

chem 5390

Advanced X-ray Analysis



LECTURE 8

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Diffraction Theory

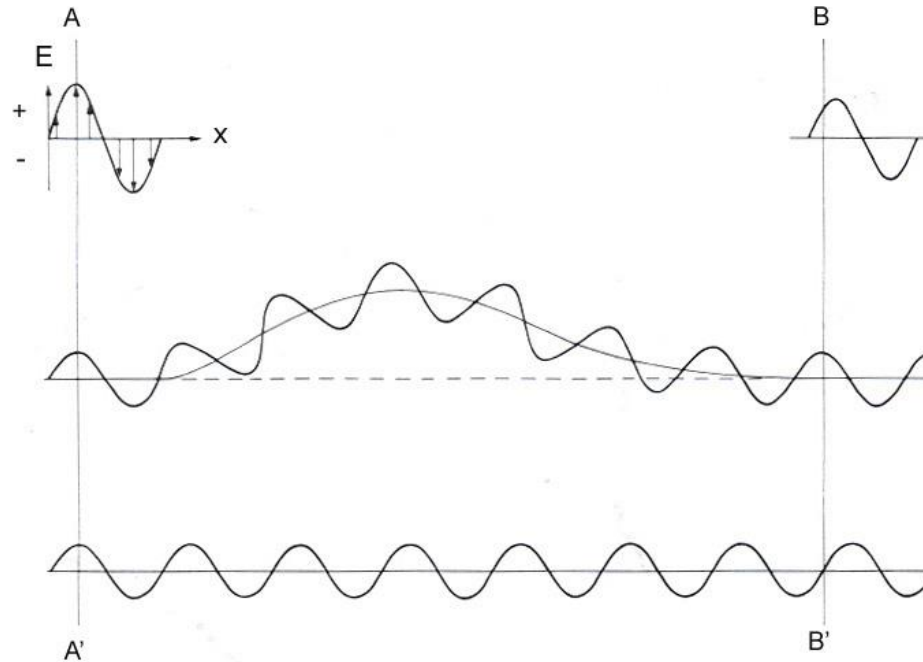
von Laue (1879 - 1960) - proposed that crystals are composed of regularly spaced atoms which may scatter x-rays, if the x-rays were electromagnetic waves of wavelength equal to the interatomic distance in crystals. He used a CuSO_4 crystal with photographic plates to prove his theory.

W. H. Bragg (1862 - 1942) and his son W. L. Bragg (1890 - 1971) read Laue's experiments and began to form equations for the diffraction process. Eventually the son solved the NaCl, KCl, KBr, and KI crystal structures.

Diffraction Theory

A. Diffraction

1. Phase relations

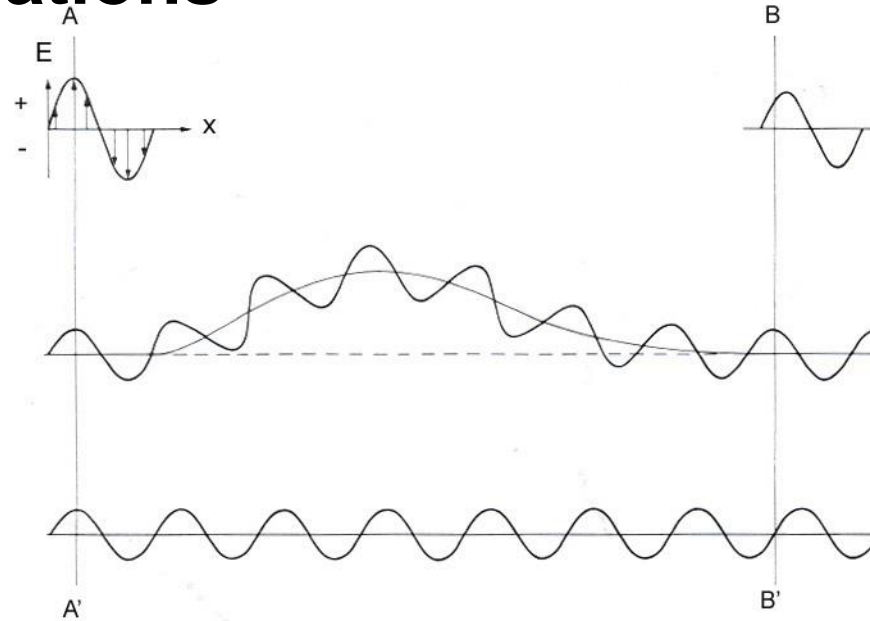


At the wave front BB' the two waves are out of phase. A difference in path length leads to a difference in phase.

Diffraction Theory

A. Diffraction

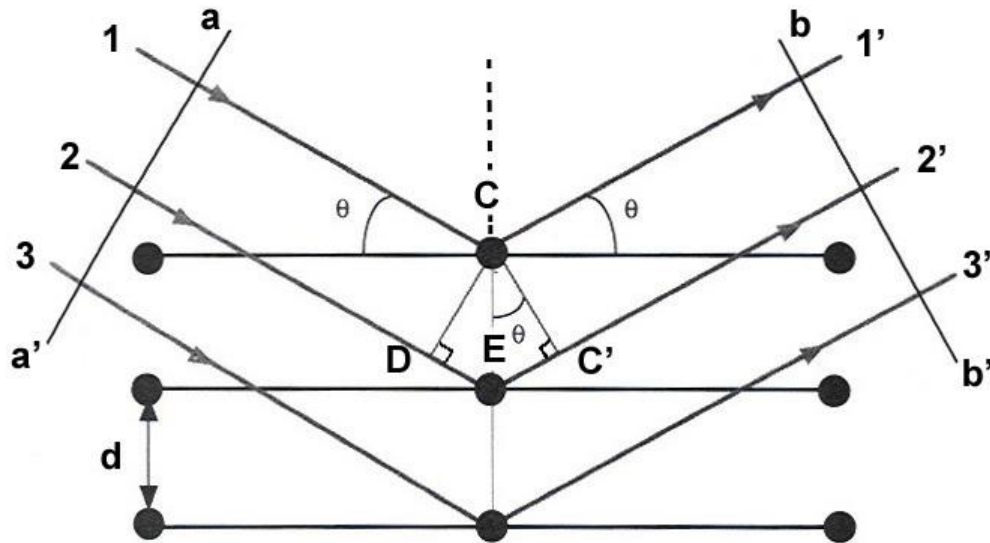
1. Phase relations



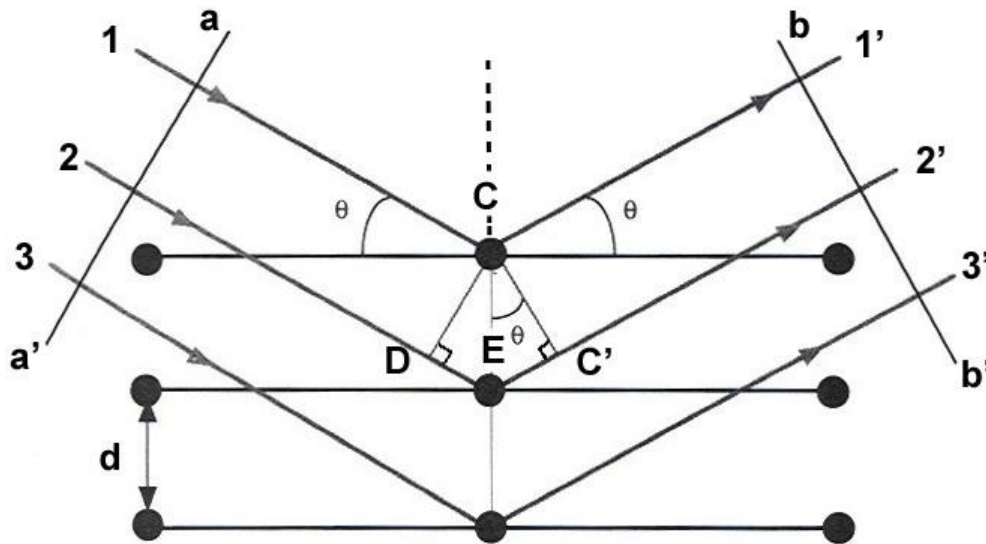
The two waves are in-phase whenever their path lengths differ either by zero or by a whole number of wavelengths.

Diffraction Theory

Scattering from an array of atoms is shown here, with the incident beam represented as 1, 2, and 3 and the diffracted beam as 1', 2', and 3'.



Diffraction Theory



$n\lambda = \text{path difference } (\delta) \quad (\text{where } n \text{ is a whole number})$

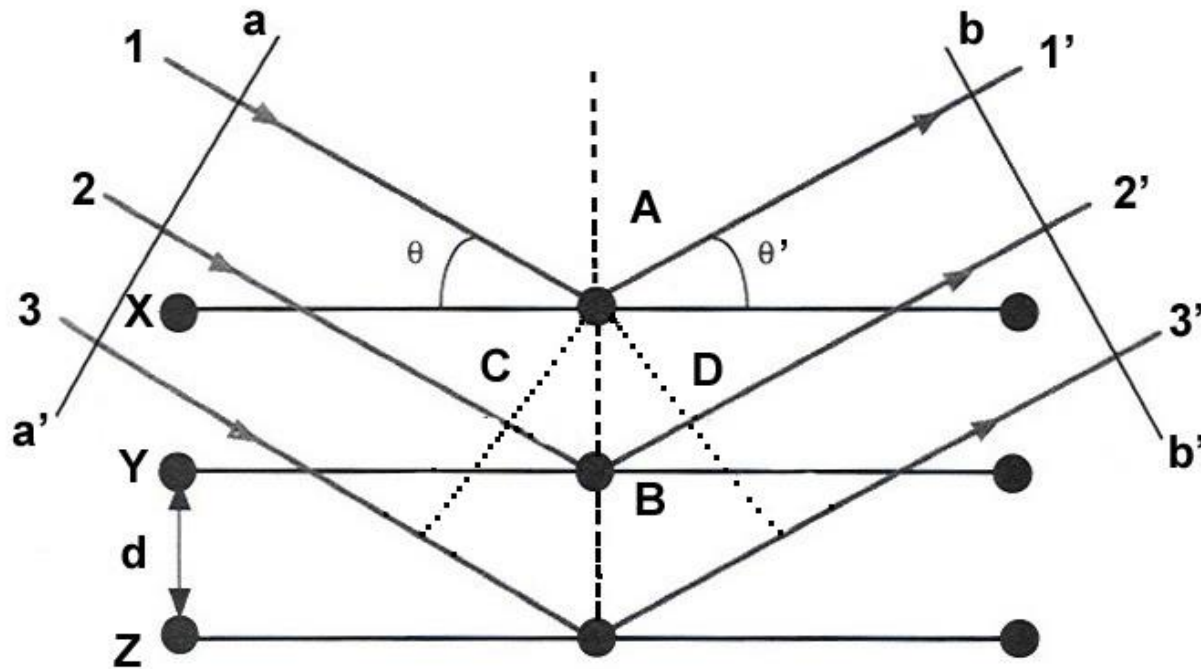
$$\delta = DE + EC' = 2EC' = CE\sin\theta + CE\sin\theta \quad \delta = 2CE\sin\theta$$

Since CE equals interplanar spacing, d , then

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

Bragg's Law

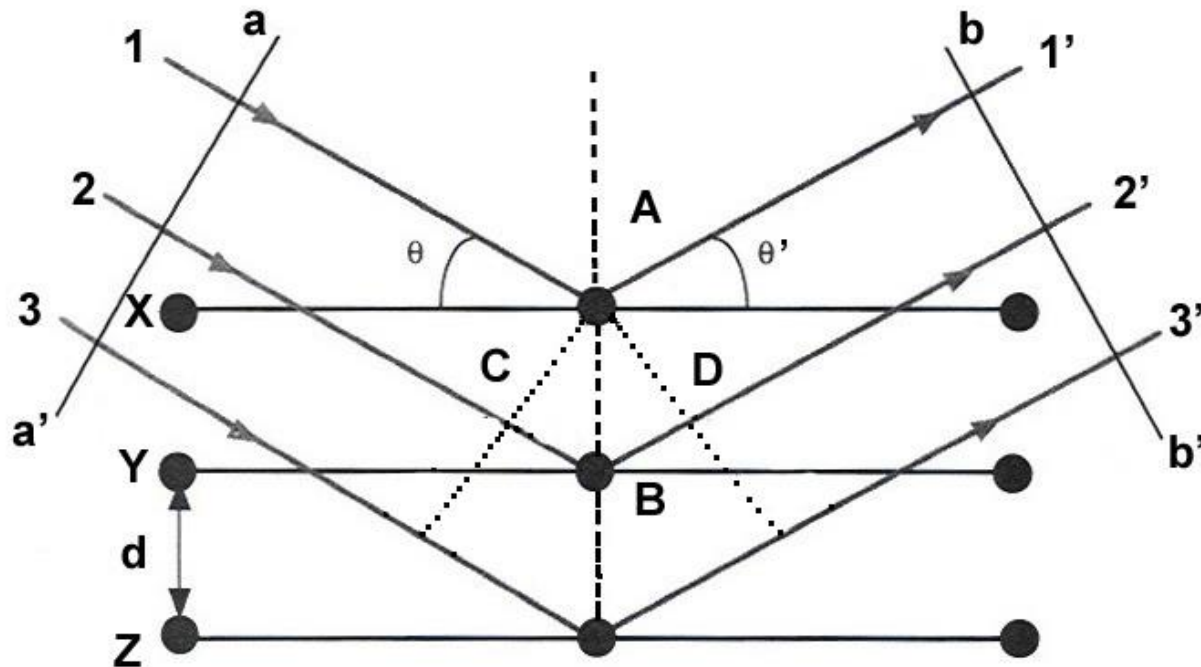
Diffraction Theory



Derivation of Bragg's law:

For planes of atoms X, Y, and Z to have a diffracted beam, the x-rays at bb' must all be exactly in phase. Rays 2 and 3 must travel further than ray 1 to reach bb' . If rays $1'$, $2'$, and $3'$ are to arrive at bb' in phase with one another, then $2'$ and $3'$ must have path length exactly a whole integer wavelength longer than ray $1'$.

Diffraction Theory



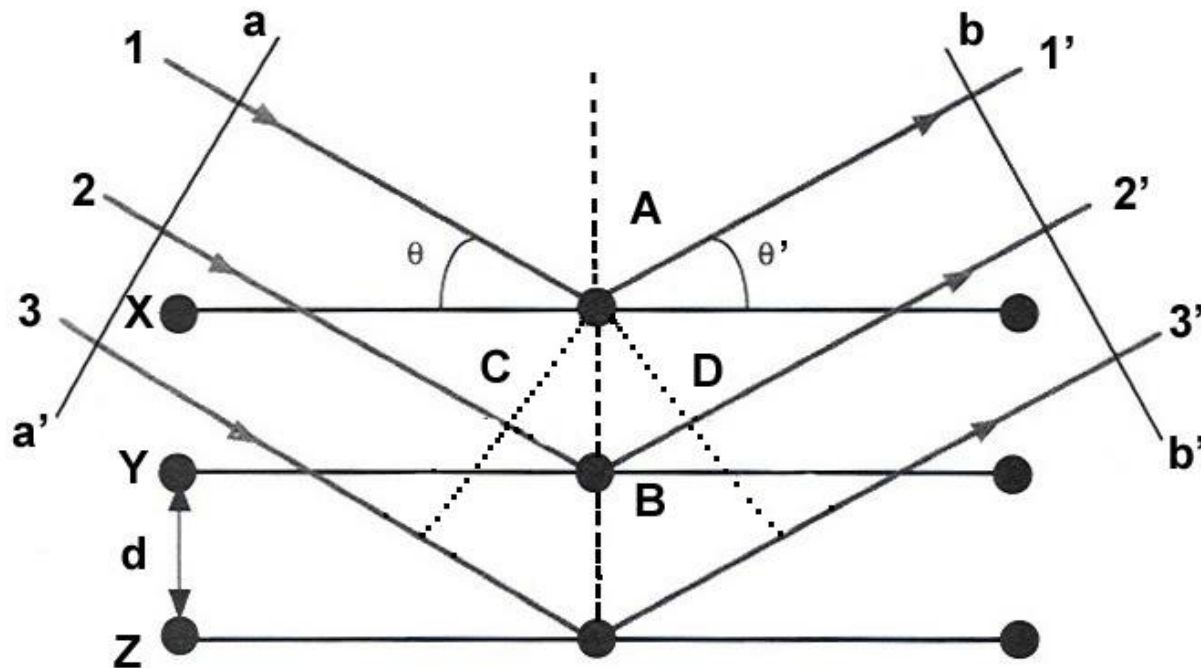
How can we prove this?

Ray 2 -2' must travel the additional distance of $CB + BD$.

This distance ($CB + BD$) must equal some whole number of wavelengths.

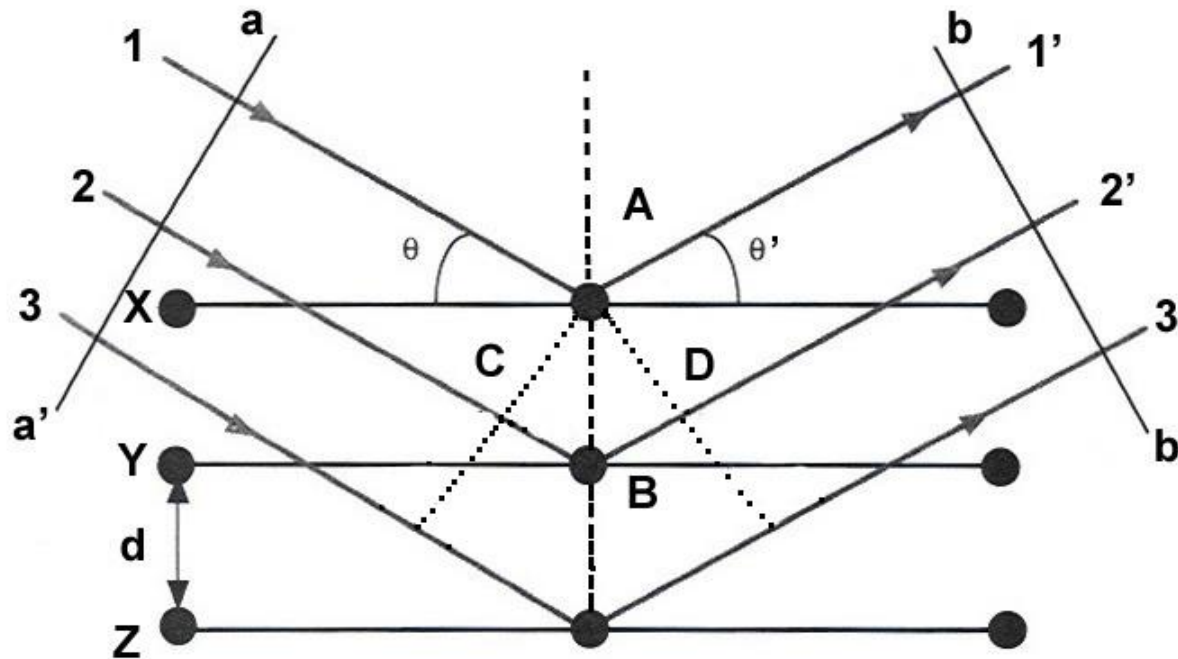
Notice the two triangles CBA and DBA have a common side, AB , that is also the spacing d between rows of atoms.

Diffraction Theory



Also notice that the angle CAB equals θ , since CA is perpendicular to ray 1 and AB is perpendicular to row X. Since row X and ray 1 make the angle θ , and CAB represents a 90° rotation of this angle, the two angles are equal.

Diffraction Theory



So, $\sin\theta = CB/AB$

$AB\sin\theta = CB$

Since $\theta = \theta'$,

$2d\sin\theta = CB + BD$

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

and

and

$2AB\sin\theta = CB + BD$

$n\lambda = CB + BD$

Bragg's Law

$\sin\theta' = BD/AB$ so,

$AB\sin\theta' = BD$

$d = AB$

Diffraction Theory

A. Diffraction

Bragg's Law refers to the direction of diffraction but does not give the intensity of the diffracted beam.

In fact, Bragg's Law can be satisfied but the intensity may be very low or even zero.

Diffraction Theory

A. Diffraction

Factors that affect the Intensity of the diffracted beam:

- 1) Structure factor
- 2) Polarization factor
- 3) Lorentz factor
- 4) Multiplicities
- 5) Temperature factor
- 6) Absorption factor - absorption of x-rays by the sample
- 7) Preferred orientation
- 8) Extinction coefficient - applies to single crystals - not applicable to powders

Diffraction Theory

A. Diffraction

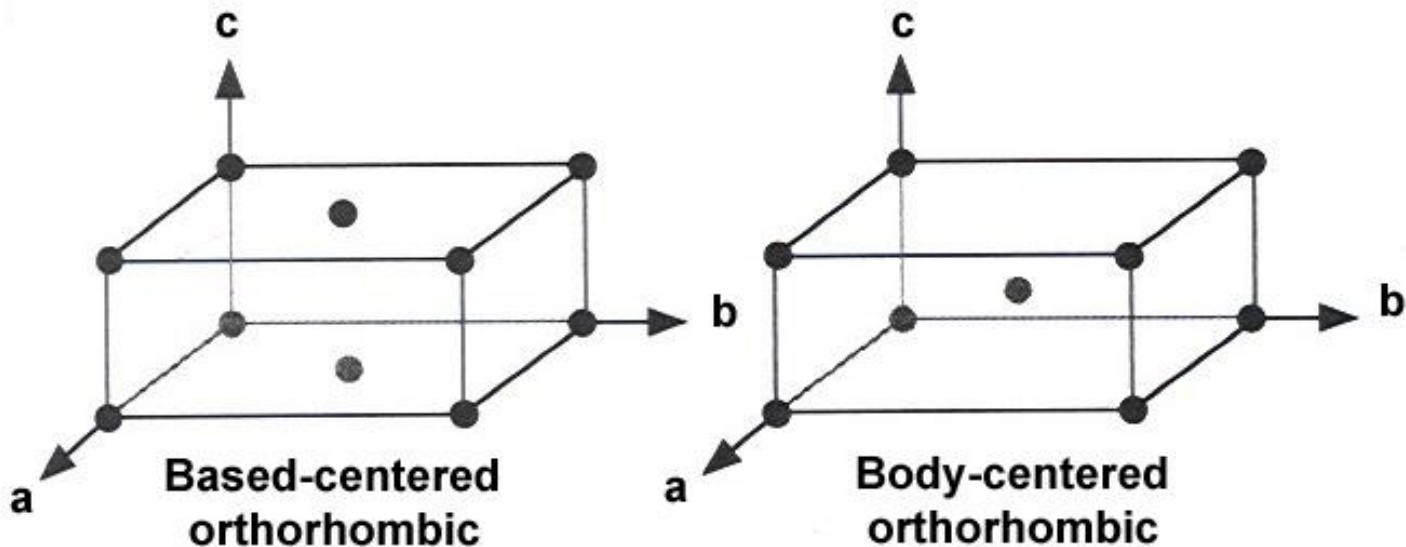
2. Structure, Scattering, and Intensity

Structure factor, F - describes the effect of crystal structure on the intensity of the diffracted beam.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

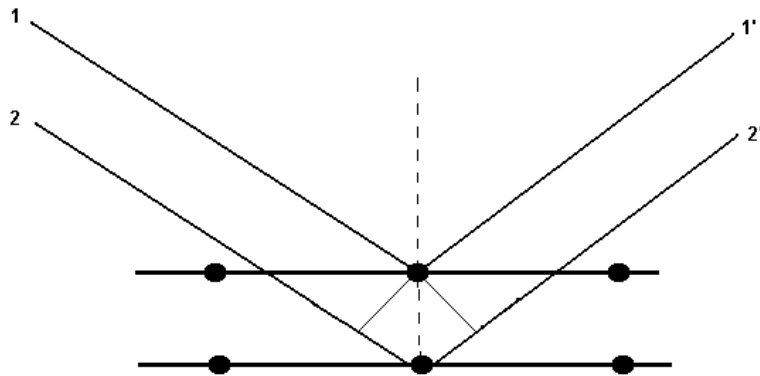


If we diffract from the (001) plane of each structure, then,

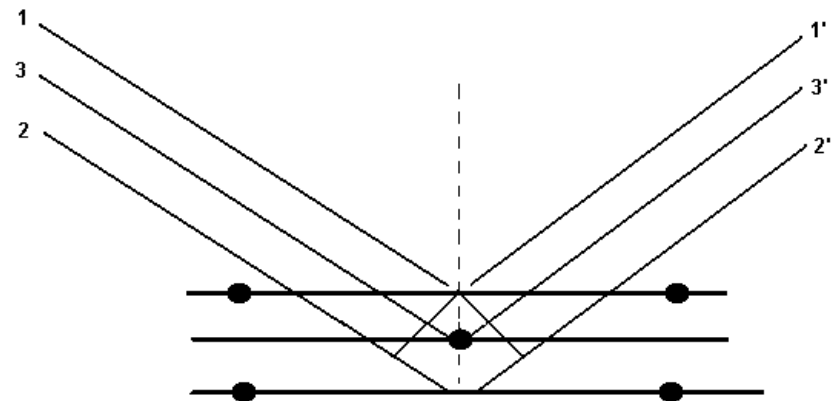
Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity



Based-centered (001) plane
1 & 2 are in-phase to give a
(001) reflection.



Body-centered (001) plane
3 is out of phase with 1 & 2
and cancel each other out.

There is no (001) reflection for a body-centered lattice.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

We consider each atom to be a point source for scattering of the x-ray beam.

The scattering efficiency of an atom is represented by f .

The scattering efficiency of a unit cell is represented by F .

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

F is always somewhat less than the sum of the scattering of the individual atoms in the unit cell.

Since the value of F depends on the way atoms are arranged in a unit cell,

F is called the structure factor.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

To get F we need:

the sum of the amplitude of the beams scattered from each atom in the unit cell adjusted for the amount of interference caused by phase differences, ϕ .

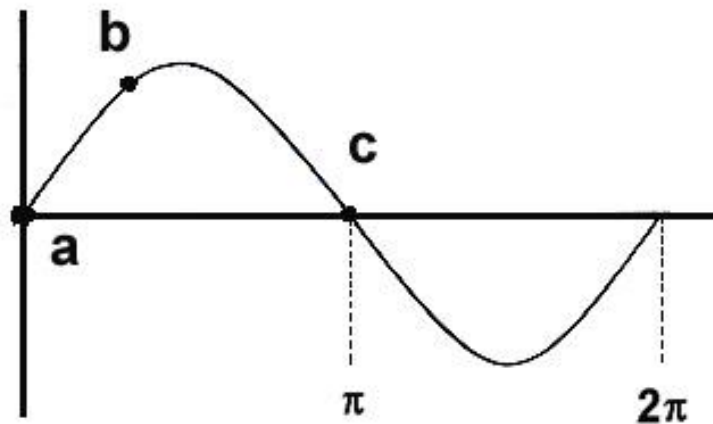
Since the x-rays are represented by sine waves and a point on a wave can be described as the phase angle, ϕ ,

ϕ can be expressed in terms of a fraction of a circle (360°) or 2π radians.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity



$$a = 0^{\circ}$$

$$b = 60^{\circ}$$

$$c = 180^{\circ}$$

convert to radians:

$$a = 0\text{rads}$$

$$b = (60/360)(2\pi) = 1.047\text{rads}$$

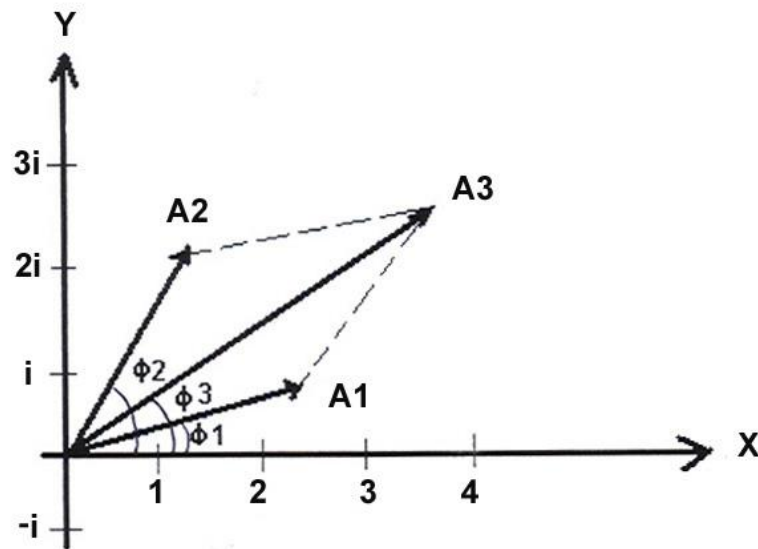
$$c = 3.14\text{rads}$$



Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity



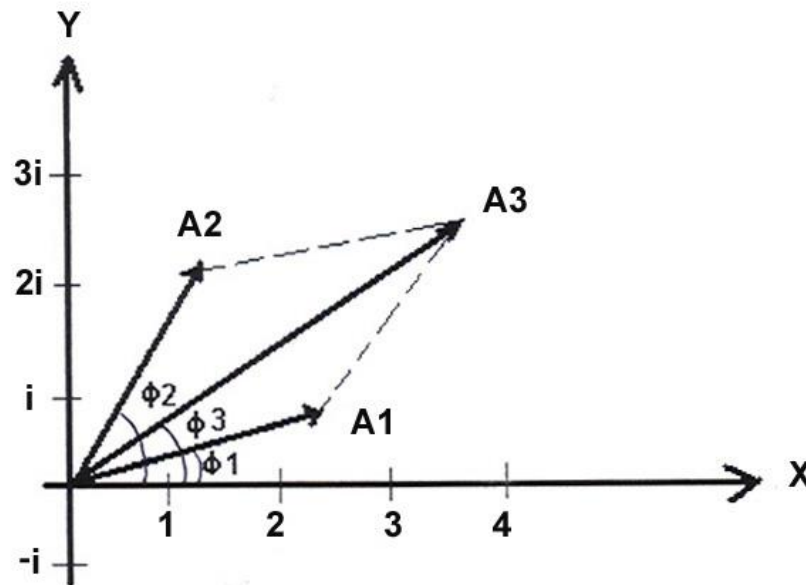
Not only phase, but also amplitude of the wave needs to be described.

Use an XY coordinate - amplitude can be represented by the length of a vector.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

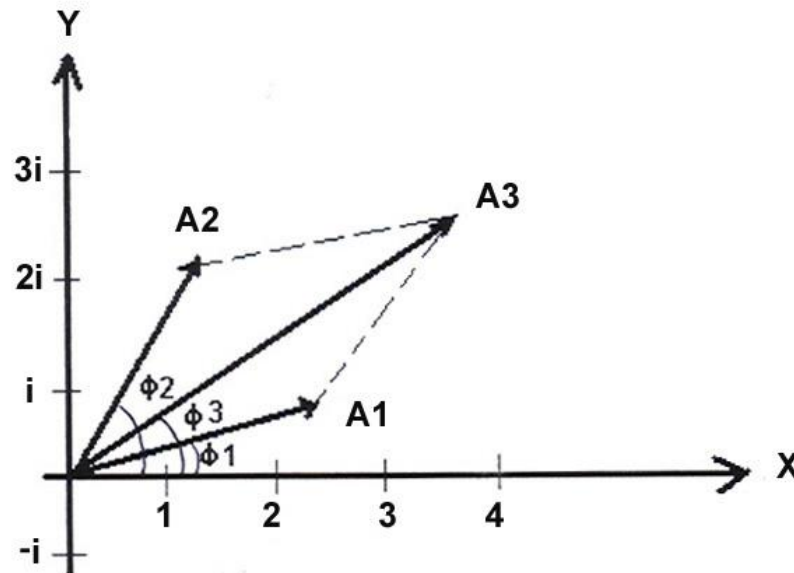


For two waves, the resulting vector A_3 represents the resulting amplitude of the resultant phase angle, ϕ_3 .

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity



The X axis is the axis of real numbers and the Y axis is the axis of imaginary numbers and any point in the X-Y plane is a complex number.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

Unit of measurement for imaginary numbers is i , defined as:

$$i = (-1)^{1/2}$$

(See Klug and Alexander (pp. 152ff, 1974) for complete derivization.)

$$F = \sum_i f_i e^{2\pi i(hu_i + kv_i + lw_i)}$$

f - atomic scattering factor.

u , v , and w - atom positions in the unit cell.

h , k , and l - Miller indices of the reflection.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

$$F = \sum_i f_i e^{2\pi i(hu_i + kv_i + lw_i)}$$

This equation tells us what reflections h, k, l to expect in a diffraction process from a given crystal structure of atoms located at positions u, v, w .

These are known as selection rules.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

Reflections for which $F = 0$ will have zero intensity and will not appear in the diffraction pattern, the reflection is forbidden.

The equation is general it applies to all crystal lattices.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

Let's digress to discuss f - the atomic scattering factor.

How efficient an atom scatters in a given direction is given by:

$f = \text{Amplitude of wave scattered by an atom} / \text{Amplitude of wave scattered by one electron}$

Heavier atoms scatter more since they possess more electrons.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

f is dependent on θ - because the waves must take different path lengths.

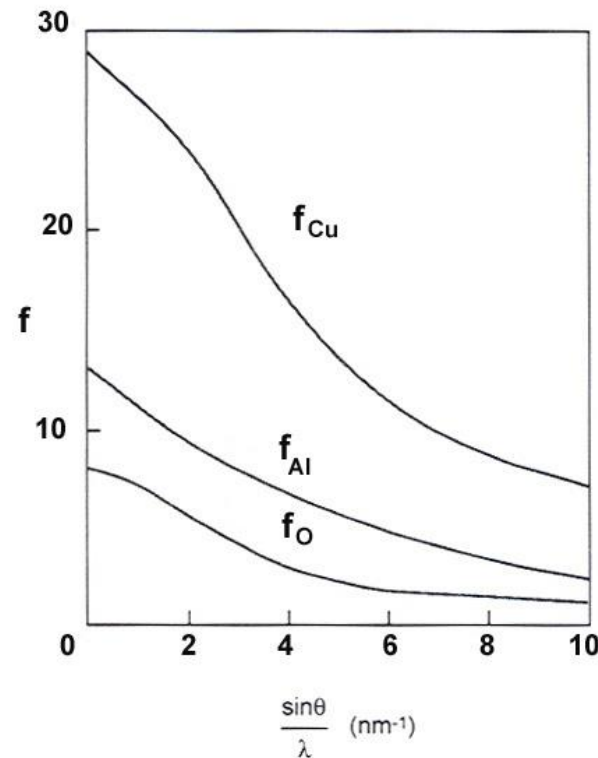
The atomic scattering factor also depends on the wavelength of the incident x-rays. For a fixed value of θ , f is smaller for shorter wavelength radiation.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

Plot f vs $\sin\theta/\lambda$



For the plot, the curves begin at the atomic number (Z) of the element.

Cu - 29

Al - 13

O - 8

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

To do calculations for the structure factor remember:

$$e^{\pi i} = e^{3\pi i} = e^{5\pi i} = -1$$

$$e^{2\pi i} = e^{4\pi i} = e^{6\pi i} = 1$$

$$e^{n\pi i} = (-1)^n, \text{ where } n \text{ is any integer}$$

$$e^{n\pi i} = e^{-n\pi i}, \text{ where } n \text{ is any integer}$$

$$e^{ix} + e^{-ix} = 2\cos x$$

Crystallography

A. Diffraction

Number of lattice points per cell is:

$$N = N_i + N_f/2 + N_c/8$$

N_i - number of interior points.

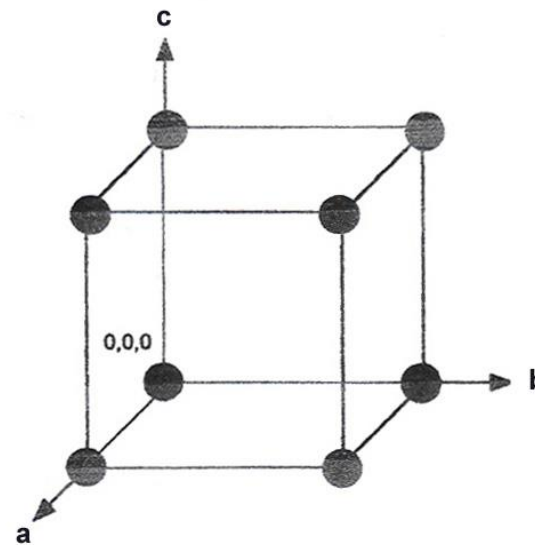
N_f - number of points on faces (shared).

N_c - number of points on corners (shared).

Diffraction Theory

A. Diffraction

Example 1. Simple cubic structure



Number of lattice points per cell is:

$$N = N_i + N_f/2 + N_c/8$$

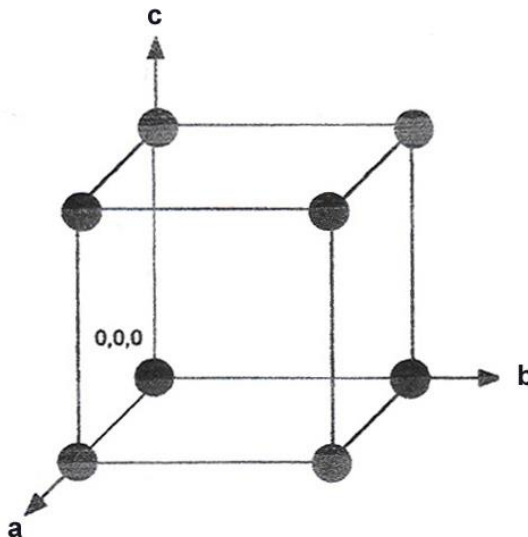
$$N = 1$$

0, 0, 0 for u, v, w

Diffraction Theory

A. Diffraction

Example 1. Simple cubic structure



$$F = \sum_i f_i e^{2\pi i(hu_i + kv_i + lw_i)}$$

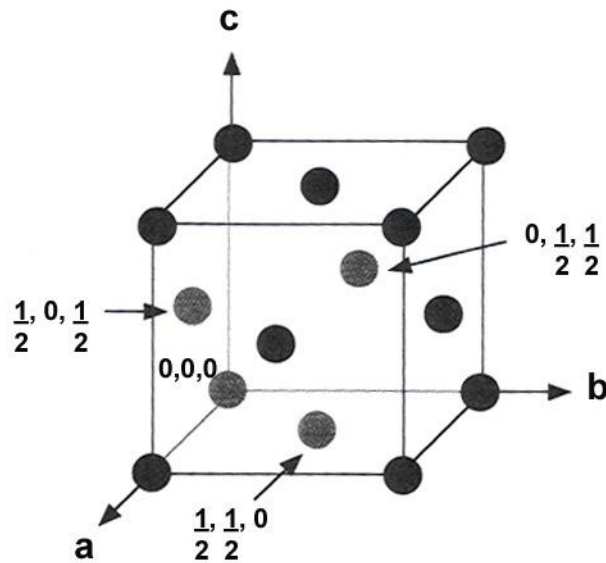
$$F = fe^{2\pi i(0)} = fe^0 = f(1) = f$$

F is independent of h, k, l, so all reflections are allowed.

Diffraction Theory

A. Diffraction

Example 2. fcc structure



$N = 4$ $0, 0, 0$

$1/2, 1/2, 0$

$1/2, 0, 1/2$

$0, 1/2, 1/2$

$$F = \sum_i f_i e^{2\pi i(hu_i + kv_i + lw_i)}$$

Diffraction Theory

A. Diffraction

Example 2. fcc structure

$$F = fe^{2\pi i(0)} + fe^{2\pi i(h/2 + k/2)} + fe^{2\pi i(h/2 + l/2)} + fe^{2\pi i(k/2 + l/2)}$$

$$F = f[1 + e^{\pi i(h + k)} + e^{\pi i(h + l)} + e^{\pi i(k + l)}]$$

If h , k , and l are all even or all odd, then the $h = k$, $k = l$, $k = l$ are even integers and since $e^{2\pi i} = e^{4\pi i} = e^{6\pi i} = 1$ then:

$$F = f[1 + 1 + 1 + 1] = 4f \quad (\text{for unmixed indices})$$

Diffraction Theory

A. Diffraction

Example 2. fcc structure

If h , k , and l are mixed,

i.e. $h = 0$, $k = 1$, $l = 2$ (012),

$$h + k = 0 + 1 = 1 \quad h + l = 0 + 2 = 2 \quad k + l = 1 + 2 = 3$$

Since $e^{\pi i} = e^{3\pi i} = e^{5\pi i} = -1$

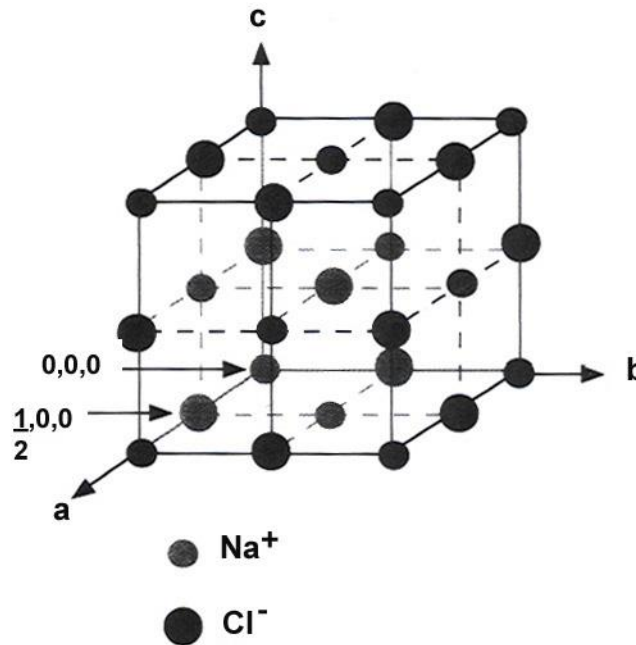
$$F = f[1 + (-1) + (1) + (-1)] = f(0) = 0 \quad (\text{for mixed indices})$$

So for fcc structure, you will see (111), (200), and (220) but not (100), (110), (210), (211), etc...

Diffraction Theory

A. Diffraction

Example 3. 2 atoms per lattice point



NaCl structure fcc

$N = 8$

Diffraction Theory

A. Diffraction

Example 3. 2 atoms per lattice point

The basis is one Na at 0, 0, 0, and one Cl at 1/2, 1/2, 1/2

$$F = [f_{\text{Na}} e^{2\pi i(0)} + f_{\text{Cl}} e^{2\pi i(h/2 + k/2 + l/2)}][1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}]$$

$$[f_{\text{Na}} e^{2\pi i(0)} + f_{\text{Cl}} e^{2\pi i(h/2 + k/2 + l/2)}] - \text{basis term}$$

$$[1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}] - \text{fcc term}$$

Diffraction Theory

A. Diffraction

Example 3. 2 atoms per lattice point

$$F = [f_{\text{Na}} + f_{\text{Cl}} e^{\pi i(h+k+l)}][1 + e^{\pi i(h+k)} + e^{\pi i(h+l)} + e^{\pi i(k+l)}]$$

If h , k , and l are mixed then the second term is equal to zero $F = 0$

If h , k , and l are even $F = 4[f_{\text{Na}} + f_{\text{Cl}}]$

Diffraction Theory

A. Diffraction

Example 3. 2 atoms per lattice point

If h , k , and l are odd $F = 4[f_{\text{Na}} - f_{\text{Cl}}]$

The 111 reflection will be weaker than the 200 reflection for a NaCl structure

This is the short hand version instead of using $N = 8$, we can use the basis x the Bravais lattice of the crystal structure.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity, con't

The intensity of the diffracted beam does not only depend on F , but also on other factors.

$$I = F^2 p \left(\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) e^{-2M}$$

I - intensity of the beam

F - structure factor

p - multiplicity

$(1 + \cos^2 2\theta / \sin^2 \theta \cos \theta)$ - Lorentz-polarization factor

e^{-2M} - temperature factor

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity, con't

a. p - We have already discussed the multiplicity factor (how many planes in a family of planes), so let's look at the other terms.

b. Lorentz-Polarization Factor

Polarization factor

The x-ray incident beam is unpolarized and can be resolved into two plane polarized components.

The total scattered intensity of the x-ray beam is the sum of the intensities of these two components.

This sum is dependent on angle (2θ)

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity, con't

b. Lorentz-Polarization Factor

Polarization factor

Polarization is at a maximum at $2\theta = 0^\circ$ and at a minimum at $2\theta = 90^\circ$

At 0° it is similar to a beam of light polarized by reflecting off the hood of a car.

Polarization factor = $(1 + \cos^2 2\theta/2)$ where θ is the angle between the incident beam and reflecting plane.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity, con't

b. Lorentz-Polarization Factor

Lorentz factor

A combination of two geometric factors

1st factor - related to the volume of the crystal exposed to irradiation, spot size changes from a circle to an eclipse as angle becomes more steep.

2nd factor - related to the number of crystals favorably oriented for diffraction at any Bragg angle, θ_B .

The Lorentz factor differs for powders and single crystals

Diffraction Theory

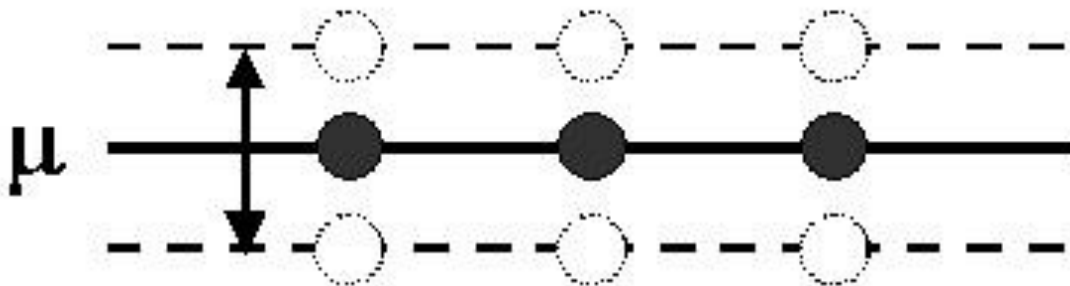
A. Diffraction

2. Structure, Scattering, and Intensity, con't

c. Temperature factor

Effect of temperature on intensity

Atoms vibrate within a crystal, intensities decrease as temperature increases. The set of parallel planes at the Bragg angle move in and out.

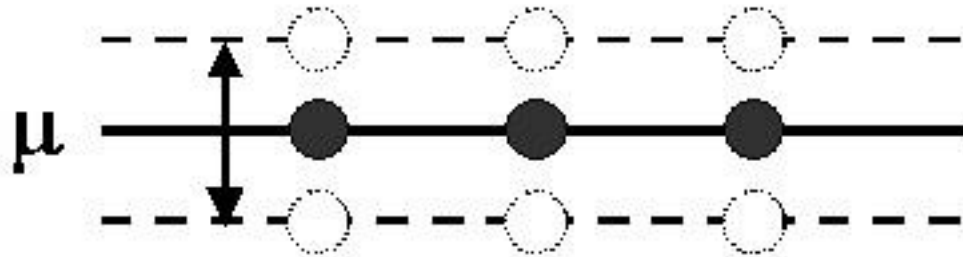


Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity, con't

c. Temperature factor



μ - Average displacement of an atom from it's mean position.

The temperature factor = e^{-2M} ,

Where M is proportional to μ and 2θ

The calculation of the temperature factor is quite involved and usually neglected for many materials.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity, con't

d. Absorption Factor - A

This factor is the number by which the calculated intensity must be multiplied. The calculation of A depends on the geometry of the diffraction method.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity, con't

d. Absorption Factor - A

For a diffractometer – the specimen is usually on a flat plate, giving equal angles for the incident and diffracted beams.

Absorption is independent of angle, because of area versus depth.

The larger the absorption coefficient of the sample, the lower the intensity of the diffracted beam.

Diffraction Theory

A. Diffraction

2. Intensity Equation

The intensity equation is valid when:

- the crystals making up the specimen are randomly oriented in space.
- the crystals consist of small mosaic blocks
 - “ideally imperfect” crystal

Diffraction Theory

A. Diffraction

2. Intensity Equation

The intensity equations becomes invalid when preferred orientation is present in the sample.

If the crystal grains are not randomly oriented but have preferred orientation, the observed intensities will be much different from a random sample.

Diffraction Theory

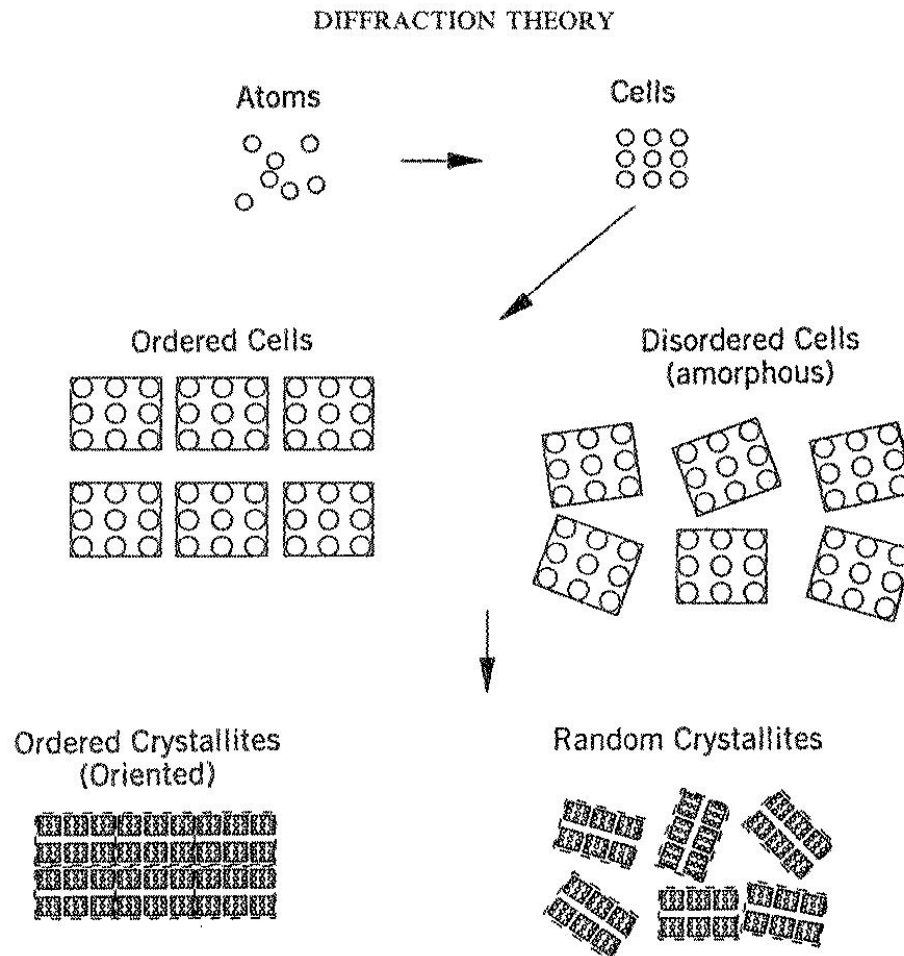
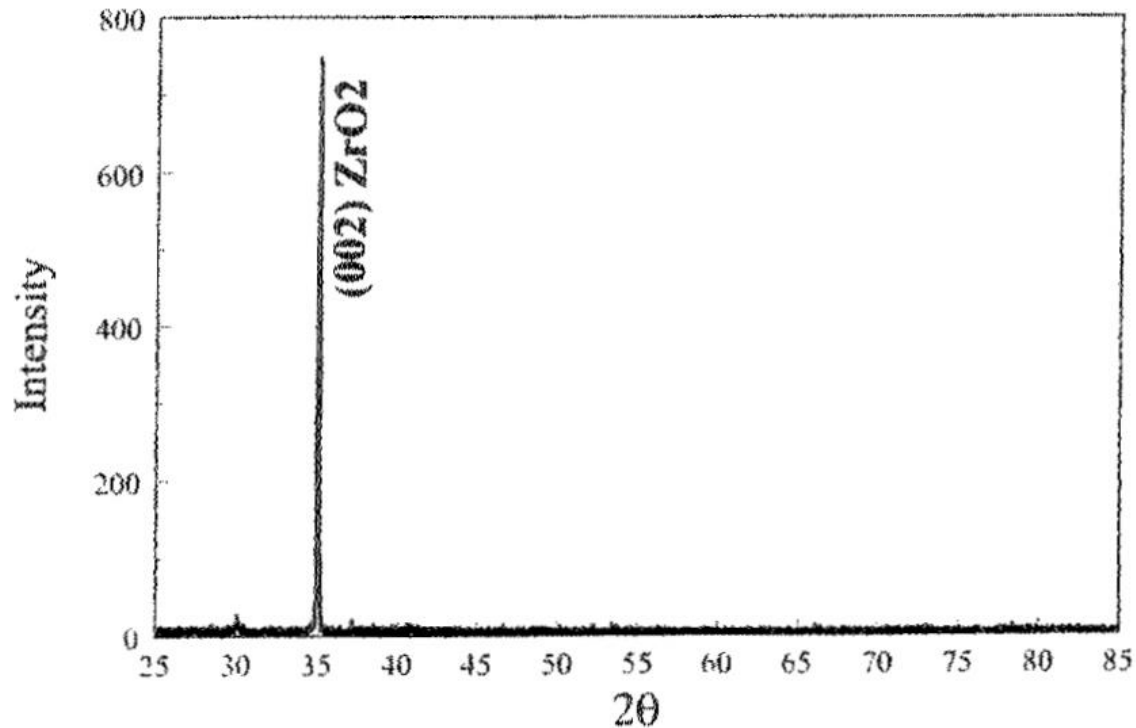


Figure 3.20. The structural makeup of solids.

Diffraction Theory



(b) Observation of a zirconia film in which the grains are oriented so as to have the (002) planes parallel to the surface of the sample. The incidence angle ω is equal to the Bragg angle $\theta_{(002)}$

Figure 7.9. Illustration of a preferential orientation

ZrO₂ – cubic, tetragonal, monoclinic

Diffraction Theory

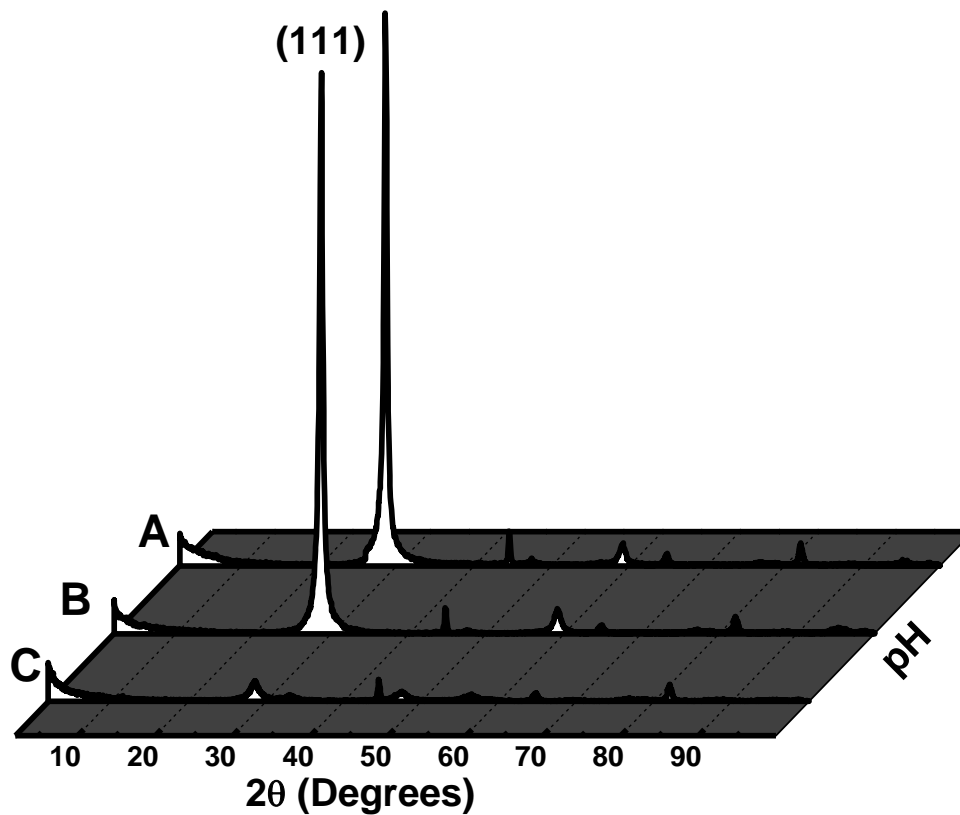


Figure 5 in Wang & Golden
"Anodic Electrodeposition..."

Diffraction Theory

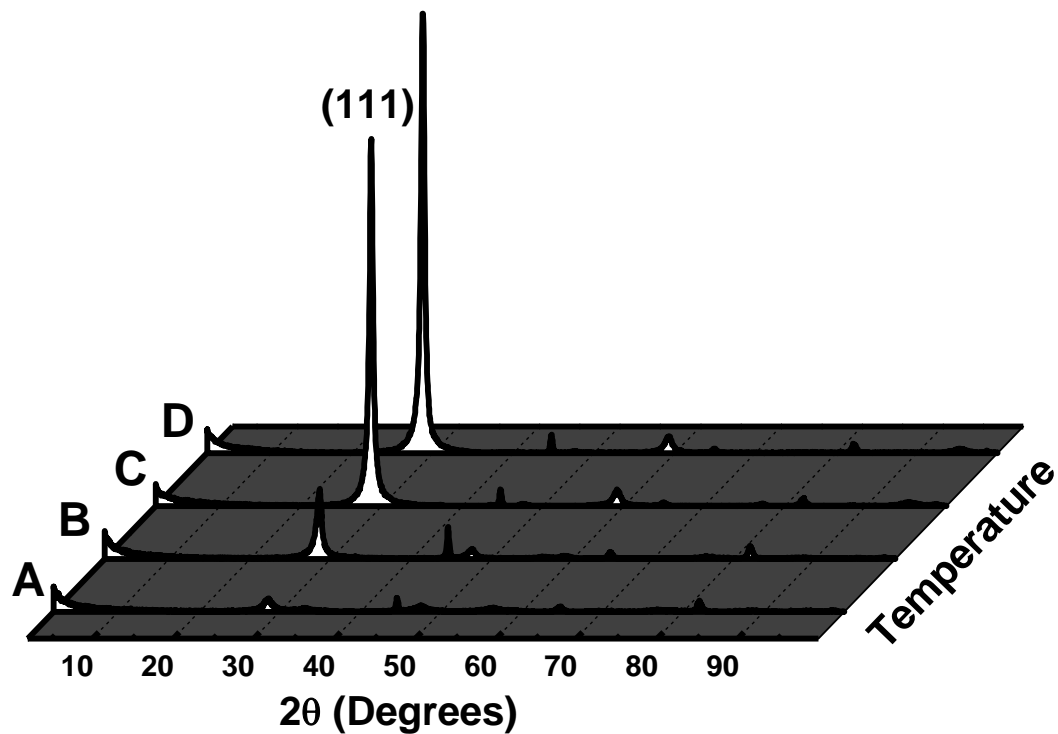


Figure 4 in Wang & Golden
"Anodic Electrodeposition..."

Diffraction Theory

2θ(°)	hkl	25°C	40°C	50°C	60°C	70°C	80°C
28.54	111	100	100	100	100	100	100
33.03	200	29	---	---	---	---	---
47.51	220	47	12	14	3.0	---	---
56.34	311	33	2	2	---	---	---
59.36	222	7	4	3	3	3	3
CeO₂(111)/ ss(110)		0.684	1.25	5.208	3.096	20.41	22.73

Table 2. The preferred orientation of CeO₂ at temperatures of: 25, 40, 50, 60, 70 and 80°C (Data from Figure 4).

Diffraction Theory

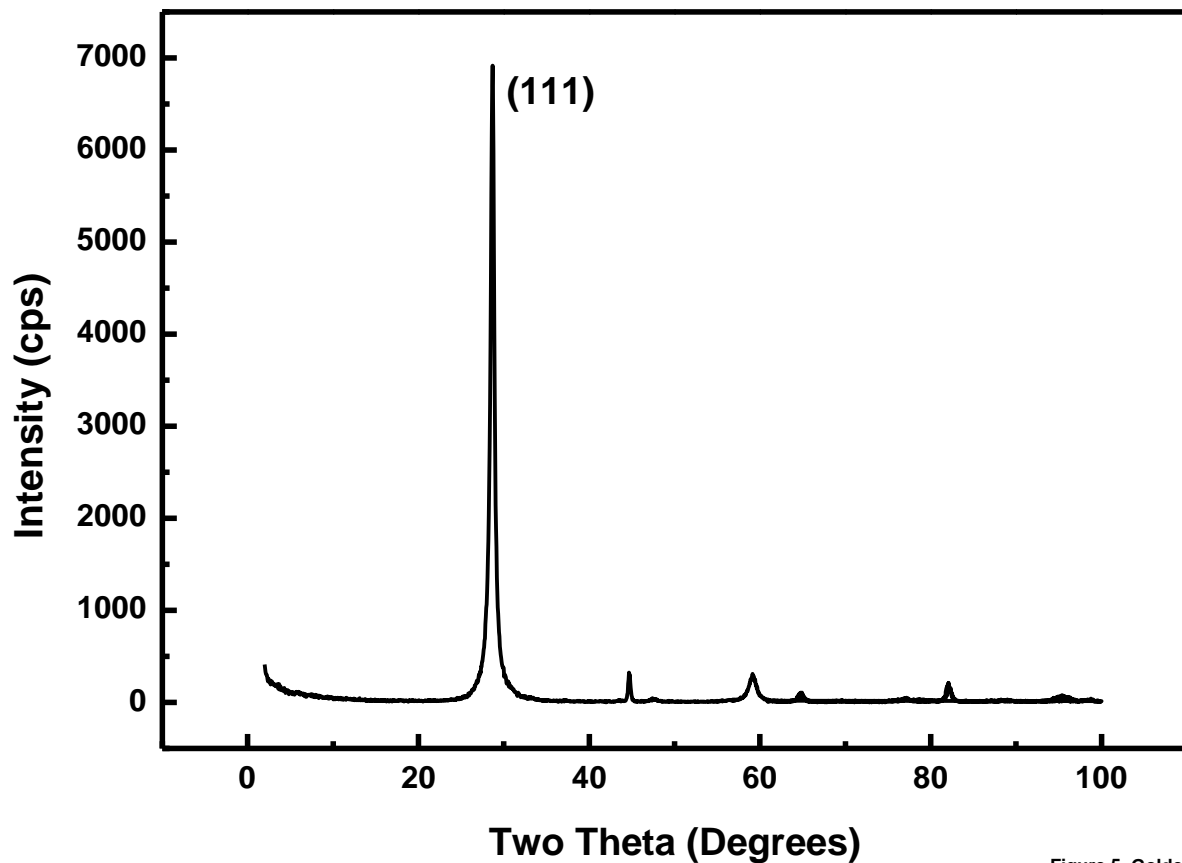


Figure 5, Golden & Wang
"Anodic Oxidation of..."

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

Preferred orientation or texture is common.

It can occur due to the synthesis conditions or to the forming (working) conditions of the material (i.e. wire drawing, sheet rolling, cold working, hot working...)

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

If due to the working conditions – it is called a deformation texture.

There is a tendency of the grains to rotate during plastic deformation, causing slipping and rotation of adjoining grains and resulting in texture.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

Preferred orientation not only happens in metals but also rocks, ceramics, semiconductors, thin films, etc...

Preferred orientation may or may not be beneficial.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

Properties may be enhanced by having all the aggregates in the same direction, i.e.

Steel for electric motor cores have all the grains oriented with their $\{100\}$ planes parallel to the sheet surface. That direction is magnetic when lines up.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

However, some steels that are textured are more likely to crack during severe deformation.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity

Most common way to evaluate preferred orientation (texture) is to measure the pole figure for a particular direction.

Diffraction Theory

A. Diffraction

2. Intensity Equation

The intensity equation is valid when:

- the crystals making up the specimen are randomly oriented in space.
- the crystals consist of small mosaic blocks
 - “ideally imperfect” crystal

Diffraction Theory

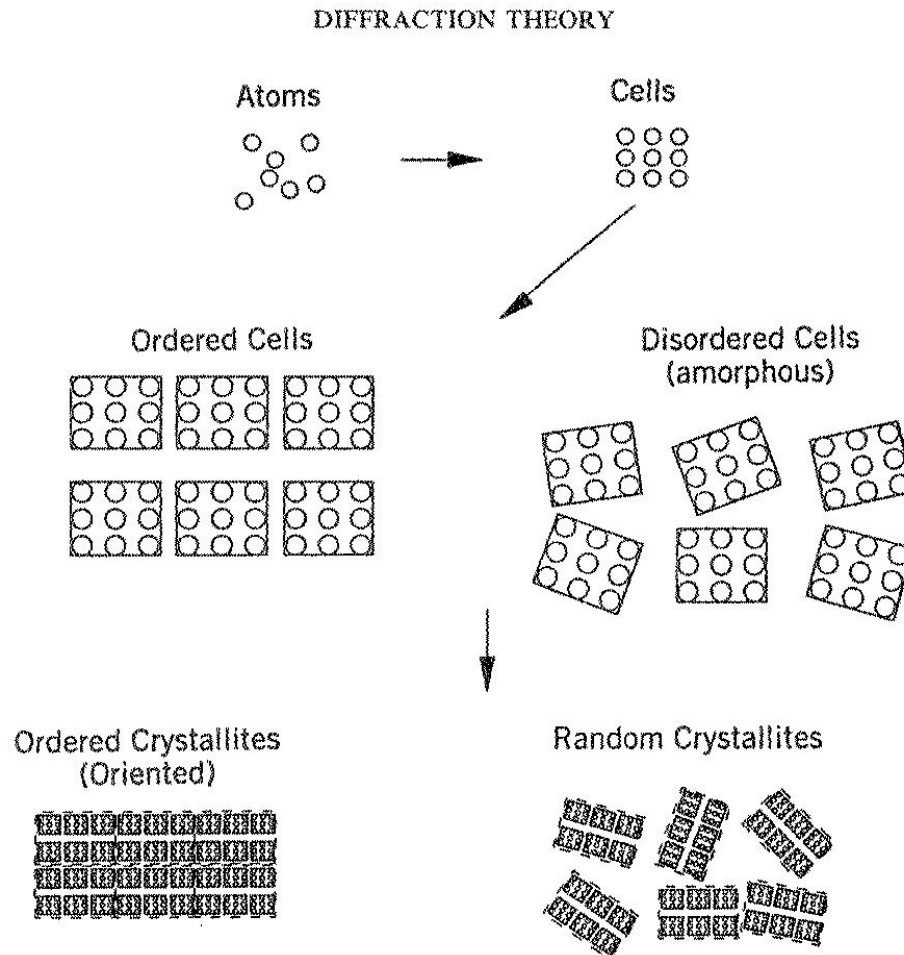


Figure 3.20. The structural makeup of solids.

Diffraction Theory

A. Diffraction

2. Intensity Equation

A crystal made up of large mosaic blocks is more nearly perfect and has a lower diffracting power.

This decrease in the integrated intensity of the diffracted beam as the crystal becomes more nearly perfect is called extinction.

Diffraction Theory

A. Diffraction

2. Intensity Equation

Extinction is absent for the ideally imperfect crystal.

Any method that will make a crystal more imperfect will reduce extinction.

This includes grinding of the sample to fine powders. Grinding reduces the crystal size and populates the diffraction cones more fully, and tends to decrease the mosaic block size, disorient the blocks, and make nonuniform.

Diffraction Theory

A. Diffraction

2. Structure, Scattering, and Intensity, con't

So to sum up: The factors that affect intensity:

- 1) Structure factor
- 2) Polarization factor
- 3) Lorentz factor
- 4) Multiplicities
- 5) Temperature factor
- 6) Absorption factor - absorption of x-rays by the sample
- 7) Preferred orientation
- 8) Extinction coefficient - applies to single crystals - not applicable to powders

Diffraction Theory

Allowed Reflections for cubic system

Bravais Lattice	Reflections which <i>may be</i> present	Reflections necessarily absent
Simple	all	None
Body centred	$(h + k + l)$ even	$(h + k + l)$ odd
Face centred	h, k and l unmixed	h, k and l mixed
End centred	h and k unmixed <i>C centred</i>	h and k mixed <i>C centred</i>

Diffraction Theory

Allowed Reflections for cubic system

Bravais Lattice	Allowed Reflections
SC	All
BCC	$(h + k + l)$ even
FCC	h, k and l unmixed
DC	h, k and l are all odd <i>Or</i> all are even $(h + k + l)$ divisible by 4

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



Reading Assignment:

Read Chapter 3 and 4 from Cullity

Read Chapter 3 from Jenkins

Read Chapter 2 from Norton

Homework 4 Due 10/10/24

