Crystal Structure Analysis

X-ray Diffraction

Electron Diffraction

Neutron Diffraction

Essence of diffraction: Bragg Diffraction

Reading: West 5
A/M 5-6
G/S 3

REFERENCES

Elements of Modern X-ray Physics, *2nd Ed*. by Jens Als-Nielsen and Des McMorrow, John Wiley & Sons, Ltd., 2011 (Modern x-ray physics & new developments)

X-ray Diffraction, by B.E. Warren, General Publishing Company, 1969, 1990 (Classic X-ray physics book)

Elements of X-ray Diffraction, 3rd Ed., by B.D. Cullity, Addison-Wesley, 2001 (Covers most techniques used in traditional materials characterization)

High Resolution X-ray Diffractometry and Topography, by D. Keith Bowen and Brian K. Tanner, Taylor & Francis, Ltd., 1998 (Semiconductors and thin film analysis)

Modern Aspects of Small-Angle Scattering, by H. Brumberger, Editor, Kluwer Academic Publishers, 1993 (SAXS techniques)

Principles of Protein X-ray Crystallography, *3rd Ed*. by Jan Drenth, Springer, 2007 (Crystallography)

SCATTERING

Scattering is the process in which waves or particles are forced to deviate from a straight trajectory because of *scattering centers* in the propagation medium.

X-rays scatter by interaction with the electron density of a material.
Neutrons are scattered by nuclei and by any magnetic moments in a sample.
Electrons are scattered by electric/magnetic fields.

Momentum transfer: $\mathbf{p}' - \mathbf{p} = \hbar \mathbf{q}$

Energy change: $E' - E = h\nu$

For X-rays: $E = pc$

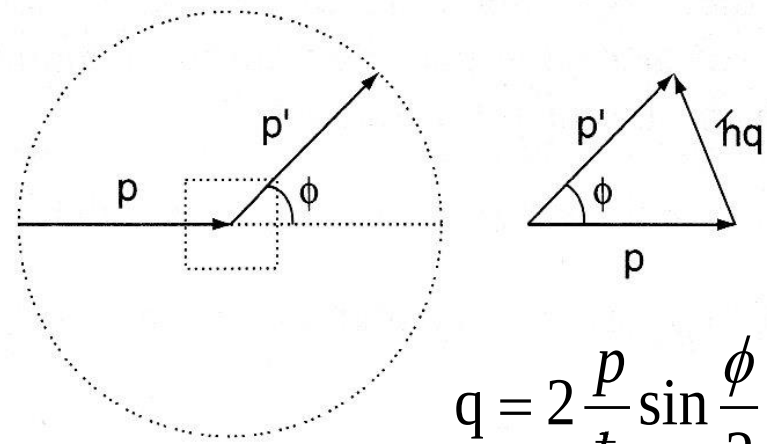
Elastic ($E' = E$)

- Rayleigh ($\lambda >> d_{object}$)
- Mie ($\lambda \approx d_{object}$)
- Geometric ($\lambda << d_{object}$)
- Thompson (X-rays)

Inelastic ($E' \neq E$)

- Compton (photons + electrons)
- Brillouin (photons + quasiparticles)
- Raman (photons + molecular vib./rot.)

Elastic scattering geometry

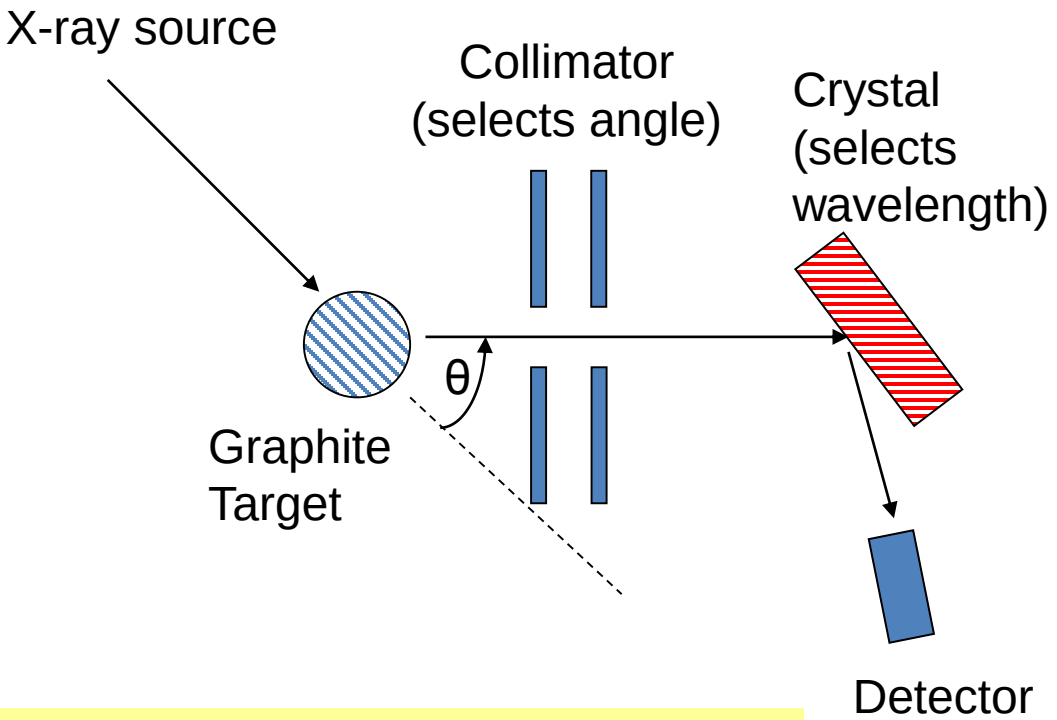


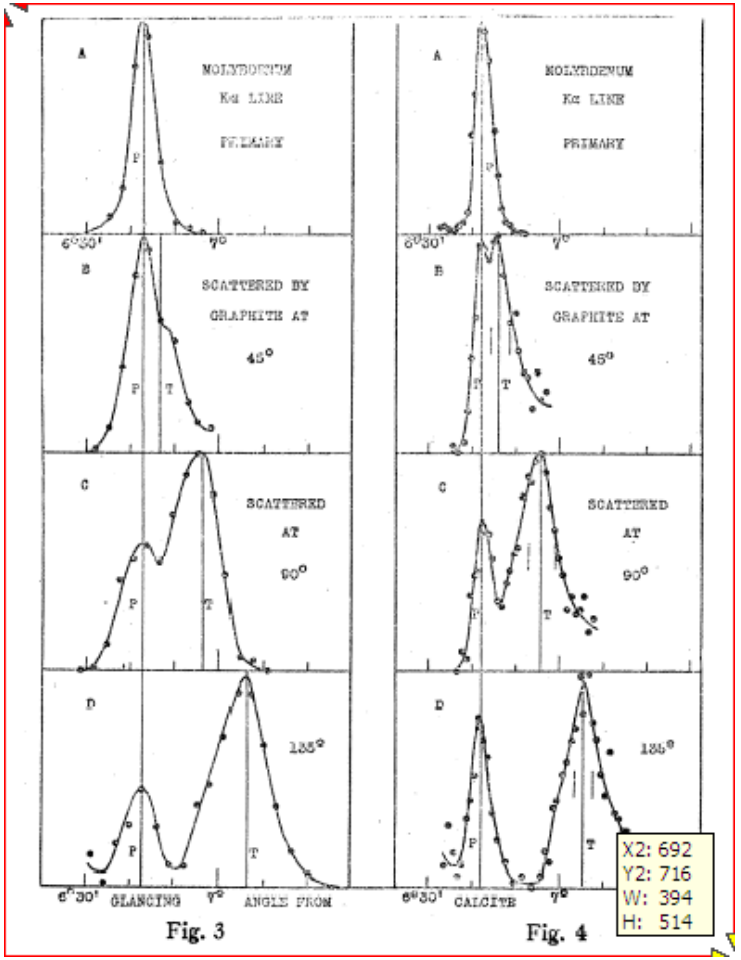
$$q = 2\frac{p}{\hbar}\sin\frac{\phi}{2}$$

COMPTON SCATTERING

Compton (1923) measured intensity of scattered X-rays from solid target, as function of wavelength for different angles. He won the 1927 Nobel prize.

Compton





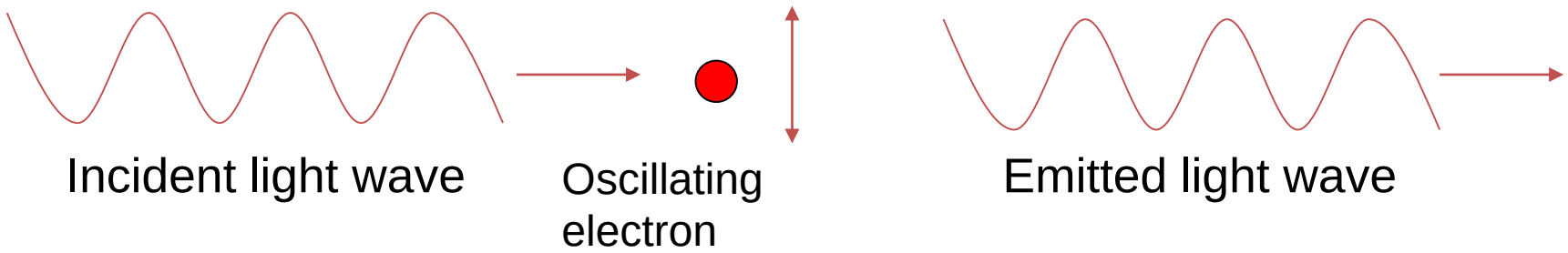
Result: peak in scattered radiation shifts to longer wavelength than source. Amount depends on θ (but not on the target material).

A. H. Compton. *Phys. Rev.* **22,** 409 (1923).

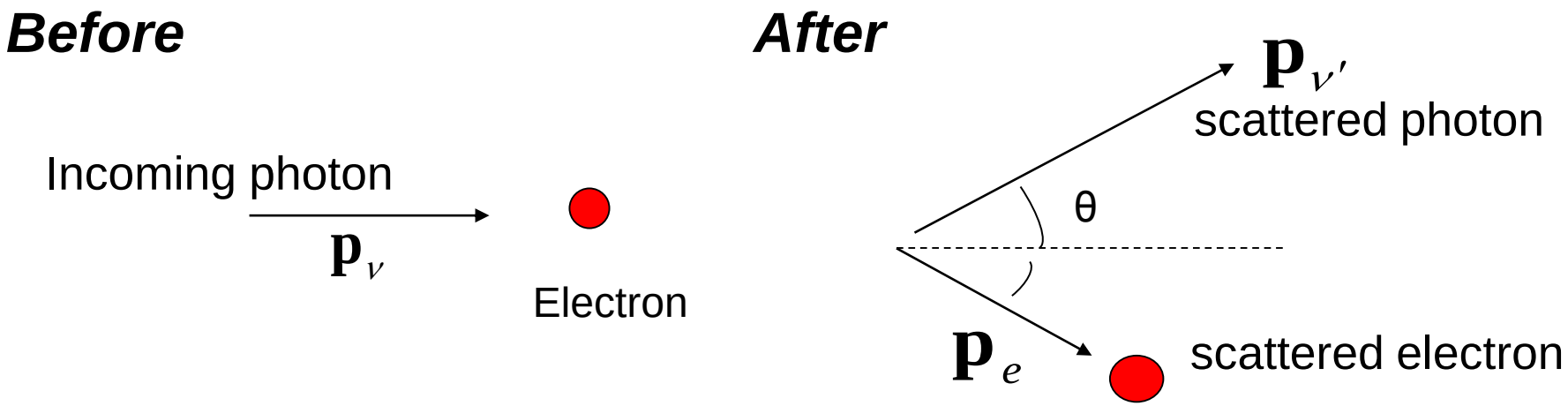
COMPTON SCATTERING

Classical picture: oscillating electromagnetic field causes oscillations in positions of charged particles, which re-radiate in all directions at *same frequency and wavelength* as incident radiation (Thompson scattering).

Change in wavelength of scattered light is completely unexpected classically

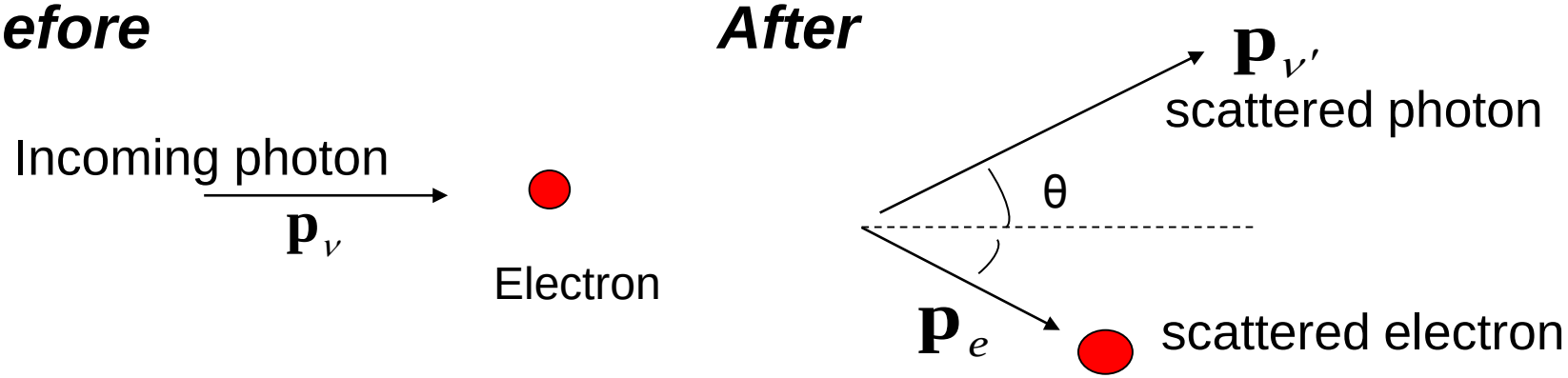


Compton's explanation: "billiard ball" collisions between particles of light (X-ray photons) and electrons in the material



COMPTON SCATTERING

Before ***After***



Conservation of energy

$$h\nu + m_e c^2 = h\nu' + \left(p_e^2 c^2 + m_e^2 c^4\right)^{1/2}$$

Conservation of momentum

$$\mathbf{p}_\nu = \frac{h}{\lambda}\hat{\mathbf{i}} = \mathbf{p}_{\nu'} + \mathbf{p}_e$$

From this Compton derived the change in wavelength:

$$\boxed{\begin{aligned}\lambda' - \lambda &= \frac{h}{m_e c}\left(1 - \cos\theta\right) \\ &= \lambda_c\left(1 - \cos\theta\right) \geq 0\end{aligned}}$$

$$\lambda_c = \text{ Compton wavelength } = \frac{h}{m_e c} = 2.4 \times 10^{-12}\,\text{m}$$

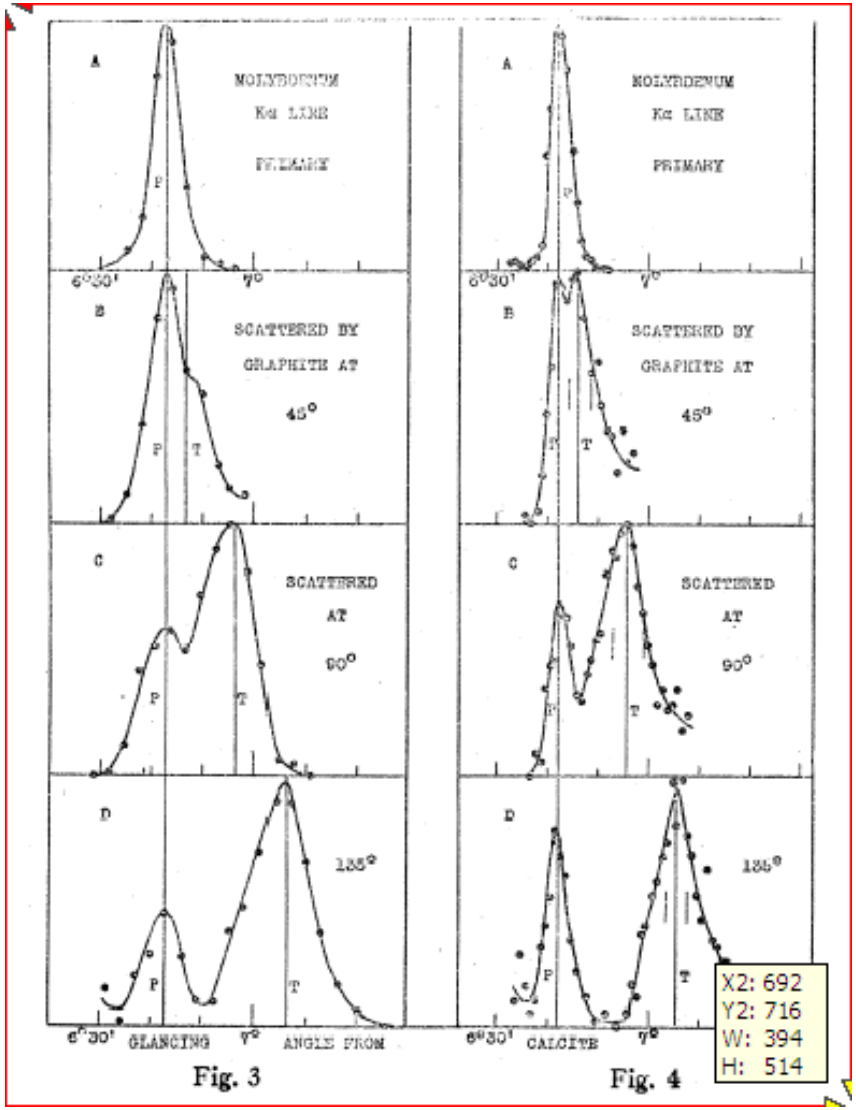
COMPTON SCATTERING

Note that there is also an unshifted peak at each angle.

Most of this is elastic scatter. Some comes from a collision between the X-ray photon and the nucleus of the atom.

$$\lambda' - \lambda = \frac{h}{m_N c}\left(1 - \cos\theta\right) \approx 0$$

since $m_N >> m_e$

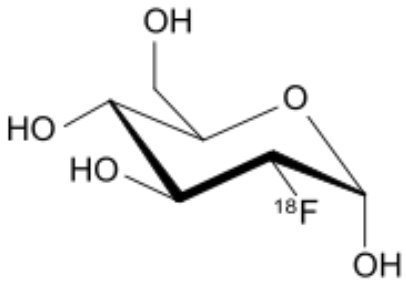


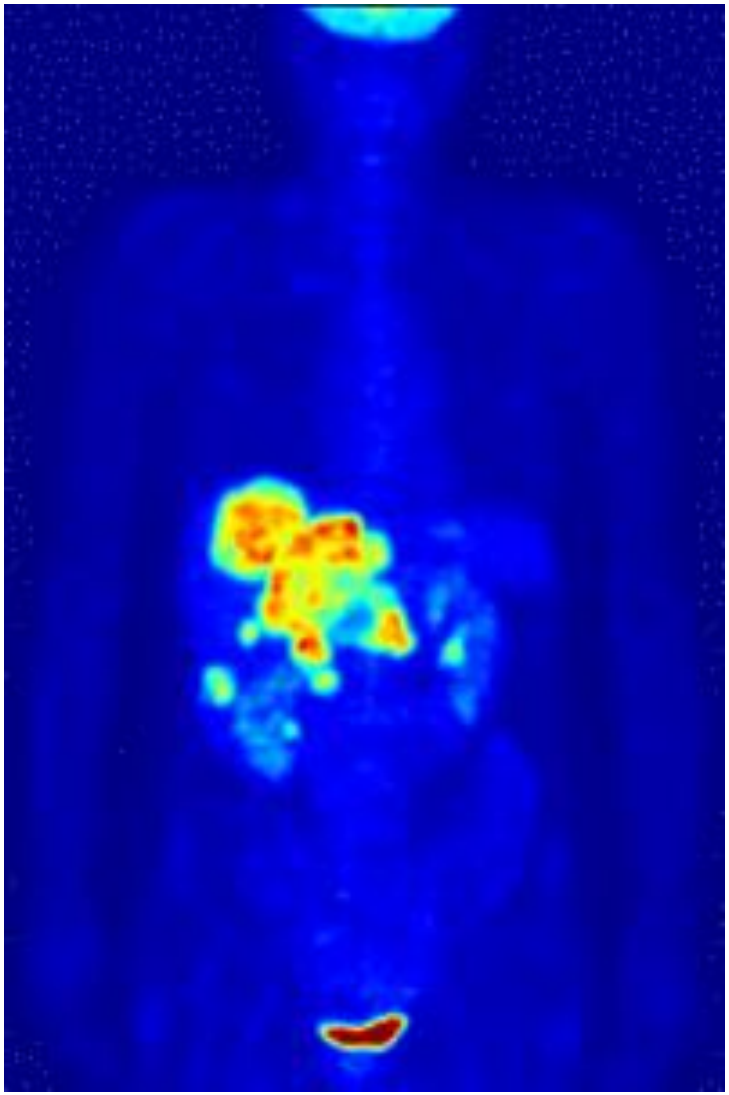
COMPTON SCATTERING

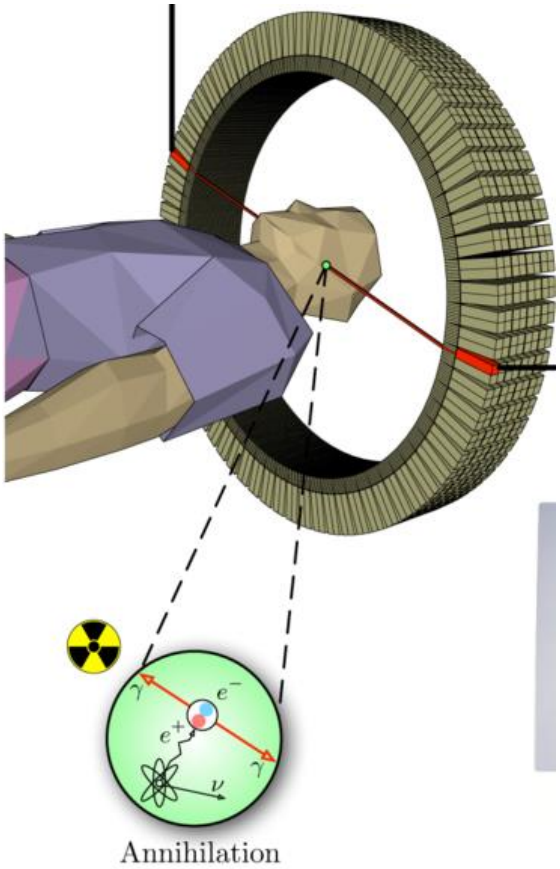
Contributes to general background noise

Diffuse background from Compton emission by gamma rays in a positron emission tomography (PET) scan.

Fluorodeoxyglucose (^{18}F)







X-RAY SCATTERING

X-rays: λ (in Å) = 12400/E (in eV)

- 100 eV ("soft") – 100 keV ("hard") photons
- 12,400 eV X-rays have wavelengths of 1 Å, somewhat smaller than interatomic distances in solids

➡ Diffraction from crystals!

Roentgen
1901 Nobel

elastic (Thompson, $\Delta E = 0$)

- wide-angle diffraction ($\theta > 5°$)
- small-angle diffraction (θ close to 0°)
- X-ray reflectivity (films)

inelastic ($\Delta E \neq 0$)

- Compton X-ray scattering
- resonant inelastic X-ray scattering (RIXS)
- X-ray Raman scattering

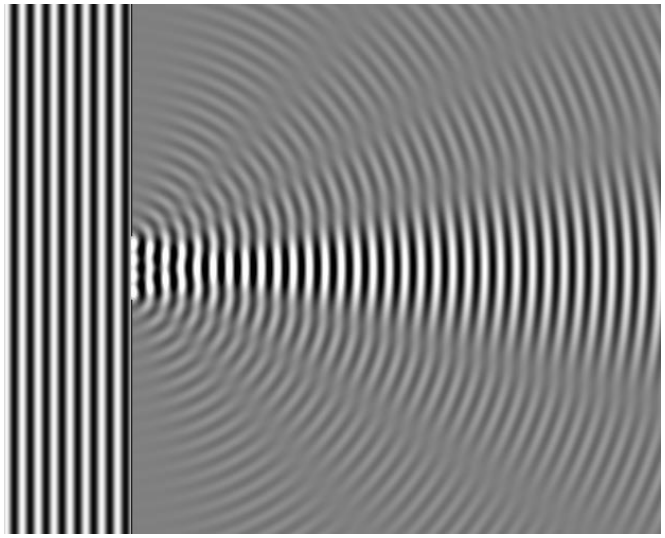
First X-ray: 1895

DIFFRACTION

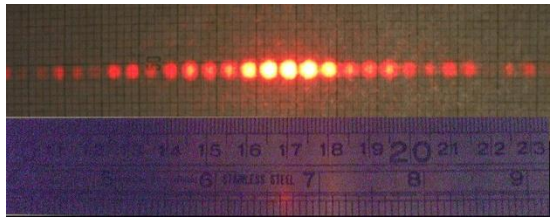
Diffraction refers to the apparent bending of waves around small objects and the spreading out of waves past small apertures.

In our context, diffraction is the scattering of a coherent wave by the atoms in a crystal. A diffraction pattern results from interference of the scattered waves.

Refraction is the change in the direction of a wave due to a change in its speed.

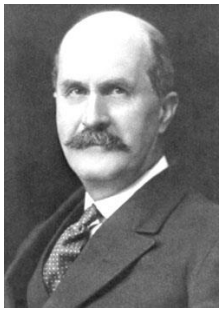


diffraction of plane waves

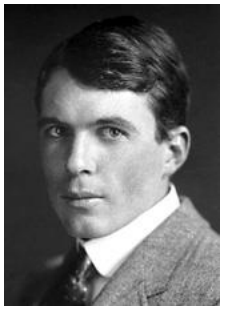


Crystal diffraction

I. Real space description (Bragg)
II. Momentum (k) space description (von Laue)



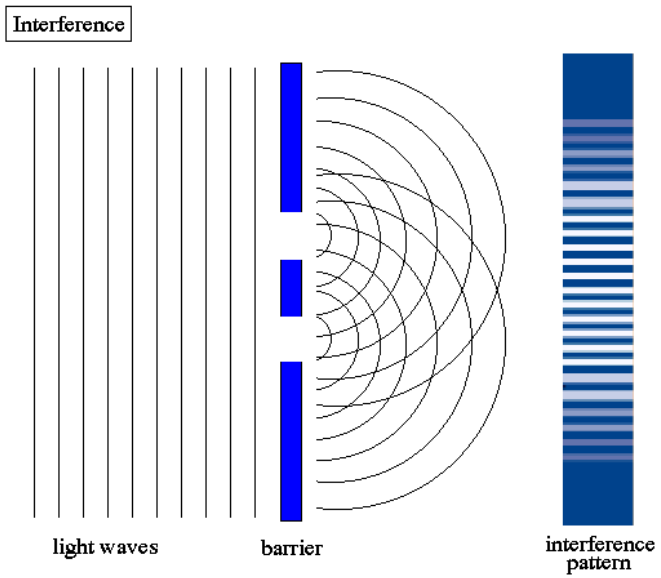
W. H. Bragg

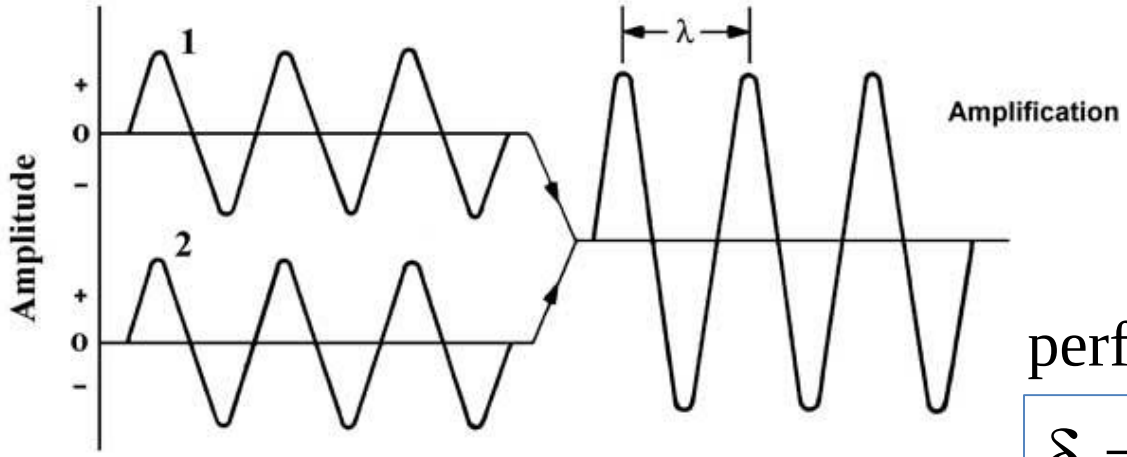


W. L. Bragg

von Laue

OPTICAL INTERFERENCE



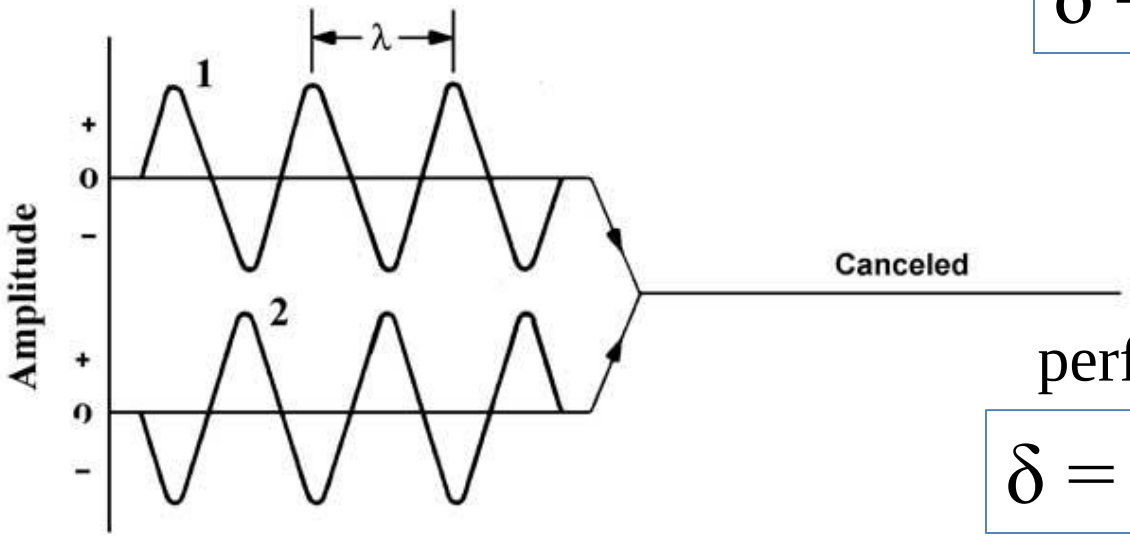


perfectly in phase:

$$\delta = n\lambda, \quad n = 0, 1, 2, \ldots$$

δ: phase difference

n: order



perfectly out of phase:

$$\delta = n\lambda, \quad n = 1/2, 3/2, \ldots$$

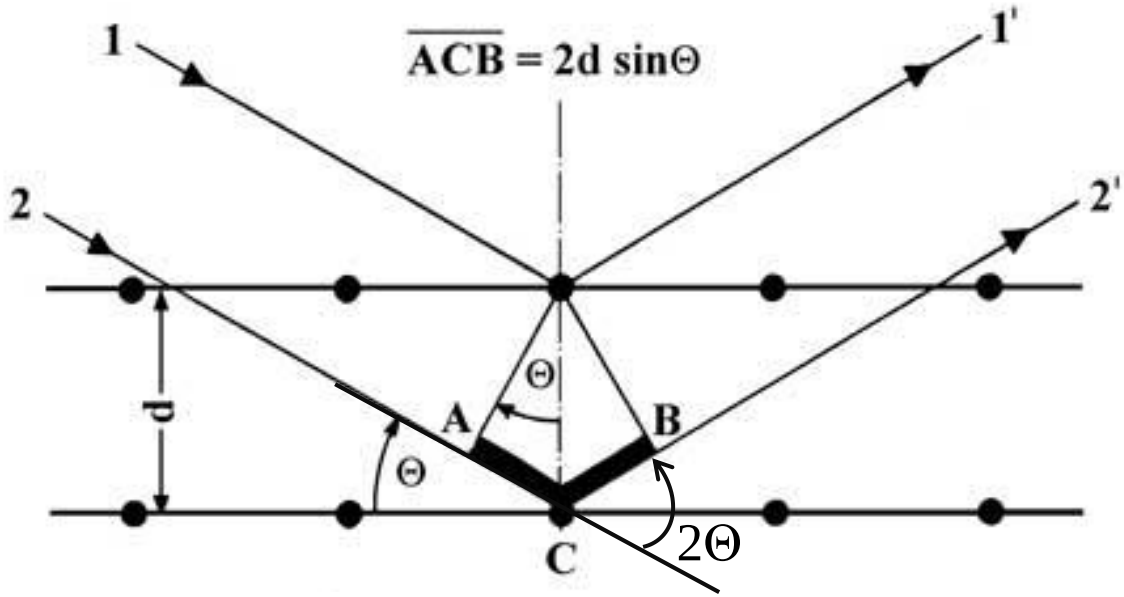
BRAGG'S LAW OF DIFFRACTION

When a collimated beam of X-rays strikes pair of parallel lattice planes in a crystal, each atom acts as a scattering center and emits a secondary wave.
→ All of the secondary waves interfere with each other to produce the diffracted beam

Bragg provided a simple, intuitive approach to diffraction:

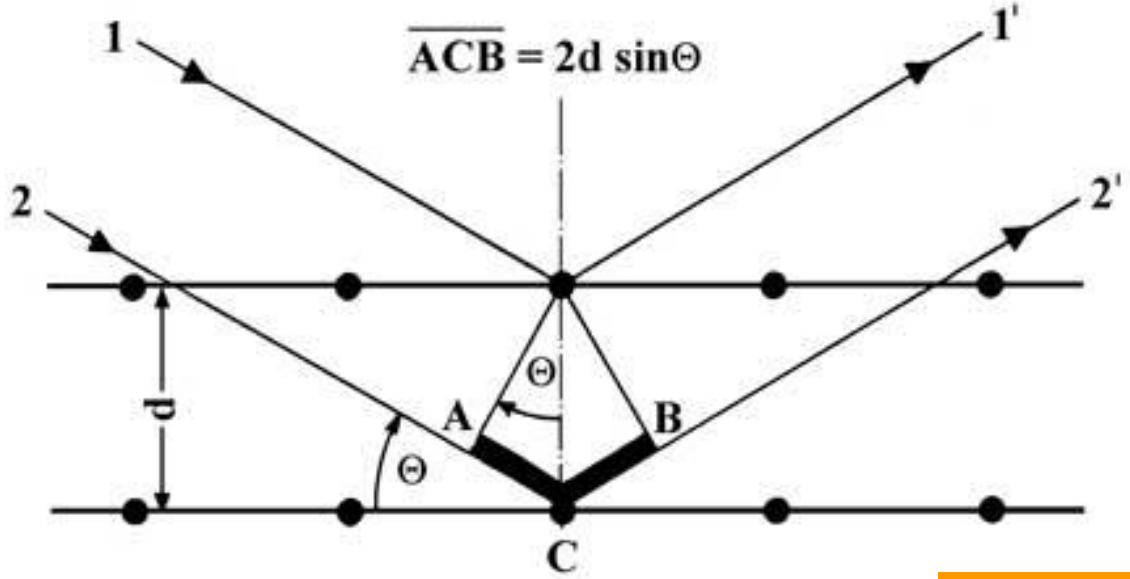
- Regard crystal as parallel planes of atoms separated by distance *d*
- Assume specular reflection of X-rays from any given plane

→ Peaks in the intensity of scattered radiation will occur when rays from successive planes interfere constructively



BRAGG'S LAW OF DIFFRACTION

No peak is observed unless the condition for constructive interference ($\delta = n\lambda$, with n an integer) is precisely met:



$$\overline{AC} = d \sin\theta$$

$$\overline{ACB} = 2d \sin\theta$$

$$n\lambda = \overline{ACB}$$

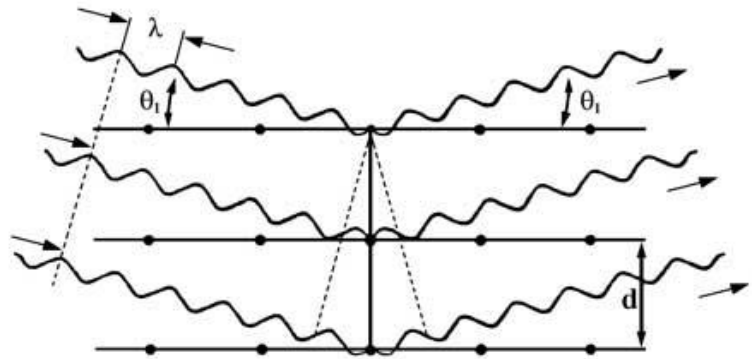
Bragg's Law: $$n\lambda = 2d \sin\theta$$

When Bragg's Law is satisfied, "reflected" beams are in phase and interfere constructively. Specular "reflections" can occur only at these angles.

DIFFRACTION ORDERS

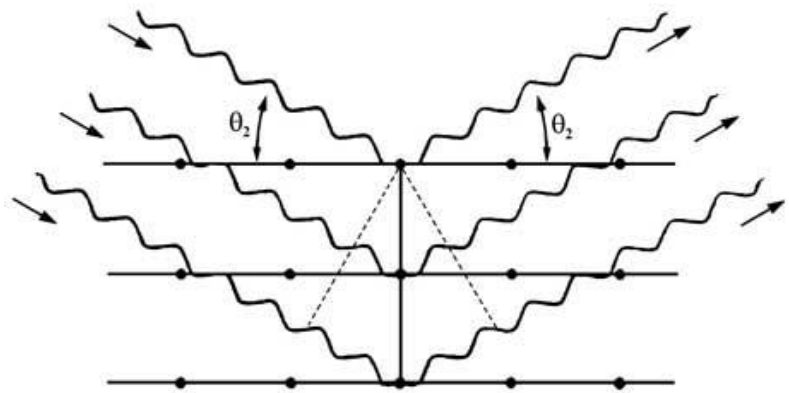
1st order:

$$\lambda = 2d\sin\theta_1$$



2nd order:

$$2\lambda = 2d\sin\theta_2$$



By convention, we set the diffraction order = 1 for XRD.

For instance, when n=2 (as above), we just halve the d-spacing to make n=1.

$$2\lambda = 2d\sin\theta_2 \quad \Rightarrow \quad \lambda = 2(d/2)\sin\theta_2$$

e.g. the 2nd order reflection of d_{100} occurs at same θ as 1st order reflection of d_{200}

XRD TECHNIQUES AND APPLICATIONS

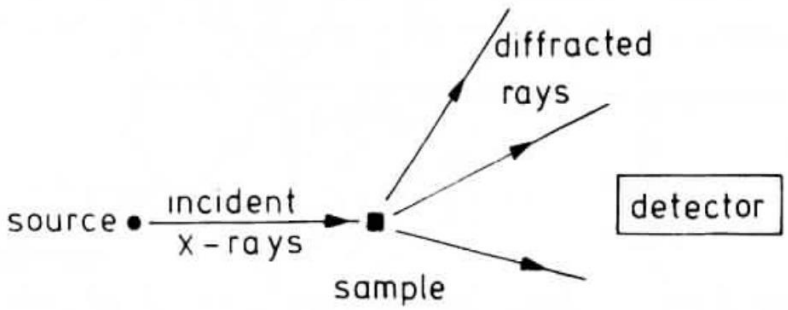


Fig. 3.6 The X-ray diffraction experiment

- powder diffraction
- single-crystal diffraction
- thin film techniques
- small-angle diffraction

Uses:

- phase identification
- crystal structure determination
- radial distribution functions
- thin film quality
- crystallographic texture
- percent crystalline/amorphous
- crystal size
- residual stress/strain
- defect studies
- in situ analysis (phase transitions, thermal expansion coefficients, etc)
- superlattice structure

POWDER X-RAY DIFFRACTION

- uses monochromatic radiation, scans angle
- sample is powder → all orientations simultaneously presented to beam
- some crystals will always be oriented at the various Bragg angles
- this results in cones of diffracted radiation
- cones will be spotty in coarse samples (those w/ few crystallites)

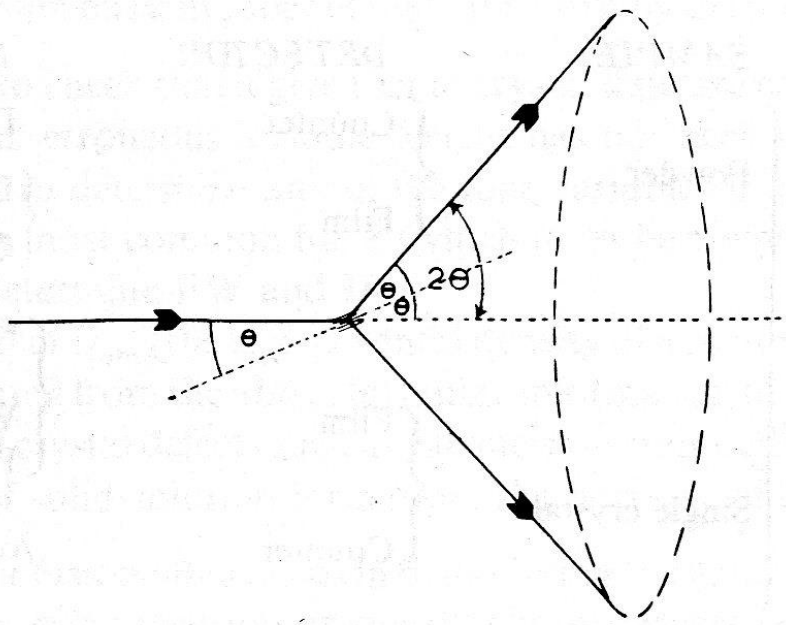
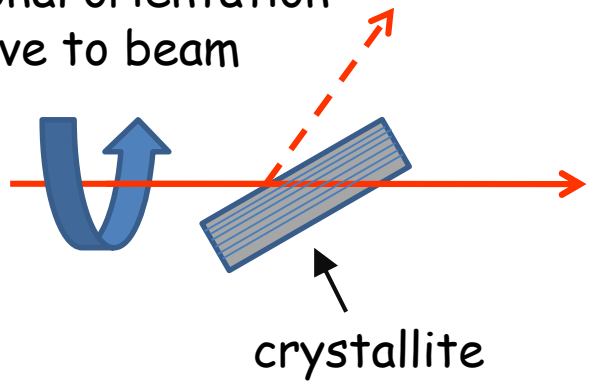
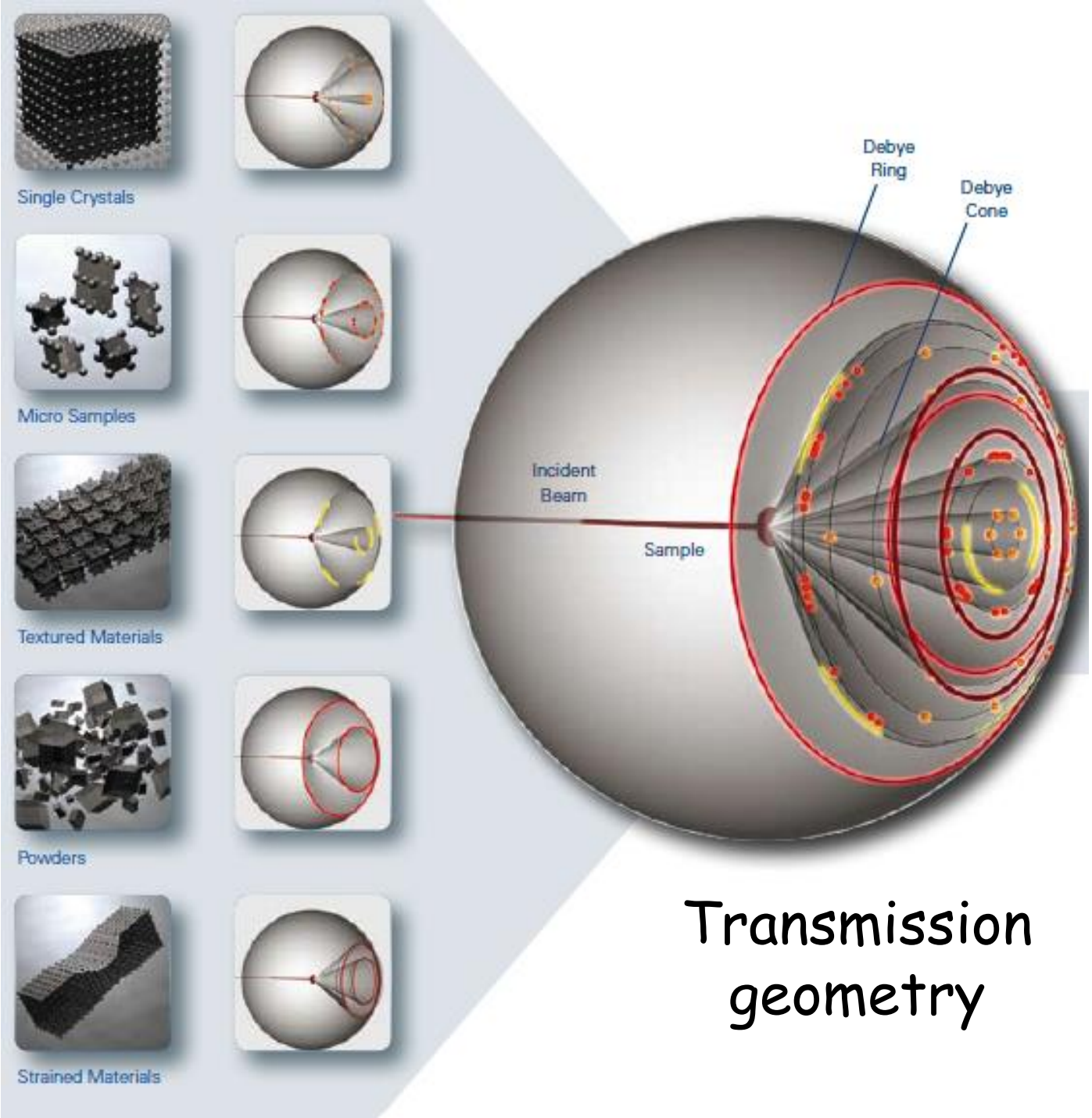


Fig. 5.29 The formation of a cone of diffracted radiation in the powder method

no restriction
on rotational orientation
relative to beam



$$\lambda = 2d_{hkl} \sin \theta_{hkl}$$

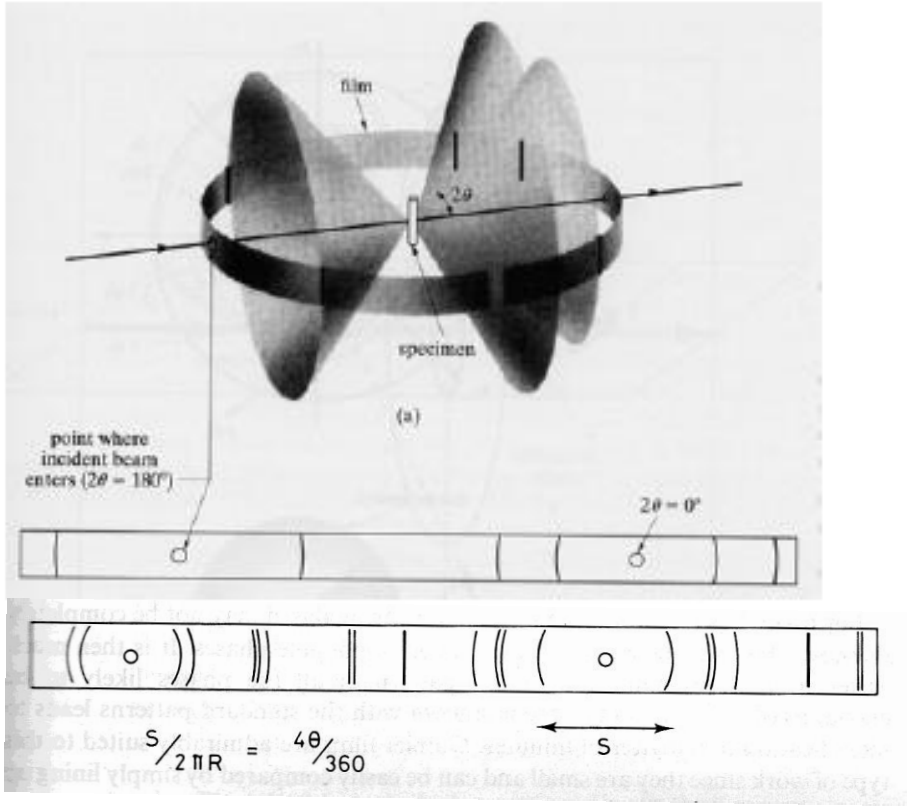


Transmission geometry

DEBYE-SCHERRER METHOD

Can record sections on these cones on film or some other x-ray detector

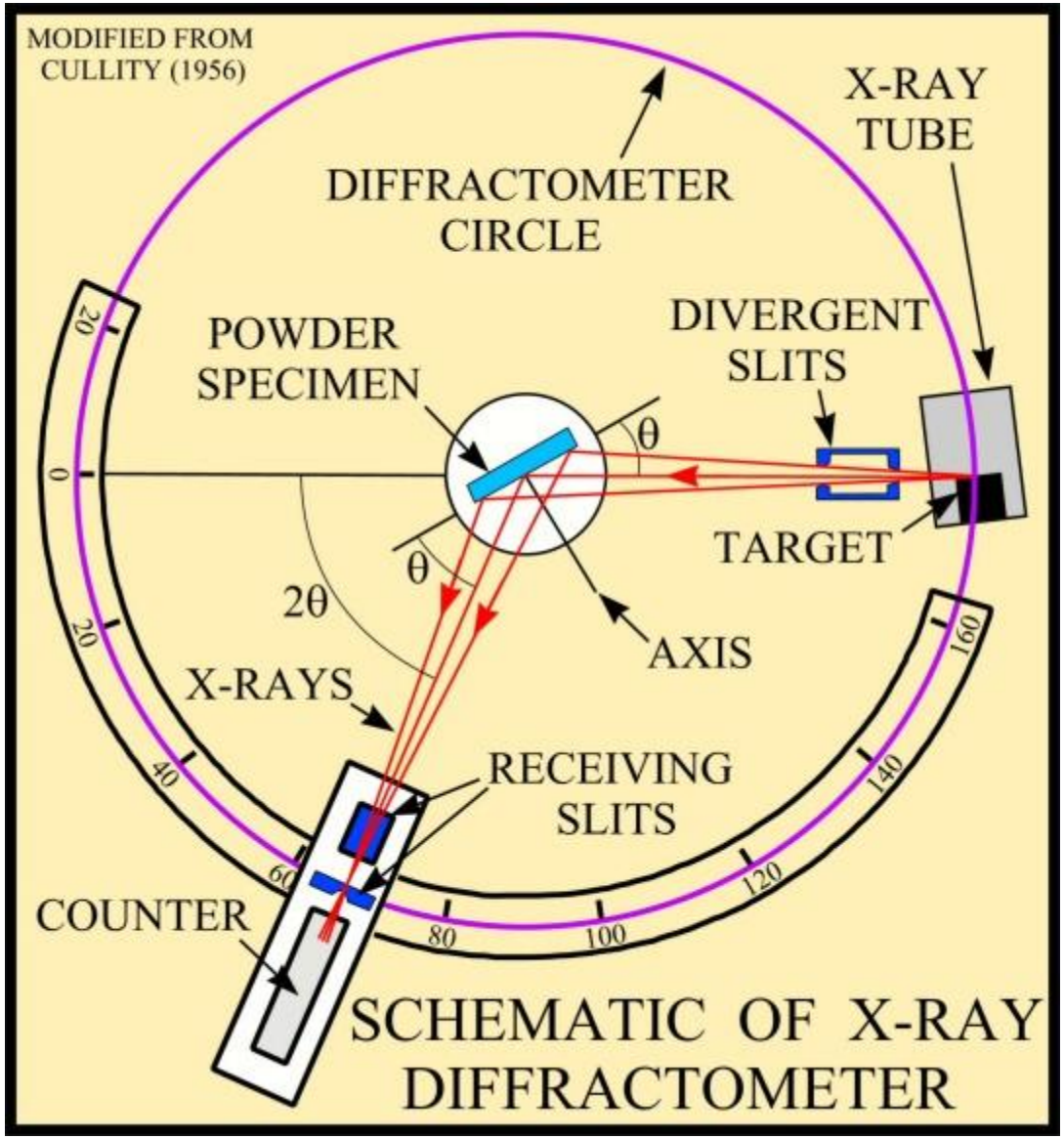
- Simplest way of doing this is to surround a capillary sample with a strip of film
- Can covert line positions on film to angles and intensities by electronically scanning film or measuring positions using a ruler and guessing the relative intensities using a "by eye" comparison



$$\lambda = 2d_{hkl}\sin\theta_{hkl}$$

…or we can use a diffractometer to intercept sections of the cones

BASIC DIFFRACTOMETER SETUP

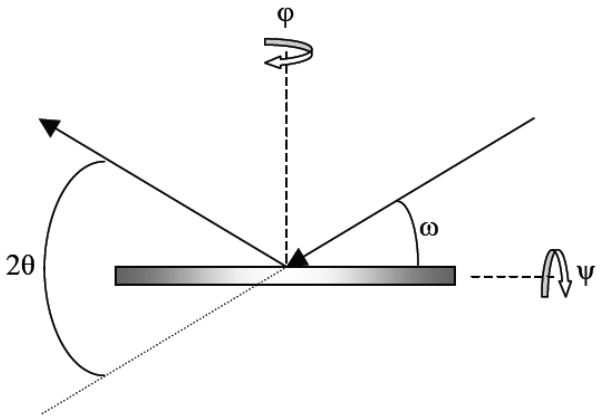


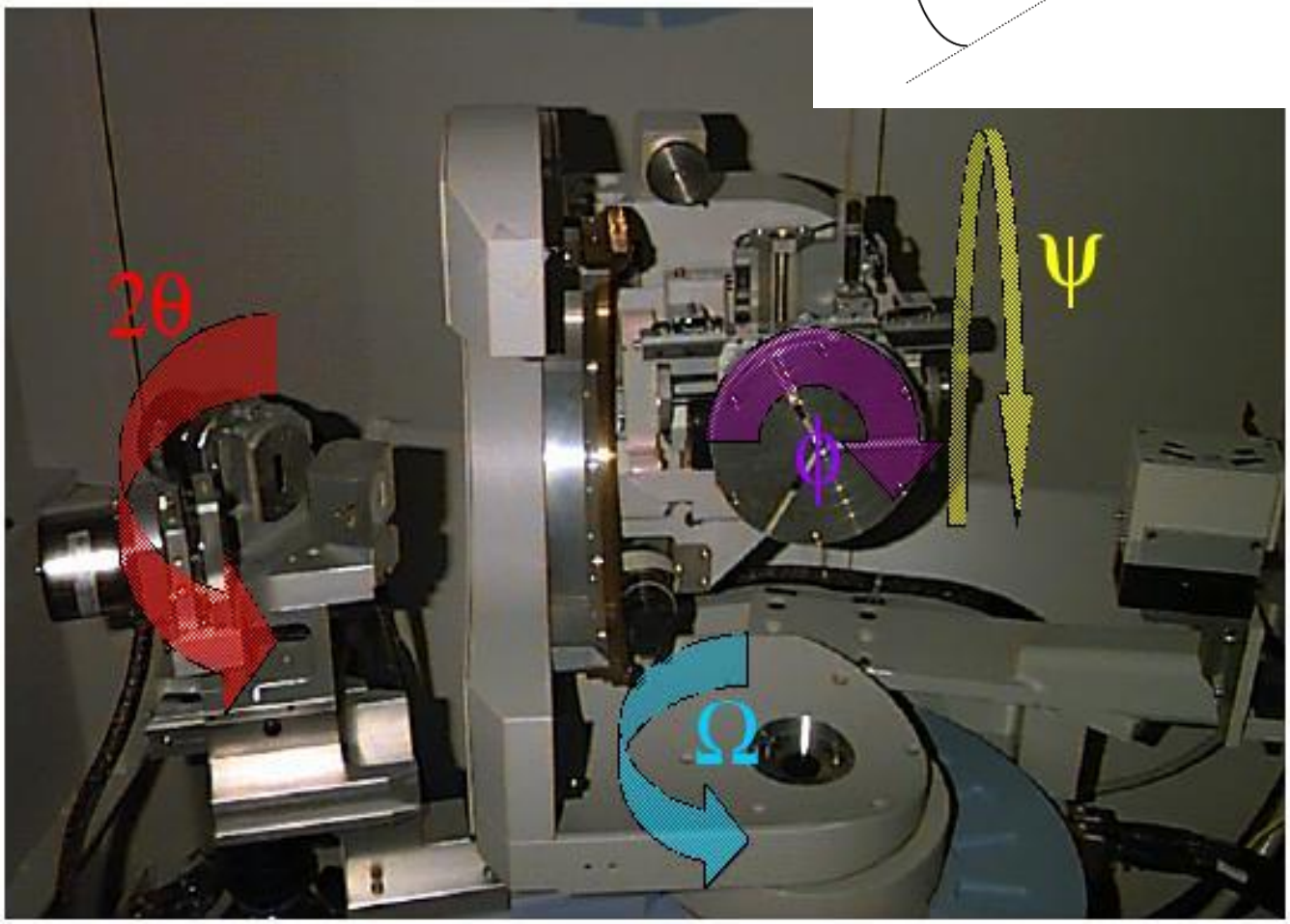
DIFFRACTOMETERS

General Area Detector Diffraction System (GADDS)

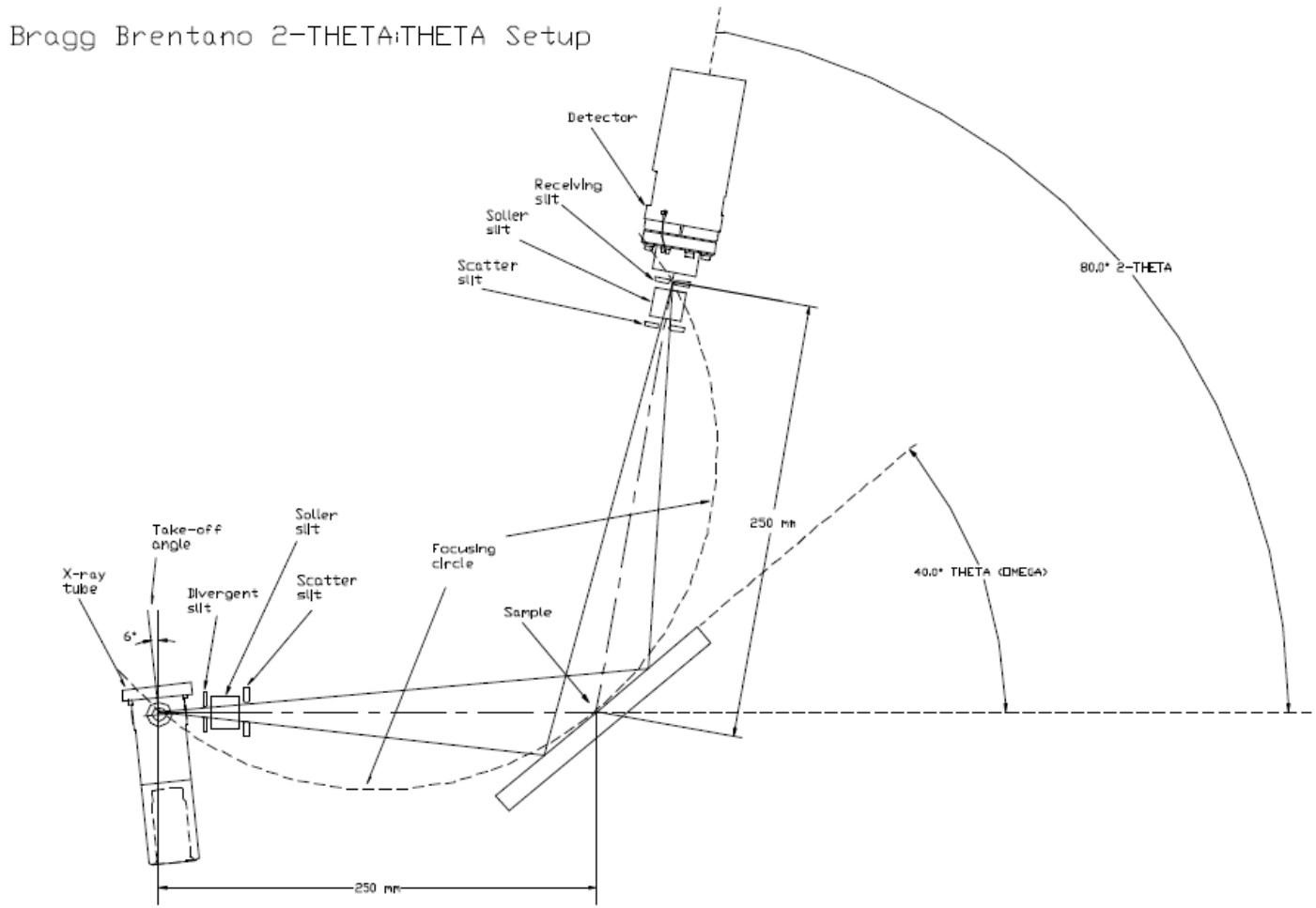
THIN FILM SCANS

4-axis goniometer



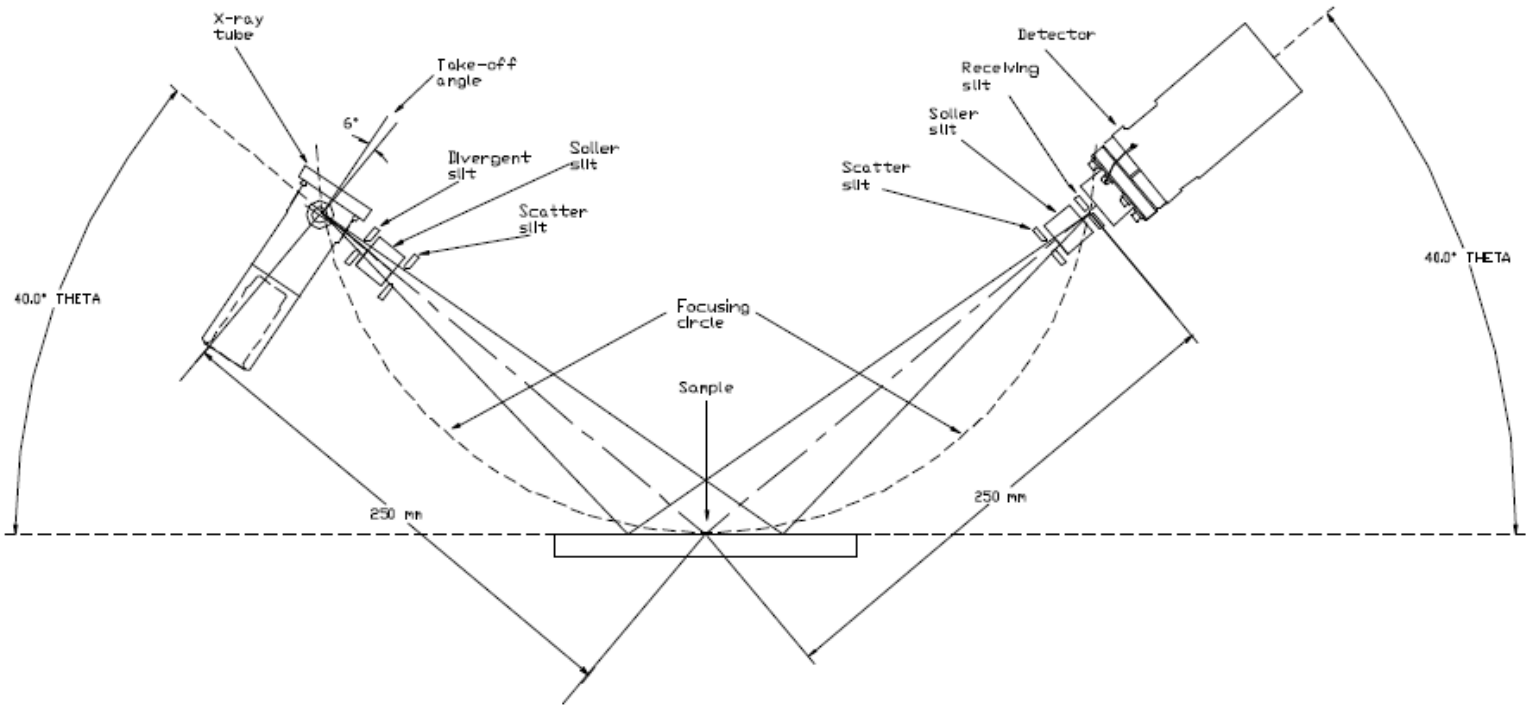


THETA-2THETA GEOMETRY



- X-ray tube stationary
- sample moves by angle theta, detector by 2theta

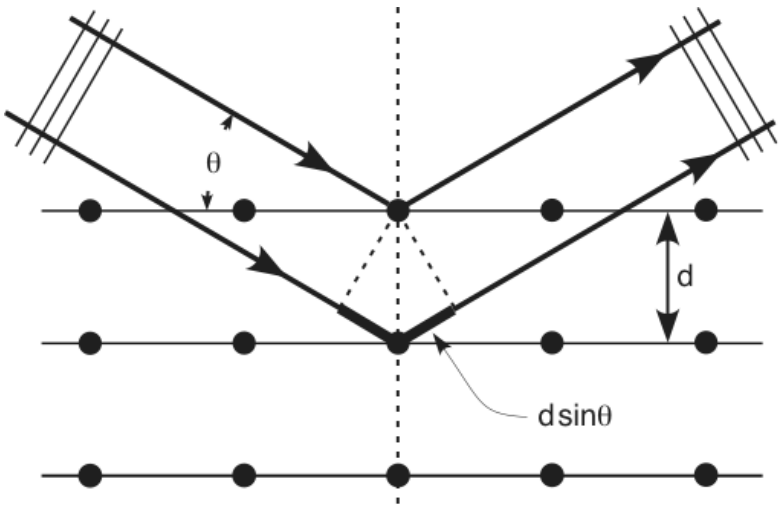
THETA-THETA GEOMETRY



- sample horizontal (good for loose samples)
- tube and detector move simultaneously through theta

POWDER DIFFRACTOGRAMS

In powder XRD, a finely powdered sample is probed with monochromatic X-rays of a known wavelength in order to evaluate the *d*-spacings according to Bragg's Law.



BRAGG LAW

$$2d(\sin\theta) = \lambda_o$$

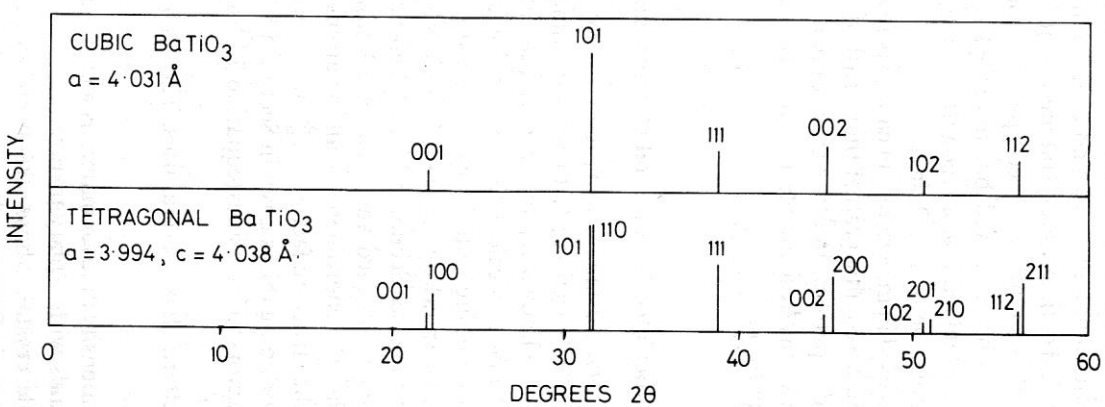
where:

d = lattice interplanar spacing of the crystal

θ = x-ray incidence angle (Bragg angle)

λ = wavelength of the characteristic x-rays

Cu Ka radiation: λ = 1.54 Å



peak positions depend on:

- *d*-spacings of {hkl}
- "systematic absences"

Minimum d?

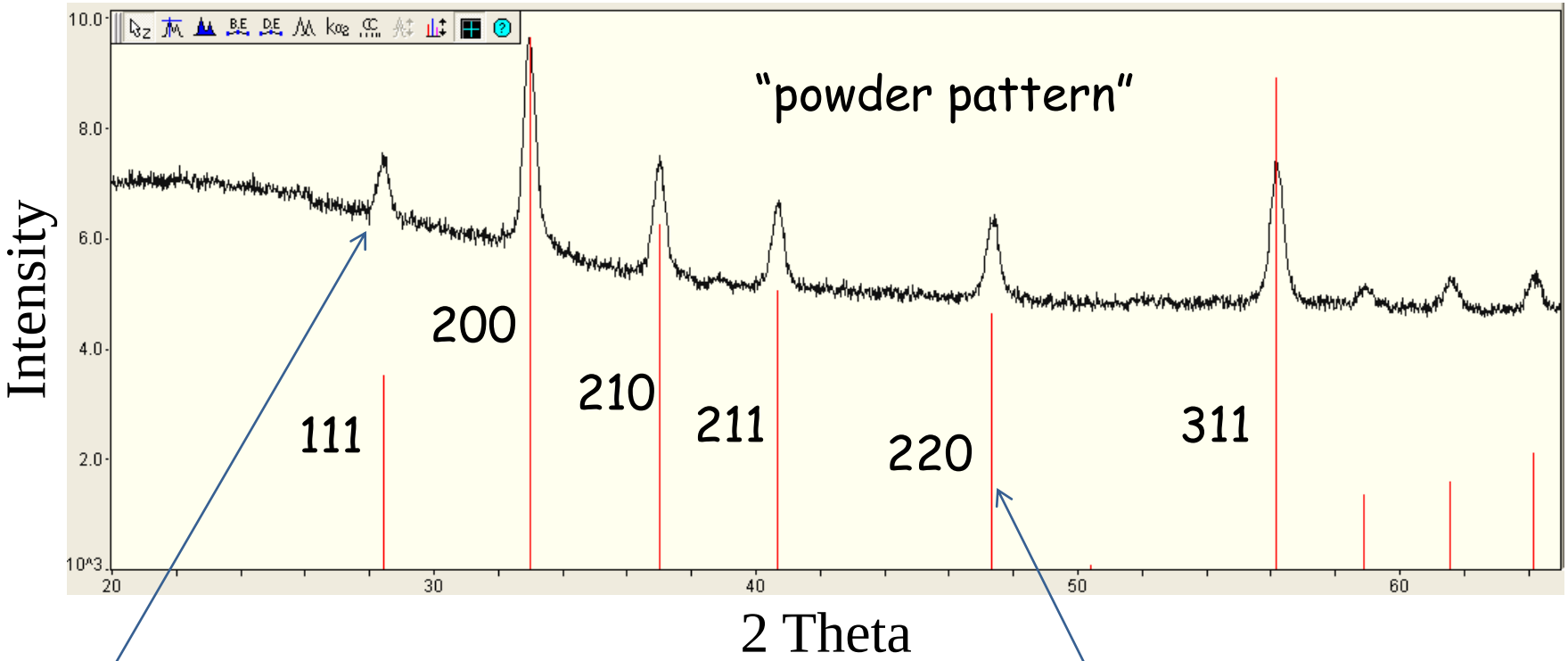
$$d_{\min} = \lambda / 2$$

increasing θ, **decreasing** *d*

ACTUAL EXAMPLE: PYRITE THIN FILM

FeS_2 – cubic (a = 5.43 Å)
Random crystal orientations

Cu Kα = 1.54 Å



$2\theta = 28.3° \rightarrow d = 1.54/[2\sin(14.15)]$
$= 3.13$ Å $= d_{111}$

reference pattern from ICDD
(1,004,568+ datasets)

On casual inspection, peaks give us d-spacings, unit cell size, crystal symmetry, preferred orientation, crystal size, and impurity phases (none!)

d-SPACING FORMULAS

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

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

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

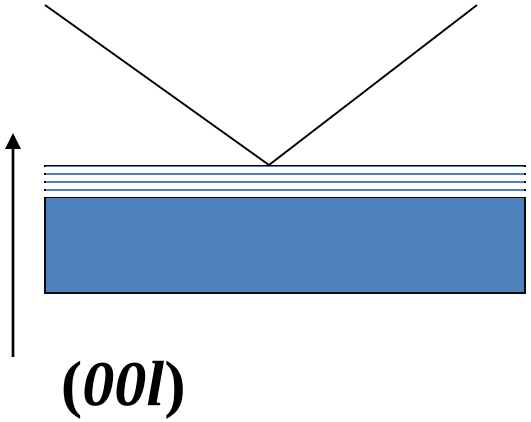
Hexagonal
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

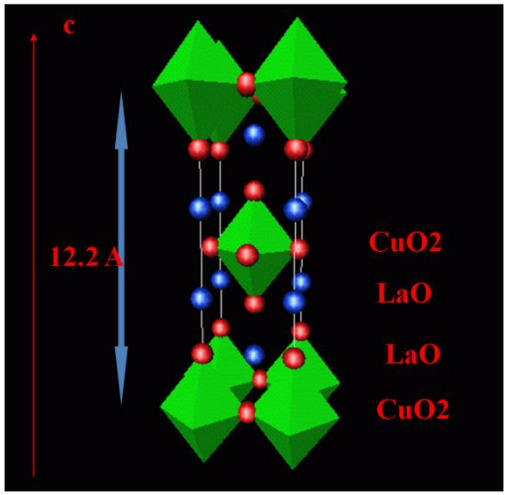
Monoclinic
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic
$$\begin{aligned}\frac{1}{d^2} = \frac{1}{V^2}[&h^2b^2c^2\sin^2\alpha + k^2a^2c^2\sin^2\beta \\ &+ l^2a^2b^2\sin^2\gamma + 2hkabc^2(\cos\alpha\cos\beta - \cos\gamma) \\ &+ 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha) \\ &+ 2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)]\end{aligned}$$

EXAMPLE 2: textured La_2CuO_4

Layered Cuprate Thin film, growth oriented along c axis





$$2d_{00l}\sin\theta = \lambda$$

c = 12.2 Å

Epitaxial film is *textured*.
(It has crystallographic orientation).
Many reflections are "missing"

2 theta	*d*	(*hkl*)
7.2	12.2	(001)
14.4	6.1	(002)
22	4.0	(003)

POWDER DIFFRACTION

Peak positions determined by size and shape of unit cell

Peak intensities determined by the position and atomic number of the various atoms within the unit cell

Peak widths determined by instrument parameters, temperature, and crystal size, strain, and imperfections

we will return to this later…

GENERATION OF X-RAYS

X-rays beams are usually generated by colliding high-energy electrons with metals.

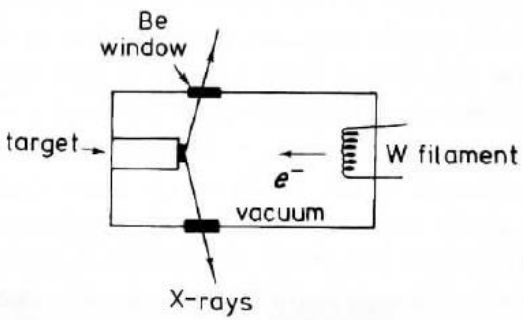
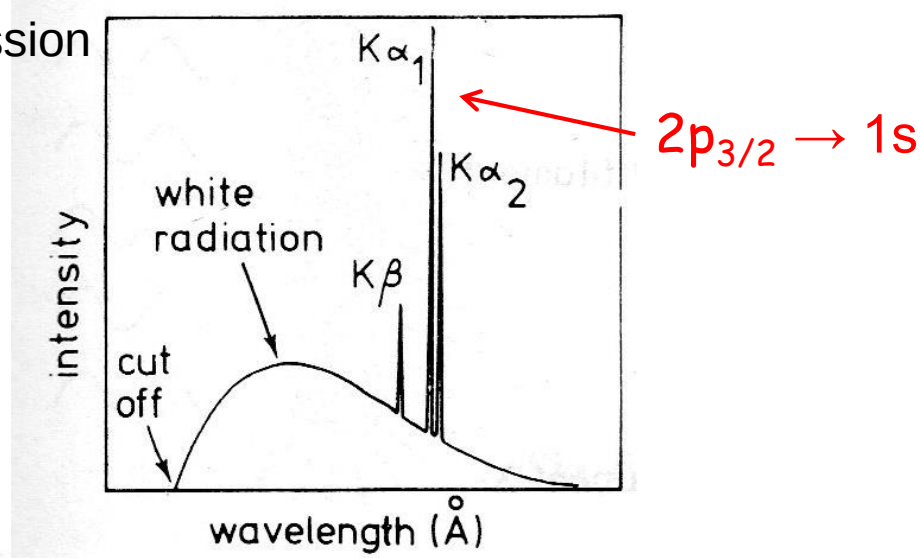
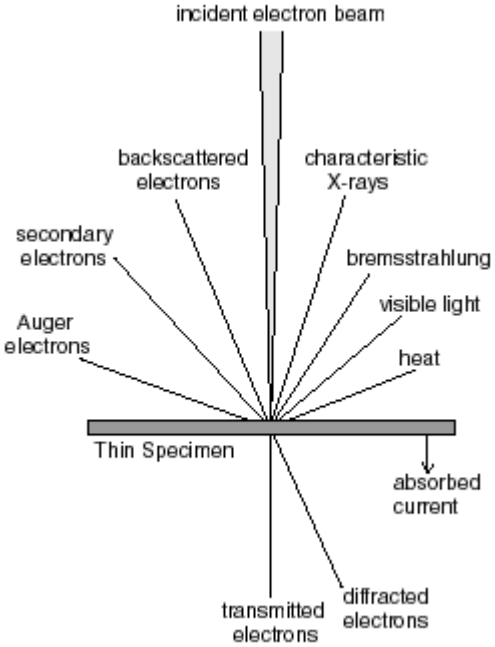


Fig. 3.2 Schematic design of a filament X-ray tube

X-ray emission spectrum





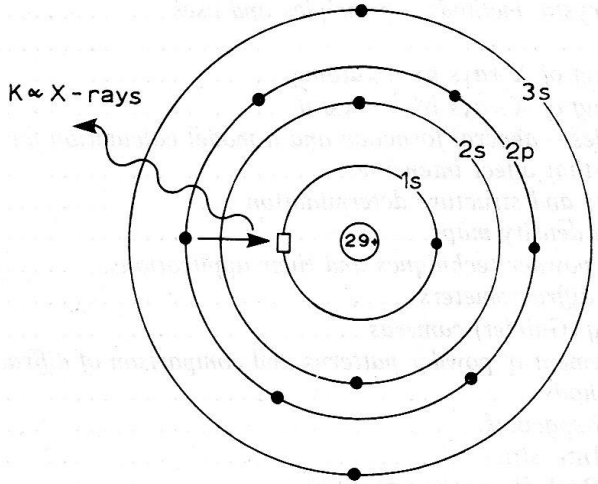
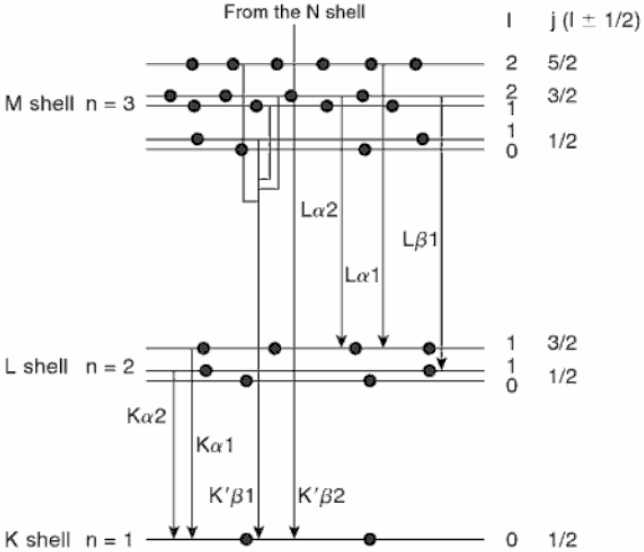
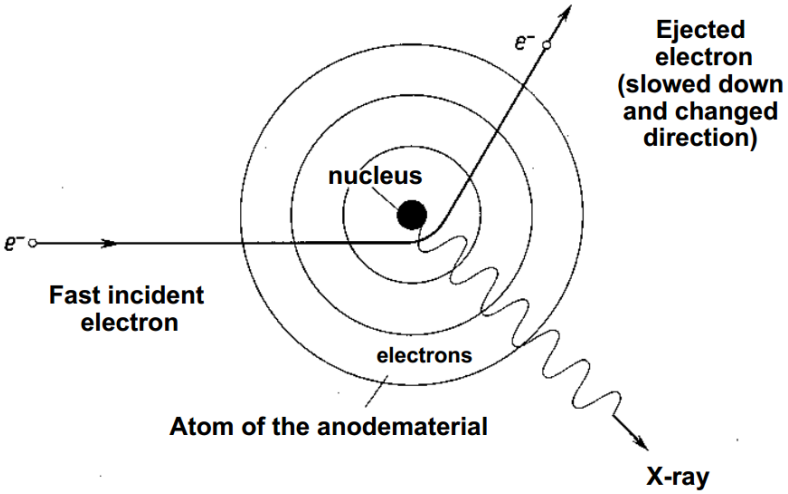


Fig. 5.1 Generation of Cu $K\alpha$ X-rays. A $2p$ electron falls into the empty $1s$ level (□) and the excess energy is released as X-rays

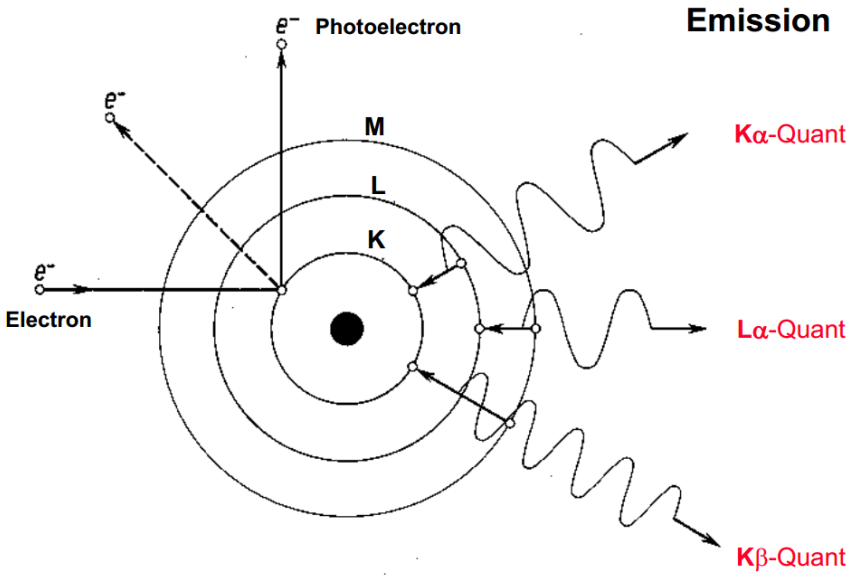


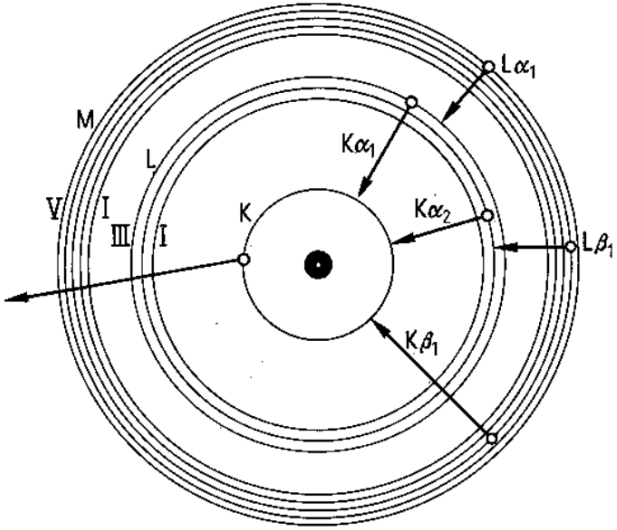
Siegbahn notation

Generating Bremsstrahlung



Generating Characteristic X-rays

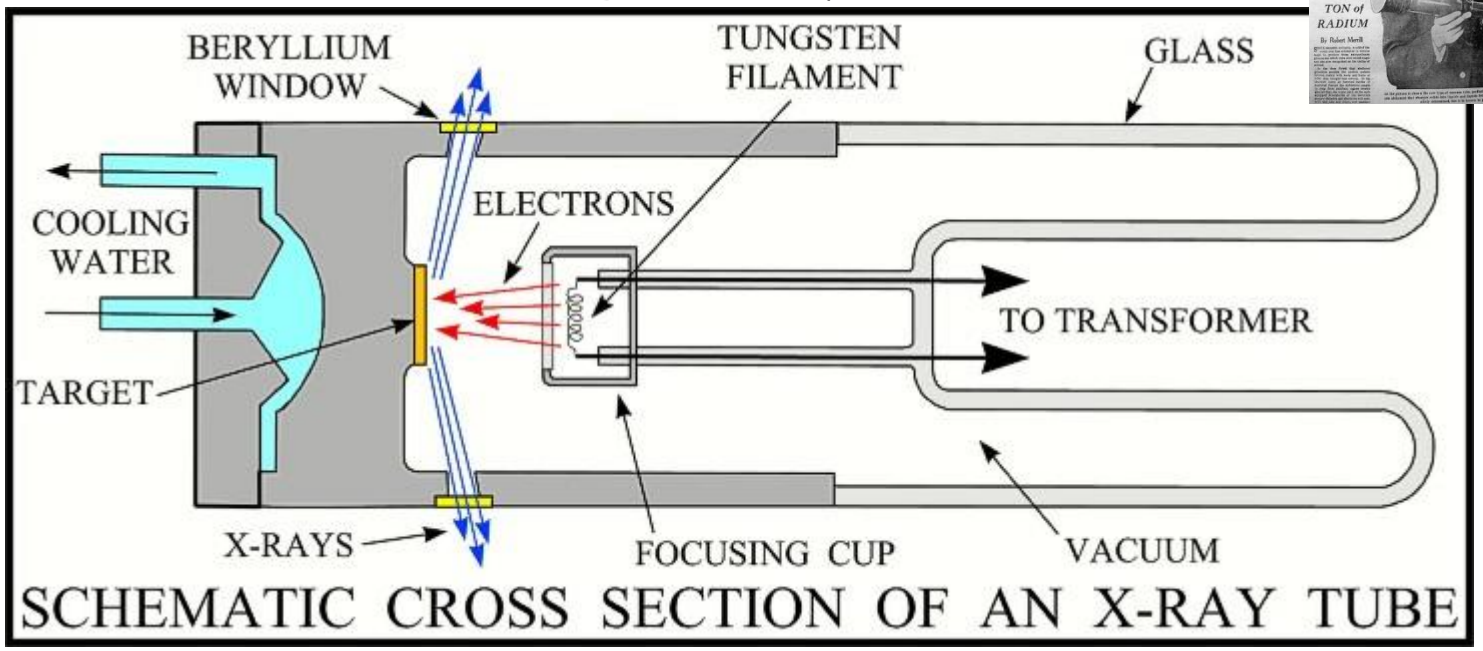




Bohr`s model

GENERATION OF X-RAYS

Side-window Coolidge X-ray tube



X-ray energy is determined by anode material, accelerating voltage, and monochromators:

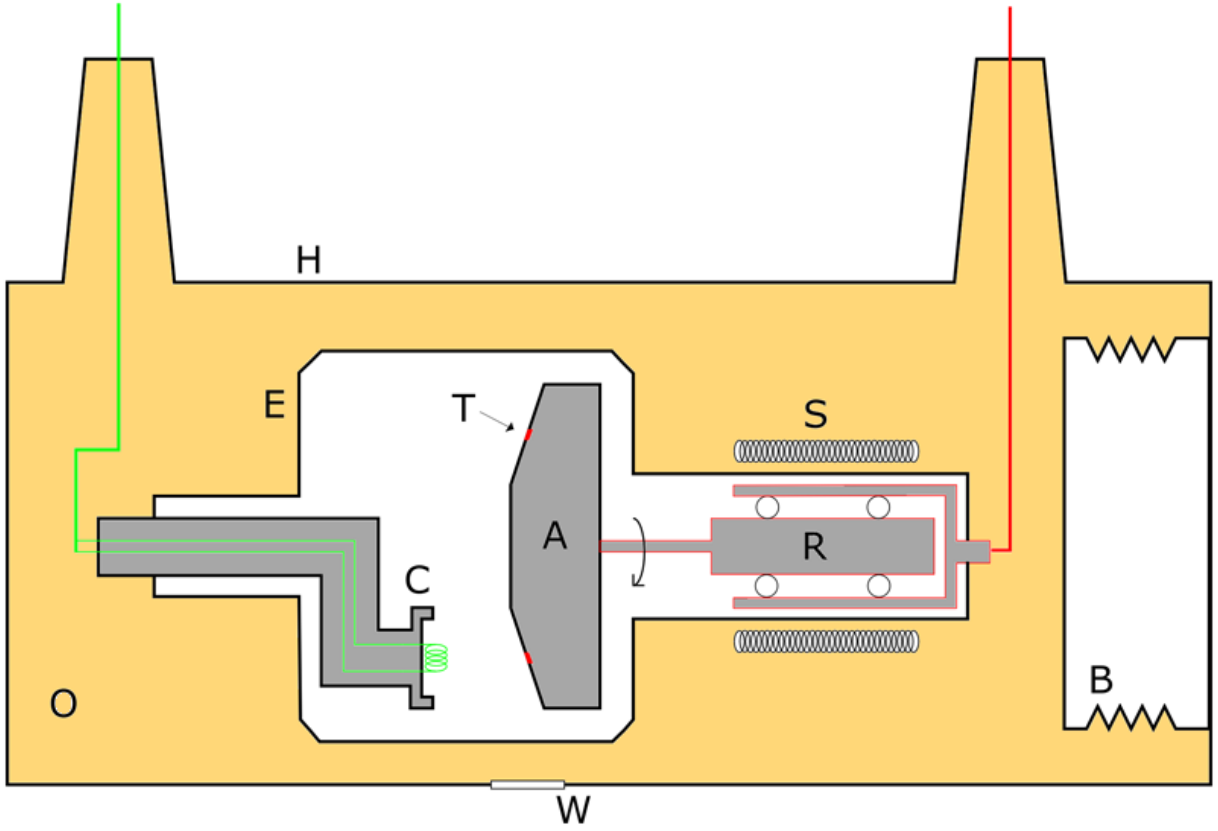
$$E = h\nu = hc/\lambda$$

Moseley's Law: $\lambda^{-1/2} = C(Z - \sigma)$

Co $K\alpha_1$: 1.79 Å
Cu $K\alpha_1$: 1.54 Å (~8 keV)
Mo $K\alpha_1$: 0.71 Å

ROTATING ANODES

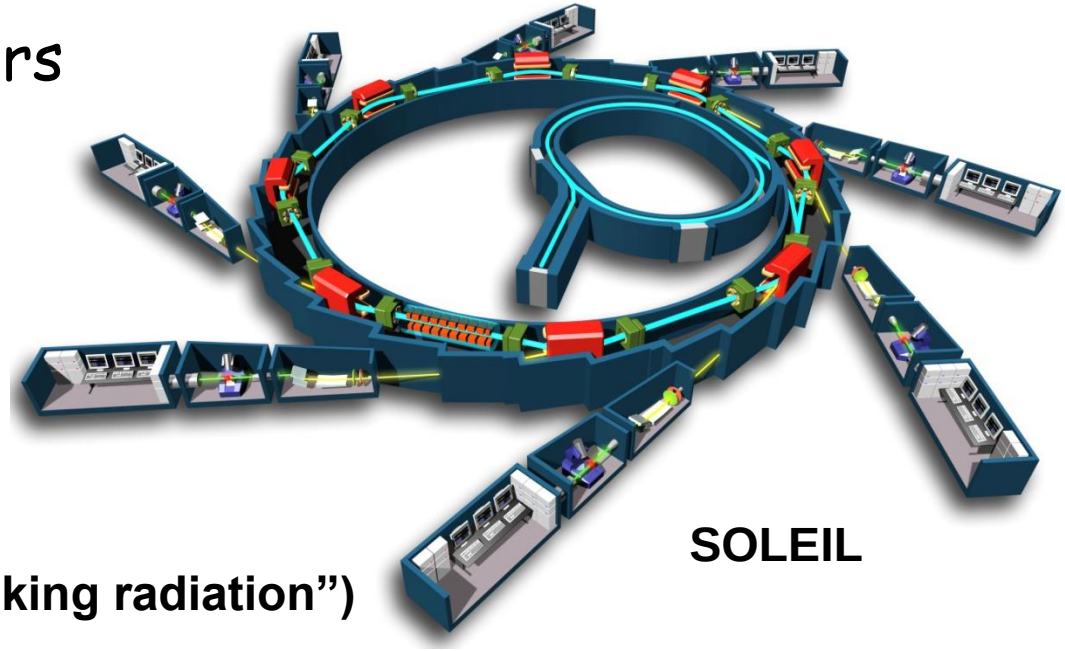
- 100X higher powers possible by spinning the anode at > 6000 rpm to prevent melting it → brighter source



SYNCHROTRON LIGHT SOURCES

GeV electron accelerators

- brightest X-ray sources
- high collimation
- tunable energy
- pulsed operation



SOLEIL

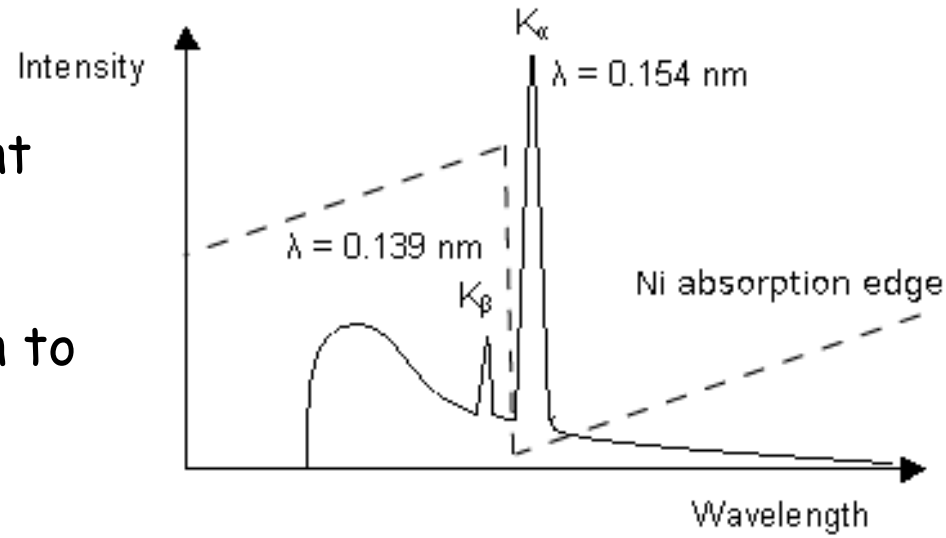
Bremsstrahlung ("braking radiation")

Australian Synchrotron

MONOCHROMATIC X-RAYS

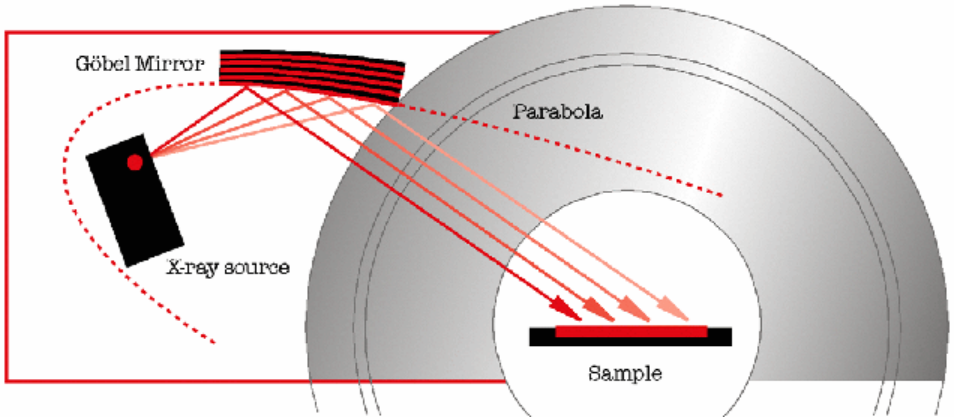
Filters (old way)

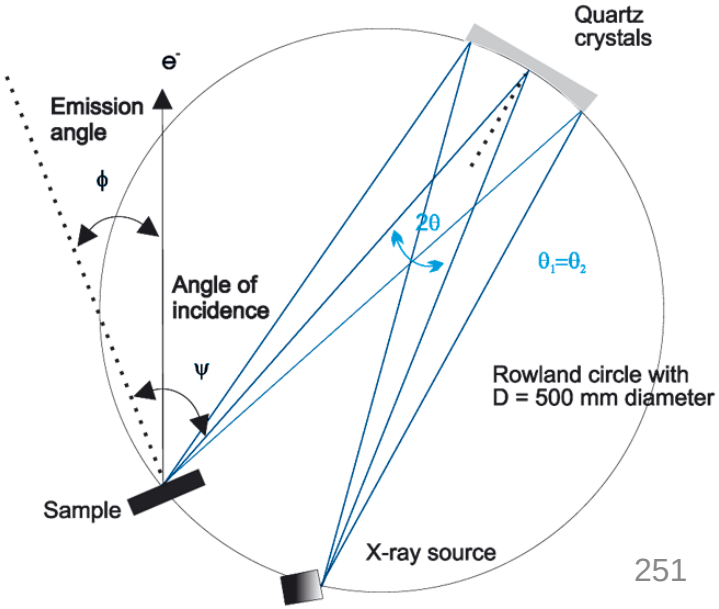
A foil of the next lightest element (Ni in the case of Cu anode) can often be used to absorb the unwanted higher-energy radiation to give a clean K_α beam



Crystal Monochromators

Use diffraction from a curved crystal (or multilayer) to *select* X-rays of a specific wavelength





DETECTION OF X-RAYS

Detection principles

- gas ionization
- scintillation
- creation of e-h pairs

- Point detectors
- Strip detectors
- Area detectors

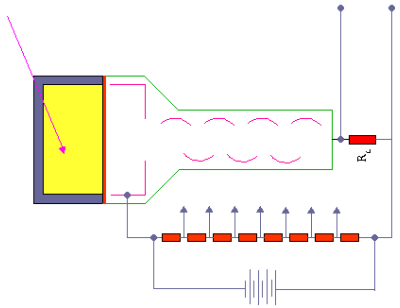
Table 4-2. *Properties of common x-ray detectors; ΔE is measured as FWHM.*

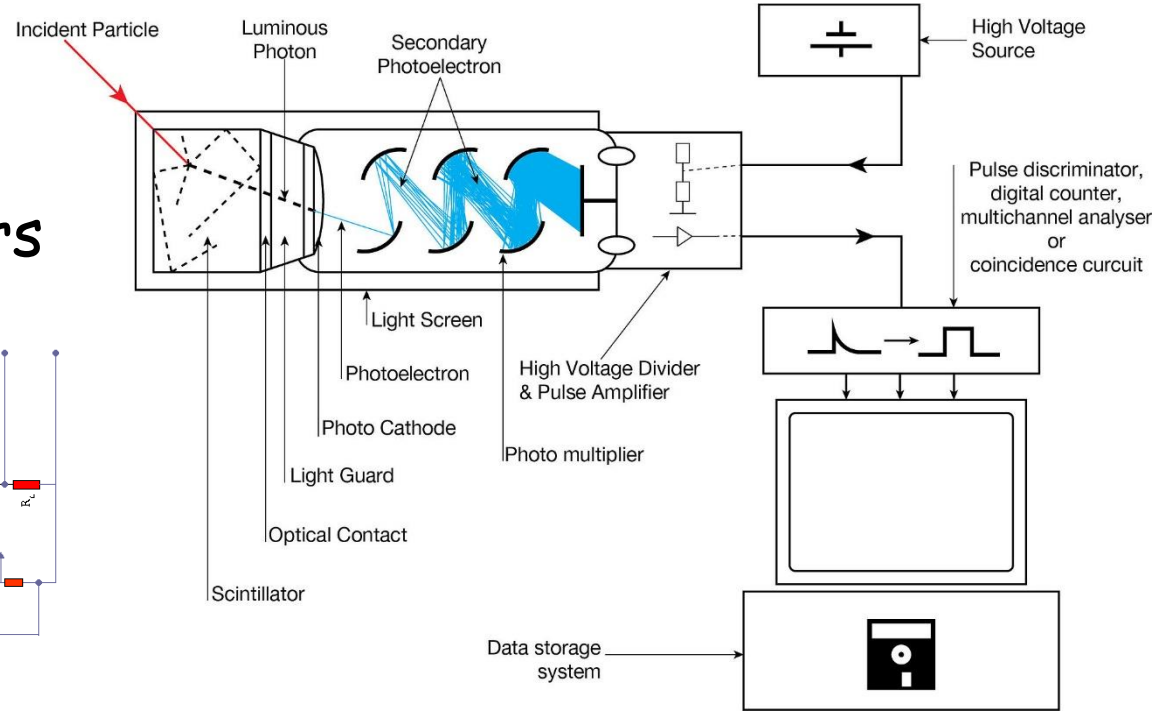
Detector	Energy range (keV)	$\Delta E/E$ at 5.9 keV (%)	Dead time/event (μs)	Maximum count rate (s^{-1})
Gas ionization (current mode)	0.2–50	n/a	n/a	10^{11a}
Gas proportional	0.2–50	15	0.2	10^6
Multiwire and microstrip proportional	3–50	20	0.2	$10^6/mm^2$
Scintillation [NaI(Tl)]	3–10,000	40	0.25	2×10^6
Energy-resolving semiconductor	1–10,000	3	0.5–30	2×10^5
Surface-barrier (current mode)	0.1–20	n/a	n/a	10^8
Avalanche photodiode	0.1–50	20	0.001	10^8
CCD	0.1–70	n/a	n/a	n/a
Superconducting	0.1–4	< 0.5	100	5×10^3
Image plate	4–80	n/a	n/a	n/a

DETECTION OF X-RAYS

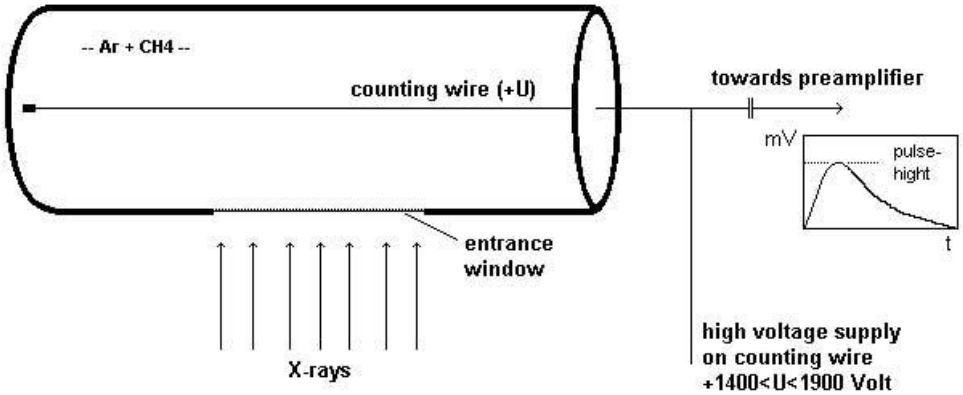
Point detectors

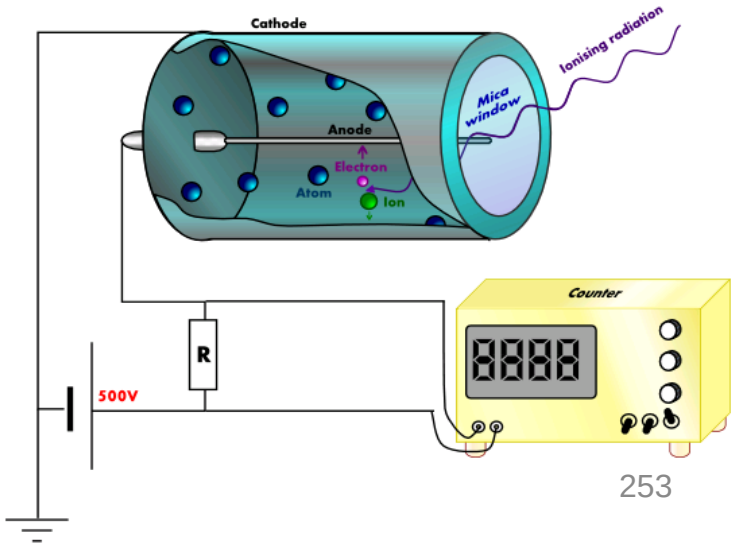
Scintillation counters





Gas proportional counters



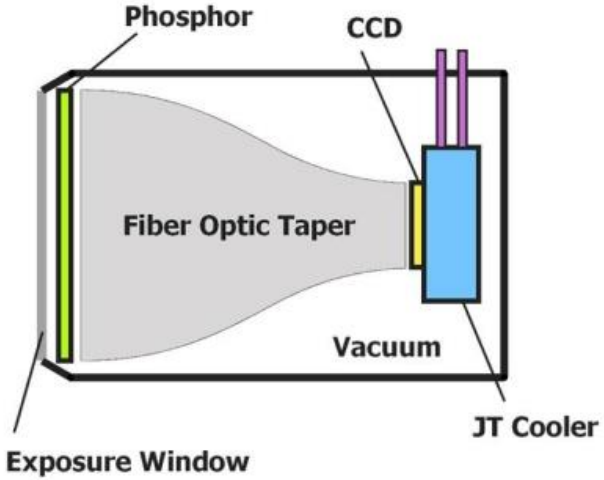


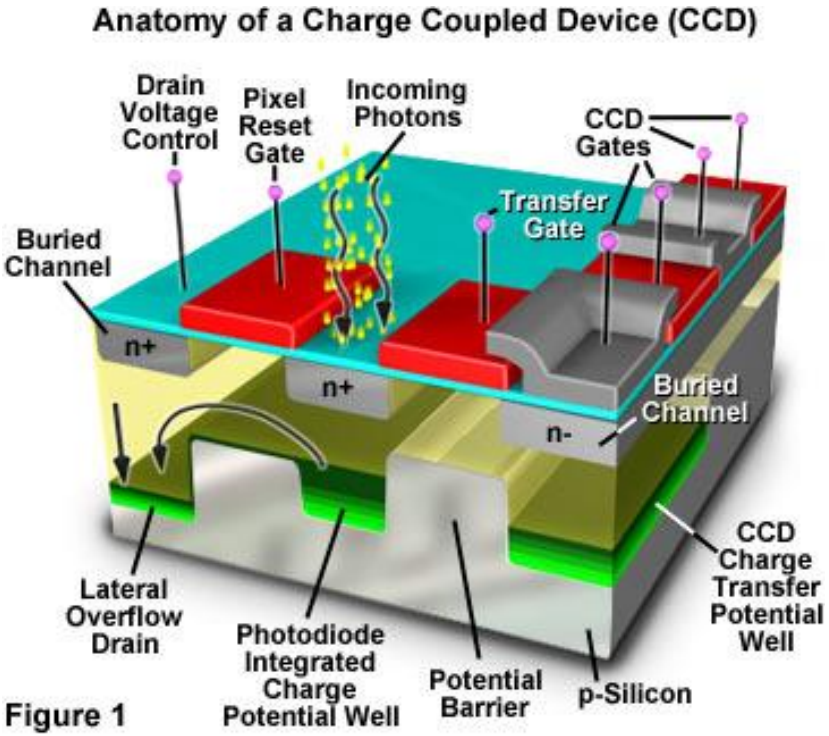
X-RAY DETECTORS

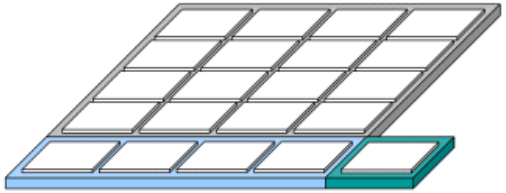
Area detectors

- film
- imaging plate
- CCD
- multiwire

Charge-coupled devices



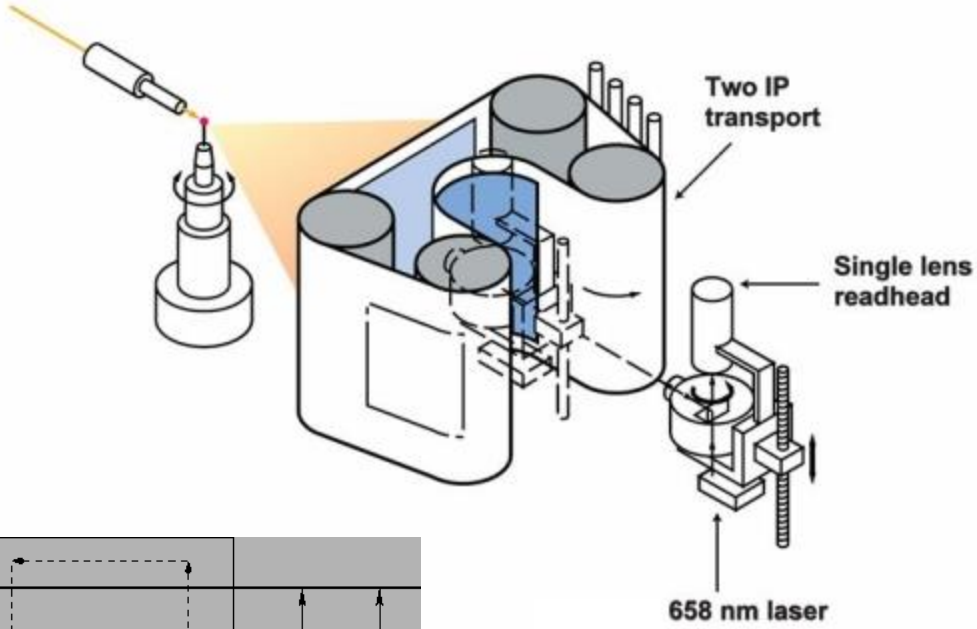


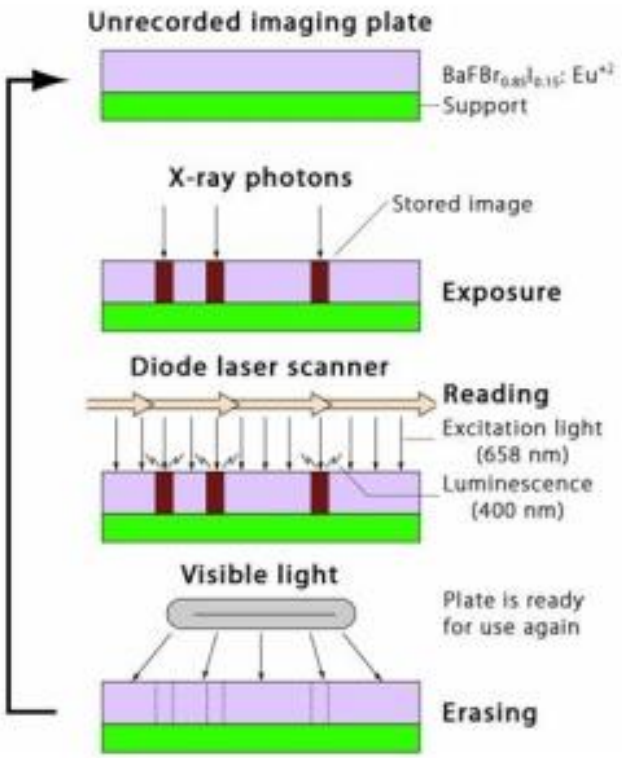


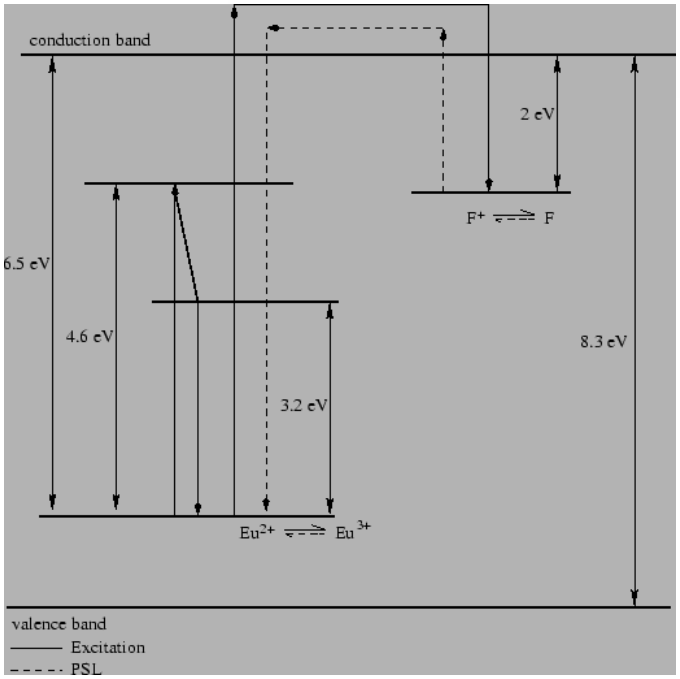
X-RAY DETECTORS

Imaging plates

photostimulated luminescence from $BaFBr_{0.85}I_{0.15}:Eu^{2+}$



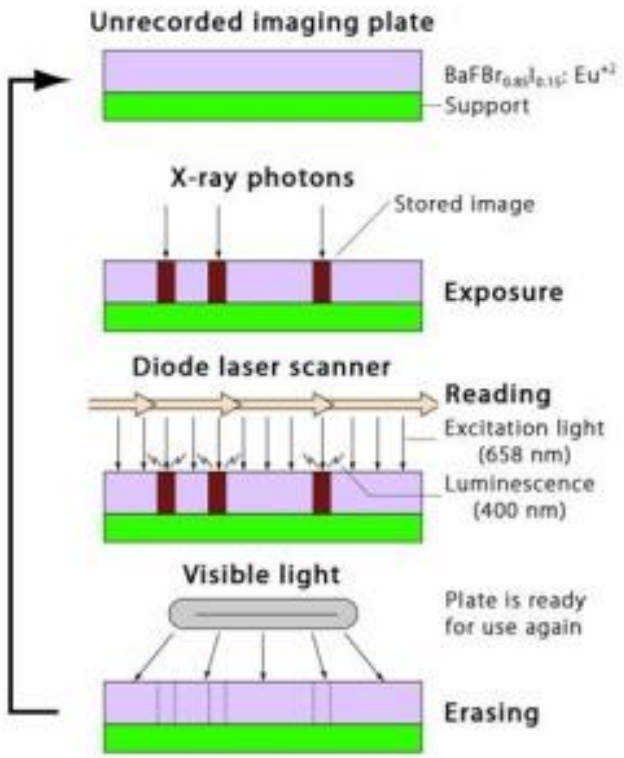


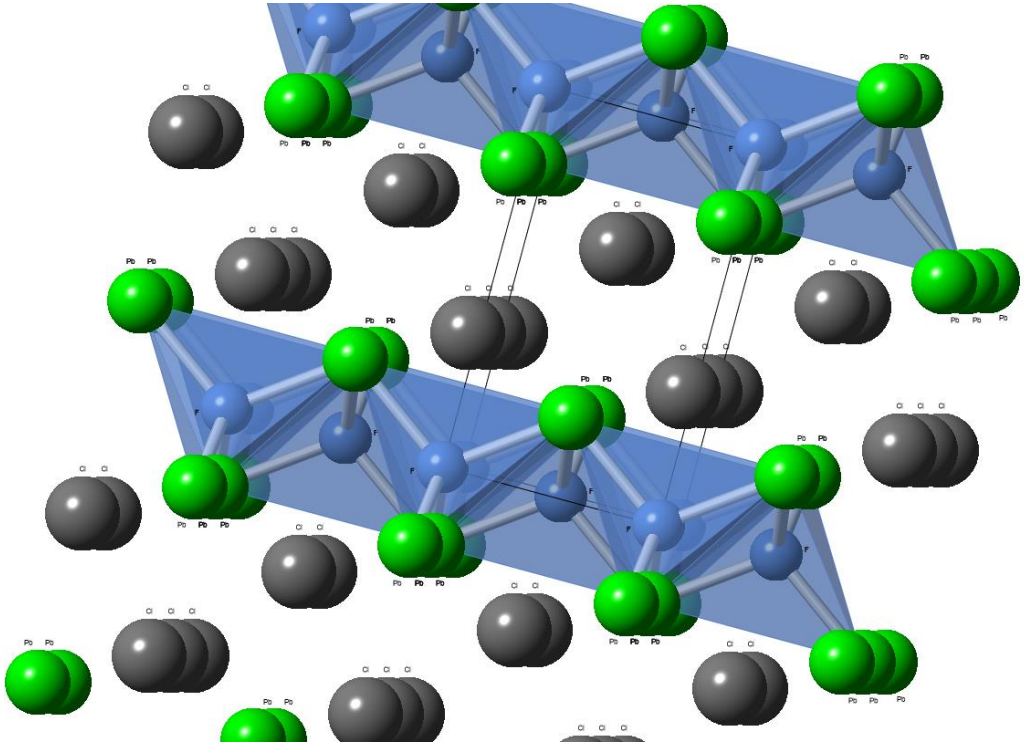


X-RAY DETECTORS

Imaging plates

photostimulated luminescence
from $BaFBr_{0.85}I_{0.15}:Eu^{2+}$





tetragonal Matlockite structure (PbFCl)
9-coordinate Ba!

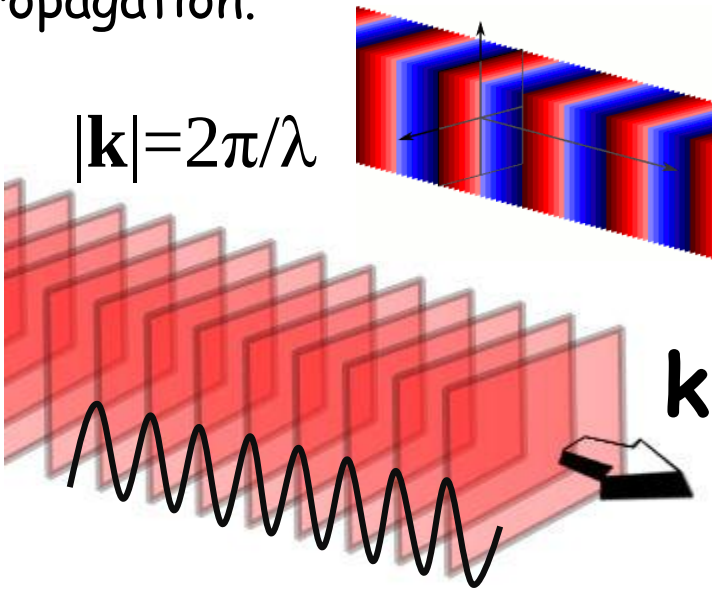
The Reciprocal Lattice and the Laue Description of Diffraction

Reading: A/M 5-6
G/S 3

PLANE WAVES

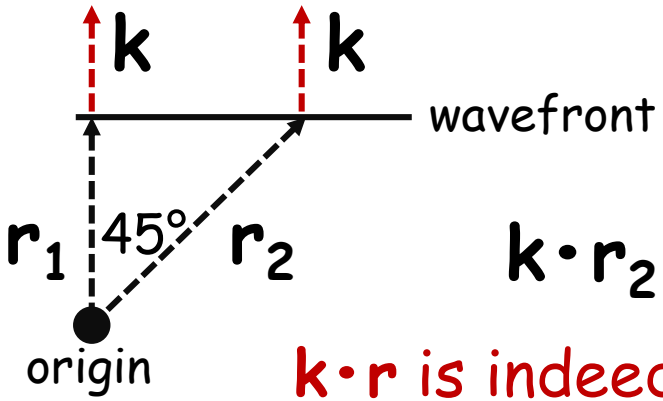
A wave whose surfaces of constant phase are infinite parallel planes of equal spacing normal to the direction of propagation.

$$\psi(r) = Ae^{i\mathbf{k}\cdot\mathbf{r}}$$



ψ: wave amplitude at point r
A: max amplitude of wave
k: wave vector
r: space vector from arbitrary origin

Amplitude is constant in any plane normal to **k** because **k**•**r** is a constant for such planes:



$$\mathbf{k}\cdot\mathbf{r}_1 = kr_1$$

$$\mathbf{k}\cdot\mathbf{r}_2 = kr_1\sqrt{2}(\cos 45) = kr_1$$

k•**r** is indeed constant on wavefronts

THE RECIPROCAL LATTICE

The reciprocal lattice of a Bravais lattice is the set of all vectors **K** such that

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1$$

for all real lattice position vectors **R**.

Reciprocal lattice: The set of all wave vectors **K** that yield plane waves with the periodicity of a given Bravais lattice.

Direct lattice position vectors: $\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$

Reciprocal lattice vectors: $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$

where the primitive vectors of the reciprocal lattice are:

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_2 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

$$\mathbf{b}_3 = 2\pi \frac{\mathbf{a}_1 \times \mathbf{a}_2}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)}$$

and $\{n_i\}$ and $\{h,k,l\}$ are integers

$$e^{i\mathbf{K}\cdot\mathbf{R}} = 1$$ is satisfied when $\mathbf{K}\cdot\mathbf{R} = 2\pi n$, with n an integer

To verify that the $\{\mathbf{b}_i\}$ are primitive vectors of the reciprocal lattice, let's first show that $\mathbf{b}_i\cdot\mathbf{a}_j = 2\pi\delta_{ij}$

$$\mathbf{b}_1\cdot\mathbf{a}_1 = 2\pi\frac{\mathbf{a}_2\times\mathbf{a}_3}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}\cdot\mathbf{a}_1 = 2\pi\frac{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)} = 2\pi$$

$$\mathbf{b}_2\cdot\mathbf{a}_1 = 2\pi\frac{\mathbf{a}_3\times\mathbf{a}_1}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}\cdot\mathbf{a}_1 = 0$$

(since cross product of two vectors is perpendicular to both)

$$\mathbf{b}_3\cdot\mathbf{a}_1 = 2\pi\frac{\mathbf{a}_1\times\mathbf{a}_2}{\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3)}\cdot\mathbf{a}_1 = 0$$

Indeed, $\mathbf{b}_i\cdot\mathbf{a}_j = 2\pi\delta_{ij}$

so, $\mathbf{K}\cdot\mathbf{R} = (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)\cdot(n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3)$

$= 2\pi(hn_1 + kn_2 + ln_3) = 2\pi \times \text{integer}$

$\mathbf{K}$ is indeed a reciprocal lattice vector

WHAT IS A RECIPROCAL LATTICE VECTOR?

The reciprocal lattice is defined at the lattice generated from the set of all vectors **K** that satisfy

$$e^{i\mathbf{K}\bullet\mathbf{R}} = 1$$

for all direct lattice position vectors **R**.

What is K?

a wave vector of a plane wave that has the periodicity of the direct lattice

The direct lattice is periodic (invariant under translation by **R**)

$$\psi(\mathbf{r}+\mathbf{R}) = e^{i\mathbf{K}\bullet(\mathbf{r}+\mathbf{R})} = e^{i\mathbf{K}\bullet\mathbf{r}} = \psi(\mathbf{r})$$

$$\Downarrow$$

$$e^{i\mathbf{K}\bullet\mathbf{R}} = 1$$

Reciprocal lattice vectors = wave vectors of plane waves that are unity at all direct lattice sites

THE RECIPROCAL LATTICE

- the reciprocal lattice is defined in terms of a Bravais lattice
- the reciprocal lattice is itself one of the 14 Bravais lattices
- the reciprocal of the reciprocal lattice is the original direct lattice

e.g., simple cubic direct lattice

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \qquad \mathbf{a}_2 = a\hat{\mathbf{y}} \qquad \mathbf{a}_3 = a\hat{\mathbf{z}}$$

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot \left(\mathbf{a}_2 \times \mathbf{a}_3\right)} = 2\pi \frac{a^2}{a^3}\hat{\mathbf{x}} = \frac{2\pi}{a}\hat{\mathbf{x}}$$

$$\mathbf{b}_2 = \frac{2\pi}{a}\hat{\mathbf{y}} \qquad \mathbf{b}_3 = \frac{2\pi}{a}\hat{\mathbf{z}}$$

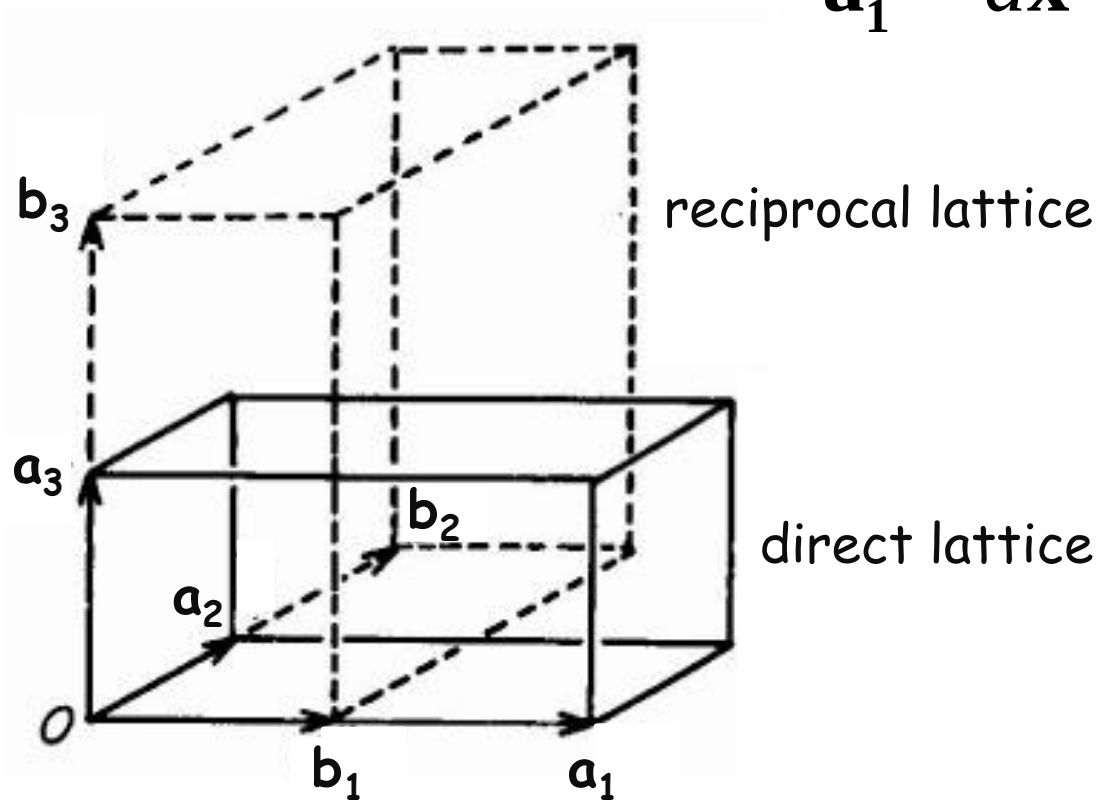
→ simple cubic reciprocal lattice with lattice constant $2\pi/a$

→ b_1 parallel to a_1, etc.

Crystals with orthogonal axes (cubic, tetragonal, orthorhombic)

b_1, b_2, b_3 are parallel to a_1, a_2, a_3, respectively.

$$\mathbf{a}_1 = a\hat{\mathbf{x}} \quad \mathbf{a}_2 = b\hat{\mathbf{y}} \quad \mathbf{a}_3 = c\hat{\mathbf{z}}$$

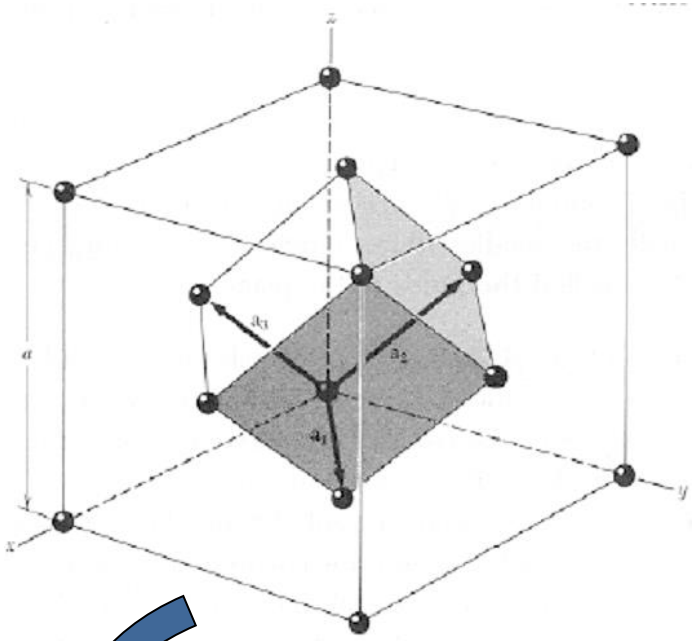


$$\mathbf{b}_1 = \frac{2\pi}{a}\hat{\mathbf{x}}$$

$$\mathbf{b}_2 = \frac{2\pi}{b}\hat{\mathbf{y}}$$

$$\mathbf{b}_3 = \frac{2\pi}{c}\hat{\mathbf{z}}$$

RECIPROCAL LATTICE OF FCC IS BCC



FCC primitive vectors:

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}}),$$

$$\mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}),$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}}).$$

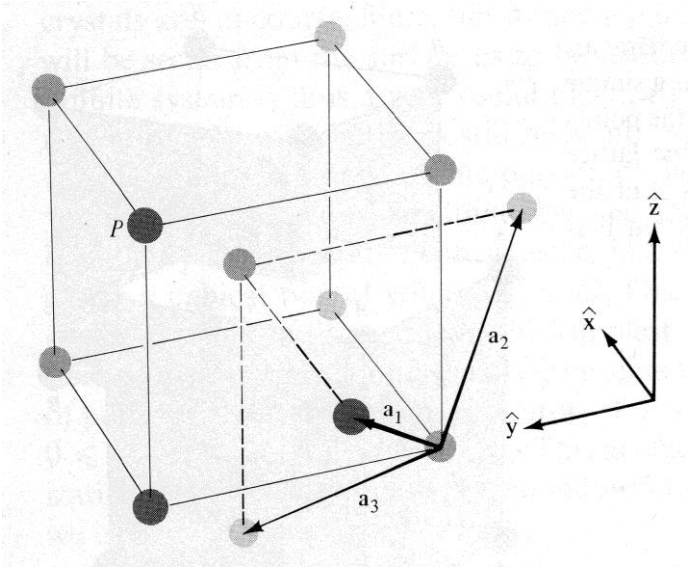
Note: not orthogonal

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} = 2\pi \frac{\frac{a^2}{4}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})}{\frac{a^3}{8}(2)} = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}})$$

$$\mathbf{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}) \qquad \mathbf{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

→ BCC reciprocal lattice with lattice constant $4\pi/a$

RECIPROCAL LATTICE OF BCC IS FCC



BCC primitive vectors (not orthogonal):

$$\mathbf{a}_1 = \frac{a}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}} - \hat{\mathbf{x}}), \quad \mathbf{a}_2 = \frac{a}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}),$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}}).$$

$$\mathbf{b}_1 = 2\pi \frac{\mathbf{a}_2 \times \mathbf{a}_3}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} = 2\pi \frac{\frac{a^2}{4}(2\hat{\mathbf{y}} + 2\hat{\mathbf{z}})}{\frac{a^3}{8}(4)} = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{y}} + \hat{\mathbf{z}})$$

$$\mathbf{b}_2 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{z}} + \hat{\mathbf{x}}) \qquad \mathbf{b}_3 = \frac{4\pi}{a}\frac{1}{2}(\hat{\mathbf{x}} + \hat{\mathbf{y}})$$

→ FCC reciprocal lattice with lattice constant $4\pi/a$

RECIPROCAL LATTICES

- simple orthorhombic → simple orthorhombic
- FCC → BCC
- BCC → FCC
- simple hexagonal → simple hexagonal (rotated)

The reciprocal lattice

Similar: **hexagonal/trigonal**, i.e. $\gamma^* = 180^\circ - \gamma$

Case studies:

II) **Monoclinic crystal system**:

Orientations:

$\vec{a}^* \perp$ (1, 0, 0), the b,c-plane. => $\vec{a}^*$ **NOT** $\parallel \vec{a}$

$\vec{b}^* \perp$ (0, 1, 0), the a,c-plane. => $\vec{b}^* \parallel \vec{b}$

$\vec{c}^* \perp$ (0, 0, 1), the a,b-plane. => $\vec{c}^*$ **NOT** $\parallel \vec{c}$

Lengths: generally $a^* = 1/d_{100}$, $b^* = 1/d_{010}$, $c^* = 1/d_{001}$

here: $d_{100} = a\sin\beta$, $d_{010} = b$, $d_{001} = c\sin\beta$;

thus: $a^* = 1/(a\sin\beta)$, $b^* = 1/b$, $c^* = 1/(c\sin\beta)$,

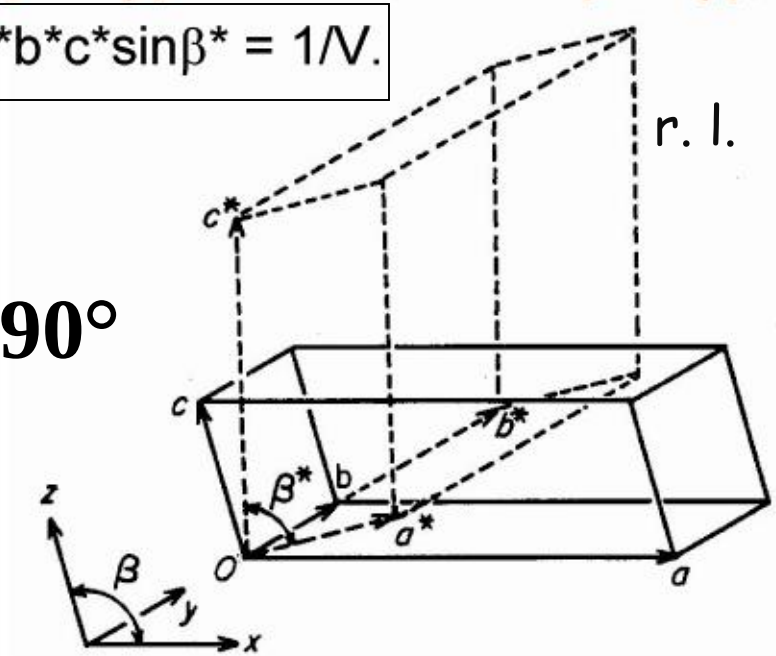
$V^* = a^*b^*c^*\sin\beta^* = 1/V.$

$\vec{a}^* = b_1$

$\vec{b}^* = b_2$

$\vec{c}^* = b_3$

$\beta \neq 90^\circ$



$\alpha^* = \alpha = 90^\circ$

$\beta^* = 180^\circ - \beta$

$\gamma^* = \gamma = 90^\circ$

The reciprocal lattice

Case studies:

III) **Triclinic crystal system**:

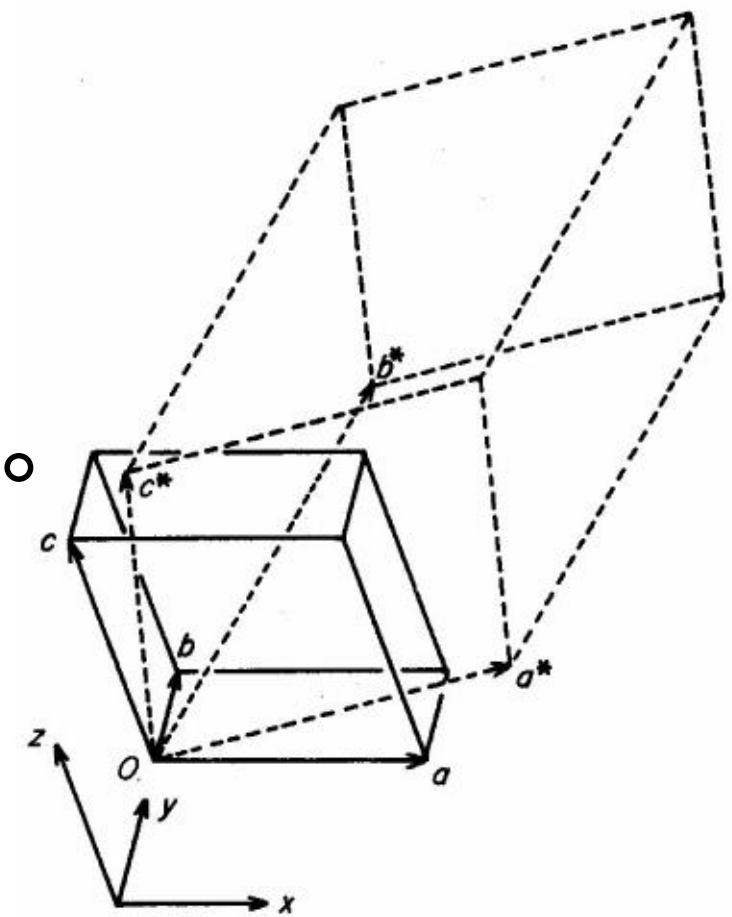
Orientations:

$\vec{a}^* \perp$ (1, 0, 0), the b,c-plane. => $\vec{a}^*$ **NOT** $\parallel$ $\vec{a}$

$\vec{b}^* \perp$ (0, 1, 0), the a,c-plane. => $\vec{b}^*$ **NOT** $\parallel$ $\vec{b}$

$\vec{c}^* \perp$ (0, 0, 1), the a,b-plane. => $\vec{c}^*$ **NOT** $\parallel$ $\vec{c}$

$\alpha,\beta,\gamma \neq 90°$



Lengths/angles:
quite complex;
see next slide.

The reciprocal lattice

Case studies:

III) **Triclinic crystal system**:

Formulas correct for all systems!
But often much simpler, when
e.g. $\alpha = 90^o \Rightarrow \sin\alpha = 1, \cos\alpha = 0$

$$a^* = \frac{bc \sin \alpha}{V} \qquad a = \frac{b^* c^* \sin \alpha^*}{V^*}$$

$$b^* = \frac{ac \sin \beta}{V} \qquad b = \frac{a^* c^* \sin \beta^*}{V^*}$$

$$c^* = \frac{ab \sin \gamma}{V} \qquad c = \frac{a^* b^* \sin \gamma^*}{V^*}$$

Note that these formulas are missing a factor of 2π

$$V = \frac{1}{V^*} = abc\sqrt{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}$$

$$V^* = \frac{1}{V} = a^* b^* c^* \sqrt{1 - \cos^2 \alpha^* - \cos^2 \beta^* - \cos^2 \gamma^* + 2 \cos \alpha^* \cos \beta^* \cos \gamma^*}$$

$$\cos \alpha^* = \frac{\cos \beta \cos \gamma - \cos \alpha}{\sin \beta \sin \gamma} \qquad \cos \alpha = \frac{\cos \beta^* \cos \gamma^* - \cos \alpha^*}{\sin \beta^* \sin \gamma^*}$$

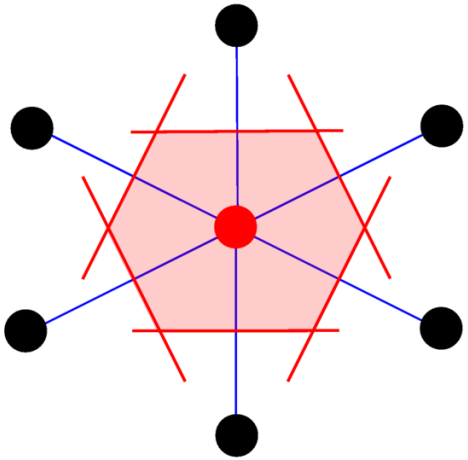
$$\cos \beta^* = \frac{\cos \alpha \cos \gamma - \cos \beta}{\sin \alpha \sin \gamma} \qquad \cos \beta = \frac{\cos \alpha^* \cos \gamma^* - \cos \beta^*}{\sin \alpha^* \sin \gamma^*}$$

$$\cos \gamma^* = \frac{\cos \alpha \cos \beta - \cos \gamma}{\sin \alpha \sin \beta} \qquad \cos \gamma = \frac{\cos \alpha^* \cos \beta^* - \cos \gamma^*}{\sin \alpha^* \sin \beta^*}$$

FIRST BRILLOUIN ZONES

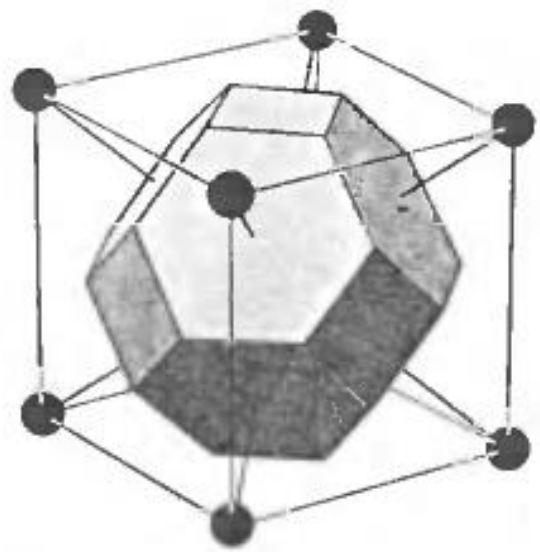
The Wigner-Seitz cell of the reciprocal lattice is called the first Brillouin zone (FBZ).

Wigner-Seitz cell: primitive cell with lattice point at its center



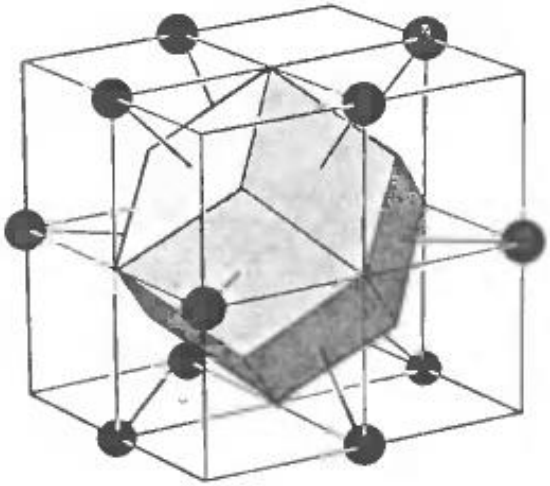
enclosed region is W-S cell for 2D hexagonal lattice

d.l. FCC
r.l. BCC
1st Brillouin zone:



truncated octahedron

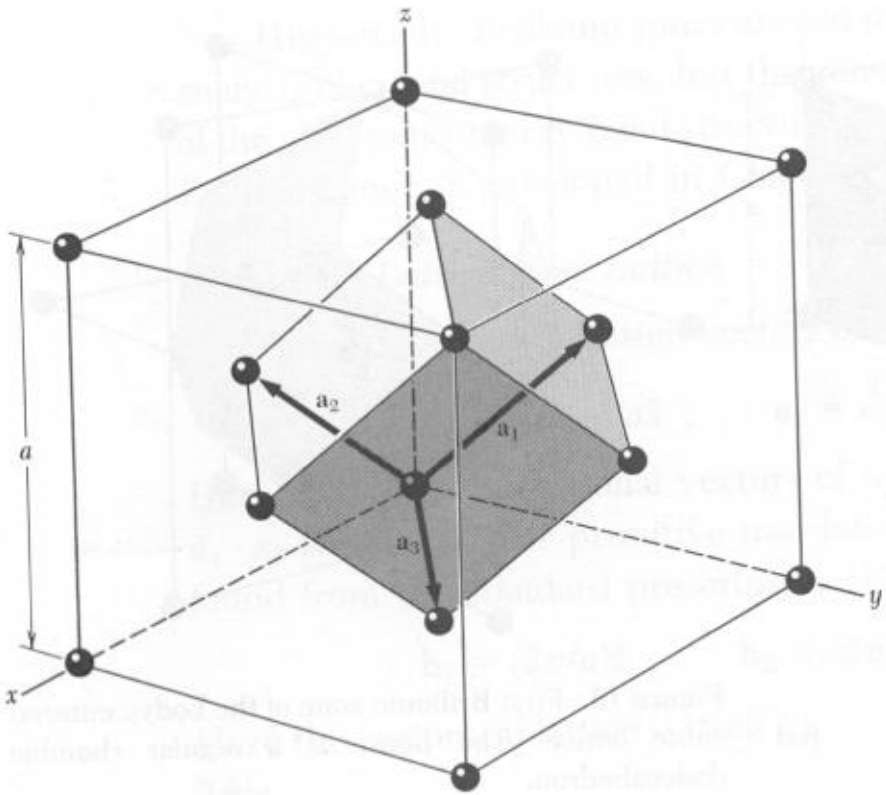
d.l. BCC
r.l. FCC
1st Brillouin zone:

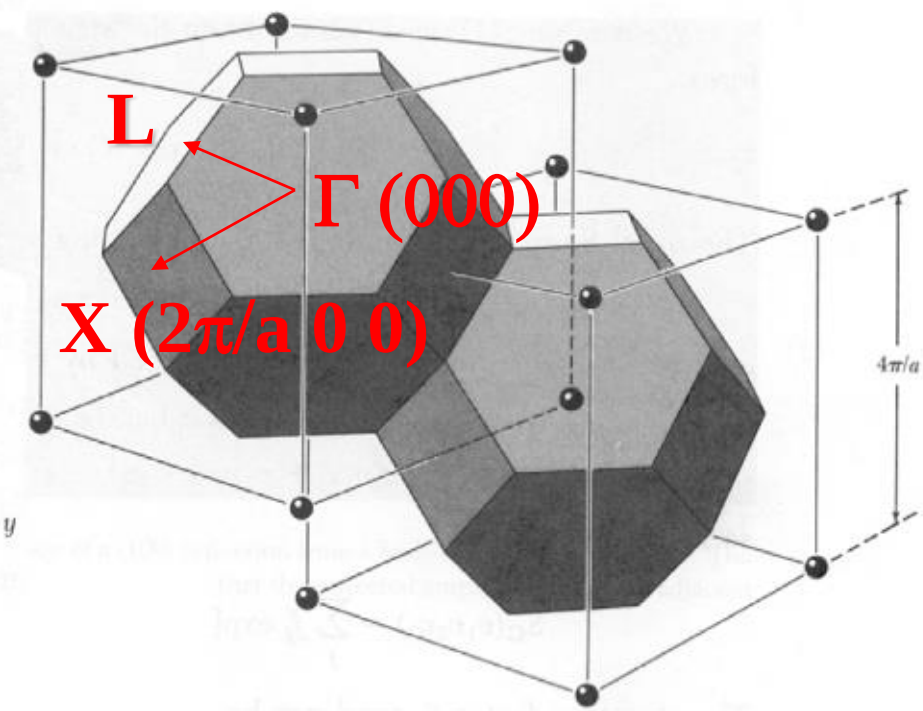


rhombic dodecahedron

Examples for Brillouin zones

face-centered cubic

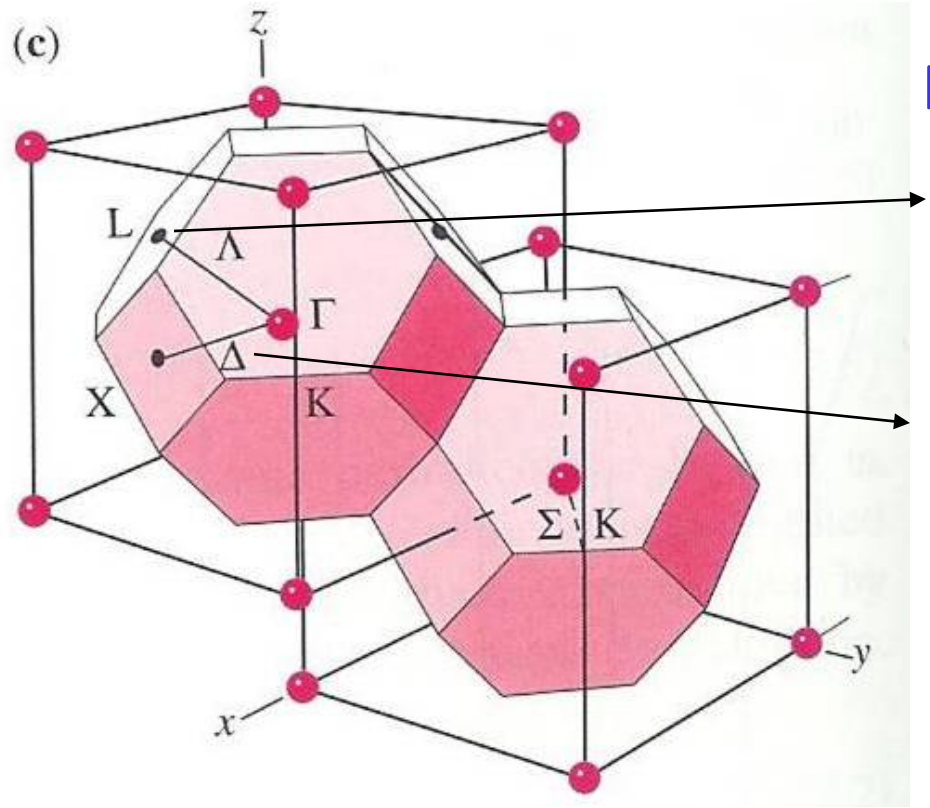




d.l.: centered and primitive cell

r.l.: 1st Brillouin zone

Brillouin Zone of Diamond and Zincblende Structure (FCC Lattice)



Notation:

- Zone Edge or surface : Roman alphabet
- Interior of Zone: Greek alphabet
- Center of Zone or origin: Γ

Notation:

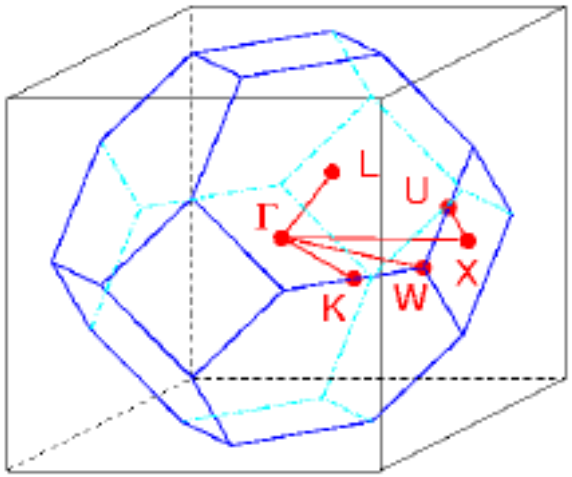
Δ<=>[100] direction

X<=>BZ edge along [100] direction

Λ<=>[111] direction

L<=>BZ edge along [111] direction

The first Brillouin zone



$4\pi/a_0$

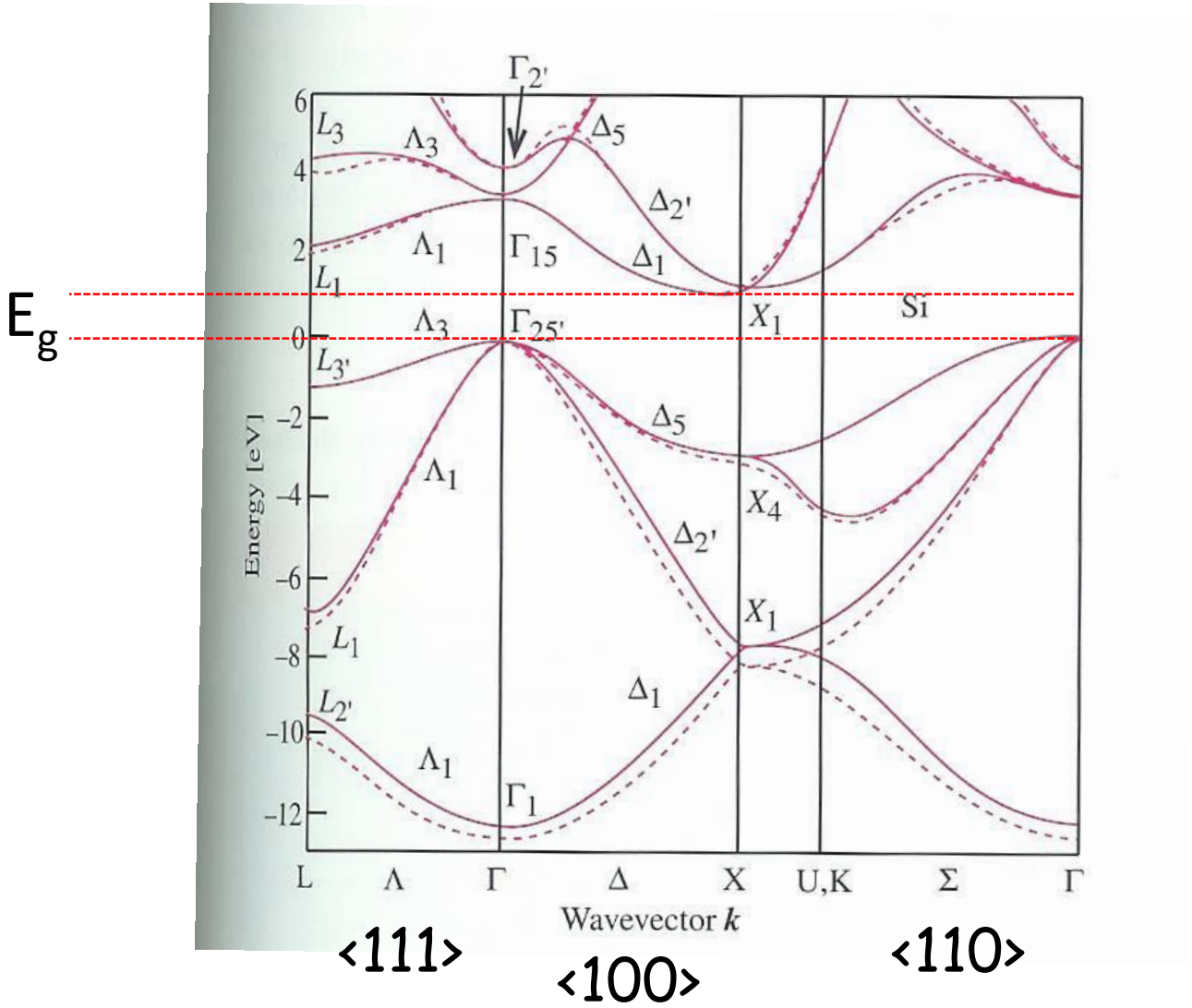
High symmetry points and directions

$\Gamma = 2\pi/a_0[0, 0, 0]$
$X = 2\pi/a_0[1, 0, 0]$
$L = 2\pi/a_0[\frac{1}{2}, \frac{1}{2}, \frac{1}{2}]$
$U = 2\pi/a_0[1, \frac{1}{4}, \frac{1}{4}]$
$W = 2\pi/a_0[1, \frac{1}{2}, 0]$
$K = 2\pi/a_0[\frac{3}{4}, \frac{3}{4}, 0]$

$\Delta = 2\pi/a_0[\xi, 0, 0]$,	$0 \le \xi \le 1$
$\Lambda = 2\pi/a_0[\xi, \xi, \xi]$,	$0 \le \xi \le \frac{1}{2}$
$\Sigma = 2\pi/a_0[\xi, \xi, 0]$,	$0 \le \xi \le \frac{3}{4}$
$Z = 2\pi/a_0[1, \xi, 0]$,	$0 \le \xi \le \frac{1}{2}$
$Q = 2\pi/a_0[1-\xi, \frac{1}{2}, \xi]$,	$0 \le \xi \le \frac{1}{2}$
$S = 2\pi/a_0[1, \xi, \xi]$,	$0 \le \xi \le \frac{1}{4}$

Electronic band structure is calculated within the 1st Brilluoin zone

Electronic Band Structure of Si



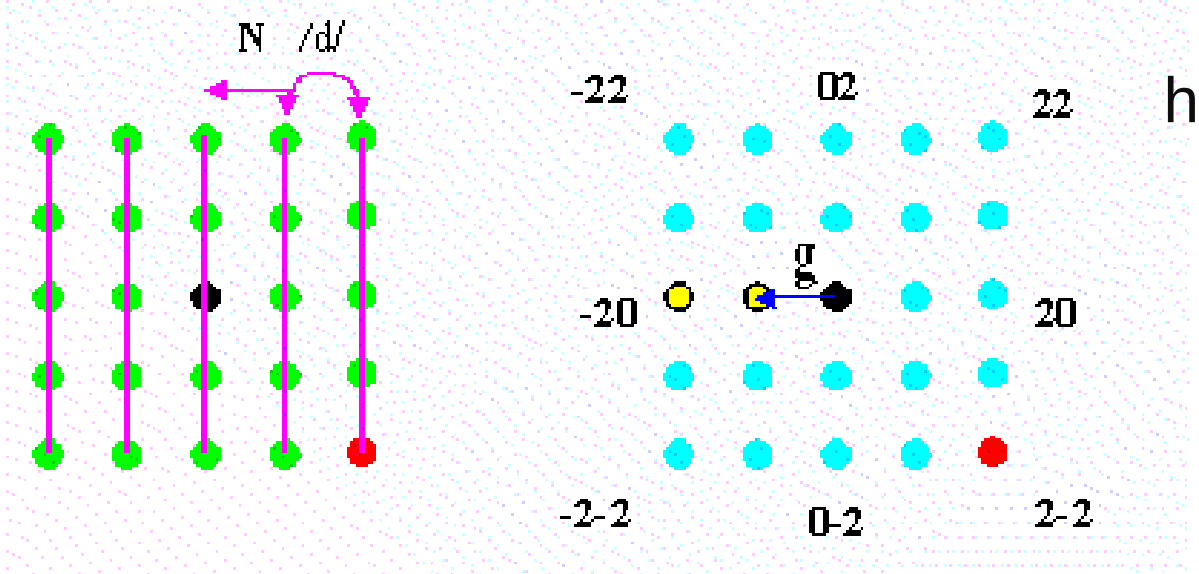
K and LATTICE PLANES

Theorem:

For any family of lattice planes separated by distance d, there are reciprocal lattice vectors perpendicular to the planes, the shortest of which has a length of $2\pi/d$.

Conversely, any reciprocal lattice vector **K** has a family of real-space planes normal to it, separated by d.

Real Lattice $\boxed{\mathbf{K} = 2\pi n/\mathbf{d}}$ **Reciprocal Lattice**



here, **g** = **K**

hk in 2D
hkl in 3D

MILLER INDICES OF LATTICE PLANES

Orientation of a plane is determined by its normal vector

It is natural to pick the shortest perpendicular reciprocal lattice vector to represent the normal

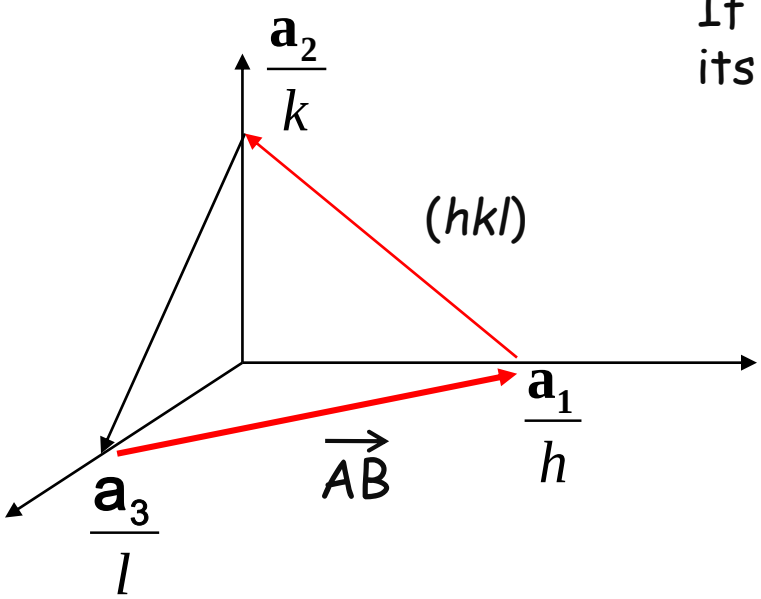
Miller indices: coordinates of this reciprocal lattice vector

i.e., A plane with Miller indices hkl is normal to the reciprocal lattice vector $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$

→ Definition #2: directions in *k*-space

(Definition #1 was inverse intercepts in the real lattice)

Proof that $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is normal to (hkl)



If $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is normal to the plane at left, its dot product with any in-plane vector is zero.

Consider vector AB that lies in the plane.

By vector addition, $\frac{\mathbf{a}_1}{h} - \frac{\mathbf{a}_3}{l} = \mathbf{AB}$

The dot product,

$$\mathbf{AB} \bullet \mathbf{K} = \left(\frac{\mathbf{a}_1}{h} - \frac{\mathbf{a}_3}{l}\right) \bullet (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)$$

$$= 2\pi - 2\pi = 0 \qquad \text{etc.}$$

So the reciprocal vector formed by using the Miller indices of a plane as its components forms a vector in space that is normal to the Miller plane.

Furthermore, the length of the shortest vector **K** is equal to $2\pi/d_{hkl}$.

In the figure above, the spacing between the planes is the projection of $\frac{\mathbf{a}_1}{h}$ on $\frac{\mathbf{K}}{|\mathbf{K}|}$:

$$d_{hkl} = \frac{\mathbf{a}_1}{h} \bullet \frac{\mathbf{K}}{|\mathbf{K}|} = \frac{h}{h}\frac{2\pi}{|\mathbf{K}|} = \frac{2\pi}{|\mathbf{K}|} \quad \rightarrow \quad \boxed{|\mathbf{K}| = \frac{2\pi}{d_{hkl}} = K_0}$$

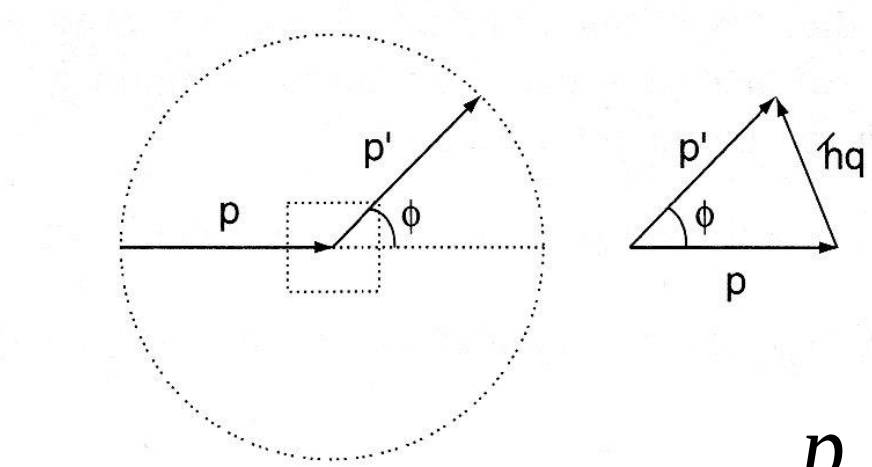
REMINDER on ELASTIC SCATTERING

scattering vector

Momentum conservation: $\mathbf{p}' - \mathbf{p} = \hbar \mathbf{q}$

elastic scattering: $|\mathbf{p}'| = |\mathbf{p}| = p$

Elastic scattering geometry



$$q = 2\frac{p}{\hbar}\sin\frac{\phi}{2}$$

von LAUE DESCRIPTION OF DIFFRACTION

- reciprocal space description, equivalent to Bragg description but more powerful for crystallography & solid state physics

Equivalence to Bragg picture:

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

$$2k\sin\theta = n\frac{2\pi}{d} = nK_0 = K$$

since scattering is elastic and $\mathbf{p} = \hbar\mathbf{k}$,

$$q = 2\frac{p}{\hbar}\sin\frac{\phi}{2} = 2k\sin\theta = K$$

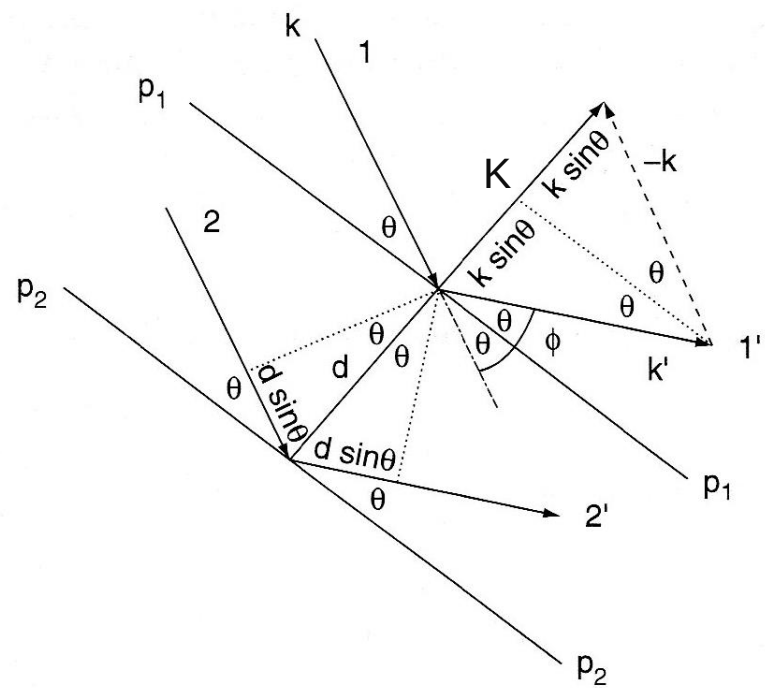


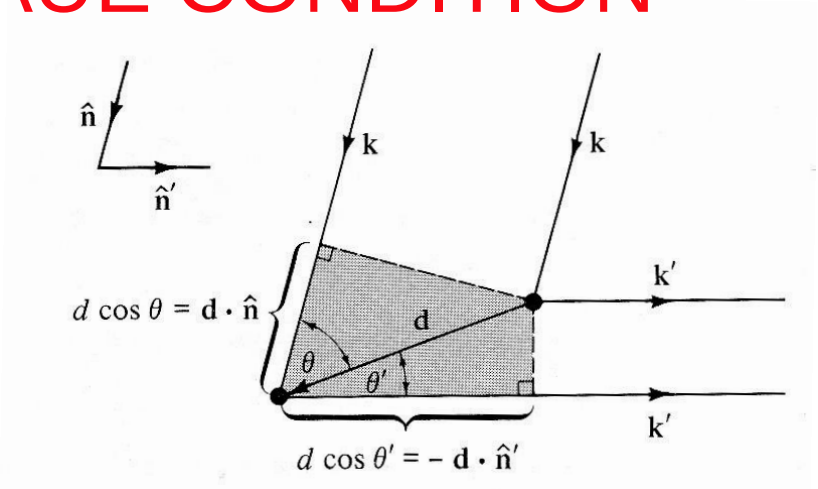
Figure 3.6. Diffraction from two lattice planes.

$$q = K$$

von Laue: "Constructive interference occurs when scattering vector is a reciprocal lattice vector."

DERIVATION of von LAUE CONDITION

Consider two scatterers:



Path difference between the rays: $d\cos\theta + d\cos\theta' = \mathbf{d}\bullet(\hat{\mathbf{n}} - \hat{\mathbf{n}}')$

Condition for constructive interference: $\mathbf{d}\bullet(\hat{\mathbf{n}} - \hat{\mathbf{n}}') = n\lambda$

Multiply through by $2\pi/\lambda$: $\mathbf{d}\bullet(\mathbf{k} - \mathbf{k}') = 2\pi n$

For the Bravais lattice of scatterers: $\mathbf{R}\bullet(\mathbf{k} - \mathbf{k}') = 2\pi n$

Multiply by i and raise to e: $\boxed{e^{i(\mathbf{k}'-\mathbf{k})\bullet\mathbf{R}} = e^{i2\pi n} = 1}$

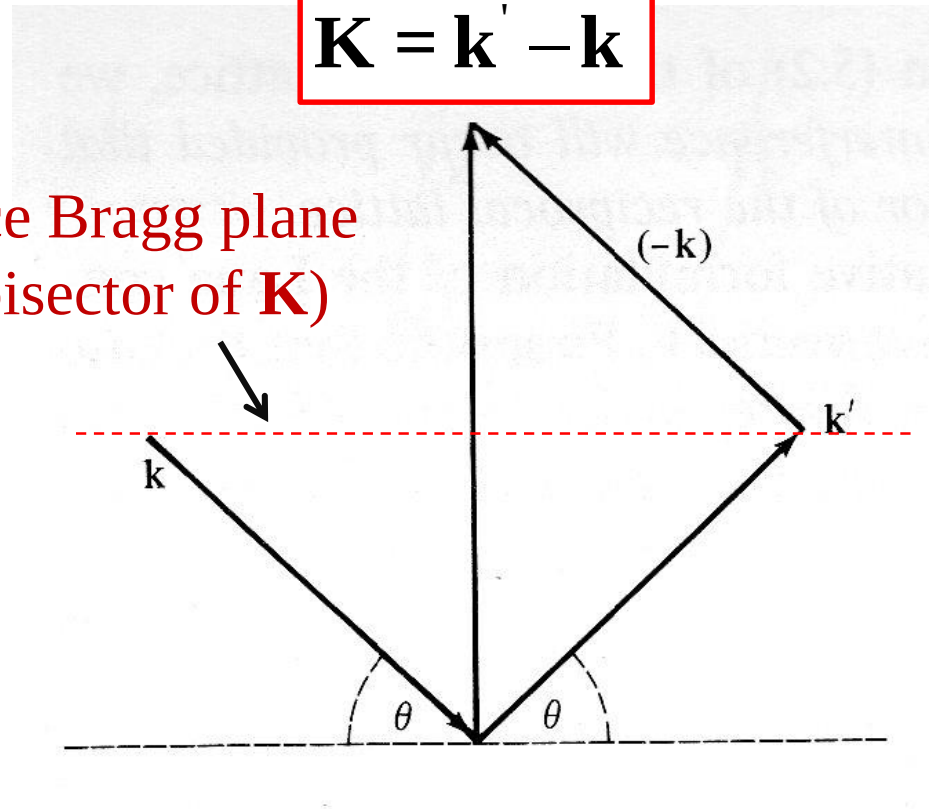
So, $\mathbf{k}' - \mathbf{k} = \mathbf{K}$

Diffraction occurs when the change in wave vector, **k'-k**, is a vector of the reciprocal lattice.

$$\mathbf{K} = \mathbf{k}' - \mathbf{k}$$

Laue condition

k-space Bragg plane
(per. bisector of **K**)



Alternatively,

$$\mathbf{k}' \cdot \mathbf{K} = K^2/2$$

Reciprocal lattice vectors are perpendicular to direct lattice planes

Bragg: diffraction when path length difference = $n\lambda$

Laue: diffraction when scattering vector = recip. vector

equivalently, when tip of wave vector lies on a *k*-space Bragg plane

EWALD ("e-val") SPHERE

A geometrical construction that provides the relationship between the orientation of a crystal and the direction of the beams diffracted by it.

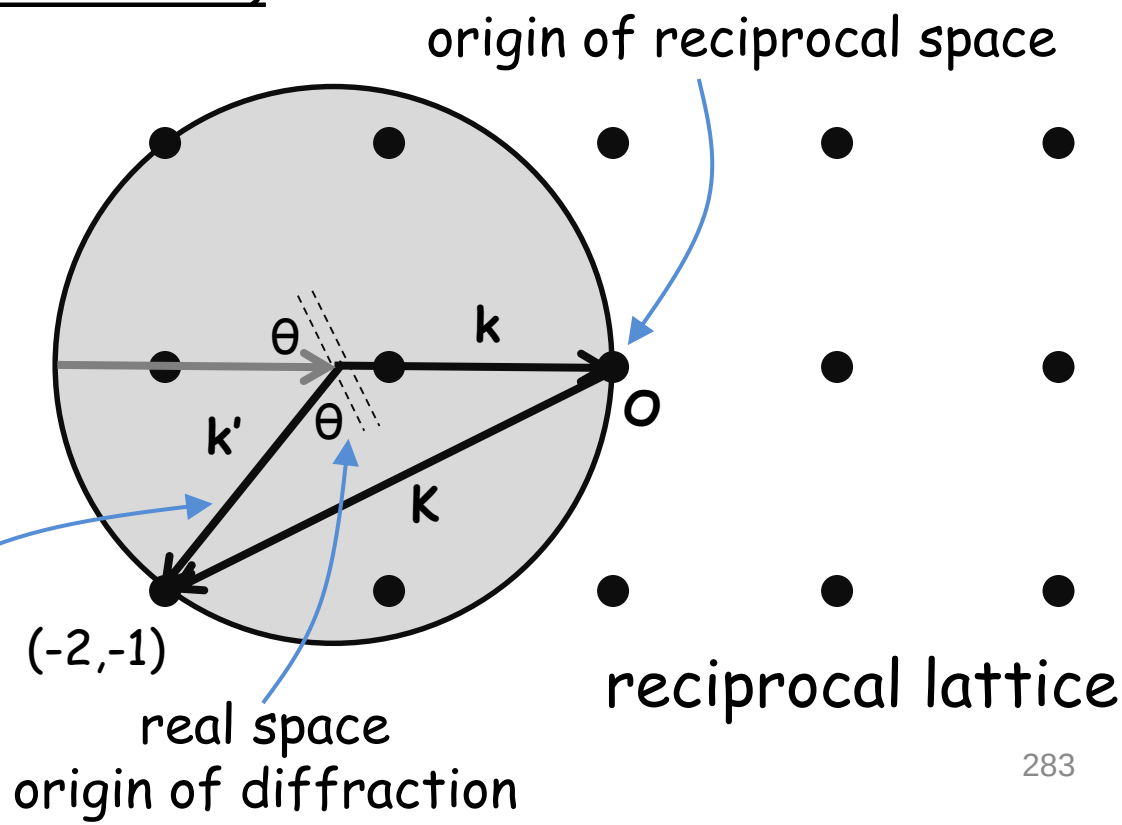
A sphere of radius k centered on the base of the incident wave vector **k** drawn to the origin O (hkl = 000) of the reciprocal lattice.

<u>Projected Ewald sphere (Ewald circle)</u>

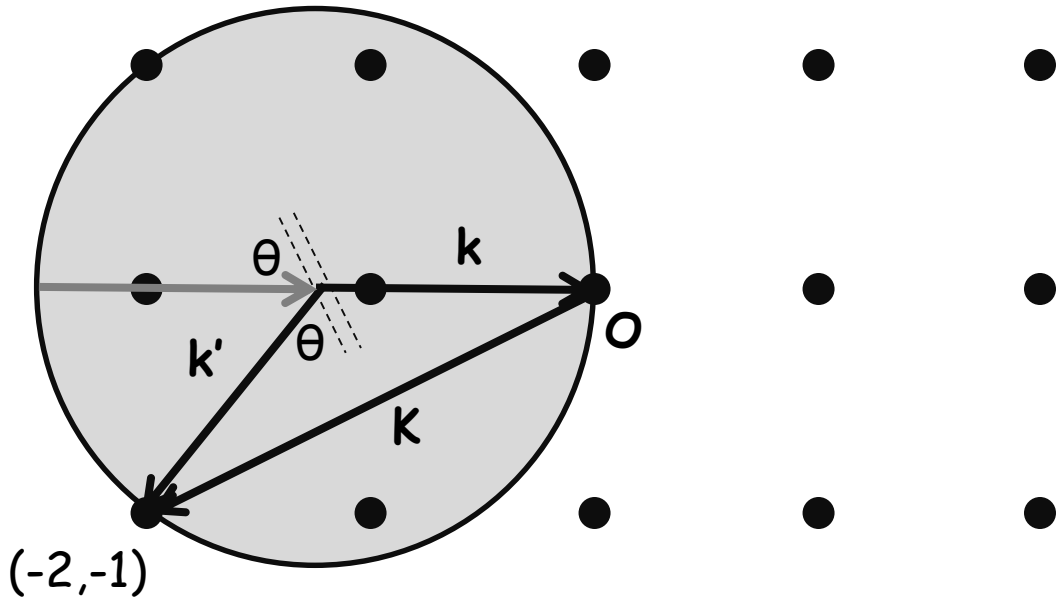
radius = k

Laue condition:

$$\mathbf{K} = \mathbf{k}' - \mathbf{k}$$

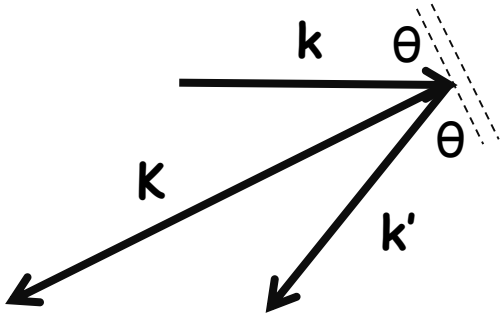


Diffraction occurs only when a reciprocal lattice point lies on the surface of the Ewald sphere.



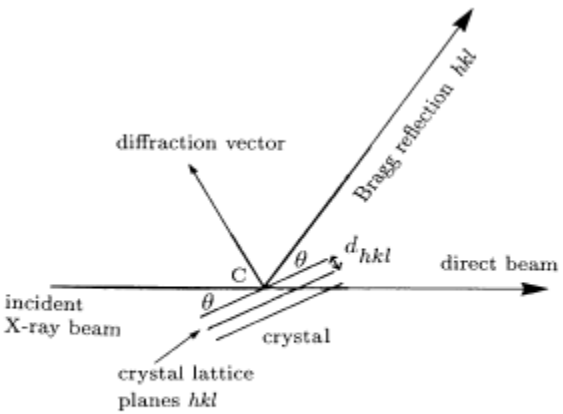
Laue condition:

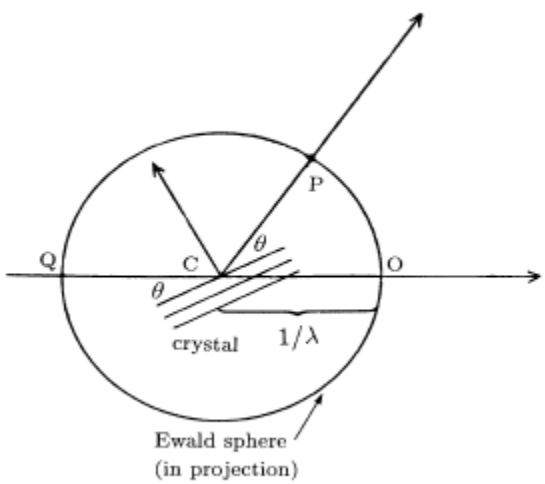
$$\mathbf{K} = \mathbf{k}' - \mathbf{k}$$

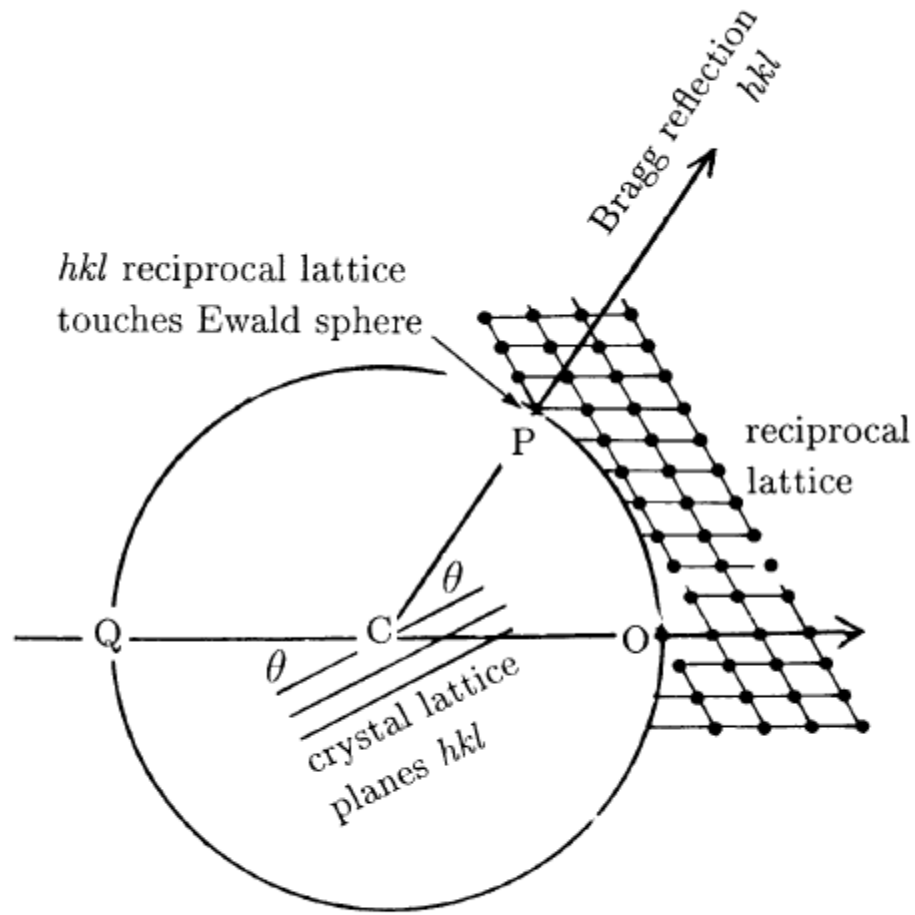


$$|\mathbf{K}| = 2\pi / d_{210}$$

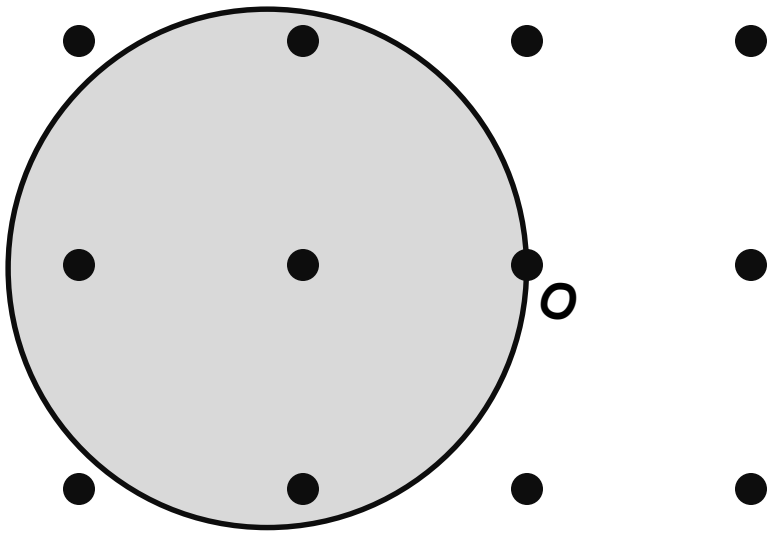
In this case, *hkl* = -2,-1,0 so diffraction occurs from the $(\bar{2}\bar{1}0)$ planes and the diffracted beam moves off along **k'**.


diffraction vector
Bragg reflection hkl
C
θ
d_{hkl}
direct beam
incident
X-ray beam
θ
crystal
crystal lattice
planes hkl


P
Q
C
θ
O
θ
crystal
1/λ
Ewald sphere
(in projection)


Bragg reflection
hkl
hkl reciprocal lattice
touches Ewald sphere
P
reciprocal
lattice
θ
Q
C
O
θ
crystal lattice
planes hkl

In general, a sphere in *k*-space with the origin on its surface will have no other reciprocal lattice points on its surface:



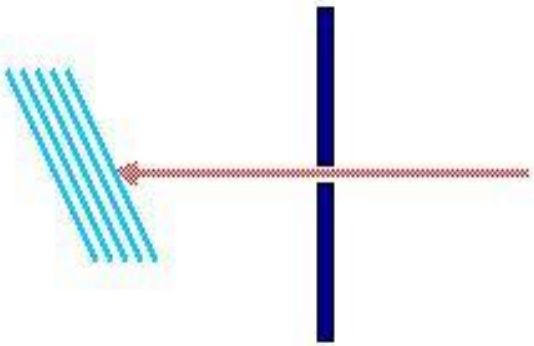
No Bragg peaks for a general incident X-ray!

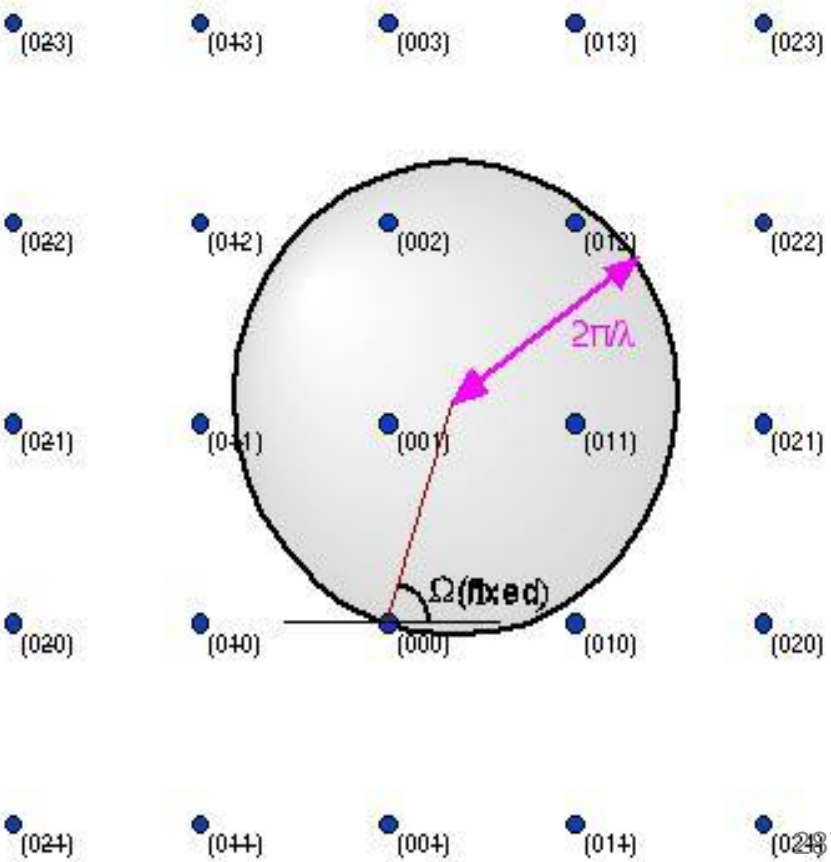
In order to record diffraction patterns, we must either:

- use polychromatic radiation (vary the sphere size) → Laue method
- rotate the crystal (and thus the reciprocal lattice) → rot. cryst. method
- use a powder sample (equivalent to rotating reciprocal space about all angles) → powder method

Monochromatic source + single crystal

- **Only one crystal orientation**
  - Fixed Ω
  - Only points on surface of fixed sphere diffract
  - Almost zero probability of diffraction

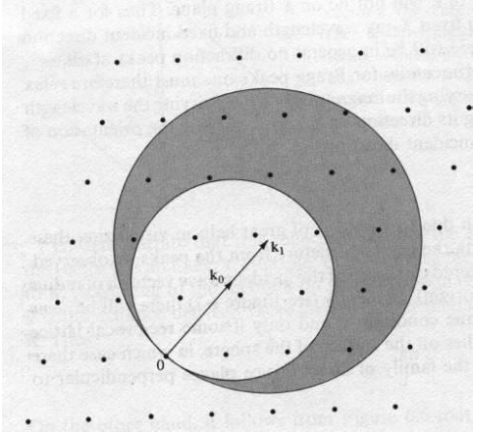


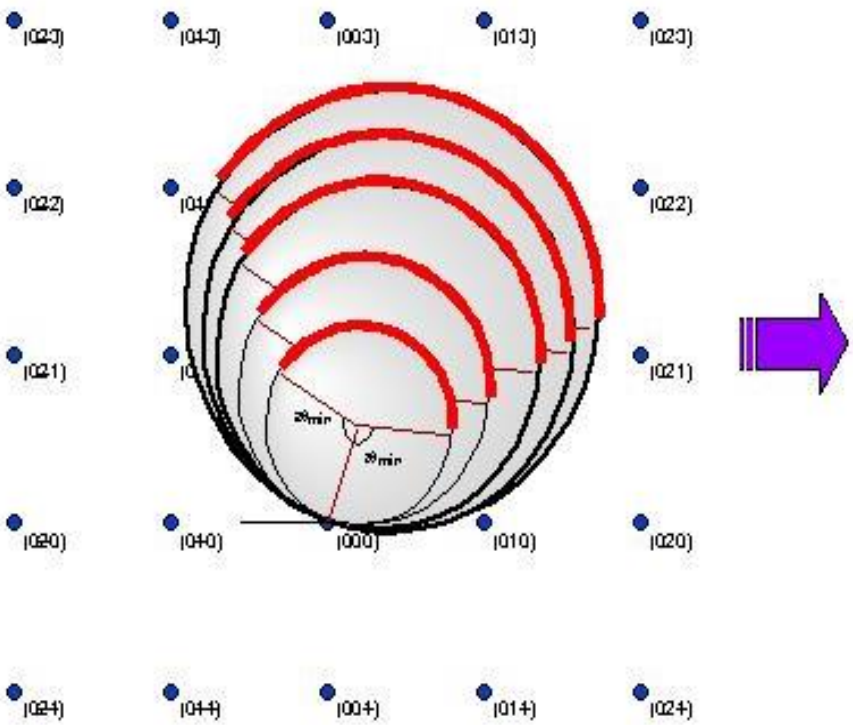


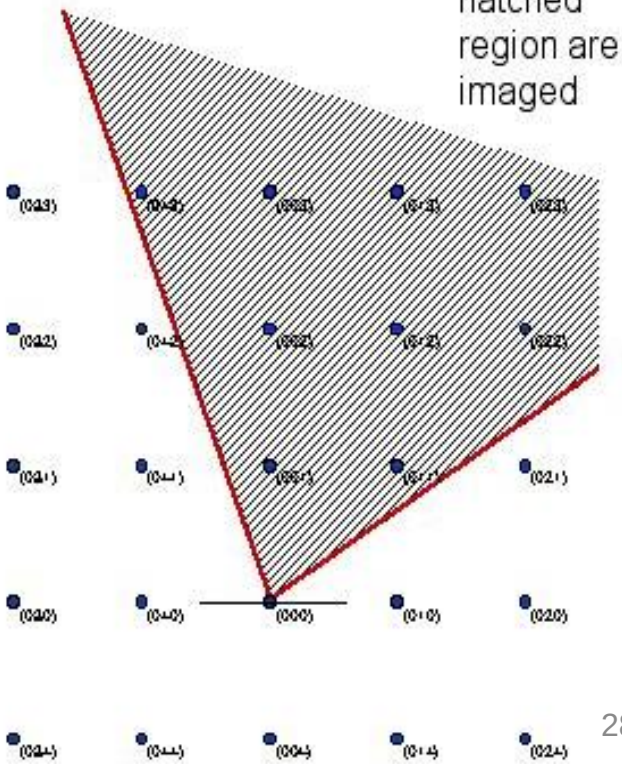
LAUE METHOD

"White" source + single-xtal sample

- fixed crystal & angle, many wavelengths
  - **All possible wavelengths (ideally)**
    - Sample has only one value of Ω
    - Points swept out by surface of variable size sphere diffract
    - Finite camera angle restricts diffraction to certain portion of sphere
    - Interpretation of photographs difficult



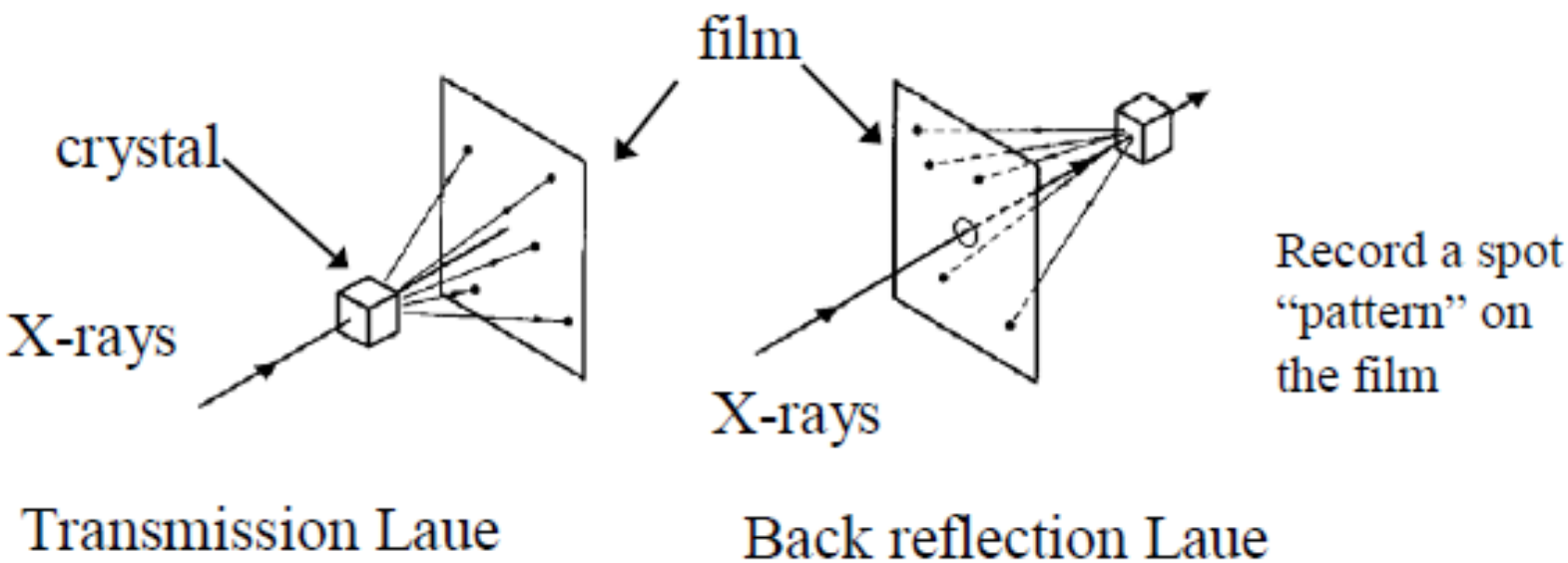




Points in hatched region are imaged

As used in Laue's original experiment

- Use the "white" Bremsstrahlung radiation from the tube so that many different wavelengths are incident on the sample
  - » Many reflections will simultaneously satisfy Bragg's law without rotating the crystal

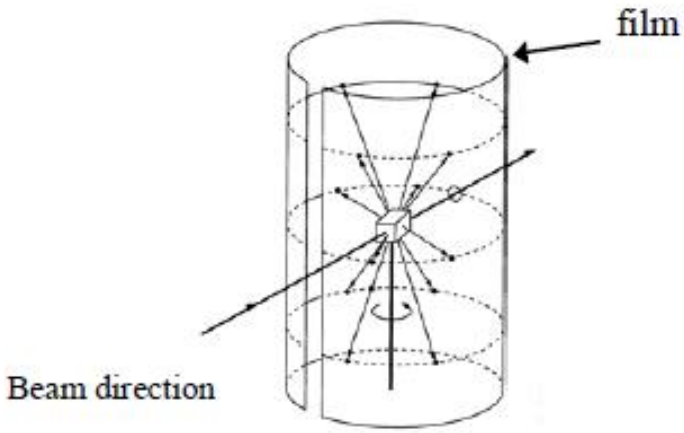


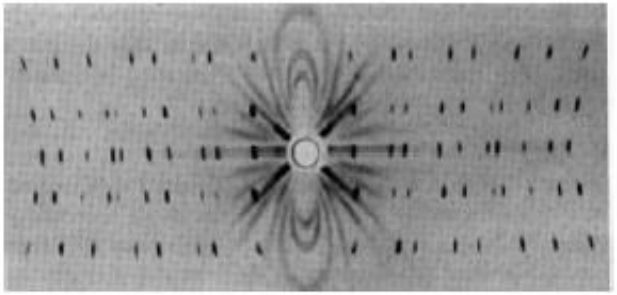
The Laue method is mainly used to determine the orientation of large single crystals.

When the zone axis lies along the symmetry axis of the crystal, the pattern of Bragg spots will have the same symmetry.

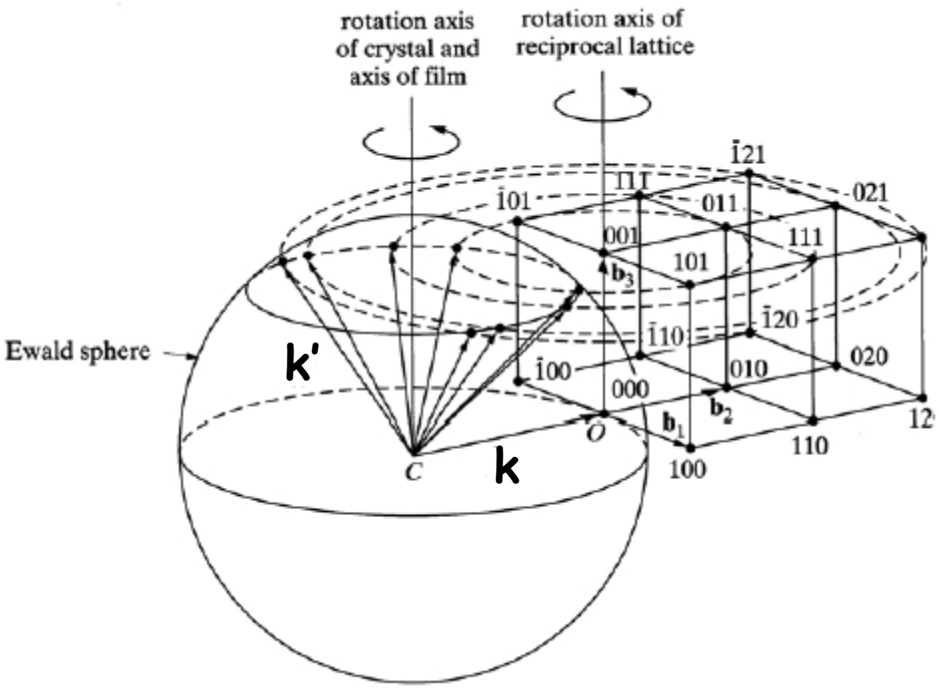
ROTATING CRYSTAL METHOD

- single wavelength
- aligned crystal is rotated about one axis to rotate reciprocal lattice
- produces spots on layer lines



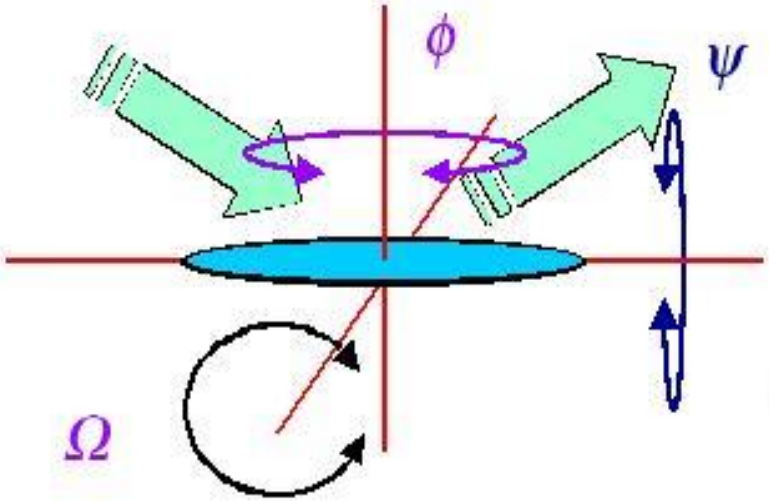


Rotation photograph of quart
showing spots on layer lines

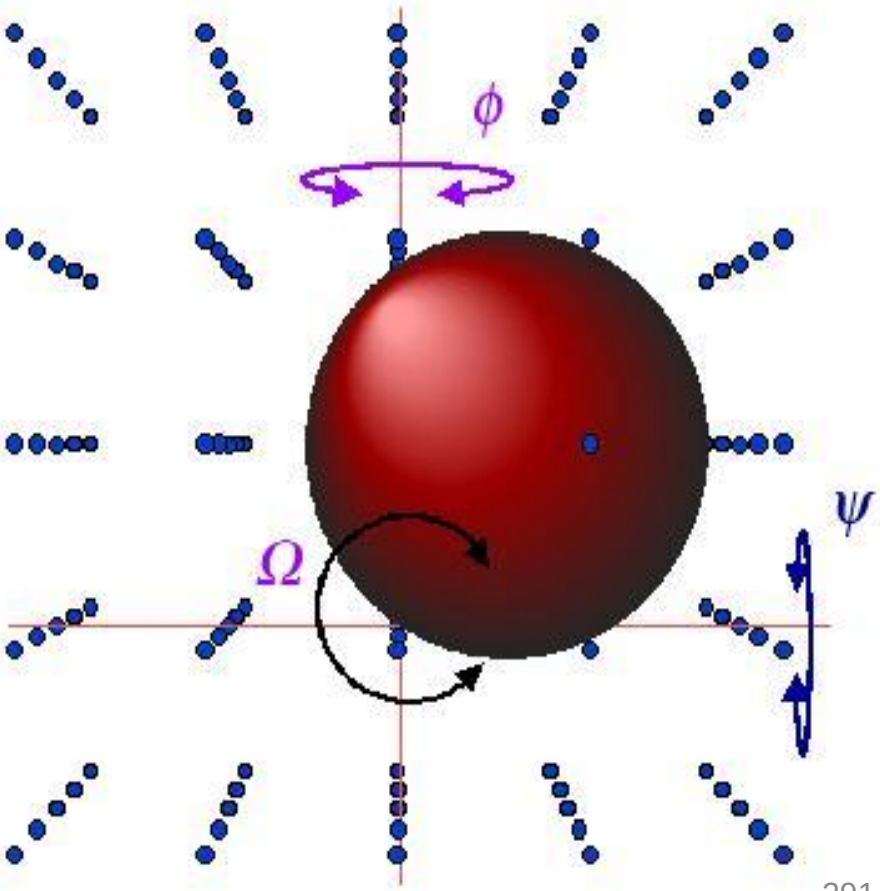


http://escher.epfl.ch/x-ray/diff.mpeg

Other rotation axes

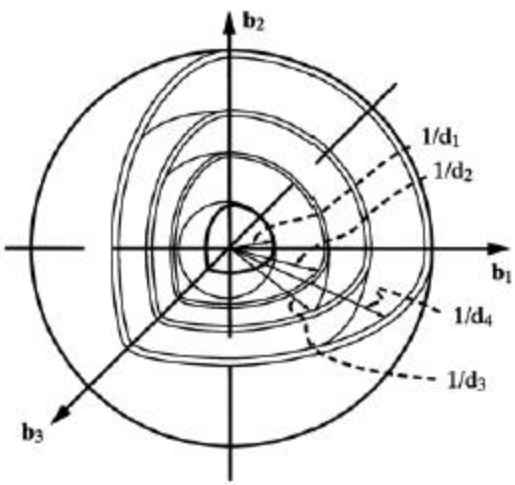


- Simplest scanning geometry has:
  - $\Omega = 2\theta/2$
  - $\psi = 0$
  - ϕ irrelevant
- Applicable only to powder samples
- More complex scanning systems required for aligned materials

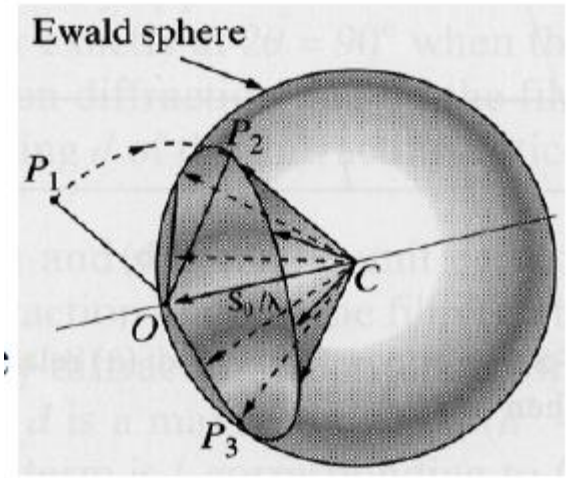


POWDER (DEBYE-SCHERRER) METHOD

- single wavelength
- fixed powder sample
- equivalent to rotating the reciprocal lattice through all possible angles about the origin



every point in reciprocal space traces out a shell of radius K



Each shell with radius $K < 2k$ intersects the Ewald sphere to form a circle.

All the diffracted beams from a powder lie on the surface of cones

PEAK INTENSITIES

Peak intensities depend on (in large part):
1) intensity scattered by individual atoms (form factors)
2) the resultant wave from atoms in unit cell (structure factor)

In many cases, the intensity from certain planes (*hkl*) is zero.

Possible reasons:
- symmetry of crystal causes complete cancellation of beam
  "systematic absences"
- happenstance

Other factors that affect intensity:
- scattering angle
- multiplicities
- temperature factor
- absorption factor
- preferred orientation

MONOATOMIC BASES

up to now we have considered diffraction only from Bravais lattices with single atom bases (i.e., atoms only at the lattice points **R**).

We found the diffraction condition: $e^{i(\mathbf{k}'-\mathbf{k})\bullet\mathbf{R}} = e^{i2\pi n} = 1$

which is the same as: $e^{i\mathbf{K}\bullet\mathbf{R}} = 1$

The scattering amplitude $F_{\mathbf{K}}$ is the sum over the lattice sites:

$$F_{\mathbf{K}} = \sum_{\mathbf{R}} f_{\mathbf{R}}(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{R}}$$

where $f_{\mathbf{R}}(\mathbf{K})$ is the "atomic form factor" for a given atom (disc. later).

The scattered intensity is proportional to the absolute square of the amplitude:

$$I_{\mathbf{K}} \propto I_0 \left| F_{\mathbf{K}} \right|^2$$

…this is what is actually measured in an experiment.

n-ATOM BASES

Crystals with n atoms in each primitive cell must be further analyzed into a set of scatterers at positions $\mathbf{d}_1$, $\mathbf{d}_2$ … $\mathbf{d}_n$ within each primitive cell.

The positions of the atoms are: $$\mathbf{A}_j(\mathbf{R}) = \mathbf{R} + \mathbf{d}_j$$

making the scattering amplitude: $$F_{\mathbf{K}} = \sum_{\mathbf{R}} \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot(\mathbf{R}+\mathbf{d}_j)}$$

$$= \sum_{\mathbf{R}} e^{i\mathbf{K}\cdot\mathbf{R}} \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

$$L = \sum_{\mathbf{R}} e^{i\mathbf{K}\cdot\mathbf{R}}$$

"Lattice sum"

$$\Phi_{\mathbf{K}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

"Structure factor" of the basis

*If the structure factor = 0, there is no diffraction peak.

STRUCTURE FACTOR

The structure factor gives the amplitude of a scattered wave arising from the atoms with a single primitive cell.

$$\Phi_{\mathbf{K}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

For crystals composed of only one type of atom, it's common to split the structure factor into two parts:

$$\Phi_{\mathbf{K}} = f_j(\mathbf{K}) S_{\mathbf{K}}$$

"atomic form factor"

$$S_{\mathbf{K}} = \sum_j e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

"geometric structure factor"

S = 0 gives a systematic absence (i.e., absence of expected diff. peak).

STRUCTURE FACTORS

The amplitude of the rays scattered at positions $d_1, \ldots, d_n$ are in the ratios:

$$e^{i\mathbf{K}\bullet\mathbf{d}_1} \quad \ldots \quad e^{i\mathbf{K}\bullet\mathbf{d}_n}$$

The net ray scattered by the entire cell is the sum of the individual rays:

Geometric structure factor

$$S_{\mathbf{K}} = \sum_{j=1}^{n} e^{i\mathbf{K}\cdot\boldsymbol{d}_j}$$

-Adds up scattered waves from unit cell

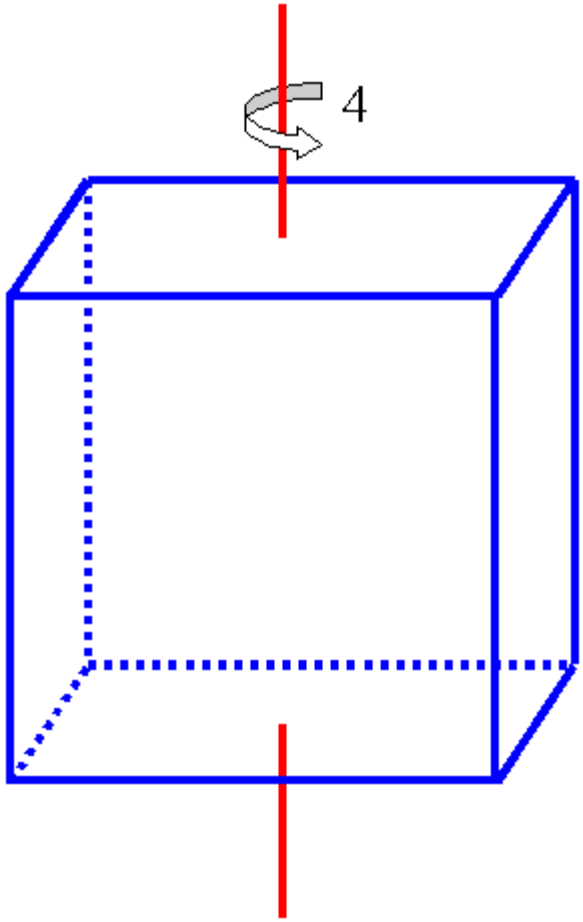
$$I_{(hkl)} \propto \left|S_{\mathbf{K}}\right|^2$$

-In particular, no peak when $S_K = 0$

SIMPLE CUBIC

For simple cubic: one atom basis (0,0,0)

$$\mathbf{d}_1 = 0\mathbf{a}_1 + 0\mathbf{a}_2 + 0\mathbf{a}_3$$



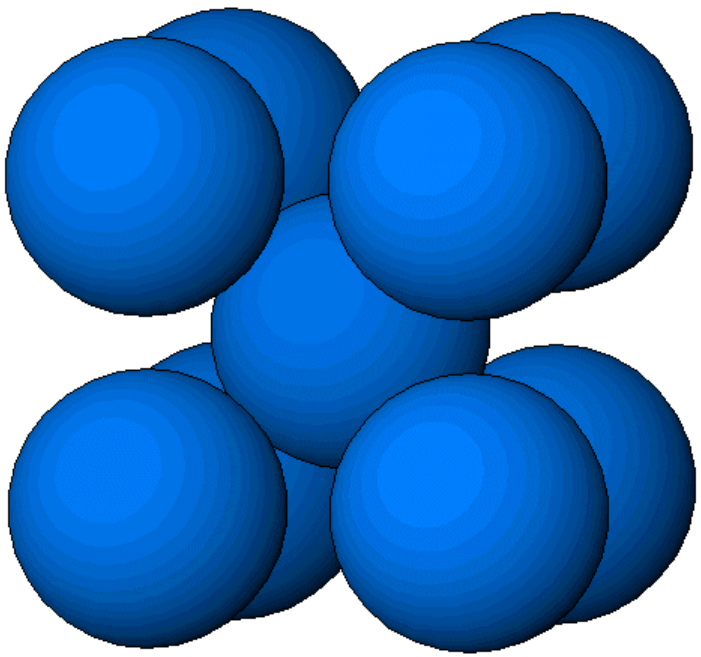
$$S_{\mathbf{K}} = e^{i\mathbf{K}\cdot 0} = 1$$

Same result as simple monatomic basis

MONATOMIC BCC

For monoatomic BCC:

we can think of this as SC with two point basis (0,0,0), (½,½,½)



$$S_{\mathbf{K}} = \sum_{j=1}^{2} e^{i\mathbf{K}\cdot\boldsymbol{d}_j} = e^{i\mathbf{K}\cdot 0} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{x}+\vec{y}+\vec{z})}$$

For SC, $\mathbf{K} = \frac{2\pi}{a}(h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}})$

$$= 1 + e^{i\pi(h+k+l)}$$

$$= 1 + (-1)^{h+k+l}$$

S = 2, when h + k + l even
S = 0, when h + k + l odd (systematic absences)

e.g. consider the powder pattern of BCC molybdenum

PDF#00-042-1120(RDB): QM=Star(S); d=Diffractometer; I=Diffractometer

Reference Lines(7) Cu 8

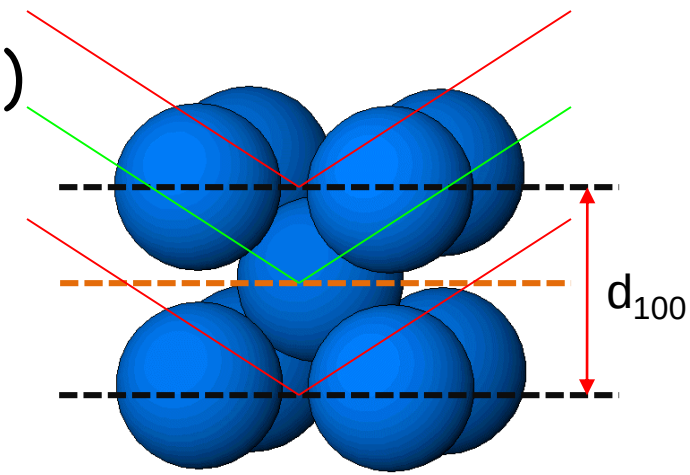
#	2-Theta	d(Å)	I(f)	(h k l)	Theta	1/(2d)	2pi/d	n^2
1	40.516	2.2247	100.0	(1 1 0)	20.258	0.2247	2.8243	2
2	58.609	1.5738	16.0	(2 0 0)	29.304	0.3177	3.9924	4
3	73.683	1.2847	31.0	(2 1 1)	36.842	0.3892	4.8909	6
4	87.597	1.1129	9.0	(2 2 0)	43.799	0.4493	5.6456	8
5	101.412	0.9953	14.0	(3 1 0)	50.706	0.5023	6.3127	10
6	115.968	0.9085	3.0	(2 2 2)	57.984	0.5504	6.9162	12
7	132.645	0.8411	24.0	(3 2 1)	66.323	0.5945	7.4702	14

Powder card shows only even hkl sums b/c Mo is BCC

Why?

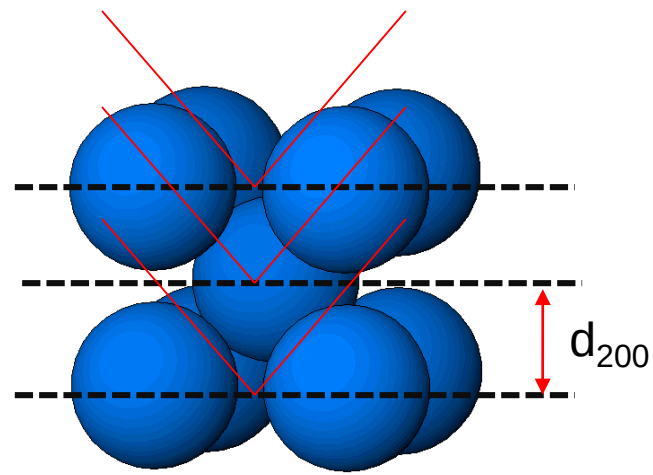
- Diffraction from other (hkl) results in destructive interference:

(100)



Beam cancels b/c body center atoms scatter exactly 180° out of phase

(200)

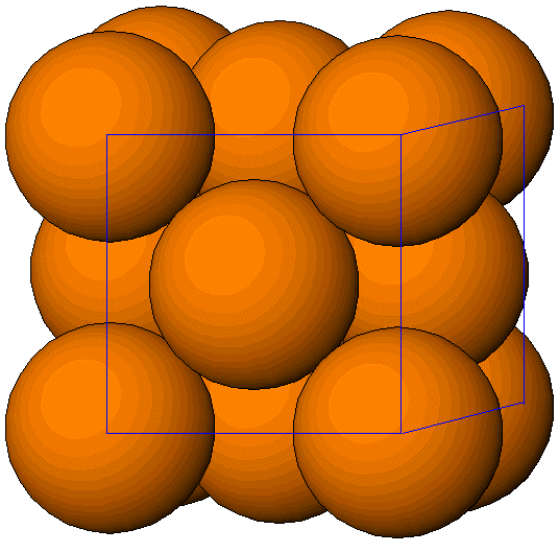


Strong reflection b/c all atoms lie on 200 planes and scatter in phase

MONATOMIC FCC

For monoatomic FCC:

SC with four point basis (0,0,0), (½,½,0), (0,½,½), (½,0,½)



$$S_{\mathbf{K}} = \sum_{j=1}^{4} e^{i\mathbf{K}\cdot\mathbf{d}_j} = e^{i\mathbf{K}\cdot 0} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{x}+\vec{y})} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{y}+\vec{z})} + e^{i\mathbf{K}\cdot\frac{a}{2}(\vec{x}+\vec{z})}$$

For SC, $\mathbf{K} = \frac{2\pi}{a}(h\hat{\mathbf{x}} + k\hat{\mathbf{y}} + l\hat{\mathbf{z}})$

$$S_{\mathbf{K}} = 1 + e^{i\pi(h+k)} + e^{i\pi(k+l)} + e^{i\pi(h+l)}$$

S = 4 when *h* + *k*, *k* + *l*, *h* + *l* all even (*h*, *k*, *l* <u>all even</u> or <u>all odd</u>)

S = 0 otherwise.

POLYATOMIC STRUCTURES

Atoms of different *Z* in the unit cell have different scattering powers, so we explicitly include the form factors:

Total structure factor

$$\Phi_{\mathbf{K}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

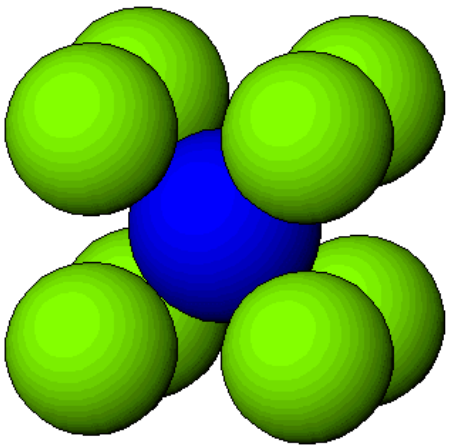
$\{f_j\}$: atomic form factors
$\propto$ # of electrons

CsCl STRUCTURE

Cesium Chloride is primitive cubic

Cs (0,0,0)

Cl (1/2,1/2,1/2)



$$\Phi_{\mathbf{K}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

$$\Phi_{\mathbf{K}} = f_{Cs} + f_{Cl} e^{i\pi(h+k+l)}$$

$\Phi = f_{Cs} + f_{Cl}$ **when** $h + k + l$ **even**

$\Phi = f_{Cs} - f_{Cl}$ **when** $h + k + l$ **odd**

Cs^+ and Cl^- are <u>not</u> isoelectronic
→ systematic absences unlikely

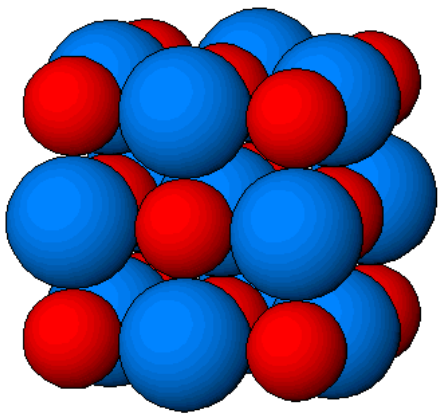
but what about CsI?

Cs^+ and I^- are isoelectronic, so CsI looks like BCC lattice:

(hkl)	CsCl	CsI
(100)	√	
(110)	√	√
(111)	√	
(200)	√	√
(210)	√	
(211)	√	√
(220)	√	√
(221)	√	
(300)	√	
(310)	√	√
(311)	√	

***h + k + l* even**

Diatomic FCC Lattices

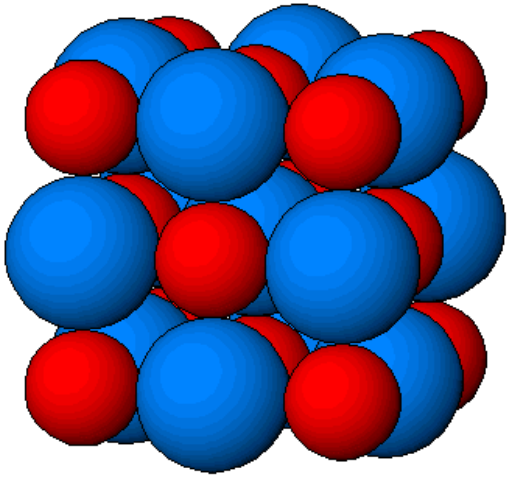


Sodium Chloride (NaCl)

Na: (0,0,0)(0,1/2,1/2)(1/2,0,1/2)(1/2,1/2,0)

Add (1/2,1/2,1/2)

Cl: (1/2,1/2,1/2) (1/2,1,1)(1,1/2,1)(1,1,1/2)



$$\Phi_{\mathbf{K}} = [\, f_{Na} + f_{Cl} e^{i\pi(h+k+l)}][S_{\mathbf{K},FCC}]$$

$$\Phi_{\mathbf{K}} = [\, f_{Na} + f_{Cl} e^{i\pi(h+k+l)}][1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(l+k)}]$$

$\Phi = 4(f_{Na} + f_{Cl})$ when *h*, *k*, *l*, all even

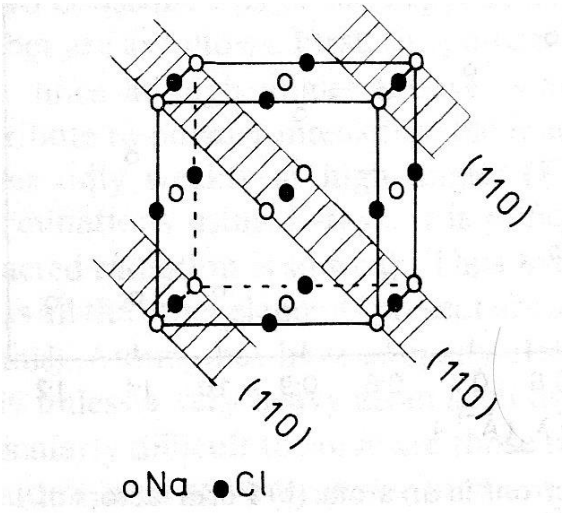
$\Phi = 4(f_{Na} - f_{Cl})$ when *h*, *k*, *l* all odd

$\Phi = 0$ otherwise

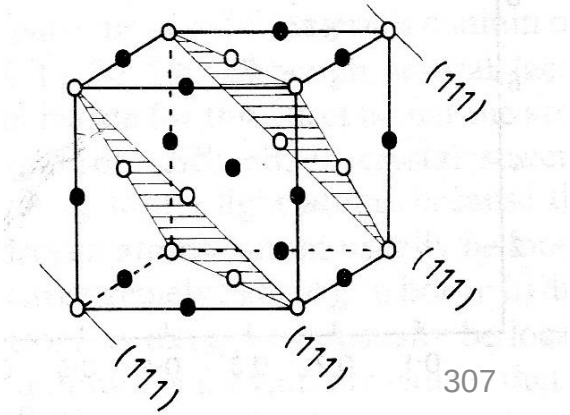
Once again, there are more systematic absences for isoelectronic ions (e.g., K and Cl)

(hkl)	NaCl	KCl
(100)		
(110)		
(111)	√	
(200)	√	√
(210)		
(211)		
(220)	√	√
(221)		
(300)		
(310)		
(311)	√	

(110) always absent in RS



(111) sometimes absent



For RS, we expect the intensity of the all odd reflections to increase with increasing ΔZ between cation and anion:

Table 5.7 *X-ray powder diffraction patterns for potassium halides.* (Data from Joint Committee on Powder Diffraction Standards, Swarthmore)

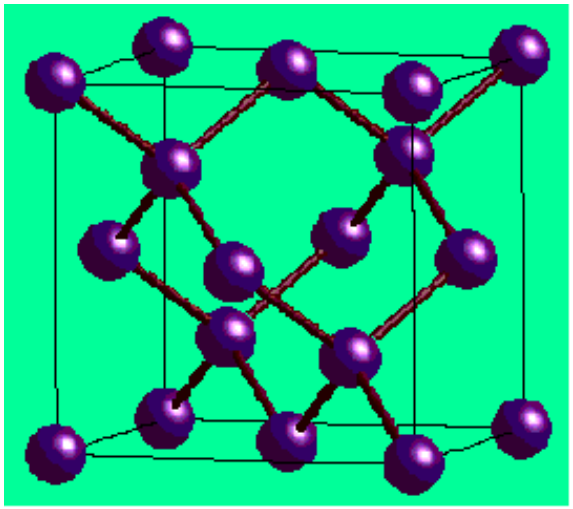
	KF, $a = 5.347$ Å		KCl, $a = 6.2931$ Å		KI, $a = 7.0655$ Å	
(*hkl*)	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
111	3.087	29		—	4.08	42
200	2.671	100	3.146	100	3.53	100
220	1.890	63	2.224	59	2.498	70
311	1.612	10	—	—	2.131	29
222	1.542	17	1.816	23	2.039	27
400	1.337	8	1.573	8	1.767	15

$I_{111,311}$: KCl < KF < KBr < KI

Less complete destructive interference between cation and anion sublattices.

DIAMOND STRUCTURE

Diamond: FCC lattice with two-atom basis (0,0,0,), (¼,¼,¼)



$$S_{\mathbf{K},diamond} = [e^{iK\cdot 0} + e^{iK\cdot\frac{a}{4}(\vec{x}+\vec{y}+\vec{z})}][S_{\mathbf{K},FCC}]$$

$$= [1 + e^{i(\pi/2)(h+k+l)}][S_{\mathbf{K},FCC}]$$

Only for all even or all odd *hkl* is S ≠ 0. For these unmixed values,

Additional condition:

S = 8	***h + k + l* twice an even number**
S = 4(1 ± i)	***h + k + l* odd**
S = 0	***h + k + l* twice an odd number**

I_{FCC} : all nonvanishing spots have equal intensity.

$I_{diamond}$: spots allowed by FCC have relative intensities of 64, 32, or 0.

	FCC	diamond
(*hkl*)	Al	Si
(100)		
(110)		
(111)	√	√
(200)	√	
(210)		
(211)		
(220)	√	√
(221)		
(300)		
(310)		
(311)	√	√

What about zinc blende?

SUMMARY OF SYSTEMATIC ABSENCES

crystal structure	condition for peak to occur
SC	any h,k,l
BCC	$h + k + l$ = even
FCC	h,k,l all even or all odd
NaCl	h,k,l all even, or all odd if $f_A \neq f_B$
diamond	h,k,l all even and twice an even #, or all odd
HCP	any h,k,l <u>except</u> when $h + 2k = 3n$ and l is odd

$$\Phi_{\mathbf{K}} = \sum_j f_j(\mathbf{K}) e^{i\mathbf{K}\cdot\mathbf{d}_j}$$

SIMPLE ANALYSIS OF SIMPLE PATTERNS

What will we see in XRD patterns of SC, BCC, FCC?

Miller Indices of the Diffracting Planes for BCC and FCC Lattices

Cubic planes {*hkl*}	$h^2 + k^2 + l^2$	Sum $\Sigma(h^2 + k^2 + l^2)$	Cubic diffracting planes {*hkl*} FCC	BCC
{100}	$1^2 + 0^2 + 0^2$	1		
{110}	$1^2 + 1^2 + 0^2$	2	...	110
{111}	$1^2 + 1^2 + 1^2$	3	111	
{200}	$2^2 + 0^2 + 0^2$	4	200	200
{210}	$2^2 + 1^2 + 0^2$	5		
{211}	$2^2 + 1^2 + 1^2$	6	...	211
...		7		
{220}	$2^2 + 2^2 + 0^2$	8	220	220
{221}	$2^2 + 2^2 + 1^2$	9		
{310}	$3^2 + 1^2 + 0^2$	10	...	310
		SC	FCC	BCC

$$h^2 + k^2 + l^2$$

SC: 1,2,3,4,5,6,8,9,10,11,12,…

BCC: 2,4,6,8,10,12,...

FCC: 3,4,8,11,12,16,24,…

Observable diffraction peaks for monoatomic crystals

We can take ratios of ($h^2 + k^2 + l^2$) to determine structure.

SIMPLE ANALYSIS OF SIMPLE PATTERNS

$$2d\sin\theta = n\lambda \quad \Rightarrow \quad \sin^2\theta \propto \frac{1}{d_{hkl}^2}$$

For cubic crystals: $d_{hkl} = \dfrac{a}{\sqrt{h^2+k^2+l^2}}$

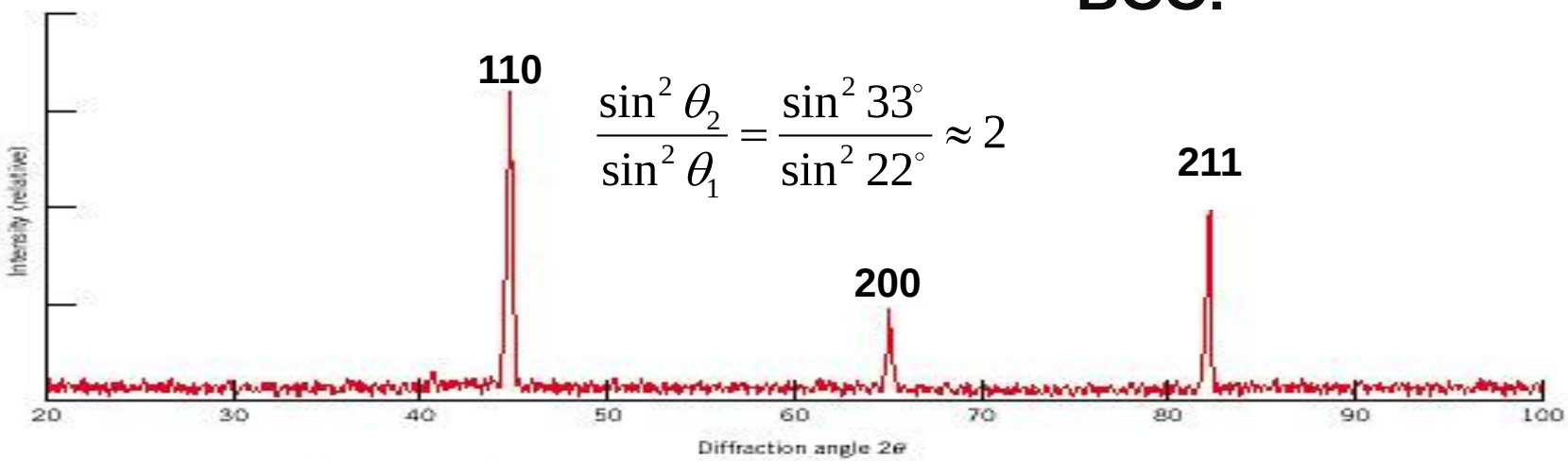
$$\sin^2\theta \propto (h^2+k^2+l^2)$$

$$\frac{\sin^2\theta_{n\text{th peak}}}{\sin^2\theta_{1\text{st peak}}} = \frac{(h^2+k^2+l^2)_{n\text{th peak}}}{(h^2+k^2+l^2)_{1\text{st peak}}}$$

SIMPLE ANALYSIS OF SIMPLE PATTERNS

α-Fe is cubic. Is it FCC or BCC?

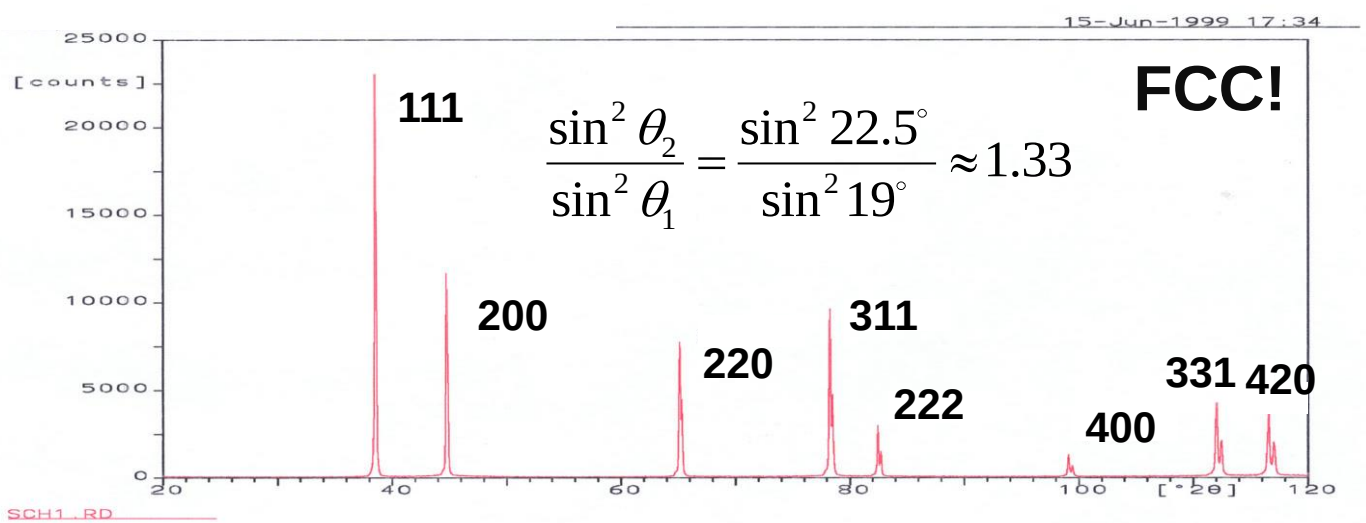
BCC!



$$\frac{\sin^2\theta_2}{\sin^2\theta_1} = \frac{\sin^2 33^\circ}{\sin^2 22^\circ} \approx 2$$

FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

What about Al?



$$\frac{\sin^2\theta_2}{\sin^2\theta_1} = \frac{\sin^2 22.5^\circ}{\sin^2 19^\circ} \approx 1.33$$

FCC!

Ex: An element, BCC or FCC, shows diffraction peaks at 2θ: 40, 58, 73, 86.8,100.4 and 114.7. Determine:(a) Crystal structure?(b) Lattice constant? (c) What is the element?

2theta	theta	$\sin^2\theta$	normalized $h^2+k^2+l^2$	(*hkl*)
40	20	0.117	1	(110)
58	29	0.235	2	(200)
73	36.5	0.3538	3	(211)
86.8	43.4	0.4721	4	(220)
100.4	50.2	0.5903	5	(310)
114.7	57.35	0.7090	6	(222)

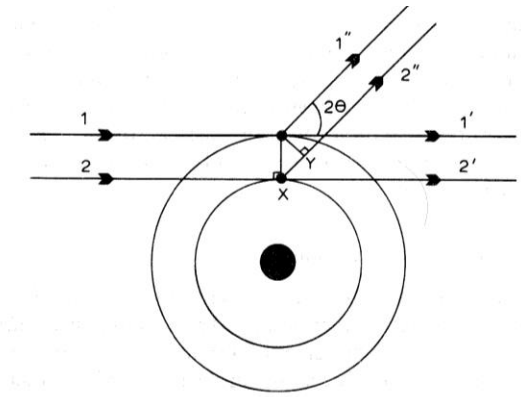
BCC, *a* =3.18 Å → W

ELASTIC X-RAY SCATTERING BY ATOMS

Atoms scatter X-rays because the oscillating electric field of an X-ray sets each electron in an atom into vibration. Each vibrating electron acts as a secondary point source of coherent X-rays (in elastic scattering).

The X-ray scattered from an atom is the resultant wave from all its electrons

Particle picture:



- zero phase difference for forward/backward scattering
  → scattering factor (form factor, *f*) proportional to atomic number, *Z*
- increasingly destructive interference with larger scattering angle (to 90°)
- for a given angle, intensity decreases with decreasing X-ray wavelength

Thomson relation:

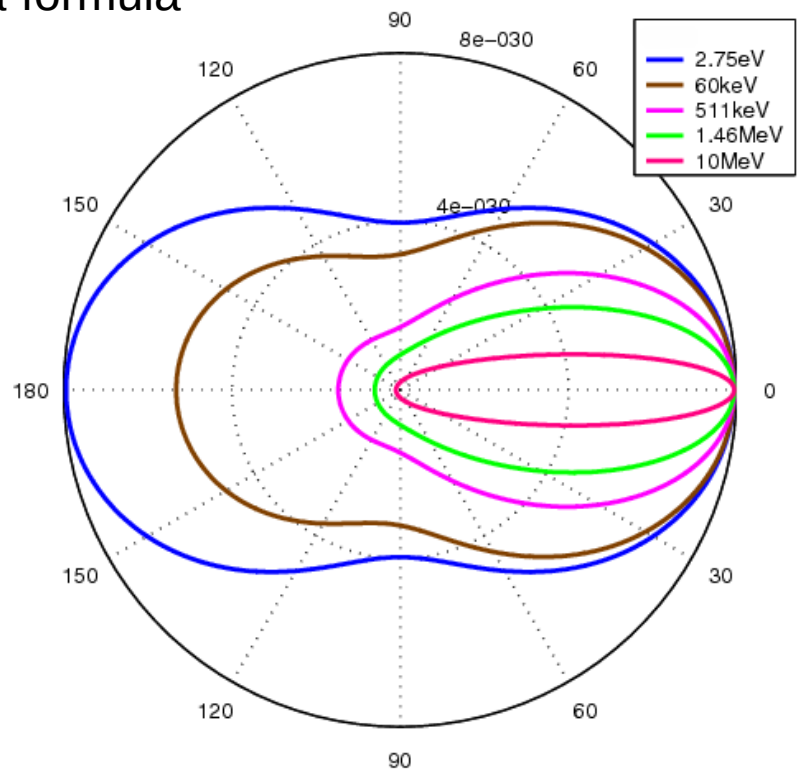
$$I \propto \frac{1}{2}(1+\cos^2 2\theta)$$

- max scattering intensity at 2θ = 0 & 180°
- gradual decrease to 50% as 2θ approaches 90°

SCATTERING OF X-RAYS BY ATOMS

scattering angle probabilities for a free electron:

Klein–Nishina formula



Low energy: Thomson
High energy: Compton

Thomson relation:

$$I \propto \frac{1}{2}(1+\cos^2 2\theta)$$

ATOMIC FORM FACTORS

Form factor *f* = scattering amplitude of a wave by an isolated atom

For X-rays, *f* depends on:
- Z (# electrons)
- scattering angle
- X-ray wavelength

} scattering vector **q**

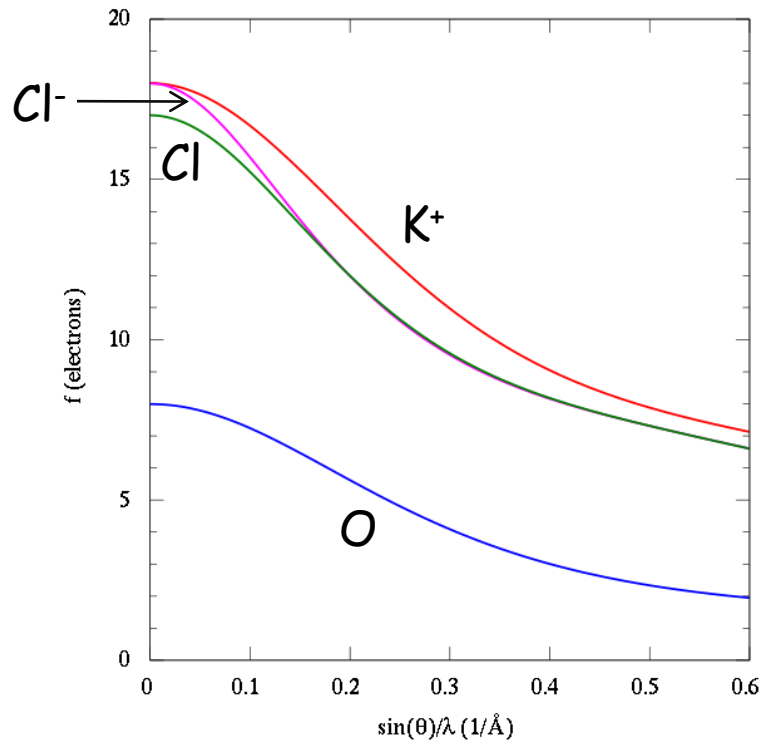
General elastic formula:

$$f_j(\mathbf{q}) = \int \rho_j(\mathbf{r}) e^{-i\mathbf{q}\cdot\mathbf{r}} d^3\mathbf{r}$$

with, $q = \dfrac{4\pi \sin\theta}{\lambda}$

For θ = 0 (forward scattering),

$$f_j(0) = \int \rho(\mathbf{r}) d^3\mathbf{r} = \#\ electrons$$



θ = 37°

consequences:
- powder patterns show weak lines at large 2θ.
- light atoms scatter weakly and are difficult to see.

ELECTRON DENSITY MAPS

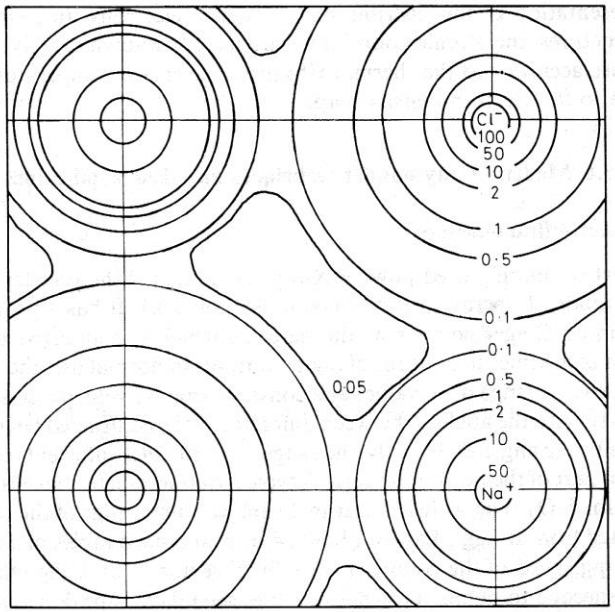
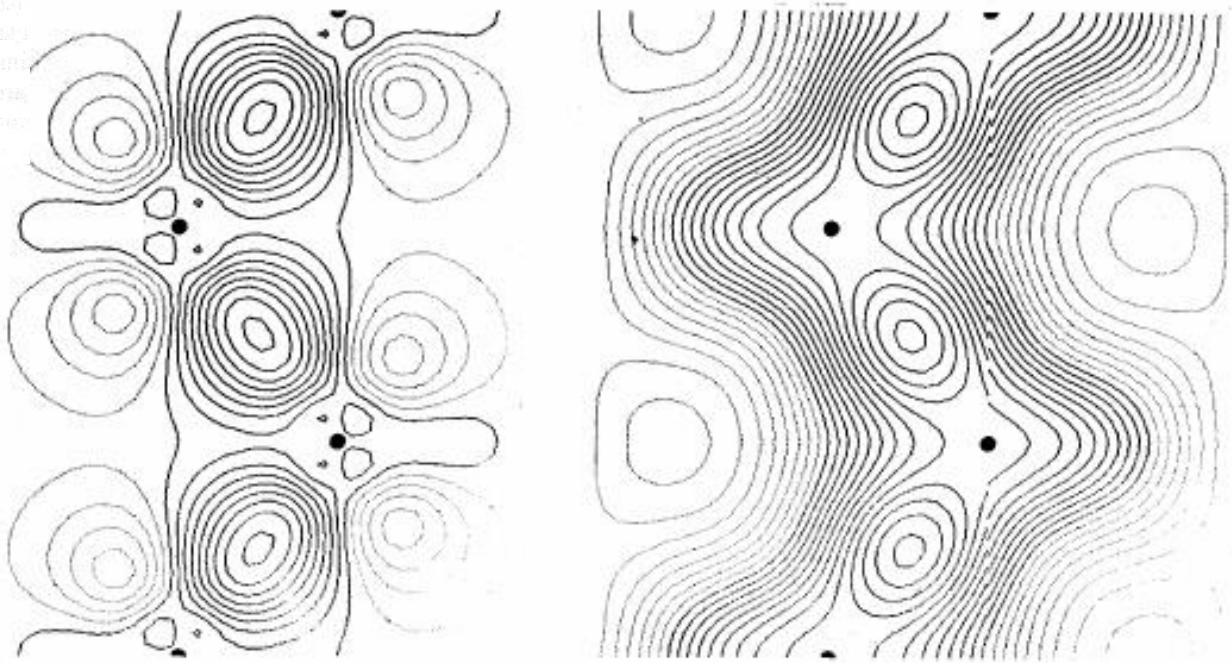


Fig. 5.39 Electron density map for NaCl

The electron density as a function of position *x*,*y*,*z* is the inverse Fourier transform of the structure factors:

$$\rho(xyz) = \frac{1}{V}\sum_{hkl}\Phi_{hkl}e^{-i2\pi(hx+ky+lz)}$$

The electron density map describes the contents of the unit cells averaged over the whole crystal (not the contents of a single unit cell)



(a) Si EXPERIMENT (b) Ge EXPERIMENT

PEAK WIDTHS

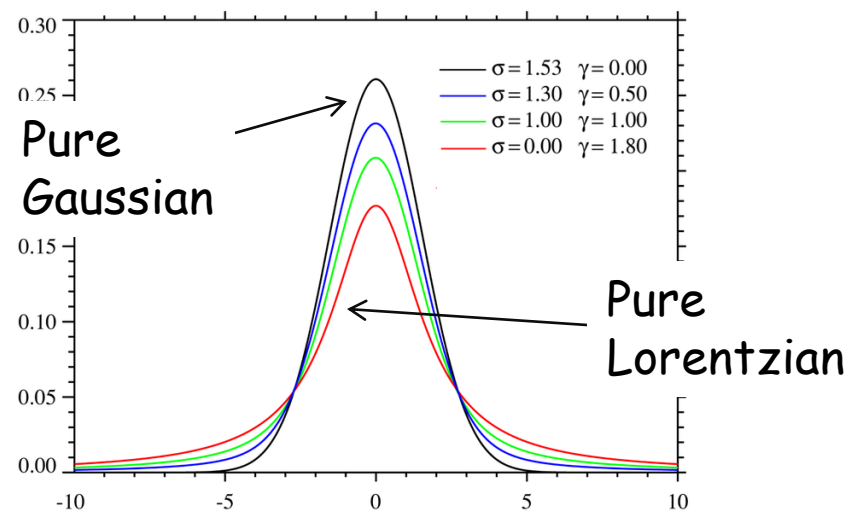
Peak **shape** is a Voigt function (mixture of Gaussian and Lorentzian)

- Gaussian component arises from natural linewidth and strain
- Lorentzian component arises from coherent domain size

$$V(x;\sigma,\gamma) = \int_{-\infty}^{\infty} G(x';\sigma)L(x-x';\gamma)\,dx'$$

$$G(x;\sigma) \equiv \frac{e^{-x^2/(2\sigma^2)}}{\sigma\sqrt{2\pi}}$$

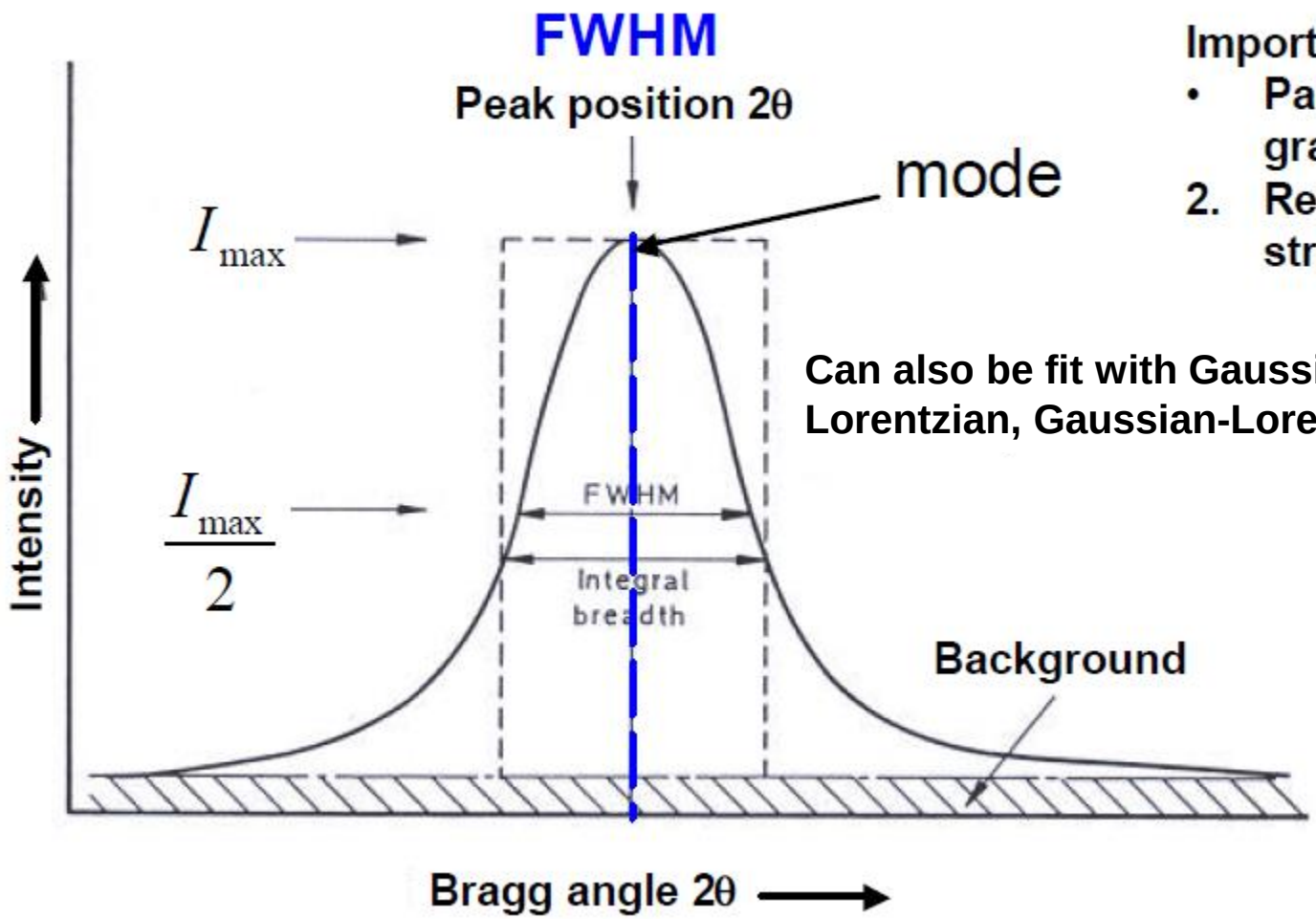
$$L(x;\gamma) \equiv \frac{\gamma}{\pi(x^2+\gamma^2)}.$$



Peak **width** (broadening) is determined by several factors:

- natural linewidth of X-ray emission
- instrumental effects (polychromatic λ, focusing, detector)
- specimen effects
  1) **crystallite size**
  2) **crystallite strain**

FULL WIDTH AT HALF MAXIMUM (FWHM)



Important for:

- Particle or grain size
2. Residual strain

Can also be fit with Gaussian, Lorentzian, Gaussian-Lorentzian etc.

Instrument and Sample Contributions to the Peak Profile must be Deconvoluted

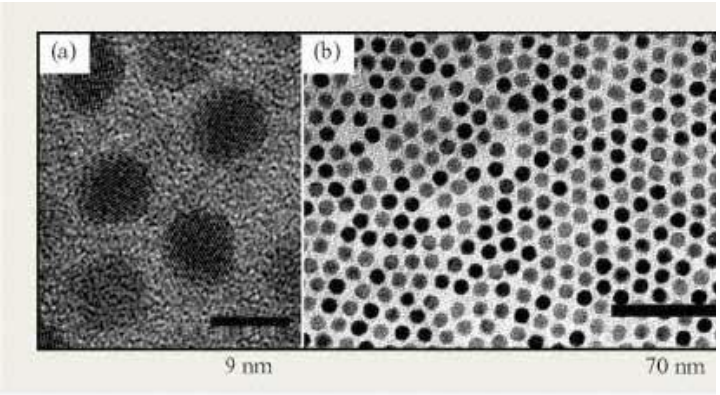
- In order to analyze crystallite size, we must deconvolute:
  - Instrumental Broadening FW(I)
    - also referred to as the Instrumental Profile, Instrumental FWHM Curve, Instrumental Peak Profile
  - Specimen Broadening FW(S)
    - also referred to as the Sample Profile, Specimen Profile

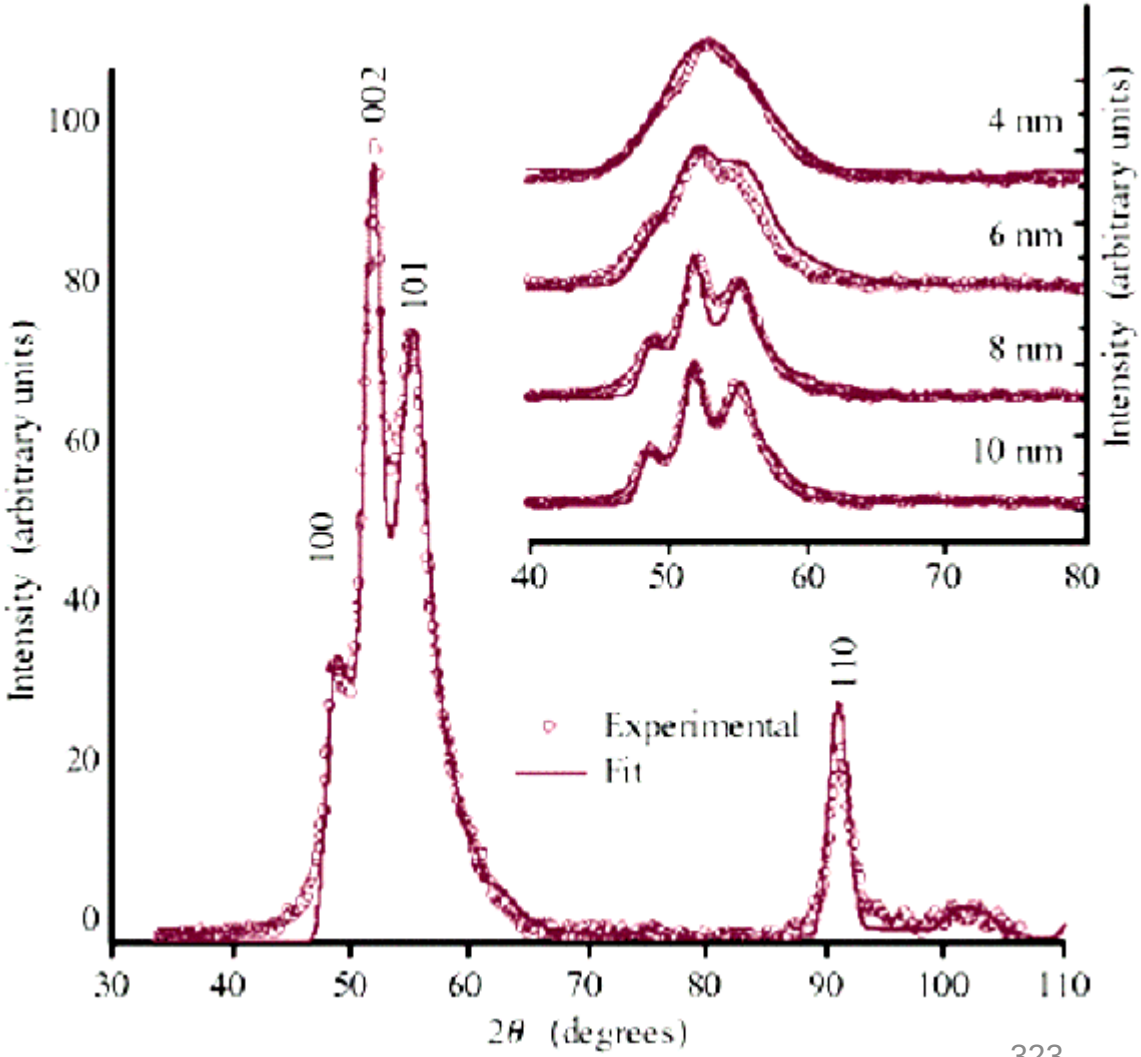
- We must then separate the different contributions to specimen broadening
  - Crystallite size and microstrain broadening of diffraction peaks

SIZE BROADENING

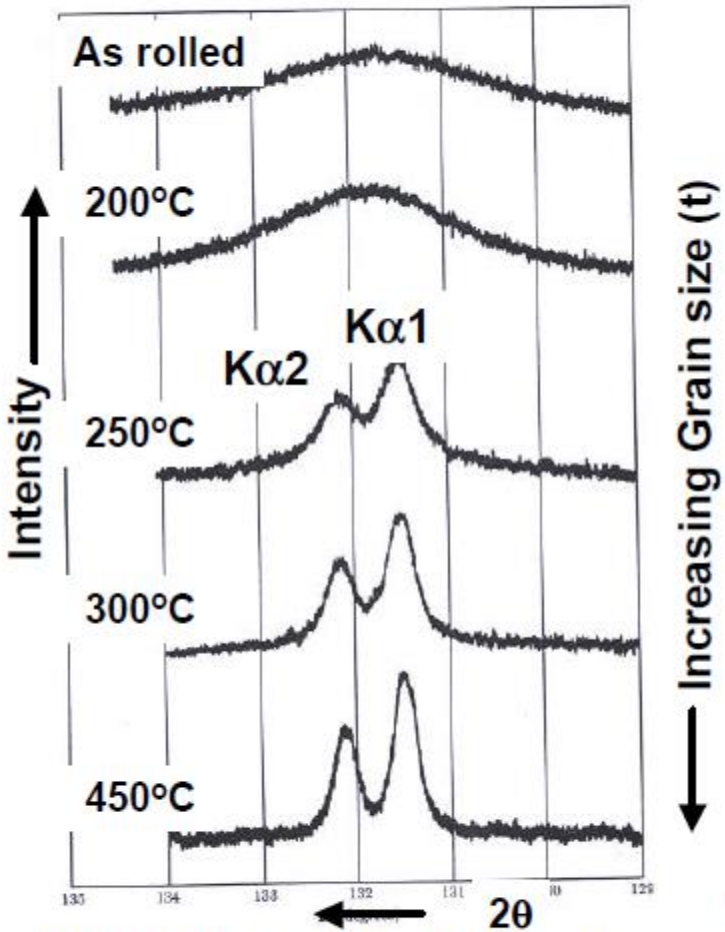
Small crystallites (< 200 nm) show broadened diffraction lines

Nanocrystal X-ray Diffraction

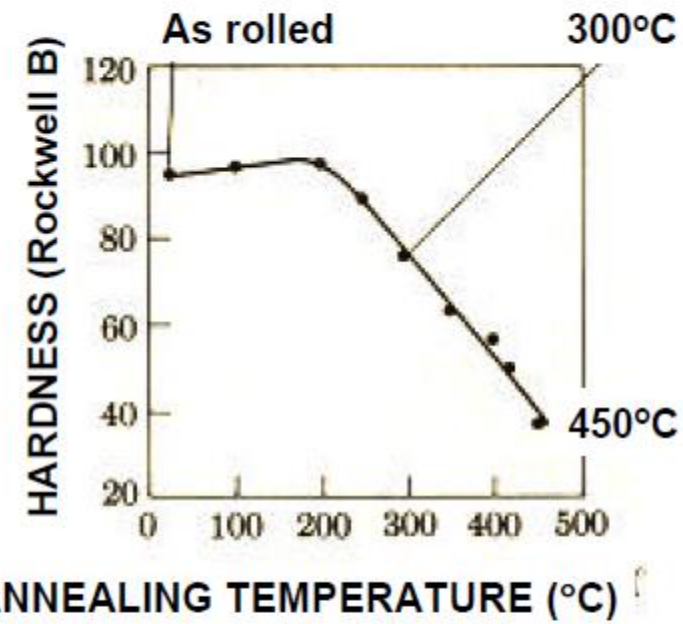




Effect of Coherent Domain Size



(331) Peak of cold-rolled and Annealed 70Cu-30Zn (brass)

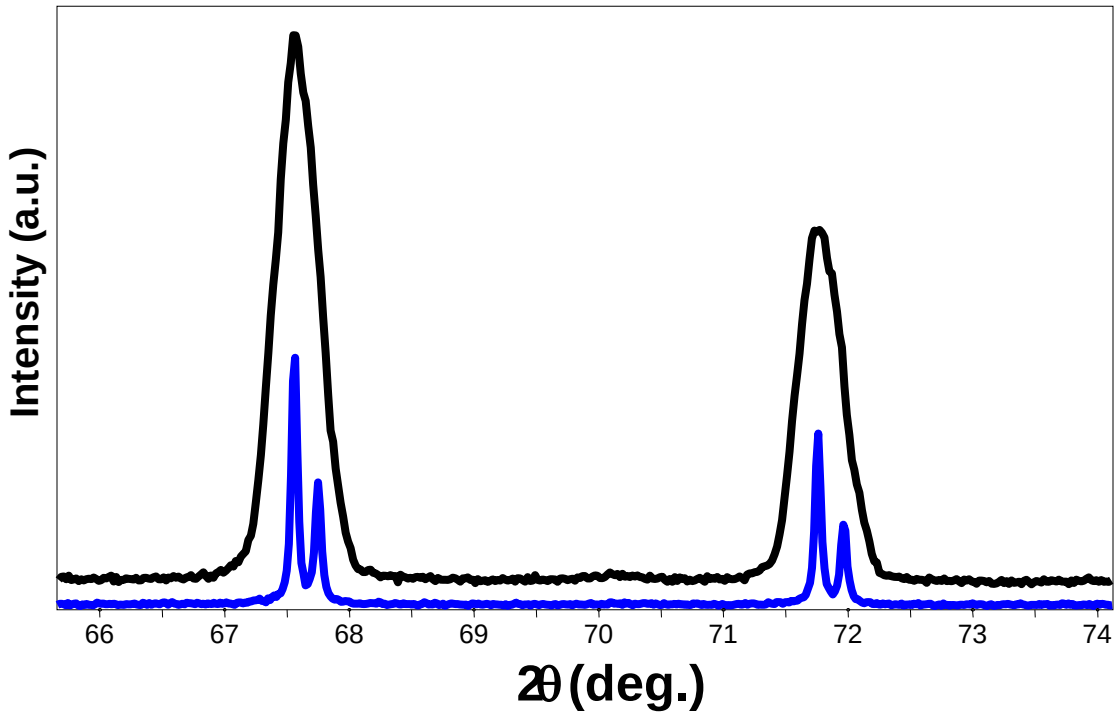


$$B = \frac{0.9 \cdot \lambda}{t \cdot Cos\theta}$$

Peak Broadening
Scherrer Model

As grain size decreases hardness increases and peaks become broader

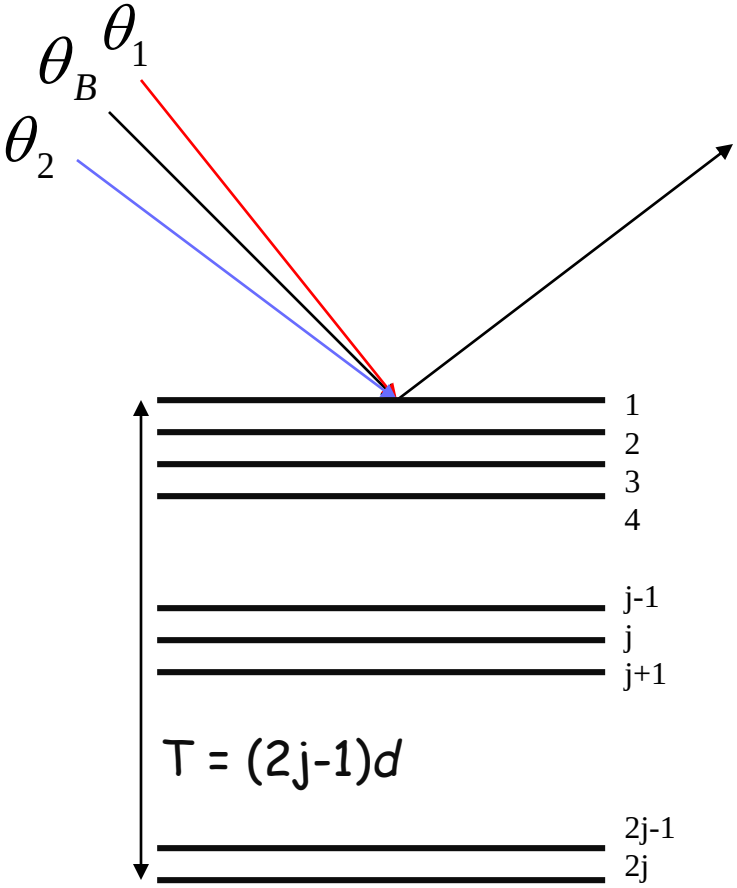
Which of these diffraction patterns comes from a nanocrystalline material?



These diffraction patterns were produced from the <u>same sample!</u>

- Two different diffractometers, with different optical configurations, were used
- ***The apparent peak broadening is due solely to the instrumentation in this case***

The *finite size of real crystals* results in incomplete destructive interference over some range of angles



Crystal with 2j planes
Total thickness T

at Bragg angle, θ_B
phase lag between two planes = λ
perfectly in phase, constructive

At some angle $\theta_1 > \theta_B$

Phase lag between two planes: $\lambda + \delta\lambda$

At $(j+1)^{th}$ plane:
Phase lag: $\sum \delta\lambda = j \cdot \delta\lambda = \frac{\lambda}{2}$

- Rays from planes 1 and j+1 cancel
- Ditto for 2 & j+2, … j & 2j
- Net diffraction over 2j planes = 0

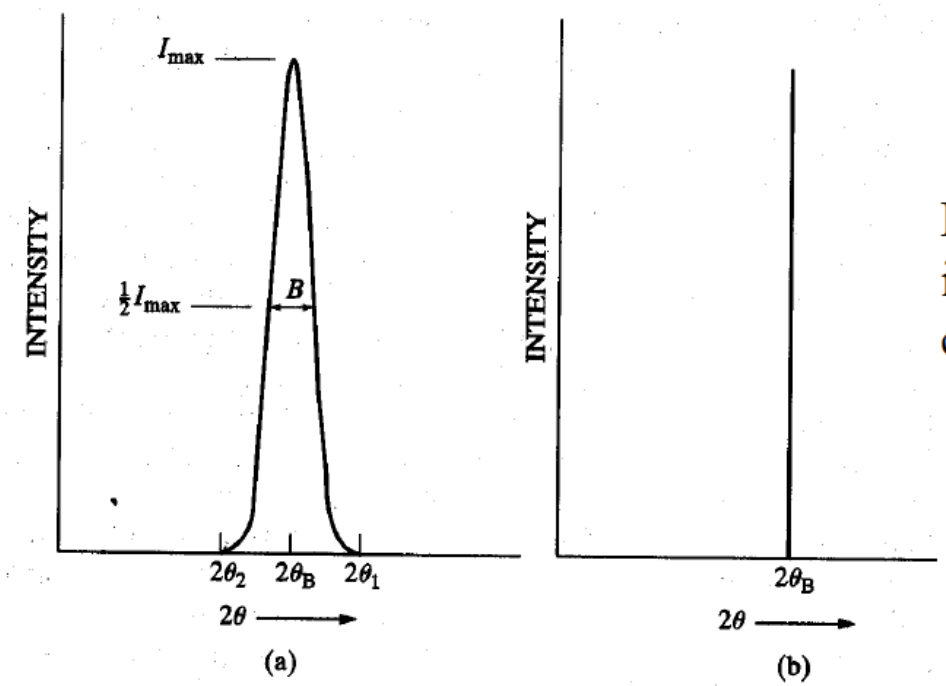
The angular range θ_B to θ_1 is the range where diffracted intensity falls from a maximum to zero (half of Bragg peak profile).

Same arguments apply to $\theta_2 < \theta_B$

So we see diffracted X-rays over all scattering angles between $2\theta_1$ and $2\theta_2$.

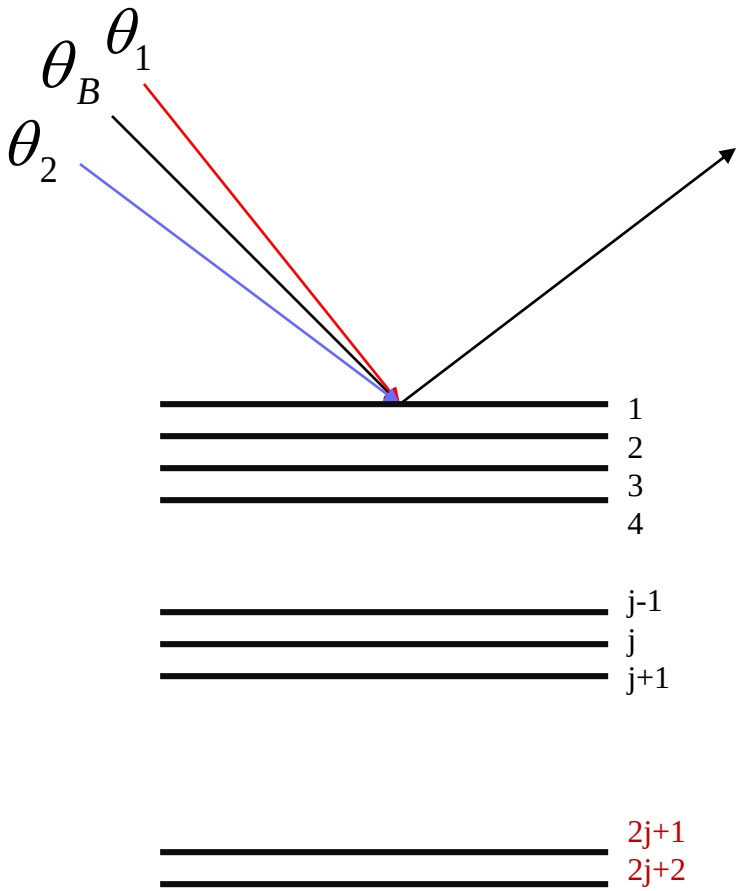
- If we assume a triangular shape for the peak, the full width at half maximum of the peak will be $B = (2\theta_1 - 2\theta_2)/2 = \theta_1 - \theta_2$

Diffraction from finite thickness crystal



Diffraction from infinitely thick crystal

If we have <u>more</u> than 2j planes:

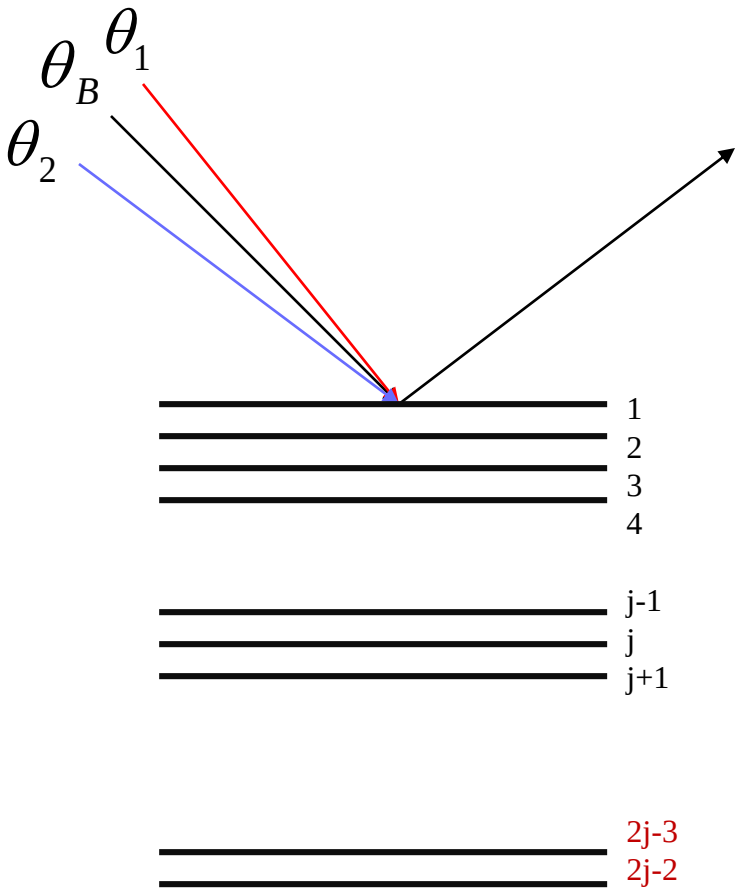


Rays from new planes are canceled

still zero intensity at θ_1

Peak sharpens!

If we have <u>fewer</u> than 2j planes:



Rays from planes j-1 & j <u>not</u> canceled

nonzero intensity at θ_1

Peak broadens!

Thinner crystals result in broader peaks!

Let's derive the relation between crystal thickness T and peak width B:

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

Considering the path length differences between X-rays scattered from the front and back planes of a crystal with 2*j*+1 planes and total thickness T:

$$2T\sin\theta_1 = (2j+1)\lambda$$

$$2T\sin\theta_2 = (2j-1)\lambda$$

Here, $T = 2jd$

$$\sin\theta_1 - \sin\theta_2 = 2\cos\frac{\theta_1+\theta_2}{2}\sin\frac{\theta_1-\theta_2}{2}$$

If we subtract them: $T(\sin\theta_1 - \sin\theta_2) = \lambda$

Using trig identity: $2T(\cos(\frac{\theta_1+\theta_2}{2})\sin(\frac{\theta_1-\theta_2}{2})) = \lambda$

Since $\frac{\theta_1+\theta_2}{2} = \theta_B$ and $\sin(\frac{\theta_1-\theta_2}{2}) \approx \frac{\theta_1-\theta_2}{2}$,

$2T(\cos\theta_B)(\frac{\theta_1-\theta_2}{2}) = \lambda.$ But, $B = 2(\frac{\theta_1-\theta_2}{2})$, so

$$T = \frac{\lambda}{B\cos\theta_B}$$

SCHERRER FORMULA

A more rigorous treatment includes a unitless shape factor:

Scherrer Formula (1918)

$$T = \frac{K\lambda}{B\cos\theta_B}$$

T = crystallite thickness
λ (X-ray wavelength, Å)
K (shape factor) ~ 0.9
B, θ_B in radians

Accurate size analysis requires correction for instrument broadening:

For Gaussian peaks: $$B^2 = B_M^2 - B_R^2$$

B_M: Measured FWHM (in radians)
B_R: Corresponding FWHM of bulk reference (large grain size, > 200 nm)

Readily applied for crystal size of 2-100 nm.
Up to 500 nm if synchrotron is used.

SCHERRER CONSTANT

$$T = \frac{K\lambda}{B\cos\theta_B} \quad \Rightarrow \quad T = \frac{0.94\lambda}{B\cos\theta_B}$$

- The constant of proportionality, K (the Scherrer constant) depends on the how the width is determined, the shape of the crystal, and the size distribution
  - the most common values for K are:
    - 0.94 for FWHM of spherical crystals with cubic symmetry
    - 0.89 for integral breadth of spherical crystals w/ cubic symmetry
    - 1, because 0.94 and 0.89 both round up to 1
  - K actually varies from 0.62 to 2.08
- For an excellent discussion of K, refer to JI Langford and AJC Wilson, “Scherrer after sixty years: A survey and some new results in the determination of crystallite size,” *J. Appl. Cryst.* **11** (1978) 102-113.

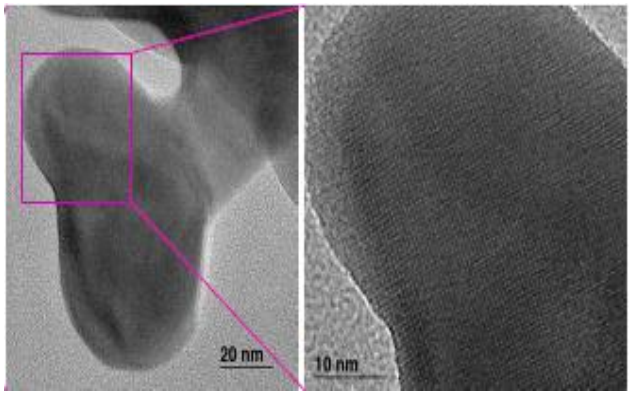
Suppose λ=1.5 Å, d=1.0 Å, and θ=49°. Then for a crystal 1 mm in diameter, the width B, due to the small crystal effect alone, would be about 2×10^{-7} radian (10^{-5} degree), too small to be observable. Such a crystal would contain some 10^7 parallel lattice planes of the spacing assumed above.

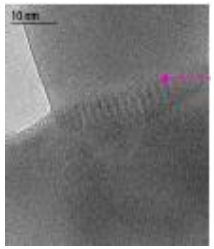
However, if the crystal were only 50 Å thick, it would contain only 51 planes, and the diffraction curve would be very broad, namely about 43×10^{-2} radian (2.46°), which is easily measurable.

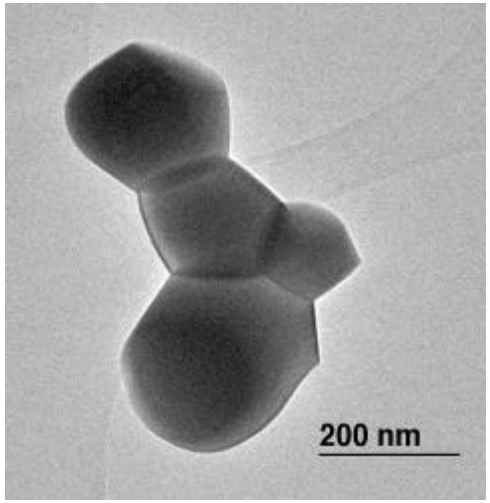
"Incomplete destructive interference at angles slightly off the Bragg angles"

What do we mean by crystallite size?
“A single-crystalline domain that scatters coherently”

- A particle may be made up of several different crystallites (also called grains)
- The crystallites, not the particles, are the coherent scattering units







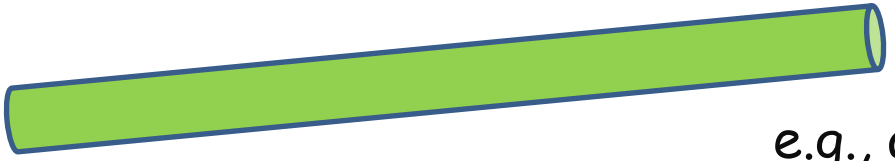
CRYSTALLITE SHAPE

- Though the shape of crystallites is usually irregular, we can often approximate them as:
  - sphere, cube, tetrahedra, or octahedra
  - parallelepipeds such as needles or plates
  - prisms or cylinders

- Most applications of Scherrer analysis assume spherical crystallite shapes

- If we know the average crystallite shape from another analysis, we can select the proper value for the Scherrer constant K

- Anisotropic crystal shapes can be identified by unequal peak broadening
  - if the dimensions of a crystallite are 2x * 2y * 200z, then (*h*00) and (0*k*0) peaks will be more broadened than (00*l*) peaks.



e.g., a nanowire

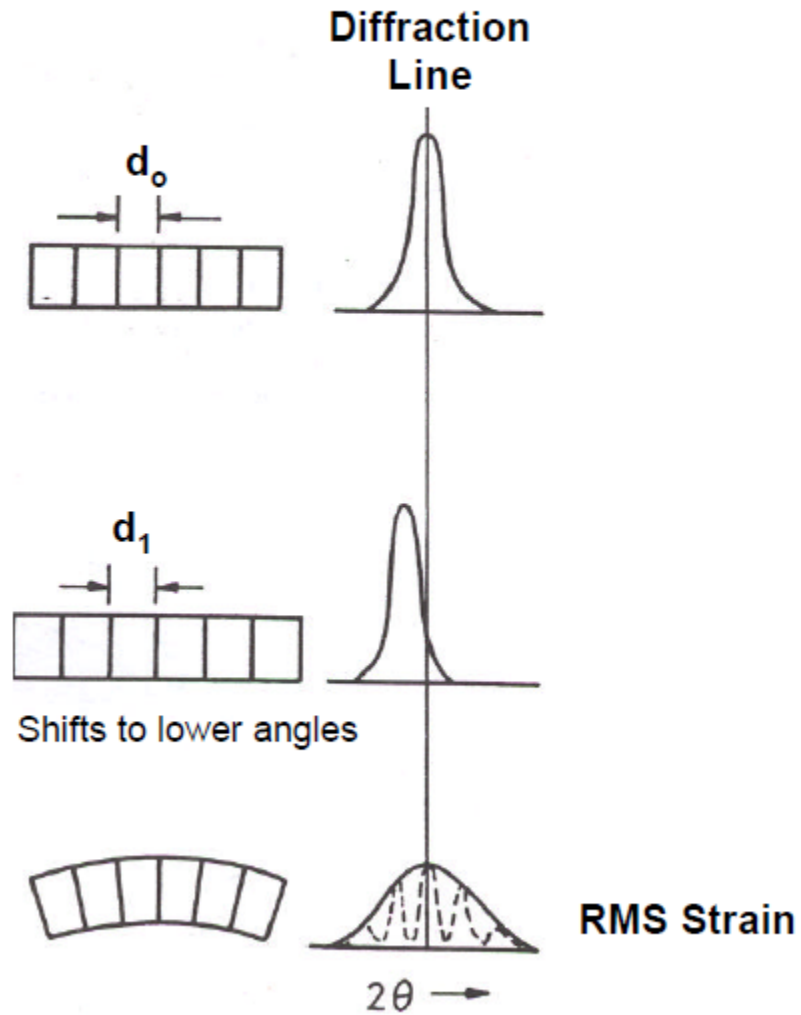
STRAIN EFFECTS

Strain: $\varepsilon = \dfrac{\Delta L}{L}$

No Strain

Uniform Strain
$(d_1 - d_o)/d_o$
Peak moves, no shape changes

Non-uniform Strain
$d_1 \neq$ constant
Peak broadens



Exceeds d_0 on top, smaller than d_0 on the bottom

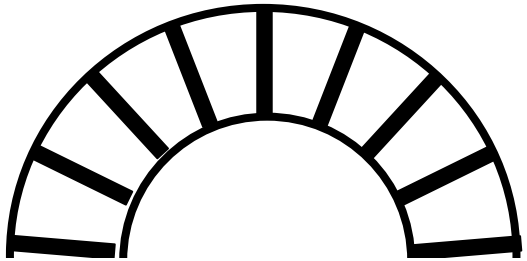
SOURCES OF STRAIN

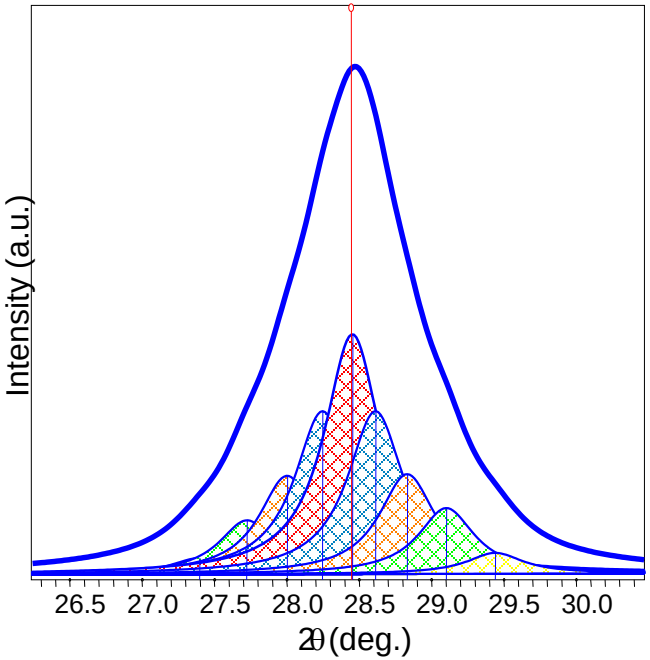
Table 1. The most typical correlations between diffraction peak aberrations, i.e. broadening, shifts or asymmetries, and the different elements of microstructure

Sources of strain	Peak aberrations				
	Peak shift	Peak broadening	Peak asymmetry	Anisotropic peak broadening	Peak shape
Dislocations		+	+	+	+
Stacking faults	+	+	+	+	+
Twinning	+	+	+	+	+
Microstresses		+			
Long-range internal stresses	+		+		
Grain boundaries	+	+			
Sub-boundaries	+	+			
Internal stresses	+				
Coherency strains	+	+	+		
Chemical heterogeneities	+	+	+		
Point defects					+
Precipitates and inclusions			+		+
Crystallite smallness		+		+	+

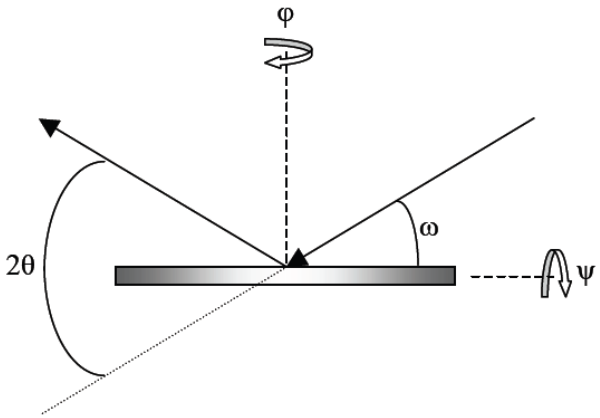
Non-Uniform Lattice Distortions

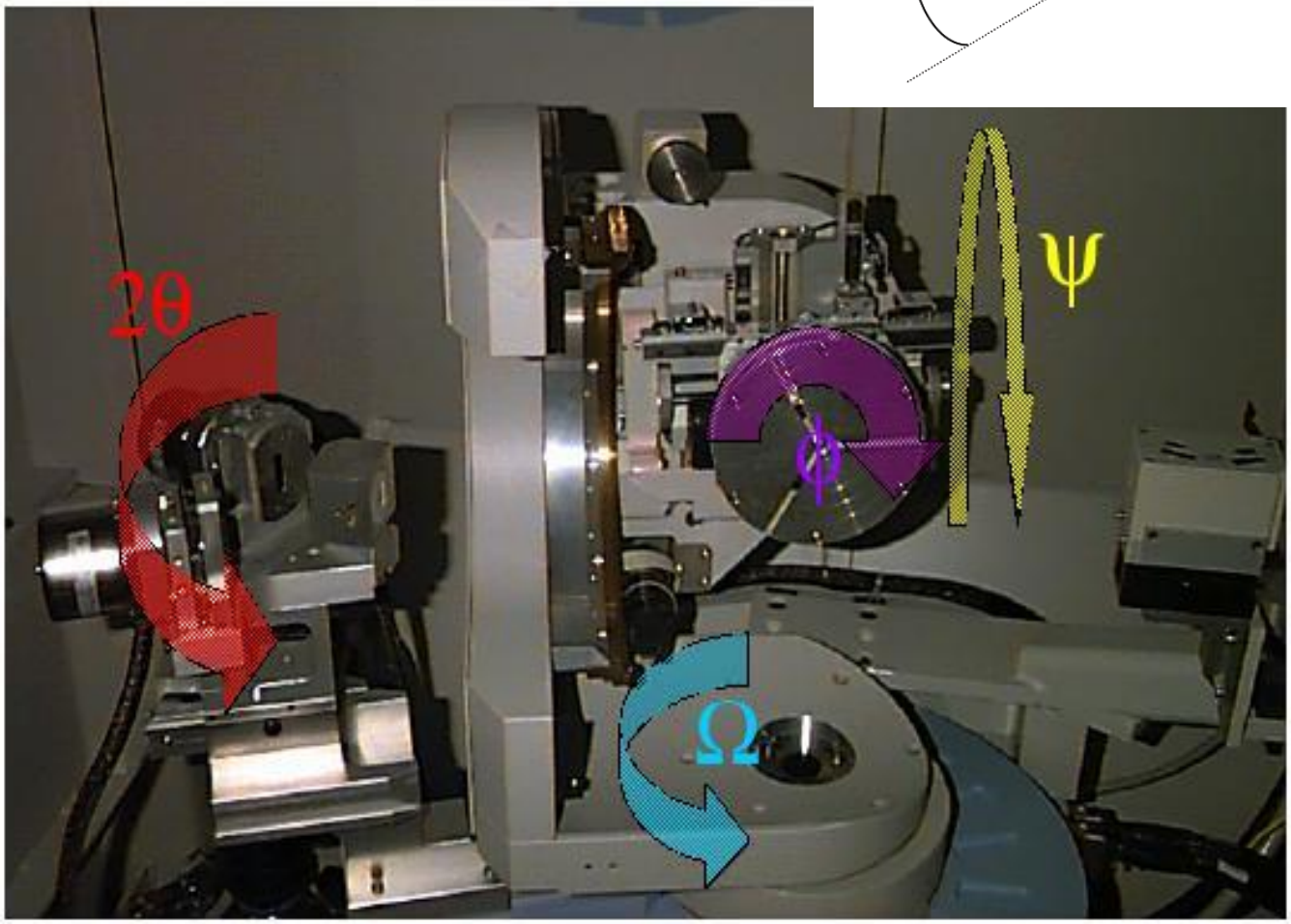
- Rather than a single *d*-spacing, the crystallographic plane has a distribution of *d*-spacings
- This produces a broader observed diffraction peak
- Such distortions can be introduced by:
  - mechanical force
  - surface tension of nanocrystals
  - morphology of crystal shape, such as nanotubes
  - interstitial impurities



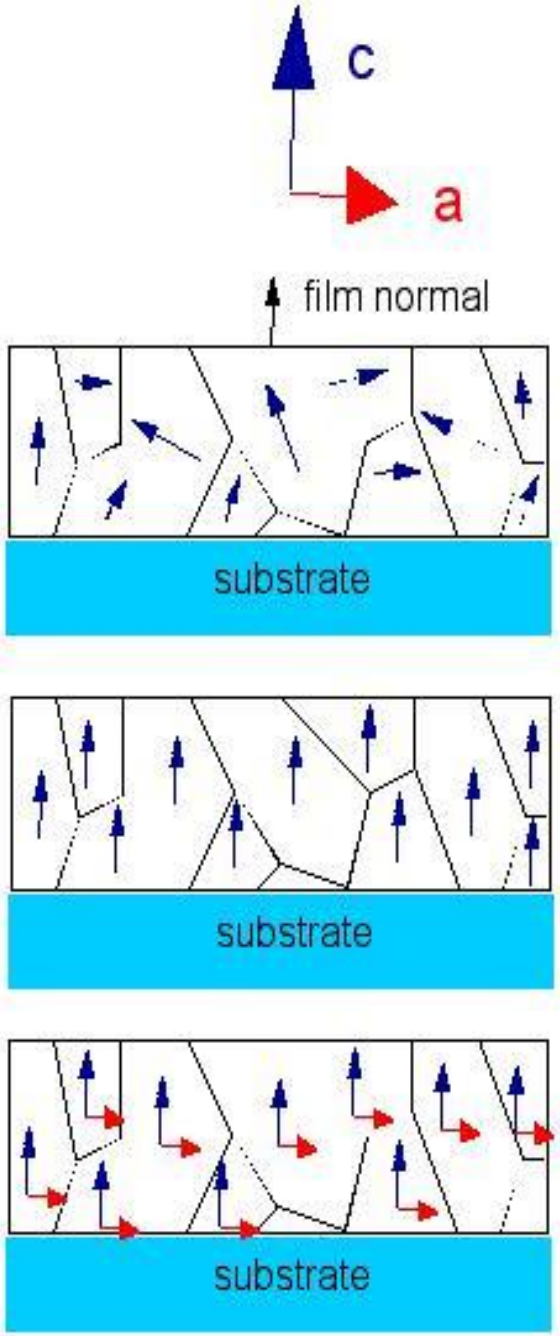


THIN FILM SCANS





Classification of thin film texture



- **Untextured**
  - rare in thin films
  - will give theoretical powder intensities

- **Uniaxial texture**
  - Can range from mild preferential orientation
  - to fully aligned (e.g. fully [100] film)

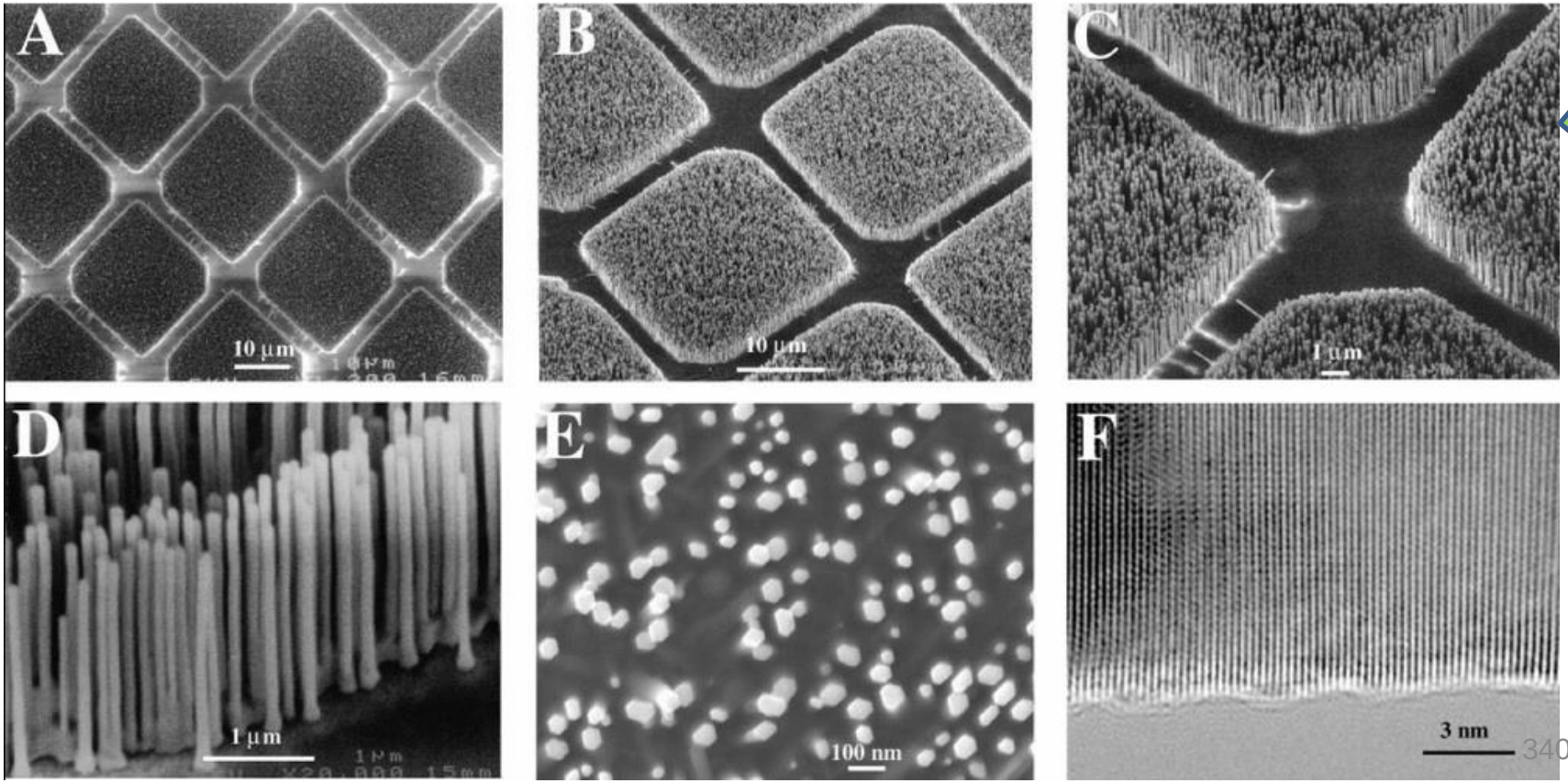
- **Biaxial texture**
  - Induced by epitaxial registration with substrate
  - Distinguished from fully aligned by texture scan

EPITAXY - "above in an ordered fashion"

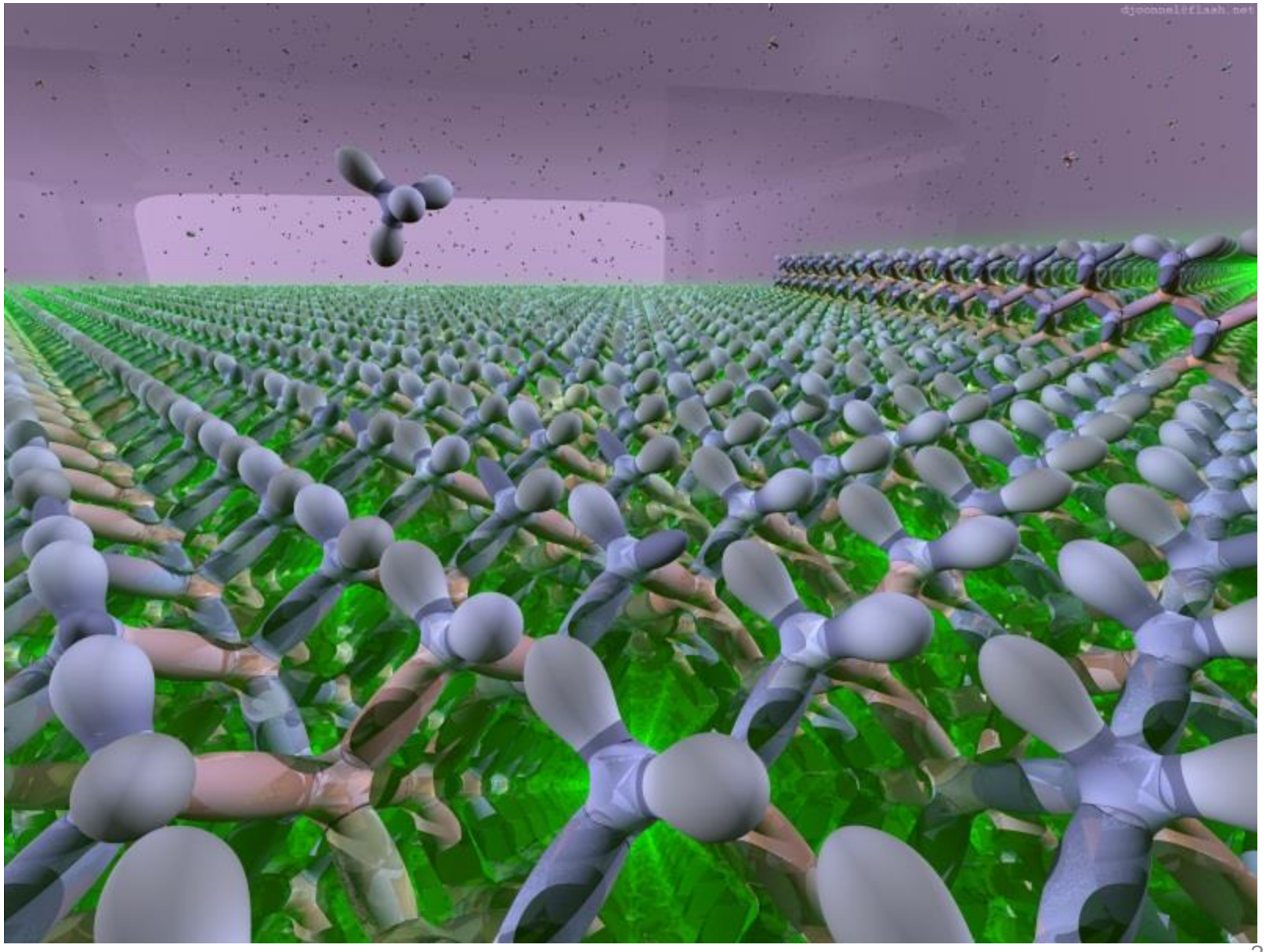
when one crystal grows on another with a well-defined 3D crystallographic relationship

Homoepitaxy: epitaxy between identical crystals (*e.g.*, Si on Si)
Heteroepitaxy: the two crystals are different (*e.g.*, ZnO on Al_2O_3)

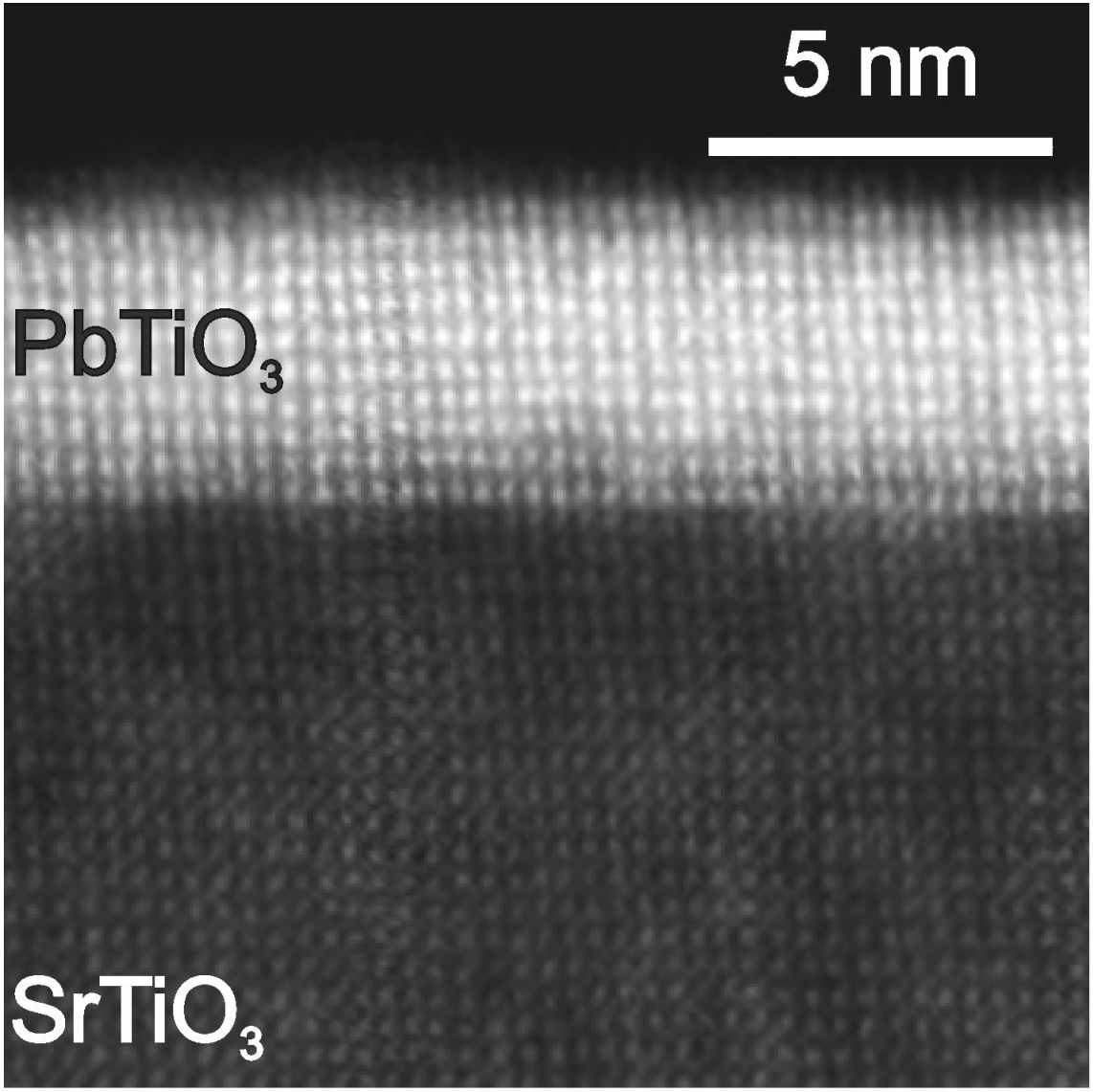
requirements: lattice symmetry & lattice constant matching



Molecular picture – Si growth on Si (100)

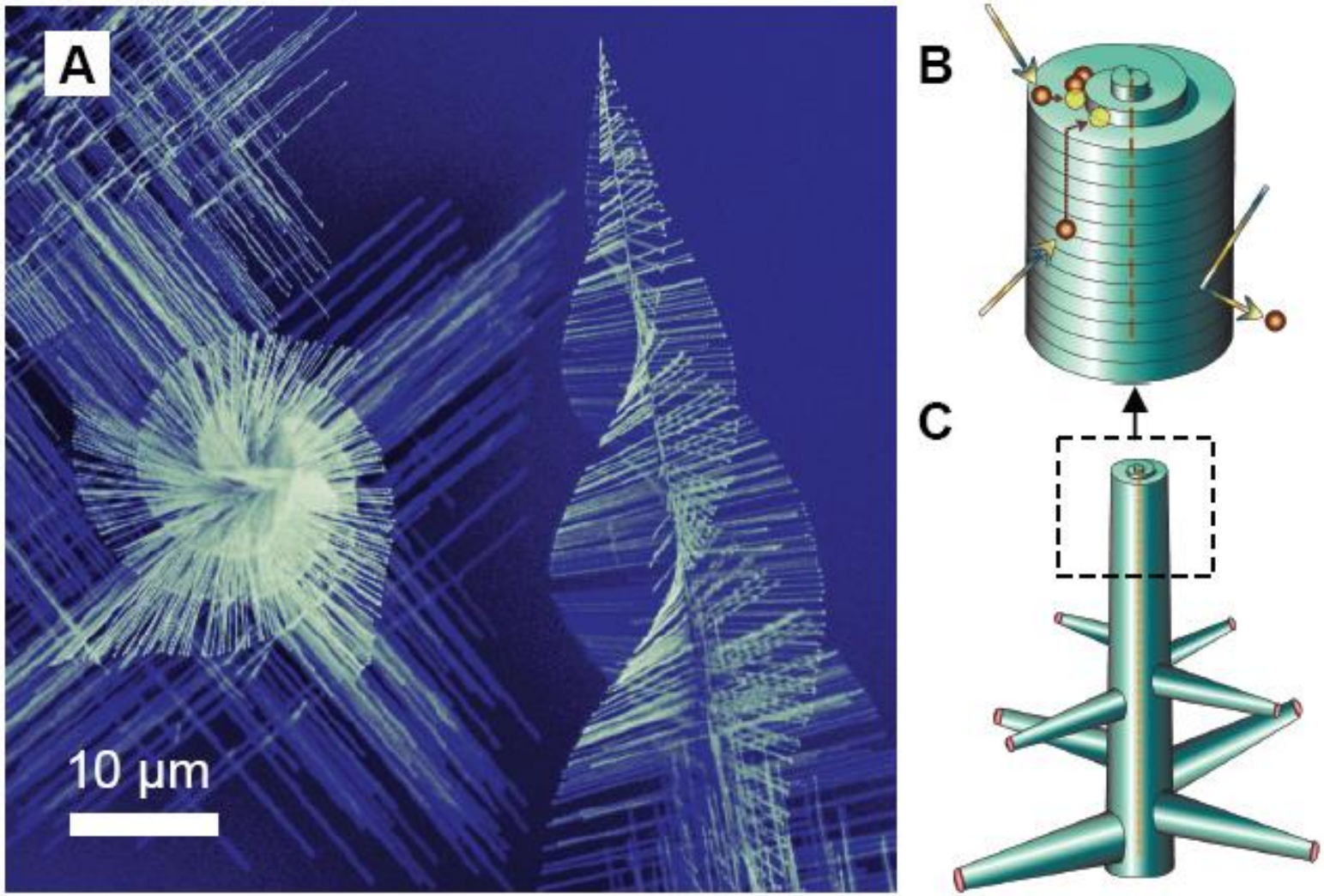


Dan Connelly



NTNU

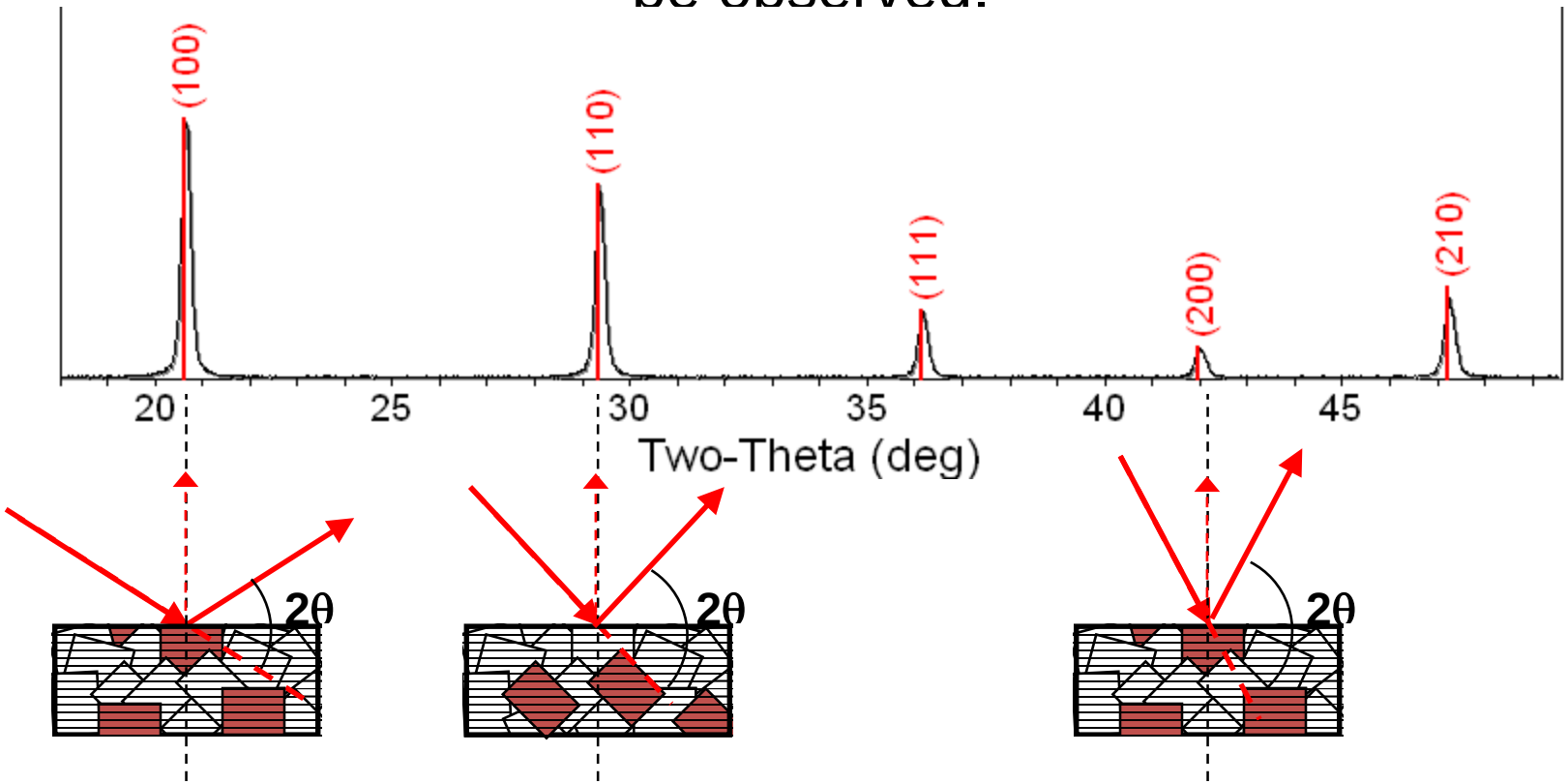
Rock salt PbS “nanotrees”



Jin group – U. Wisc.

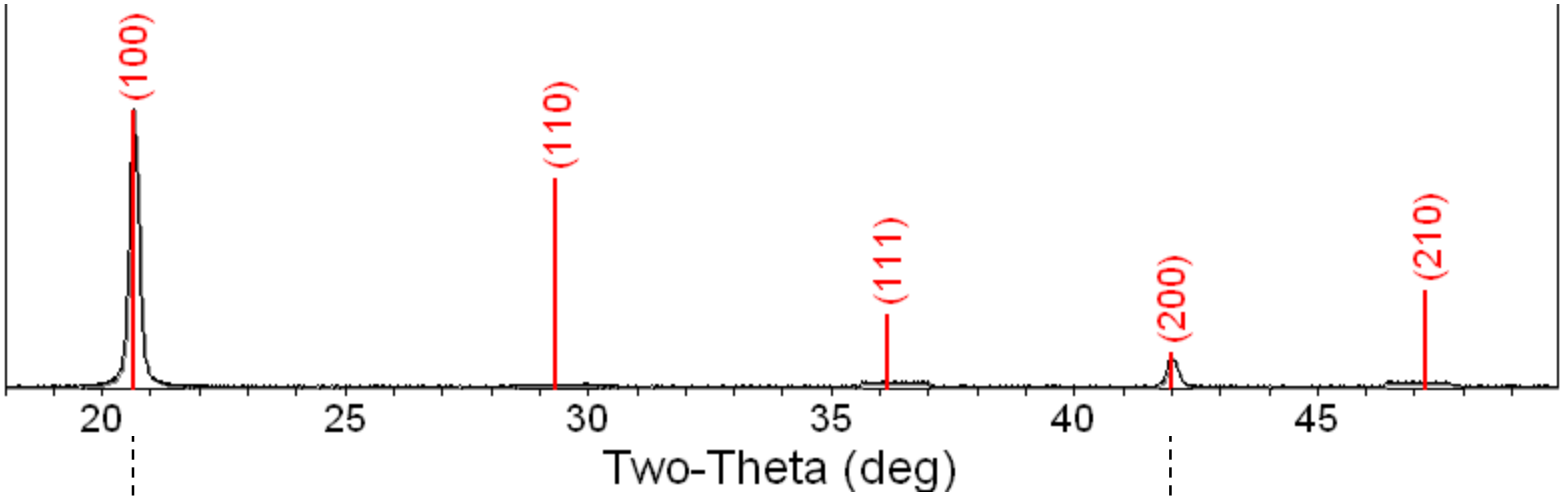
branches grow epitaxially –
each tree is a single crystal

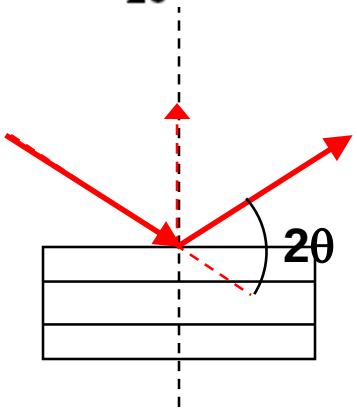
A polycrystalline sample should contain thousands of crystallites. Therefore, all possible diffraction peaks should be observed.



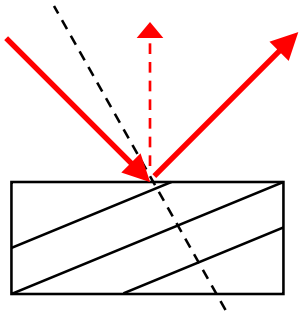
- For every set of planes, there will be a small percentage of crystallites that are properly oriented to diffract (the plane perpendicular bisects the incident and diffracted beams).
- Basic assumptions of powder diffraction are that for every set of planes there is an equal number of crystallites that will diffract and that there is a statistically relevant number of crystallites, not just one or two.

A single crystal specimen in a Bragg-Brentano diffractometer would produce only one family of peaks in the diffraction pattern.

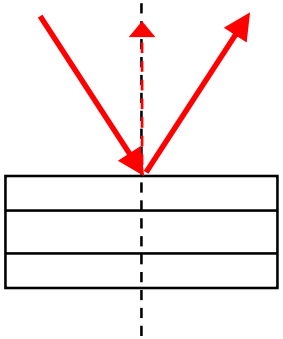




At 20.6 °2θ, Bragg's law fulfilled for the (100) planes, producing a diffraction peak.



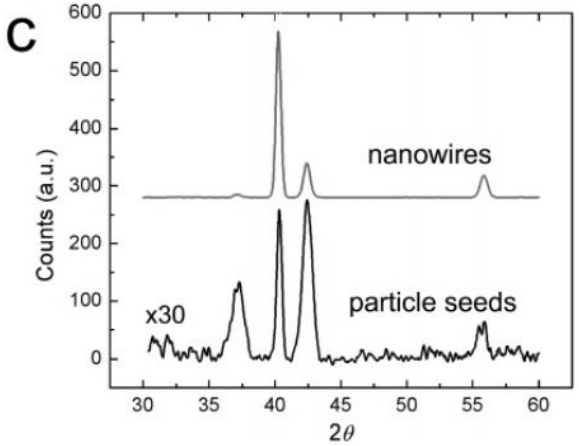
The (110) planes would diffract at 29.3 °2θ; however, they are not properly aligned to produce a diffraction peak (the perpendicular to those planes does not bisect the incident and diffracted beams). Only background is observed.

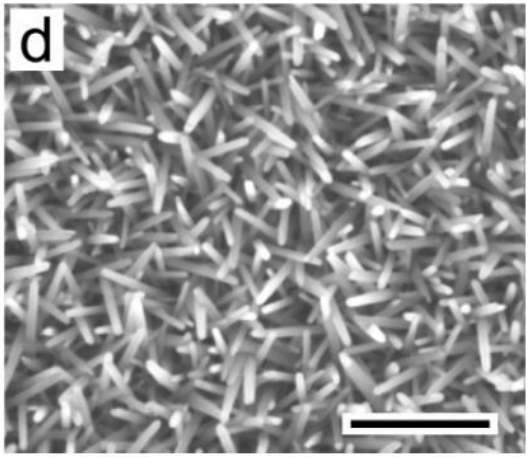


The (200) planes are parallel to the (100) planes. Therefore, they also diffract for this crystal. Since d_{200} is ½ d_{100}, they appear at 42 °2θ.

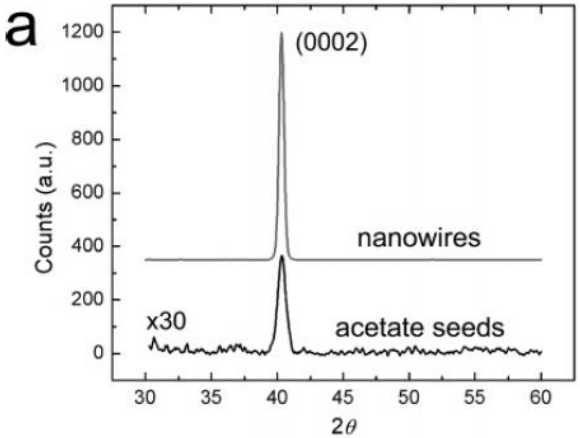
Wurtzite ZnO nanowire arrays on glass

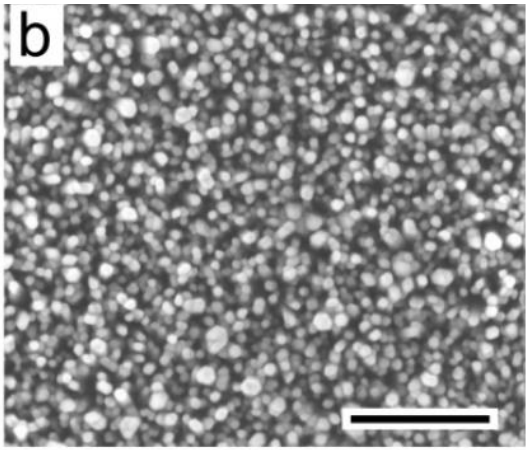
Poor uniaxial texture

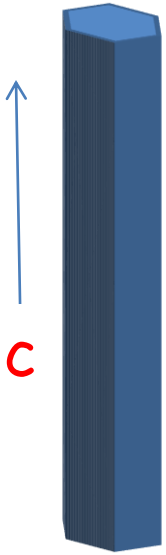




Good uniaxial texture



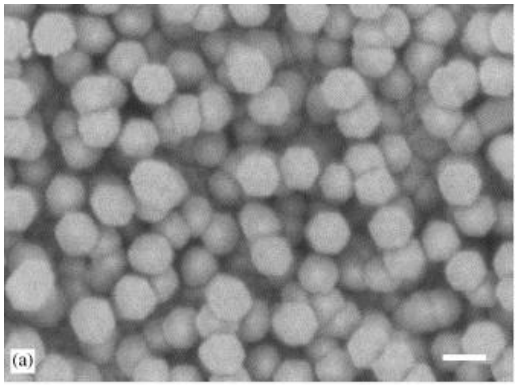




General route to vertical ZnO nanowire arrays using textured ZnO seeds.

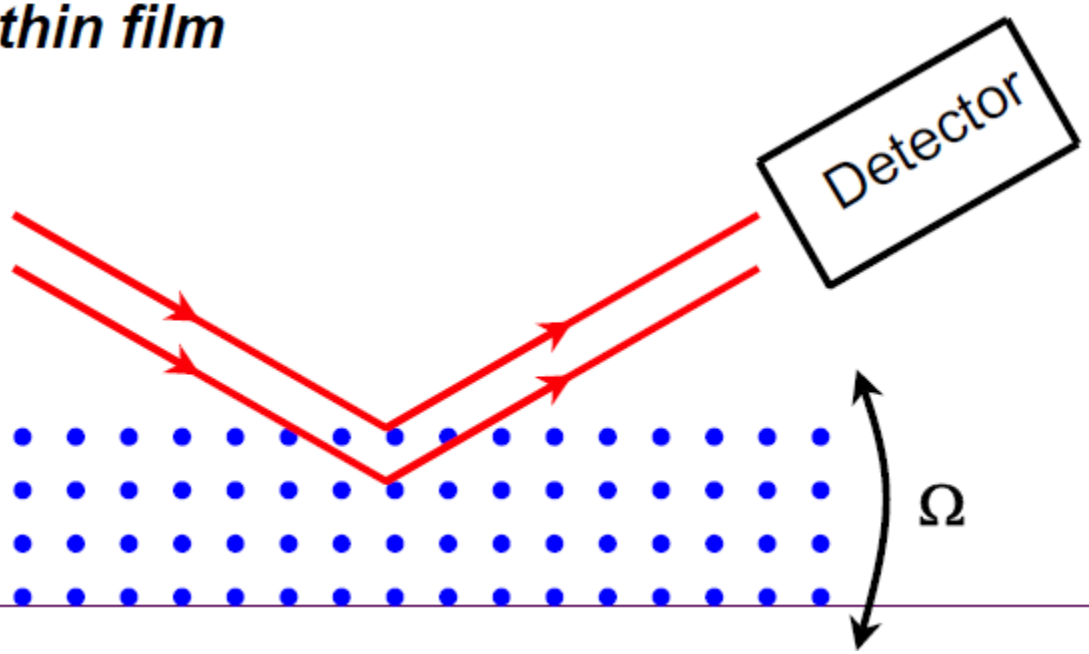
Greene, L. E., Law, M., Tan, D. H., Montano, M., Goldberger, J., Somorjai, G., Yang, P. *Nano Letters* 5, 1231-1236 (2005).

Biaxial texture (growth on Al_2O_3)



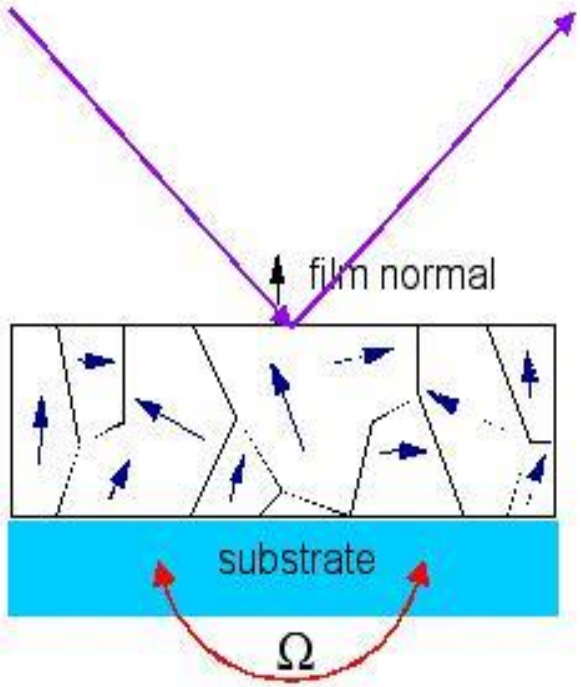
ROCKING CURVES

- ***The detector is fixed at 2θ position***
- ***The sample is scanned around θ***
- ***The defects in the sample will cause the width of the peak broaden***
- ***Rocking curve is usually used to indicate the quality of the thin film***

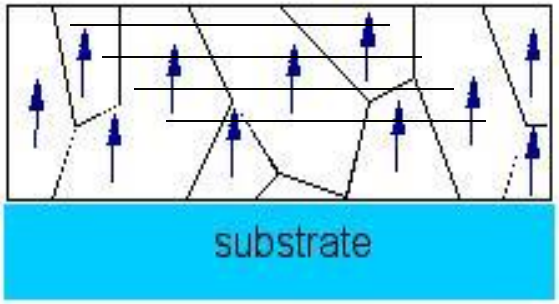


ROCKING CURVES

Ω-scans and thin film texture

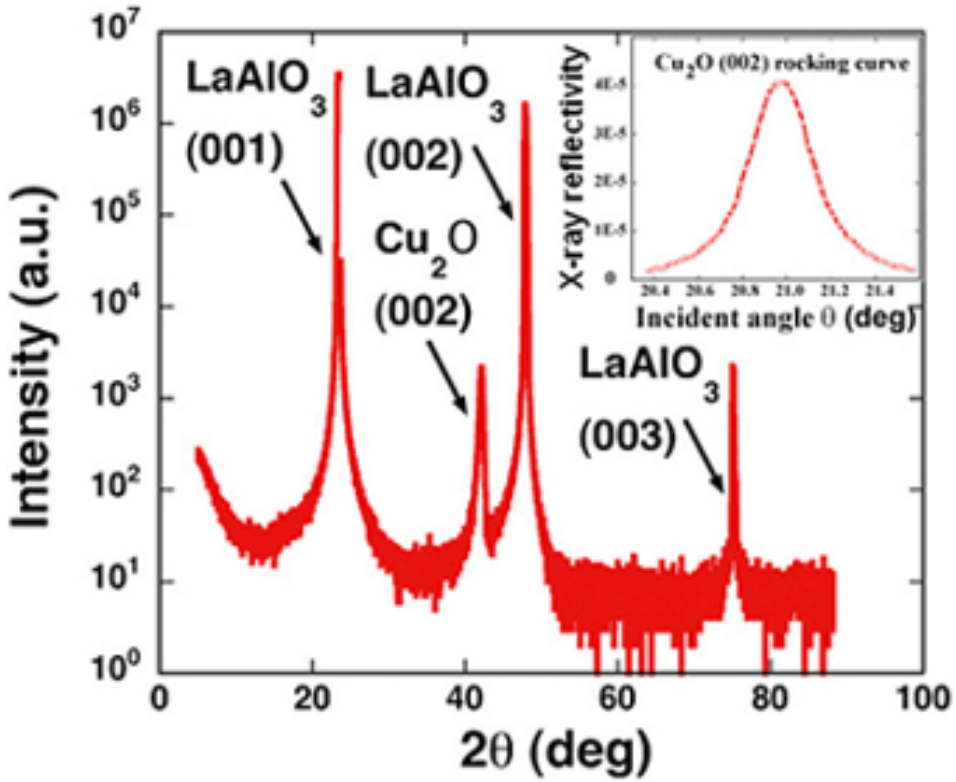


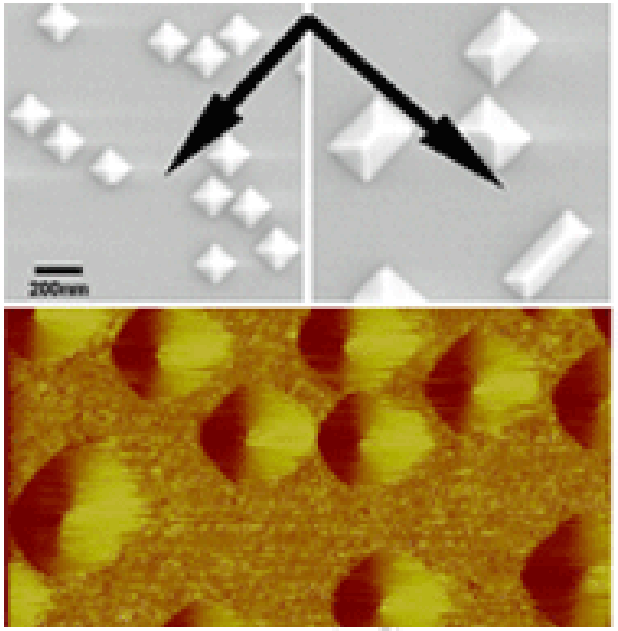
- **Untextured**
  - No intensity variation with Ω
  - will give theoretical powder intensities

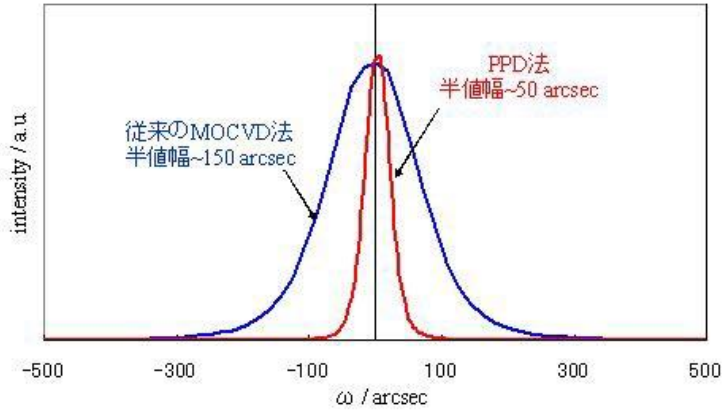


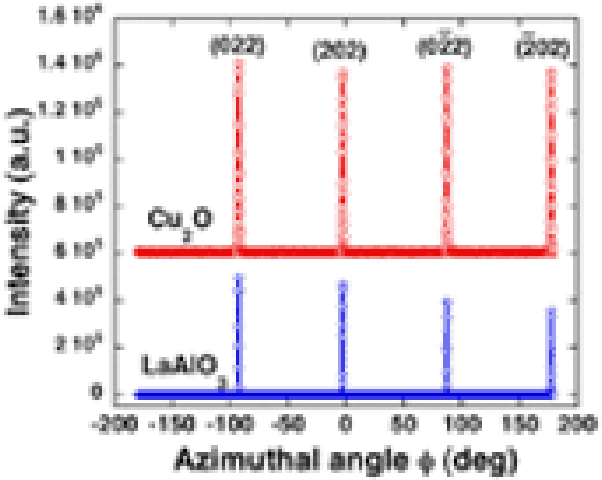
- **Textured**
  - Maximum intensity when lattice planes aligned with normal to bisector
  - Rate of decrease with Ω a measure of alignment
  - Ω-scan known as a rocking curve

ROCKING CURVE EXAMPLES



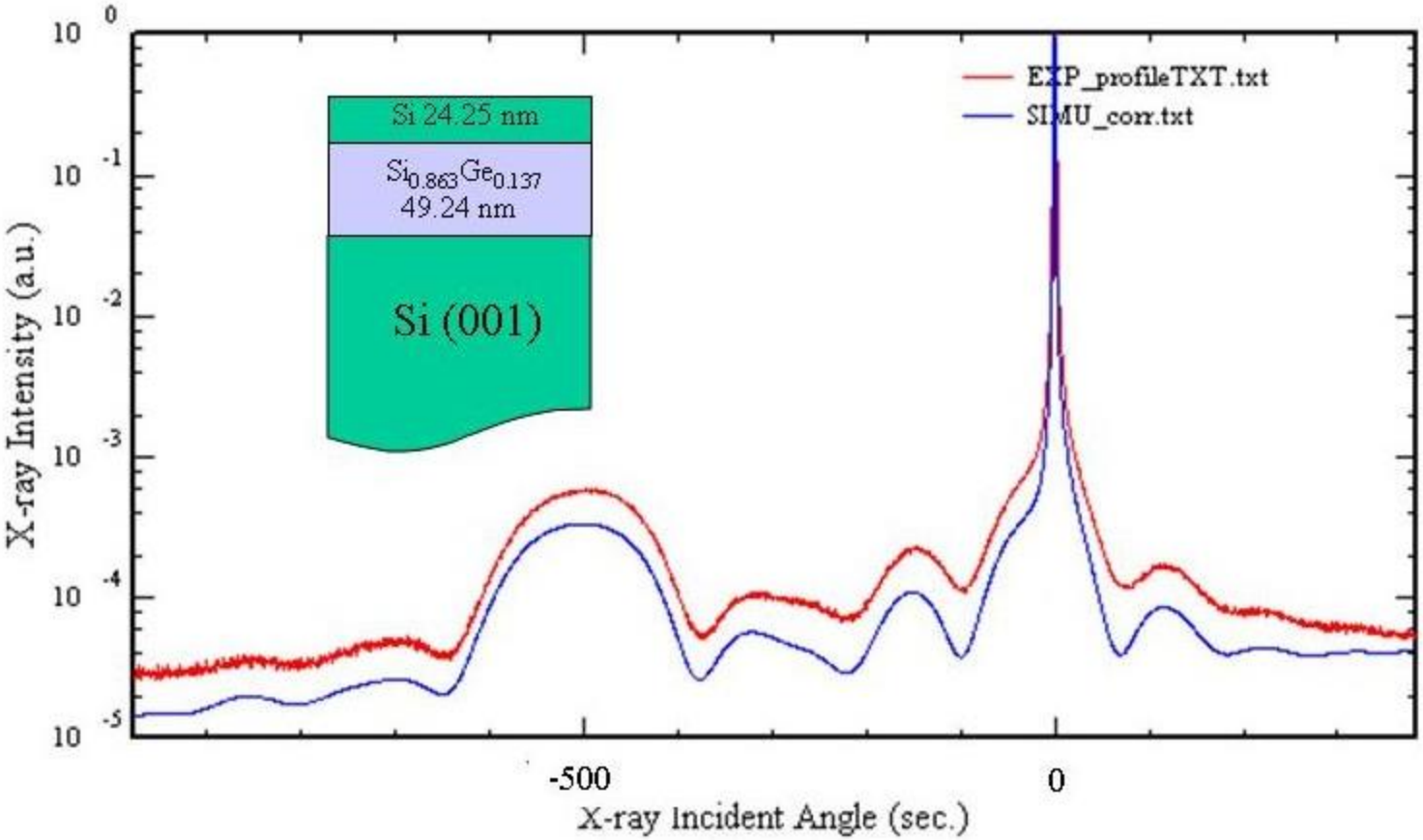






Thickness, composition, and strain state of epitaxial single crystal films

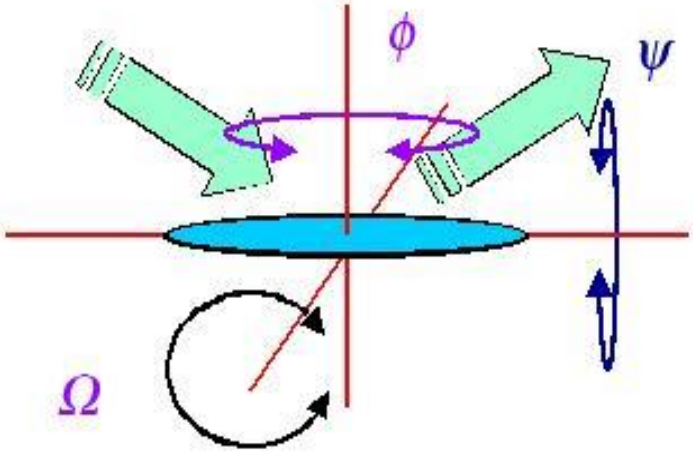
ROCKING CURVE EXAMPLE



(1° = 3600 arcsec)

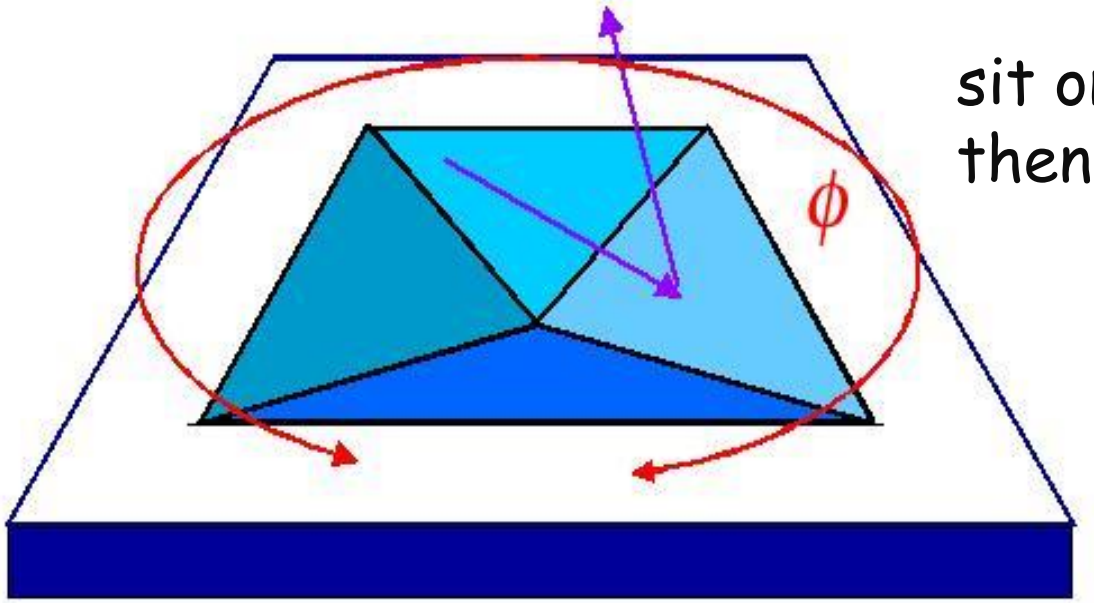
Thickness, composition, and strain state of epitaxial single crystal films

PHI SCANS



ϕ– scan

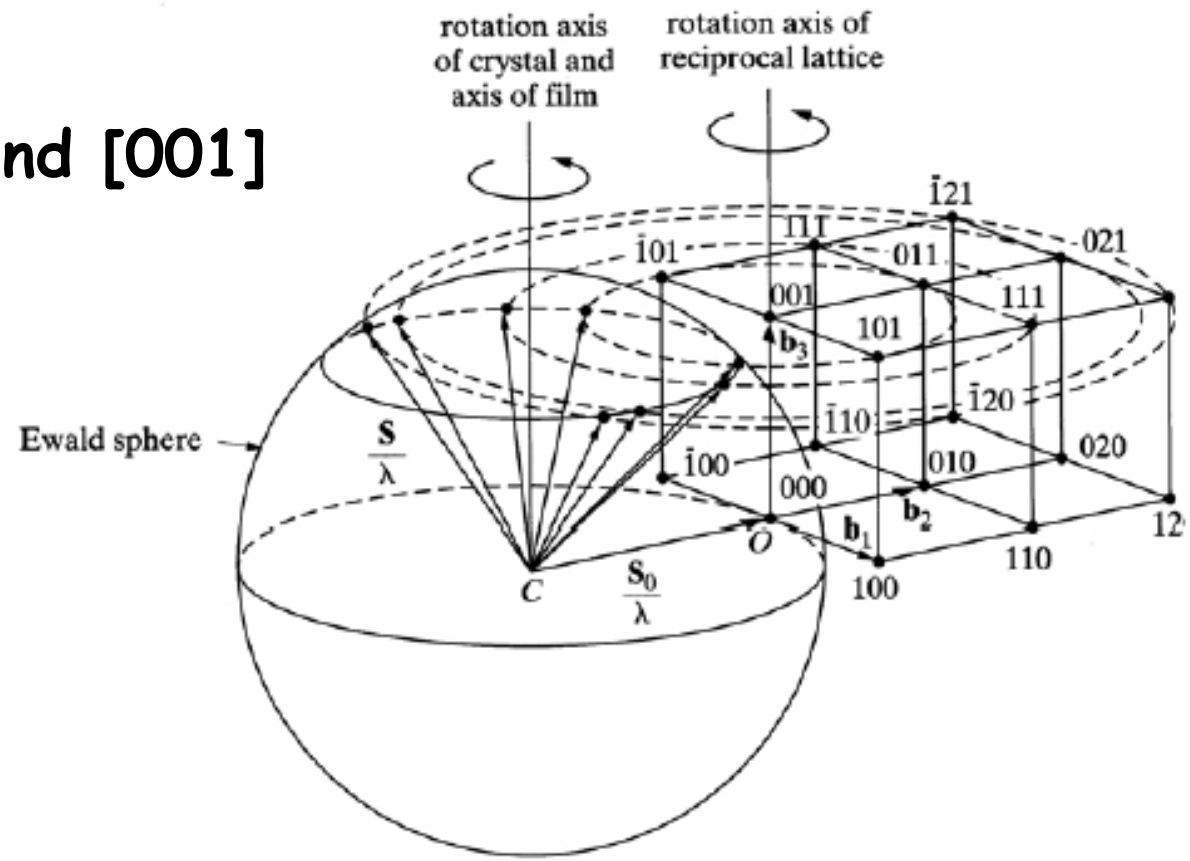
- Asymmetric reflections from powder sample
  - ϕ irrelevant
- Oriented sample
  - Depends on ϕ
- ϕ– scan enables measurement of orientation



sit on a reflection, then rotate in-plane

k-SPACE GEOMETRY

for rotation around [001] of cubic crystal:



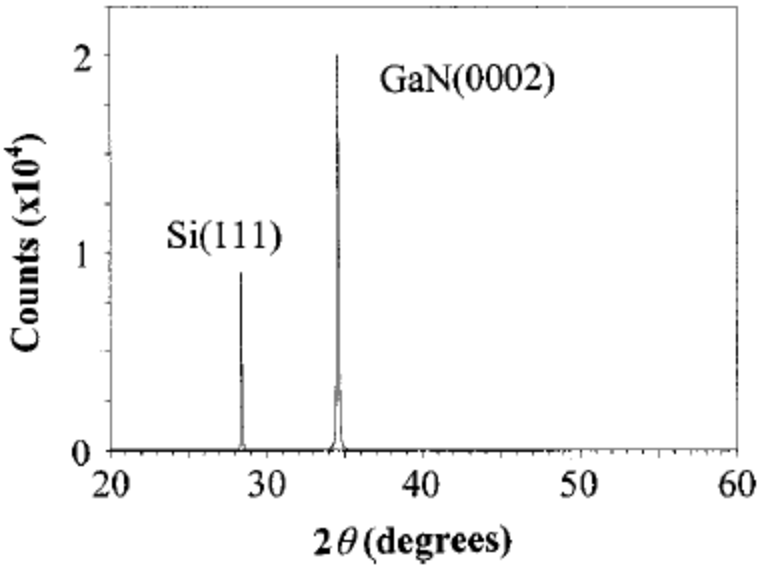
two examples:

monitor {011}: expect 4 peaks separated by 90° rotation.

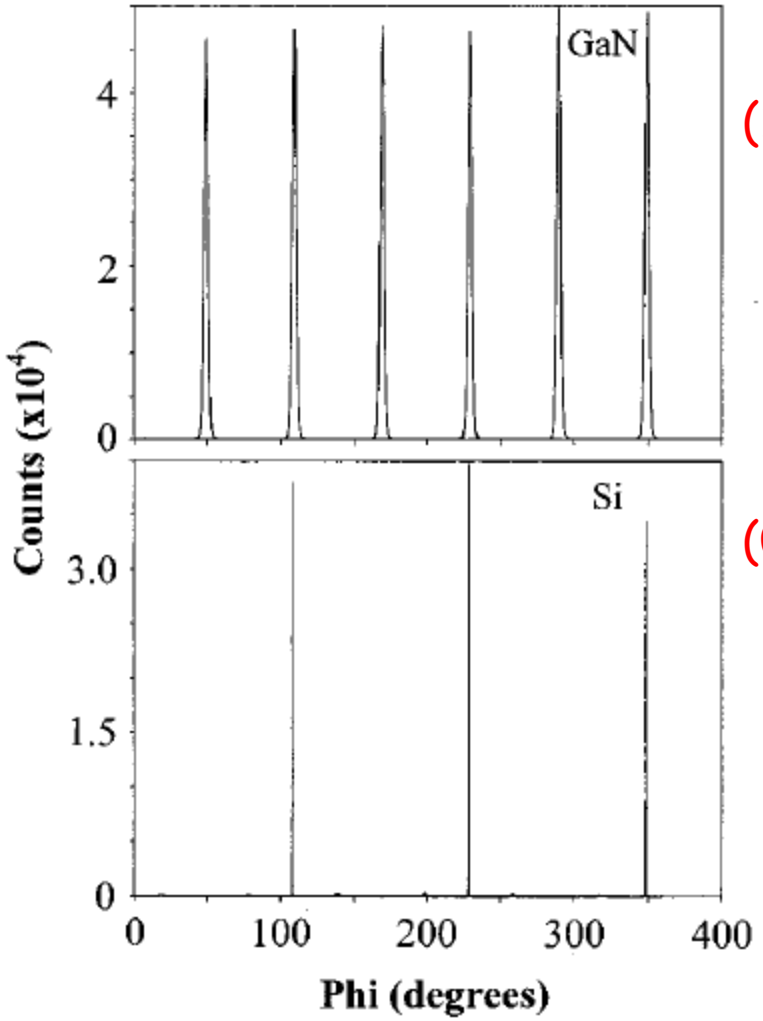
monitor {111}: expect 4 peaks separated by 90° rotation.
(ignoring possible systematic absences)

PHI SCAN EXAMPLE

1 um GaN (wurtzite) on Silicon(111)

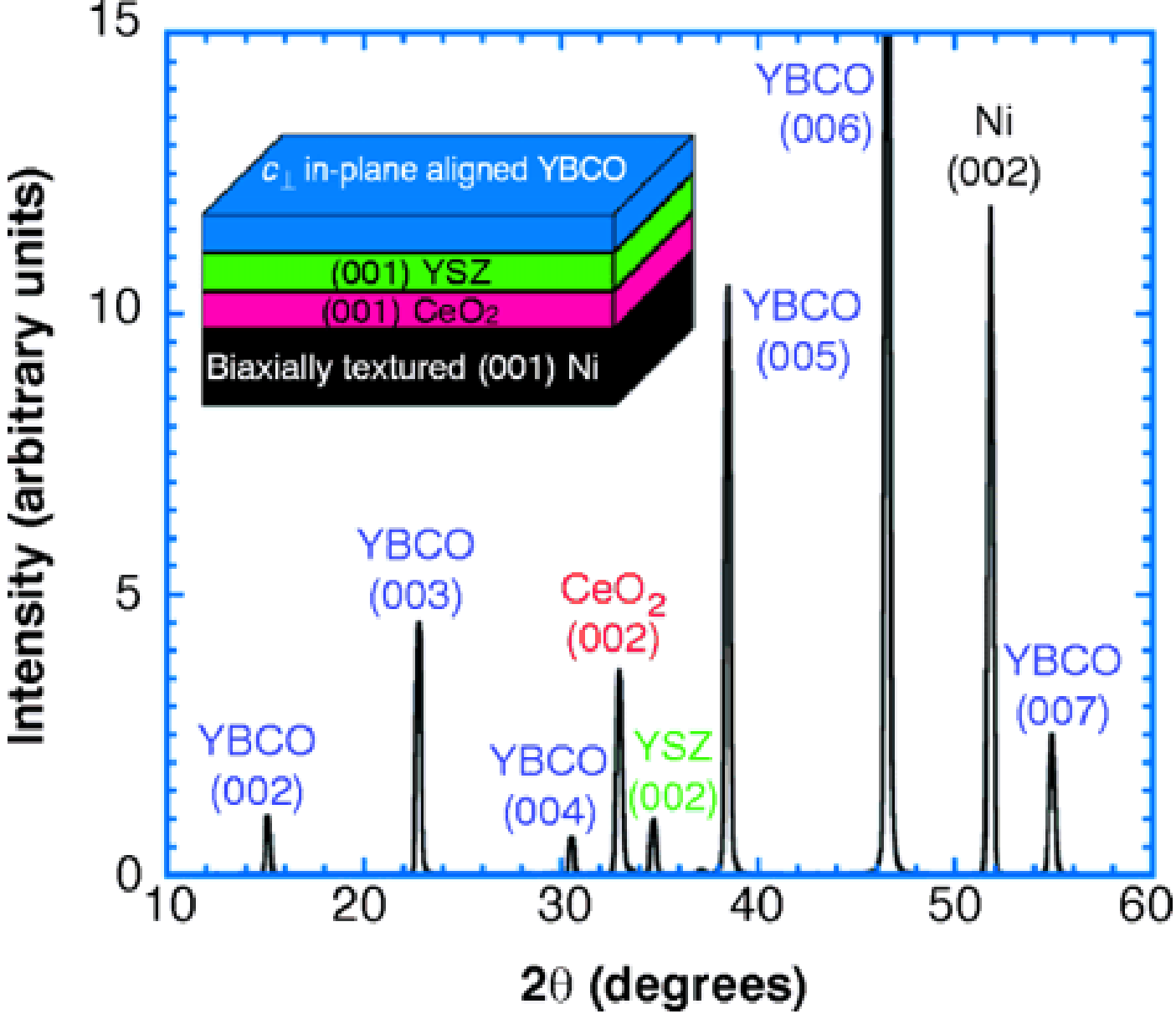


2-theta scan proves
uni-axial texture



phi scan proves
bi-axial texture (epitaxy)

In plane alignment: GaN[11$\bar{2}$0]//Si[1$\bar{1}$0]

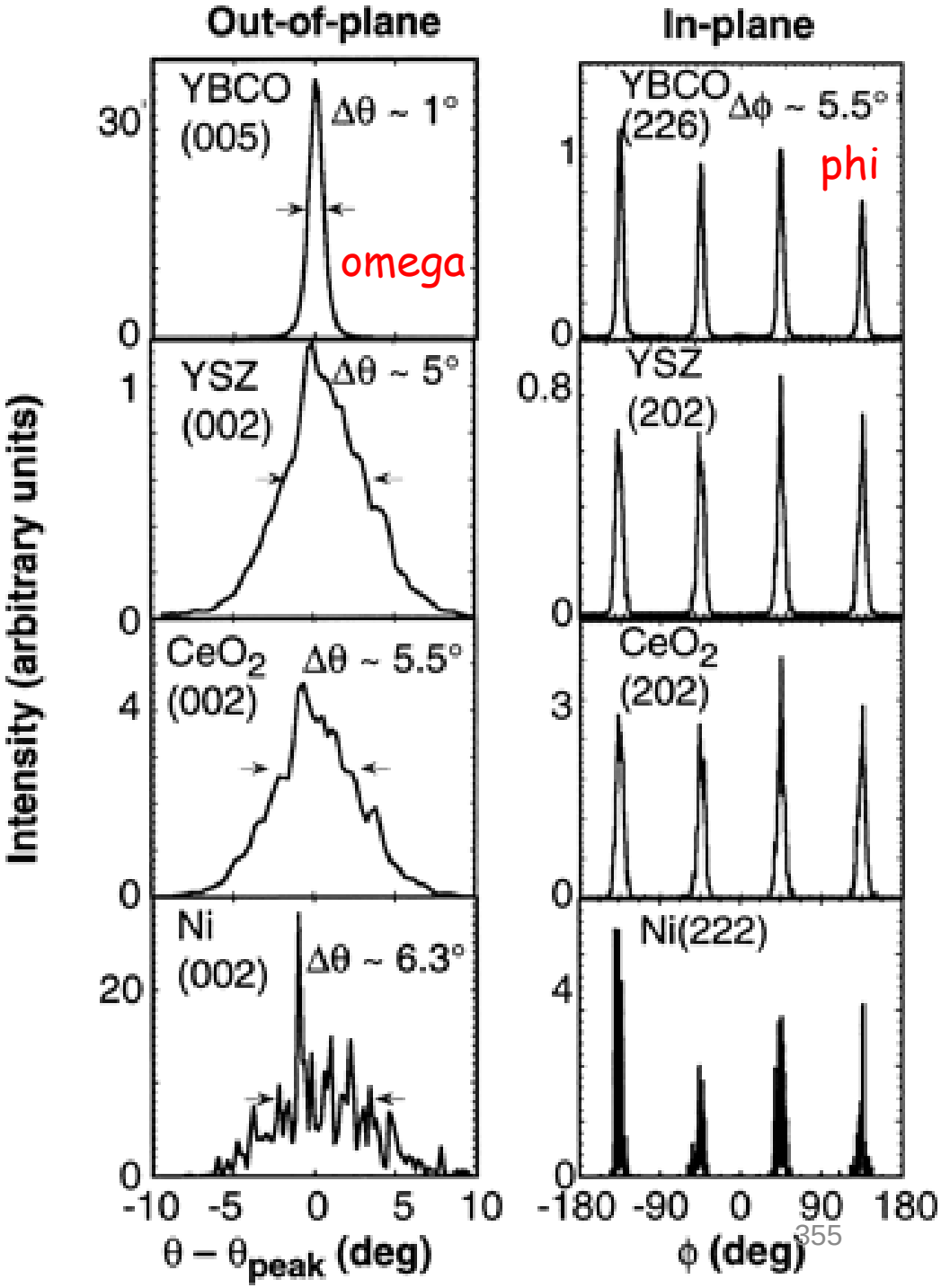


Epitaxial $YBa_2Cu_3O_7$ on Biaxially Textured Nickel (001):
An Approach to Superconducting Tapes with High Critical Current Density

Science, Vol 274, Issue 5288, 755-757 , 1 November 1996

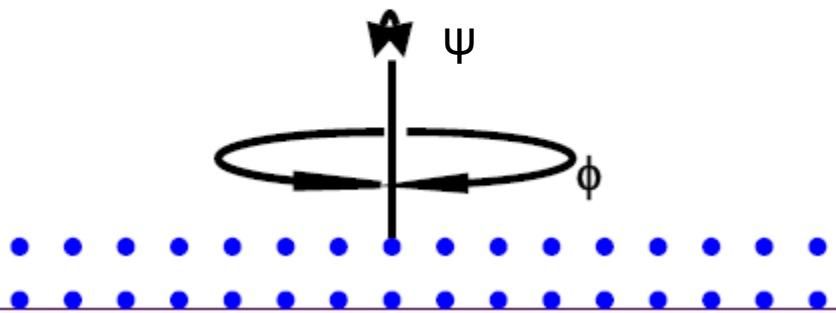
Epitaxial $YBa_2Cu_3O_7$ on Biaxially Textured Nickel (001): An Approach to Superconducting Tapes with High Critical Current Density

Science, Vol 274, Issue 5288, 755-757 , 1 November 1996



TEXTURE MEASUREMENT (POLE FIGURES)

- ***A texture measurement is also called a pole figure***
- ***It is plotted in polar coordinates around a given crystallographic orientation***
- ***The detector is fixed at 2θ position***
- ***The sample is scanned by in-plane rotation around the plane normal at different azimuthal angles***
- ***Texture measurement is used to determine the orientation distribution in a polycrystalline sample***

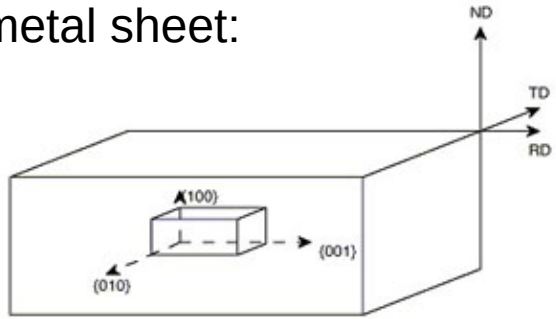


POLE FIGURES

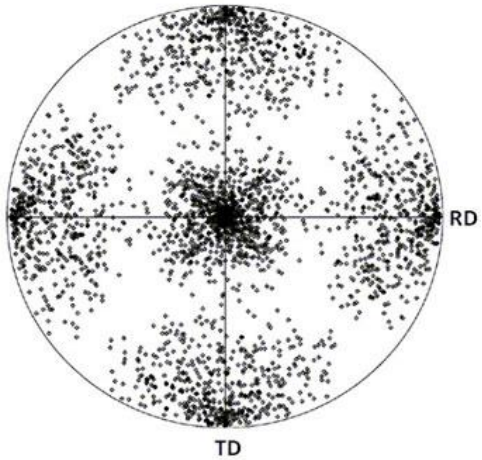
stereograms showing all poles of a particular *hkl* plane, with axes defined by an external frame of reference.

- pole figures map the intensity of a single *hkl* as a function of tilt and rotation of the sample
- most common way to map crystallographic texture

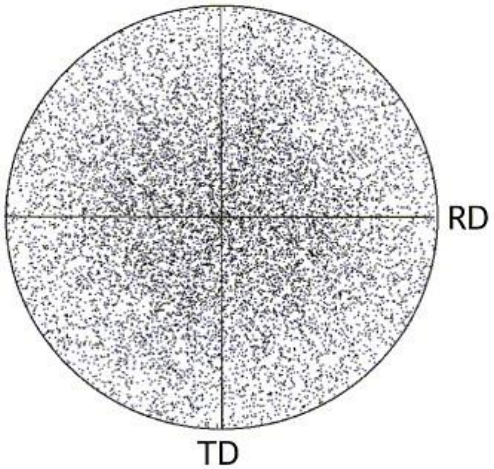
e.g., a textured polycrystalline rolled metal sheet:



textured sheet

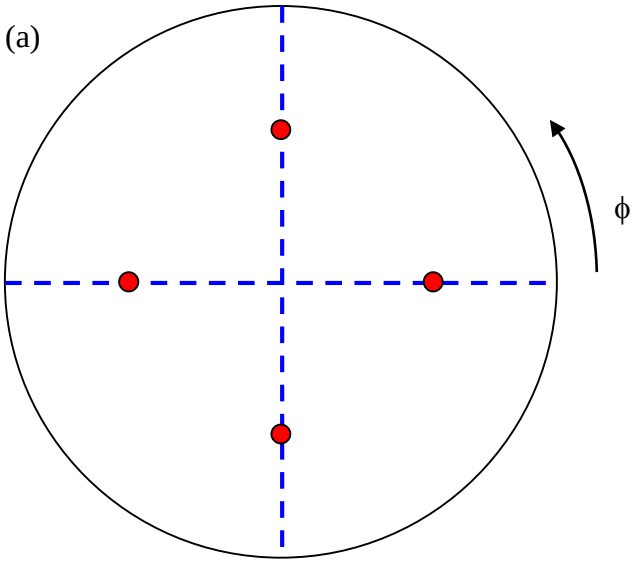


untextured sheet

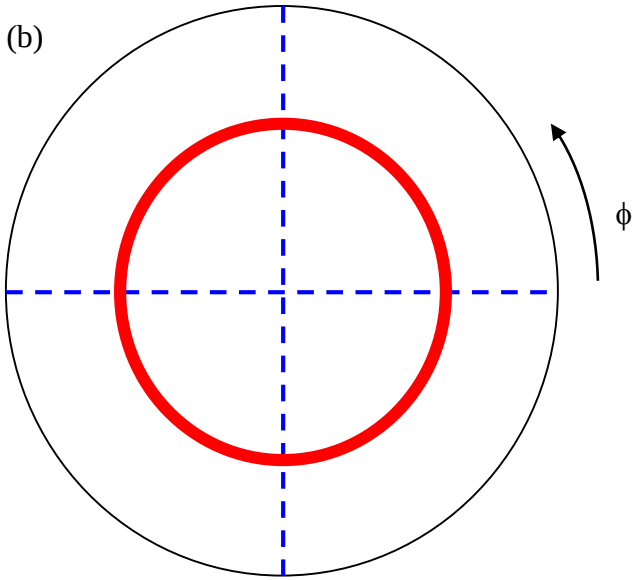


POLE FIGURE EXAMPLE – PHI ONLY

Example: c-axis aligned superconducting thin films.



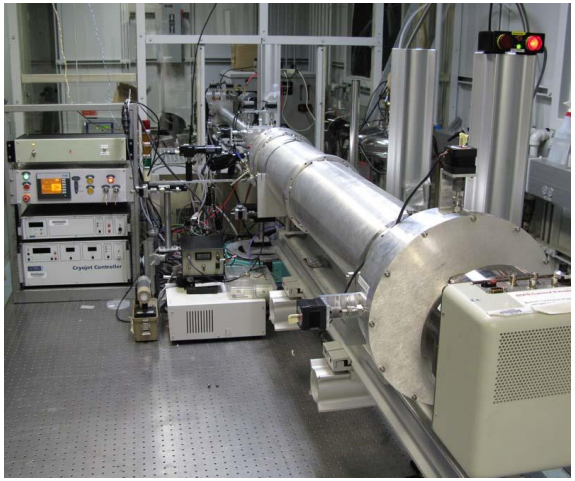
Biaxial Texture (105 planes)

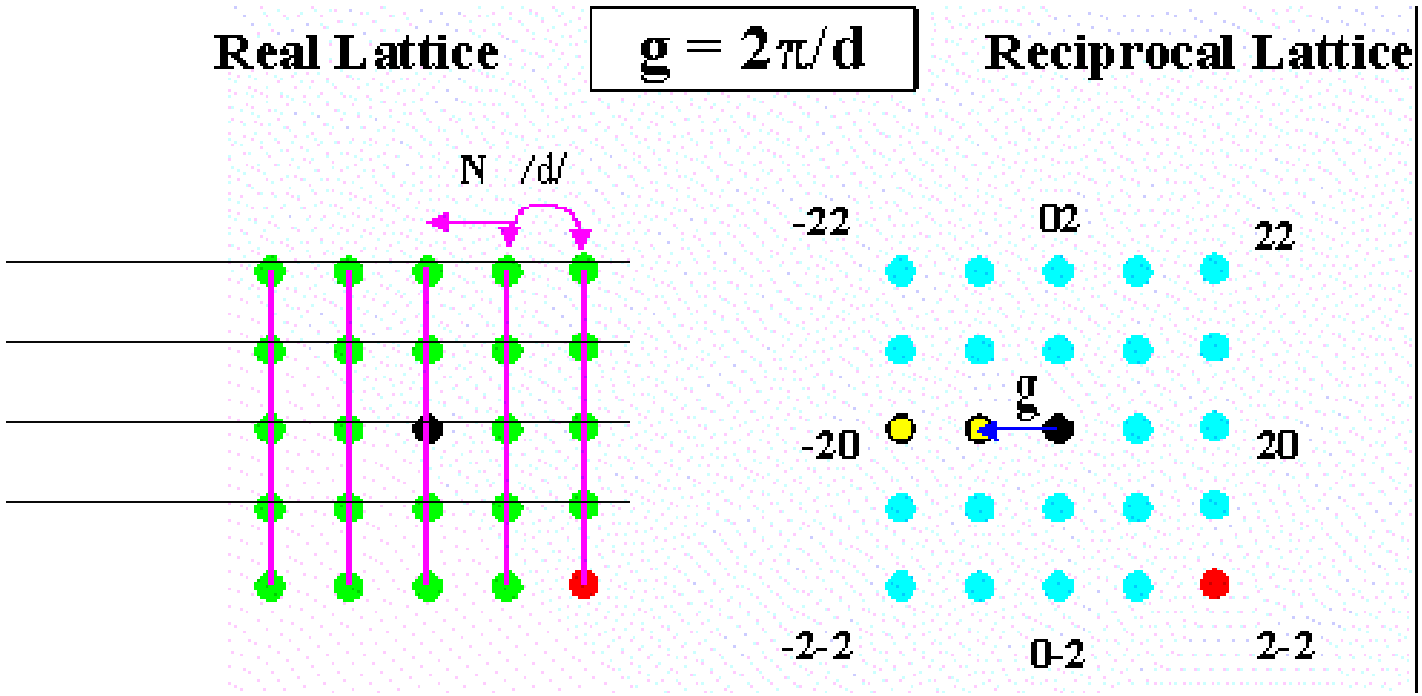


Random in-plane alignment

SMALL ANGLE X-RAY SCATTERING

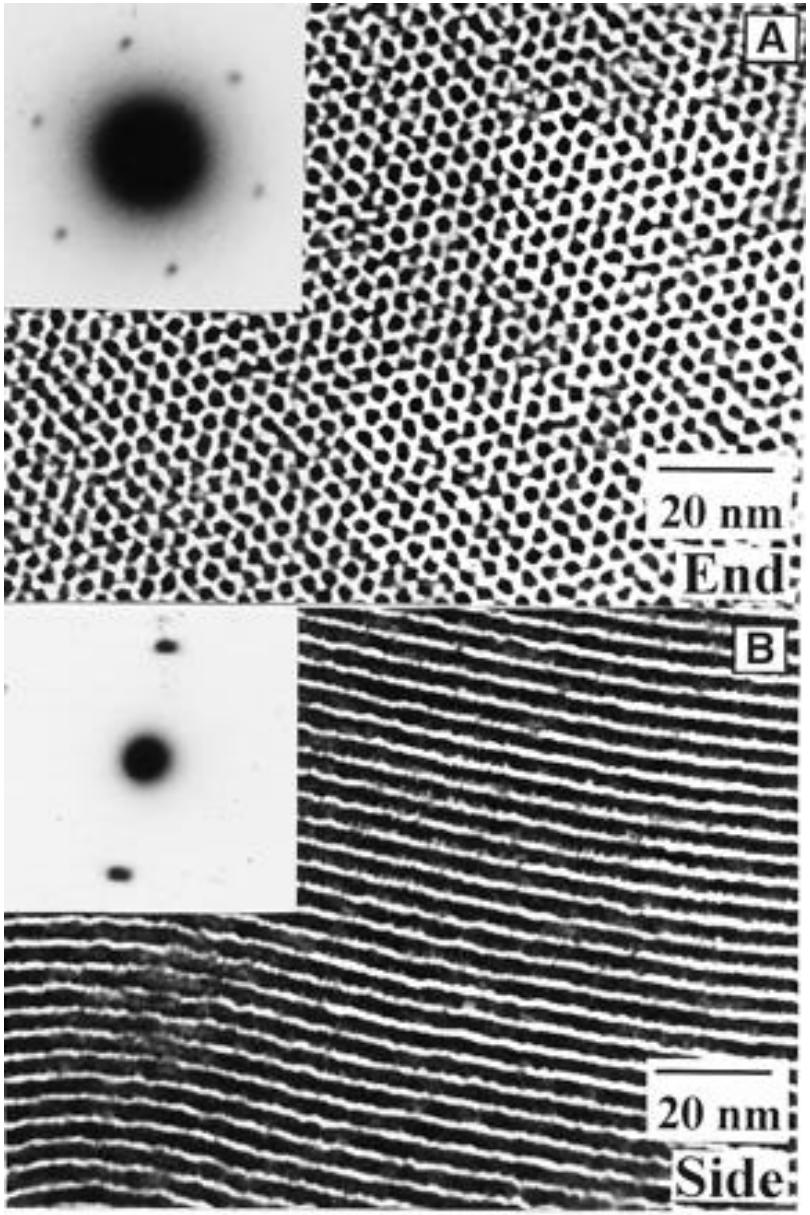
- ***SAXS technique is commonly used for large length scale structures such as self-assembled superlattices***
- ***From Bragg's law, $2d\sin\theta=n\lambda$, the scattering angle will be small for the same x-ray wavelength if the periodicity is large***
- ***SAXS typically has scattering angle $2\theta<1°$***
- ***Due to the small angular separation of the direct beam and the scattered beam, to achieve good signal-to noise ratio:***
  - *Large sample-to-detector distances*
  - *High quality collimating optics*



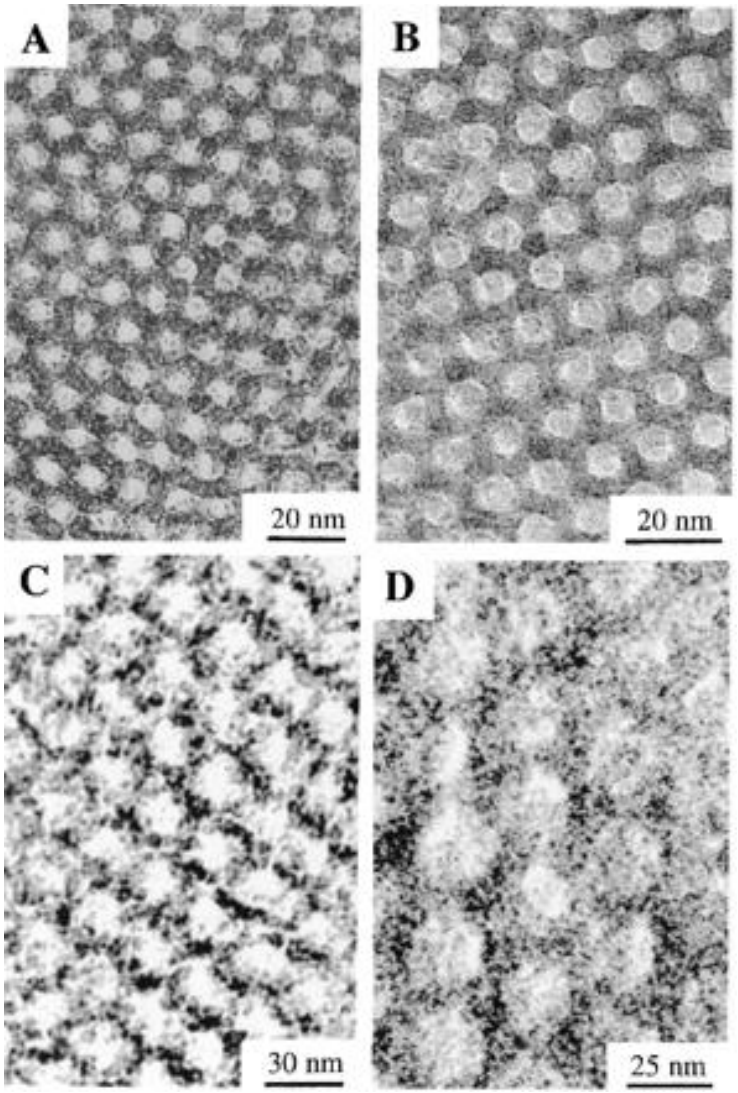


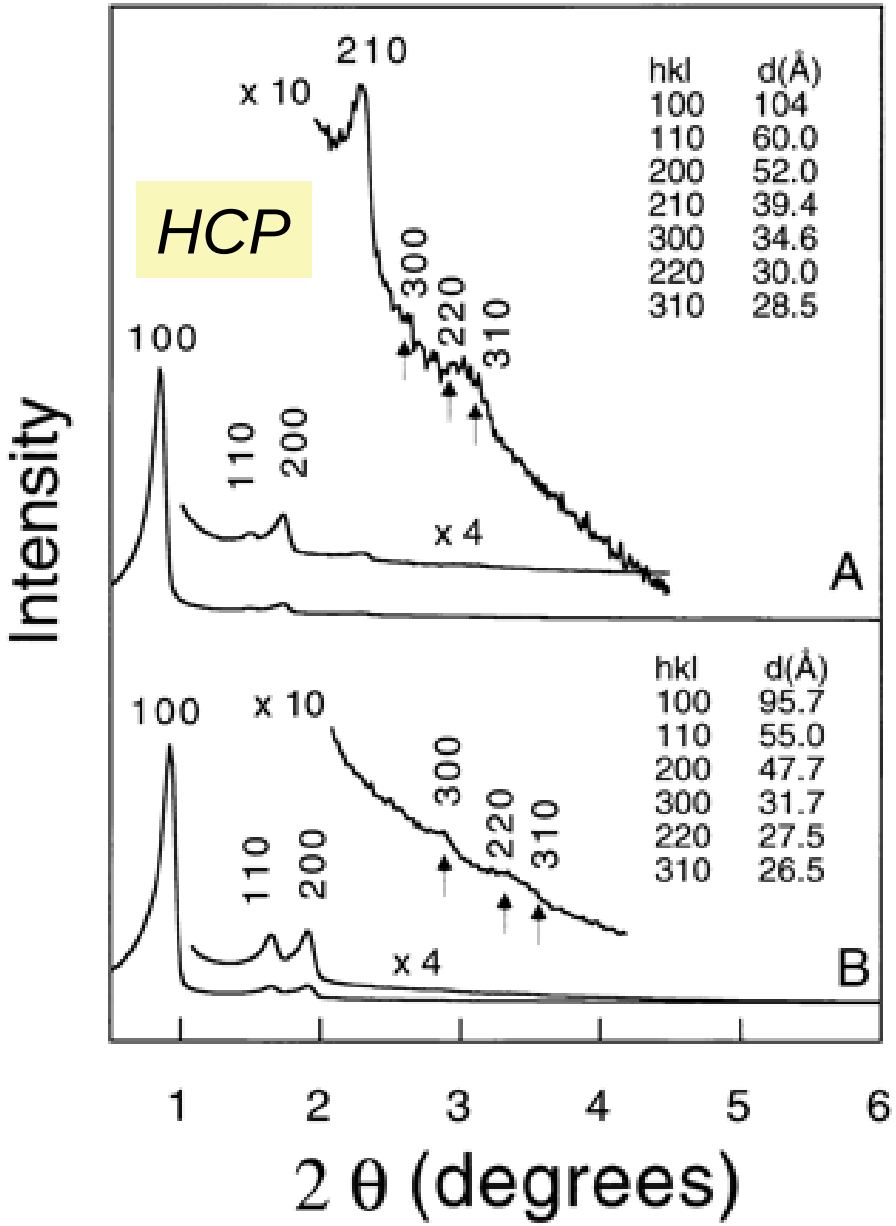
SAXS: diffraction from planes with > 1 nm d-spacing

Small Angle X-ray Diffraction



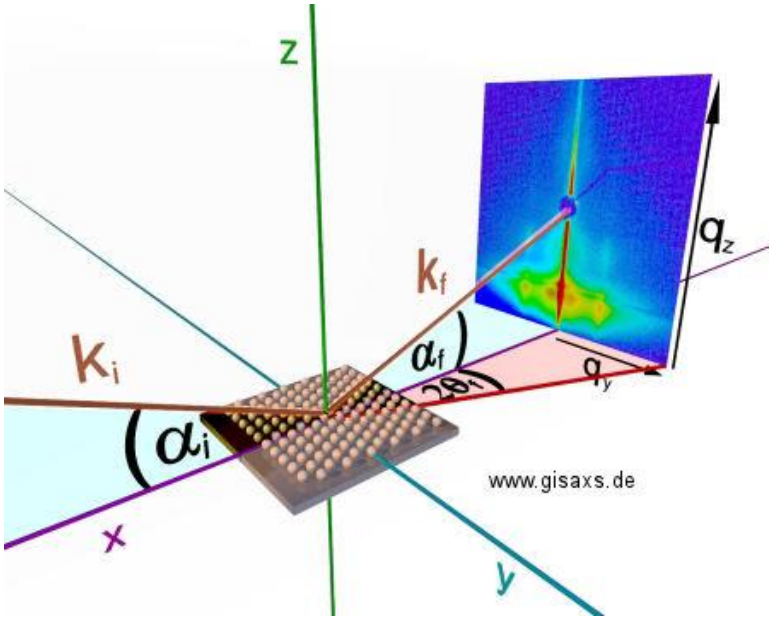
Direct Visualization of Individual Cylindrical and Spherical Supramolecular Dendrimers
Science 17 October 1997; 278: 449-452

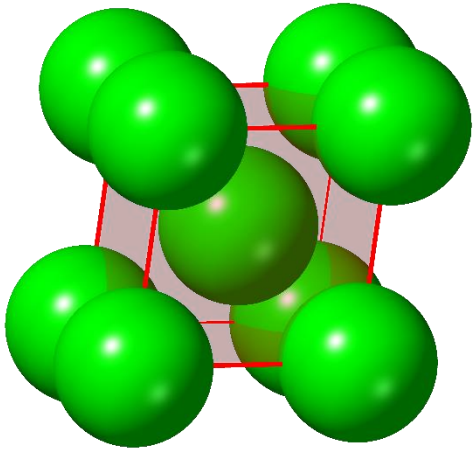


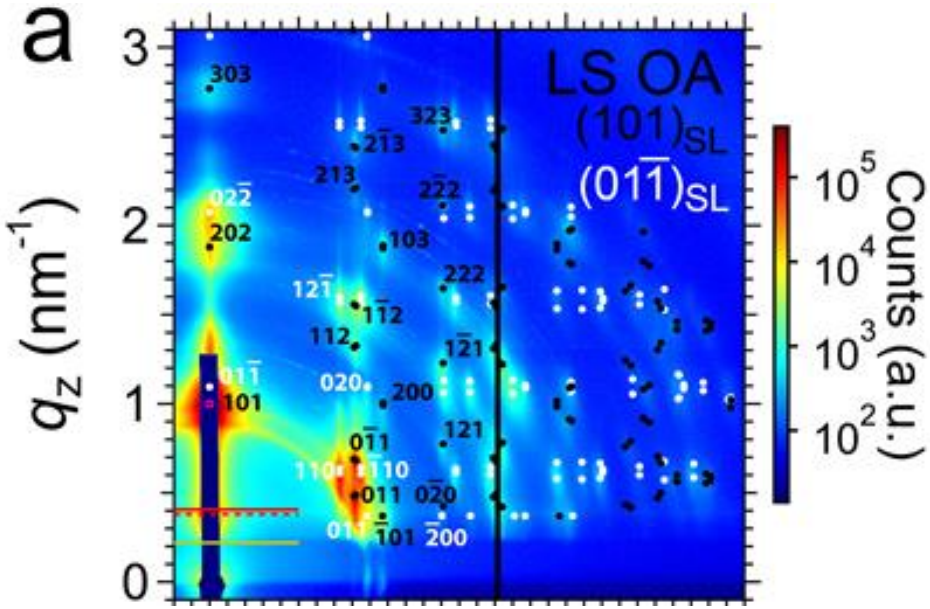


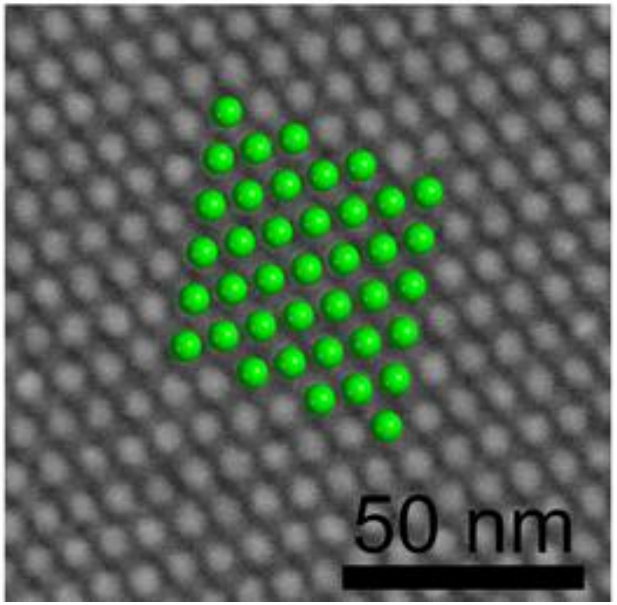
Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores Science, Vol 279, Issue 5350, 548-552 , 23 January 1998

GRAZING INCIDENCE SAXS (GISAXS)



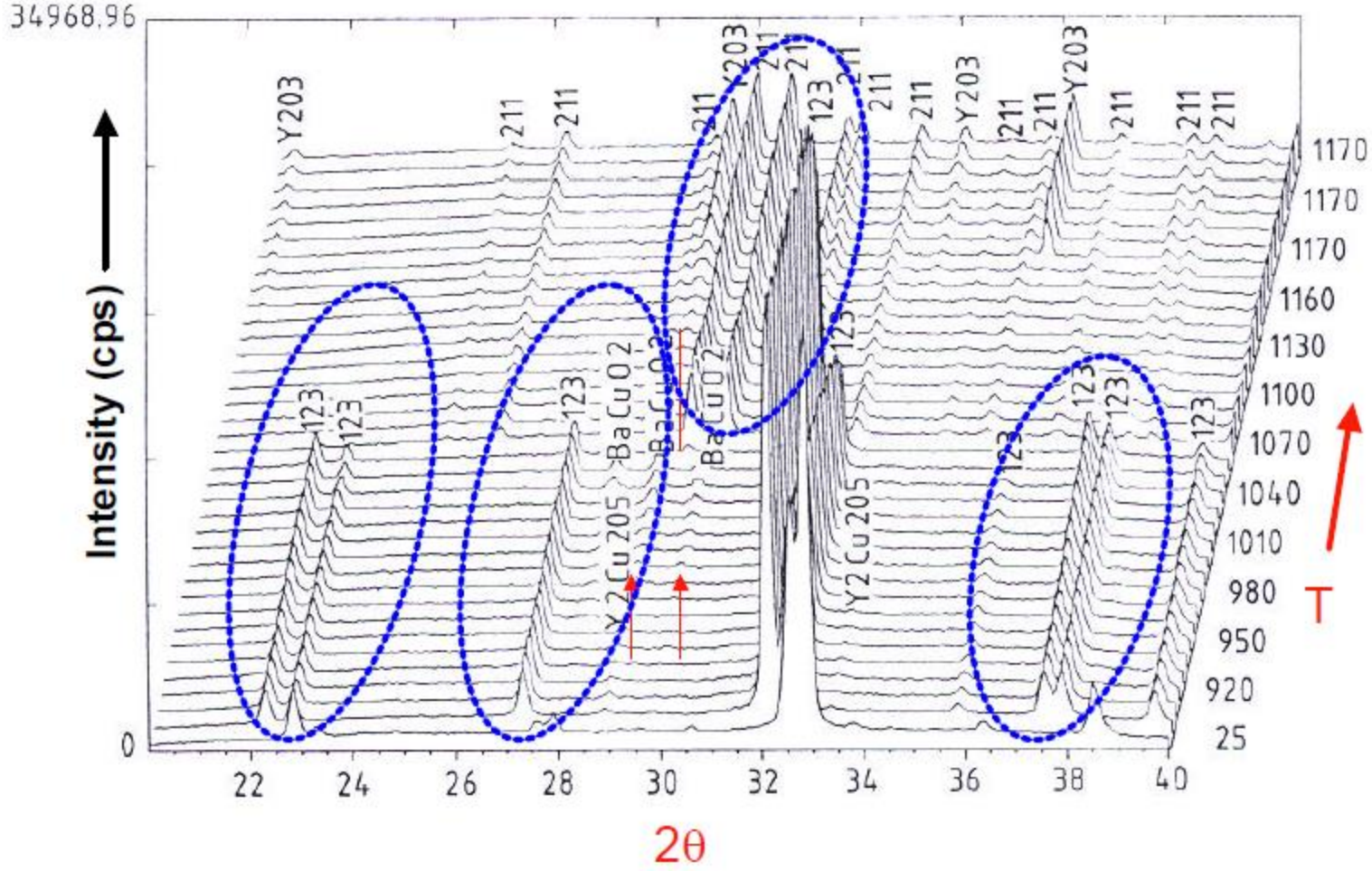






IN-SITU X-RAY DIFFRACTION

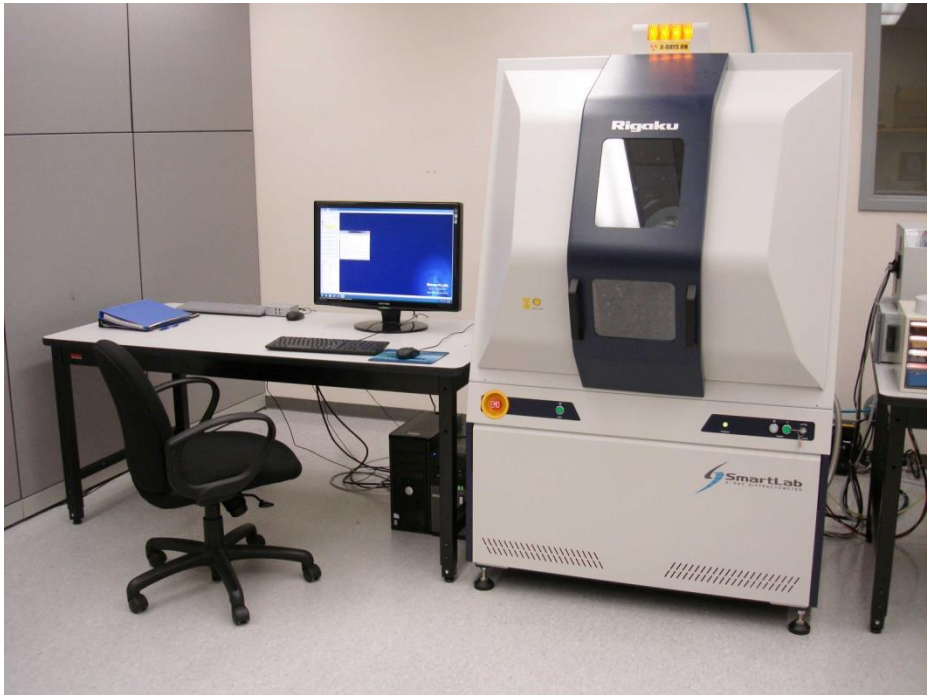
High Temperature XRD Patterns of the Decomposition of $YBa_2Cu_3O_{7-\delta}$



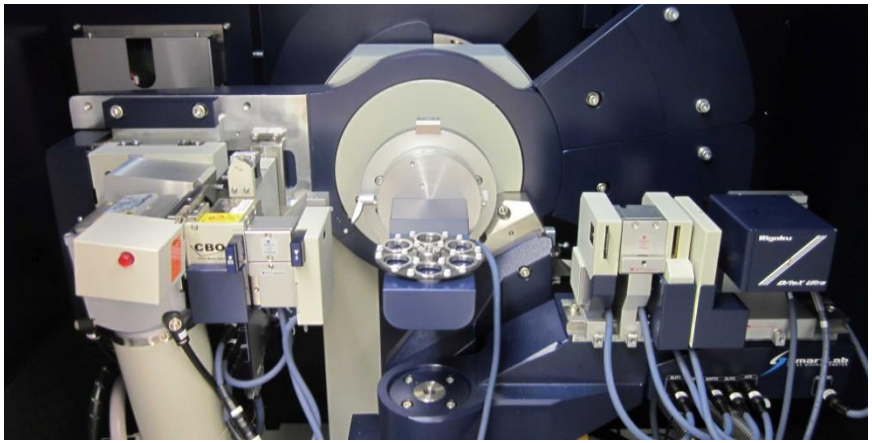
Laboratory for Electron and X-ray Instrumentation
UCI's Materials Characterization User Facility

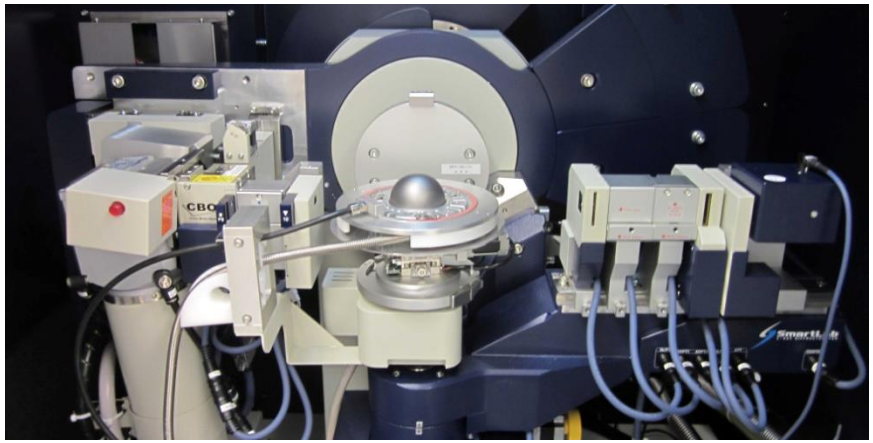
UCI XRD

Rigaku SmartLab XRD



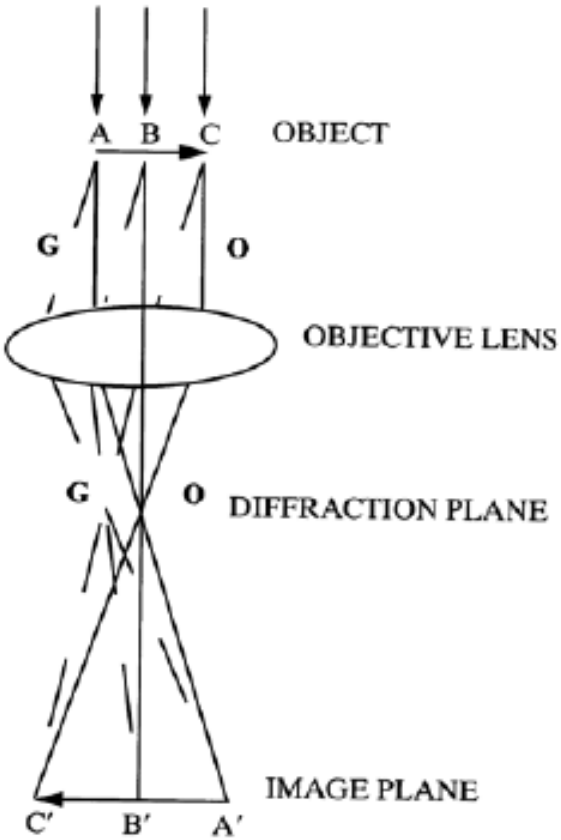
- 0D, 1D, 2D detectors
- In-plane & Out-of-plane
- Thin-film XRD
- High resolution XRD
- SAXS
- μ-XRD
- Capillary transmission
- 1500°C heating stage
- 1100°C dome stage

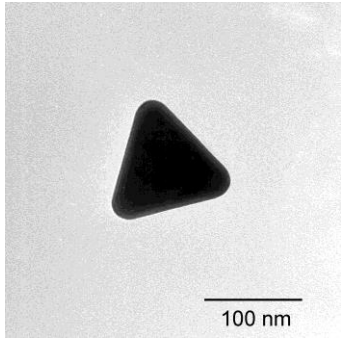


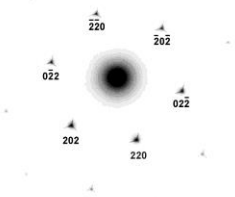


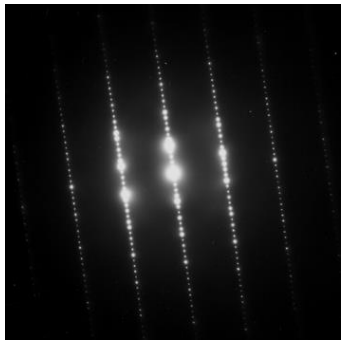
ELECTRON DIFFRACTION

In a TEM the electron beam hits the object being studied. Some electrons are diffracted and some pass through the sample. The objective lens focuses all the beams to points in the diffraction plane. So we would see a diffraction pattern here. The diffracted beams combine in the image plane to form an image. Other lenses can be used to form magnified images of either the diffraction or image planes.









Why ED patterns have so many spots

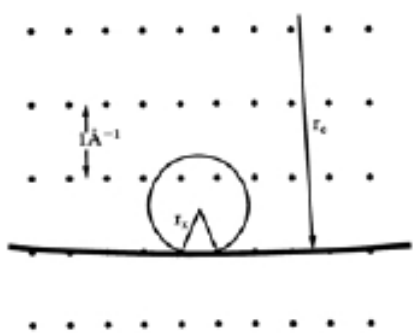
Typically, in X-ray or neutron diffraction only one reciprocal lattice point is on the surface of the Ewald sphere at one time.

In electron diffraction the Ewald sphere is not highly curved b/c of the very short wavelength electrons that are used. This nearly-flat Ewald sphere intersects with many reciprocal lattice points at once.

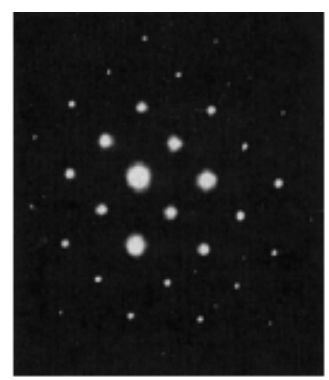
- In real crystals reciprocal lattice points are not infinitely small and in a real microscope the Ewald sphere is not infinitely thin

$$\lambda_{X\text{-}ray} = hc/E = 0.154 \text{ nm @ } 8 \text{ keV}$$

$$\lambda_{e-} = h/[2m_0eV(1 + eV/2m_0c^2)]^{1/2} = 0.0037 \text{ nm @ } 100 \text{ keV}$$



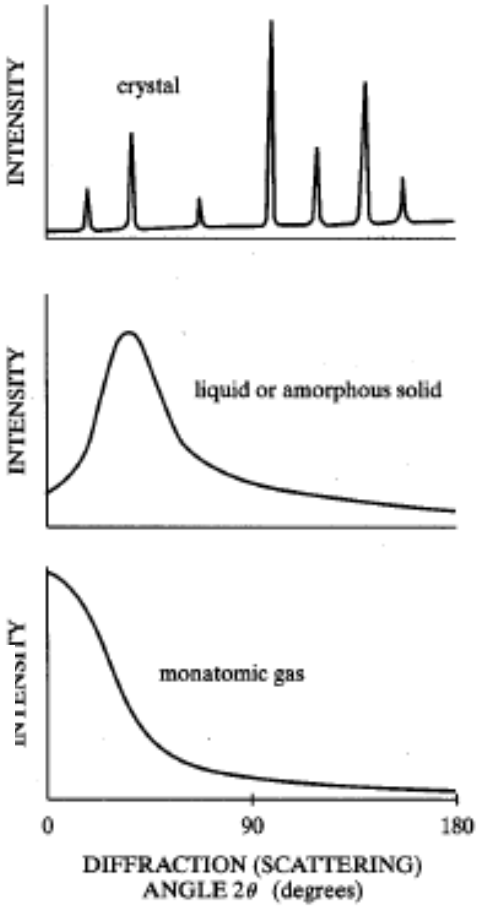
Ewald sphere for Cu radiation is much more curved than that for electrons in an electron diffraction experiment



Electron Diffraction pattern from NiAl

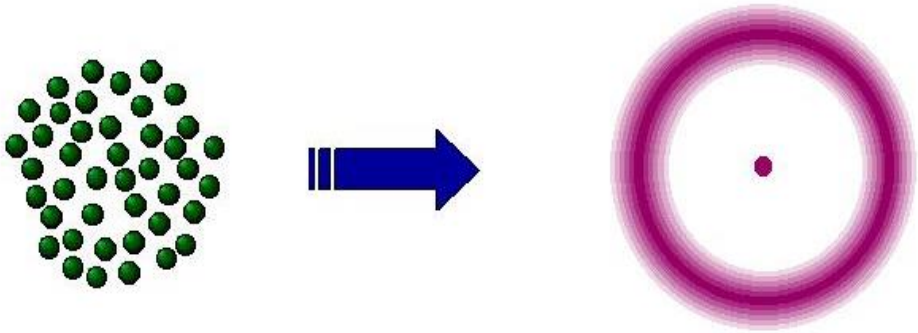
DIFFRACTION FROM DISORDERED SOLIDS

All materials scatter x-rays, even if they are not crystalline. Deviations from perfect periodicity spread the scattering out through reciprocal space, but there is still information about interatomic distances



amorphous solids

- **No long-range order**
  - Only significant order is nearest neighbour spacing
  - Diffraction pattern forms diffuse halo
  - Typical of colloidal suspensions and globular clusters
- **Diffraction is large or small angle depending on the size of the "particle"**



DIFFRACTION: WHAT YOU SHOULD KNOW

Index planes
Calculate crystal density
Calculate d-spacings
Derive/use Bragg's Law
Index diffraction peaks
Determine lattice constants
Reciprocal lattice
Ewald sphere construction
Calculate structural factors, predicting X-ray diffraction pattern (systematic absences)
Use of Scherrer relation

Term Paper and Presentation

Choose a contemporary materials topic that interests you. For example:

- Organic LEDs
- Metamaterials
- Multiferroics
- Graphene
- Photonic Crystals
- Amorphous Metals
- Colossal Magnetoresistance
- Synthetic Biomaterials
- Infrared Photodetectors
- Conducting Polymers
- Inorganic Solar Cells
- Plasmonics
- High κ Dielectrics
- Quantum Dots

In ≥10 pages of double-spaced text (+ figures and references):

1) <u>Quantitatively</u> explain the basic principles at work
2) Summarize the state-of-the-art in synthesis, properties, and apps
3) Identify a key challenge facing the field and propose an original solution to this challenge

Term Paper Due Dates

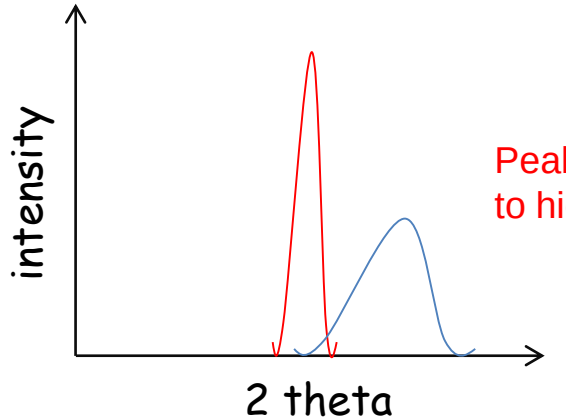
February 24: Topic selection. E-mail me with a one-paragraph abstract describing your topic, challenge, and proposed solution

8-10 am March 20: Paper submission and 5-minute presentation to educate the class on your topic.

Midterm Exam

- **February 19**
- full class period
- short answer questions
- topics up through the end of diffraction
- calculator, pens, pencils, nothing else
- focused on conceptual understanding, not memorization

(b) 4 pts. The graph below shows a single Bragg reflection from a powder sample of large crystallites. On the same graph, sketch the peak expected for a sample of this solid consisting of small crystals under substantial uniform compressive stress.



Peak will be broader and shifted to higher 2θ (smaller d-spacing)