#### **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*, 2<sup>nd</sup> *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*, 3<sup>rd</sup> 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: $\mathbf{p'} - \mathbf{p} = \hbar \mathbf{q}$

#### Elastic (E' = E)

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

#### Inelastic (E' ≠ E)

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

Energy change: 
$$E' - E = hv$$
  
For X-rays:  $E = pc$ 

Elastic scattering geometry



## X-RAY SCATTERING

**X-rays:**  $\lambda$  (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!

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

- wide-angle diffraction ( $\theta > 5^{\circ}$ )
- small-angle diffraction ( $\theta$  close to  $0^{\circ}$ )
- X-ray reflectivity (films)

#### inelastic ( $\Delta E \neq 0$ )

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



Roentgen 1901 Nobel



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

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







von Laue 226



#### 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
- $\rightarrow$  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  $(\delta = n\lambda, \text{ with } n \text{ an integer})$  is precisely met:



When Bragg's Law is satisfied, "reflected" beams are in phase and interfere constructively. Specular "reflections" can occur only at these angles. 229

#### **DIFFRACTION ORDERS**

1<sup>st</sup> order:  $\lambda = 2d \sin \theta_1$ 2<sup>nd</sup> 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.

$$2\lambda = 2d\sin\theta_2$$
  $\implies$   $\lambda = 2(d/2)\sin\theta_2$ 

e.g. the 2<sup>nd</sup> order reflection of  $d_{100}$  occurs at same  $\theta$  as 1<sup>st</sup> order reflection of  $d_{200}$ 

## **XRD TECHNIQUES AND APPLICATIONS**



Fig. 3.6 The X-ray diffraction experiment

#### Uses:

- phase identification
- crystal structure determination
- radial distribution functions
- thin film quality
- crystallographic texture
- percent crystalline/amorphous

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

- 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  $\rightarrow$  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)





#### **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**



## THETA-2THETA GEOMETRY



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

## **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.



## ACTUAL EXAMPLE: PYRITE THIN FILM

#### $FeS_2$ - cubic (a = 5.43 Å) Random crystal orientations

Cu Ka = 1.54 Å



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

#### d-SPACING FORMULAS

 $h^2 + k^2 + l^2$ Cubic  $\frac{1}{d^2} = \frac{1}{a^2}$ 1  $h^2 + k^2 l^2$ Tetragonal  $\frac{1}{d^2} = \frac{1}{a^2} + \frac{1}{c^2}$  $1 h^2 k^2 l^2$ Orthorhombic  $\frac{1}{d^2} = \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}$  $\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$ Hexagonal  $\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2h \log \beta}{ac} \right)$ Monoclinic  $\frac{1}{d^2} = \frac{1}{V^2} [h^2 b^2 c^2 \sin^2 \alpha + k^2 a^2 c^2 \sin^2 \beta]$ Triclinic  $+ l^2 a^2 b^2 \sin^2 \gamma + 2hkabc^2 (\cos \alpha \cos \beta - \cos \gamma)$  $+ 2kla^2bc(\cos\beta\cos\gamma - \cos\alpha)$ +  $2hlab^2c(\cos\alpha\cos\gamma - \cos\beta)$ ]

## POWDER DIFFRACTION

<u>Peak positions</u> determined by size and shape of unit cell

<u>Peak intensities</u> determined by the atomic number and position of the various atoms within the unit cell

<u>Peak widths</u> 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.





#### **Generating Characteristic X-rays**





Bohr`s model



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

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

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## SYNCHROTRON LIGHT SOURCES





## 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  $K_a$  beam

#### Crystal Monochromators

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





## **DETECTION OF X-RAYS**

Table 4-2. Properties of common x-ray detectors; $\Delta E$  is measured as FWHM.

#### **Detection principles**

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

- Point detectors
- Strip detectors
- Area detectors

Detector	Energy range (keV)	Δ <i>E/E</i> at 5.9 keV (%)	Dead time/event (µs)	Maximum count rate (s <sup>-1</sup> )
Gas ionization (current mode)	0.2–50	n/a	n/a	10 <sup>11a</sup>
Gas proportional	0.2-50	15	0.2	10 <sup>6</sup>
Multiwire and microstrip proportional	3–50	20	0.2	10 <sup>6</sup> /mm <sup>2</sup>
Scintillation [NaI(Tl)]	3–10,000	40	0.25	$2 \times 10^{6}$
Energy-resolving semiconductor	1-10,000	3	0.5–30	$2 \times 10^{5}$
Surface-barrier (current mode)	0.1–20	n/a	n/a	10 <sup>8</sup>
Avalanche photodiode	0.1–50	20	0.001	10 <sup>8</sup>
CCD	0.1-70	n/a	n/a	n/a
Superconducting	0.1–4	< 0.5	100	$5 \times 10^3$
Image plate	4-80	n/a	n/a	n/a <sub>251</sub>

## **DETECTION OF X-RAYS**



## **X-RAY DETECTORS**

#### Area detectors

- film
- imaging plate
- CCD
- multiwire

#### Charge-coupled devices



**Exposure Window** 







Anatomy of a Charge Coupled Device (CCD)



## **X-RAY DETECTORS**

#### Imaging plates

#### photostimulated luminescence from BaFBr<sub>0.85</sub>I<sub>0.15</sub>:Eu<sup>2+</sup>





tetragonal Matlockite structure 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.

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

\vec{\phi}: wave amplitude at point rA: max amplitude of wave

k: wave vector

**r**: space vector from arbitrary origin



Amplitude is constant in any plane normal to  $\mathbf{k}$  because  $\mathbf{k} \cdot \mathbf{r}$  is a constant for such planes:

 $\mathbf{k} \quad \mathbf{k} \quad \mathbf{r}_{1} = \mathbf{k} \mathbf{r}_{1}$   $\mathbf{r}_{1} \quad \mathbf{q}_{2} \quad \mathbf{k} \cdot \mathbf{r}_{2} \quad \mathbf{k} \cdot \mathbf{r}_{2} = \mathbf{k} \mathbf{r}_{1} \sqrt{2} (\cos 45) = \mathbf{k} \mathbf{r}_{1}$ origin  $\mathbf{k} \cdot \mathbf{r} \text{ is indeed constant on wavefronts}$ 

## 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:

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

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

and {**n**<sub>i</sub>} and {**h**,**k**,**l**} are integers

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

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

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

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

$$\mathbf{b}_2 \cdot \mathbf{a}_1 = 2\pi \frac{\mathbf{a}_3 \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3)} \cdot \mathbf{a}_1 = 0 \quad \text{(since cross product of two vectors is perpendicular to both)}$$

$$\mathbf{b}_{3} \cdot \mathbf{a}_{1} = 2\pi \frac{\mathbf{a}_{1} \times \mathbf{a}_{2}}{\mathbf{a}_{1} \cdot (\mathbf{a}_{2} \times \mathbf{a}_{3})} \cdot \mathbf{a}_{1} = 0 \qquad \text{Indeed, } \mathbf{b}_{i} \cdot \mathbf{a}_{j} = 2\pi \delta_{ij}$$

so, K·R =  $(hb_1 + kb_2 + lb_3) \cdot (n_1a_1 + n_2a_2 + n_3a_3)$ =  $2\pi(hn_1 + kn_2 + ln_3) = 2\pi \times \text{integer}$ 

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  $ho^{i{f K}\cdot{f R}}=1$ 

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)

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{K} \cdot (\mathbf{r} + \mathbf{R})} = e^{i\mathbf{K} \cdot \mathbf{r}} = \psi(\mathbf{r})$$
$$\mathbf{e}^{i\mathbf{K} \cdot \mathbf{R}} = 1$$

Reciprocal lattice vectors = wave vectors of plane waves that are unity at all direct lattice sites 260

#### 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

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

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

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

→ simple cubic reciprocal lattice with lattice constant  $2\pi/a$ → b<sub>1</sub> parallel to a<sub>1</sub>, etc. 261 Crystals with orthogonal axes (cubic, tetragonal, orthorhombic)  $b_1$ ,  $b_2$ ,  $b_3$  are parallel to  $a_1$ ,  $a_2$ ,  $a_3$ , respectively.



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# RECIPROCAL LATTICE OF FCC IS BCC



$$\mathbf{b}_{2} = \frac{4\pi}{a} \frac{1}{2} (\hat{\mathbf{z}} + \hat{\mathbf{x}} - \hat{\mathbf{y}}) \qquad \mathbf{b}_{3} = \frac{4\pi}{a} \frac{1}{2} (\hat{\mathbf{x}} + \hat{\mathbf{y}} - \hat{\mathbf{z}})$$

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

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# **RECIPROCAL LATTICE OF BCC IS FCC**



BCC primitive vectors (not orthogonal):

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

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



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

# **RECIPROCAL LATTICES**

- simple orthorhombic  $\rightarrow$  simple orthorhombic
- FCC  $\rightarrow$  BCC
- $\bullet \text{ BCC} \to \text{FCC}$
- simple hexagonal  $\rightarrow$  simple hexagonal (rotated)

# 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



truncated octahedron

# 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  $\mathbf{K}$  has a family of real-space planes normal to it, separated by d.



# 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  $\mathbf{K} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ 

 $\rightarrow$  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*)



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  $2\pi/d_{hkl}$ .

# 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: 
$$e^{i(\mathbf{k}'-\mathbf{k})\cdot\mathbf{R}} = e^{i2\pi n} = 1$$
  
which is the same as:  $e^{i\mathbf{K}\cdot\mathbf{R}} = 1$ 

The scattering amplitude  $F_{K}$  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  $f_{R}(K)$  is the "atomic form factor" for a given atom (disc. later).

The scattered intensity is proportional to the absolute square of the amplitude:  $L \propto L |E|^2$ 

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

...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  $d_1$ ,  $d_2$  ...  $d_n$  within each primitive cell.

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

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



"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:



"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  $d_1, ..., d_n$ are in the ratios:

$$e^{i\mathbf{K}\cdot\mathbf{d}_1}$$
 ...  $e^{i\mathbf{K}\cdot\mathbf{d}_n}$ 

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

> Geometric structure factor

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

-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





## MONATOMIC BCC

#### For monoatomic BCC:

we can think of this as SC with two point basis (0,0,0),  $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ 



$$S_{\mathbf{K}} = \sum_{j=1}^{2} e^{i\mathbf{K}\cdot\mathbf{d}_{j}} = e^{i\mathbf{K}\cdot\mathbf{0}} + e^{i\mathbf{K}\cdot\frac{a}{2}(\overset{\rightarrow}{x}+\overset{\rightarrow}{y}+\overset{\rightarrow}{z})}$$
  
For SC,  $\mathbf{K} = \frac{2\pi}{a}(h\hat{\mathbf{x}}+k\hat{\mathbf{y}}+l\hat{\mathbf{z}})$ 
$$= 1 + e^{i\pi(h+k+l)}$$

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

#### e.g. consider the powder pattern of BCC molybdenum



## MONATOMIC FCC

For monoatomic FCC: SC with four point basis (0,0,0),  $(\frac{1}{2}, \frac{1}{2}, 0)$ ,  $(0, \frac{1}{2}, \frac{1}{2})$ ,  $(\frac{1}{2}, 0, \frac{1}{2})$ 



S = 4 when h + k, k + l, h + l all even (h, k, l all even or all odd)

S = 0 otherwise.

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

(hkl)	NaCl	KCI
(100)		
(110)		
(111)	$\checkmark$	
(200)	$\checkmark$	$\checkmark$
(210)		
(211)		
(220)	$\checkmark$	$\checkmark$
(221)		
(300)		
(310)		
(311)	$\checkmark$	

(110) always absent in RS



(111) sometimes absent



# **DIAMOND STRUCTURE**

**Diamond:** FCC lattice with two-atom basis  $(0,0,0,), (\frac{1}{4},\frac{1}{4},\frac{1}{4})$ 



$$S_{\mathbf{K},diamond} = \left[e^{iK\cdot0} + e^{iK\cdot\frac{a}{4}(x+y+z)}\right]\left[S_{\mathbf{K},FCC}\right]$$
$$= \left[1 + e^{i(\pi/2)(h+k+l)}\right]\left[S_{\mathbf{K},FCC}\right]$$

Only for all even or all odd hkl is  $5 \neq 0$ . For these unmixed values, Additional condition: 5 = 8 h + k + l twice an even number  $5 = 4(1 \pm i)$  h + k + l odd 5 = 0 h + k + l twice an odd number

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

I<sub>diamond</sub> : spots allowed by FCC have relative intensities of 64, 32, or 0.

	FCC	diamond
(hkl)	AI	Si
(100)		
(110)		
(111)	$\checkmark$	$\checkmark$
(200)	$\checkmark$	
(210)		
(211)		
(220)	$\checkmark$	$\checkmark$
(221)		
(300)		
(310)		
(311)		

What about zinc blende?

# SUMMARY OF SYSTEMATIC ABSENCES

crystal structure	condition for peak to occur		
SC	any <i>h,k,l</i>		
BCC	h+k+l=even		
FCC	<i>h,k,l</i> all even or all odd		
NaC1	<i>h,k,l</i> all even,		
	or all odd if $f_{A} \neq f_{B}$		
diamond	<i>h,k,l</i> all even and twice an even $\#$ ,		
and Silicon	or all odd		
HCP	any $h,k,l$ except when $h + 2k = 3n$		
	and <i>l</i> 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 Piones for BCC and FCC Lattices

			12,12,12			
			Cubic diffracting planes (hki)		$h^{-} + k^{-} + l^{-}$	
Cubic					SC: 1,2,3,4,5,6,8,9,10,11,12,	
planes {hkl}	$h^2 + k^2 + l^2$	$\sum_{k=1}^{k} \sum_{k=1}^{k} \sum_{k$	FCC	BCC	BCC: 2.4.6.8.10.12	
{100}	$1^2 + 0^2 + 0^2$	1				
{110} /111	$1^2 + 1^2 + 0^2$ $1^2 + 1^2 + 1^2$	2		110	FCC · 3 / 8 11 12 16 2/	
{200}	$2^2 + 0^2 + 0^2$	3	200	200	<b>FCC</b> . <i>3</i> ,4,0,11,1 <i>2</i> ,10, <i>2</i> 4,	
{210}	$2^{2} + 1^{2} + 0^{2}$	5	200	200	▶	
{211}	$2^2 + 1^2 + 1^2$	6 7	• • •	211		
{220}	$2^2 + 2^2 + 0^2$	8	220	220	Observable diffused is	
(221)	$2^2 + 2^2 + 1^2$	9			Observable diffraction	
{310}	$3^2 + 1^2 + 0^2$	10	•••	310	neeks for monostomic	
		SC	FCC	BCC	crystals	

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

## SIMPLE ANALYSIS OF SIMPLE PATTERNS

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

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

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

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

## SIMPLE ANALYSIS OF SIMPLE PATTERNS





#### What about AI?



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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,  $a = 3.18 \text{ \AA} \rightarrow \text{W}$ 

# 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
  - $\rightarrow$  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  $2\theta = 0 \& 180^{\circ}$
- gradual decrease to 50% as 20 approaches 90°

# SCATTERING OF X-RAYS BY ATOMS

scattering angle probabilities for a free electron:



# **ATOMIC FORM FACTORS**

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



consequences: • powder patterns show weak lines at large 20.
• light atoms scatter weakly and are difficult to see.

# 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



Peak width (broadening) is determined by several factors:

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

# FULL WIDTH AT HALF MAXIMUM (FWHM)



# 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



#### **Effect of Coherent Domain Size**



# Which of these diffraction patterns comes from a nanocrystalline material?



These diffraction patterns were produced from the same sample!

- 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,  $\theta_B$ phase lag between two planes =  $\lambda$ 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  $\Theta_B$  to  $\Theta_1$  is the range where diffracted intensity falls from a maximum to zero (half of Bragg peak profile).

Same arguments apply to  $\theta_2 < \theta_R$ 

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 =  $(2\theta_1 - 2\theta_2)/2 = \theta_1 - \theta_2$ 


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



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

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i+1

2j-3 2j-2

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 2j+1 planes and total thickness T:

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

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

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

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

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  $\lambda$  (X-ray wavelength, Å) K (shape factor) ~ 0.9 B,  $\Theta_{\rm B}$  in radians

Accurate size analysis requires correction for instrument broadening:

$$B^2 = B_M^2 - B_R^2$$

B<sub>M</sub>: Measured FWHM (in radians)

B<sub>R</sub>: 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



- 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  $\lambda$ =1.5 Å, *d*=1.0 Å, and  $\theta$ =49°. Then for a crystal 1 mm in diameter, the width B, due to the small crystal effect alone, would be about 2x10<sup>-7</sup> radian (10<sup>-5</sup> degree), too small to be observable. Such a crystal would contain some 10<sup>7</sup> 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 43x10<sup>-2</sup> radian (2.46°), which is easily measurable.

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

# **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"

