CHEMISTRY 5570

Advanced Analytical Chemistry
X-ray Diffraction
Lecture 3

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Department of Chemistry

Advance X-Ray Diffraction

Class Website:

https://sites.chemistry.unt.edu/~tgolden/courses/course_downloadsFall24.xhtml

Readings:

Given at the end of each powerpoint lecture. The books are on reserve at the Willis library under CHEM 5390 (X-ray Diffraction).

Homework Assignments:

Given at the end of each powerpoint lecture. I do not accept assignments by email – all assignments must be turned in during class.

Exams:

There will be an exam in class on Tuesday, December 10th,

8:00 - 10:00 a.m.

Important for Calculations

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

where n is an integer

λ is the wavelength of the x-rays

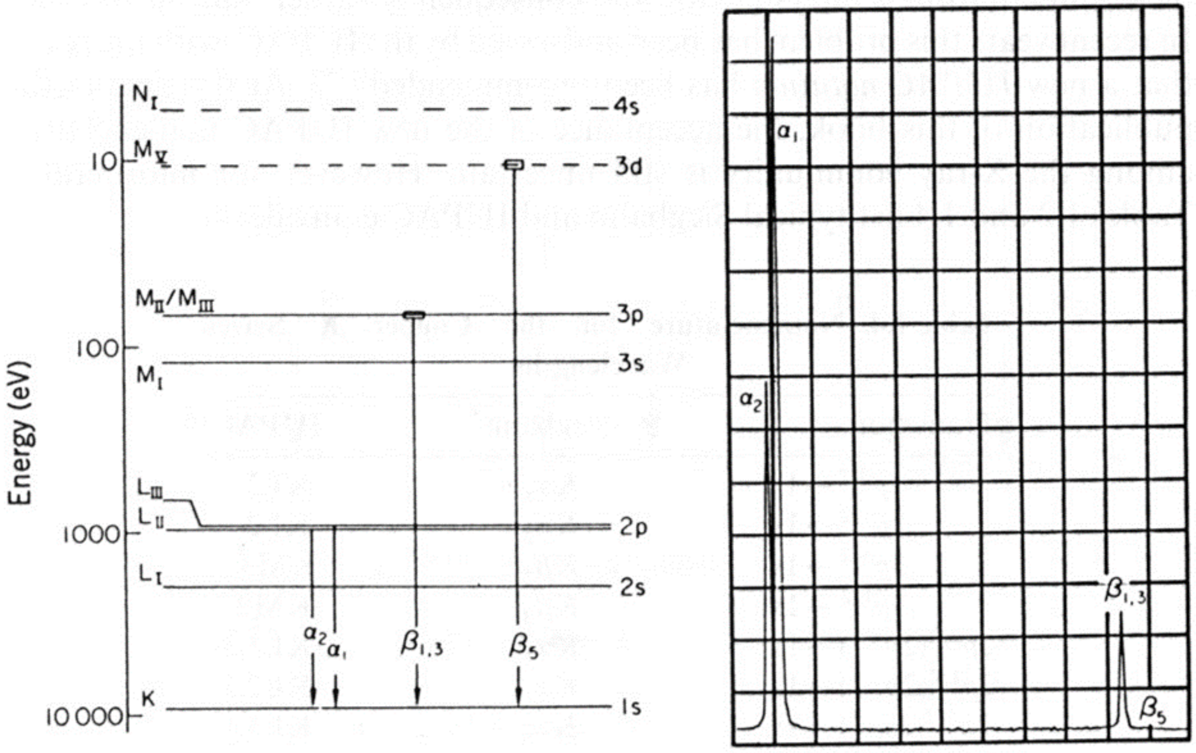
d is the interplanar spacing in the specimen

θ is the diffraction angle

Bragg Equation

Properties of X-rays

The Copper K Spectrum



The copper $K\alpha$ spectrum.

- The diagram at left shows the 5 possible Cu K transitions
- L to K “jumps:
  - **Kα_1 (8.045 keV, 1.5406Å)**
  - **Kα_2 (8.025 keV, 1.5444Å)**
- M to K
  - **Kβ_1 Kβ_3 (8.903 keV, 1.3922Å)**
  - **K β_5**

Crystallography

Solids can be generally classified as: single crystal, polycrystalline, or amorphous.

<u>Crystal</u> - solid composed of atoms arranged in a pattern periodic in three dimensions.

<u>Point lattice</u> - an array of points in space so arranged that each point has identical surroundings.

Since all points are identical we can choose a repeating group to represent a <u>unit cell</u>.

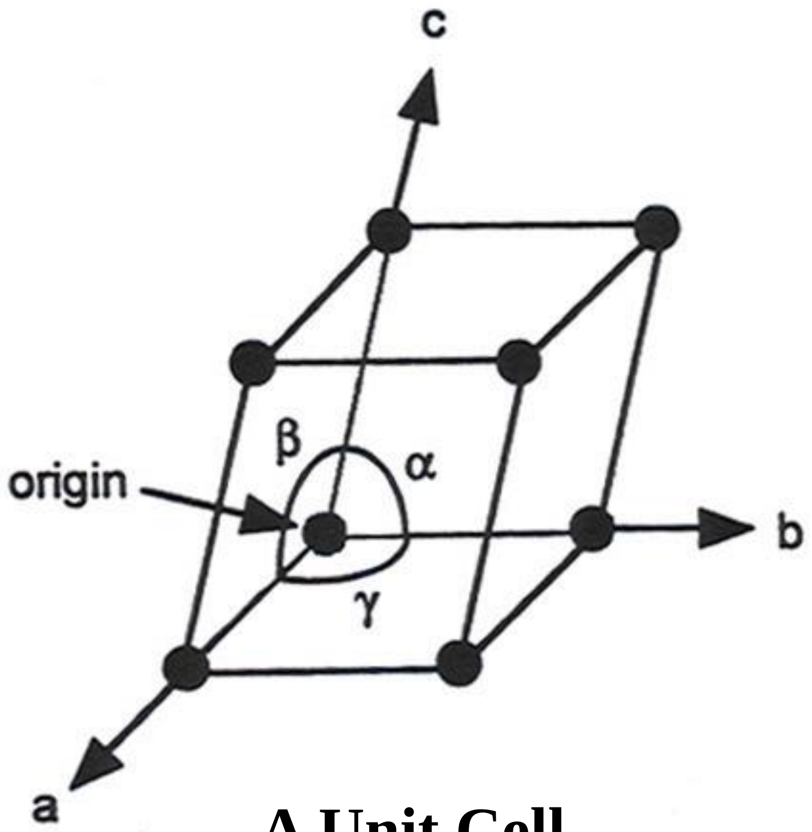
Crystallography

The size and shape of the unit cell can be described by three vectors, a, b, and c (called the <u>crystallographic axes</u> of the cell).

The unit cell can also be described in terms of lengths (a, b, c) and the angles between them (α, β, γ).

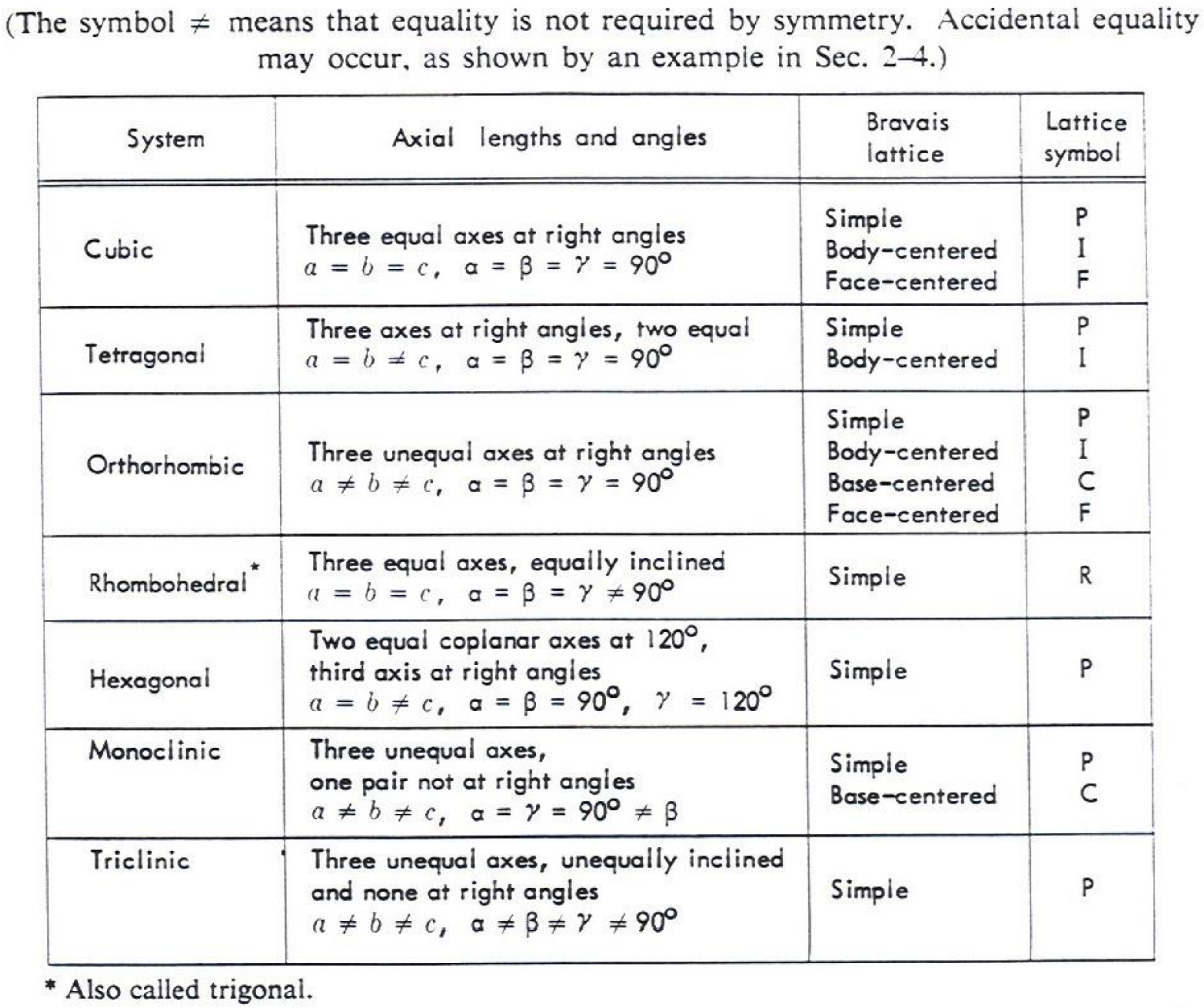
The lengths and angles are the <u>lattice constants</u> or <u>lattice parameters</u> of the unit cell.

Notice that the entire point lattice can be built by translating the unit cell.



A Unit Cell.

Axis	**a**	**b**	**c**
Lattice Parameters:			
Lengths	a	b	c
Inter-axial angle	α	β	γ

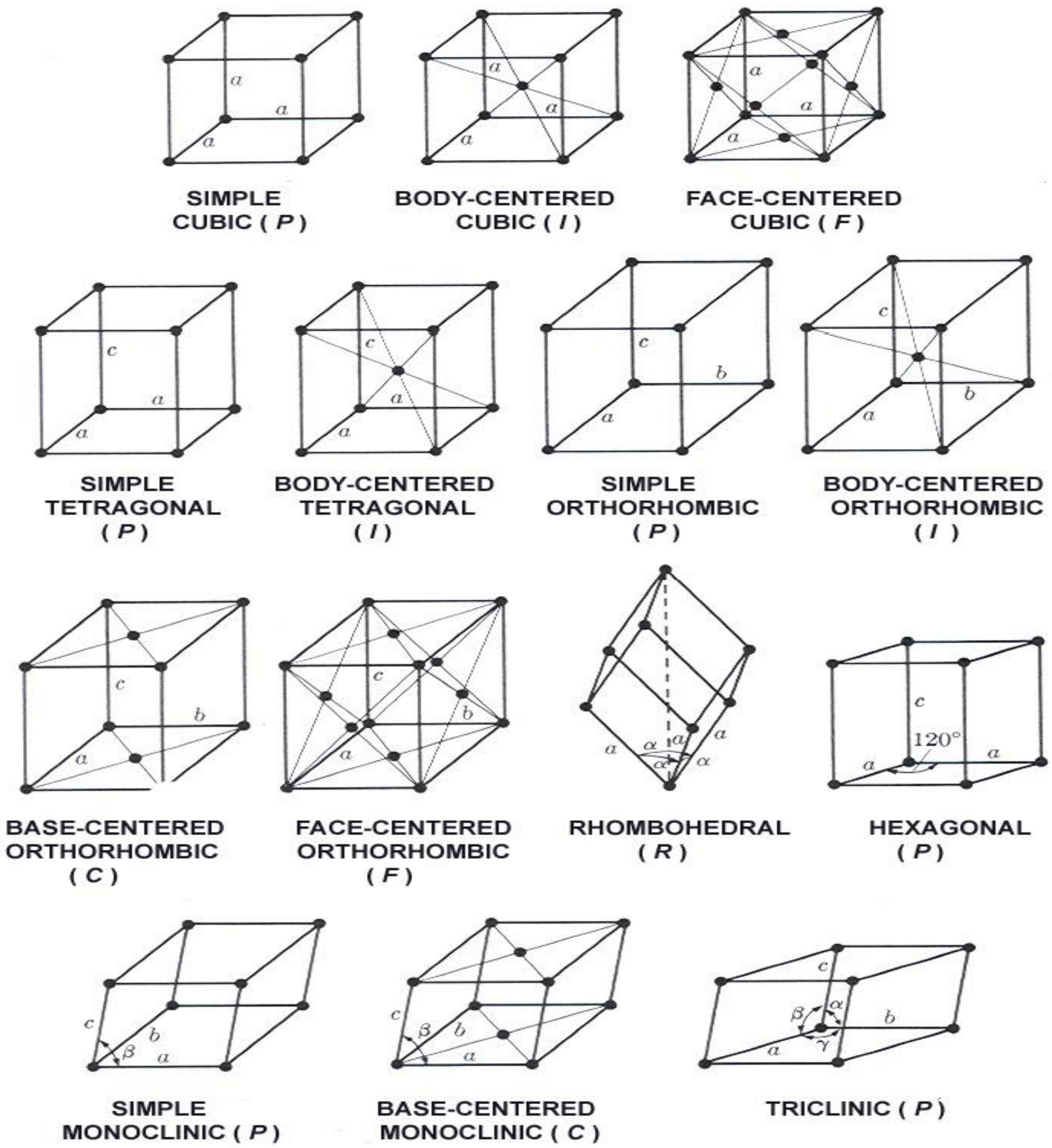


(The symbol ≠ means that equality is not required by symmetry. Accidental equality may occur, as shown by an example in Sec. 2–4.)

System	Axial lengths and angles	Bravais lattice	Lattice symbol
Cubic	Three equal axes at right angles $a = b = c, \quad \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered Face-centered	P I F
Tetragonal	Three axes at right angles, two equal $a = b \neq c, \quad \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered	P I
Orthorhombic	Three unequal axes at right angles $a \neq b \neq c, \quad \alpha = \beta = \gamma = 90^\circ$	Simple Body-centered Base-centered Face-centered	P I C F
Rhombohedral*	Three equal axes, equally inclined $a = b = c, \quad \alpha = \beta = \gamma \neq 90^\circ$	Simple	R
Hexagonal	Two equal coplanar axes at 120°, third axis at right angles $a = b \neq c, \quad \alpha = \beta = 90^\circ, \quad \gamma = 120^\circ$	Simple	P
Monoclinic	Three unequal axes, one pair not at right angles $a \neq b \neq c, \quad \alpha = \gamma = 90^\circ \neq \beta$	Simple Base-centered	P C
Triclinic	Three unequal axes, unequally inclined and none at right angles $a \neq b \neq c, \quad \alpha \neq \beta \neq \gamma \neq 90^\circ$	Simple	P

* Also called trigonal.

7 Crystal systems and 14 Bravais lattices.



The fourteen Bravais lattices.

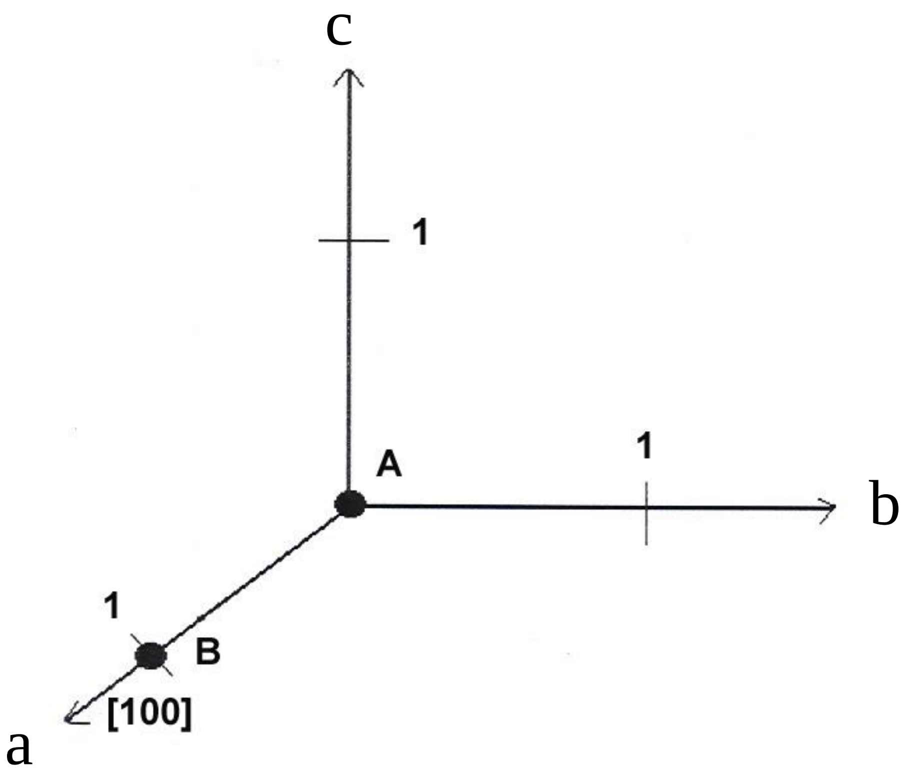
Crystallography

Geometry and the structure of crystals

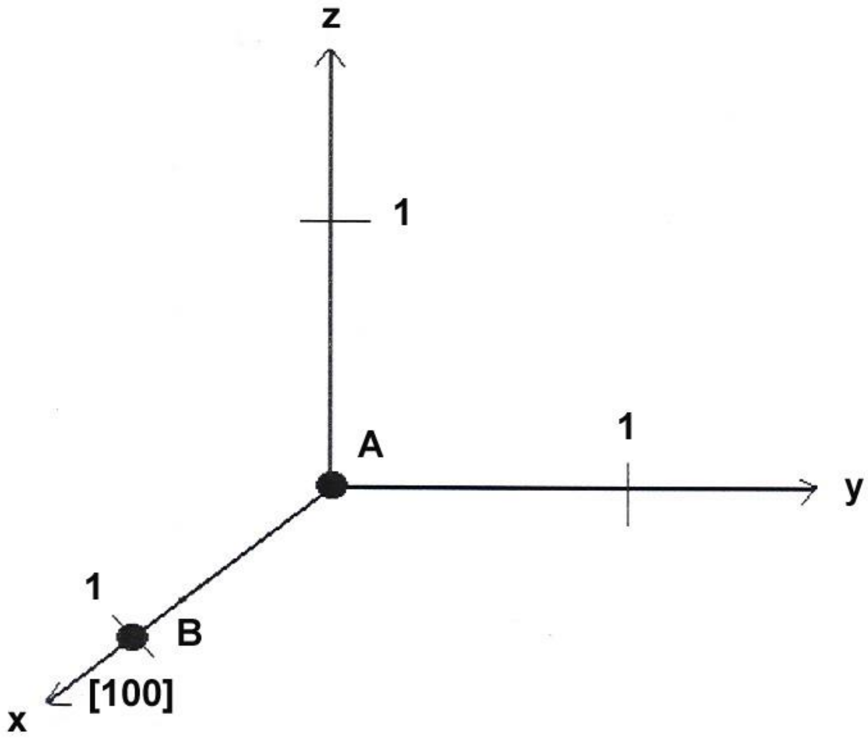
Vectors and Planes

Direction or vectors are denoted by [uvw]

[   ] - denotes an individual direction.



Crystallography



Start at A (0,0,0) origin and travel in a vector until you reach B.
So the direction of the line is [1 0 0]

The family of directions is denoted by < >
<1 0 0> - is the family of directions for all the individual directions.

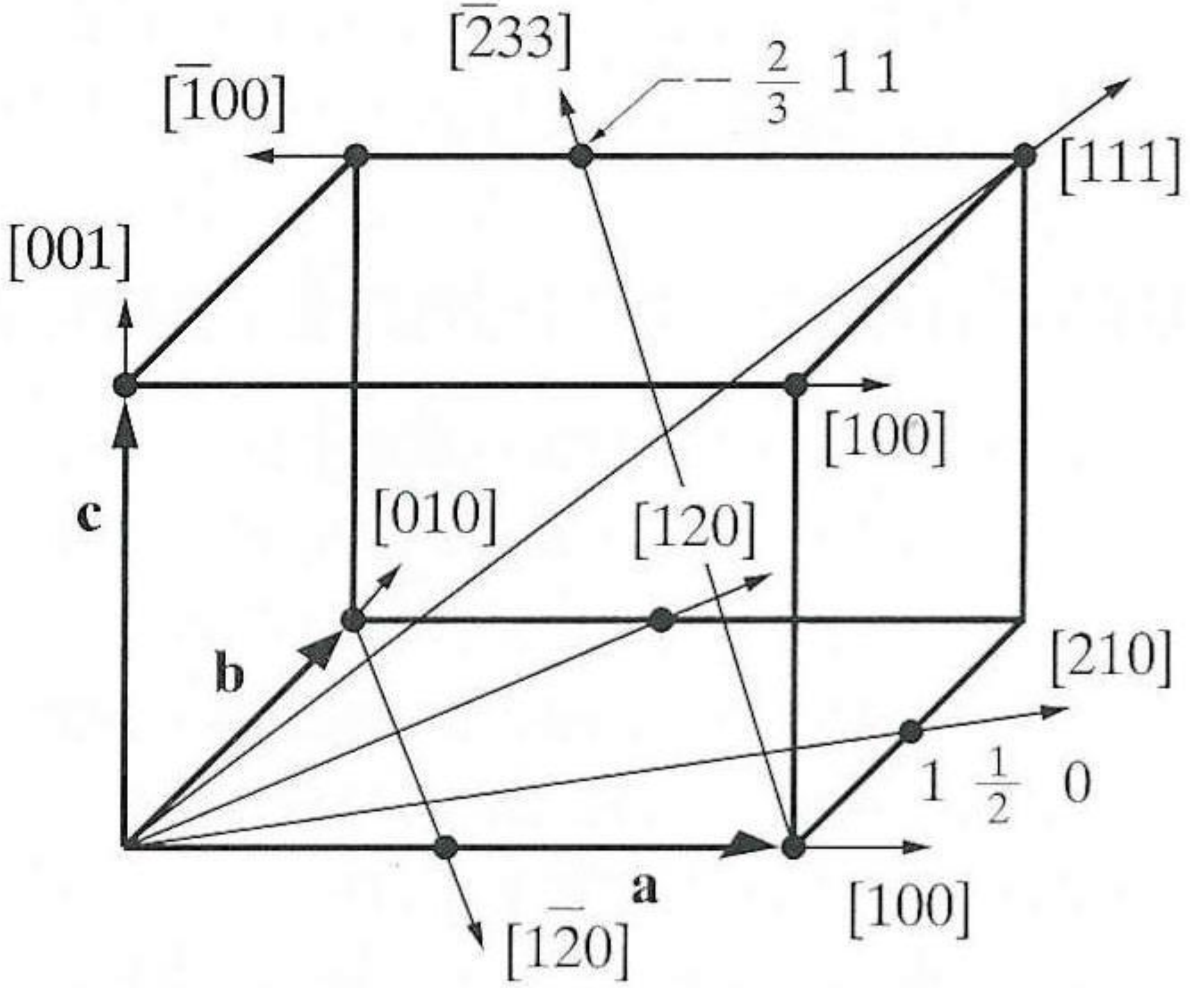
D. Vectors and Planes

$\cos\theta = (uu' + vv' + ww')/(u^2 + v^2 + w^2)^{1/2}(u'^2 + v'^2 + w'^2)^{1/2}$

Example: What is the angle between [110] and [111]?

$\theta = \arccos (1\times1 + 1\times1 + 0\times1)/ (1^2 + 1^2 + 0^2)^{1/2}(1^2 +1^2 + 1^2)^{1/2}$

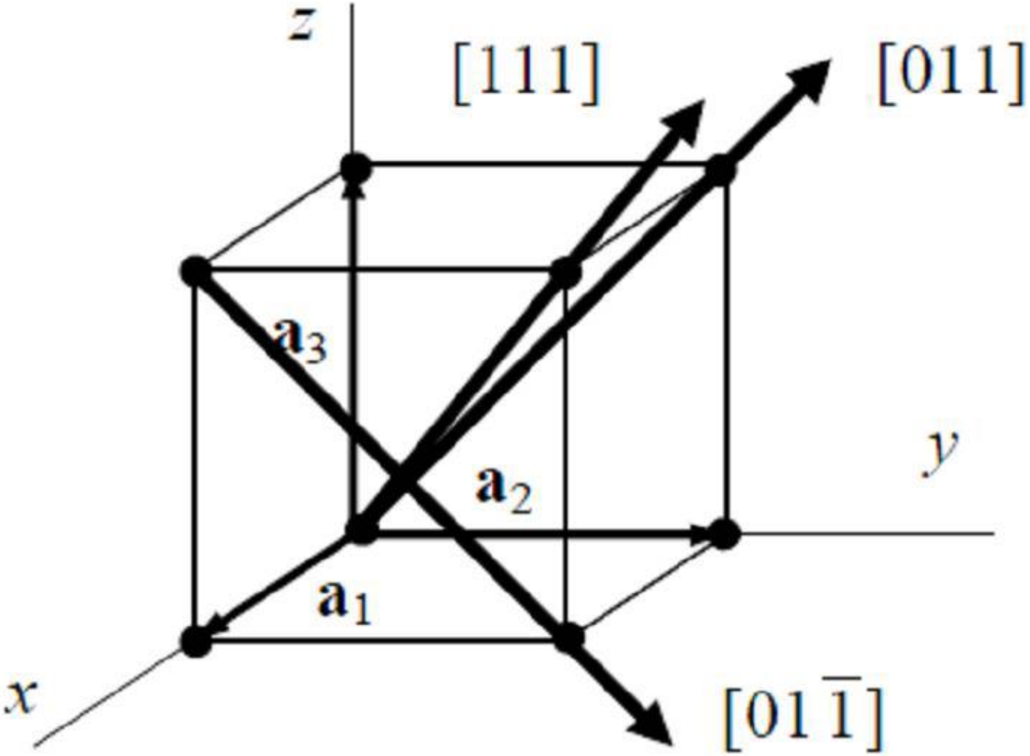
$= 35.3^o$



Indices of Directions

Crystallography

Geometry and the structure of crystals



Crystallography

Geometry and the structure of crystals

Vectors and Planes

Miller Indices

A notation used to describe various planes within a crystal lattice.

Steps to determine Miller Indices

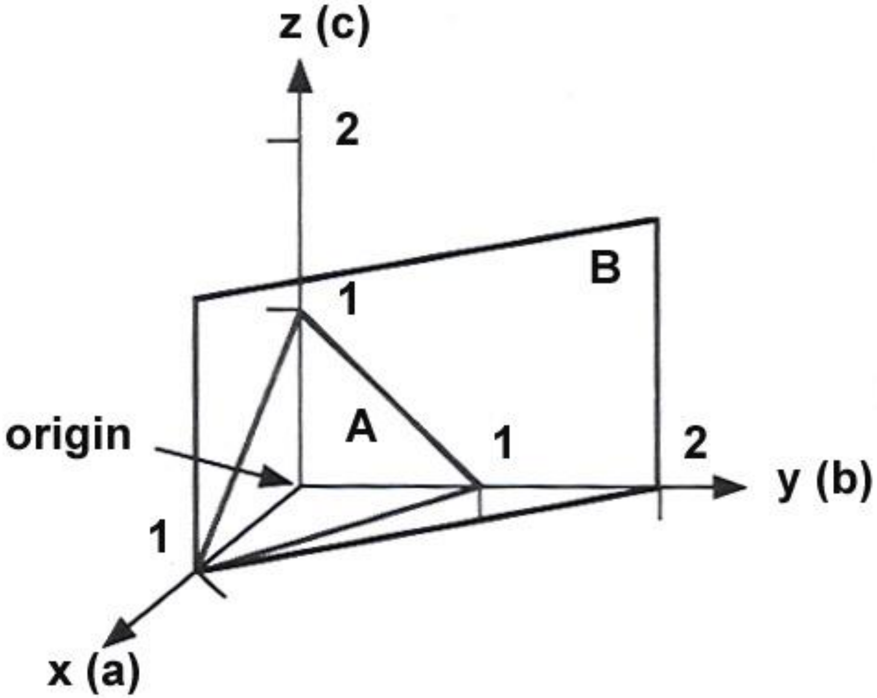
1) Identify the points at which the plane intersects the a, b, c axes. Intercept is measured in terms of fractions or multiples of the lattice parameter.

2) Take reciprocals of the intercepts. (Get rid of infinity)

3) Multiply to get a whole number (Clear the fractions)

4) Enclose numbers in (   ). Represent negative numbers with a bar (bar one).

Practice:

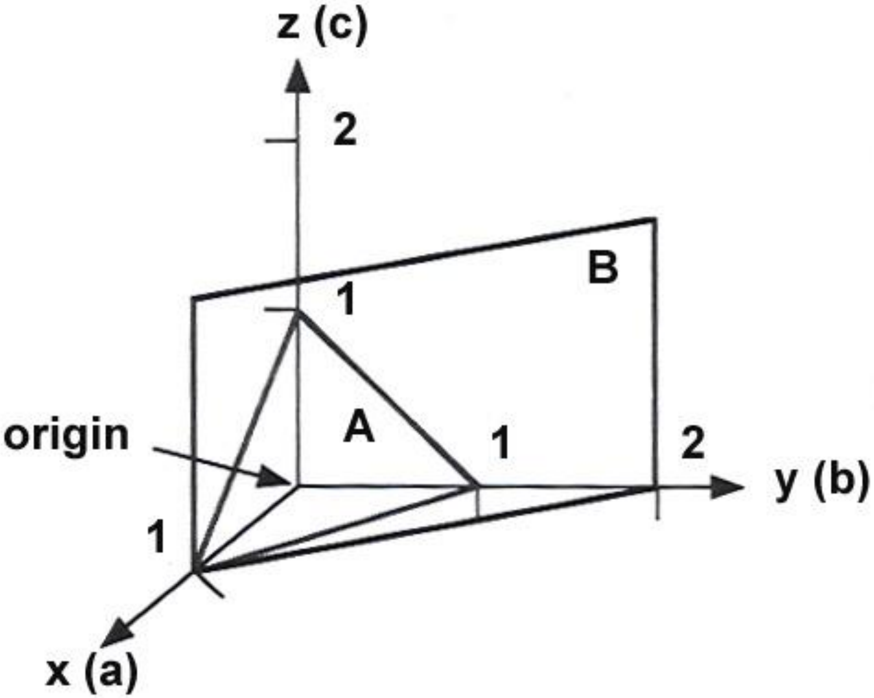


Plane A:

	a	b	c
Step 1. Intercepts	1	1	1
Step 2. Reciprocals	1	1	1
Step 3. Clear fractions	1	1	1

Step 4. Miller Indice **(1 1 1)**

Practice:

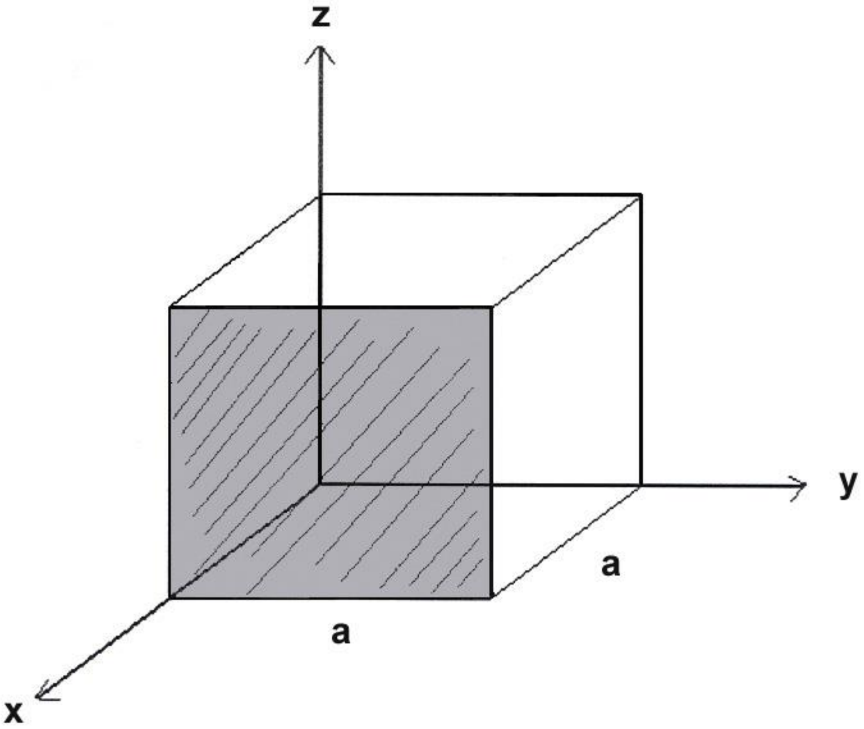


Plane B:

	a	b	c
Step 1. Intercepts	**1**	**2**	**∞**
Step 2. Reciprocals	**1**	**1/2**	**0**
Step 3. Clear fractions	**2**	**1**	**0**

Step 4. Miller Indice **(2 1 0)**

Example: Cubic System

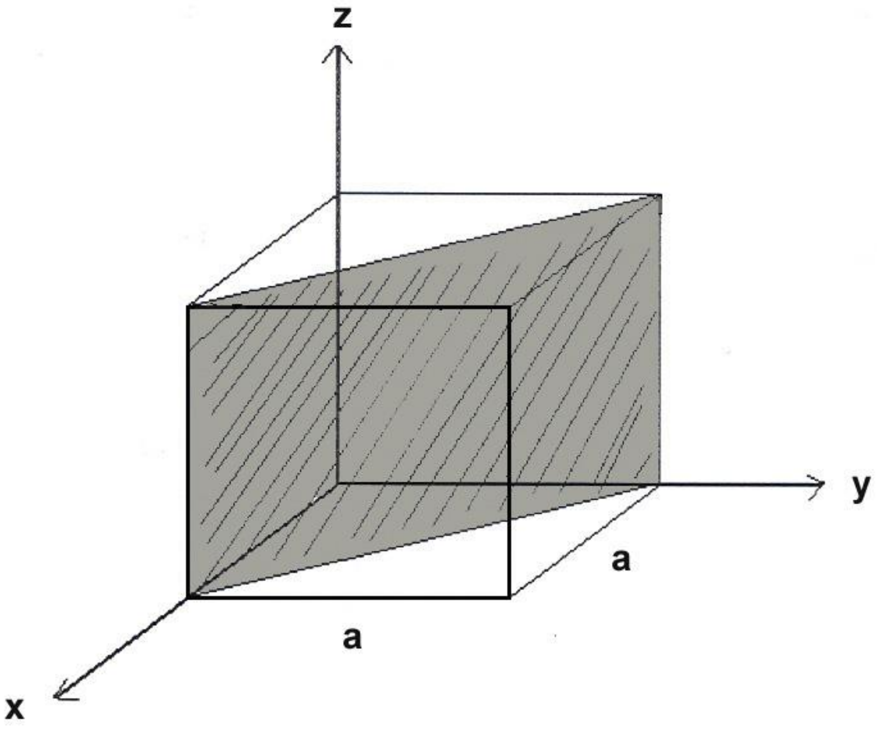


	a	b	c
Step 1. Intercepts	1	∞	∞
Step 2. Reciprocals	1	0	0
Step 3. Clear fractions	1	0	0

Step 4. Miller Indice (1 0 0)

This is the surface plane of the cubic crystal.

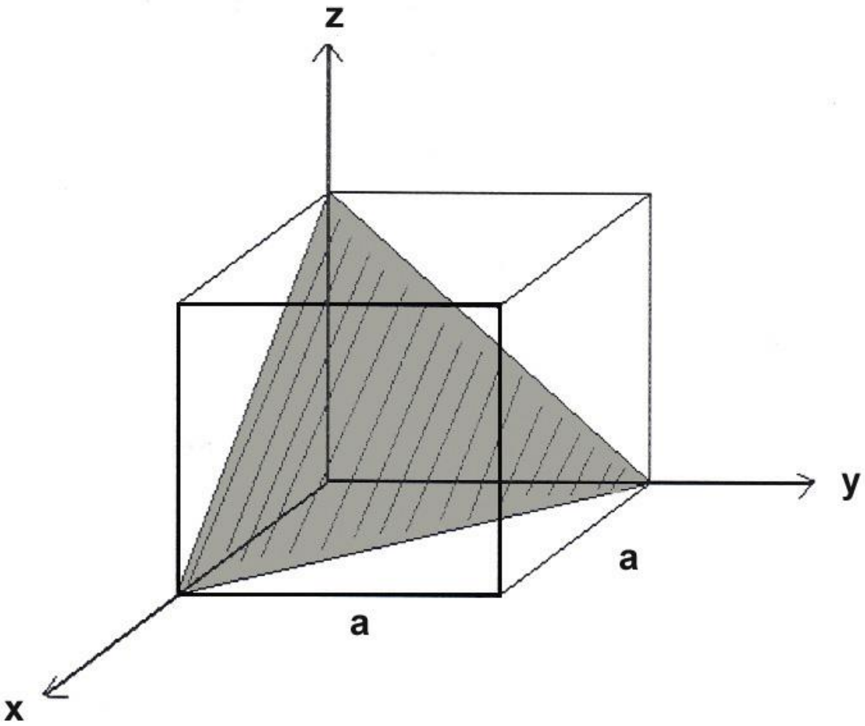
Example: Cubic System



	a	b	c
Step 1. Intercepts	**1**	**1**	**∞**
Step 2. Reciprocals	**1**	**1**	**0**
Step 3. Clear fractions	**1**	**1**	**0**

Step 4. Miller Indice **(1 1 0)**

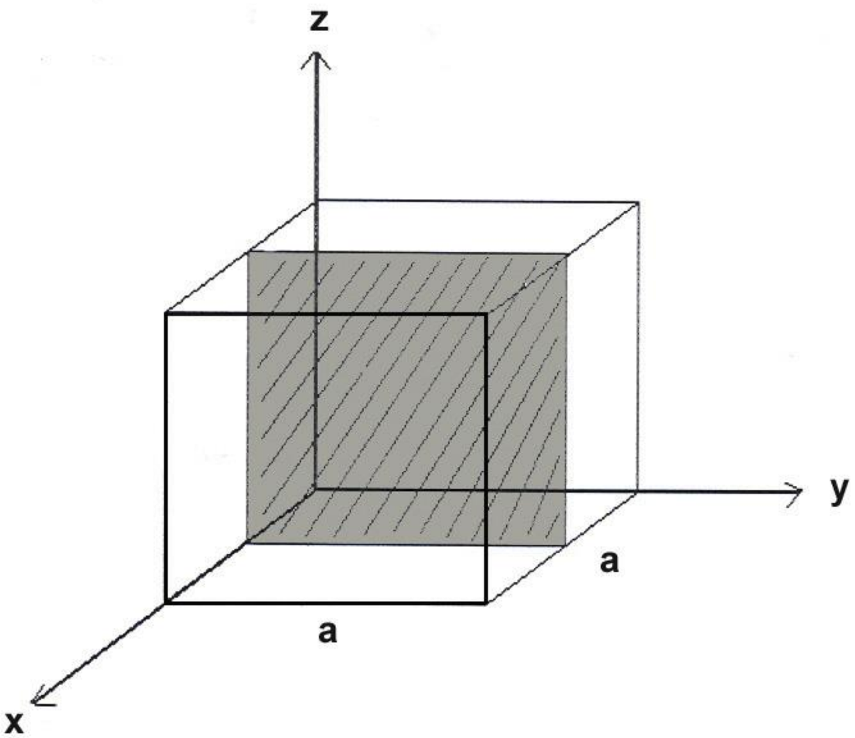
Example: Cubic System



	a	b	v
Step 1. Intercepts	1	1	1
Step 2. Reciprocals	1	1	1
Step 3. Clear fractions	1	1	1

Step 4. Miller Indice **(1 1 1)**

Example: Cubic System



	a	b	c
Step 1. Intercepts	**1/2**	**∞**	**∞**
Step 2. Reciprocals	**2**	**0**	**0**
Step 3. Clear fractions	**2**	**0**	**0**

Step 4. Miller Indice **(2 0 0)**

Notice that the (2 0 0) reflection is a multiple of (1 0 0).

$\ddot{1}$

Crystallography

Geometry and the structure of crystals

Vectors and Planes

In the cubic system there are six faces equivalent to (1 0 0).

This set is related and denoted by {1 0 0} - this set is called a <u>family</u> of planes.

{ } - denotes a family of planes

( ) - denotes an individual plane

The six planes in the {1 0 0} family are:

(1 0 0) (0 1 0) (0 0 1) ($\bar{1}$ 0 0) (0 $\bar{1}$ 0) (0 0 $\bar{1}$)

Crystallography

Geometry and the structure of crystals

Vectors and Planes

The number of planes in a family that have the same spacing is called the multiplicity factor. (This factor determines the intensity of the reflection).

Notice the (2 0 0) plane is not in the same family as the (1 0 0) plane. It is parallel to the (1 0 0) plane but the spacing is 1/2 the spacing for the (1 0 0) plane.

Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Shapes

Crystals often have facets which correspond to low index planes.

For instance, crystals with cubic symmetry

(4 – 3 fold axis) can have the form of an octahedron or cube.

Since different faces have different arrangement of atoms, then the different faces will have different reactivities.

Crystallography

Geometry and the structure of crystals

Vectors and Planes

Example:

If you crystallize NaCl with H_2O you get a cubic shaped crystal.

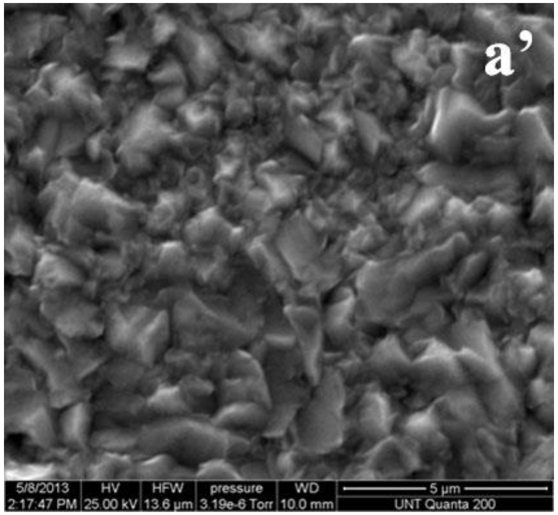
If you crystallize NaCl with urea you get an octahedron shape crystal.

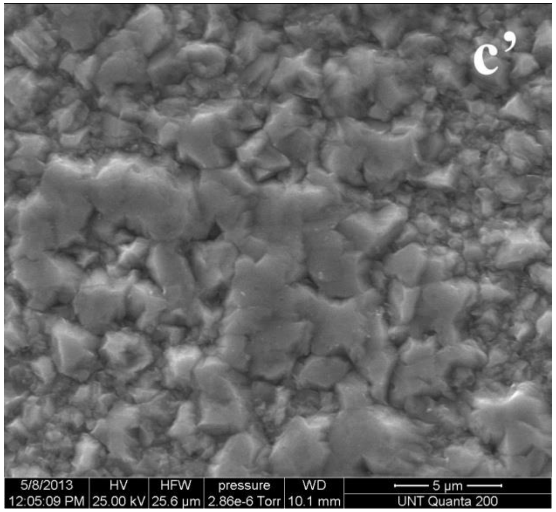
Why? – urea acts to inhibit the growth of the {111} faces, so the {100} faces grow faster and grow out.

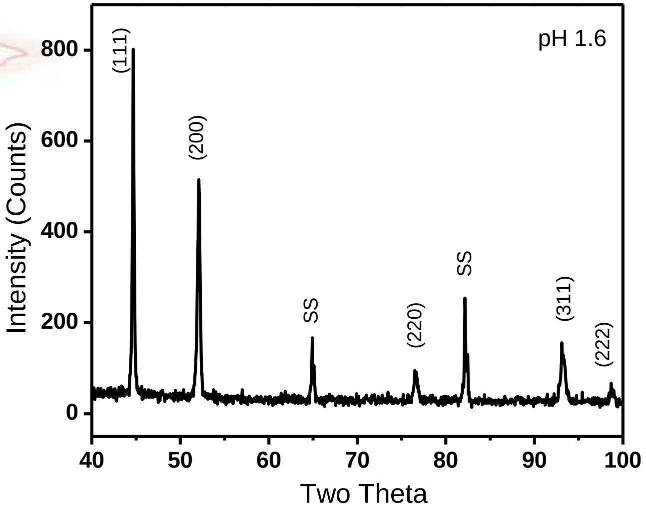
A general rule: the surfaces that are most prominent in a crystal are those that grow most slowly.

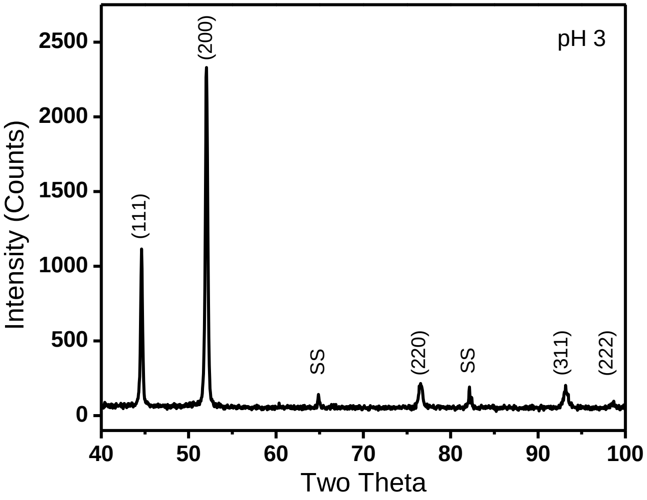
Crystallography

Geometry and the structure of crystals









Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Shapes

As seen in the previous example, the overall crystal may have the same or different shape than it’s unit cell.

Planes of low indices have the largest density of lattice points and the law of crystal growth states such planes develop at the expense of planes with high indices and few lattice points.

Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Shapes

Law of rational indices – states that the indices of naturally developed crystal faces are always composed of whole numbers, and rarely exceed 3 or 4.

Example: Faces of form {100}, {111}, {210}, etc are observed but not faces as {510}, {719}, etc.

An exception is seen in materials work for some electrodeposits or other artificially grown deposits resulting in a grains in a polycrystalline mass.

Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Shapes

Also when considering surfaces, one rule of thumb, is that the most stable solid surfaces are those with:

1. **a high surface atom density**
2. **surface atoms of high coordination number**

(Note - the two factors are obviously not independent, but are inevitably strongly correlated).

Consequently, for example, if we consider the individual surface planes of an fcc metal, then we would expect the stability to decrease in the order

fcc (111) > fcc (100) > fcc (110)

Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Defects

Imperfections in the periodic structure of the individual grains of crystalline solids.

Classified as point, line, and planar defects.

Can have large effect on the properties of the material (mechanical, optical, electrical, etc).

Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Defects

Linear defects – edge and screw dislocations. Large strains and very high dislocation densities can occur when metals are forged, rolled, machines, shot peening, or ball milling.

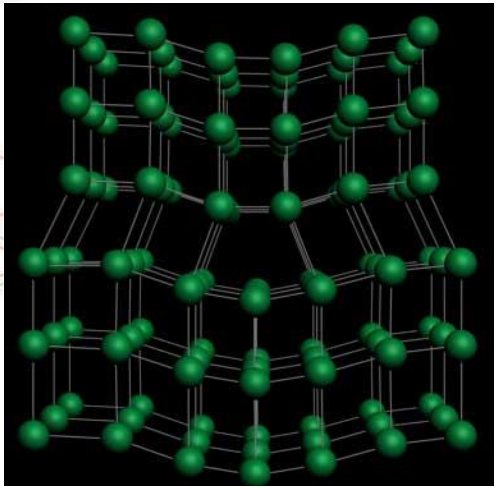
Crystallography

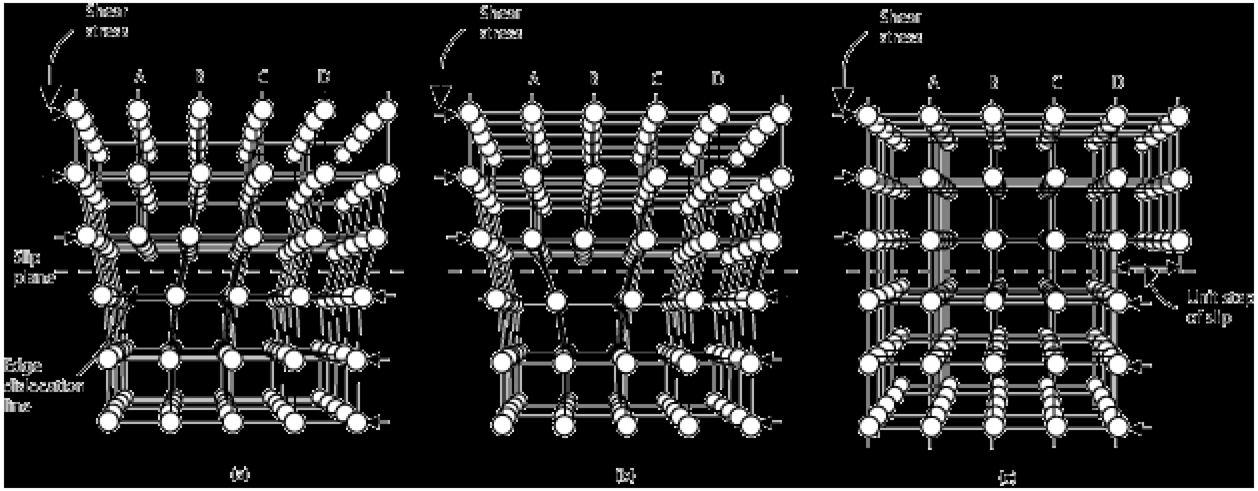
Geometry and the structure of crystals

Vectors and Planes

Crystal Defects

Linear defects – edge dislocations.





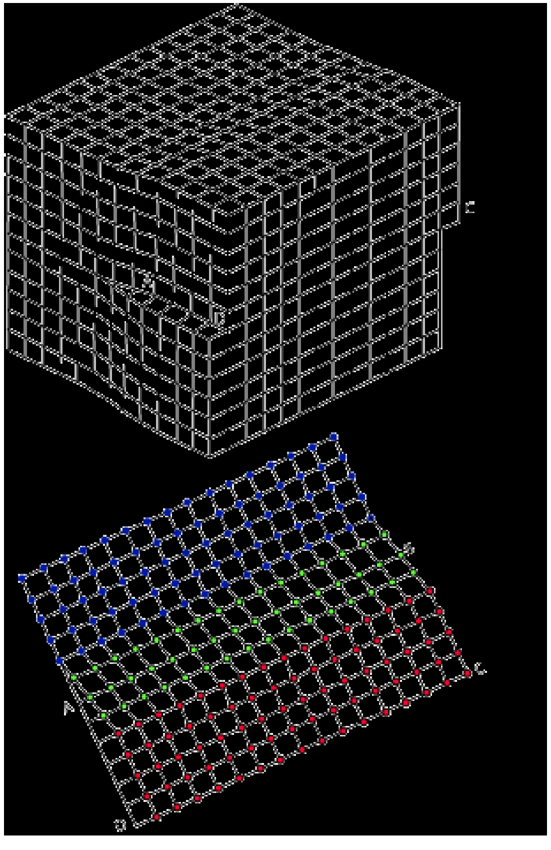
Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Defects

Linear defects – screw dislocations.



Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Defects

Planar defects – stacking faults and twins

Stacking faults – the normal stacking sequence of the close packed planes can be disrupted.

Example: For the fcc structure, the normal stacking sequence is ….ABCABCABC… but can become …ABCAB*ABC… or …ABCA*CABCA…

Crystallography

Geometry and the structure of crystals

Vectors and Planes

Crystal Defects

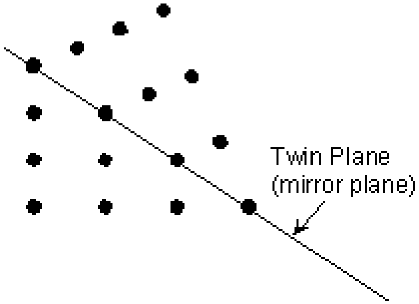
Twinned crystals – may be described by the symmetry operation to bring one in coincidence with the other.

One kind involves a 180^{o} rotation about an axis called the <u>twin axis</u>, the other involves a reflection across a plane called the <u>twin plane</u>.

The plane where the two parts of the twinned crystal unite is called the <u>composition plane</u>.

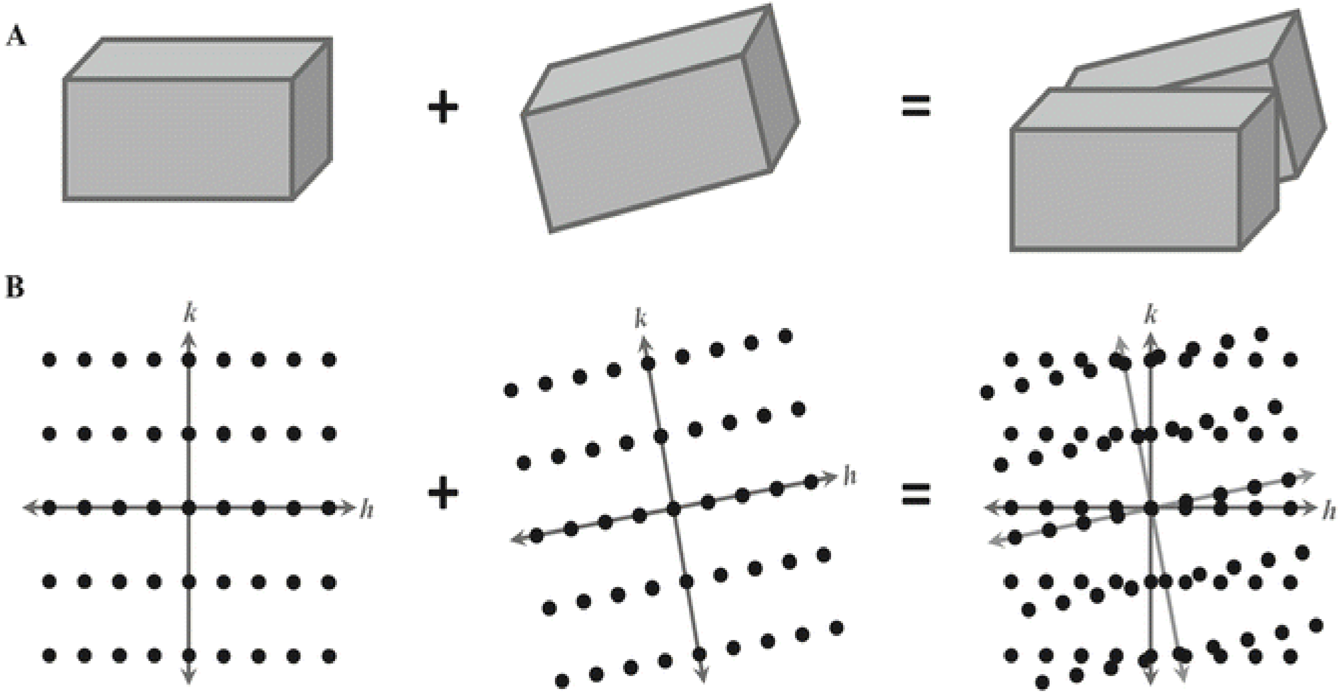
Crystallography

Geometry and the structure of crystals



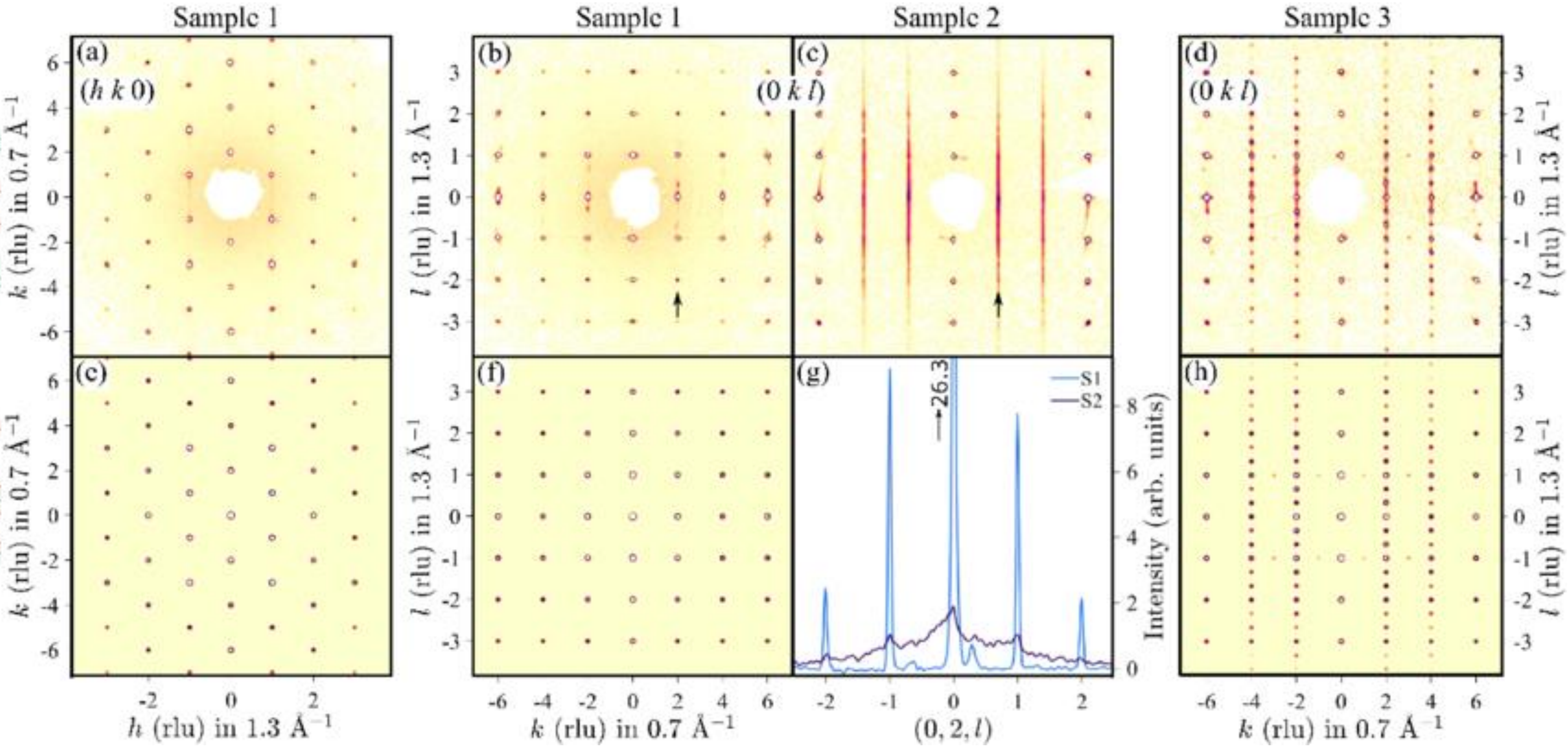
Crystallography

Geometry and the structure of crystals



Crystallography

Geometry and the structure of crystals



Crystallography

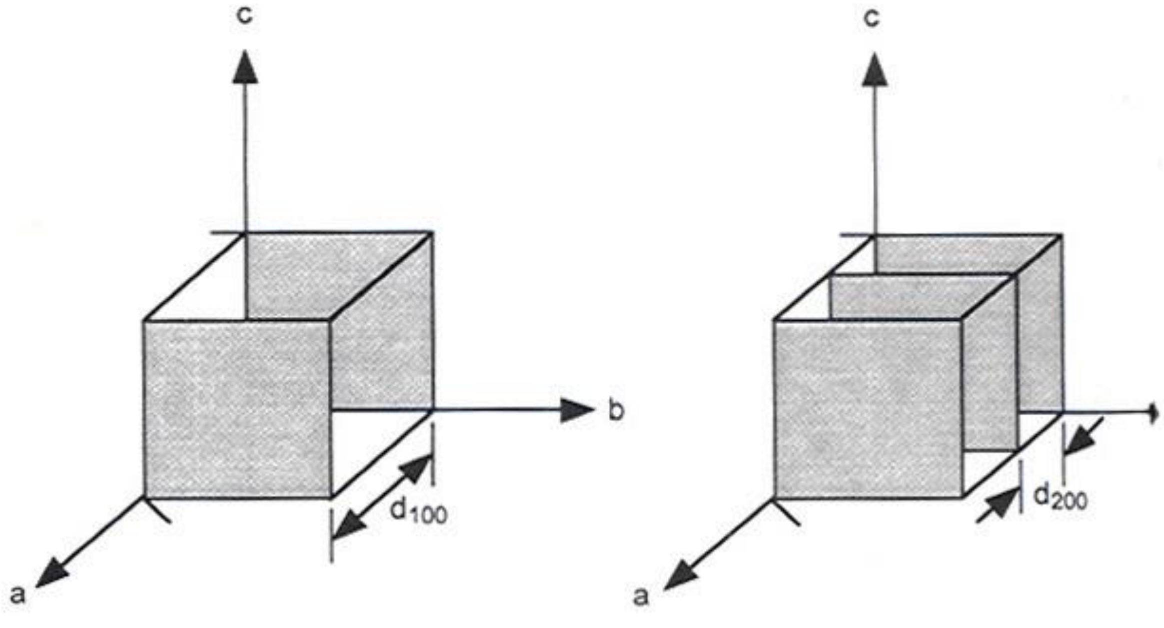
Geometry and the structure of crystals

Interplanar Spacings

The distance between an equivalent set of planes is defined as d_{hkl} - the <u>interplanar spacing</u>.

The interplanar spacing, d_{hkl}, measured at right angles to the planes, is a function both of the plane indices (hkl) and the lattice constants ($a,b,c,\alpha,\beta,\gamma$).

The distance can be directly determined by x-ray diffraction.



(a) (b)

The d_{hkl} interplanar spacing.

For a cubic system:

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

The d_{hkl} interplanar spacing.

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:

$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl) \left\{ \begin{aligned} V &= \text{volume of unit cell} \\ S_{11} &= b^2c^2\sin^2\alpha, \\ S_{22} &= a^2c^2\sin^2\beta, \\ S_{33} &= a^2b^2\sin^2\gamma, \\ S_{12} &= abc^2(\cos\alpha\cos\beta - \cos\gamma), \\ S_{23} &= a^2bc(\cos\beta\cos\gamma - \cos\alpha), \\ S_{13} &= ab^2c(\cos\gamma\cos\alpha - \cos\beta). \end{aligned} \right.$$

Crystallography

Geometry and the structure of crystals

Interplanar Spacings

For an orthorhombic system:

$1/d^2 = h^2/a^2 + k^2/b^2 + l^2/c^2$

Example: Calculate the d-spacings for an orthorhombic cell for a = 3Å, b = 4 Å, and c = 5Å if the reflections are 001, 010, 100, 011 and 101?

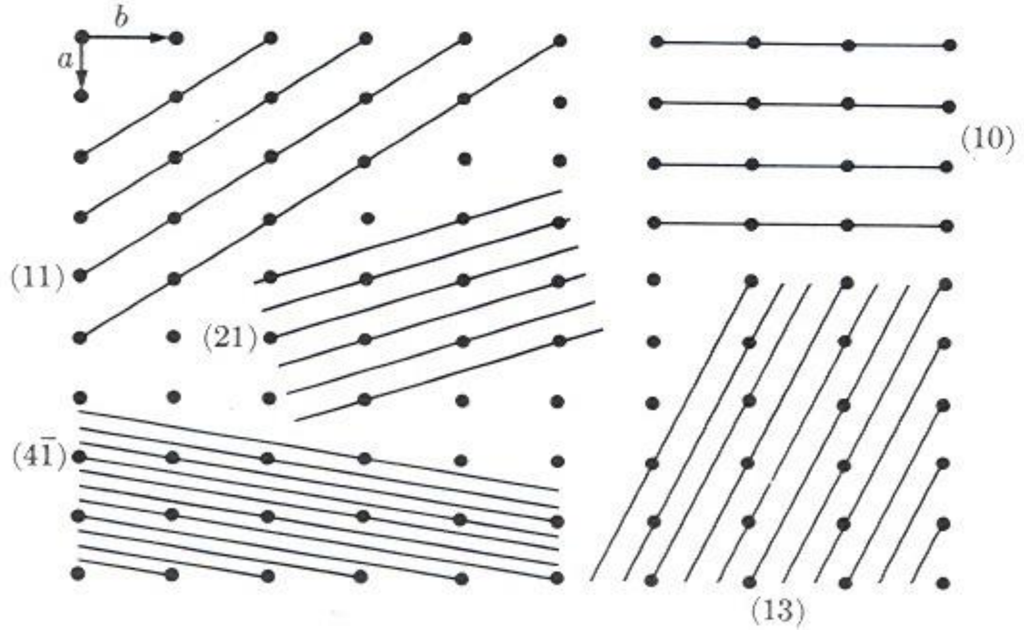
001	5
010	4
100	3
011	3.12
101	2.57

Crystallography

Geometry and the structure of crystals

Interplanar Spacings

Planes of large spacings have low indices and pass through a high density of lattice points.



Crystallography

Geometry and the structure of crystals

Interplanar Spacings

Planar density is the density of atoms on a particular plane, and can be determined by:

planar density = number of atoms on the plane/ area of the plane

Crystallography

Geometry and the structure of crystals

Interplanar Spacings

Density = mass/volume

= formula weight/molar volume

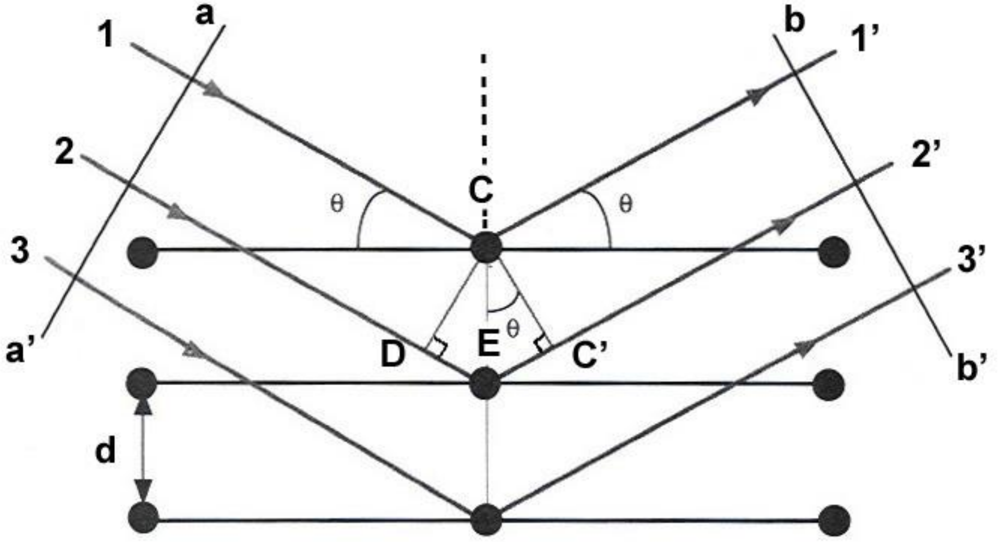
= FW/(volume of unit cell)N

= (FW x Z) / (V x N)

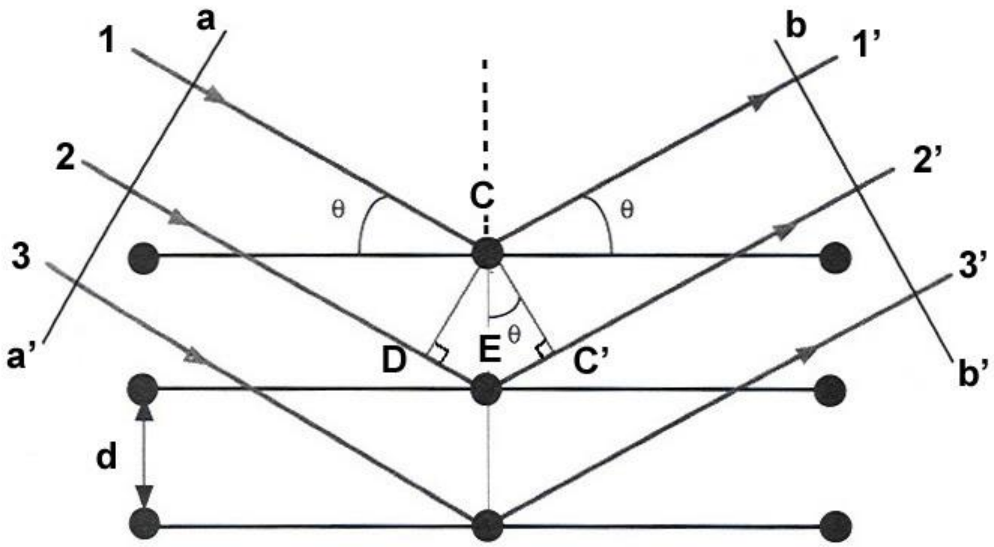
Z = # of formula units per unit cell

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



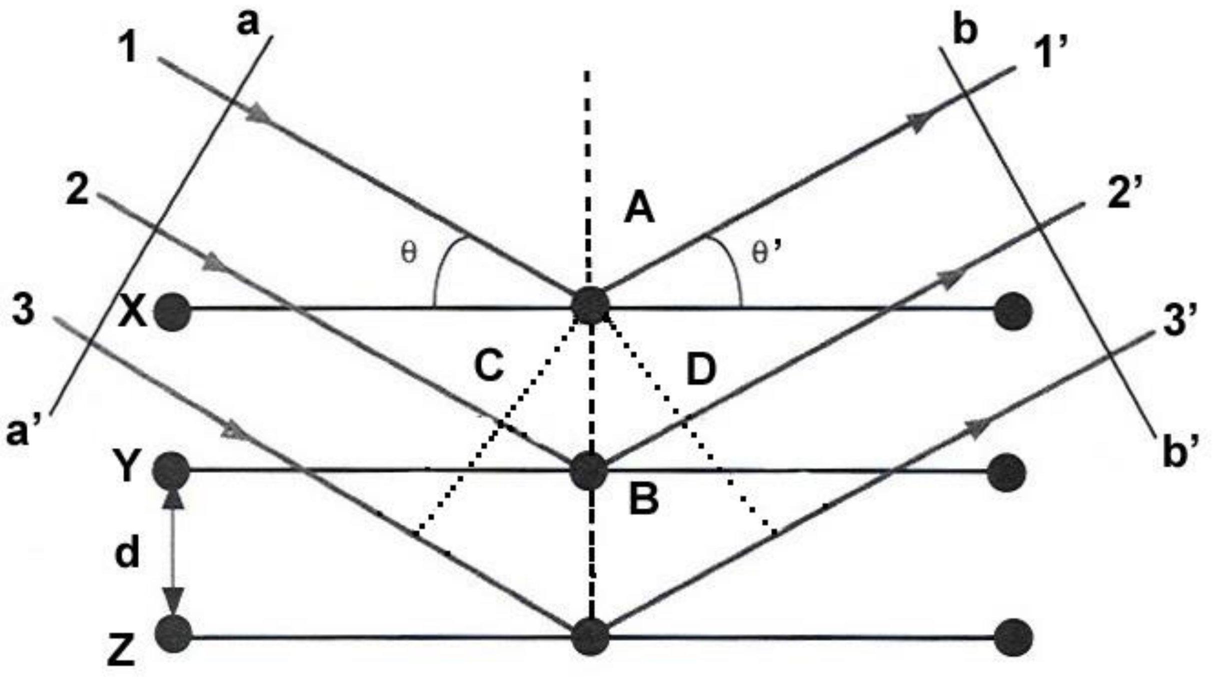
$n\lambda$ = path difference (δ)   (where n is a whole number)

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

Since CE equals interplanar spacing, d, then

$n\lambda = 2d\sin\theta$ Bragg's Law   (see next 4 slides for derivatization)

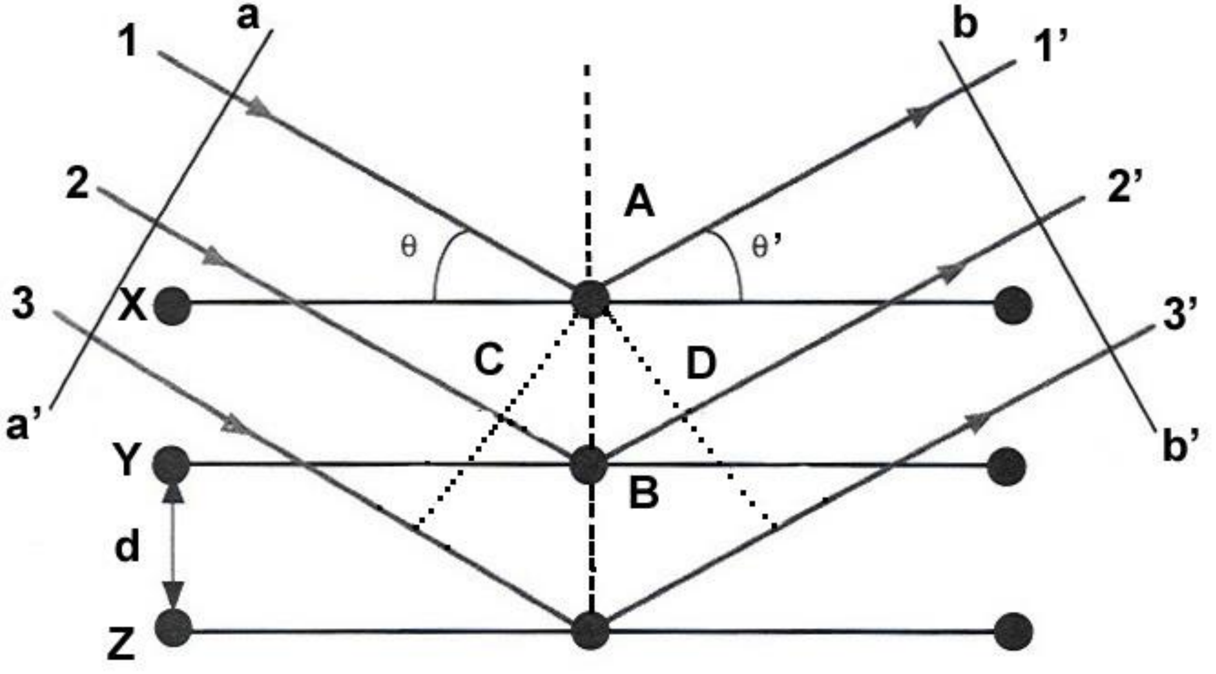
Diffraction Theory



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



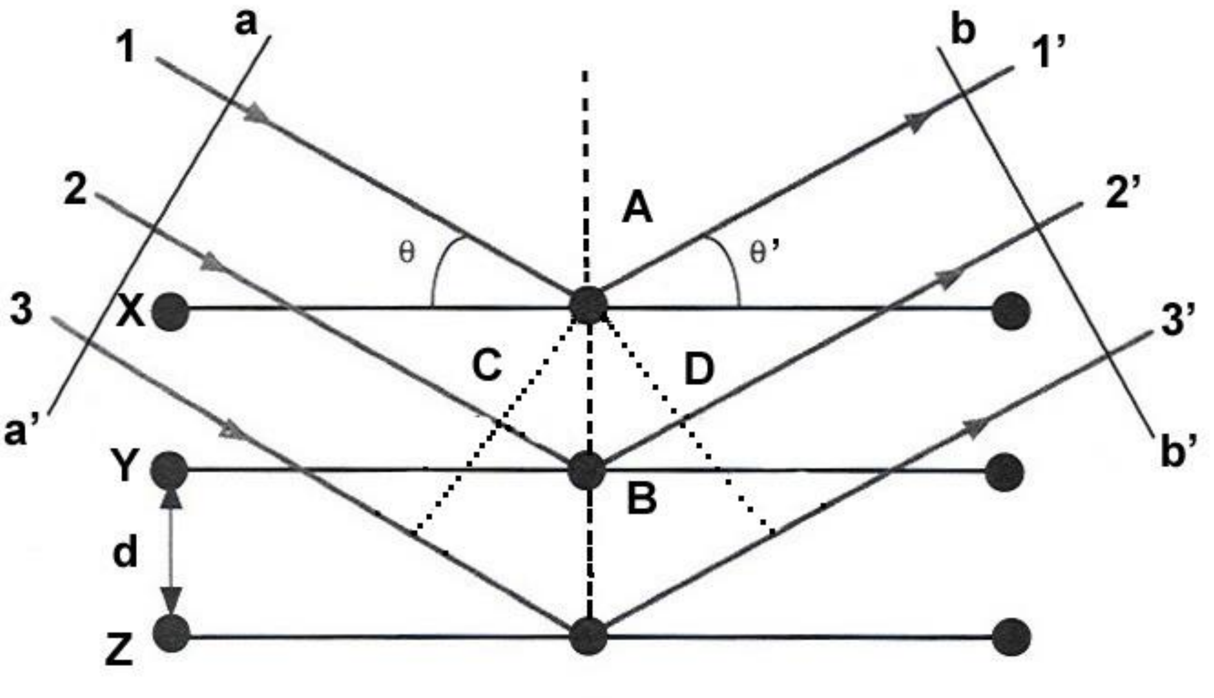
How can we prove this?

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

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

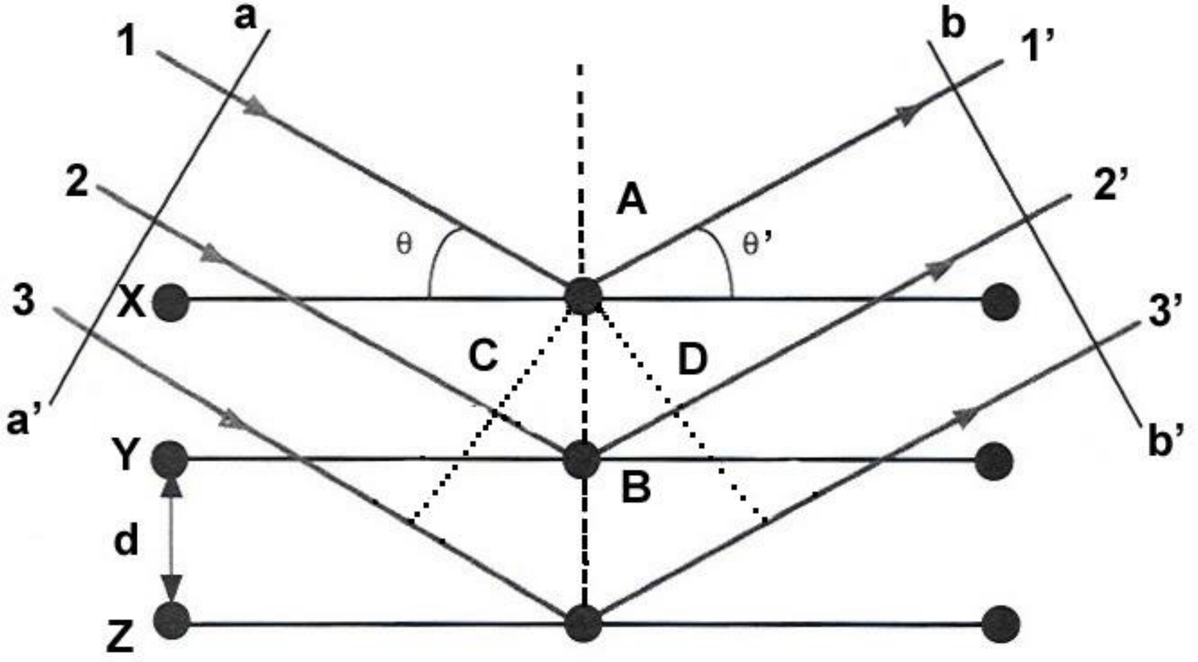
Notice the two triangles CBA and DBA have a common side, AB, that is also the spacing d between rows of atoms.

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 90^0 rotation of this angle, the two angles are equal.

Diffraction Theory



So, $\sin\theta = CB/AB$ and $\sin\theta' = BD/AB$ so,

$AB\sin\theta = CB$ and $AB\sin\theta' = BD$

Since $\theta = \theta'$, $2AB\sin\theta = CB + BD$ $d = AB$

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

$2d\sin\theta = n\lambda$ Bragg's Law

Diffraction Theory

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

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

Diffraction

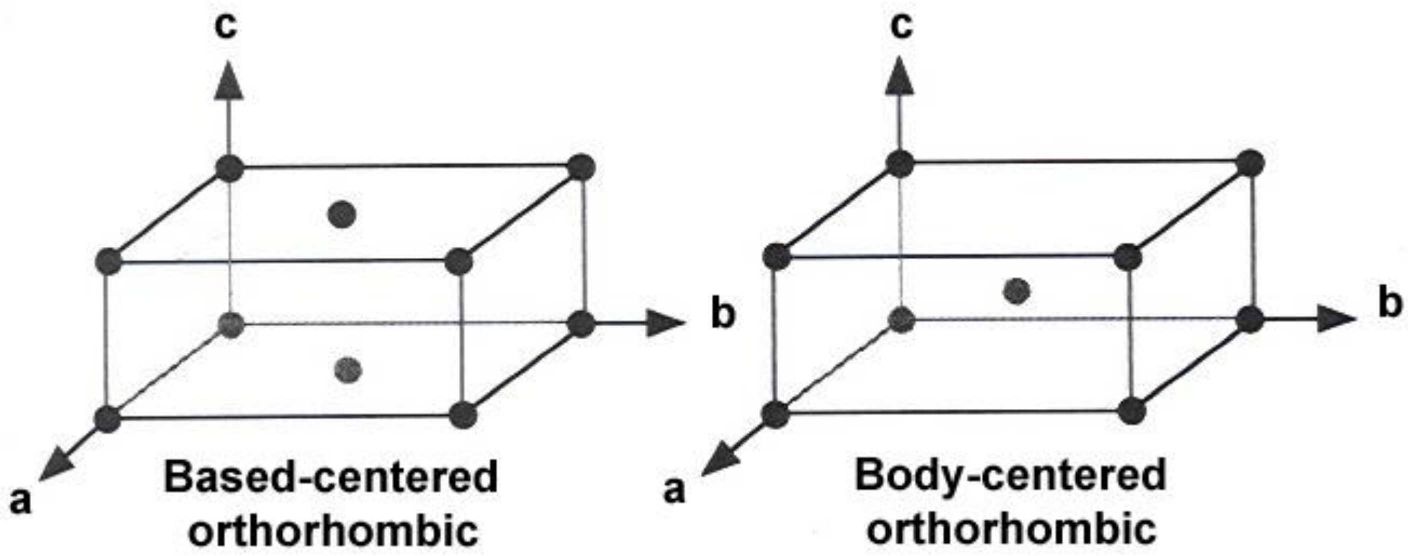
Structure, Scattering, and Intensity

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

Diffraction Theory

Example

Structure, Scattering, and Intensity



Based-centered orthorhombic

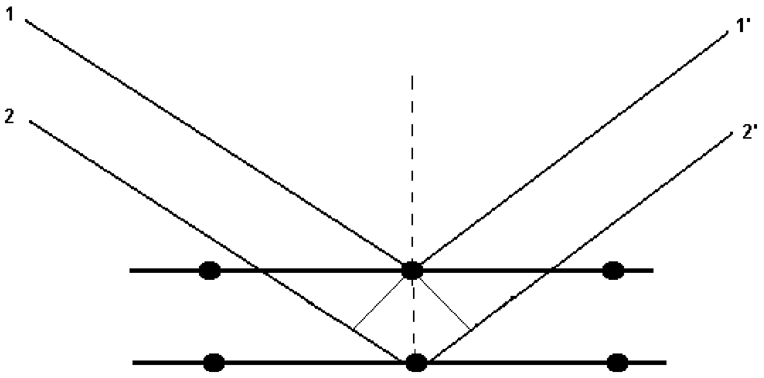
Body-centered orthorhombic

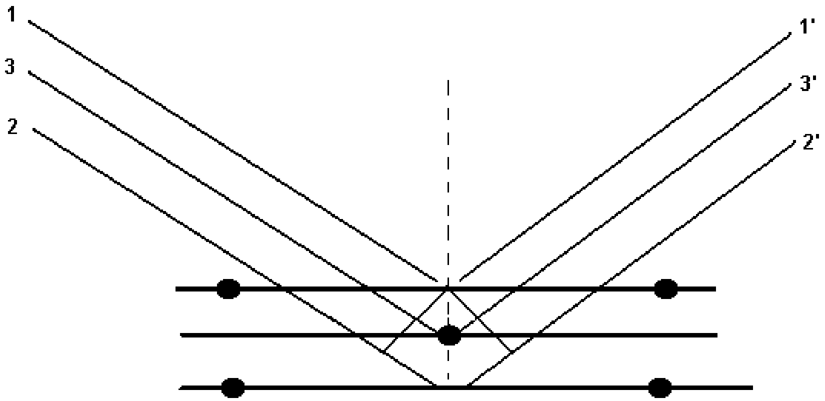
If we diffract from the (001) plane of each structure, then,

Diffraction Theory

Example

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

Diffraction

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

Diffraction

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 <u>structure factor</u>.

(we will not cover how to calculate F to get the selection rules)

Diffraction Theory

Diffraction

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

Diffraction

Structure, Scattering, and Intensity, con’t

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

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

Diffraction

Structure, Scattering, and Intensity, con’t

Lorentz-Polarization Factor

Polarization factor

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

At 0^0 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

Diffraction

Structure, Scattering, and Intensity, con't

Lorentz-Polarization Factor

<u>Lorentz factor</u>

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

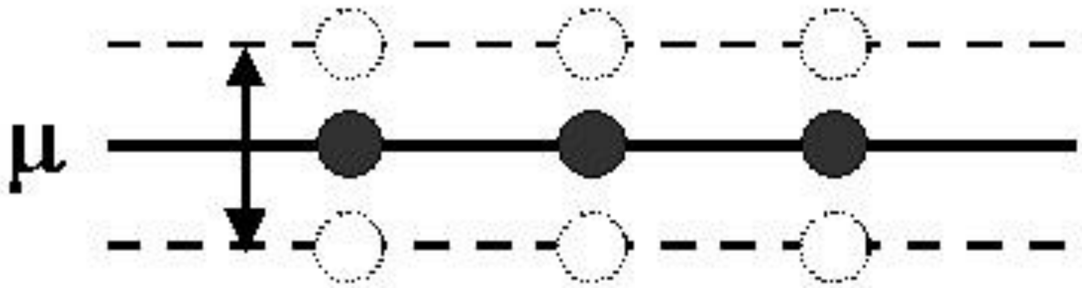
Diffraction

Structure, Scattering, and Intensity, con’t

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.

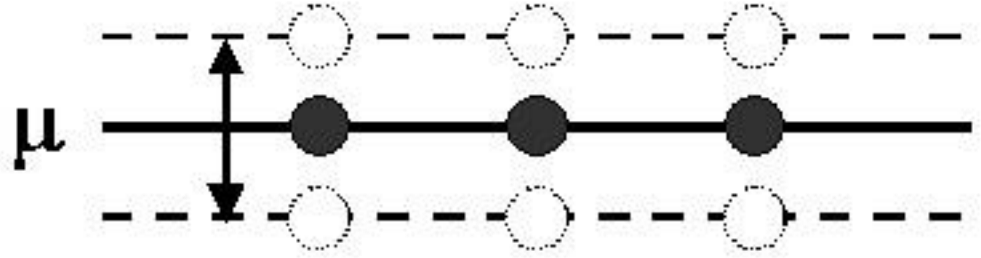


Diffraction Theory

Diffraction

Structure, Scattering, and Intensity, con't

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

Structure, Scattering, and Intensity, con’t

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.

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

Diffraction

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

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

Diffraction Theory

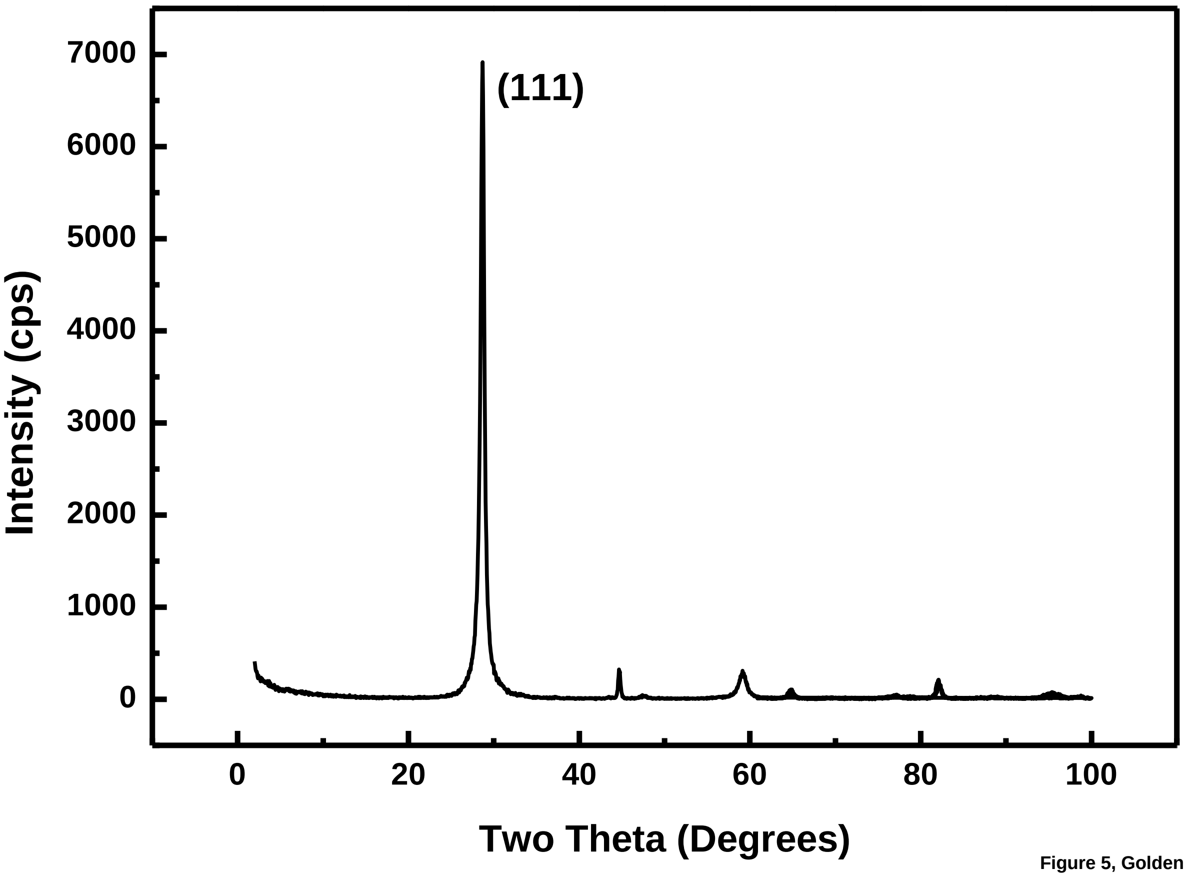


Figure 5, Golden & Wang
"Anodic Oxidation of..."

Diffraction Theory

Diffraction

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

Crystallography

Crystal Structures

Online tools

https://crystals.symotter.org/viztools/

https://www.jove.com/v/10462/single-crystal-and-powder-x-ray-diffraction

https://www.jove.com/v/10446/x-ray-diffraction-for-determining-atomic-and-molecular-structure

https://myscope.training/XRD_XRD_basics

Assignments

Homework Assignment 2: Due Today

Homework 3: Due Tuesday, 12-3-24 (see next slide)

Read this website page and listen to the videos:
https://www.sciencemuseum.org.uk/objects-and-stories/chemistry/x-ray-crystallography-revealing-our-molecular-world

Read Chapters 1&2&3 from the following textbooks:

- **X-ray Diffraction, A Practical Approach by Norton**

- **Elements of X-ray Diffraction by Cullity and Stock**

- **Introduction to X-ray powder Diffractometry by Jenkins and Synder**

Crystallography

Homework #3:

A metal oxide has the fluorite structure. It therefore has the fcc Bravais lattice with four formula units per unit cell. The density is 7.214 g/cm^3. The distance between (521) plane is 0.09879 nm.

a. What is the lattice parameter?

b. What is the spacing between the 111 planes?

c. What is the formula weight of the material?

d. What is the angle between the [741] and [123] directions?

e. What is the material?