Fundamentals of Solid State Physics

Crystal Diffraction
晶体衍射

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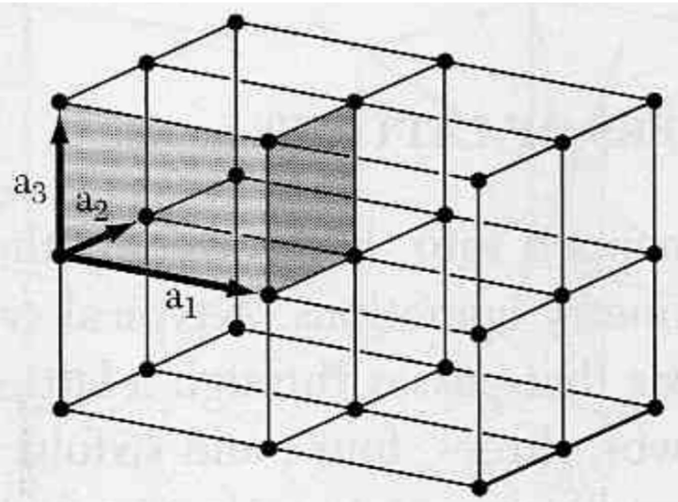
Determination of Crystal Structures

- **Crystallinity**
  - Single crystal? polycrystal? amorphous?

diamond?
glass?

- **Lattice type**
  - BCC, FCC, ... ?
- **Lattice parameter**
  - a = ?



- **Other properties**
  - Defects? Melting points? ...

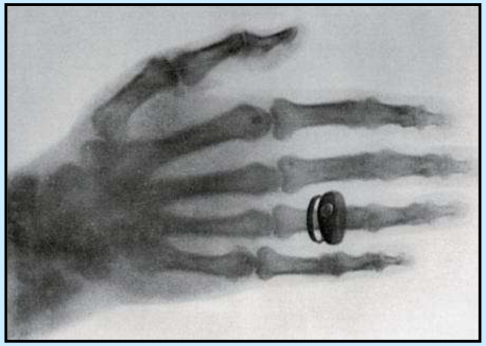
Determination of Crystal Structures

- **X-ray diffraction (XRD) X光晶体衍射**
  - the Bragg law 布拉格定律
  - cubic systems
  - XRD for polycrystals

- **Other methods**
  - electron diffraction
  - electron microscopy
  - neutron diffraction
  - ...

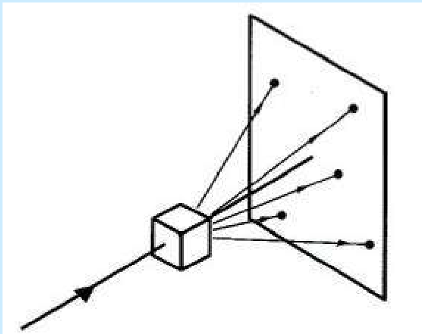
History

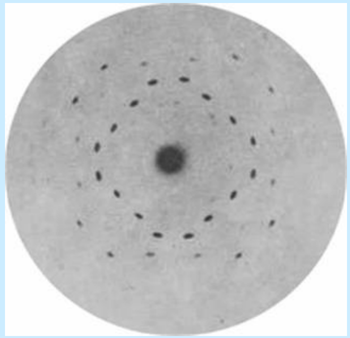
Discovery of X-ray



W. Rontgen (伦琴)
Nobel Prize in 1901

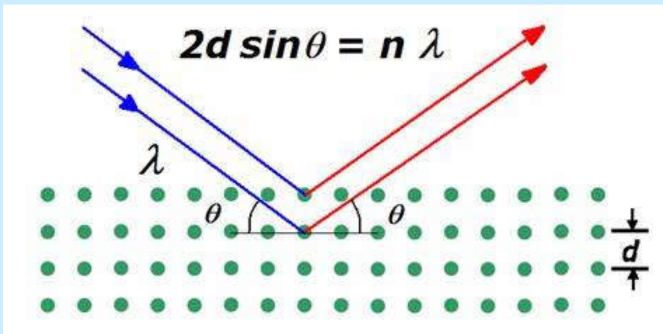
X-ray diffraction of crystals





M. von Laue (劳厄)
Nobel Prize in 1914

Bragg's law

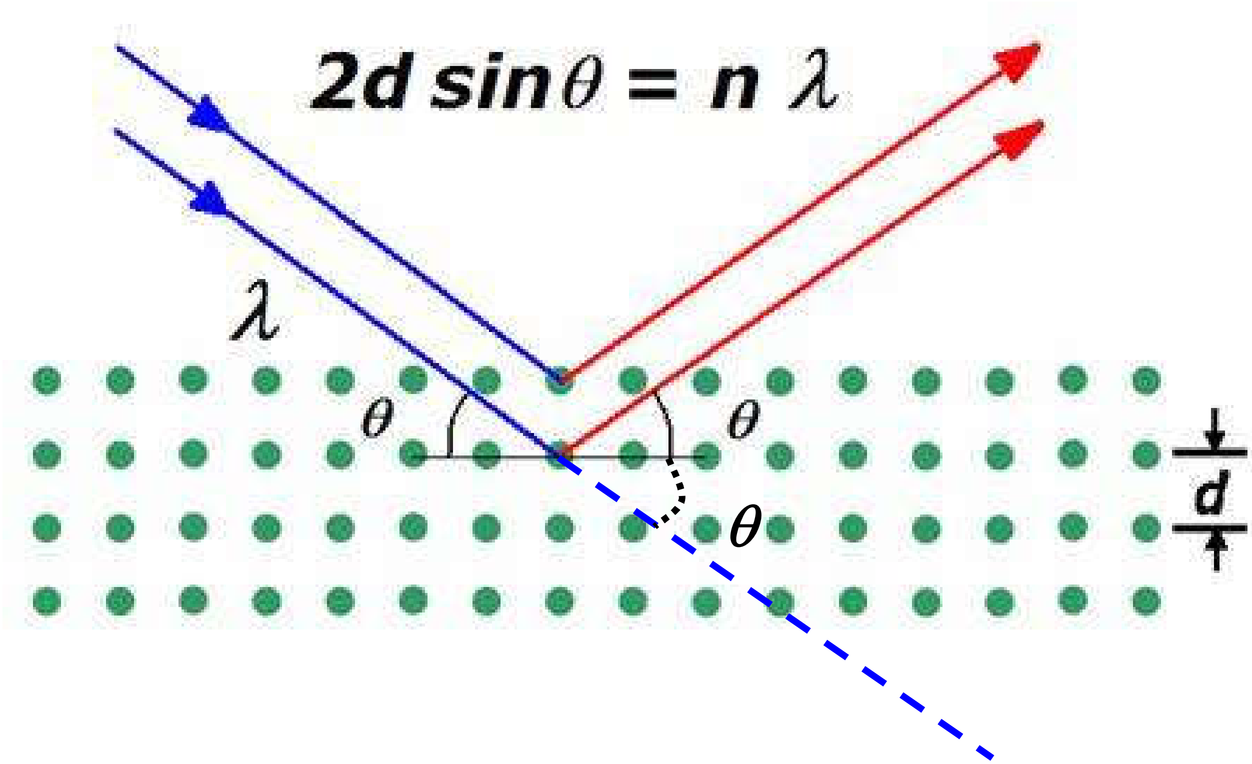


Bragg & Bragg
(布拉格父子)
Nobel Prize in 1915

the Bragg Law 布拉格定律

- **X-ray diffraction (XRD) X光晶体衍射**
  - **constructive interference among each atomic layer**

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



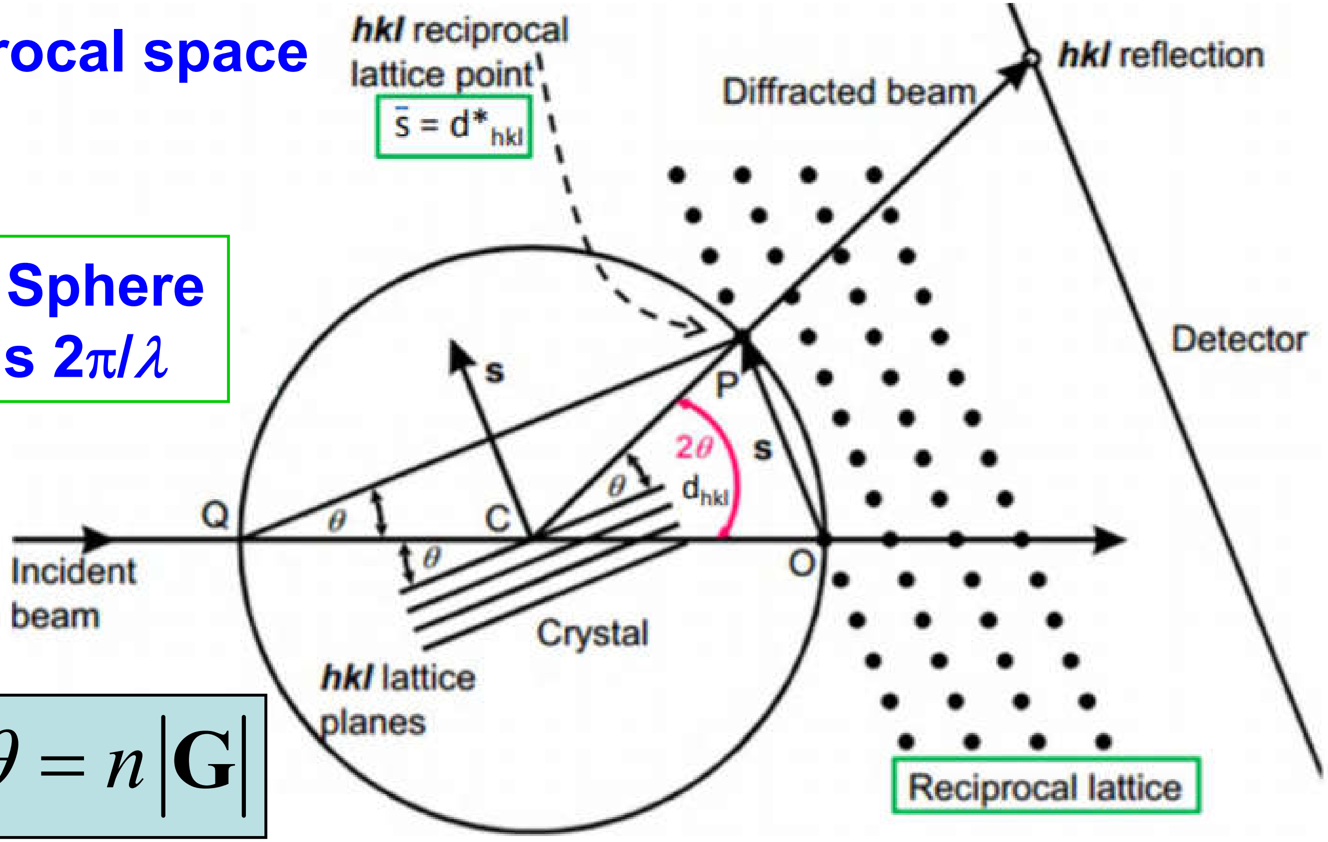
d **- interplanar spacing**
θ **- Bragg angle**
2θ **- Deflection angle**
λ **- X-ray wavelength**
n **= 1, 2, 3, ...**

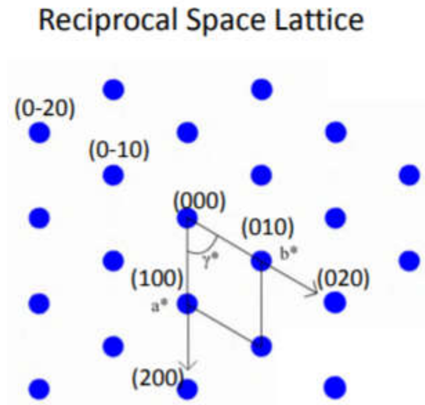
Typically, the first order diffraction (*n* = 1) has the strongest intensity.

von Laue Formulation

in reciprocal space

Ewald Sphere
radius $2\pi/\lambda$





$$\boxed{2k\sin\theta = n\left|\mathbf{G}\right|}$$

Ashcroft & Mermin p.96-p.104

$$\boxed{2\cdot\frac{2\pi}{\lambda}\cdot\sin\theta = n\left|\mathbf{G}\right| = n\frac{2\pi}{d_{(hkl)}}}$$

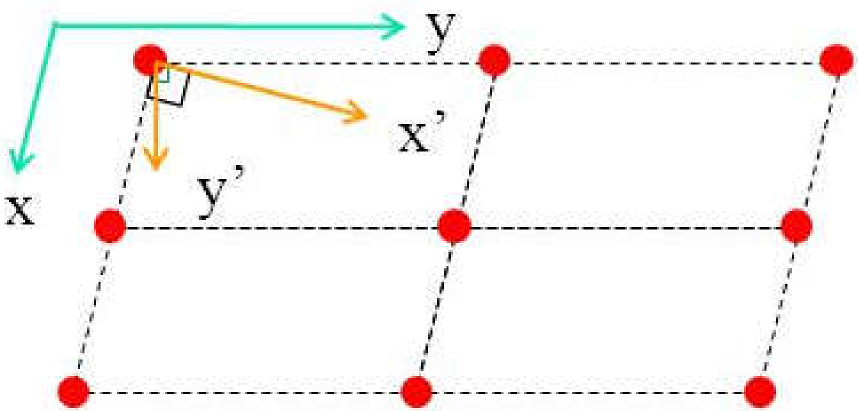
$$\rightarrow \quad \boxed{2d_{(hkl)}\sin\theta = n\lambda}$$

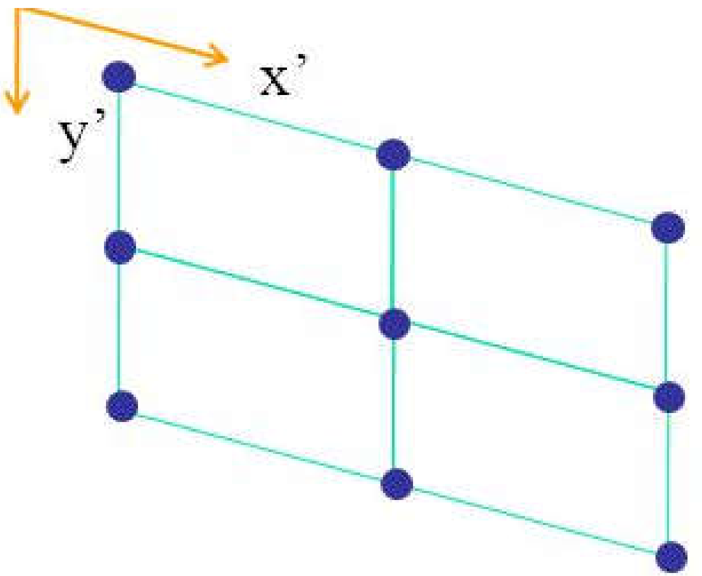
X-ray diffraction pattern is the reciprocal lattice of the crystal

Real Space vs. Reciprocal Space

Crystal Structure → **Diffraction Pattern**

Direct Lattice | **Reciprocal Lattice**



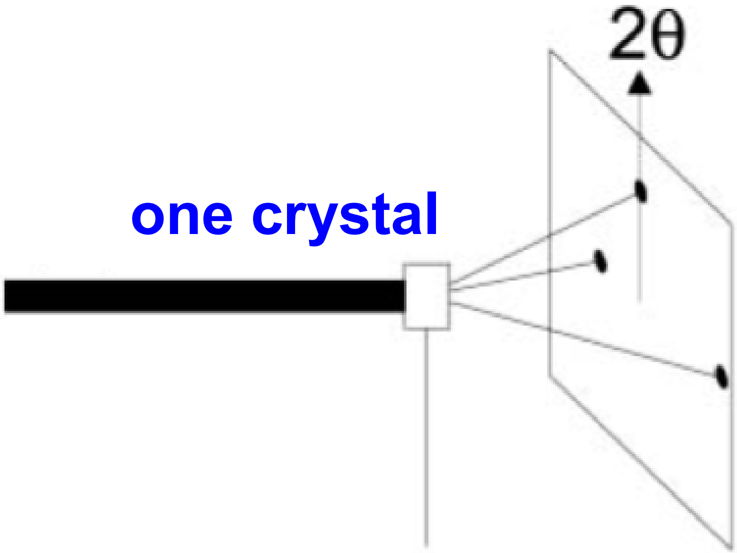


Real Space | **Reciprocal Space**

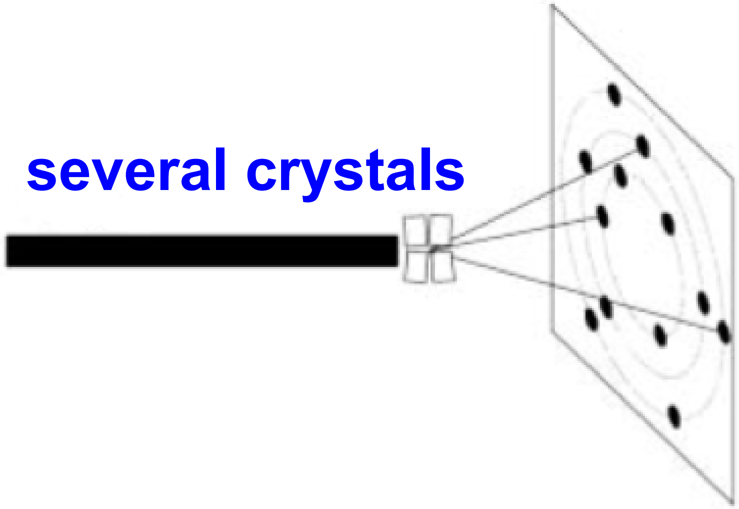
XRD of Crystals

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

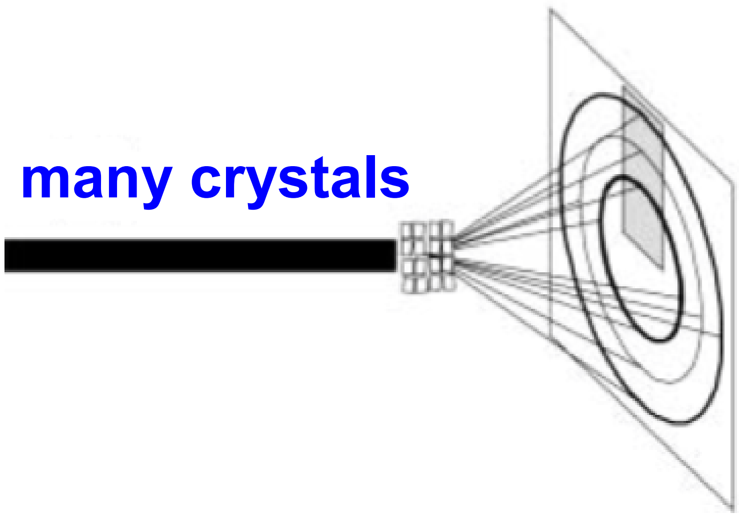
one crystal

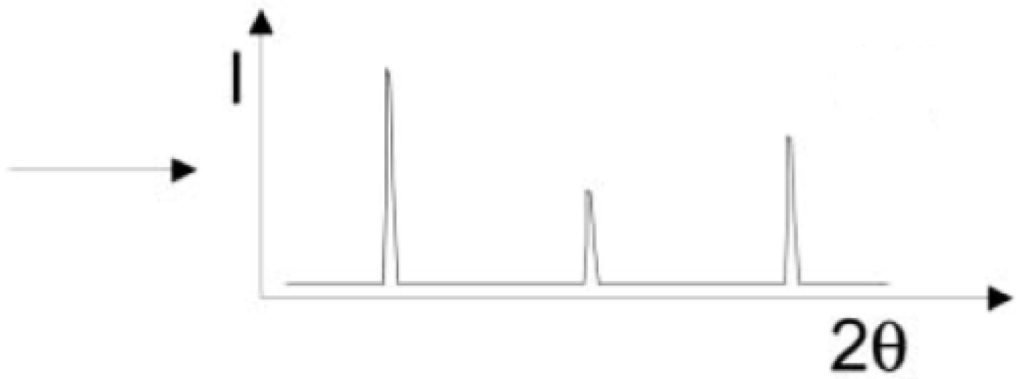


several crystals



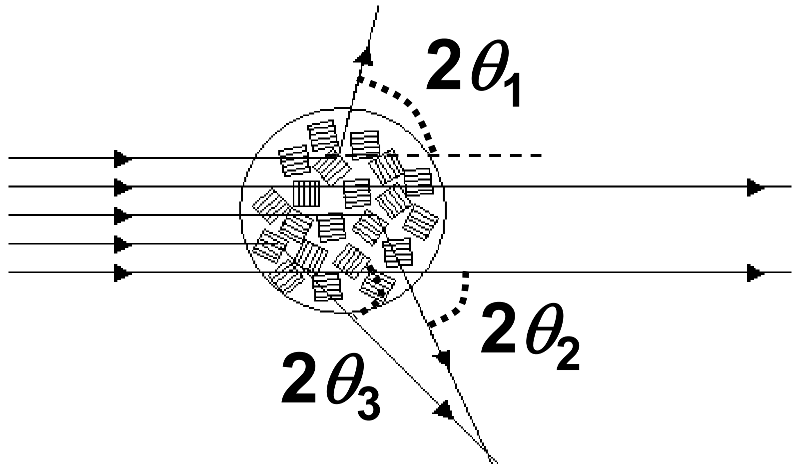
many crystals





XRD of Polycrystals

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



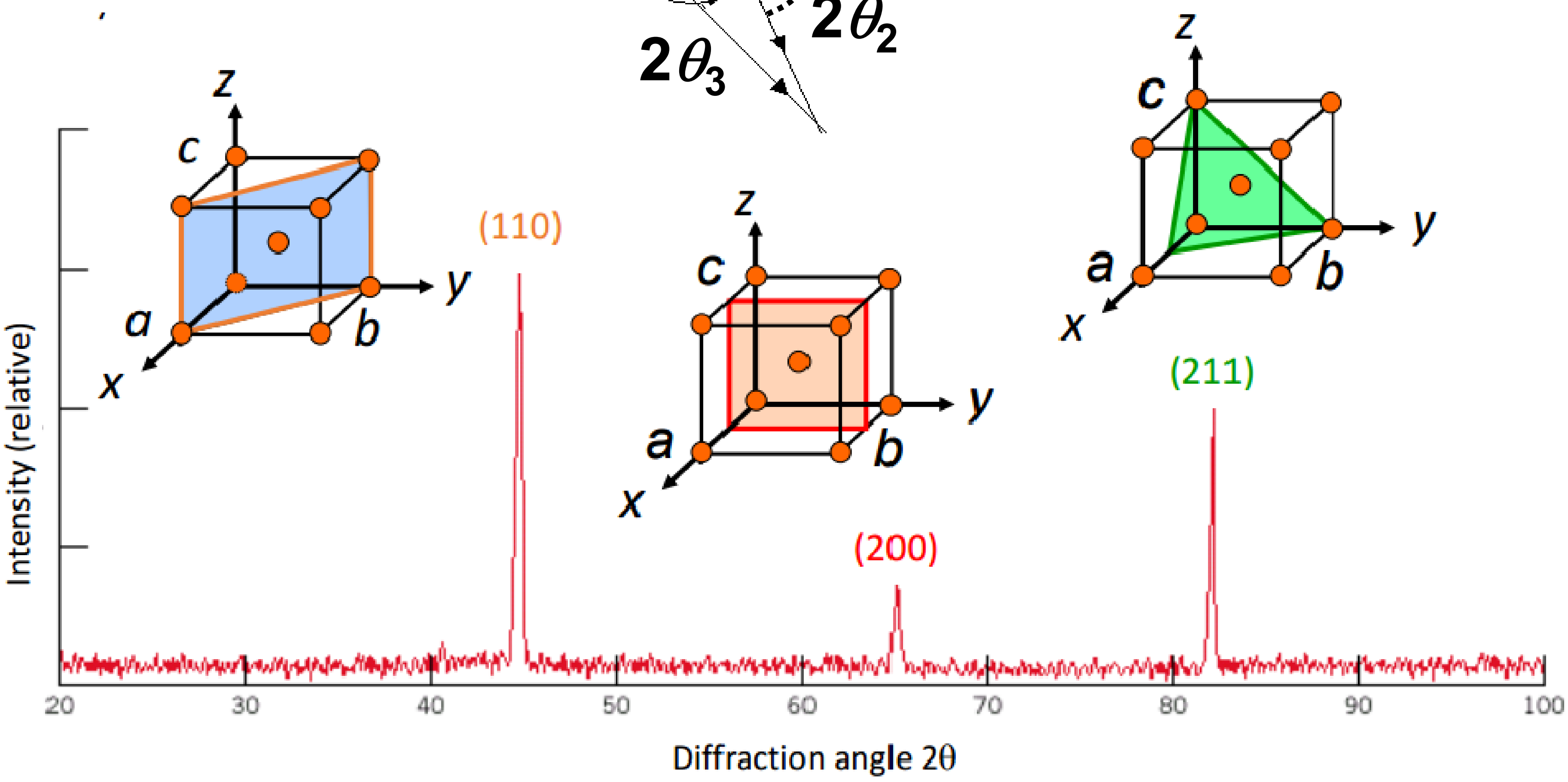
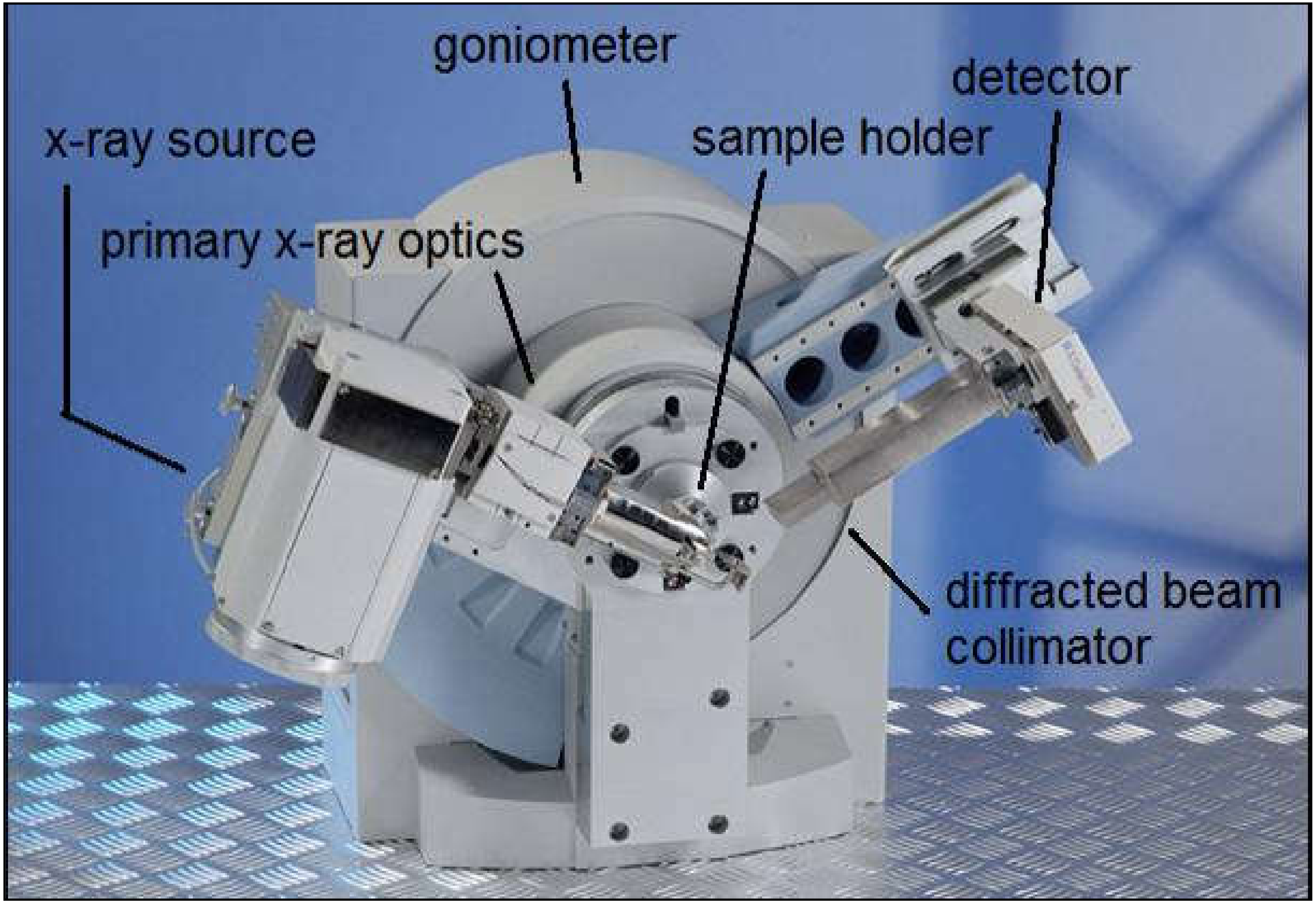


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

XRD of Polycrystals



XRD of Polycrystals

For cubic systems (SC, BCC, FCC)

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

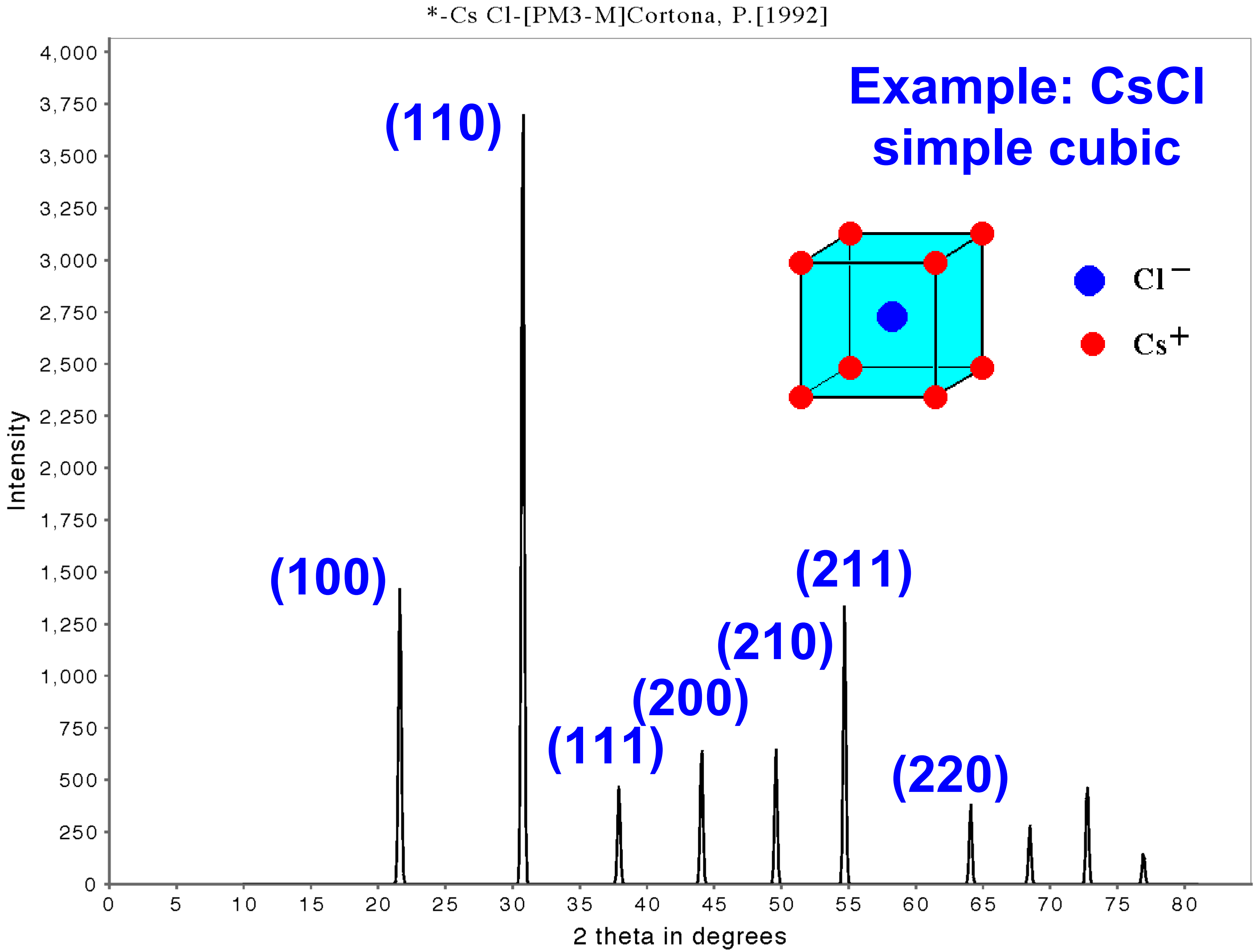
$$2d \sin\theta = n\lambda$$

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

angle	θ_1	θ_2	θ_3	θ_4	θ_5	θ_6	...
plane (*hkl*)	100	110	111	200	210	211	...

Commonly used x-ray wavelength λ = 0.154 nm generated by electrons hitting a copper metal

Example: CsCl simple cubic



https://matgenb.materialsvirtuallab.org/2013/01/01/Calculating-XRD-patterns.html

XRD of Polycrystals

- What determines the amplitude of the peaks?
- Where are other peaks like (100) and (111) here?

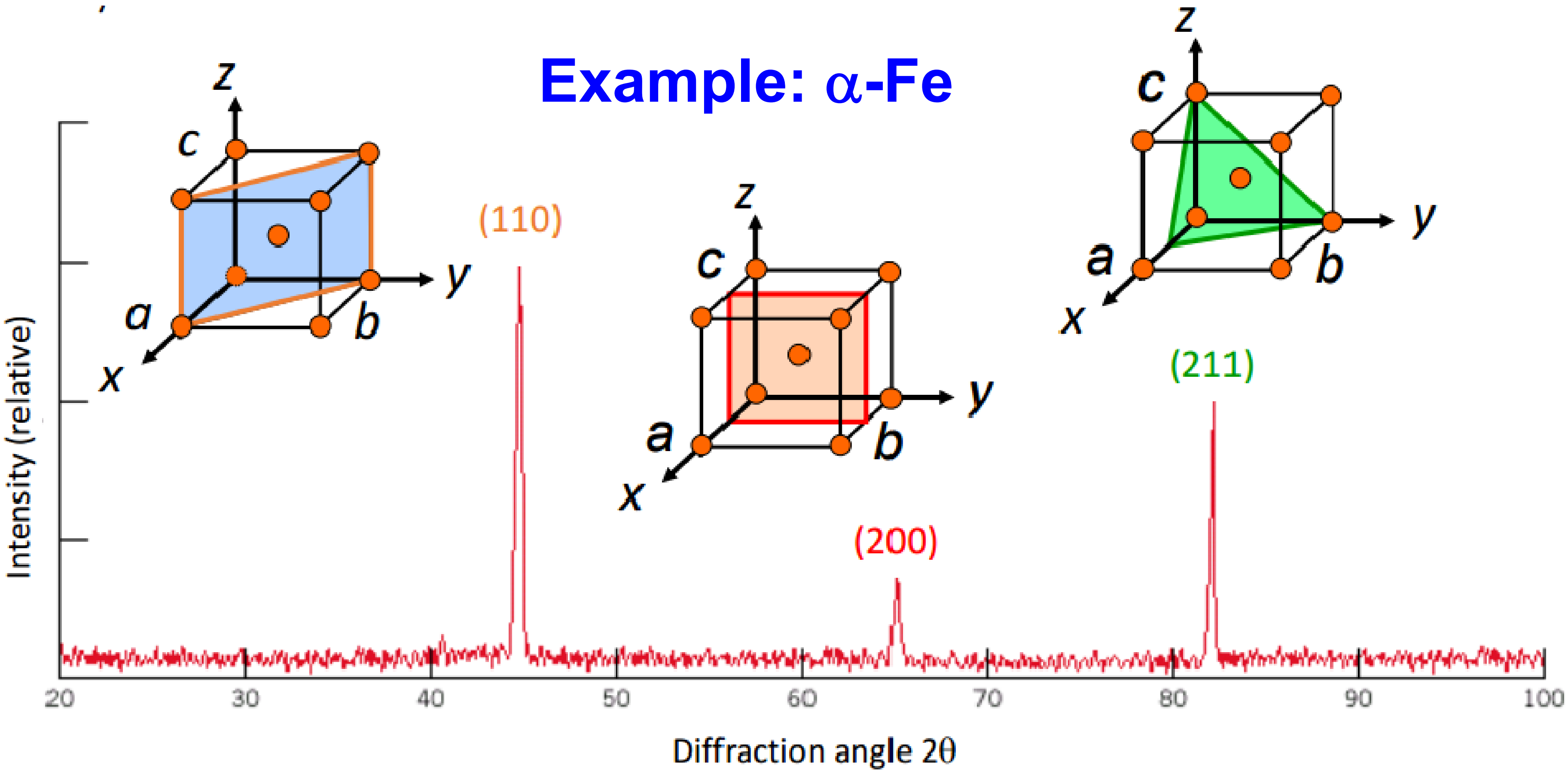


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

XRD of Polycrystals

- **What determines the amplitude of the peaks?**
  - **geometrical structure factor *S* (几何结构因子)**
  - **atomic form factor *f* (原子形状因子)**
  - **crystal orientation**
  - **crystal size**
  - **...**

Geometrical Structure Factor *S*

- **Systematic Absences 系统消光**
  - when $S = 0$, peaks are absent
  - destructive interference
- **Allowed index**
  - SC

$$\boxed{h, k, l = \text{all integers}}$$

  - BCC

$$\boxed{h + k + l = \text{even}}$$

  - FCC

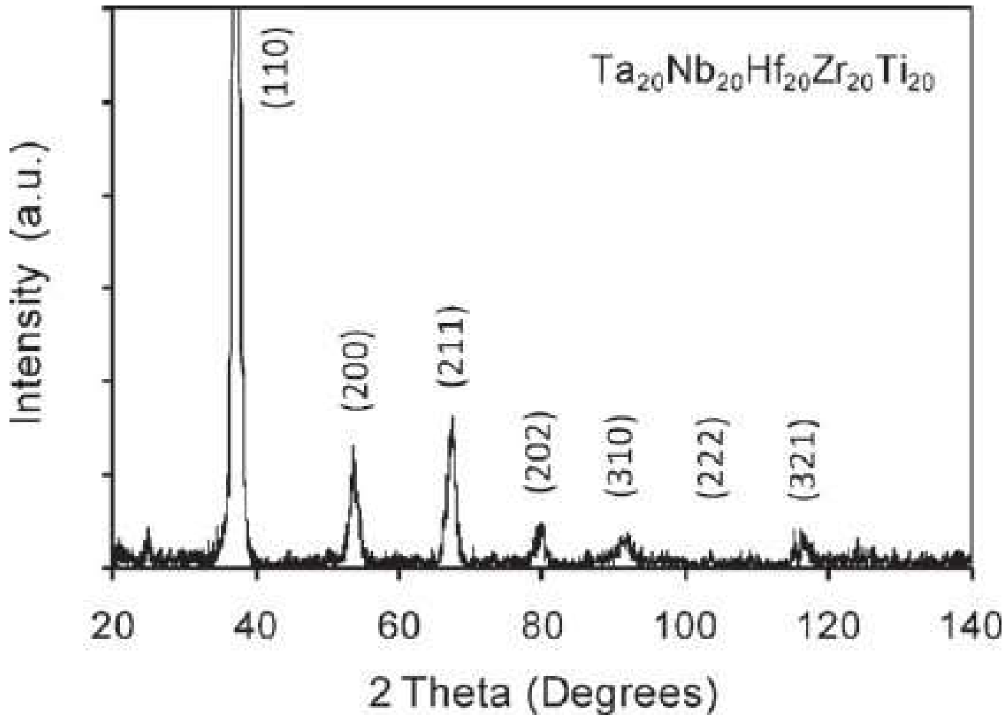
$$\boxed{h, k, l \ \text{ are all even or odd}}$$

Ashcroft & Mermin
p.104-p.107

Allowed list of $h^2 + k^2 + l^2$ for cubic crystals

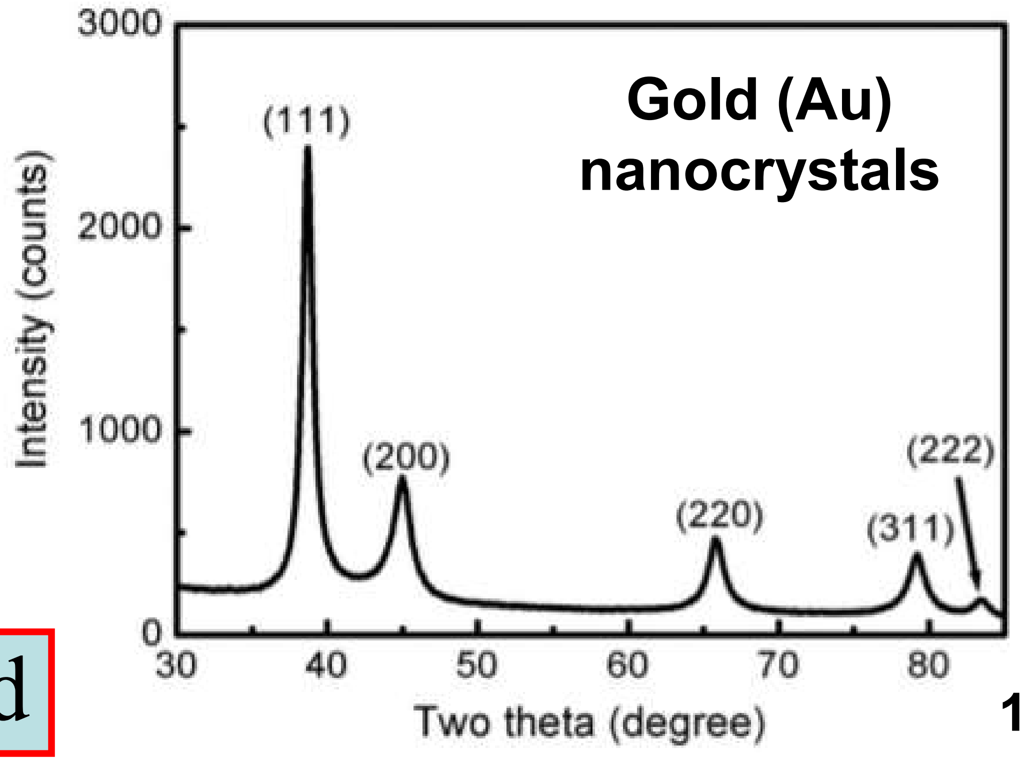
Forbidden numbers	Primitive, P	Face Centered, F	Body Centered, I	Corresponding *hkl*
	1			100
	2		2	110
	3	3		111
	4	4	4	200
	5			210
	6		6	211
7				
	8	8	8	220
	9			221, 300
	10		10	310
	11	11		311
	12	12	12	222
	13			320
	14		14	321
15				
	16	16	16	400

Geometrical Structure Factor *S*



BCC

$$\boxed{h+k+l=\text{even}}$$



FCC

$$\boxed{h,k,l\ \text{ are all even or odd}}$$

Geometrical Structure Factor *S*

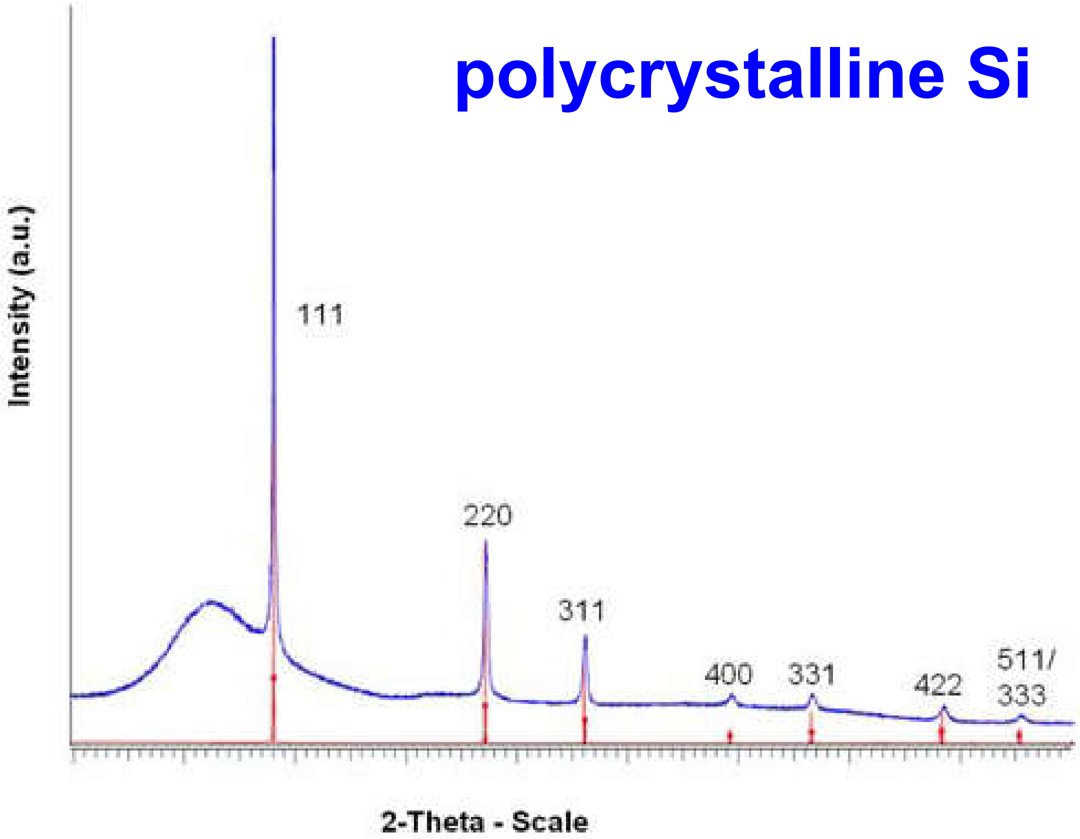
- **Allowed index for Diamond Structure (C, Si, Ge)**

$$\boxed{h,k,l \ \text{ are all odd}}$$

(111), (311), (331), ...

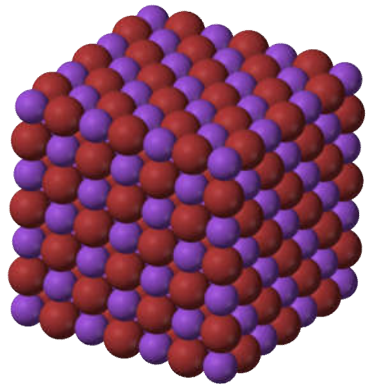
$$\boxed{\begin{array}{l} h,k,l \ \text{ are all even} \\ \text{and } h+k+l=4n \end{array}}$$

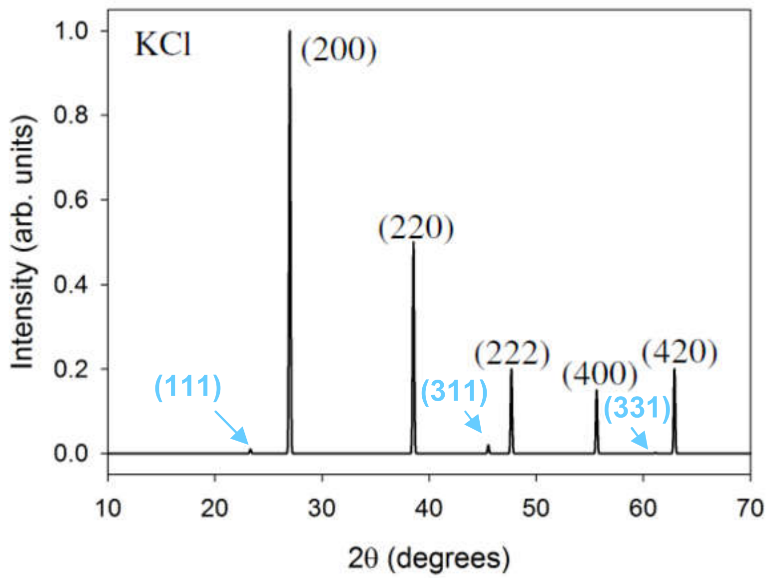
(220), (400), (422), ...

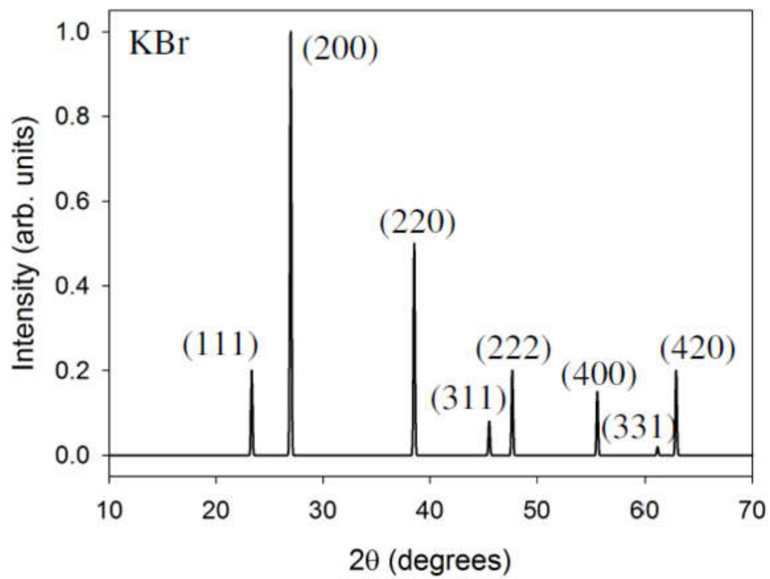


Atomic Form Factor *f*

- **Example: KCl and KBr**
  - **FCC lattice, similar lattice parameter *a***





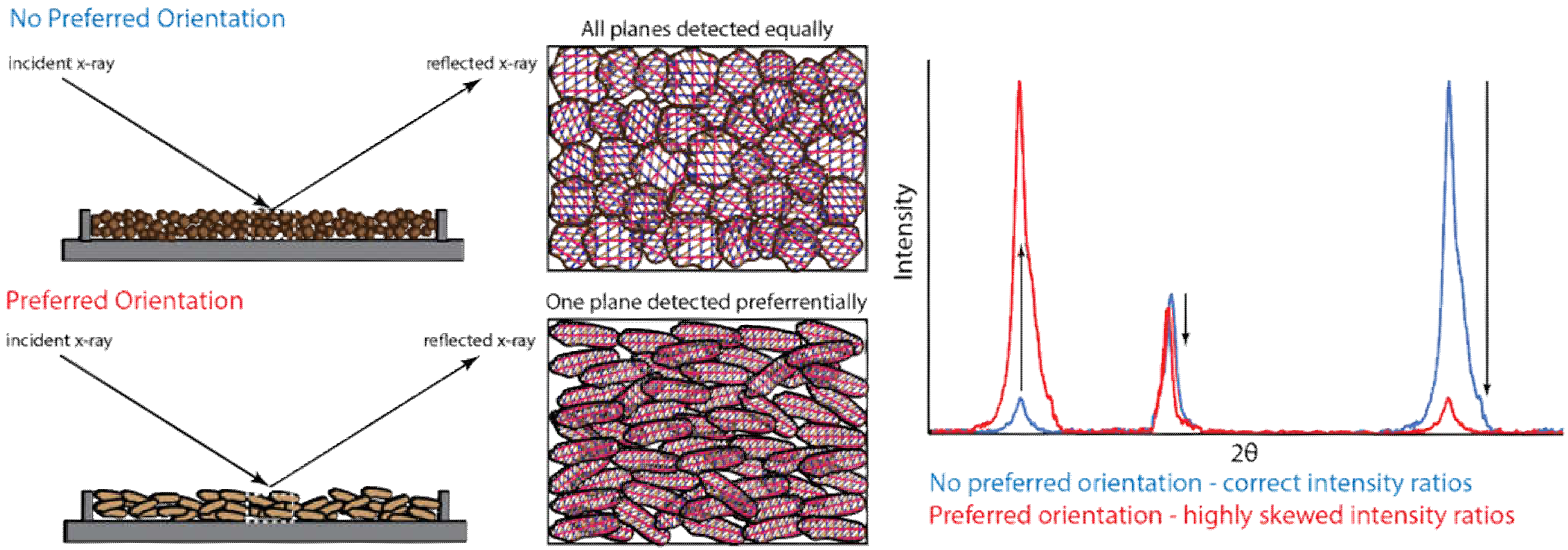


K^+ and Cl^- are very similar
KCl looks like a simple cubic with *a*/2

K^+ and Br^- are very different
KBr is a normal FCC with *a*

Crystal Orientation

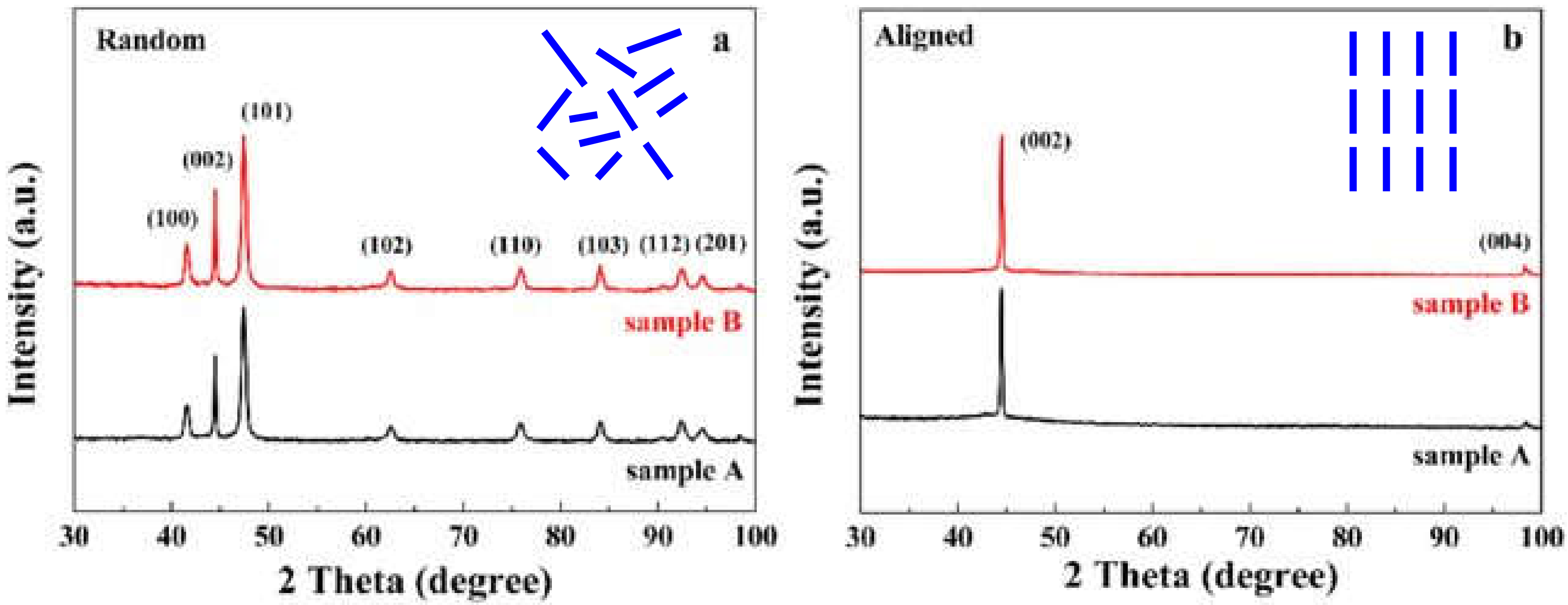
- Aligned crystals show strong orientation preference



https://cms.eas.ualberta.ca/xrd/sample-preparation/

Crystal Orientation

- **Aligned crystals show strong orientation preference**



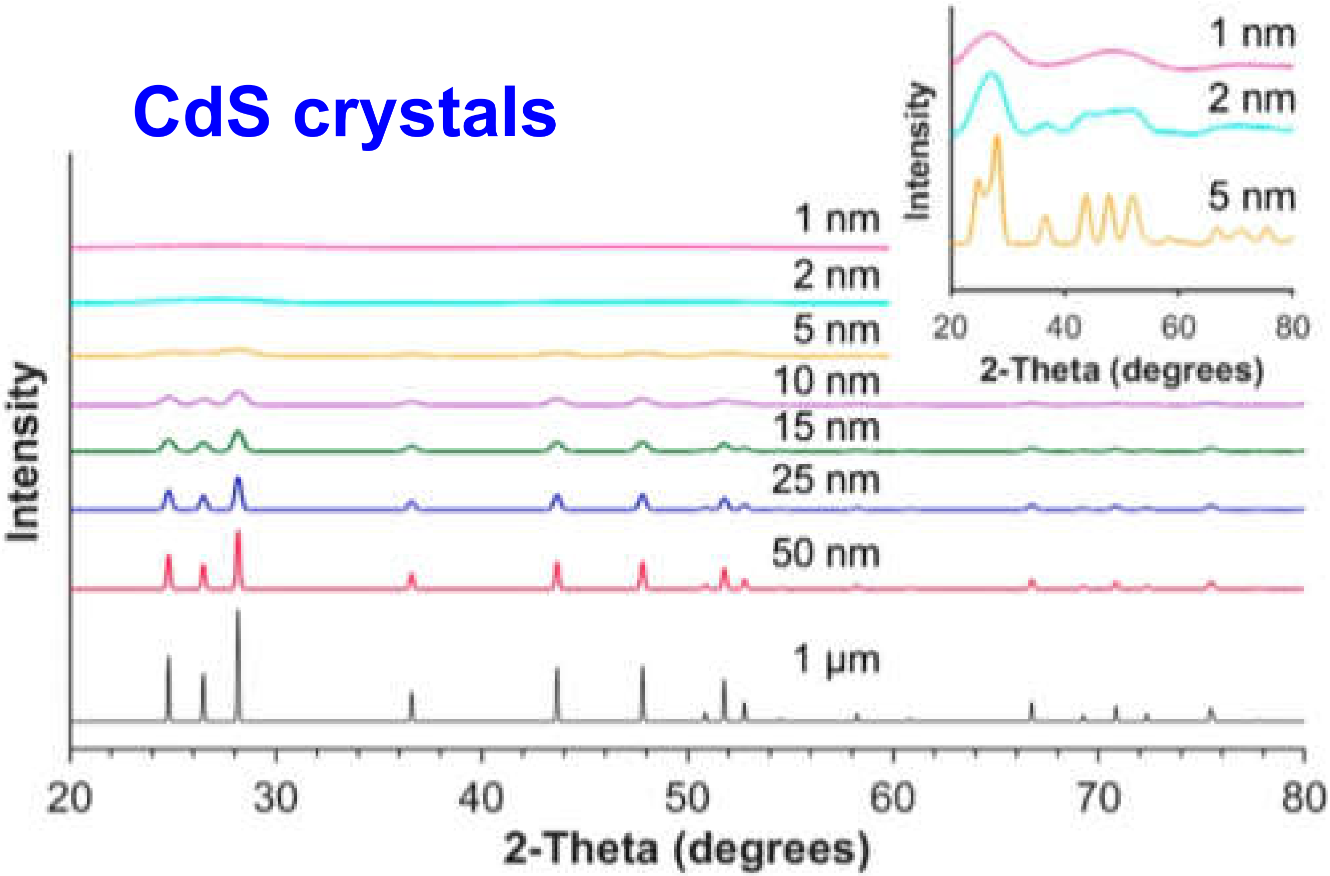
Co nanowires

H. Xu, *et al.*, *AIP Adv.* **8,** 056422 (2018)

Crystal Size

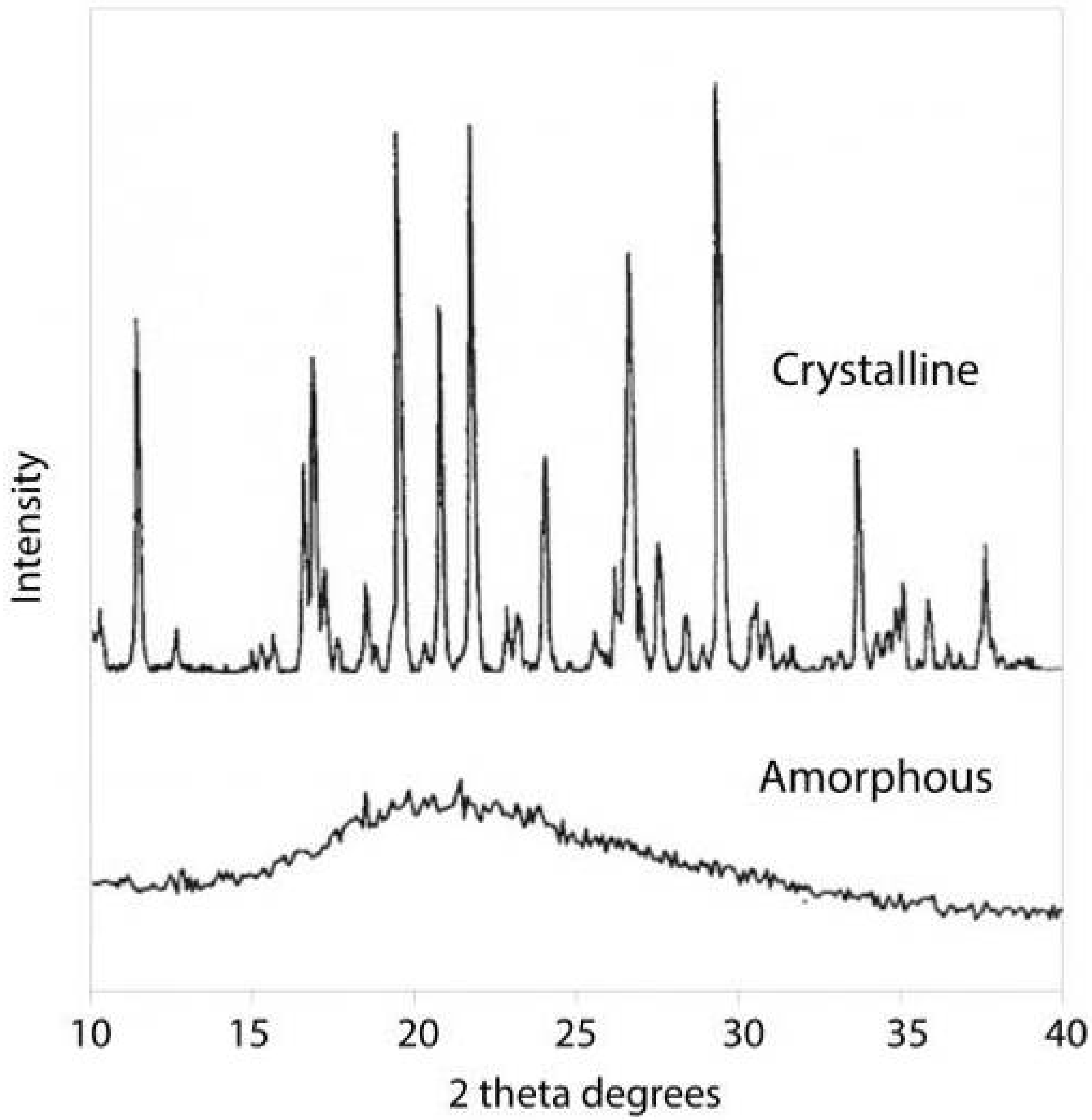
- **Smaller crystals lead to lower diffraction intensity and larger peak width.**

CdS crystals

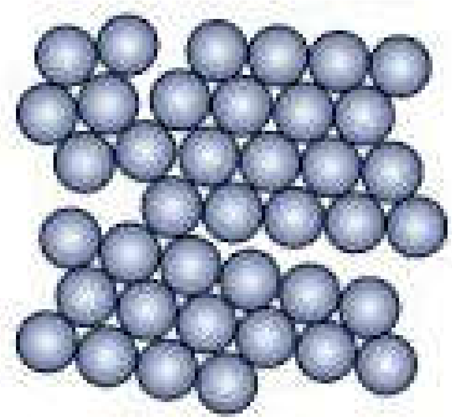


C. Holder, *et al.*, *ACS Nano* **13,** 7359 (2019)

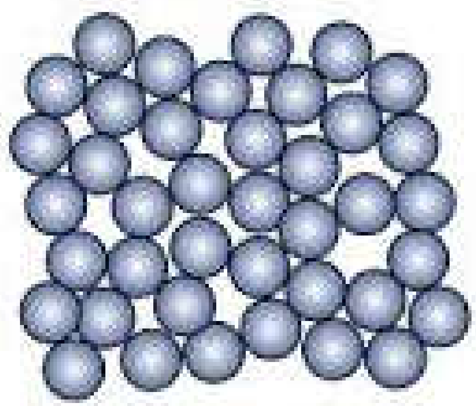
Amorphous Materials 非晶



Crystalline:
anisotropic (各向异性)

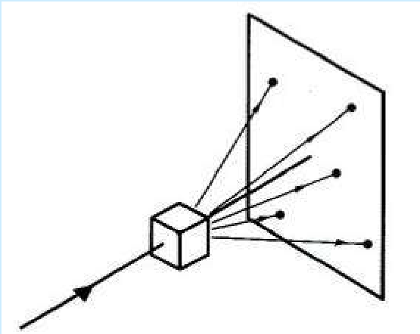


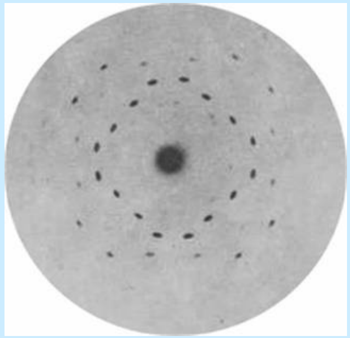
Amorphous:
isotropic (各向同性)



History of Discovery

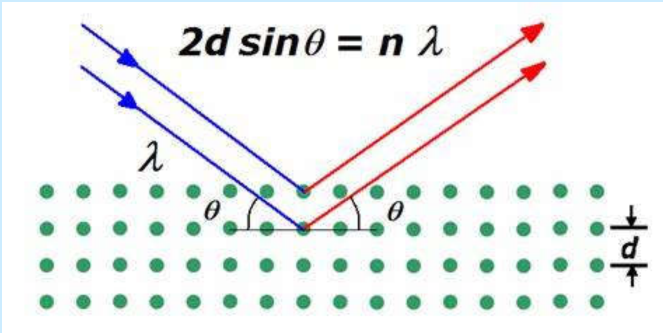
X-ray diffraction of crystals





M. von Laue (劳厄)
Nobel Prize in 1914

Bragg's law



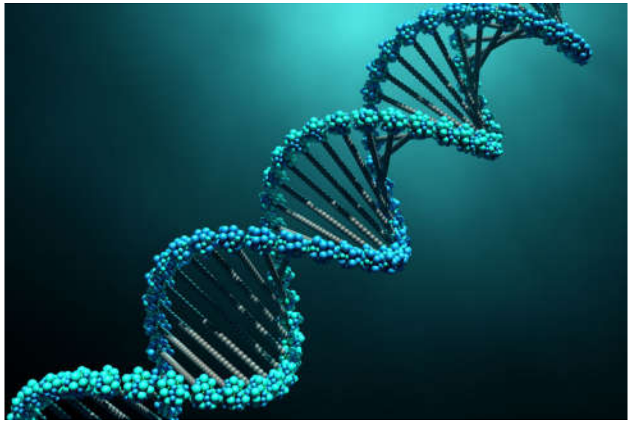
Bragg & Bragg
(布拉格父子)
Nobel Prize in 1915

Teaching

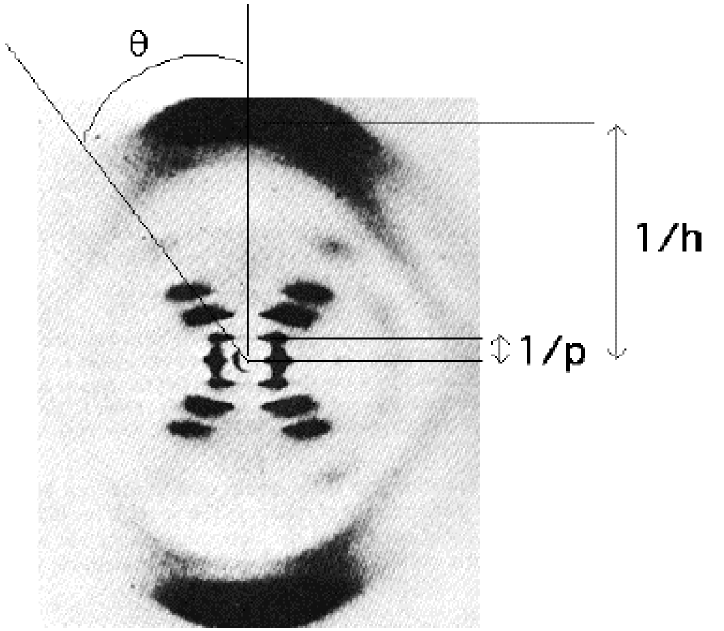
Crystal Structure ⇄ **Diffraction Pattern**

Research

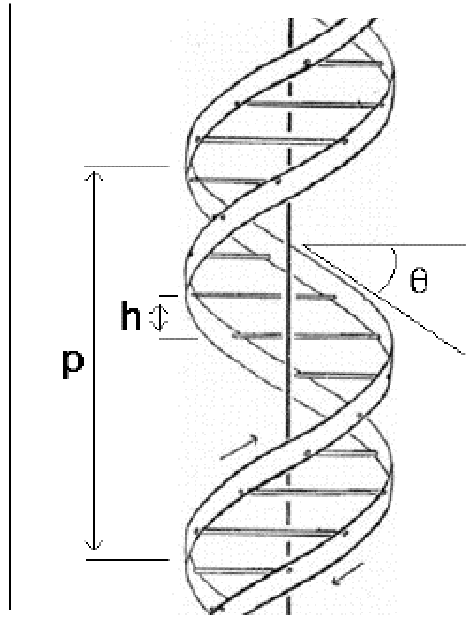
The Structure of DNA



XRD pattern



DNA structure



p = 3.4 nm
h = 0.34 nm
θ = 32º

J. Waston, F. Crick and M. Wilkins

1962 Nobel Prize in Physiology / Medicine

R. Franklin died in 1958

J. Watson, F. Crick, *Nature* **171,** 737 (1953)
M. Wilkins, *et al.*, *Nature* **171,** 738 (1953)
R. Franklin, R. Gosling, *Nature* **171,** 740 (1953)

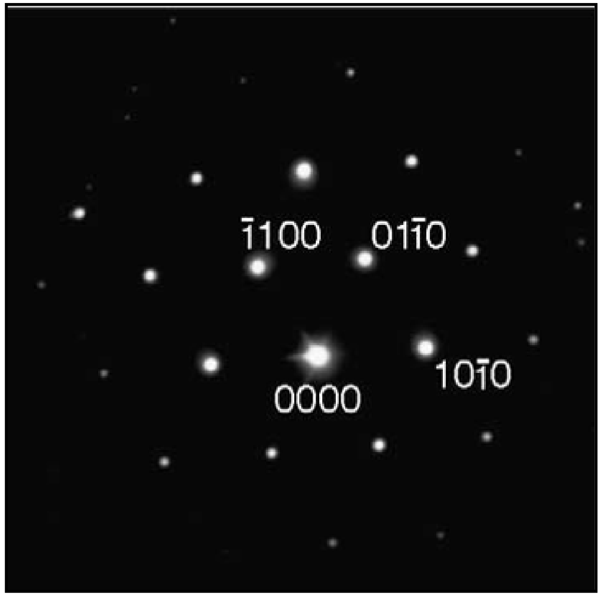
Electron Beam Diffraction

- **Electron Beam is also a wave**
  - **also follows the Bragg law**

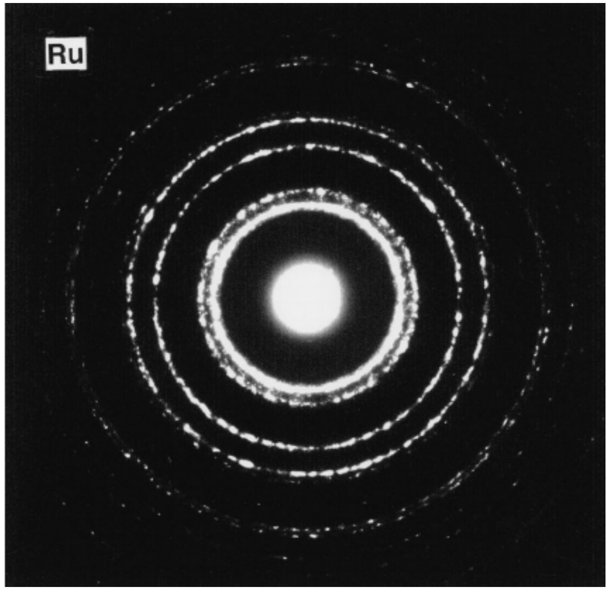
wave-particle duality

$$\lambda = \frac{h}{\text{momentum}}$$

diffraction patterns



single crystal

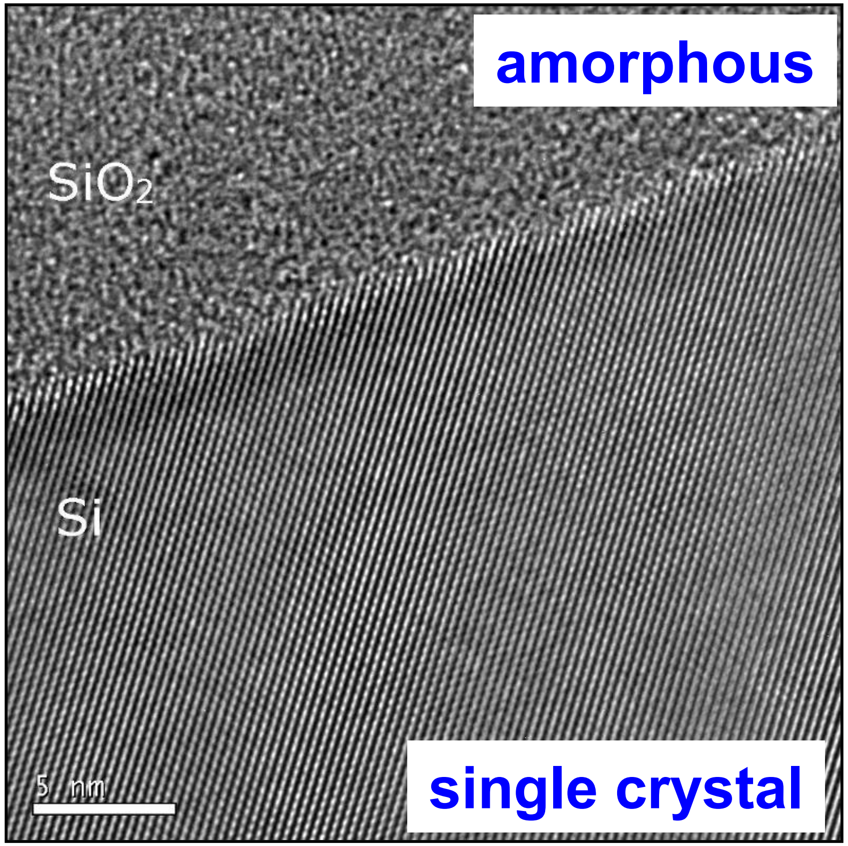


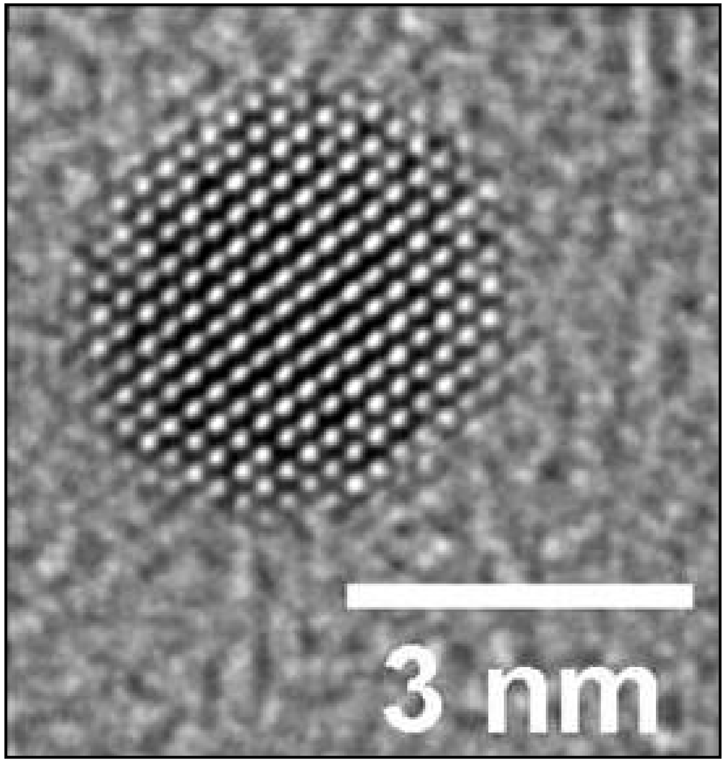
polycrystal

amorphous

Electron Microscopy

- **HRTEM**
  - **High Resolution Transmission Electron Microscope**





quantum dot

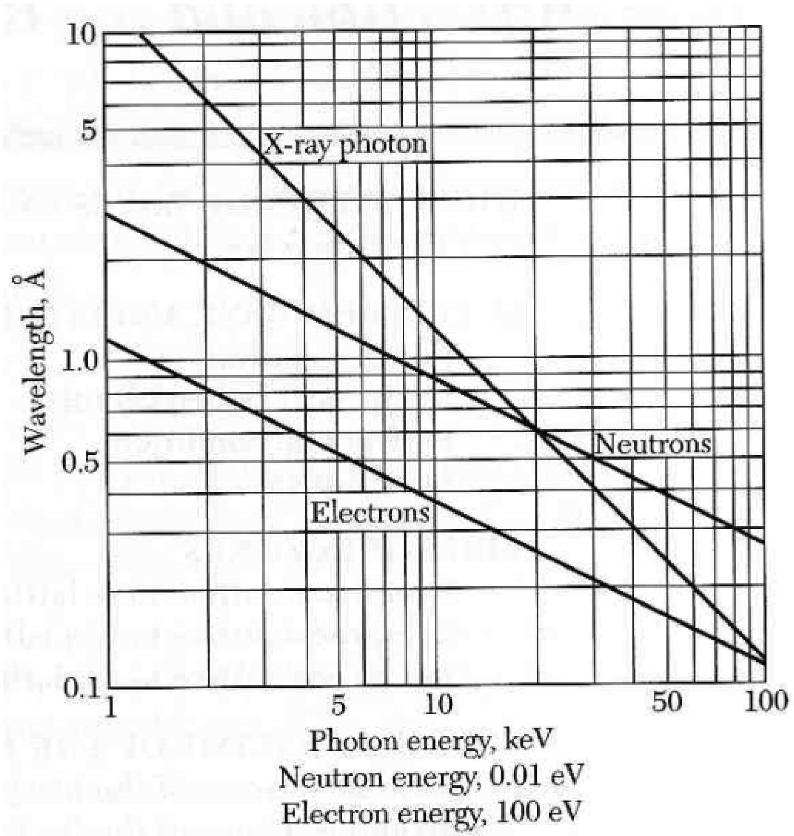
Neutron Diffraction 中子衍射

- Neutron Beam is also a wave
  - Lower energy
  - No charge
- Need a nuclear reactor

wave-particle duality

$$\lambda = \frac{h}{\text{momentum}}$$

散裂中子源，东莞



Thank you for your attention