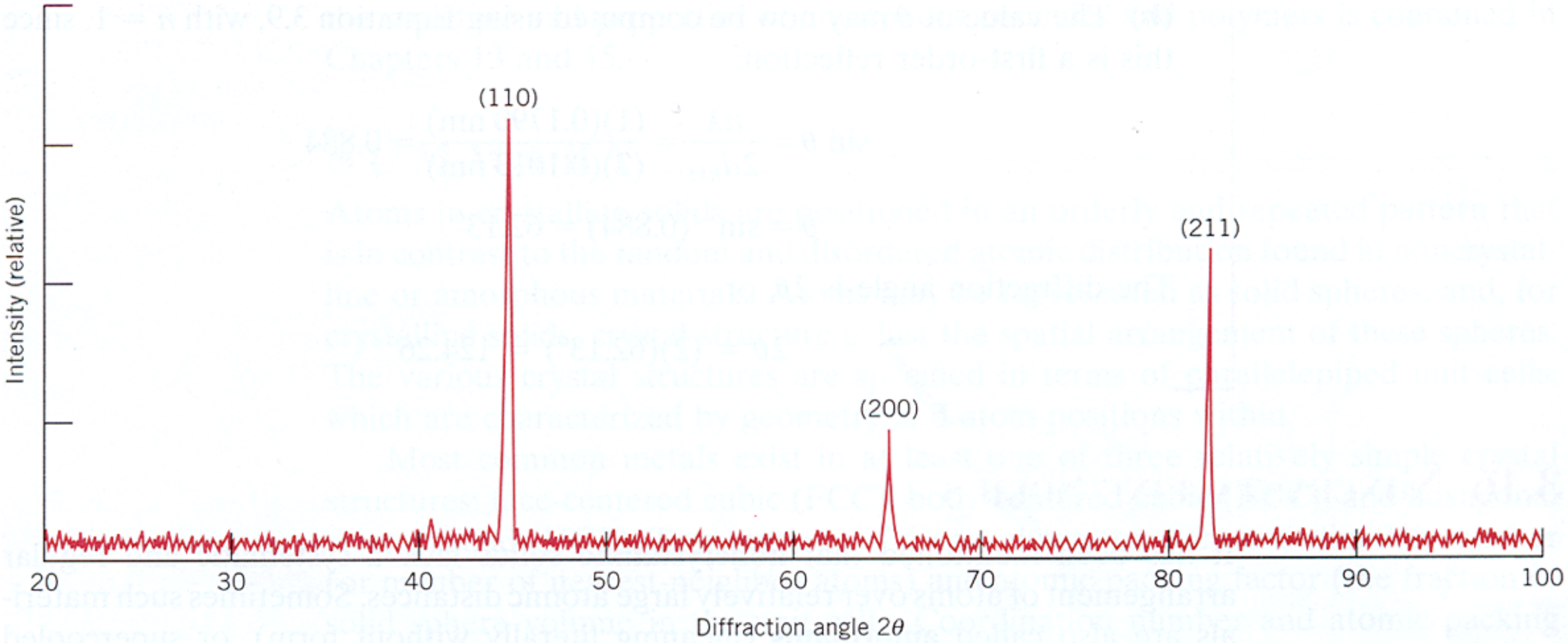
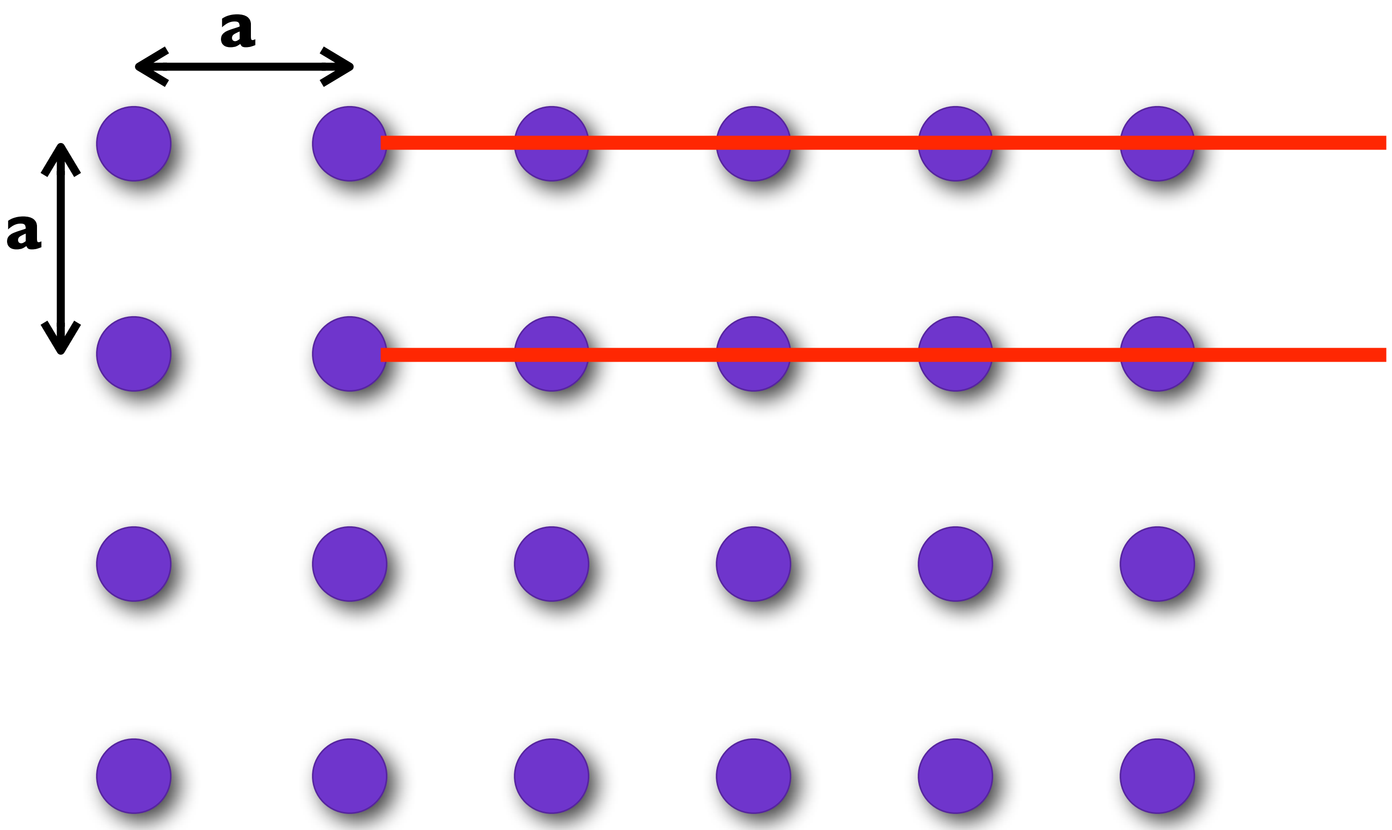


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

Nevertheless, multiple diffraction rings are observed. These diffraction rings are due to x-ray diffraction from various crystal planes.

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



d = a for this diffraction ring.

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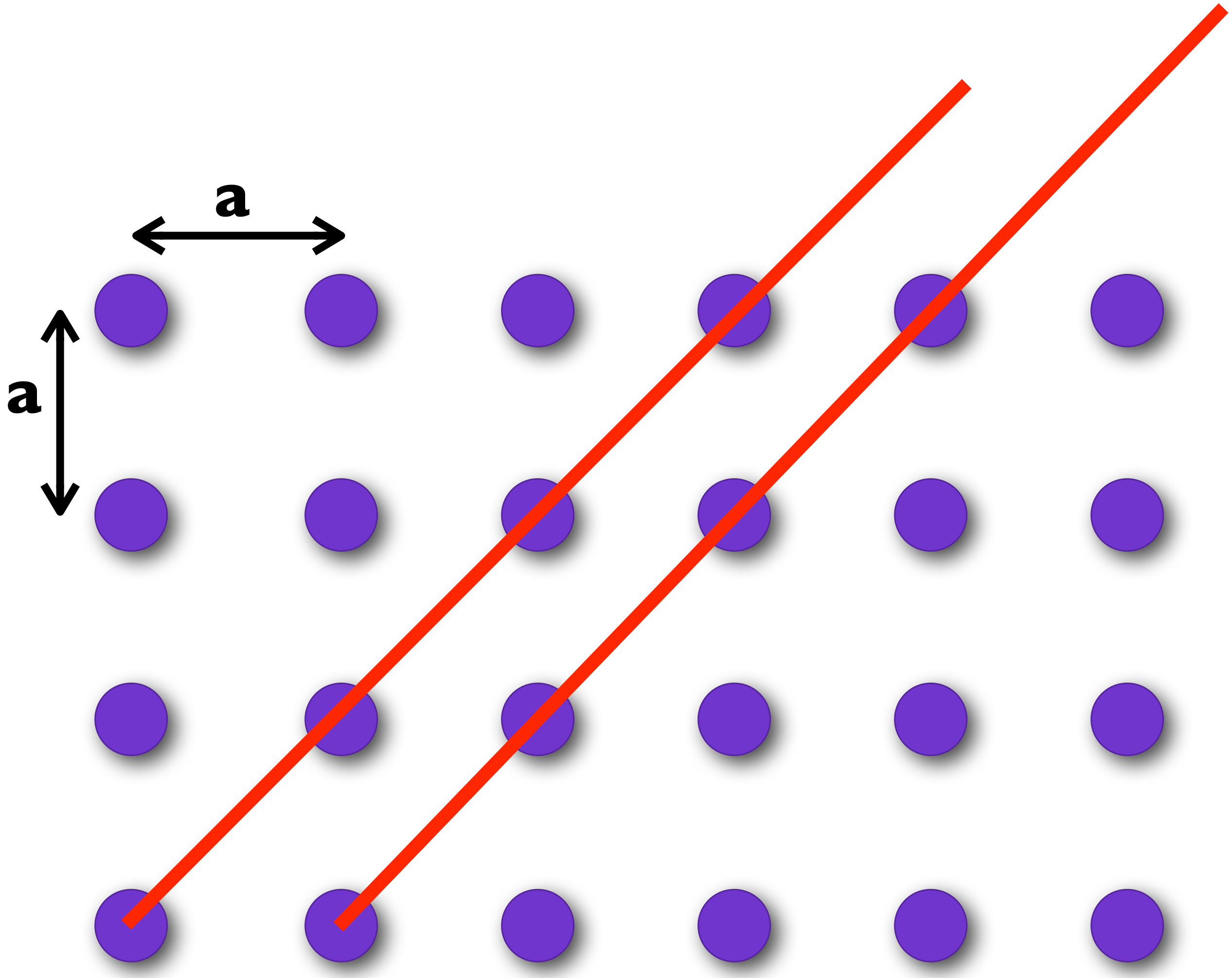
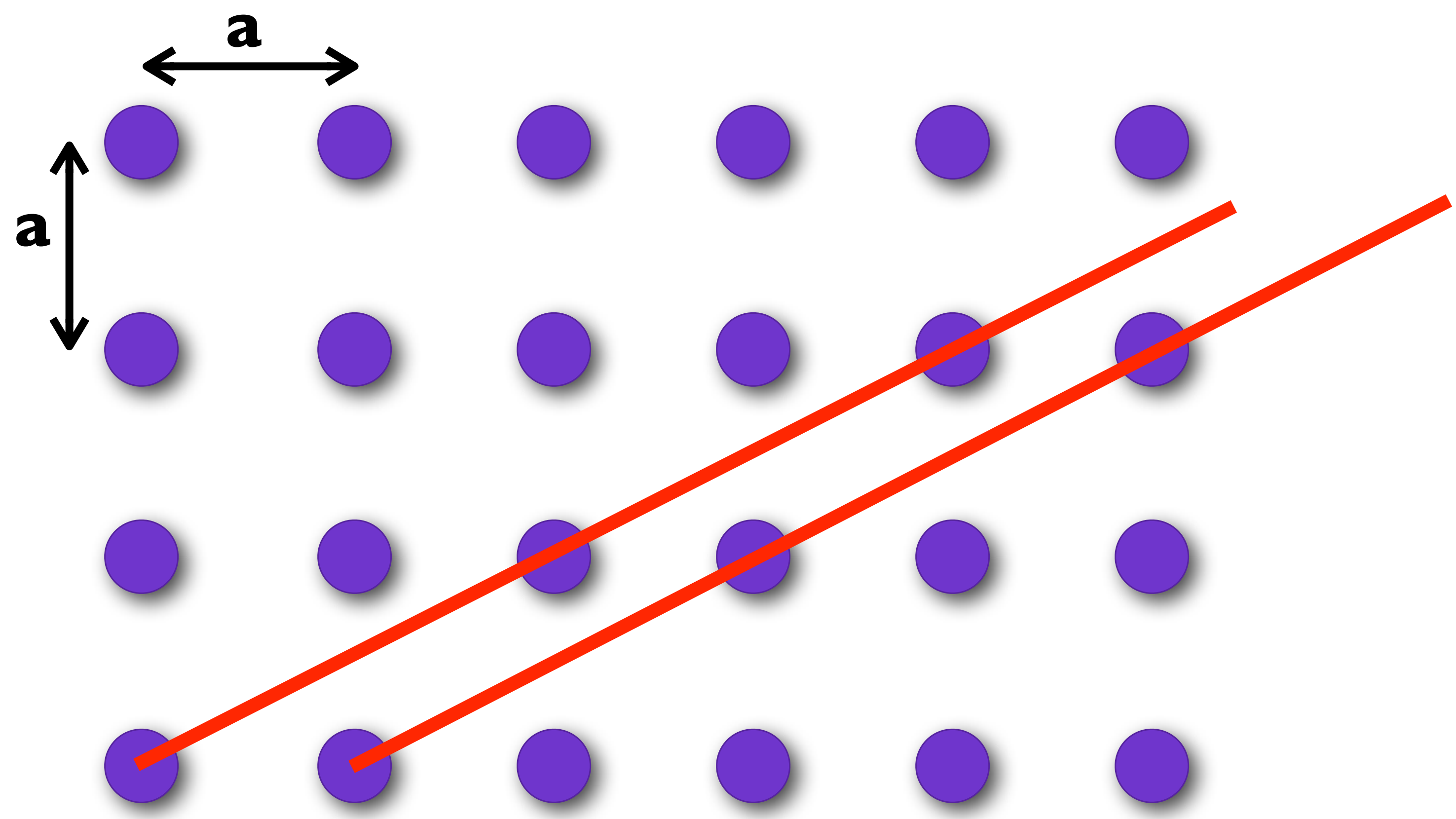


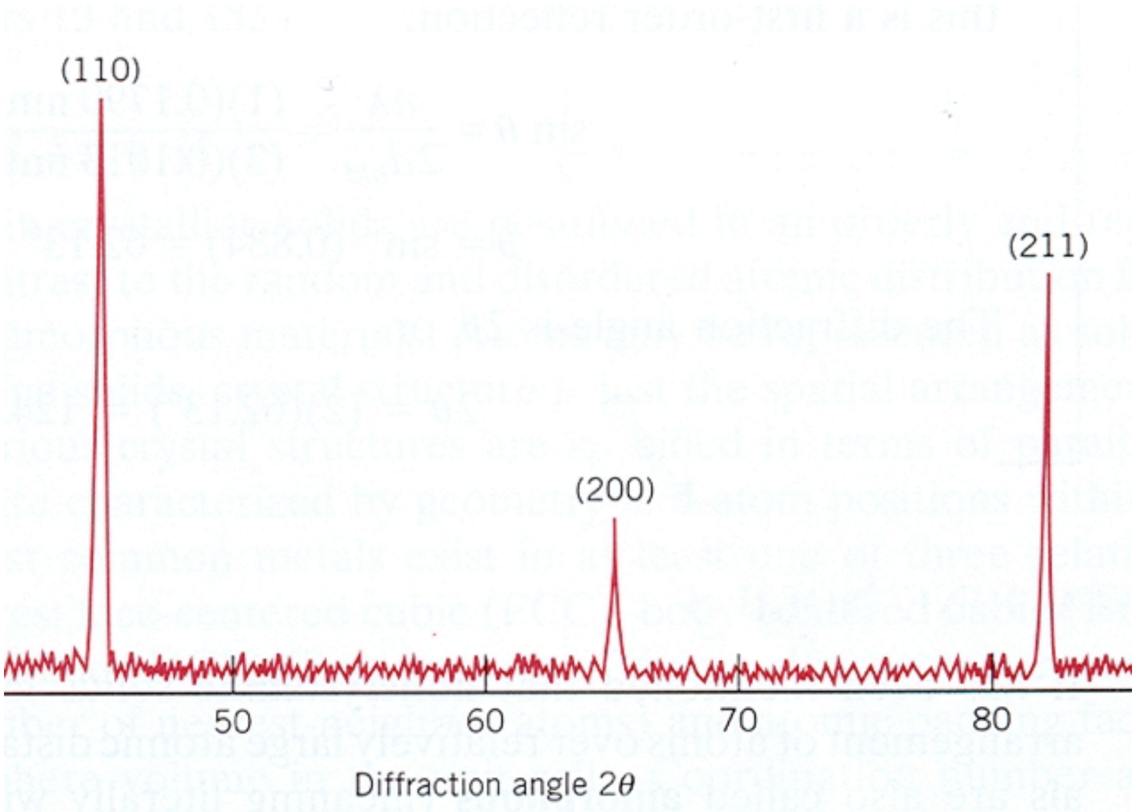
d ≠ a, diffraction occurs at a different angle

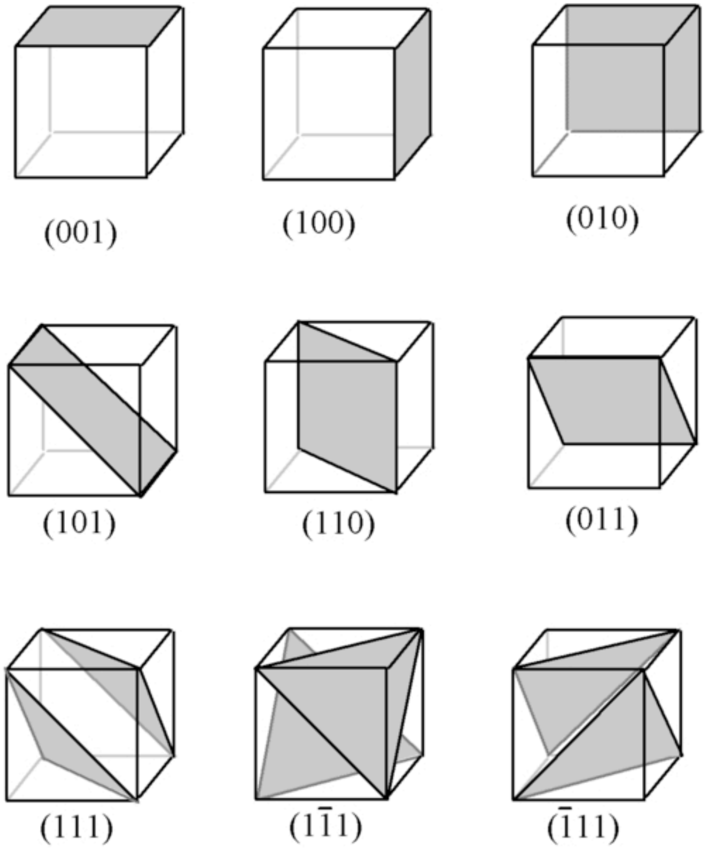
Let's take a look at the possible diffraction patterns for this 2-D crystal.



d ≠ a, diffraction occurs at yet another different angle

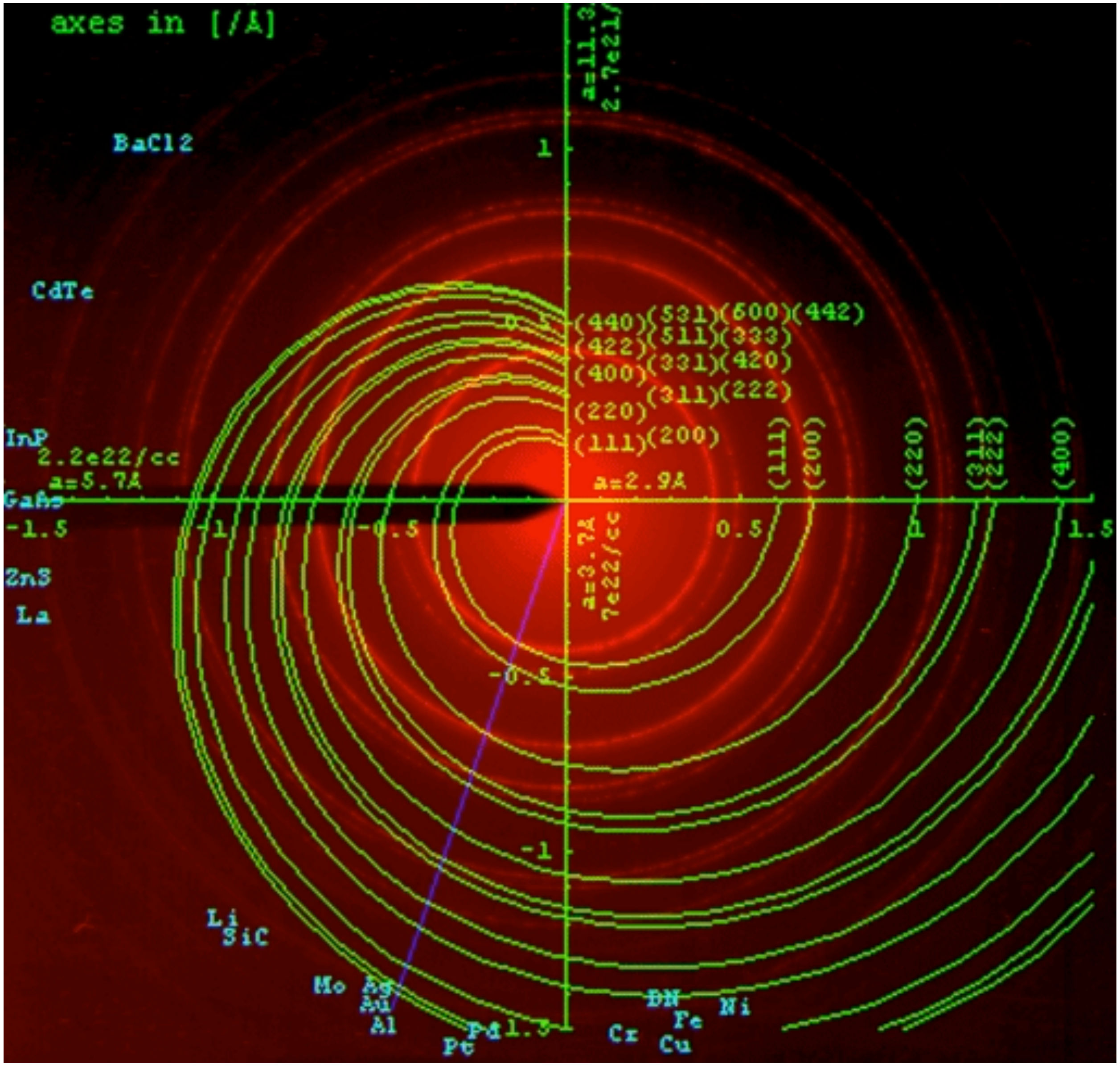
The various diffraction peaks are identified with Miller indices. (We won't go into how to get these, but it's not hard.).





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

Example: Matching the diffraction peak pattern to a calculated values yields the lattice parameter a for an FCC lattice.



FCC a values are plotted as a function of θ:

0°: a=290 pm

-90°: a=370 pm

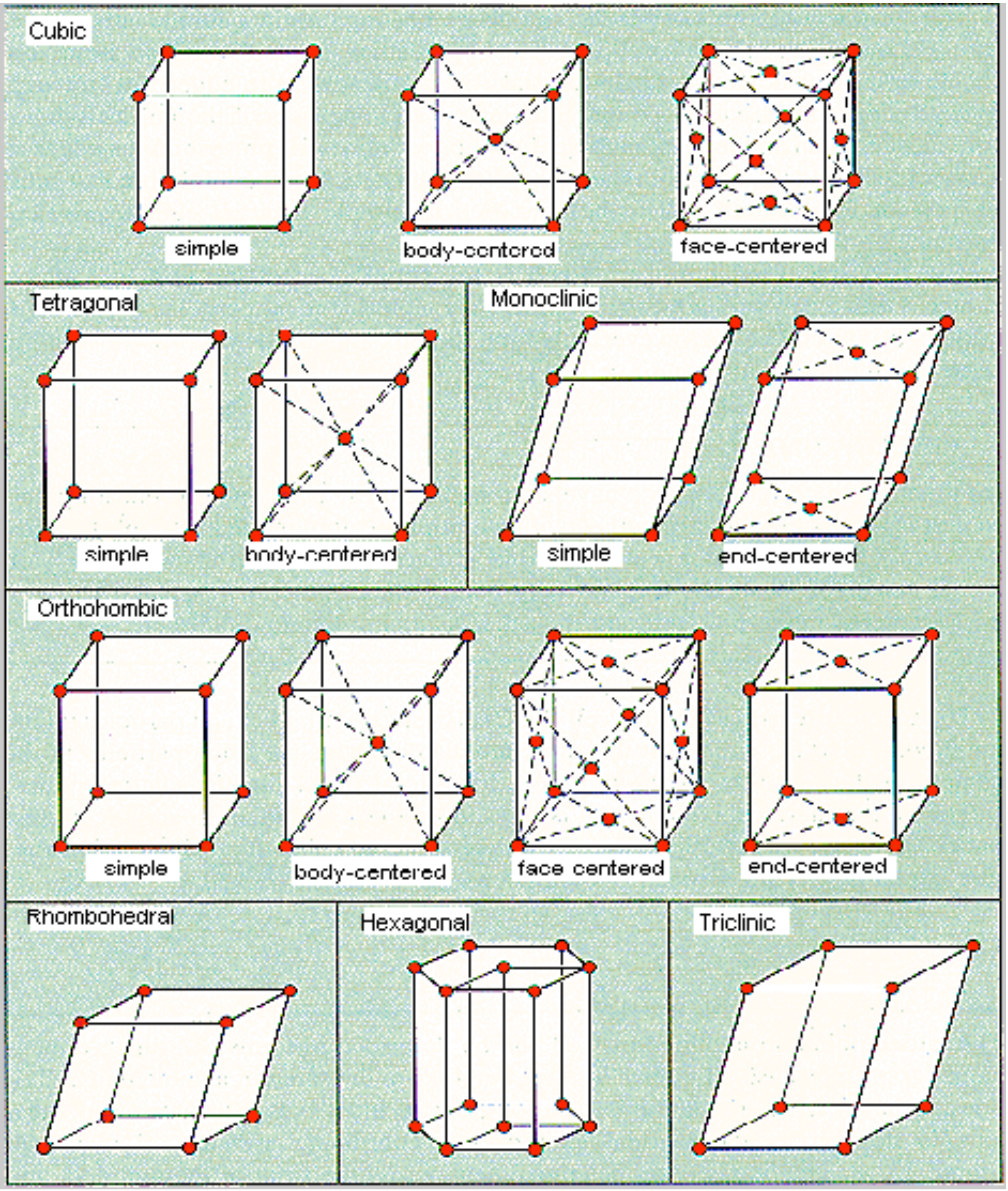
-180°: a=570 pm

-270°: a=1130 pm

Red: Al foil diffraction rings

Green: FCC calculation

Violet: Matching Point

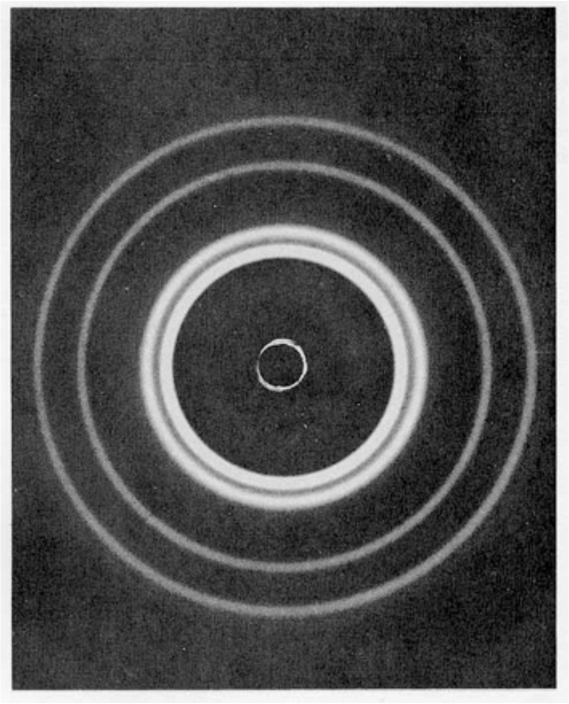


Lattice Parameters: Powder XRD

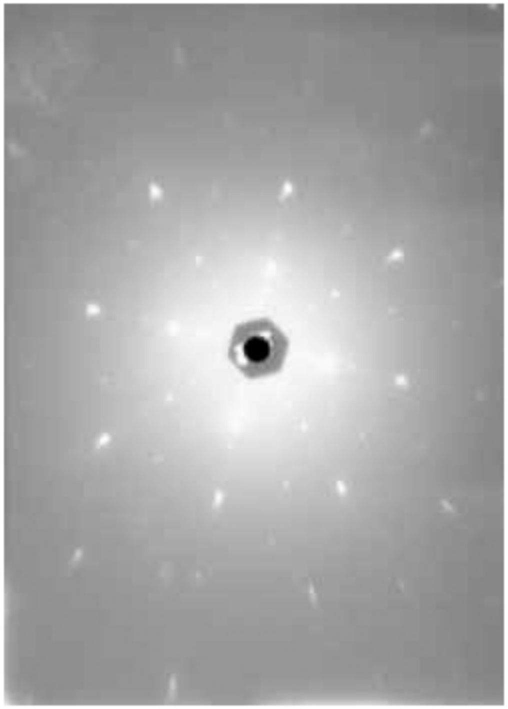
The XRD powder pattern can be used to determine the lattice parameters of the crystal.

cubic
tetragonal
monoclinic
orthorhombic
rhombohedral
hexagonal
triclinic

Single Crystal X-Ray Measurements



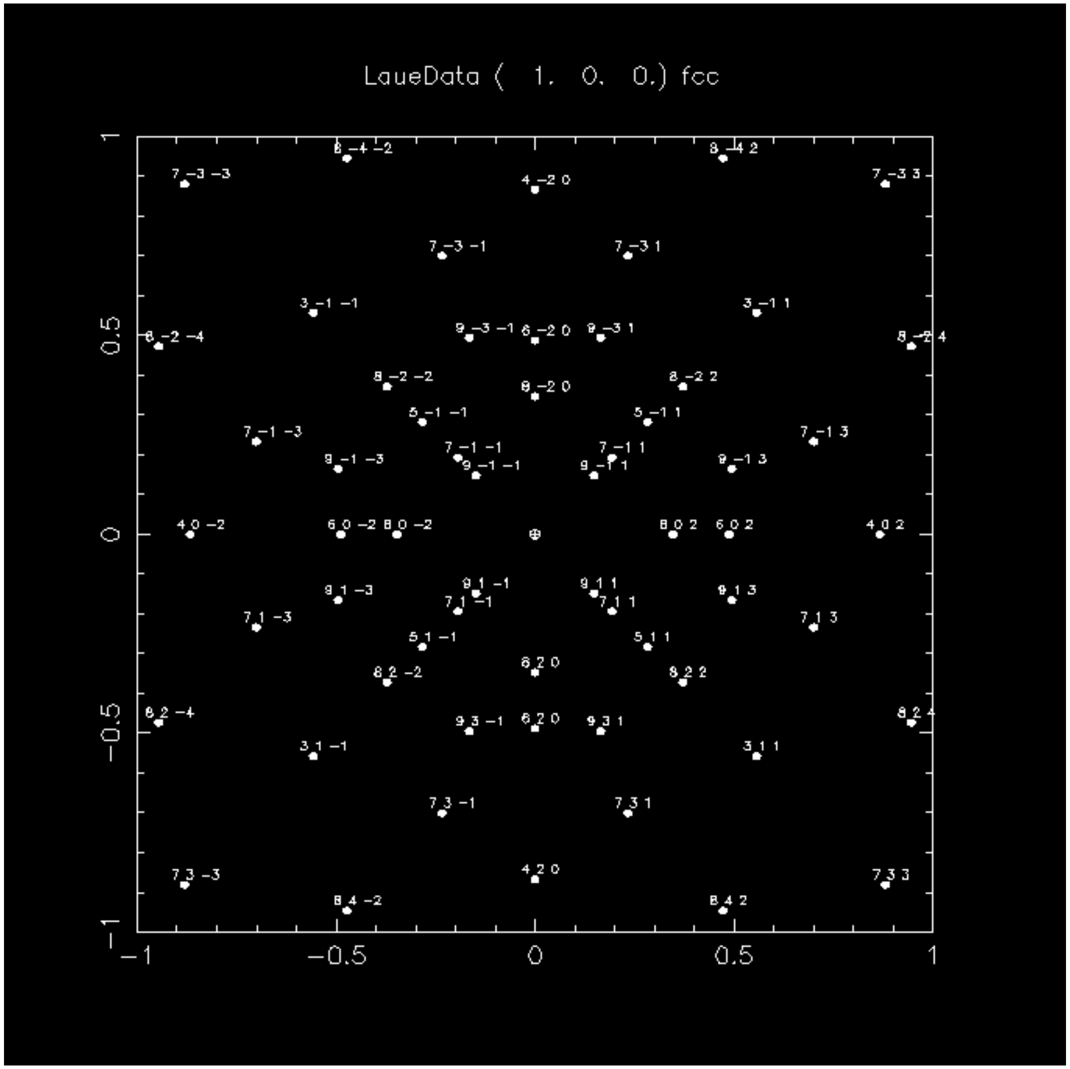
Thin foil



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.

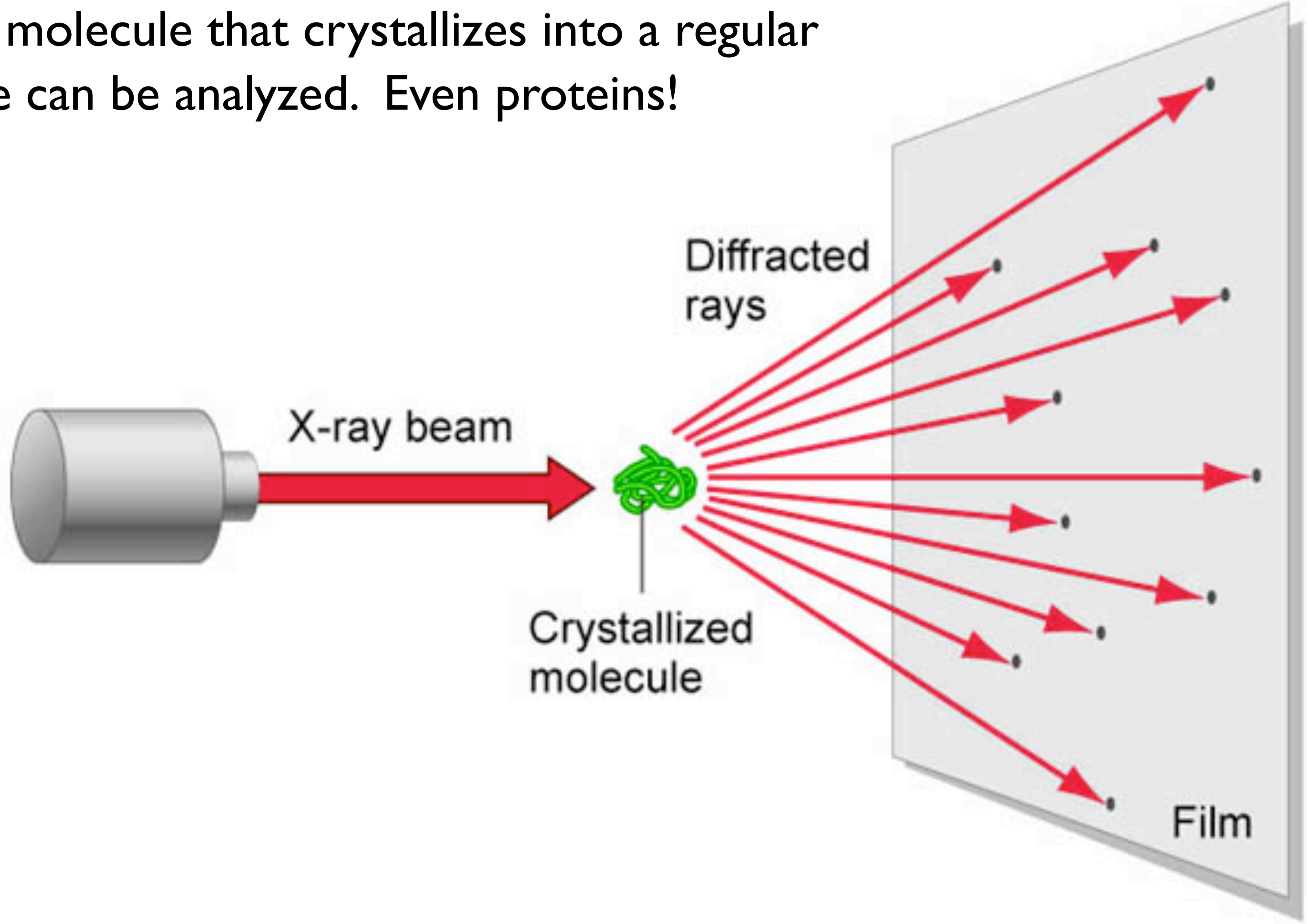
Single Crystal X-Ray Measurements



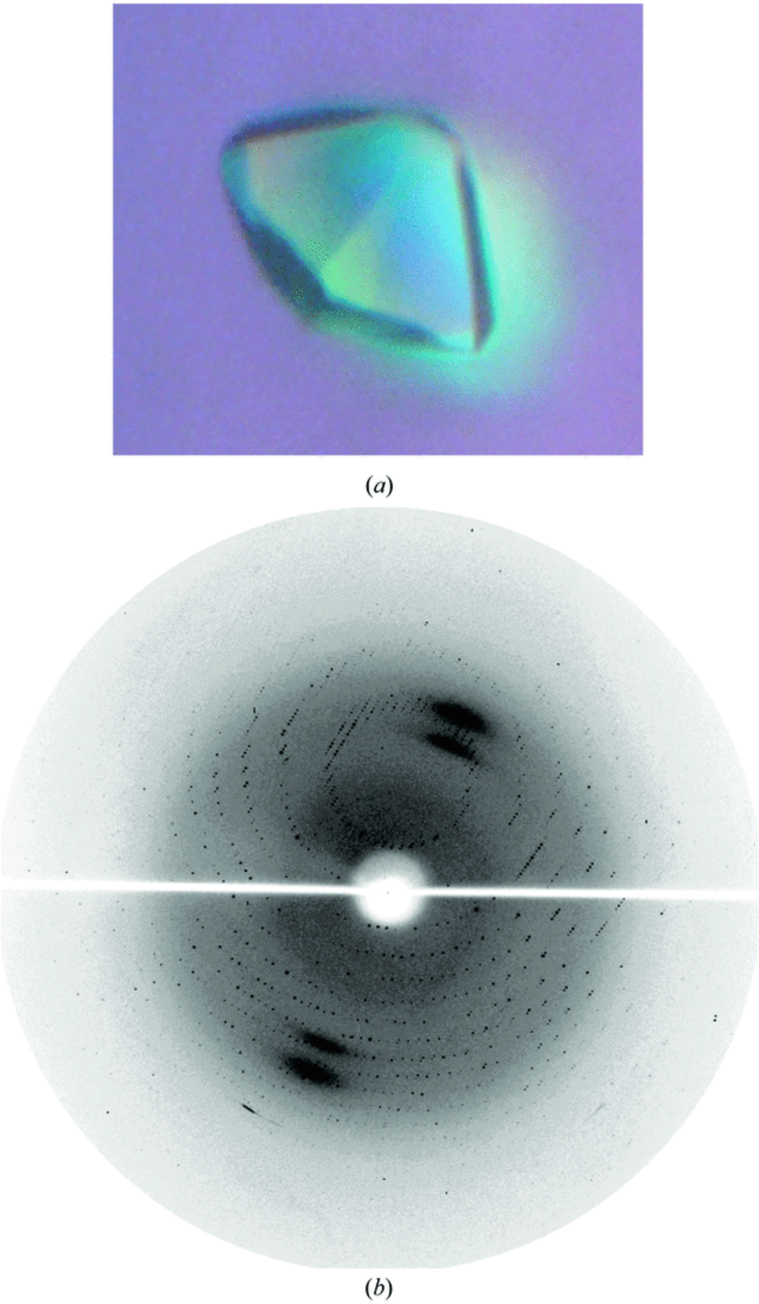
XRD pattern for diffraction from the (1,0,0) face of an fcc crystal

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

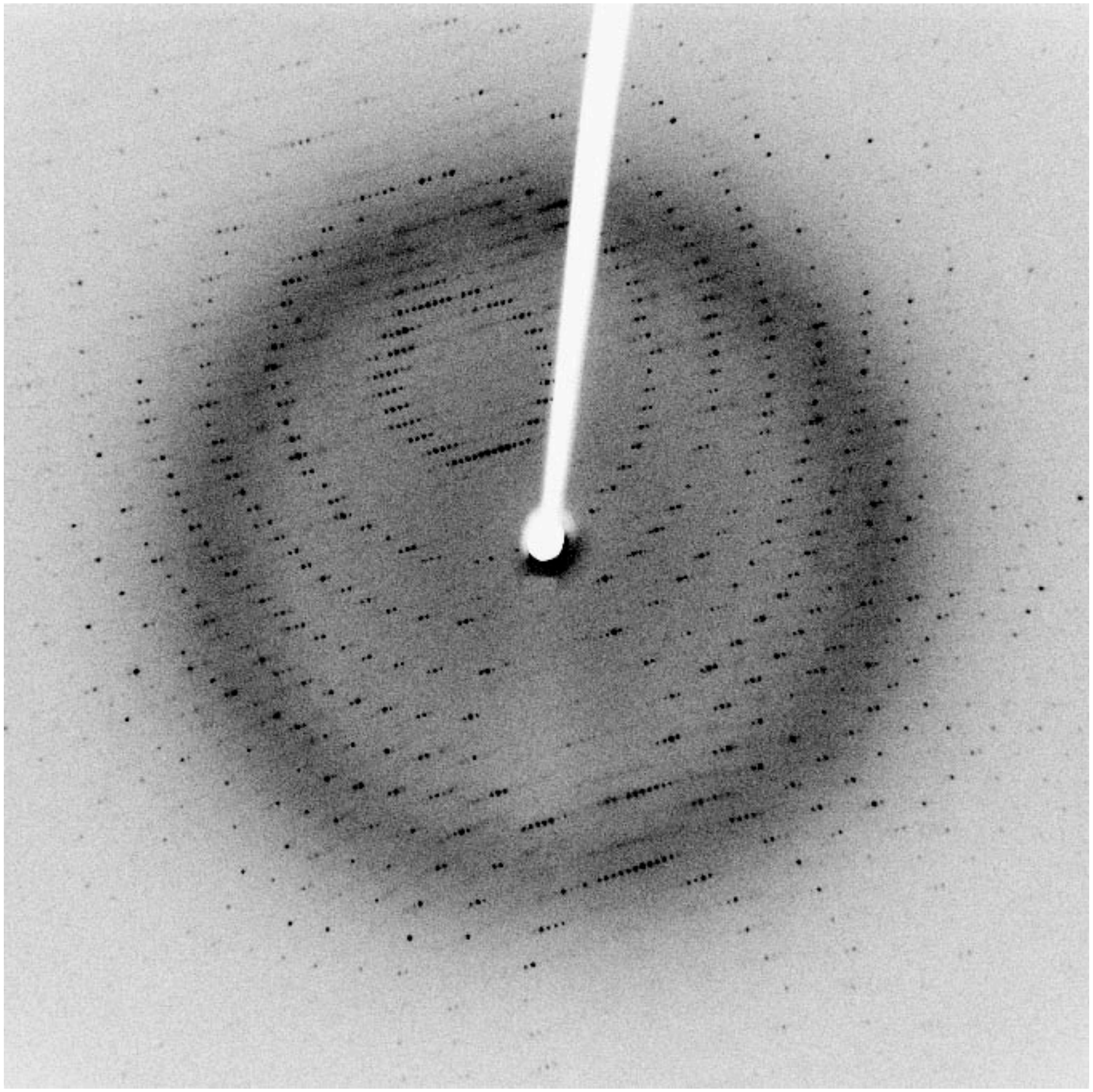
The good news is that nowadays, ANY molecule that crystallizes into a regular lattice can be analyzed. Even proteins!



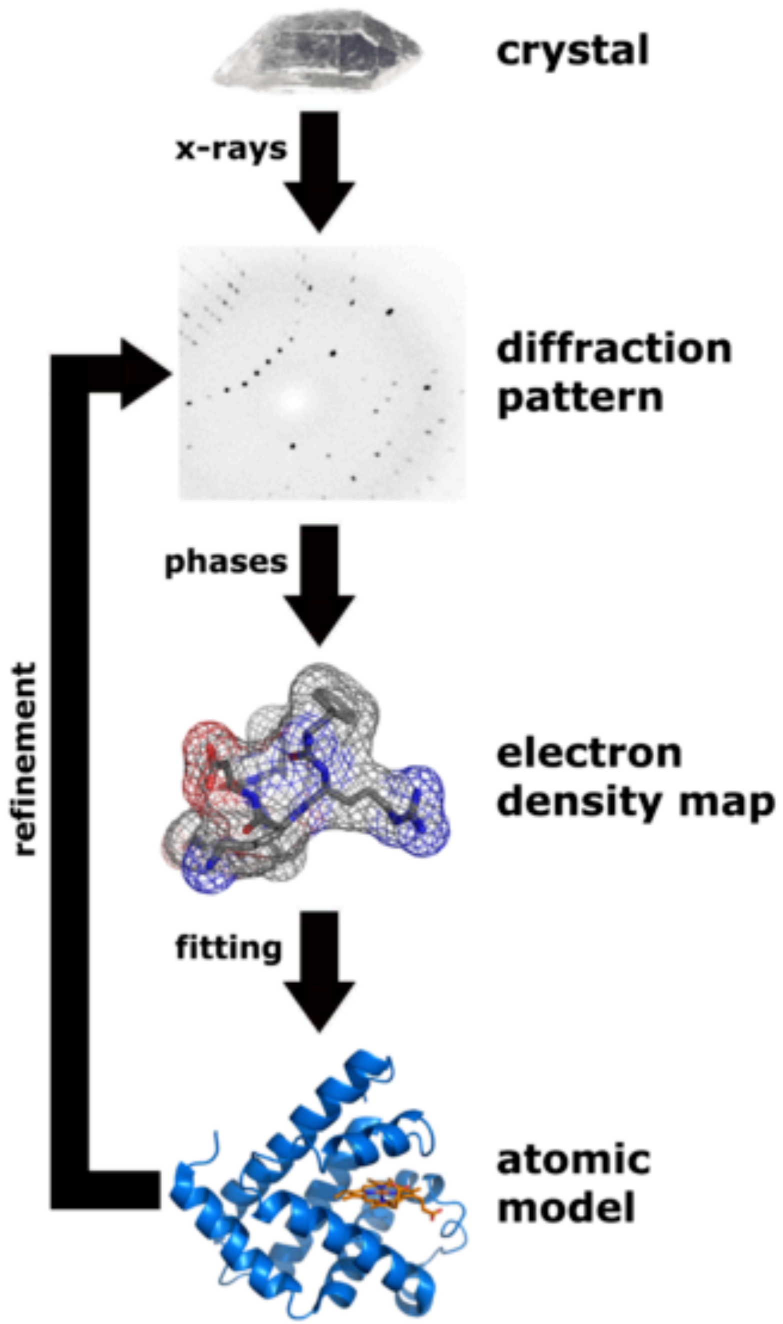
X-ray diffraction-quality crystals. (*a*) A typical crystal of *Y. pestis* SspA with dimensions of 0.1 × 0.1 × 0.1 mm. (*b*) X-ray diffraction at 2.0 Å of the crystal at the National Synchrotron Light Source.



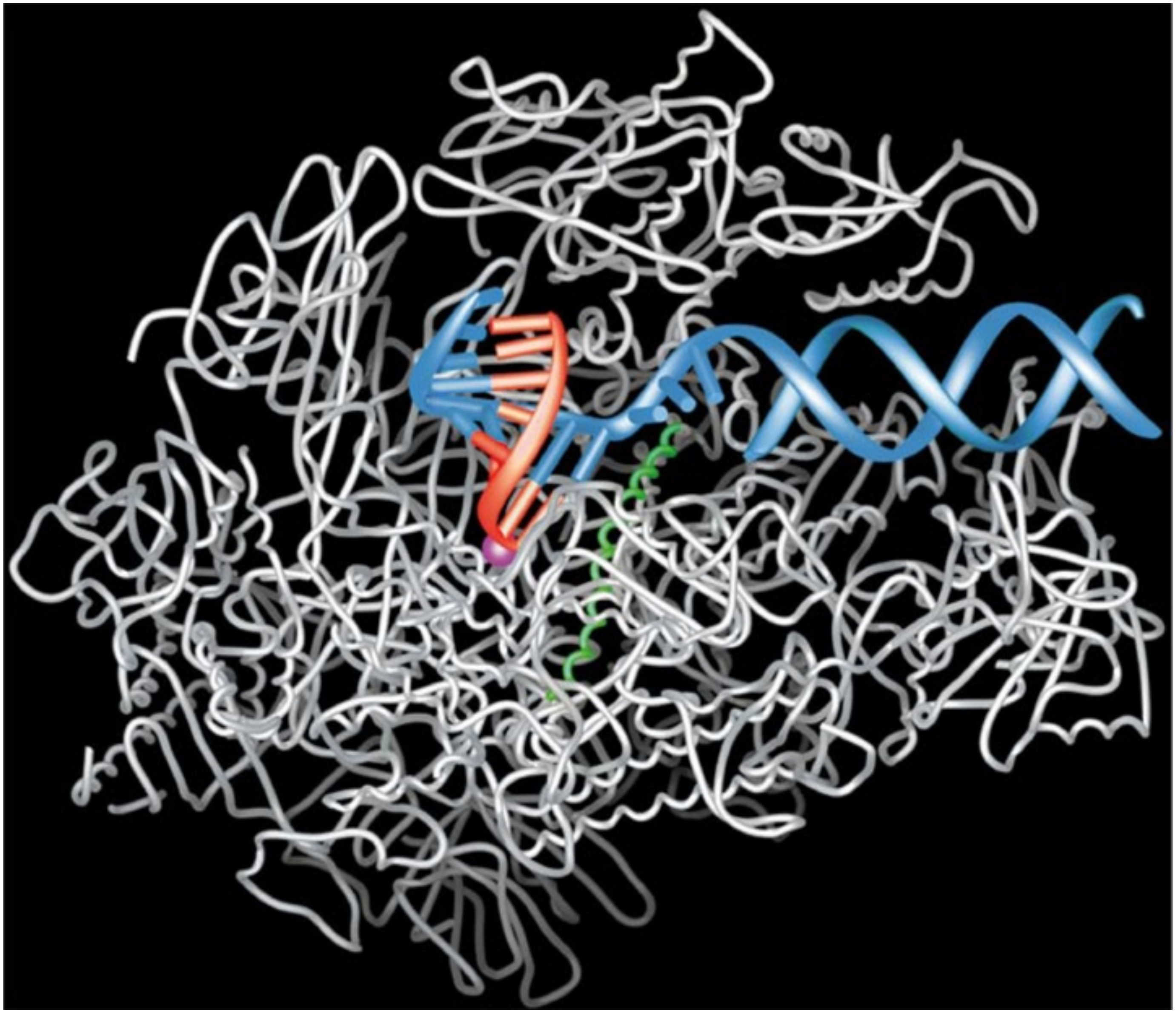
Lots of diffraction spots are obtained from many different incident angles on the crystal.



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!