XRD-2

Interaction between X-ray and Matter Peak position

> XRD-2 READ

Hammond, Chap 8 (bottom half of page 208 can be excluded.) Sherwood & Cooper, Chap 4.13; 6.1~6.3; 8.9~8.16

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Krawitz, Chap 5, p119~128

Cullity, Chap 3 (3-1~3-6)

Sherwood & Cooper, Chapter 4.1~4.3

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Interference

- Interaction between two or more trains of waves of the same frequency emitted from coherent sources.
- > A series of stationary nodes and antinodes is established, known as interference.





Diffraction, X-ray diffraction (XRD)

- > Diffraction: reinforced coherent scattering
- > Diffraction: coherent and elastic scattering of radiation

by periodic arrays of objects

resulting in concerted constructive interference at specific angles

Diffraction occurs whenever wave motion encounters a set of <u>regularly spaced</u> <u>scattering objects</u>, provided the <u>wavelength of the wave motion is the same</u> <u>order of magnitude as the repeat distance</u> between the scattering centers

Atoms/ions/molecules in crystals Lattice parameter of crystals

 λ of X-ray (few Å)

Diffraction of Water Waves





Sherwood page 94, 186





- When slit width is wide compared to the λ of the wave motion, the diffraction effects are masked.
- From the diffraction effect, info on the obstacle can be obtained.



Diffraction and information

- > When a wave interacts with an obstacle, diffraction occurs.
- > Diffracted wave contains additional information about the obstacle.
- ➤ The detailed behavior depends solely on the diffracting obstacles. → The diffracted waves can be regarded as containing information on the structure of the obstacles.



Diffraction of X-rays



Kinematical vs. Dynamical theories of diffraction

> Kinematical theory

- ✓ <u>A beam scattered once is not scattered again.</u>
- ✓ Interaction of diffracted beam with crystal is negligibly small.

> Dynamical theory

- ✓Accounts for scattering of diffracted beam & <u>other interactions</u> of waves inside the crystal.
- ✓Needed when crystals are nearly perfect or when there is a strong

interaction of the radiation with the material (electron diffraction).

Diffraction

Infinite plane wave with wave vector **k** and frequency w; $\Psi = \Psi_0 e^{i (\mathbf{k} \cdot \mathbf{r} - wt)}$

- > What happens when a wave motion interacts with an obstacle placed in its path?
- How is the wave equation modified to take account of the interaction of the wave with the obstacle?



What is X-ray Diffraction?

X-rays are an ideal probe of electromagnetic radiation for the study of crystals as the wavelength <u>λ is of the same order as the distances between</u> the atoms in crystals (Å, nm).

> Elastic scattering \rightarrow no energy transfer & no wavelength change

When the periodic array consists of crystalline matter of three dimensional (3-d) arrangement of atoms, monochromatic X-ray radiation diffracts in a number of different directions in 3-d space.

Why do we use x-rays ? read Sherwood & Cooper, Chap 6.1~6.5

Interaction of electromagnetic wave & matter

- > Electric field (E) & magnetic field (H) propagate through the matter.
- Effect of E >>> effect of H
- > When a particle of charge q is placed in **E**, $\mathbf{F} = \mathbf{q}\mathbf{E} = \mathbf{m}\mathbf{a}$ $\mathbf{a} = \frac{\mathbf{q}}{\mathbf{m}}\mathbf{E}$
- ➤ E oscillates w/ very high v. → make the charged particle oscillate. → particle radiates E-M wave (scattering).

intensity of scattered wave
$$I \propto |a|^2 \propto (\frac{q}{m})^2 E^2$$

> Neutron (no charge), proton, electron vs. E

> XRD looks at the electron distribution in a crystal.

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Must read Sherwood & Cooper 4.13

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Heavy atoms scatter X-rays more effectively than light ones.

 \rightarrow Large e' density area can be the position of nuclei of heavy atoms.

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- > XRD looks at the electron distribution in a crystal.
- > XRD does not directly look at the positions of the nuclei of atoms.
- > Atom of atomic number Z \rightarrow intensity of scattered wave $\propto (\frac{Ze}{m_e})^2$
- ➢ <u>High Z atoms (heavy atoms) are much more effective scattering centers.</u> → <u>XRD cannot give much info on light elements.</u>
- ➤ Intensities of scattered X-ray → locations of electrons in one unit cell → electron density distribution (e' density map)

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Diffraction pattern

> Each reflection (diffraction peak) has an (hkl) index and a measured intensity.

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> Each reflection index defines a set of parallel planes that slice thru the crystal.



Calculation of electron density; Fourier transform

Electron density at (xyz) = the sum of contributions to the point (xyz), of waves scattered from the plane (hkl) whose amplitude depends on the number of electrons in the plane, added with the correct relative phase relationship.



- > Given all F(hkl) (amplitude & phase for each reflection), $\rho(xyz)$ can be calculated.
- > Given $\rho(xyz)$ (i.e., the structure), F(hkl) can be calculated.

$\succ F, \varphi \leftarrow FT \rightarrow \rho(xyz)$ Chan Park, MSE-SNU Intro to Crystallography, 2021 19

Range of Applications of X-Ray Analytical Methods

- > Qualitative and quantitative element analysis (XRF)
- > Qualitative and quantitative phase analysis (XRD)
- ➢ % crystallinity
- > Micro-strain and crystallite size determination
- Residual stress and texture analysis
- Grazing incidence diffraction (GID) and reflectometry (XRR)
- Structure solution and refinement
- > Micro-diffraction (phase identification, texture, stress...)
- > Nano-structure investigations by small angle X-ray scattering (SAXS)

What can we do with XRPD (X-ray powder diffraction)?

- Identification of unknown phases (phase ID)
- > Quantitative phase analysis
- > Accurate lattice parameter measurement
- ➢ % crystallinity
- > Crystal size
- > Internal elastic strains
- Preferred orientation
- > Cation site disorder
- > Micro-diffraction (phase identification, texture, stress...)
- Structure refinement (vs. single crystal)

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For constructive interference, $(AB - CD) = a(\cos \alpha_n - \cos \alpha_0) = n_x \lambda$

Laue equation $a(\cos \alpha_n - \cos \alpha_0) = \mathbf{a} \cdot (\mathbf{s} - \mathbf{s}_0) = n_x \lambda$ $b(\cos \beta_n - \cos \beta_0) = \mathbf{b} \cdot (\mathbf{s} - \mathbf{s}_0) = n_y \lambda$ $c(\cos \gamma_n - \cos \gamma_0) = \mathbf{c} \cdot (\mathbf{s} - \mathbf{s}_0) = n_z \lambda$



Bragg's Law

- > Braggs W.H. and W.L. Bragg (father & son)
- ≻ 1913 1914
- > Realized that x-ray scattering could be imagined as reflections from planes
- > Showed how it could be used to determine atomic structure NaCl
- > Nobel prize 1915

- $n\lambda = 2d \sin\theta$ d = distance of lattice planes



reflection \neq diffraction (see Cullity chapter 3.2)





The path difference between the waves scattered by atoms from adjacent (hkl) lattice planes of spacings d_{hkl} is given by

 $(AB + BC) = (d_{hkl} \sin \theta + d_{hkl} \sin \theta) = 2d_{hkl} \sin \theta.$

Hence for constructive interference:

$$n\lambda = 2d_{hkl}\sin\theta,$$

where *n* is an integer (the order of reflection or diffraction).

$$\lambda = 2\left(\frac{d_{hkl}}{n}\right)\sin\theta = 2d_{nh\,nk\,nl}\sin\theta$$
 Bragg's law





3rd order diffaction from (111) = 1st order diffraction from 333 (**Laue index**). 333 planes have 1/3 spacing of (111). (See Hammond 8.3)





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$\lambda = 2d \sin \theta$

- Condition for diffraction
 - ✓ Incident beam
 - \checkmark Diffracted beam > co-planar
 - ✓ Plane normal

Sinθ = λ/2d (e.g. d = 4 Å)
✓ If λ = 1000 Å, sinθ = 125 → The crystal could not possibly diffract. (No θ can meet the diffraction condition.)
✓ If λ = 0.01 Å, sinθ = 0.00125 → Diffraction angle too small to be measured
✓ If λ = 2 Å, sinθ = 0.25, θ = 14.5° → Diffraction angle can be easily measured

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Laue equation vs. Bragg's Law

≻Laue

- ✓ Crystals consist of **3-D network of rows of atoms**
- ✓ Crystal behaves as a 3D diffraction grating
- ✓ Laue equations

➢ Bragg

- ✓ Crystals consist of planes of atoms which behave as reflecting planes
- ✓ Strong reflected beam is produced when the path difference between reflections from successive planes in a family is equal to whole number of wavelengths
- ✓ Bragg's law





Linear least square

4 measurements (observations) 2 unknown parameters

4 (x,y) data sets (1,6), (2,5), (3,7), (4,10)

More equations than unknowns

 \rightarrow There are no values of β_1 and β_2 that satisfy the equations exactly

 \rightarrow can get the β_1 and β_2 that satisfy the equations as much as possible (best straight line thru the points)

→ best fit = values of β_1 and β_2 that minimizes $\sum \epsilon_i^2$ when residual (error) $\epsilon_i = y - \beta_1 - \beta_2 x$



Line of linear regression



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Linear least square

$$S(\beta_1,\beta_2) = [6 - (\beta_1 + 1\beta_2)]^2 + [5 - (\beta_1 + 2\beta_2)]^2 + [7 - (\beta_1 + 3\beta_2)]^2 + [10 - (\beta_1 + 4\beta_2)]^2$$

For errors to be minimum









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If λ can change continuously \rightarrow other planes can diffract as their reciprocal lattice points successively intersect the sphere \rightarrow Laue's original X-ray experiment using <u>white radiation</u>





- > Simulated and indexed powder XRD pattern for bulk (1 µm) wurtzite CdS.
- The inset shows the crystal structure of wurtzite CdS with the (100), (002), and (101) planes highlighted.





- Graphical representation of preferred orientation for nanoparticles having different shapes: (a) spheres, (b) cubes, and (c) rods.
- Simulated XRD patterns for varying degrees of alignment (*i.e.*, preferred orientation) of wurtzite CdS particles along specific crystallographic directions: (d) [100], (e) [001], and (f) [110].



X-ray diffraction > residual stress measurement

 $\lambda = 2d \sin \Theta$

The value of d can be obtained from the peak position (2θ) of the XRD pattern

SSVV

The change of d can be obtained from XRD @ many different angles \rightarrow info on strain \rightarrow info on stress



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Cullity 3rd ed. p441

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Peak position, Intensity and Shape of diffraction lines

- 2theta
 - ✓ Geometry (crystal system, lattice parameter) (<u>size & shape</u>)
- ➤ Intensity
 - ✓ Atom type
 - ✓ Arrangement
 - ✓ Orientation
- Shape of diffraction lines
 - ✓ Instrument broadening
 - ✓ Particle dimension
 - ✓ Strain



2θ





➤ Two step process

(1) Determination of the size & shape of the unit cell ← peak positions of the diffraction pattern

(2) Determination of lattice type & distribution of the atoms in the structure ← intensities of the diffraction peaks

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 - Krawitz, Chap 5, p119~128
 - Cullity, Chap 3 (3-1~3-6)
 - Sherwood & Cooper, Chapter 4.1~4.3
- > XRD-2 Homework (due in 1 week)
 - ✓ Hammond chapter 8 --- 1, 2, 3
 - ✓ Krawitz p5.1
 - ✓ Cullity 3-3~3-6