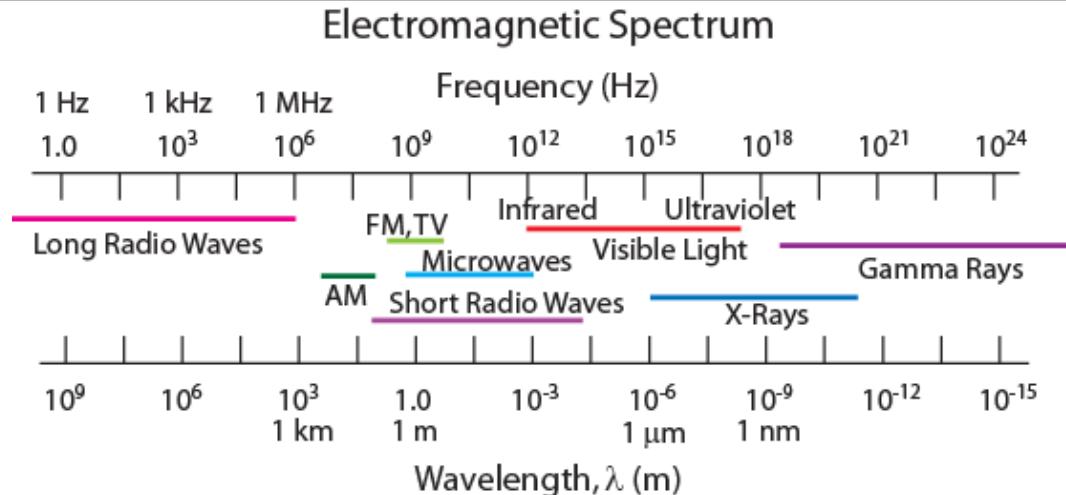




Introduction: X-Ray Diffraction

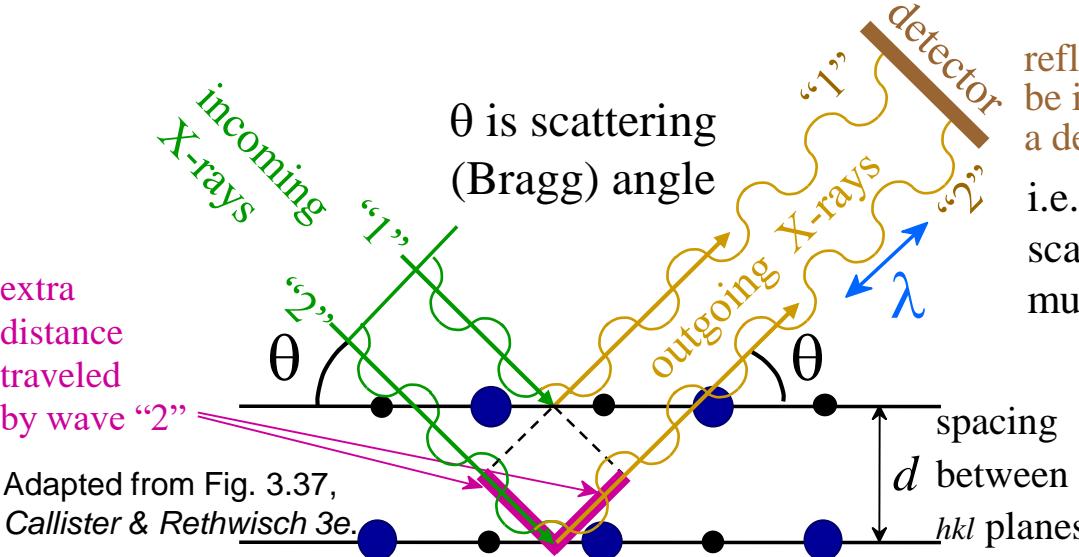


- XRD is a powerful experimental technique used to determine the
 - crystal structure and its lattice parameters ($a, b, c, \alpha, \beta, \gamma$) and
 - spacing between lattice planes (hkl Miller indices) → this interplanar spacing (d_{hkl}) is the distance between parallel planes of atoms or ions.
- Diffraction is result of radiation's being scattered by a regular array of scattering centers whose spacing is about same as the λ of the radiation.
- *Diffraction gratings* must have spacings comparable to the wavelength of diffracted radiation.
- We know that atoms and ions are on the order of 0.1 nm in size, so we think of crystal structures as being *diffraction gratings* on a sub-nanometer scale.
- For X-rays, atoms/ions are scattering centers (photon interaction with an orbital electron in the atom). Spacing (d_{hkl}) is the distance between parallel planes of atoms.....



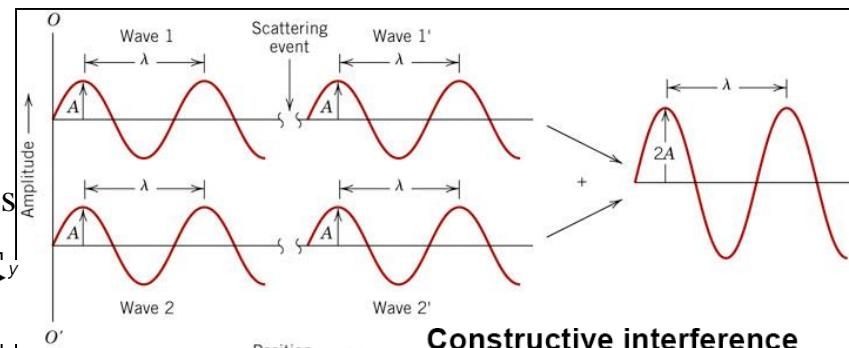
XRD to Determine Crystal Structure & Interplanar Spacing (d_{hkl})

Recall incoming X-rays **diffract** from crystal planes:



reflections must be in phase for a detectable signal

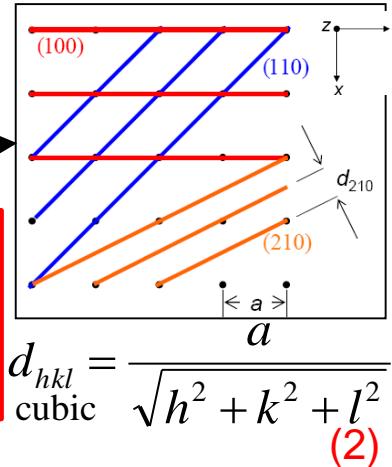
i.e., for diffraction to occur, x-rays scattered off adjacent crystal planes must be in phase:



Constructive interference
Diffracted waves are in phase and reinforce (add up)

(Bragg's Law is not satisfied)

Measurement of critical angle, θ_c , allows computation of interplanar spacing (d)

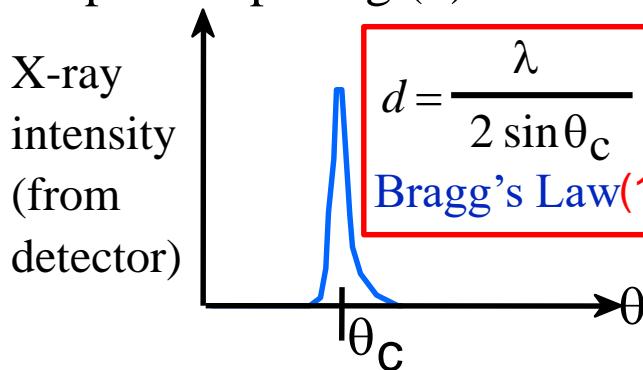


$$d = \frac{\lambda}{2 \sin \theta_c}$$

Bragg's Law(1)

$$d_{hkl} = \frac{\lambda}{\sqrt{h^2 + k^2 + l^2}}$$

Destructive interference
Diffracted waves are out of phase and cancel out





The interplanar (d_{hkl}) spacings for the 7 crystal systems

The value of d , the distance between adjacent planes in the set (hkl) , may be found from the following equations.

Cubic:

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

Tetragonal:

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

Hexagonal:

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

Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

Orthorhombic:

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

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:

$$\frac{1}{d^2} = \frac{1}{V^2} (S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

In the equation for triclinic crystals,

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

$$S_{11} = b^2 c^2 \sin^2 \alpha,$$

$$S_{22} = a^2 c^2 \sin^2 \beta,$$

$$S_{33} = a^2 b^2 \sin^2 \gamma,$$

$$S_{12} = abc^2 (\cos \alpha \cos \beta - \cos \gamma),$$

$$S_{23} = a^2 bc (\cos \beta \cos \gamma - \cos \alpha),$$

$$S_{13} = ab^2 c (\cos \gamma \cos \alpha - \cos \beta).$$

- As crystal symmetry decreases, the number of XRD peaks observed increases:

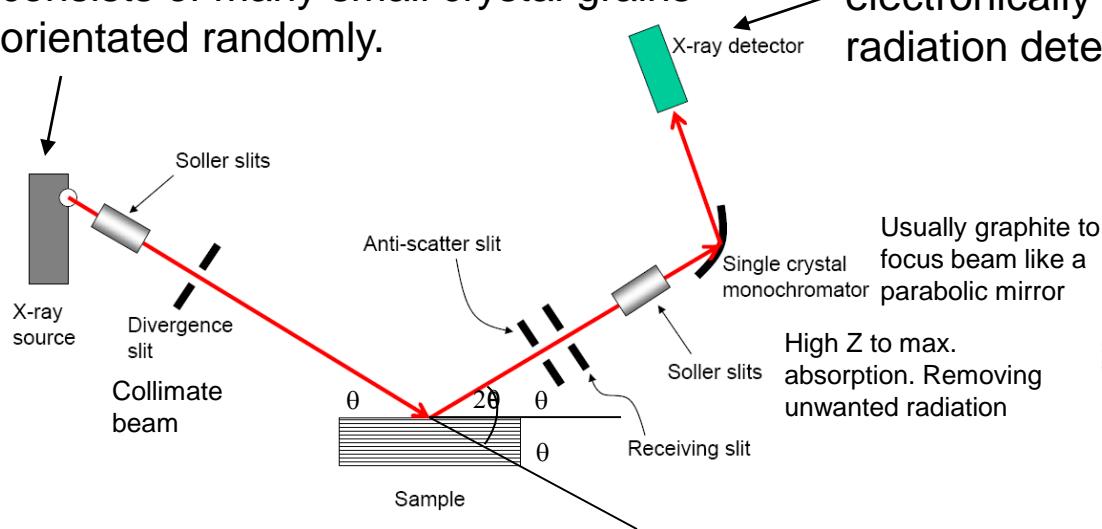
• *Cubic crystals*, highest symmetry, fewest number of XRD peaks, e.g. $(110)=(101)=(011)$, since $a=b=c \rightarrow$ all 3 have same interplanar (d_{hkl}) spacing.

• *Orthorhombic crystals*, lower symmetry, larger number of XRD peaks, e.g. $(110) \neq (101) \neq (011)$, since $a \neq b \neq c \rightarrow$ all 3 have different interplanar (d_{hkl}) spacings

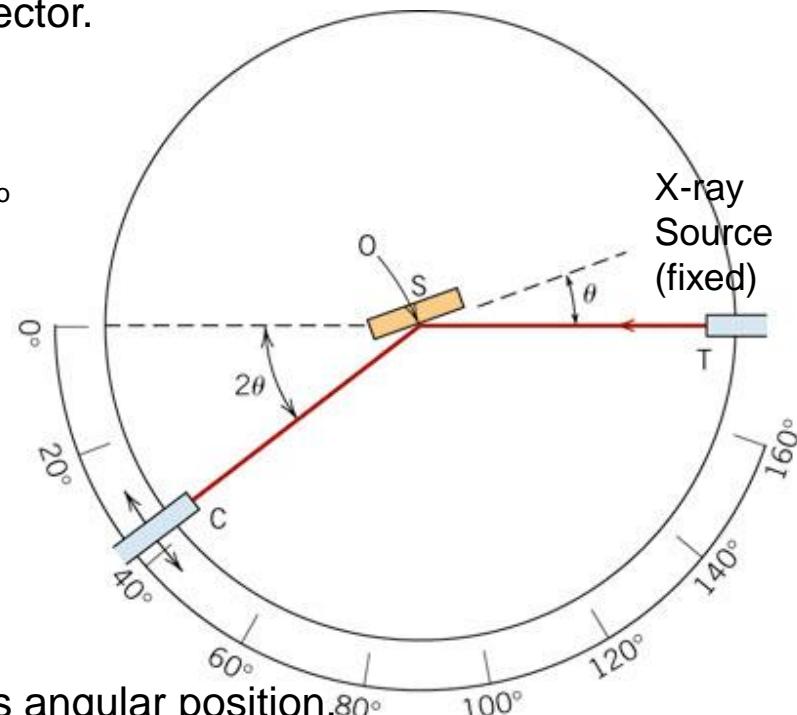


Geometry of XRD (F.Y.I.)

- A single (monochromatic) wavelength of x-ray radiation is often used to keep the number of diffraction peaks to a small workable number, since samples often consists of many small crystal grains orientated randomly.



- The diffracted beam intensity is monitored electronically by a mechanically driven scanning radiation detector.



Bragg angle = θ

Diffraction angle, what's measured experimentally = 2θ

- Counter/detector is rotated about O-axis; 2θ is its angular position.
- Counter and specimen are mechanically coupled such that a rotation of the specimen through θ is accompanied by a 2θ rotation of the counter.
- This assures that the incident and reflection angles are maintained equal to one another.



More on Bragg's Law

- Bragg's Law is a necessary ***but*** insufficient condition for diffraction.
- It only defines the diffraction condition for ***primitive unit cells***, e.g. P cubic, P tetragonal, etc., where atoms are only at unit cell corners.
- Crystal structures with non-primitive unit cells have atoms at additional lattice (basis) sites.
- These extra scattering centers can cause out-of-phase scattering to occur at certain Bragg angles.
- The net result is that some of the diffraction predicted by Bragg's Law (eqn. 1) does not occur, i.e. certain sets of planes do not exist (**forbidden reflections**).
- **Selection (or Reflection) rules:**

| Bravais Lattice | Example Compounds/Structures | Allowed Reflections | Forbidden Reflections |
|-------------------------|-------------------------------|--|--|
| Primitive (P) Cubic | Simple Cubic (α -Po) | Any h,k,l | None |
| Body-centered (I) Cubic | Body-Centred Cubic metal | $h+k+l$ even | $h+k+l$ odd |
| Face-centered (F) Cubic | Face-Centred Cubic metal | h,k,l all odd or all even | h,k,l mixed odd or even |
| Face-centered (F) Cubic | NaCl-rocksalt, ZnS-zincblende | h,k,l all odd or all even | h,k,l mixed odd or even |
| Face-centered (F) Cubic | C, Si, Ge - Diamond cubic | As FCC, but if all even then $h+k+l=4n$ (n is integer) | h,k,l mixed odd or even and if all even and $h+k+l\neq 4n$ |
| Primitive (P) Hexagonal | Hexagonal closed packed metal | All other cases | $h+2k=3n$, l odd |

These rules are calculated based on atomic scattering factors (f) and structure factors (F), which we will discuss next class (you will also see them in HW4 and possibly on the final exam).



Selection Rules for Cubic

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

where "S" is line #,
e.g. for (100) S=1 and
for (200) S=4

As we will determine later when we calculate the structure factors, these selection rules also hold for the other 5 non-primitive Bravais lattices, e.g. I-tetragonal, F-orthorhombic, etc.

| P | | I | | F | |
|----|---------|----|-------|----|-------|
| S | (hkl) | S | (hkl) | S | (hkl) |
| 1 | 100 | - | - | - | - |
| 2 | 110 | 2 | 110 | - | - |
| 3 | 111 | - | | 3 | 111 |
| 4 | 200 | 4 | 200 | 4 | 200 |
| 5 | 210 | - | - | - | - |
| 6 | 211 | 6 | 211 | - | - |
| 7 | - | - | - | - | - |
| 8 | 220 | 8 | 220 | 8 | 220 |
| 9 | 221,300 | - | - | | |
| 10 | 310 | 10 | 310 | | |
| 11 | 311 | - | - | 11 | 311 |
| 12 | 222 | 12 | 222 | 12 | 222 |

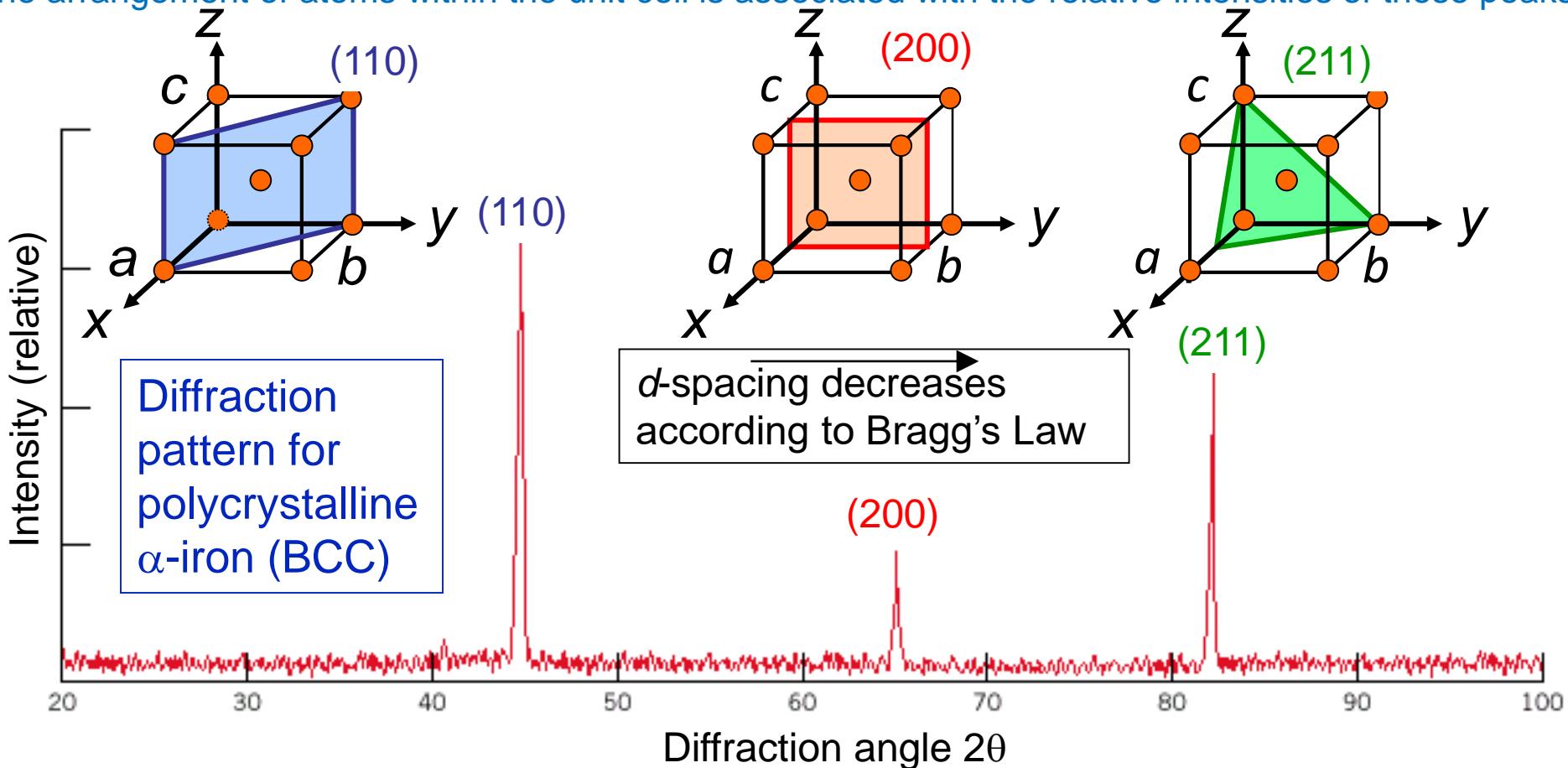
→ Odd+even
→ Odd+even
→ All odd
→ All even
→ Odd+even
→ Odd+even
→ All even
→ Odd+even
→ Odd+even
→ All odd
→ All even

class 24/6



Example of XRD Pattern

- The unit cell size and geometry may be resolved from the angular positions of the diffraction peaks.
- When the distance between the peak spacings are all pretty much the same (2θ) it is likely cubic.
- The arrangement of atoms within the unit cell is associated with the relative intensities of these peaks



→ $h+k+l$ even are only allowed according to previously shown selection rules for BCC metal.



Review of Systematic Absences in the Diffraction Patterns of 4 Cubic Structures

| $h^2 + k^2 + l^2 = S=1$ | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
|-------------------------|---|---|---|---|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|
| 100 | | | | | | | | | | | | | | | | | | | |
| 110 | | | | | | | | | | | | | | | | | | | |
| 111 | | | | | | | | | | | | | | | | | | | |
| 200 | | | | | | | | | | | | | | | | | | | |
| 210 | | | | | | | | | | | | | | | | | | | |
| 211 | | | | | | | | | | | | | | | | | | | |
| 220 | | | | | | | | | | | | | | | | | | | |
| 300, 221 | | | | | | | | | | | | | | | | | | | |
| 310 | | | | | | | | | | | | | | | | | | | |
| 311 | | | | | | | | | | | | | | | | | | | |
| 222 | | | | | | | | | | | | | | | | | | | |
| 320 | | | | | | | | | | | | | | | | | | | |
| 321 | | | | | | | | | | | | | | | | | | | |
| 400 | | | | | | | | | | | | | | | | | | | |
| 410, 322 | | | | | | | | | | | | | | | | | | | |
| 411, 330 | | | | | | | | | | | | | | | | | | | |
| 331 | | | | | | | | | | | | | | | | | | | |
| 420 | | | | | | | | | | | | | | | | | | | |

→ When indexing XRD data for your material always try cubic first (least amount of diffracting planes since most symmetric lattice parameters). class24/8



X-Ray Diffraction for Tetragonal, Hexagonal and Orthorhombic Crystals

Bragg's Law (1):

$$d = \frac{\lambda}{2 \sin \theta_c} \quad (1)$$

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2) \text{ Plane spacing for cubic crystals}$$

Combined (1) and (2):

$$\left(\frac{n\lambda}{2a}\right)^2 = \frac{\sin^2 \theta}{h^2 + k^2 + l^2} \text{ or } \sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2) \quad (3)$$

For a particular incident x-ray wavelength and cubic crystal of unit cell size a , this equation predicts all possible Bragg angles at which diffraction can occur from planes (hkl) .

→ Diffraction planes are determined solely by the shape and size (lattice parameters) of the unit cell.

Plane spacings for:

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (4)$$

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (5)$$

Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad (6)$$

If crystal is tetragonal with $a=a\neq c$ then (1) and (4) become:

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2) + \frac{\lambda^2}{4c^2} (l^2) \quad (7)$$

If crystal is hexagonal with $a=a\neq c$ then (1) and (5) become:

$$\sin^2 \theta = \frac{\lambda^2}{3a^2} (h^2 + k^2 + hk) + \frac{\lambda^2}{4c^2} (l^2) \quad (8)$$

If crystal is orthorhombic with $a\neq b\neq c$ then (1) and (6):

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2) + \frac{\lambda^2}{4b^2} (k^2) + \frac{\lambda^2}{4c^2} (l^2) \quad (9)$$

- Next class we will determine how intensities of diffracted beams are determined by positions of the atoms within the unit cell. Thus, we must measure the intensities if we are able to obtain any information at all about atom positions. (**Intensities (I) are related to Structure Factor (F), i.e., I is proportional to F**).
- We will determine that for many crystals there are particular atomic arrangements which reduce the intensities of some diffracted beams to zero, i.e. no diffracted beam at the angle (θ) predicted by Equations (3), (7), (8), (9), etc., **which means F=0**.



The Effect of Cell Distortion (Symmetry) on XRD Patterns

- As the symmetry of crystal decreases more peaks are seen, e.g. cubic \rightarrow triclinic.

- Similar with cell distortion.** If distort / cubic along [001] by 4% so c is now 4.16 \AA get / tetragonal.

- This decreases symmetry more, and shifted diffraction lines are formed (shown in the middle for tetragonal).

- If now stretch 8% along [010] axis with $a=4.00\text{\AA}$, $b=4.32\text{\AA}$, and $c=4.16\text{\AA}$ to get / orthorhombic which lowers symmetry even more thus adding more diffraction lines (shown far right).

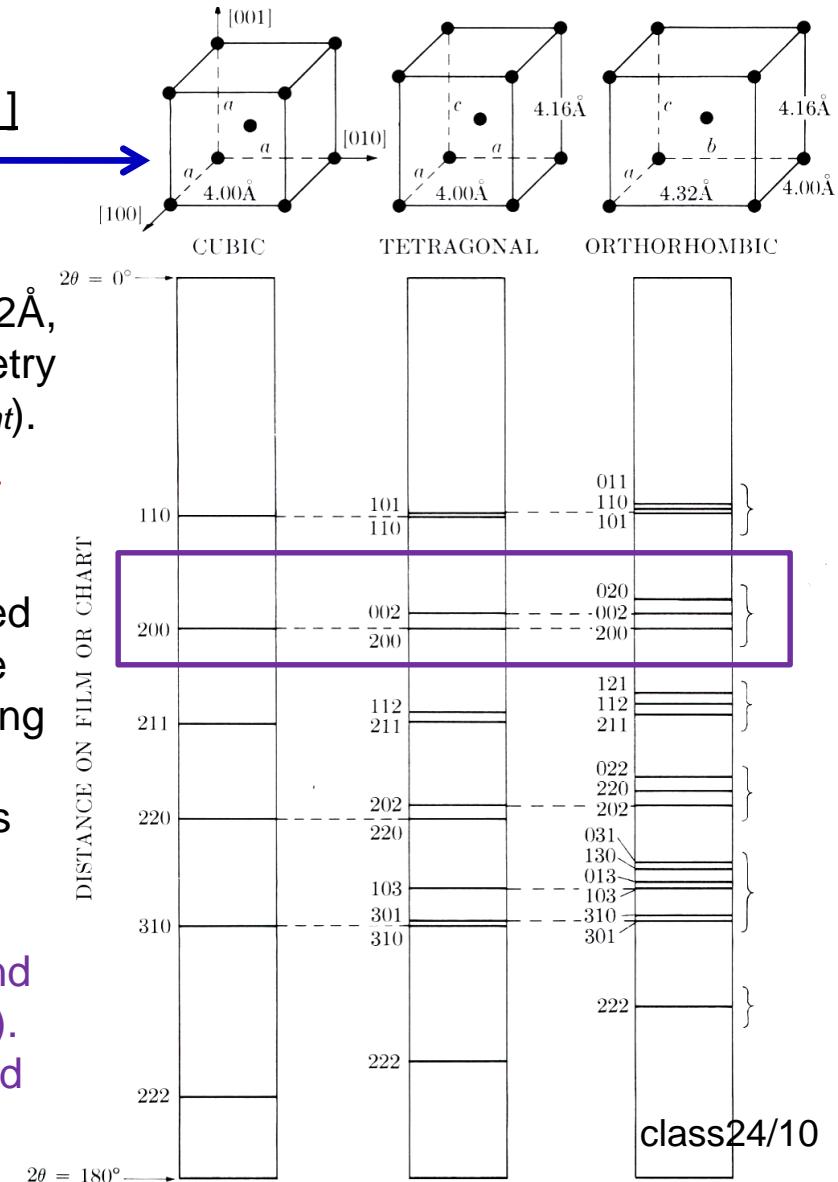
- The increase in number of lines is due to the introduction of new hkl plane d -spacings, caused by non-uniform distortion.

- Thus in cubic cell, the (200), (020) and (002) planes all have the same spacing and only one line is formed, called the (200) line. However, this line splits into two when the cell becomes tetragonal since now the (002) plane spacing differs from the other two.

- When the cell becomes orthorhombic, all three spacings are different and three lines are formed.

- Common in phase transformations, e.g. carbon steel slowly cooled get Ferrite (BCC) \rightarrow Cementite (orthor.), and quench from austenite (FCC) \rightarrow martensite (I-tetragonal).

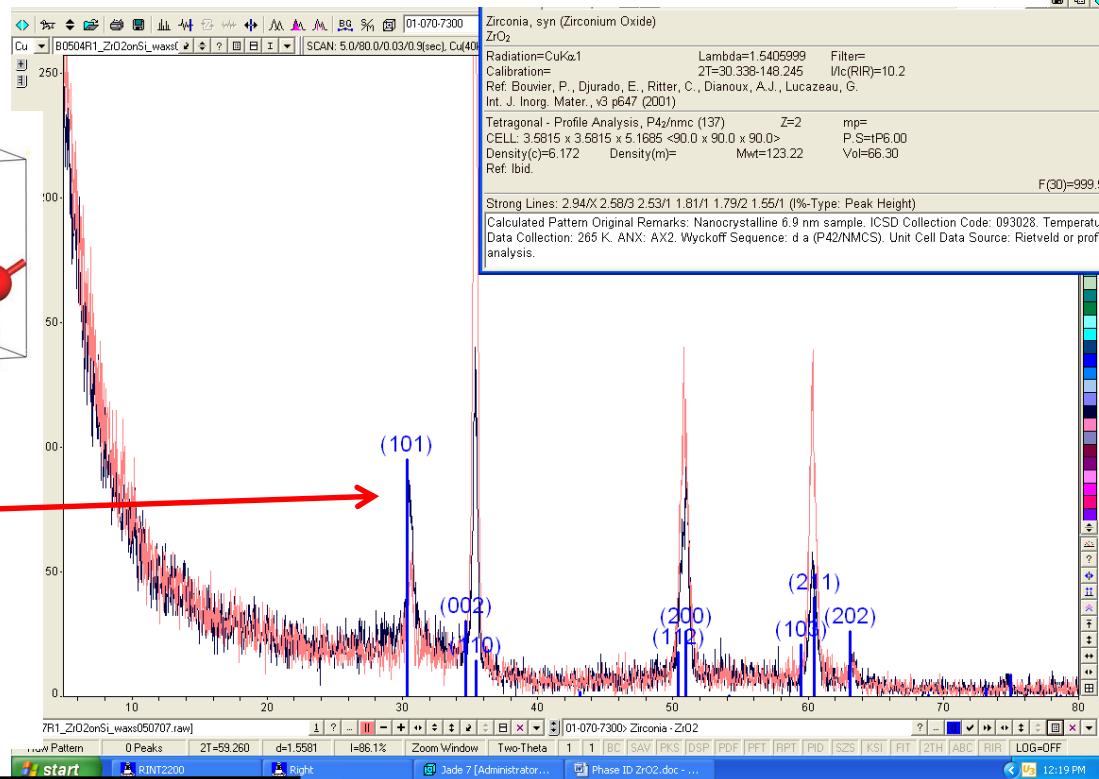
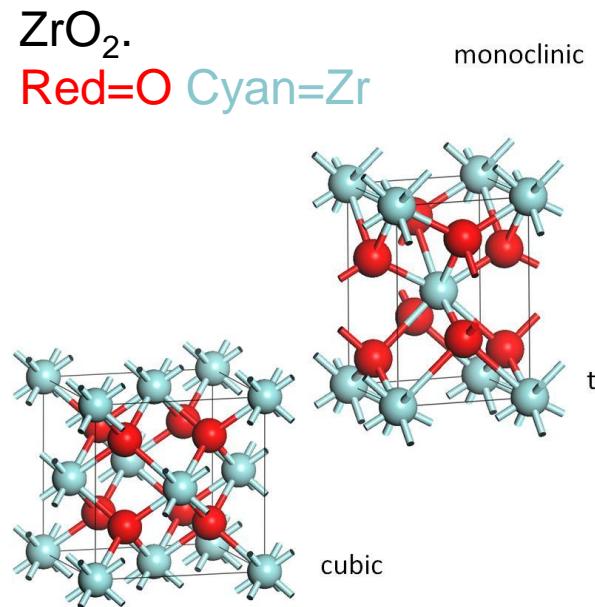
- In disorder-order reactions (CuAu), cubic in disordered state but becomes either tetragonal or orthorhombic (depending on temperature) when ordered.





Example: Phase Transformations in ZrO_2

Low-pressure forms of
 ZrO_2 .
Red=O Cyan=Zr



| Property | Cubic ZrO_2 | Tetragonal ZrO_2 | Monoclinic ZrO_2 |
|-------------------------------------|---|---|---|
| Lattice parameters (\AA) | | | |
| a | 5.034 | 5.037 | 5.098 |
| b | 5.034 | 5.037 | 5.171 |
| c | 5.034 | 5.113 | 5.264 |
| Temperature (K) | >2570 | 1400 to 2570 | <1400 |
| Coordination | Zr=8; O ₁ =4; O ₂ =4 | Zr=8; O ₁ =4; O ₂ =4 | Zr=7; O ₁ =3; O ₂ =4 |
| Volume (\AA^3) | 127.57 | 129.73 | 136.77 |
| Density (g/cc) | 6.17 | 6.172 | 5.814 |
| Space Group | Fm-3m | P4 ₂ /nmc | P2 ₁ /c |

XRD scan of a tetragonal ZrO_2 thin film taken from UNT's Rigaku Ultima III high-resolution XRD

