Fundamentals of Solid State Physics

Crystal Diffraction
晶体衍射

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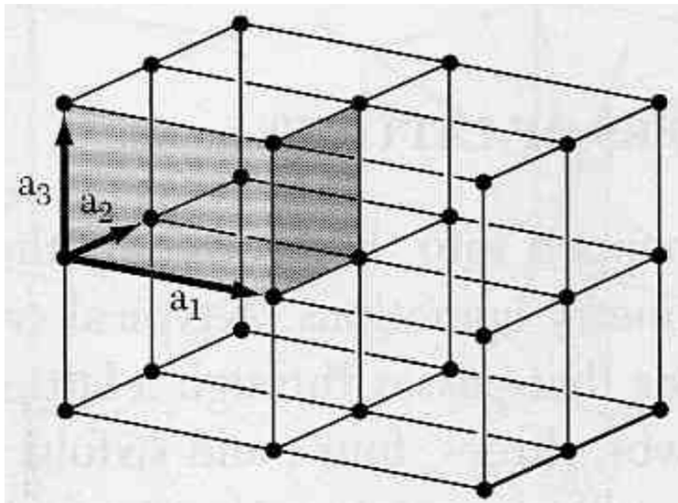
Determination of Crystal Structures

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

diamond?
glass?

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



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

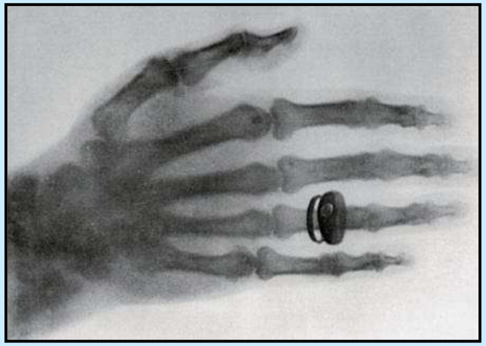
Determination of Crystal Structures

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

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

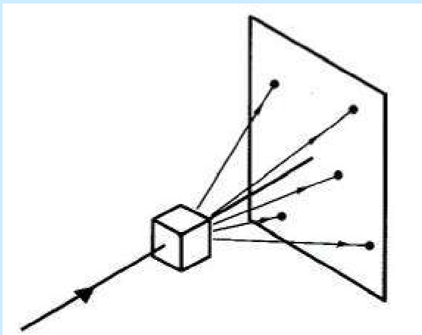
History

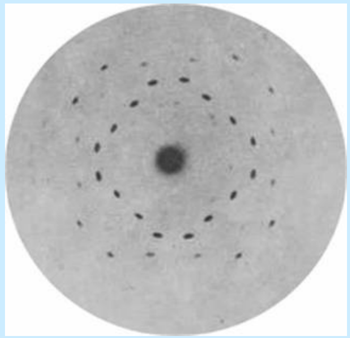
Discovery of X-ray



W. Rontgen (伦琴)
Nobel Prize in 1901

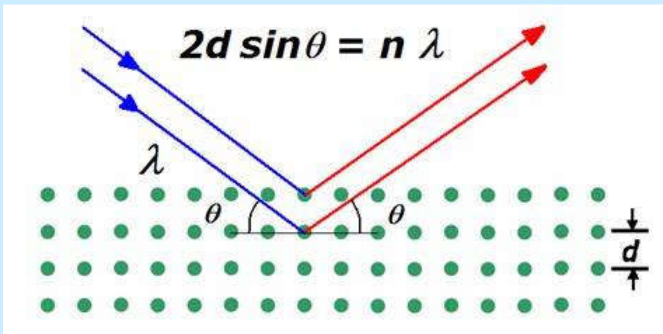
X-ray diffraction of crystals





M. von Laue (劳厄)
Nobel Prize in 1914

Bragg's law

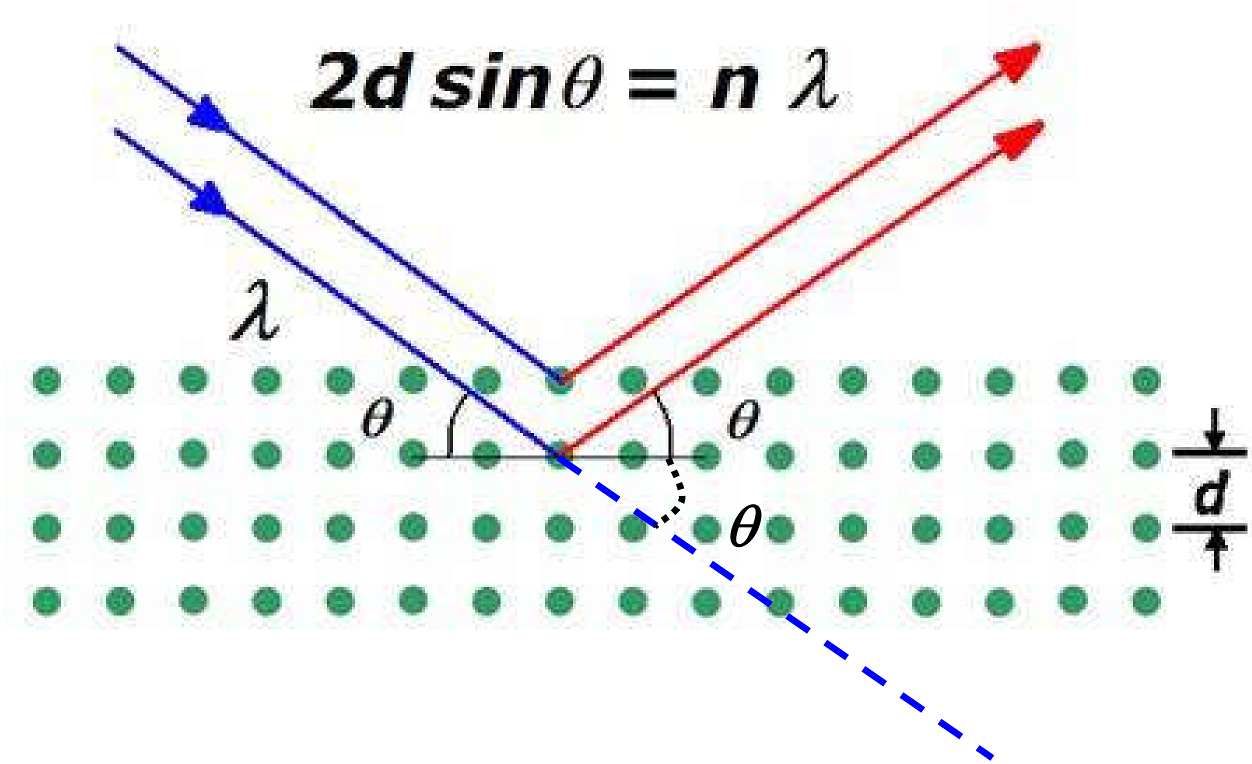


Bragg & Bragg (布拉格父子)
Nobel Prize in 1915

the Bragg Law 布拉格定律

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

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



d **- interplanar spacing**

θ **- Bragg angle**

2*θ* - Deflection angle

λ **- X-ray wavelength**

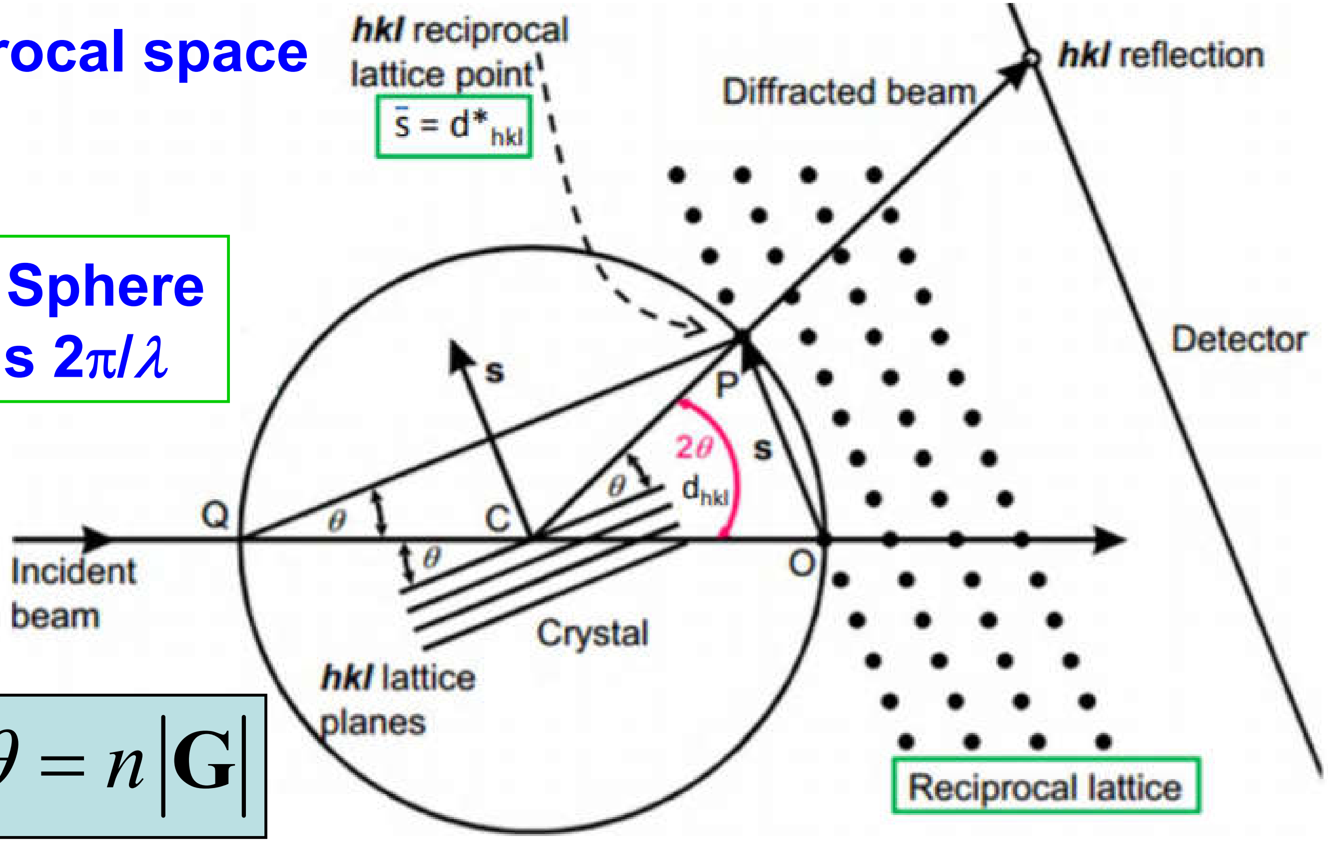
n **= 1, 2, 3, ...**

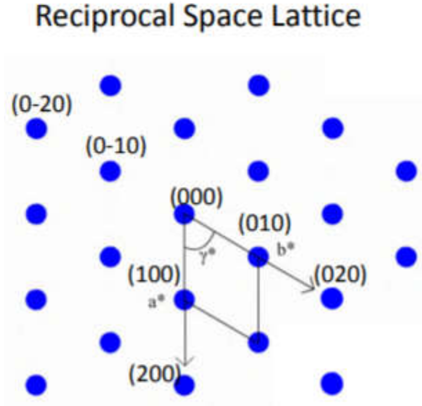
Typically, the first order diffraction (*n* = 1) has the strongest intensity.

von Laue Formulation

in reciprocal space

Ewald Sphere
radius $2\pi/\lambda$





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

Ashcroft & Mermin
p.96-p.104

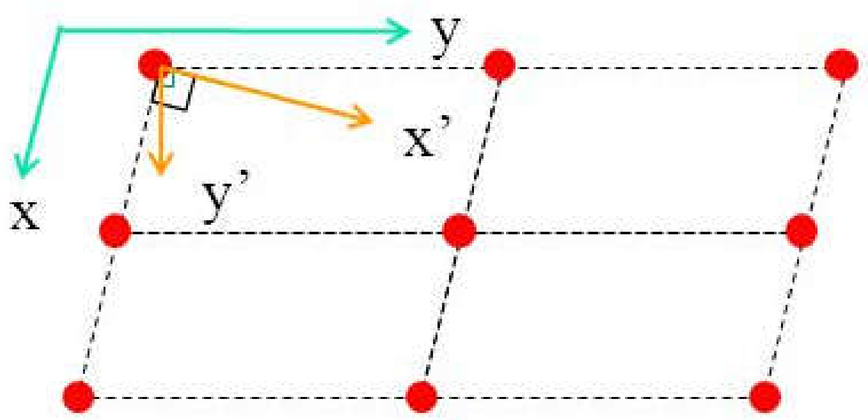
$$2\cdot\frac{2\pi}{\lambda}\cdot\sin\theta = n\left|\mathbf{G}\right| = n\frac{2\pi}{d_{(hkl)}} \rightarrow 2d_{(hkl)}\sin\theta = n\lambda$$

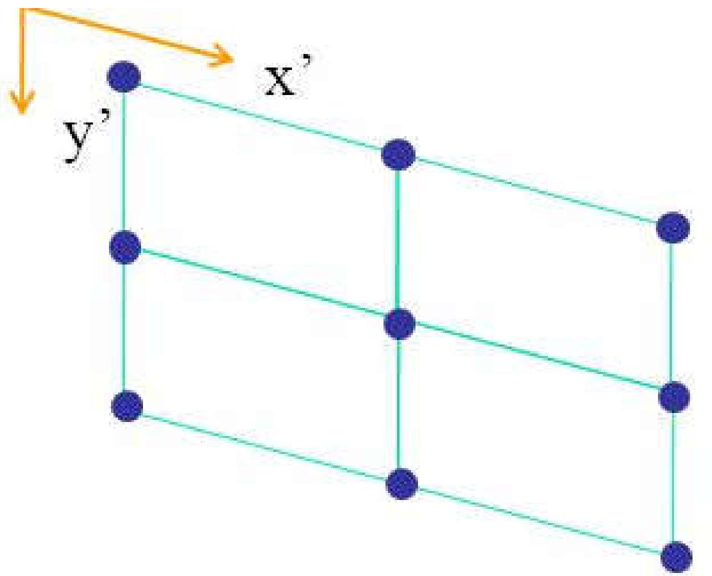
X-ray diffraction pattern is the reciprocal lattice of the crystal

Real Space vs. Reciprocal Space

Crystal Structure → **Diffraction Pattern**

Direct Lattice | **Reciprocal Lattice**

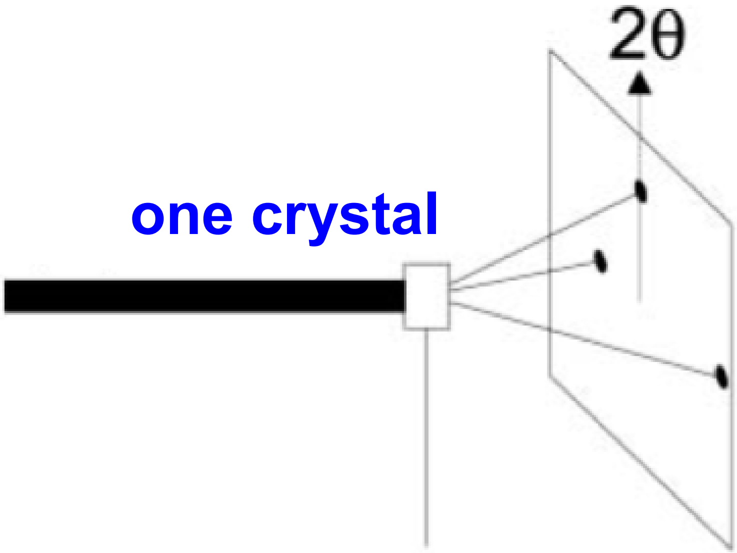


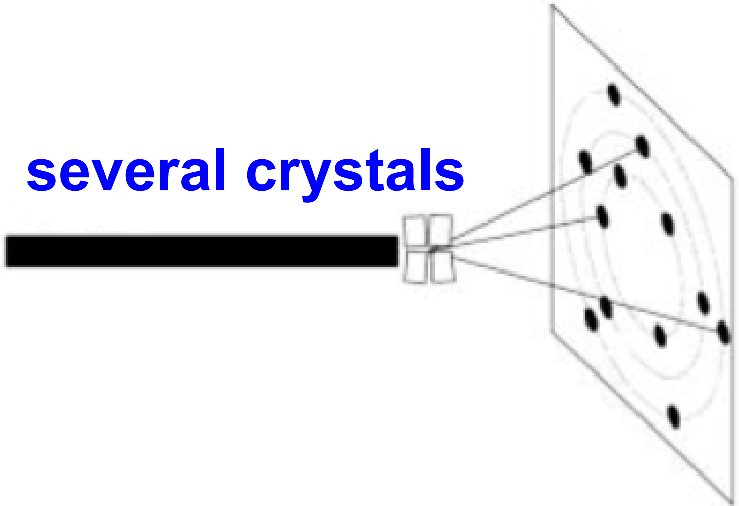


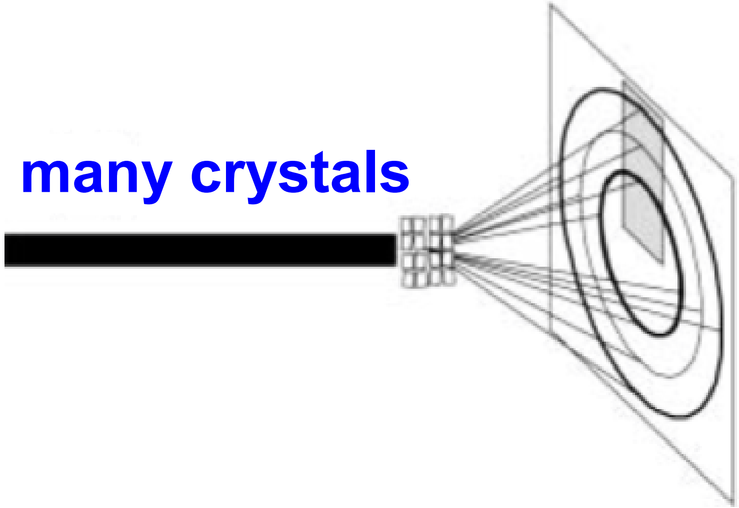
Real Space | **Reciprocal Space**

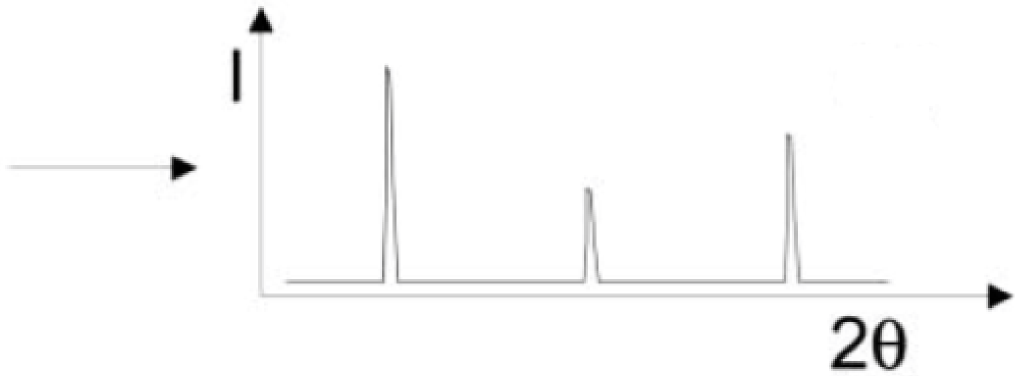
XRD of Crystals

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









XRD of Polycrystals

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

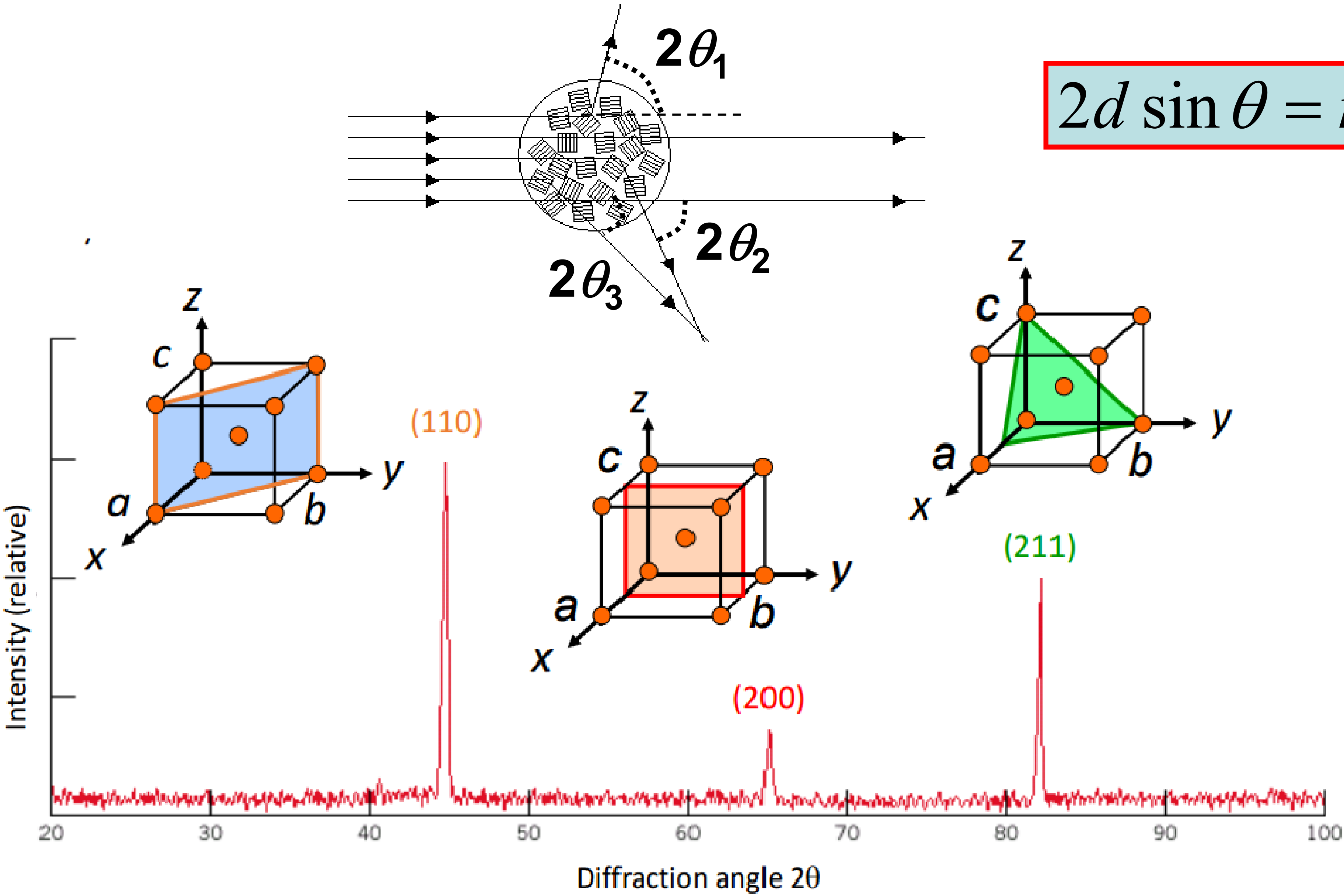
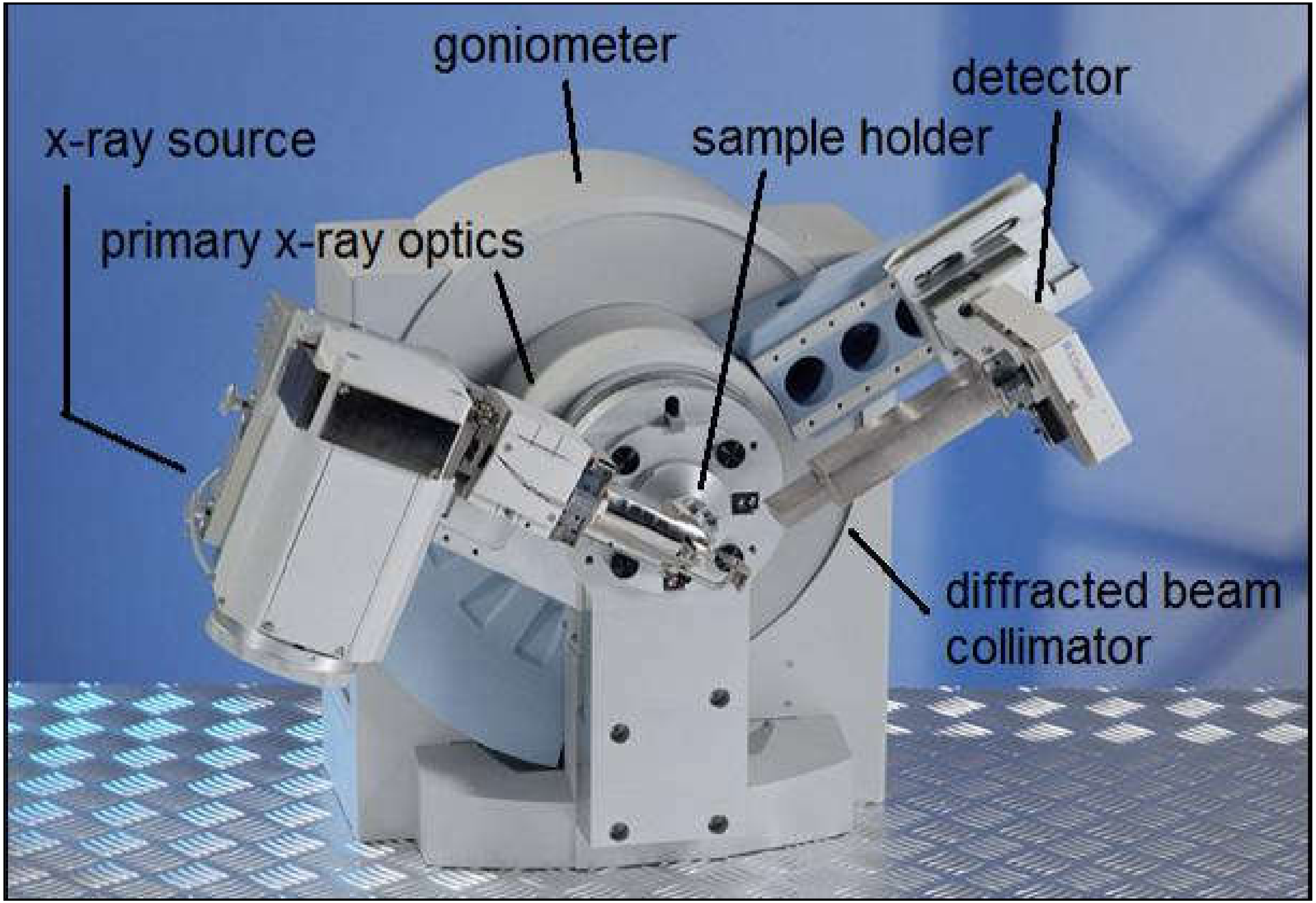


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

XRD of Polycrystals



XRD of Polycrystals

For cubic systems (SC, BCC, FCC)

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

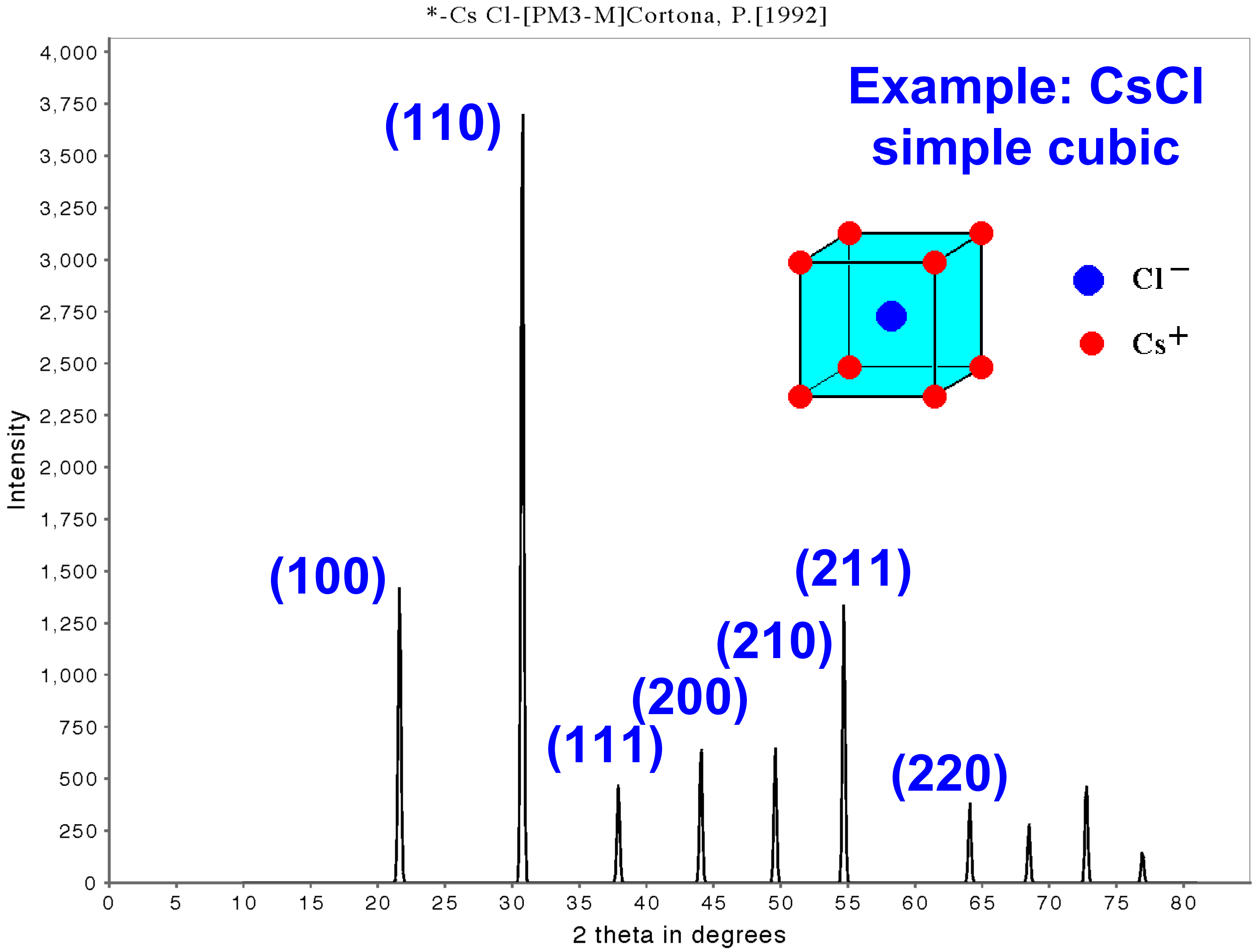
$$2d\sin\theta = n\lambda$$

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

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

Typically, *n* = 1

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



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?

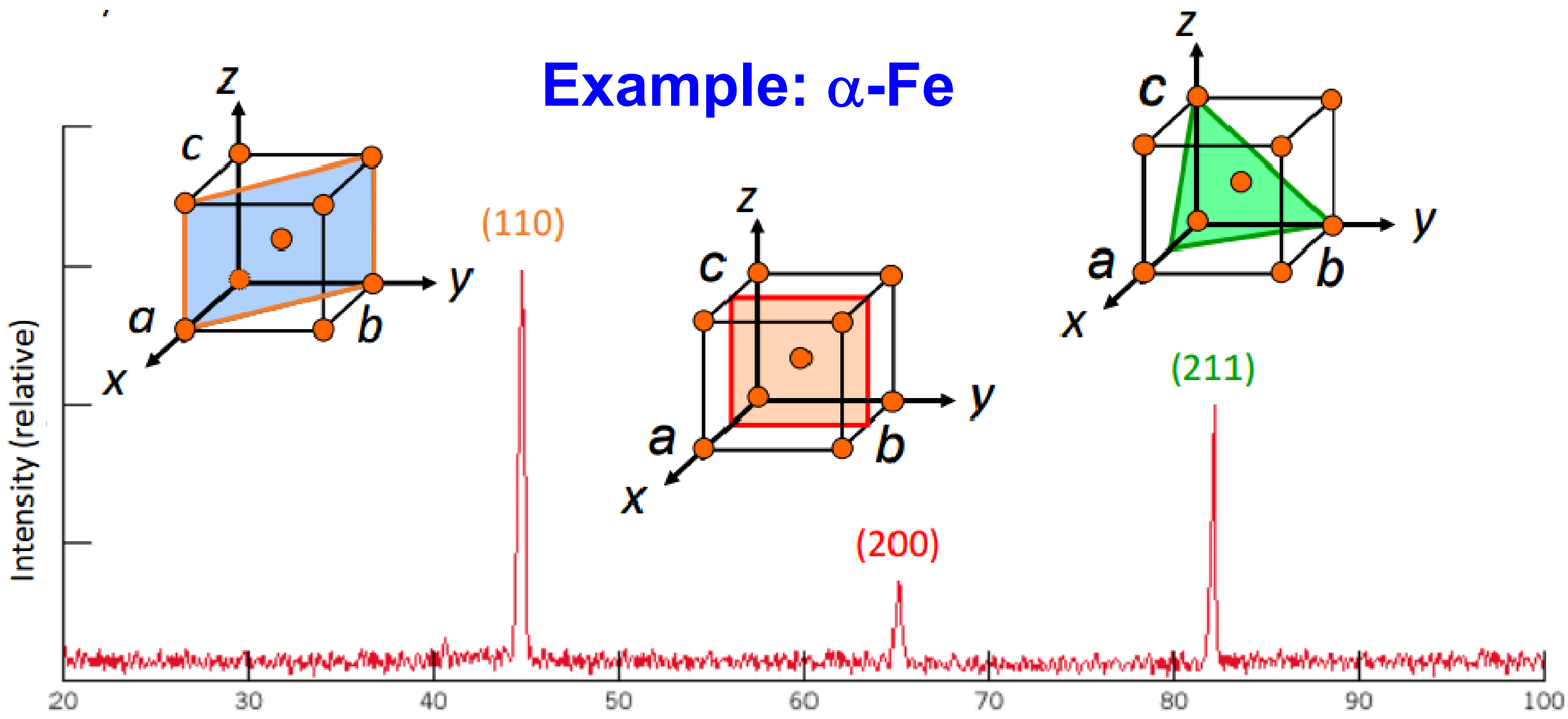


FIGURE 3.20 Diffraction pattern for polycrystalline α-iron.

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

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

  - BCC

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

  - FCC

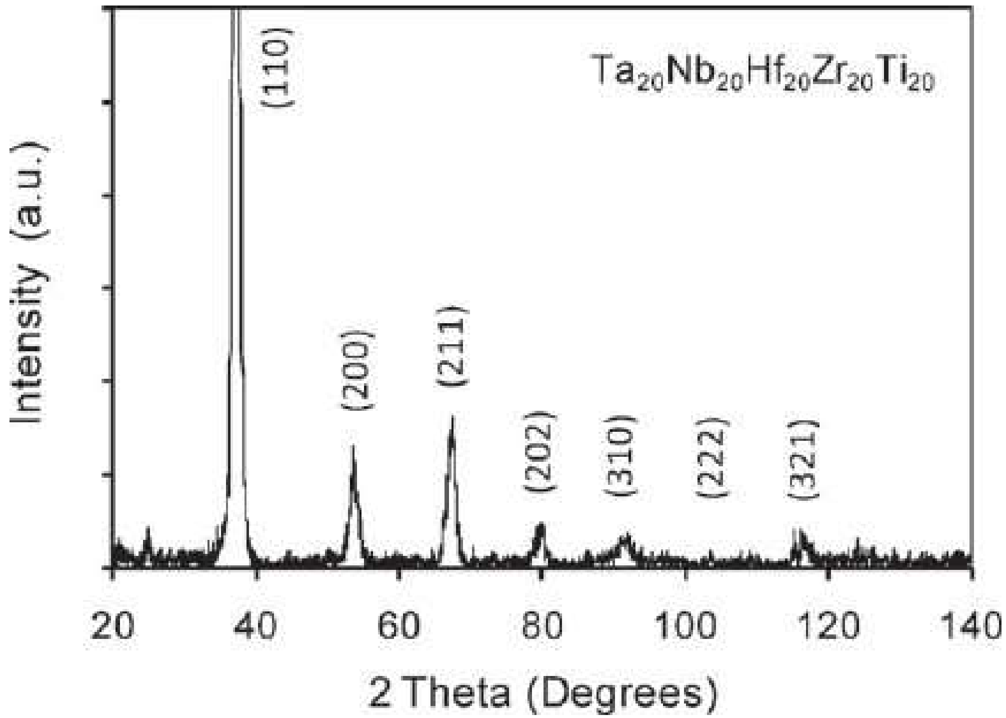
$$h, k, l \ \text{ are all even or odd}$$

Ashcroft & Mermin p.104-p.107

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

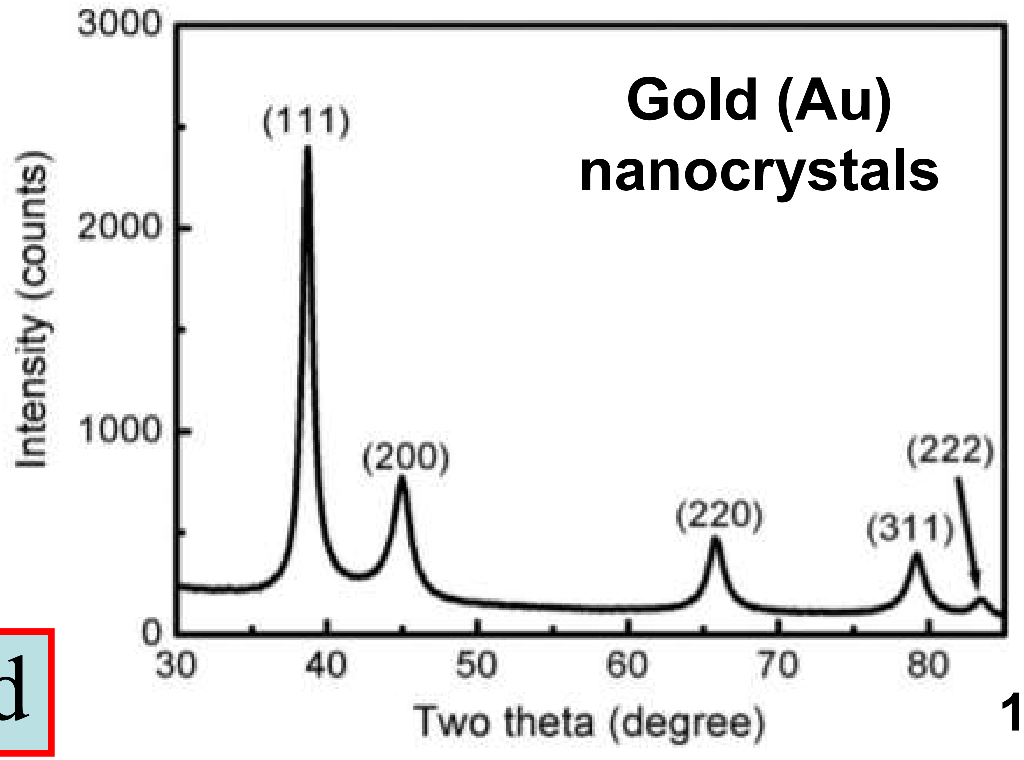
Forbidden numbers	Primitive, P	Face Centered, F	Body Centered, I	Corresponding *hkl*
	1			100
	2		2	110
	3	3		111
	4	4	4	200
	5			210
	6		6	211
7				
	8	8	8	220
	9			221, 300
	10		10	310
	11	11		311
	12	12	12	222
	13			320
	14		14	321
15				
	16	16	16	400

Geometrical Structure Factor *S*



BCC

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



FCC

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

Geometrical Structure Factor *S*

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

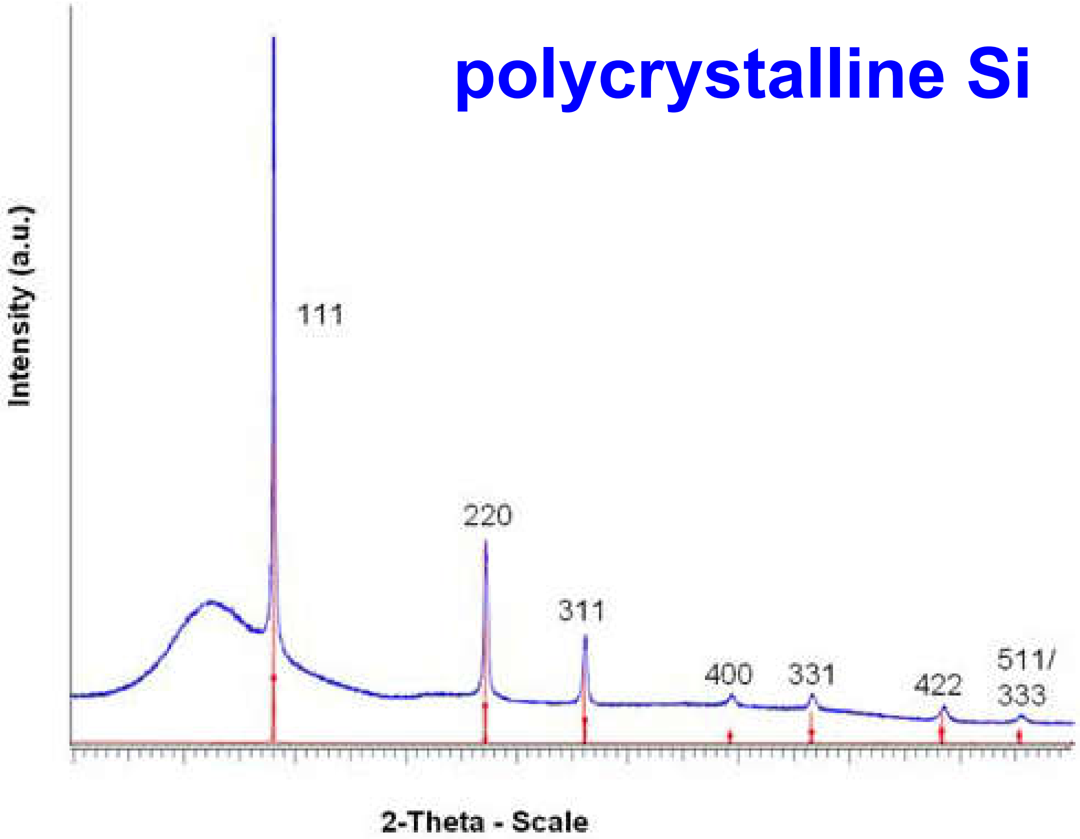
h, k, l are all odd

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

h, k, l are all even and $h + k + l = 4n$

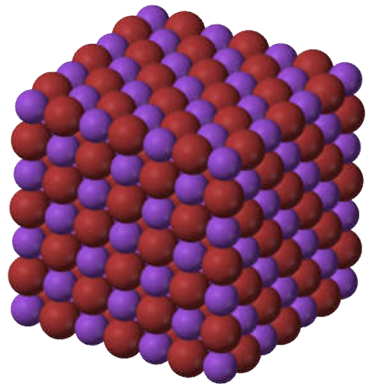
(220), (400), (422), ...

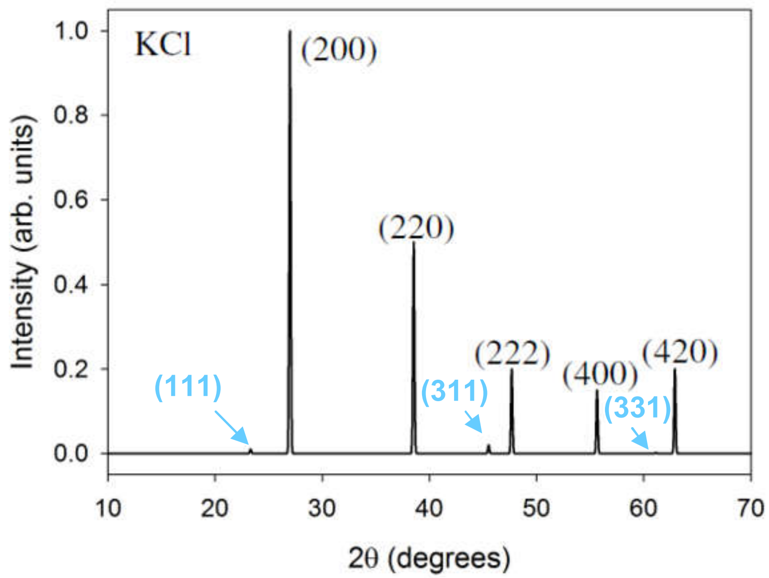
polycrystalline Si

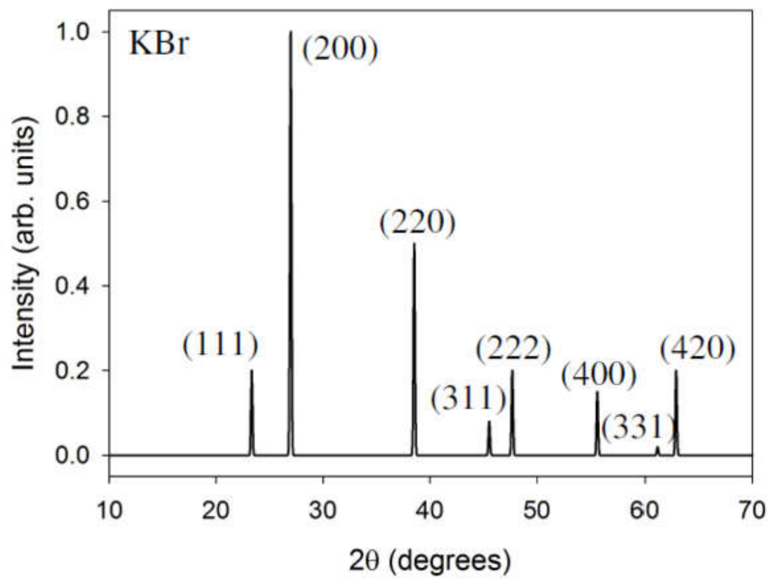


Atomic Form Factor *f*

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





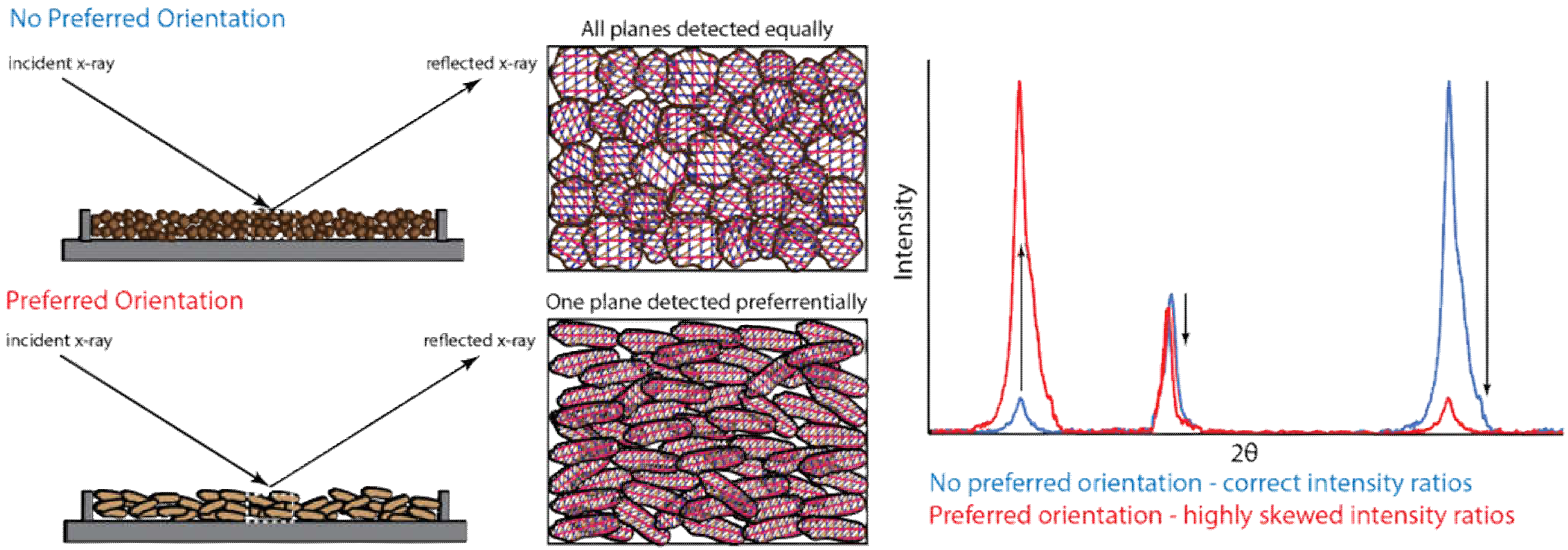


K^+ and Cl^- are very similar
KCl looks like a simple cubic with *a*/2

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

Crystal Orientation

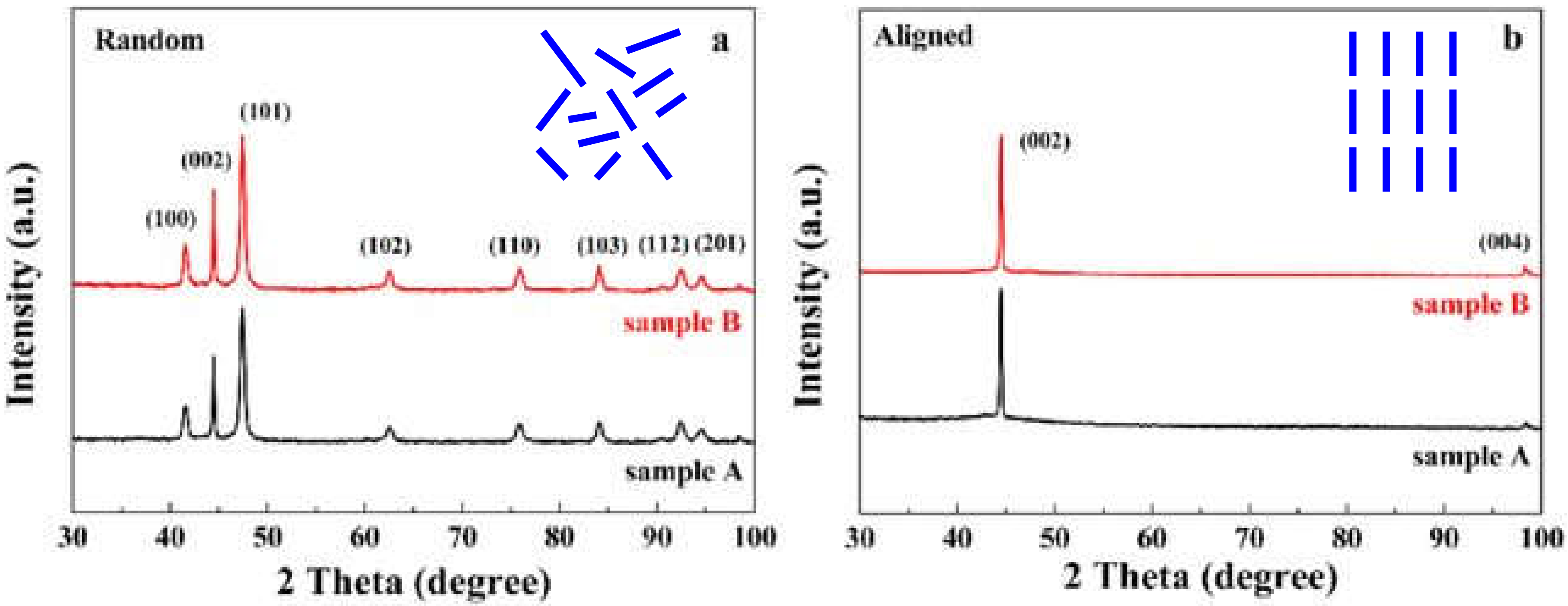
- **Aligned crystals show strong orientation preference**



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

Crystal Orientation

- **Aligned crystals show strong orientation preference**



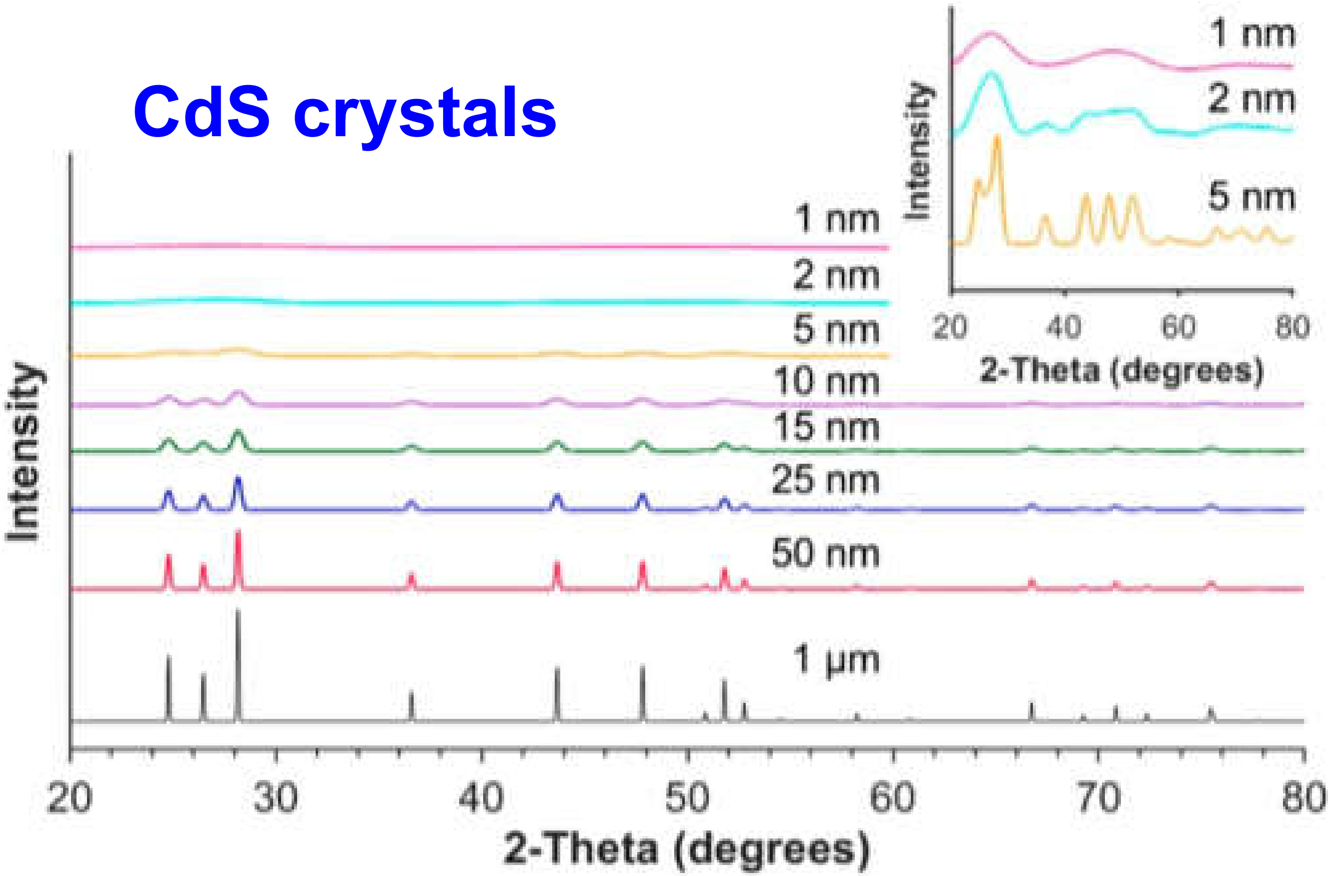
Co nanowires

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

Crystal Size

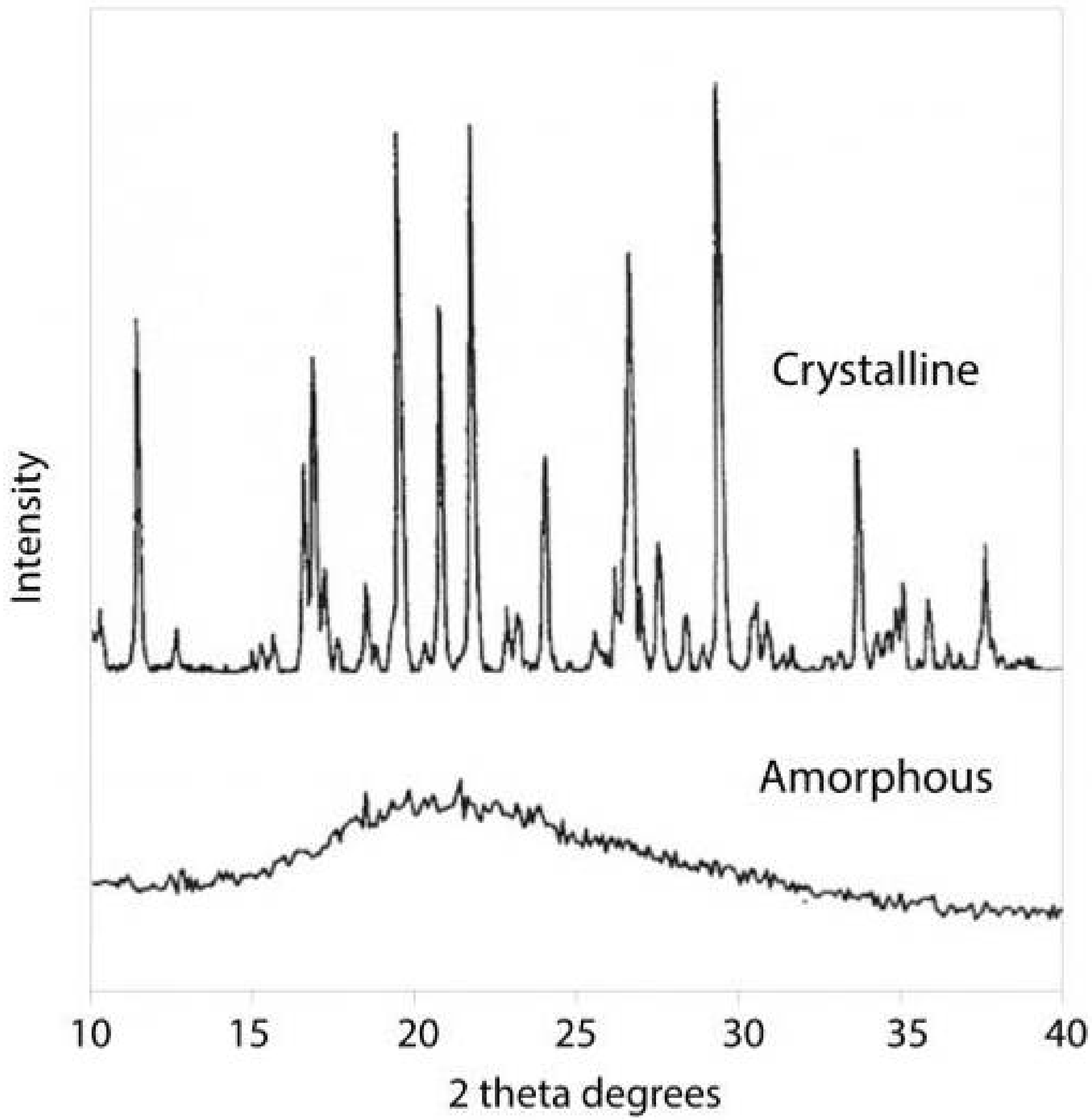
- **Smaller crystals lead to lower diffraction intensity and larger peak width.**

CdS crystals

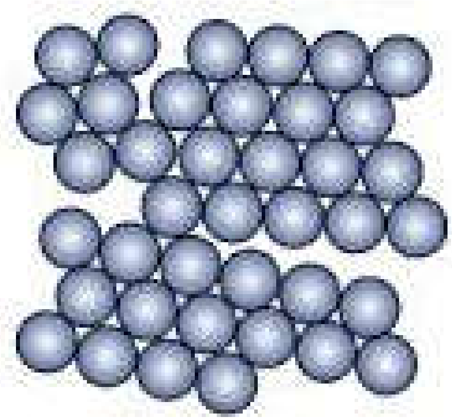


C. Holder, *et al.*, *ACS Nano* **13,** 7359 (2019)

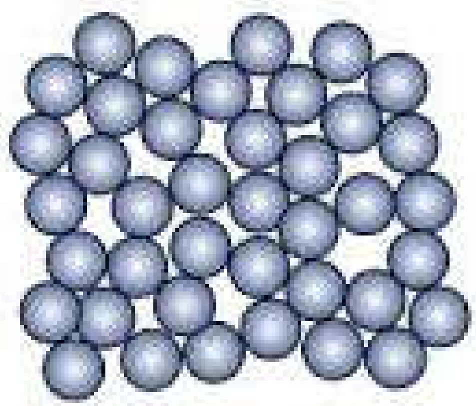
Amorphous Materials 非晶



Crystalline:
anisotropic (各向异性)

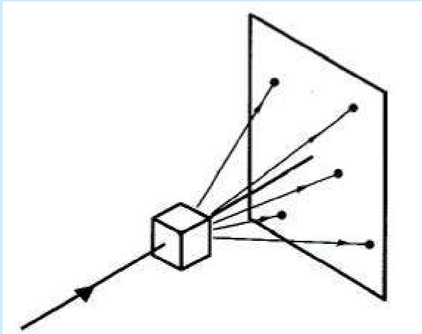


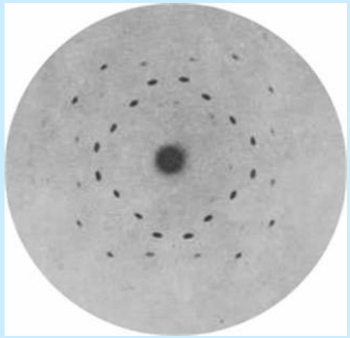
Amorphous:
isotropic (各向同性)



History of Discovery

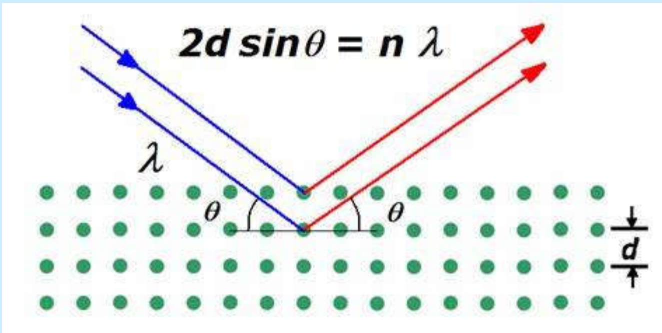
X-ray diffraction of crystals





M. von Laue (劳厄)
Nobel Prize in 1914

Bragg's law



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

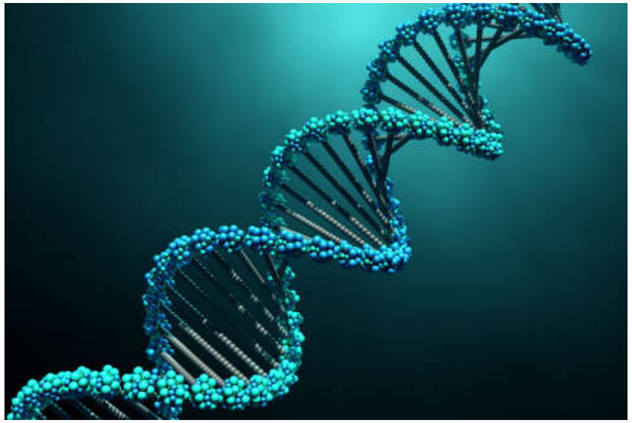
Teaching

Crystal Structure → **Diffraction Pattern**

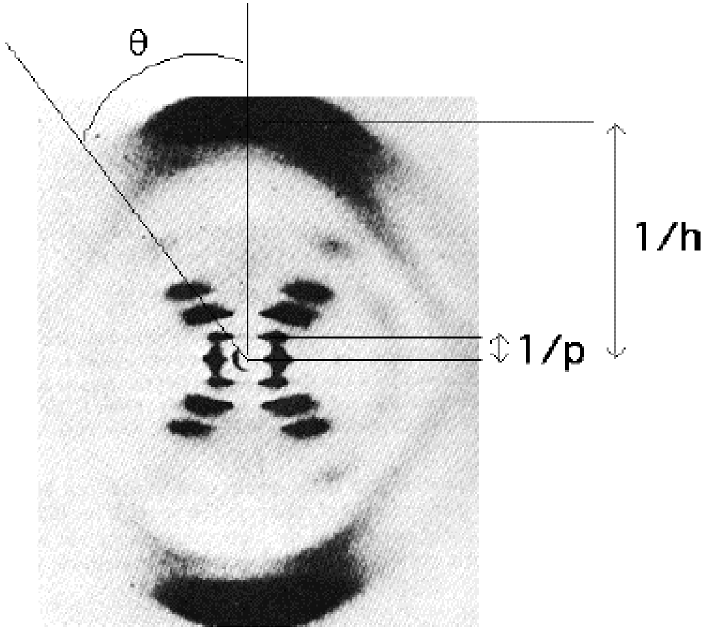
Crystal Structure ← **Diffraction Pattern**

Research

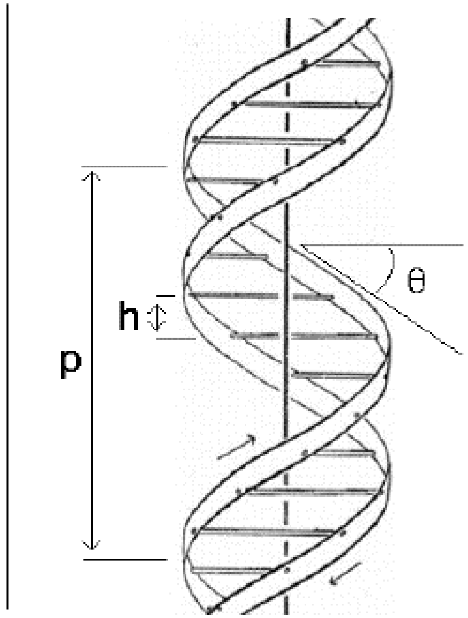
The Structure of DNA



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)

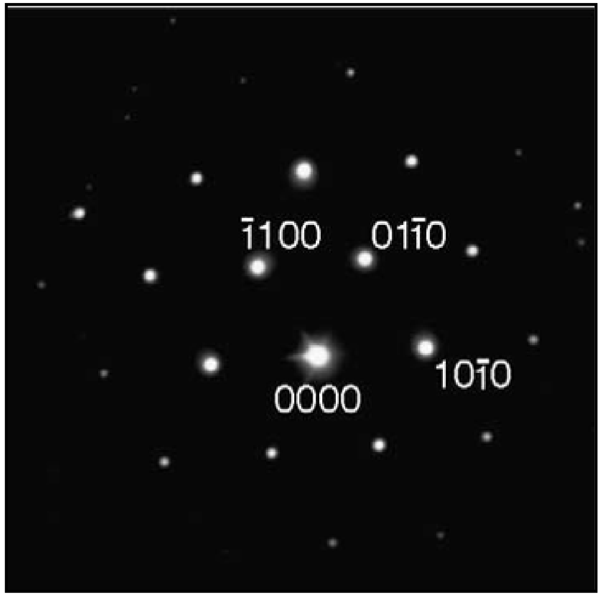
Electron Beam Diffraction

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

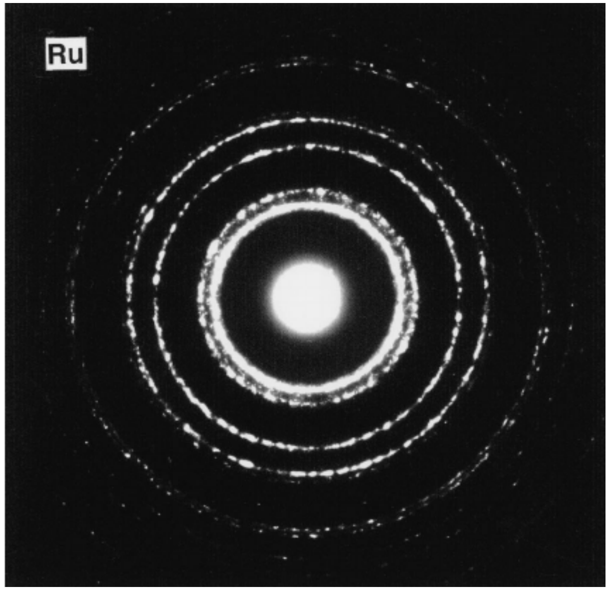
wave-particle duality

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

diffraction patterns



single crystal

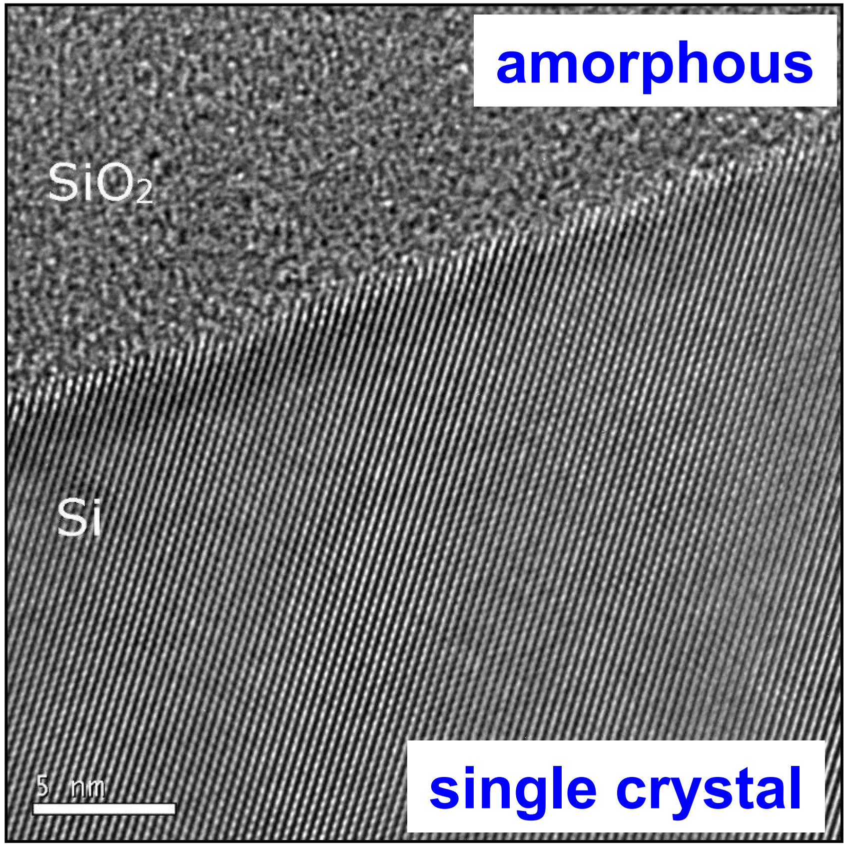


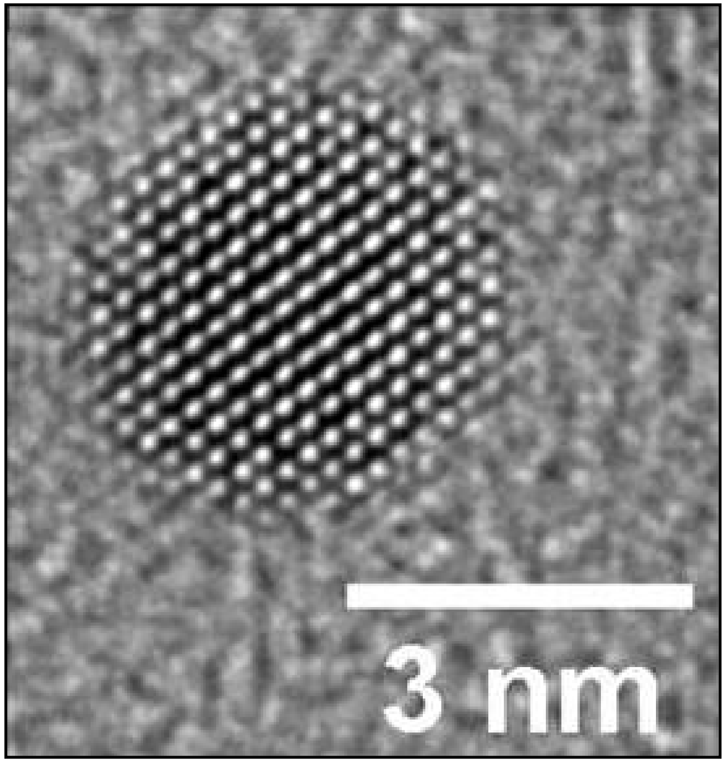
polycrystal

amorphous

Electron Microscopy

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





quantum dot

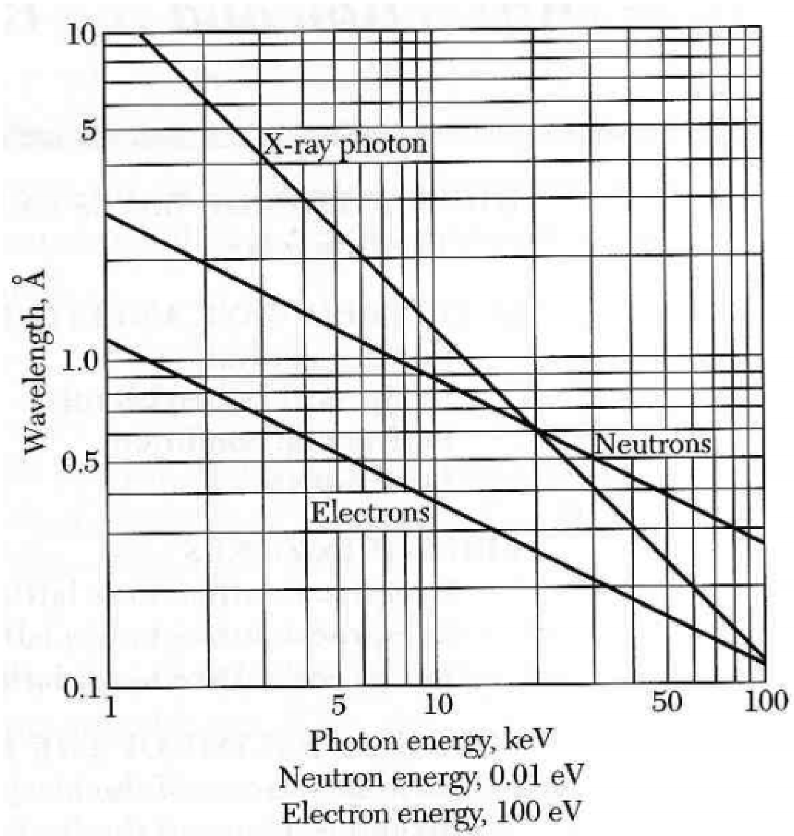
Neutron Diffraction 中子衍射

- 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