

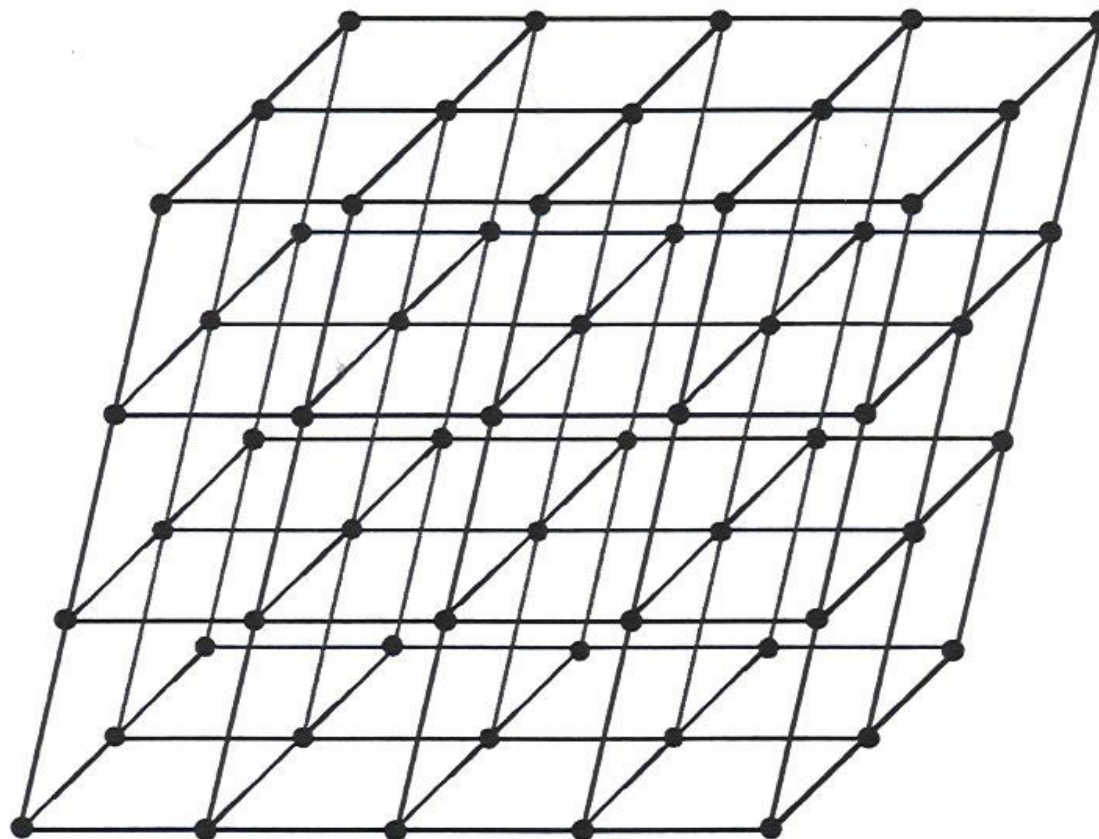
chem 5390

Advanced X-ray Analysis



LECTURE 6

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Department of Chemistry



A Point Lattice.

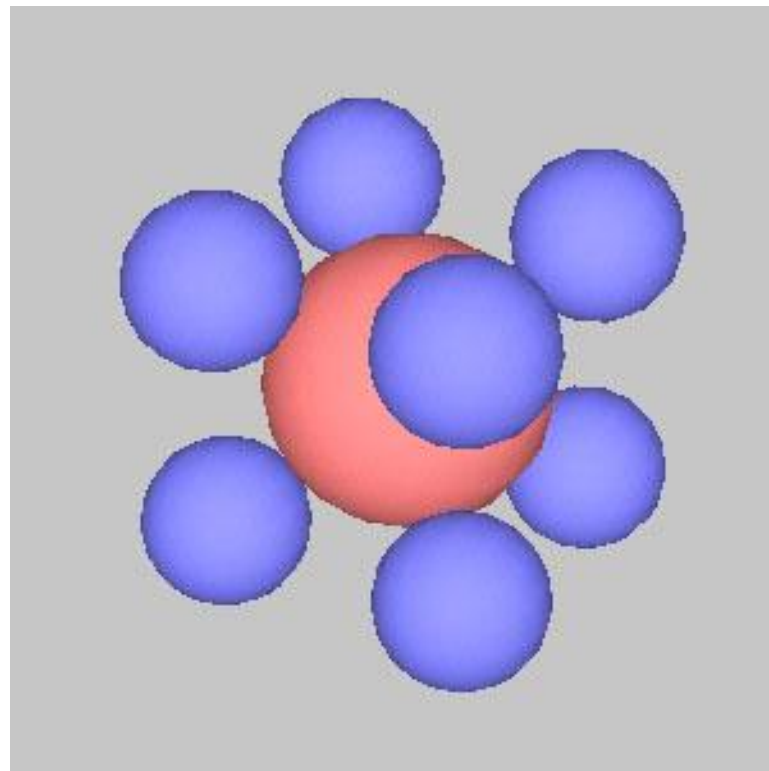
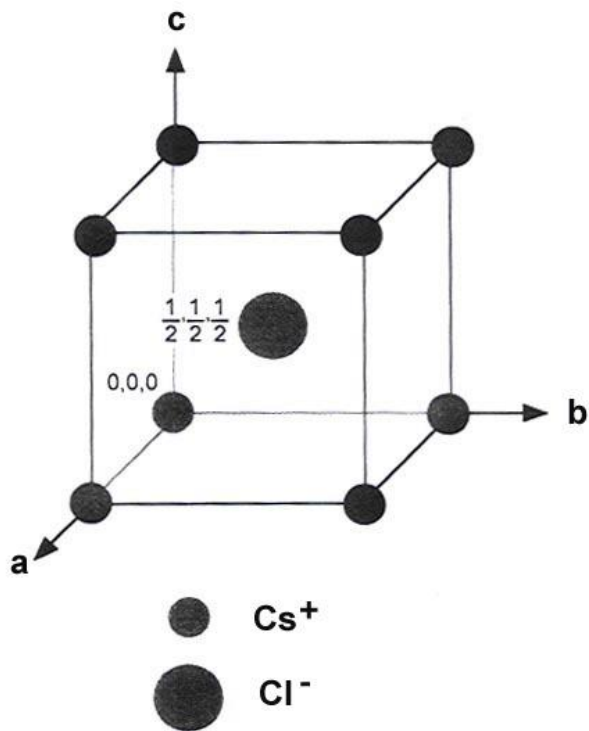
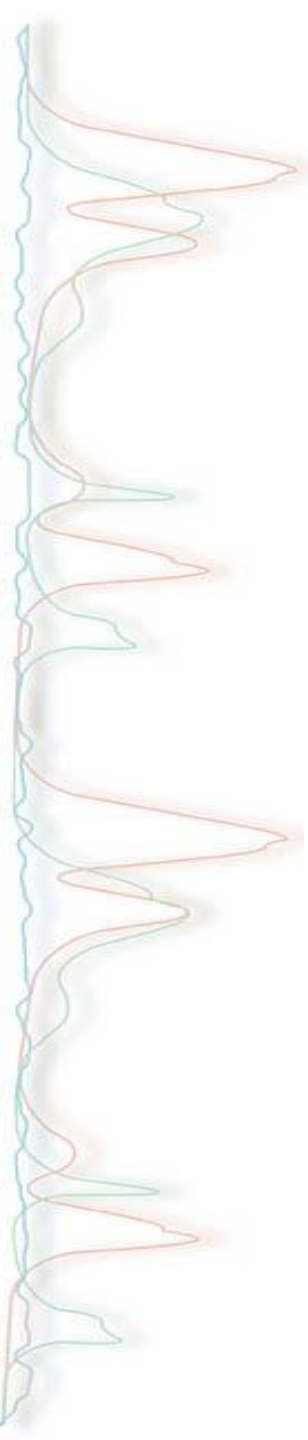
Crystallography

C. Crystal Structures

3. Two Different Atoms per Lattice Point

a. Cesium Chloride Structure

Primitive cubic (P) lattice + 2 atoms \rightarrow CsCl structure



Cesium chloride (CsCl) structure.

Crystallography

C. Crystal Structures

3. Two Different Atoms per Lattice Point

a. Cesium Chloride Structure

Cs is at $0, 0, 0$ and a Cl at $1/2, 1/2, 1/2$ to form the basis.

Why is this primitive cubic and not bcc? If we translate Cs at $0, 0, 0$ to $1/2, 1/2, 1/2$, this position is not an equivalent.

The CsCl is two interpenetrating cubes, one with Cs atoms and one with Cl atoms, all displaced $1/2, 1/2, 1/2$ with respect to each other.

Crystallography

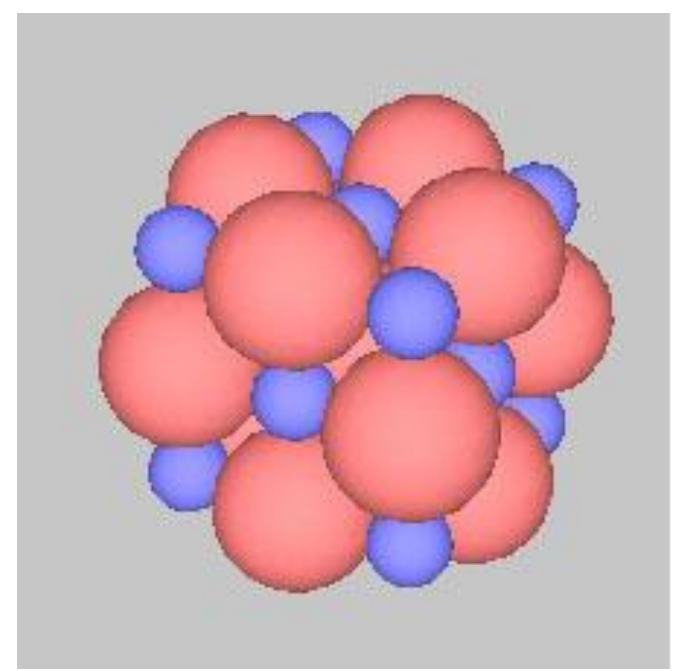
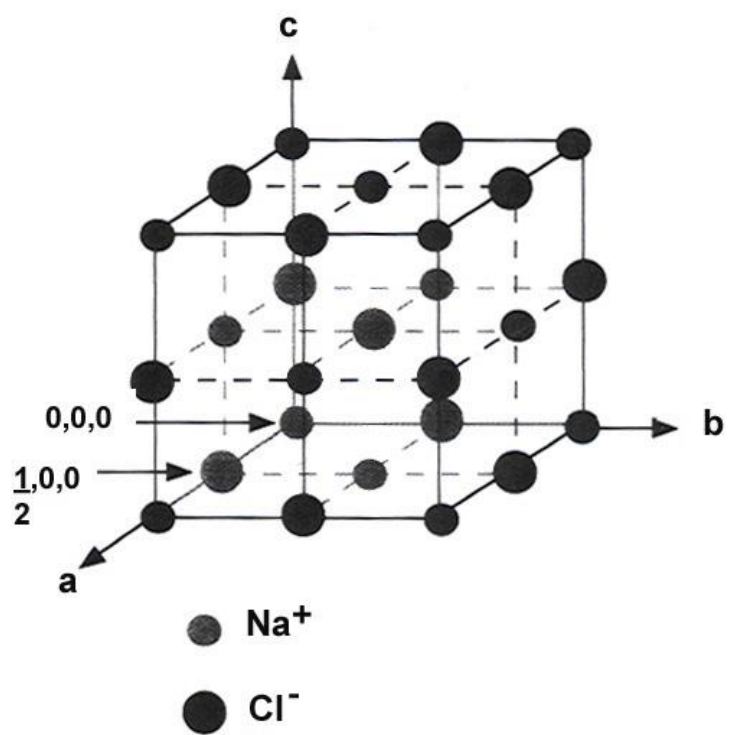
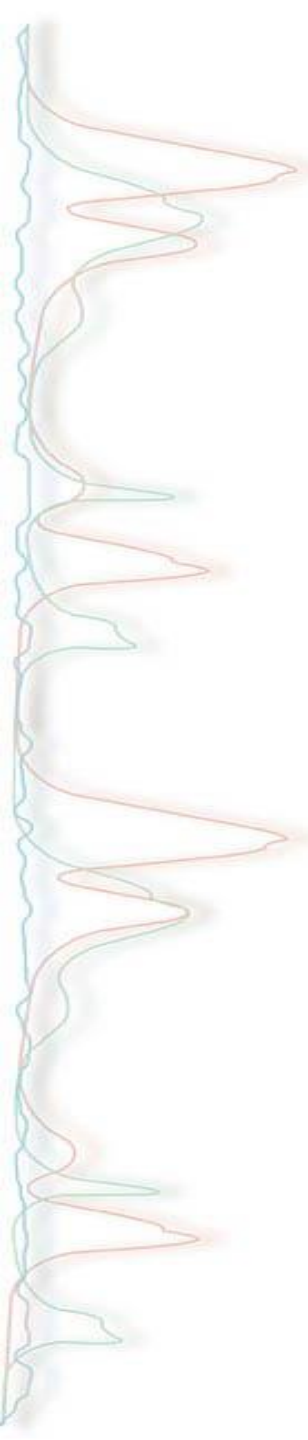
C. Crystal Structures

3. Two Different Atoms per Lattice Point

b. Sodium Chloride Structure or Rocksalt Structure

Face-centered cubic (F) lattice + 2 atoms --->
Rocksalt structure

There are a basis of two atoms at $0, 0, 0$, for Na and $1/2, 0, 0$ for Cl.



Sodium Chloride (NaCl) structure.

Crystallography

C. Crystal Structures

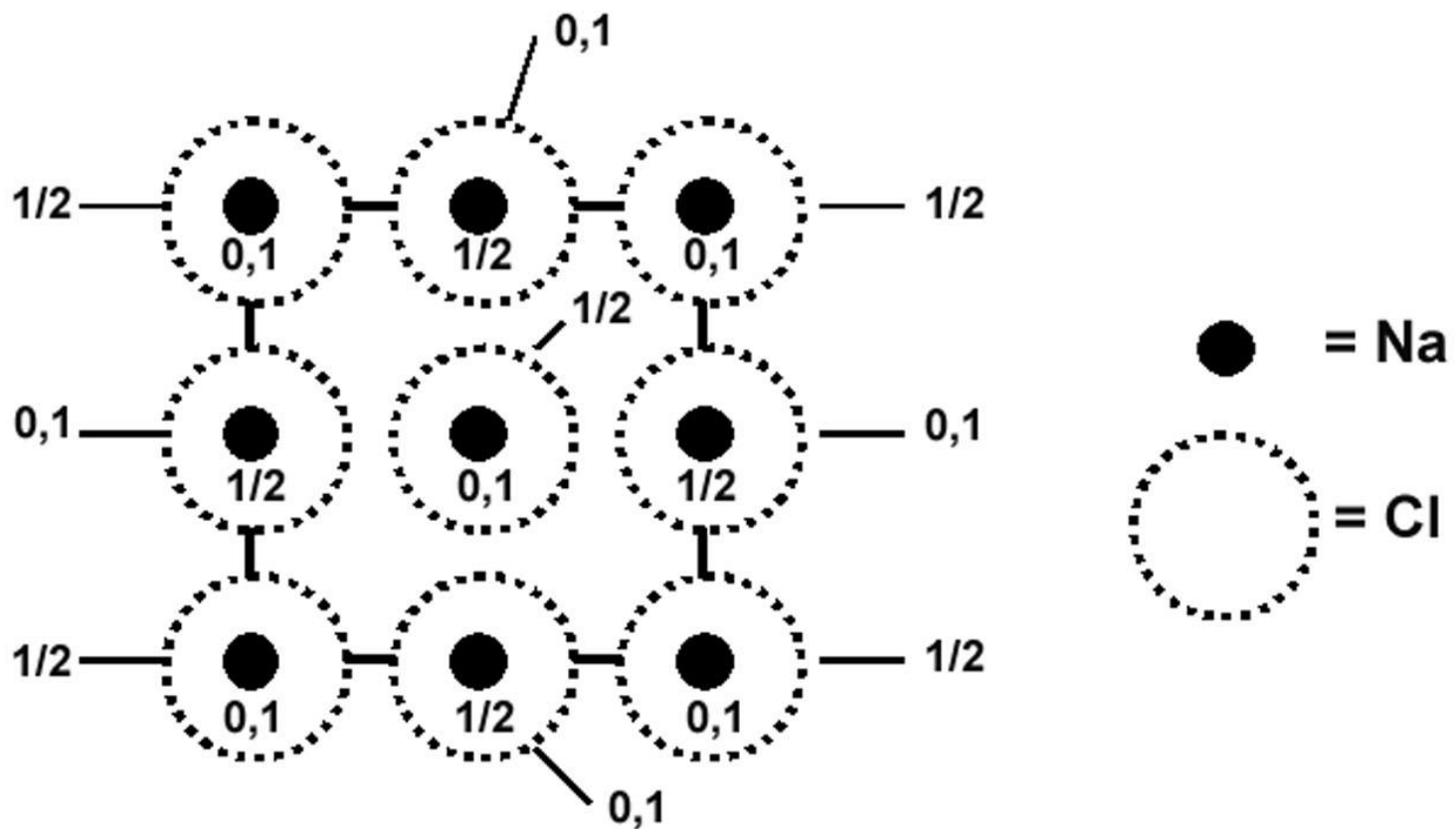
3. Two Different Atoms per Lattice Point

b. Sodium Chloride Structure or Rocksalt Structure

Na at 0, 0, 0	1/2, 1/2, 0	1/2, 0, 1/2	0, 1/2, 1/2
Cl at 1/2, 0, 0	0, 1/2, 0	0, 0, 1/2	1/2, 1/2, 1/2

Na atoms are in a face centered cubic arrangement, translate 1/2 and Cl is also in face centered cubic arrangement.

What would the planar representation look like?



Planar representation of sodium chloride structure.

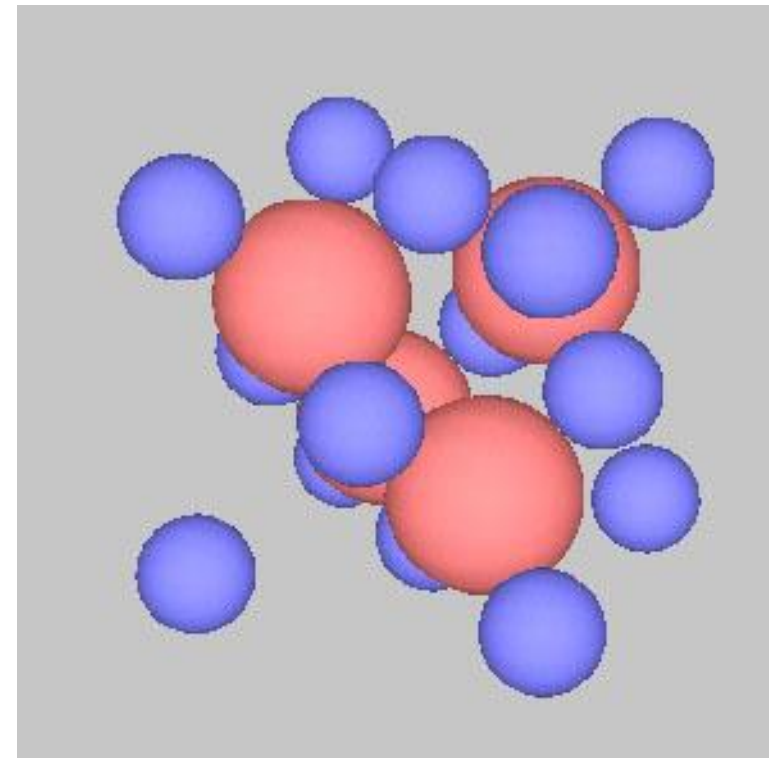
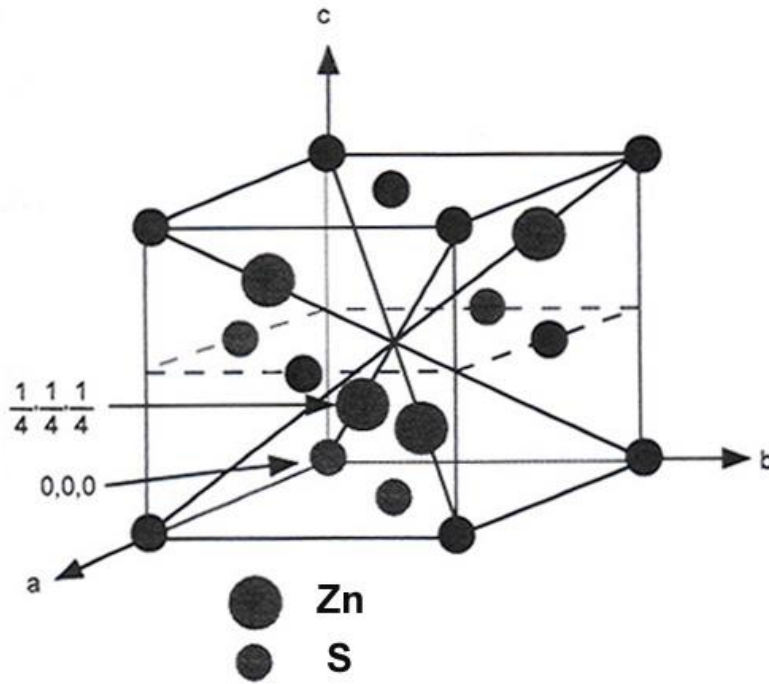
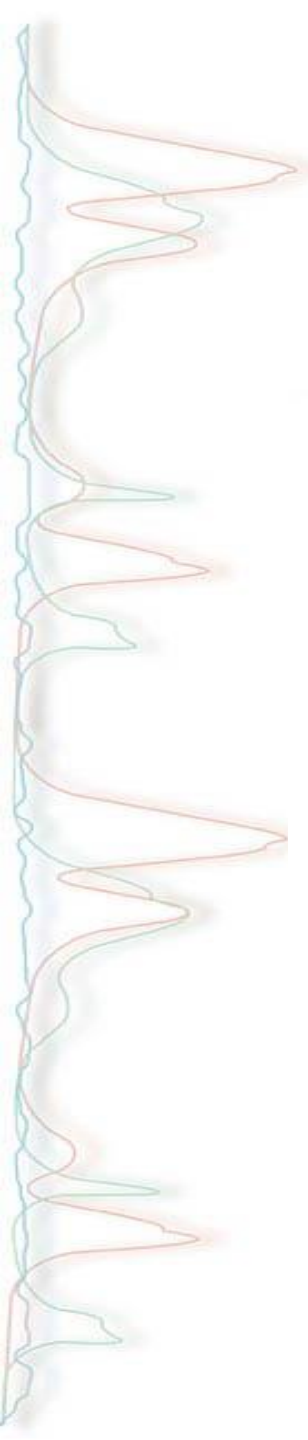
Crystallography

C. Crystal Structures

3. Two Different Atoms per Lattice Point

c. Zinc Blende Structure (Sphalerite) (ZnS)

Face-centered cubic (F) lattice + 2 atoms \rightarrow Zinc blende structure



Zinc Blende (ZnS) structure.

Crystallography

C. Crystal Structures

3. Two Different Atoms per Lattice Point

c. Zinc Blende Structure (Sphalerite) (ZnS)

S atoms at 0, 0, 0	1/2, 1/2, 0	1/2, 0, 1/2	0, 1/2, 1/2
Zn atoms at 1/4, 1/4, 1/4	3/4, 3/4, 1/4	3/4, 1/4, 3/4	1/4, 3/4, 3/4

For S start at 0, 0, 0 and do a fcc translation

For Zn start at 1/4, 1/4, 1/4 and do a fcc translation

Crystallography

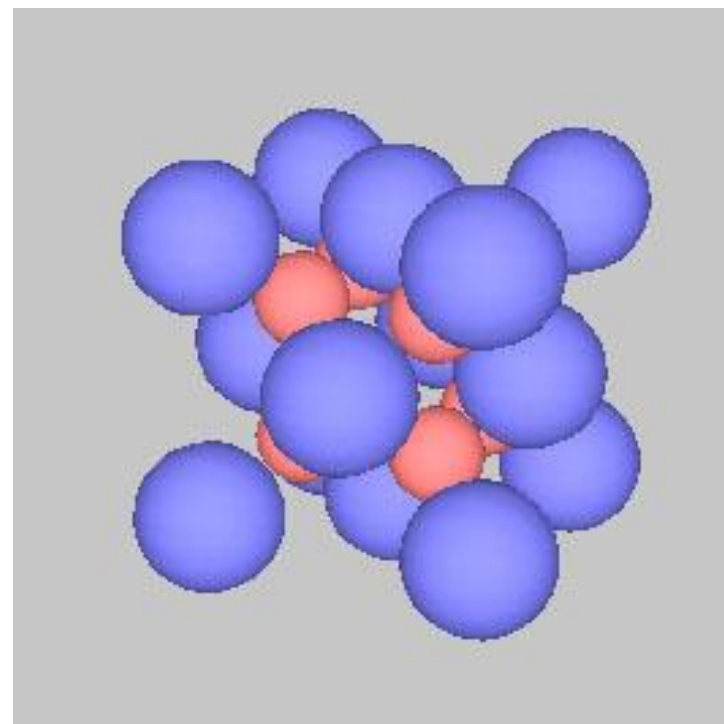
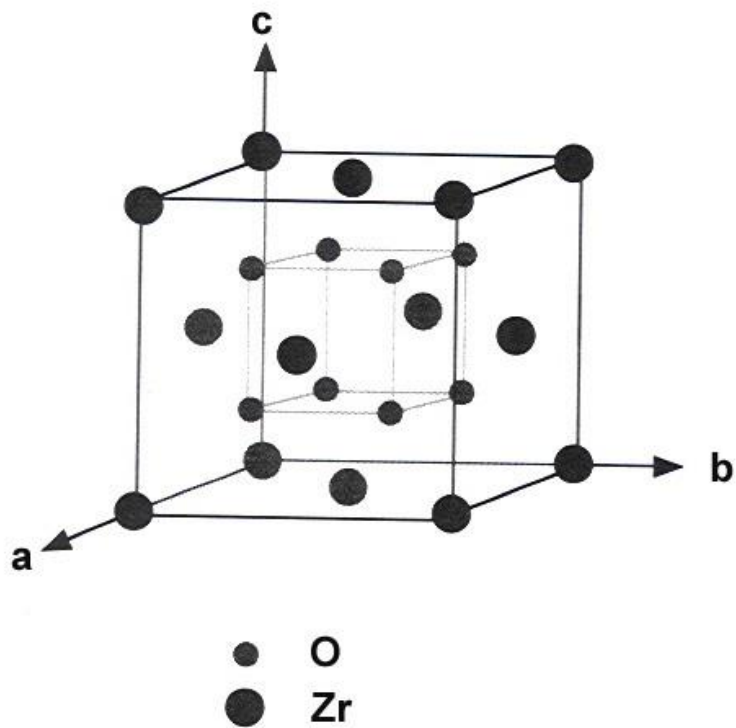
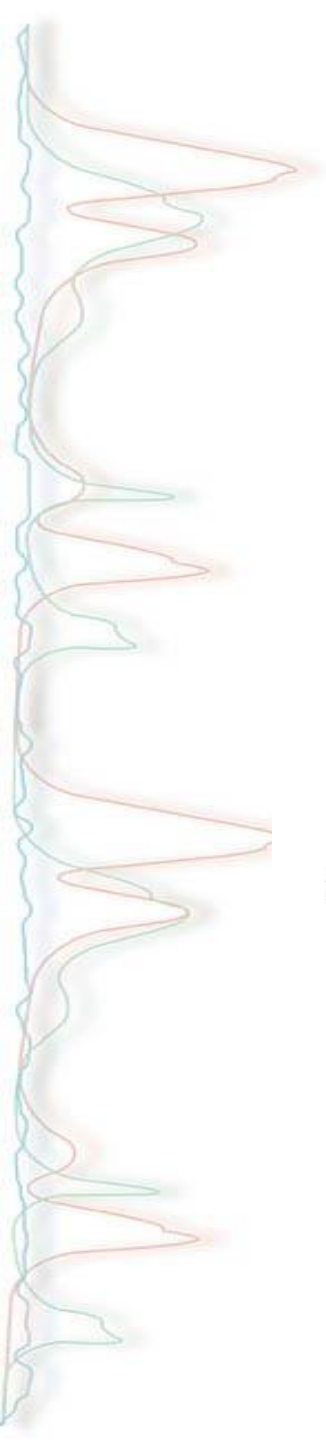
C. Crystal Structures

4. More complex structures

Can have more than two atoms associated with each lattice point.

Common example:

Face centered cubic lattice + 3 atoms ---> Fluorite structure



Fluorite Structure.

Crystallography

C. Crystal Structures

4. More complex structures

Name of Structure	Corresponding Materials	Other Materials
Rocksalt	NaCl	KCl, LiF, MgO, TiN
Zinc blende	ZnS	BeO, GaAs, β -SiC
Rutile	TiO ₂	GeO ₂ , SnO ₂
Corundum	Al ₂ O ₃	Fe ₂ O ₃ , Cr ₂ O ₃
Wurtzite	ZnS	ZnO, AlN, α -SiC
Perovskite	CaTiO ₃	BaTiO ₃ , SrTiO ₃
Spinel	MgAl ₂ O ₄	FeAl ₂ O ₄ , ZnAl ₂ O ₄

Crystallography

C. Crystal Structures

4. 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

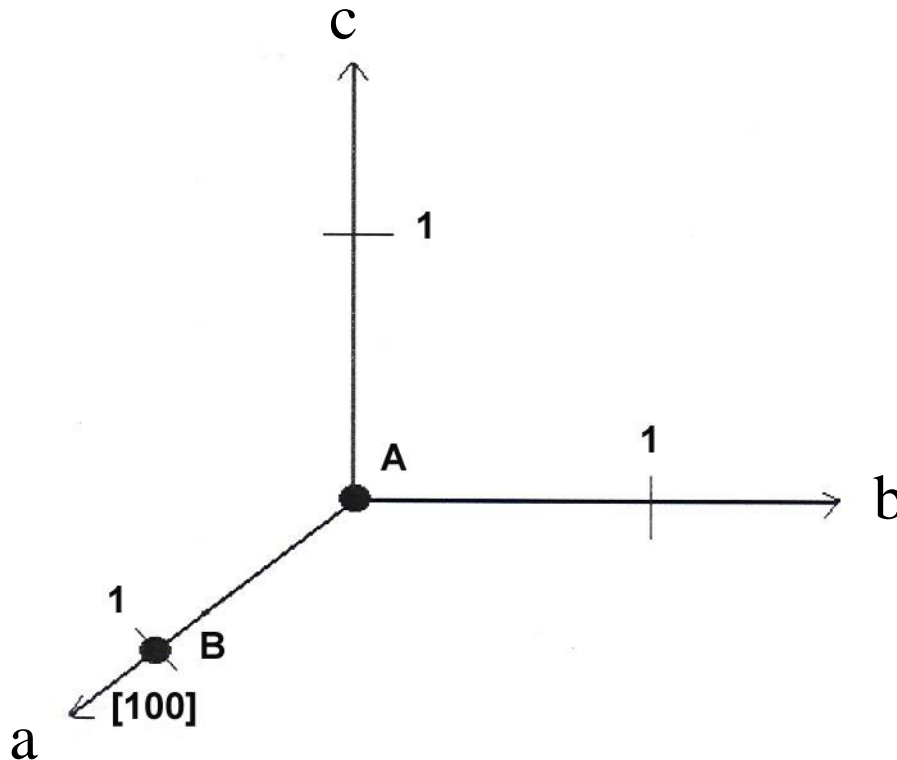
Crystallography

Geometry and the structure of crystals

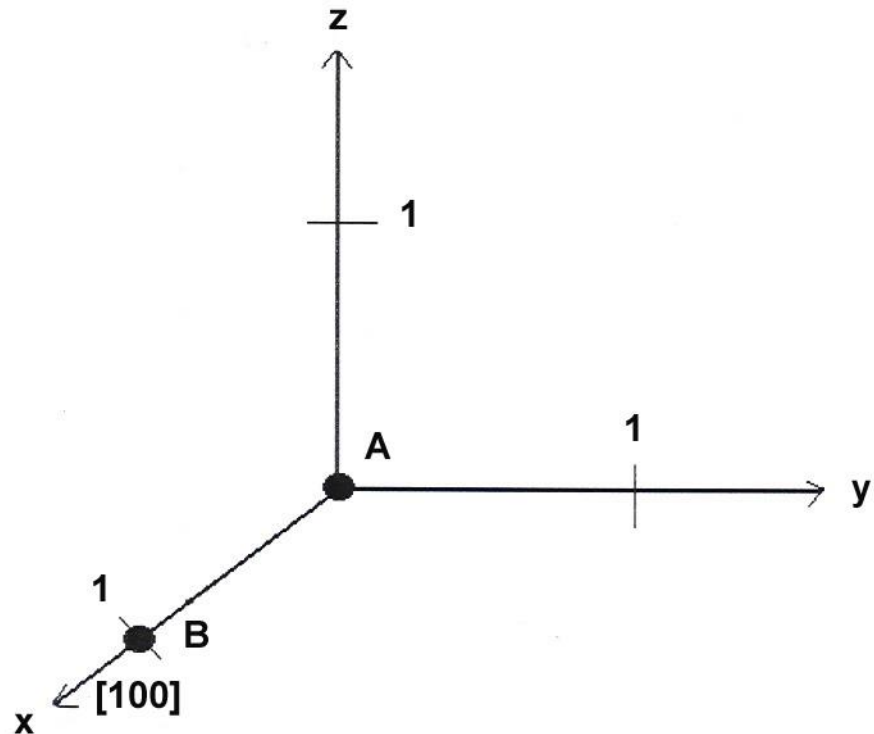
D. Vectors and Planes

Direction or vectors are denoted by $[uvw]$

$[\quad]$ - 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 $\langle \quad \rangle$
 $\langle 1\ 0\ 0 \rangle$ - is the family of directions for all the individual directions.

Crystallography

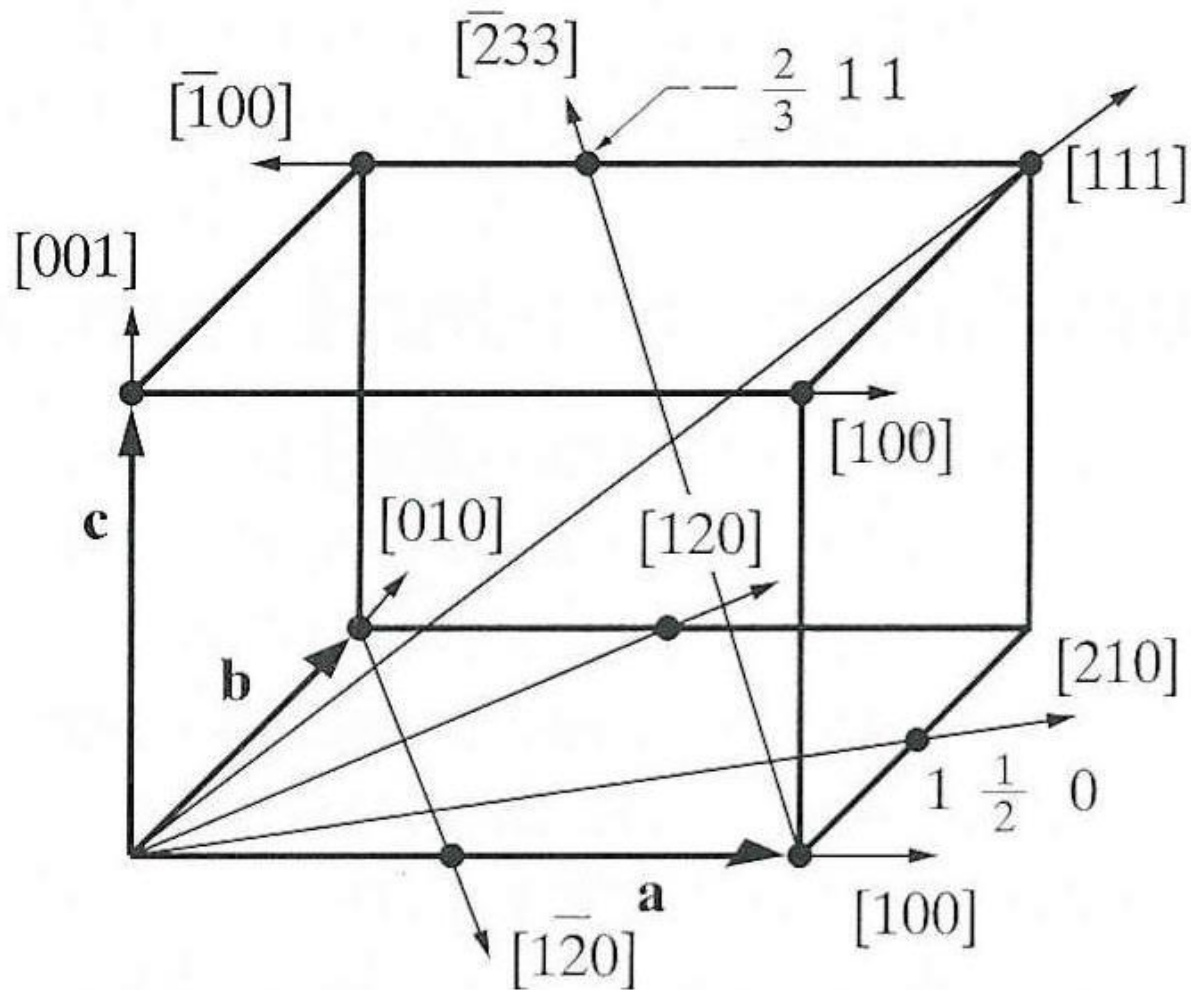
Geometry and the structure of crystals

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]?

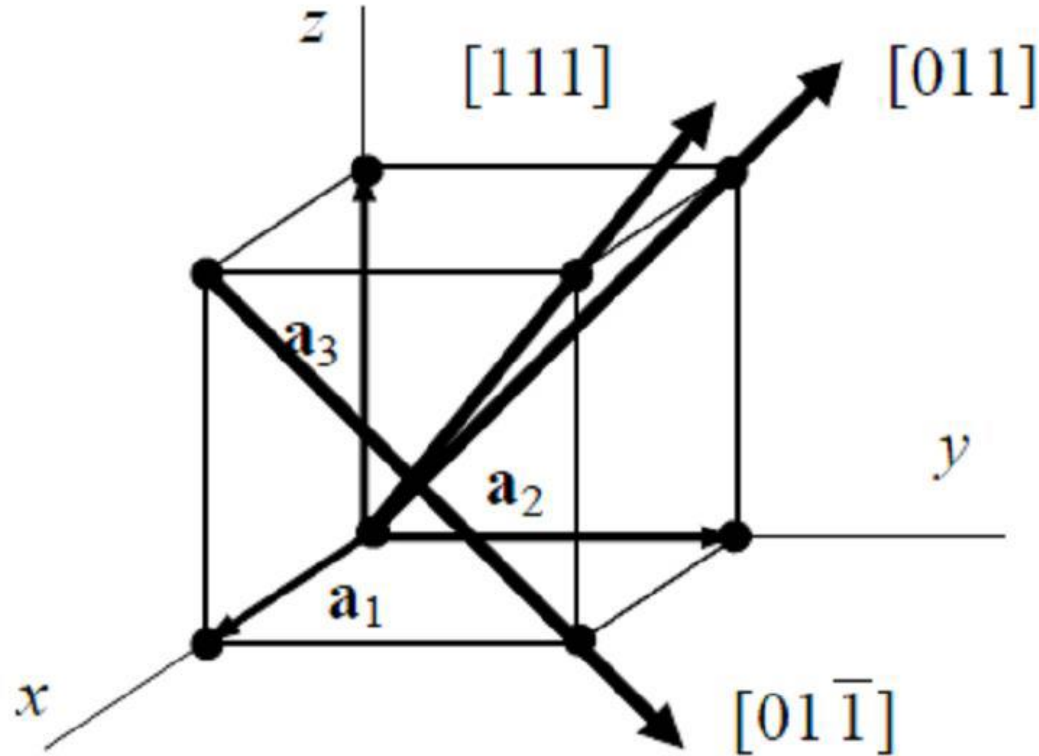
$$\begin{aligned} \theta &= \arccos (1 \times 1 + 1 \times 1 + 0 \times 1) / (1^2 + 1^2 + 0^2)^{1/2} (1^2 + 1^2 + 1^2)^{1/2} \\ &= 35.3^\circ \end{aligned}$$



Indices of Directions

Crystallography

Geometry and the structure of crystals



Crystallography

Geometry and the structure of crystals

D. Vectors and Planes

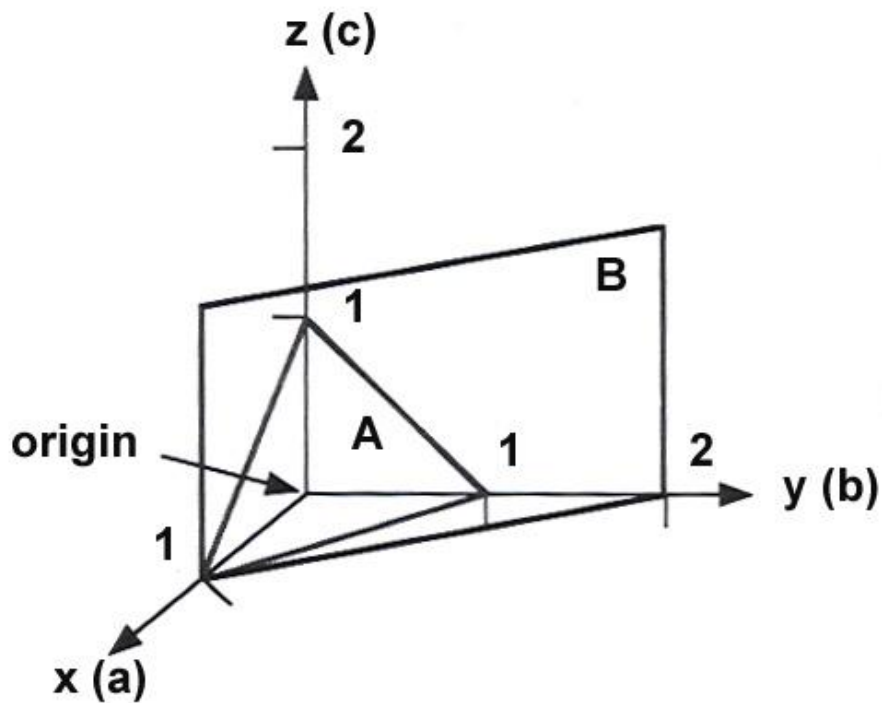
Miller Indices

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:

Step 1. Intercepts

Step 2. Reciprocals

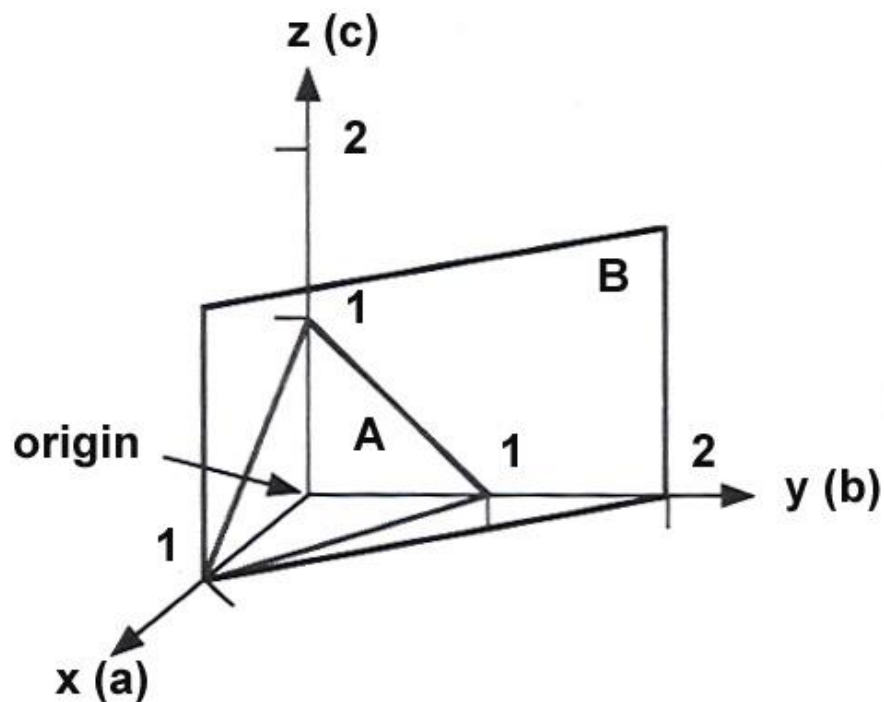
Step 3. Clear fractions

Step 4. Miller Indices

a	b	c
1	1	1
1	1	1
1	1	1

(1 1 1)

Practice:



Plane B:

Step 1. Intercepts

Step 2. Reciprocals

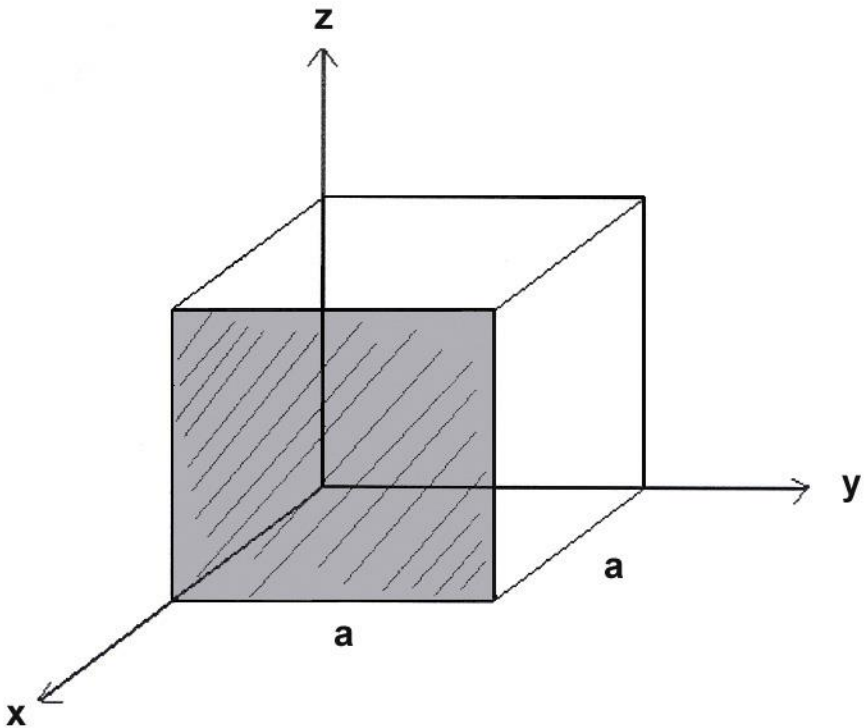
Step 3. Clear fractions

Step 4. Miller Indices

a	b	c
1	2	∞
1	1/2	0
2	1	0

(2 1 0)

Example: Cubic System



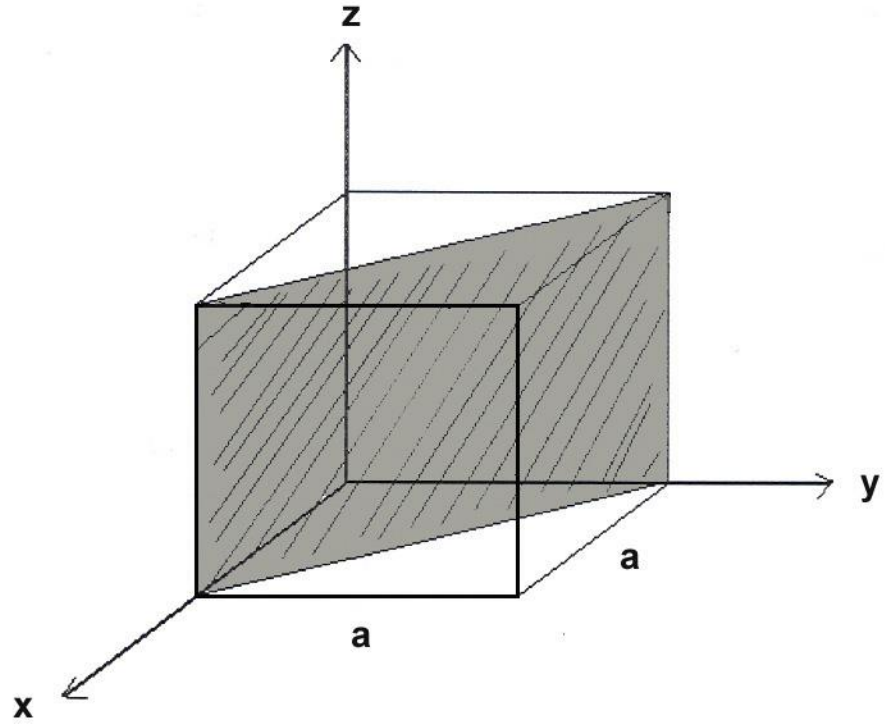
- Step 1. Intercepts
- Step 2. Reciprocals
- Step 3. Clear fractions
- Step 4. Miller Indices

a	b	c
1	∞	∞
1	0	0
1	0	0

(1 0 0)

This is the surface plane of the cubic crystal.

Example: Cubic System

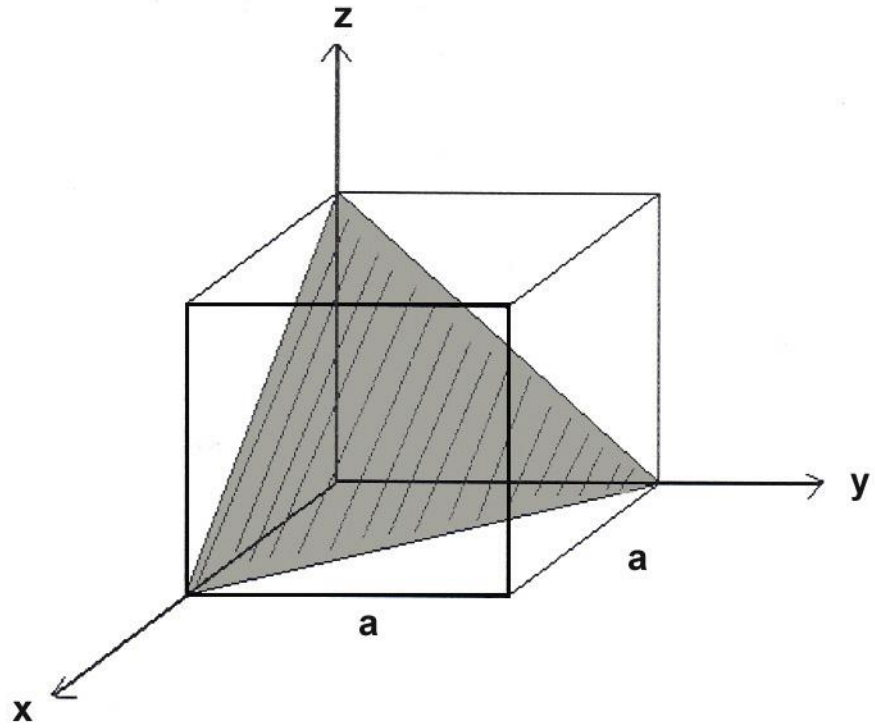


- Step 1. Intercepts
- Step 2. Reciprocals
- Step 3. Clear fractions
- Step 4. Miller Indices

a	b	c
1	1	∞
1	1	0
1	1	0

(1 1 0)

Example: Cubic System

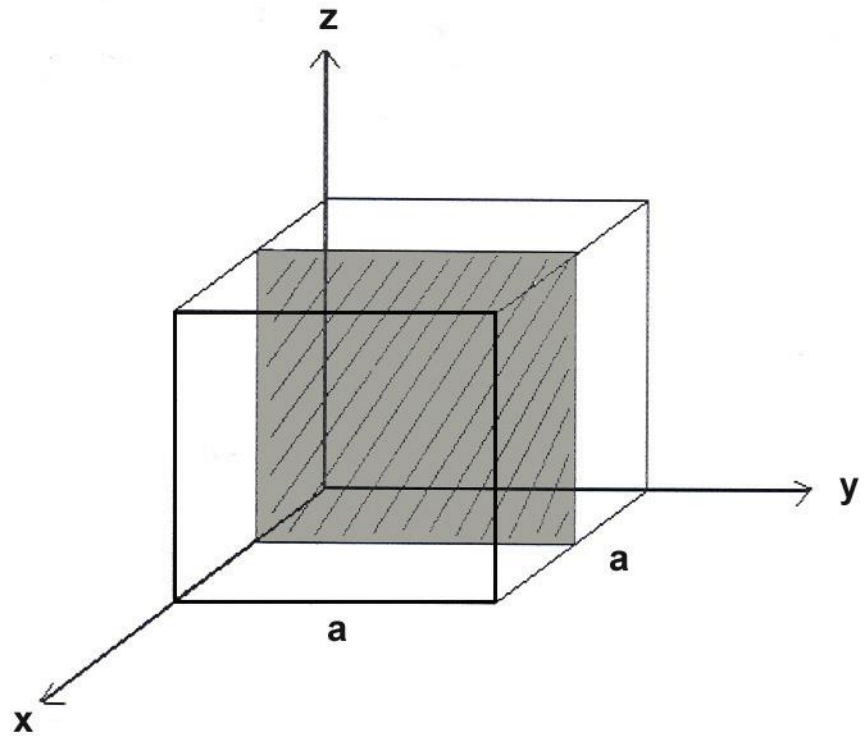


- Step 1. Intercepts
- Step 2. Reciprocals
- Step 3. Clear fractions
- Step 4. Miller Indices

a	b	v
1	1	1
1	1	1
1	1	1

(1 1 1)

Example: Cubic System



Step 1. Intercepts
 Step 2. Reciprocals
 Step 3. Clear fractions

a	b	c
1/2	∞	∞
2	0	0
2	0	0

Step 4. Miller Indices

(2 0 0)

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

Crystallography

Geometry and the structure of crystals

D. 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 family of planes.

$\{ \quad \}$ - denotes a family of planes

(\quad) - 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

D. 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

D. 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

D. Vectors and Planes

Example:

If you crystallize NaCl with H₂O you get a cubic shaped crystal.

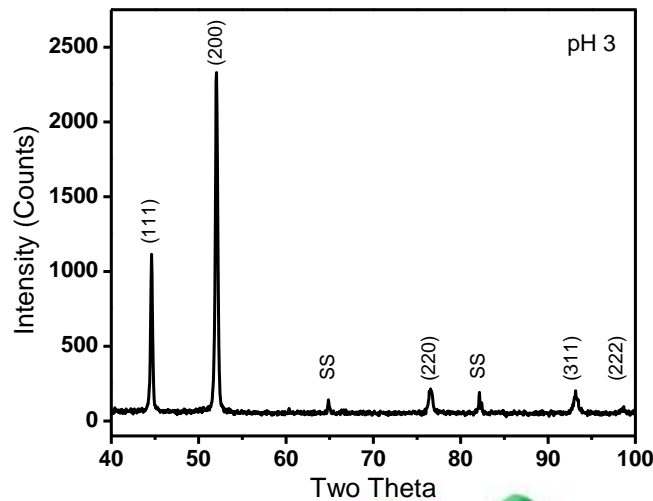
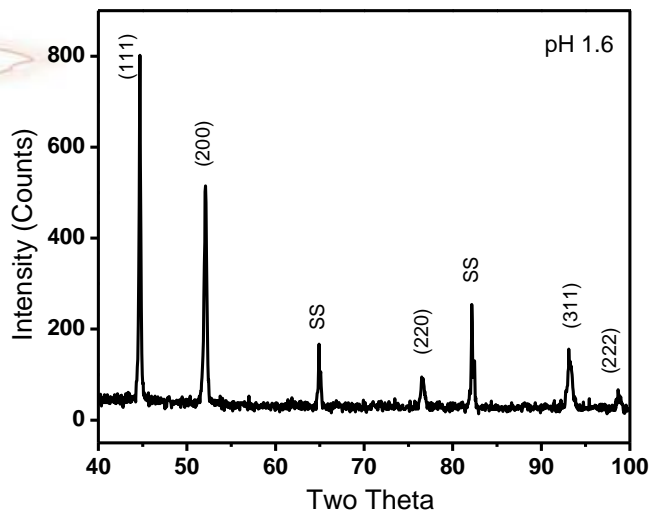
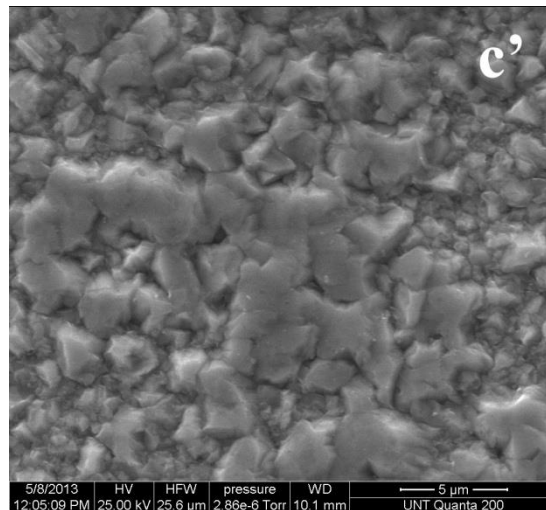
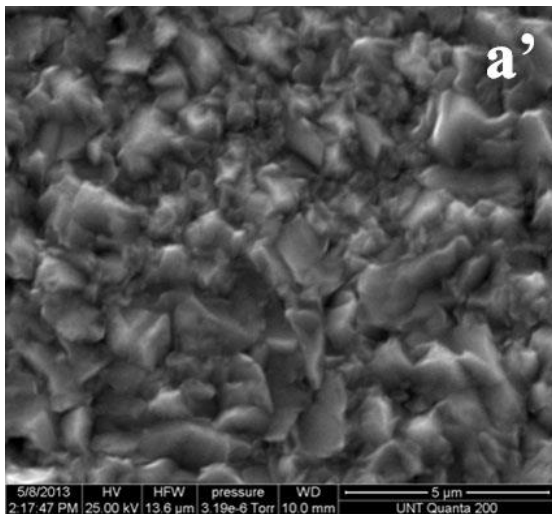
If you crystallize NaCl with urea you get an octahedron shape crystal.

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

D. Vectors and Planes

Crystal Shapes

As seen in the previous example, the overall crystal may have the same or different shape than its 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

D. 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

D. 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

$$\text{fcc (111)} > \text{fcc (100)} > \text{fcc (110)}$$

Crystallography

Geometry and the structure of crystals

D. 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

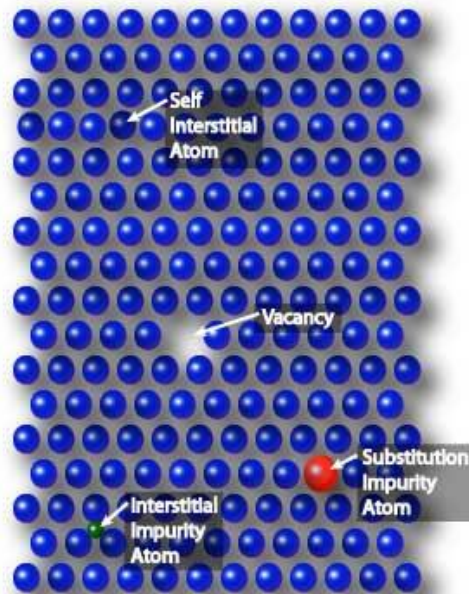
Geometry and the structure of crystals

D. Vectors and Planes

Crystal Defects

Point defects – substitutional or interstitial impurities.

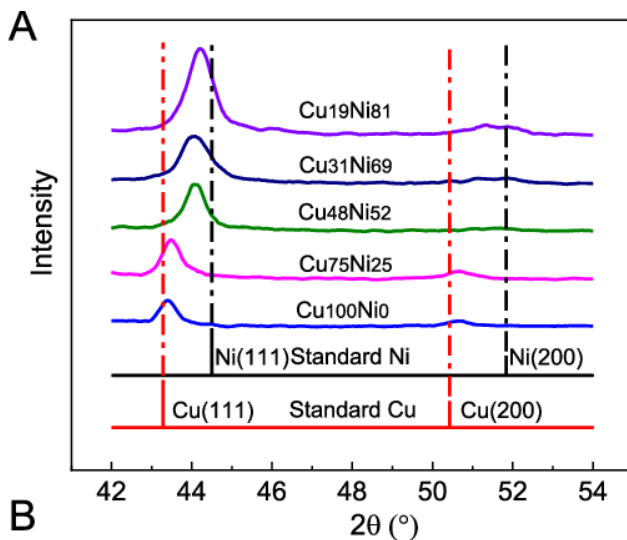
Vegard's law – volume of unit cells in a substitutional solid solution is linearly proportional to the fraction of sites substituted.



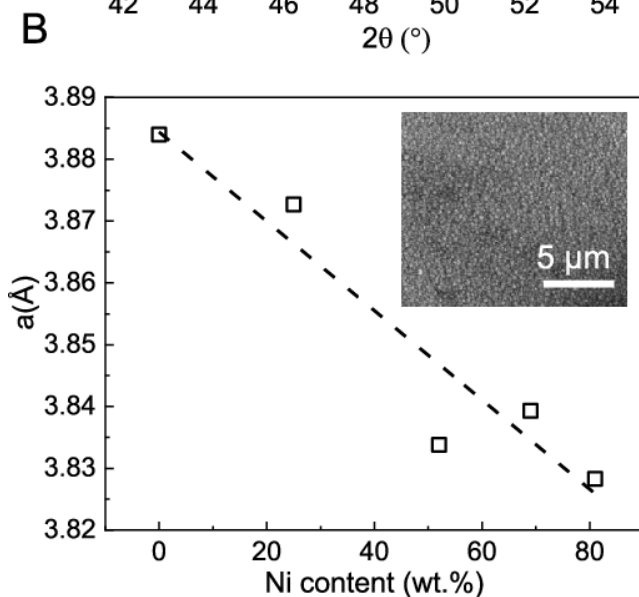
Crystallography

Geometry and the structure of crystals

D. Vectors and Planes



Vegard's law



Crystallography

Geometry and the structure of crystals

Vegard's Law

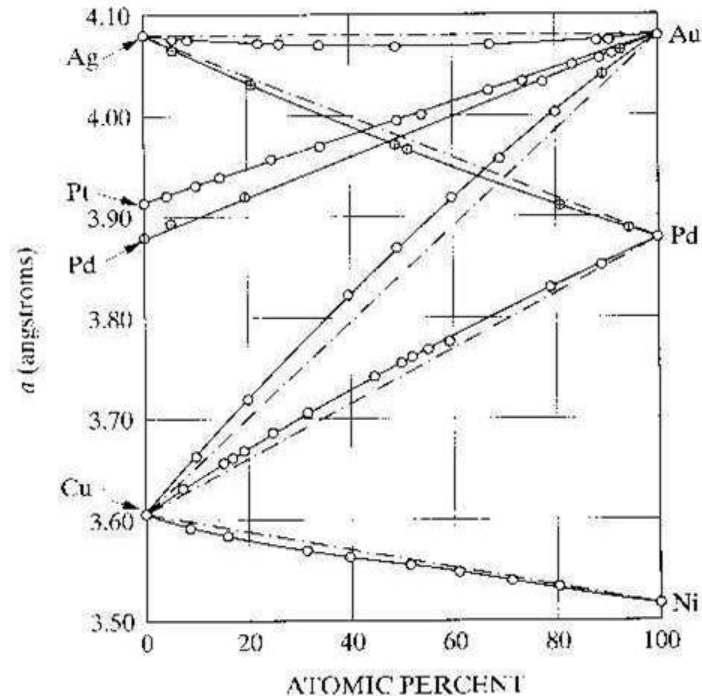
Good for alloys with
continuous solid solutions

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

Ex) Au-Pd

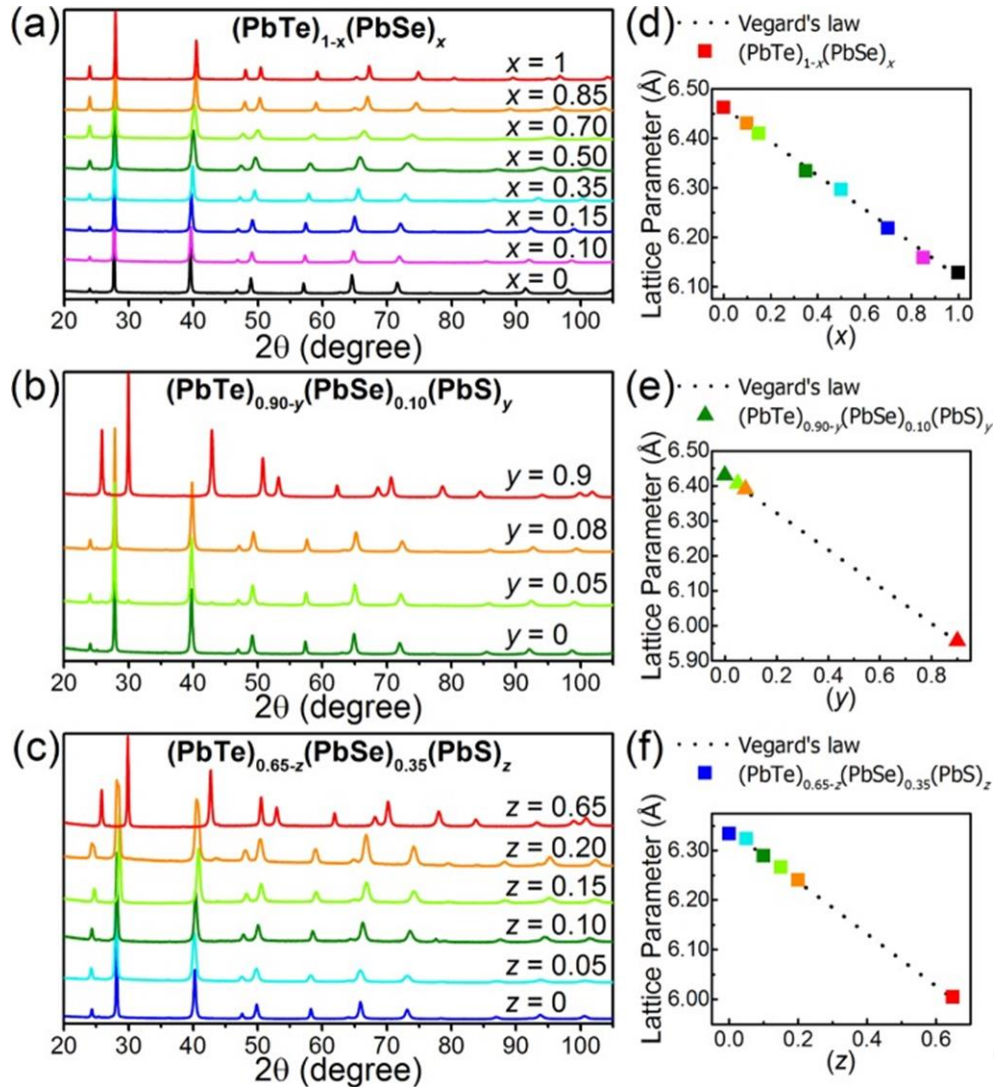
- To create the plot on the right
 - Using the crystal structure of the alloy calculate "a" for each metal
 - Draw a straight line between them as shown on the chart to the left.
- To calculate the composition
 - Calculate "a" from d-spacings
 - "a" will be an atomic weighted fraction of "a" of the two metal

Figure 11-6 Lattice parameters of some continuous solid solutions. Dot-dash lines indicate Vegard's law. Barrett [1.7].



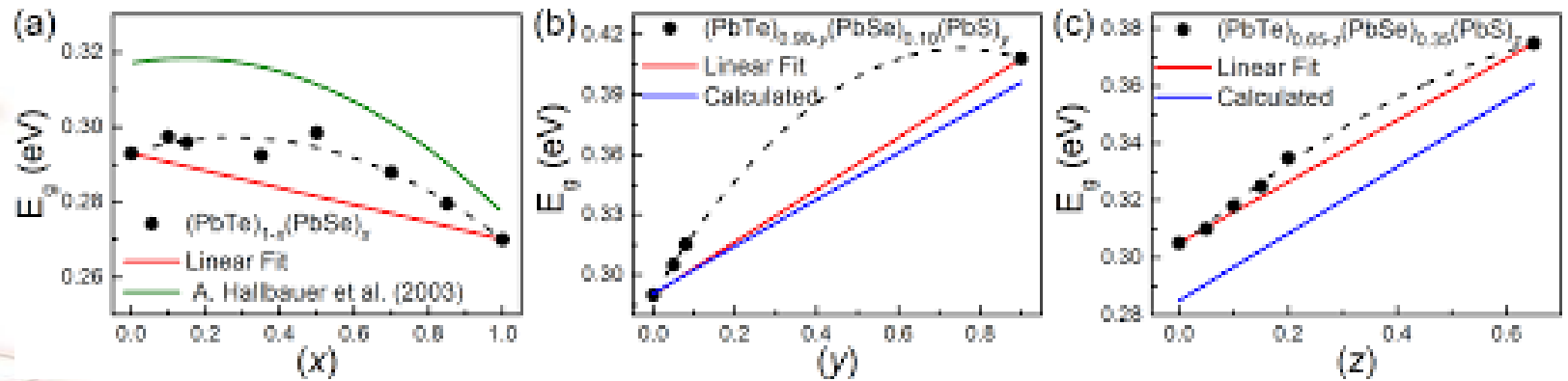
Crystallography

Geometry and the structure of crystals



Crystallography

Geometry and the structure of crystals



Crystallography

Geometry and the structure of crystals

D. 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, machined, shot peening, or ball milling.

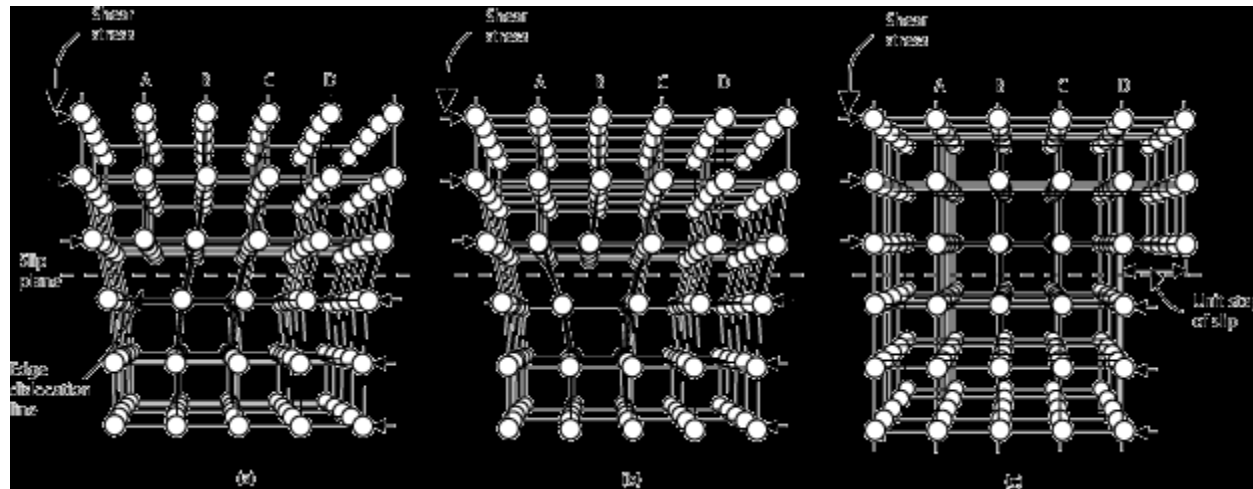
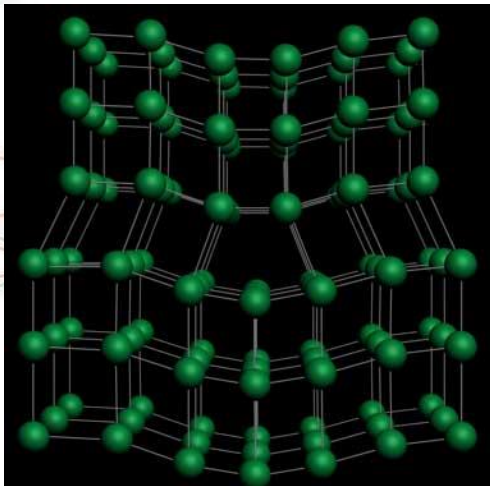
Crystallography

Geometry and the structure of crystals

D. Vectors and Planes

Crystal Defects

Linear defects – edge dislocations.



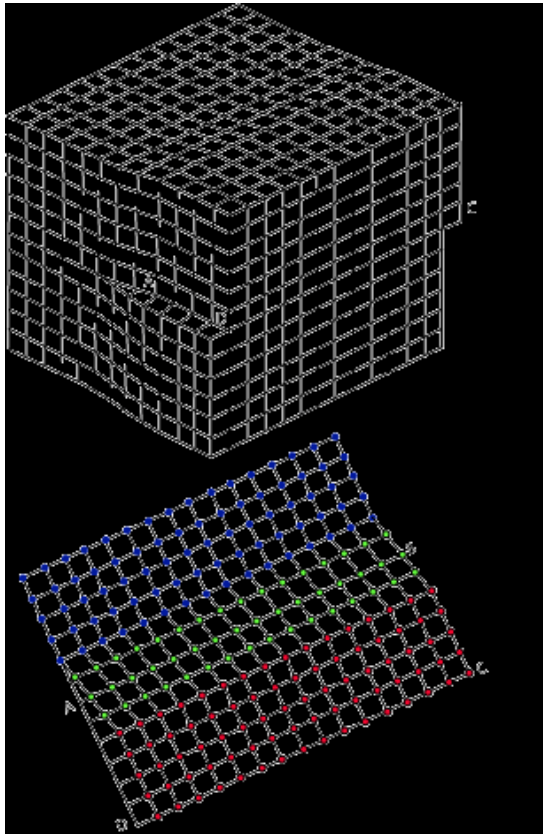
Crystallography

Geometry and the structure of crystals

D. Vectors and Planes

Crystal Defects

Linear defects – screw dislocations.



Crystallography

Geometry and the structure of crystals

D. Vectors and Planes

Crystal Defects

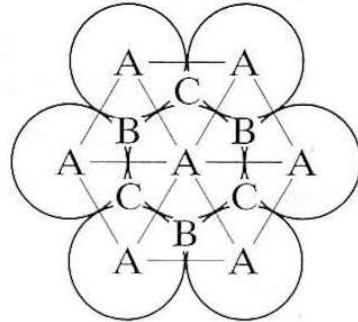
Planar defects – stacking faults and twins

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

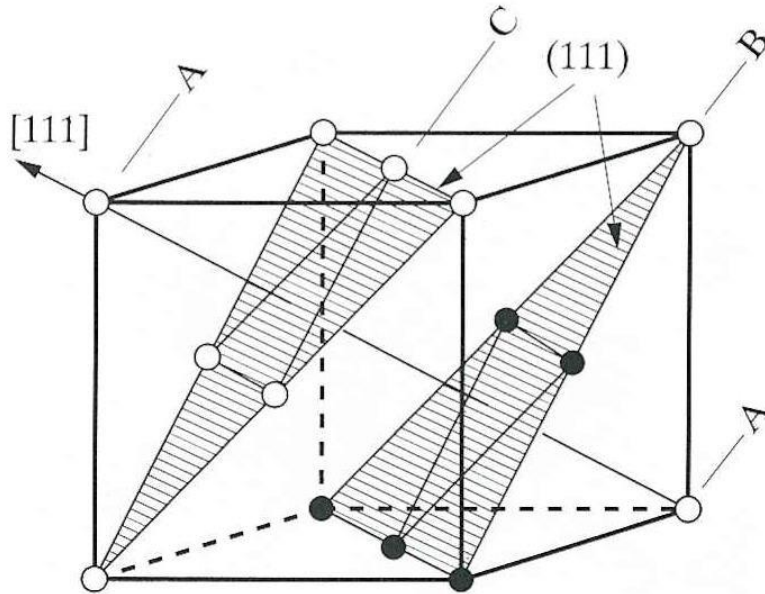
Example: For the fcc structure, the normal stacking sequence is ...ABCABCABC... but can become ...ABCAB*ABC... or ...ABCA*CABCA...

Crystallography

Geometry and the structure of crystals



STACKING OF (111) PLANES



FACE-CENTERED CUBIC

Crystallography

Geometry and the structure of crystals

D. Vectors and Planes

Crystal Defects

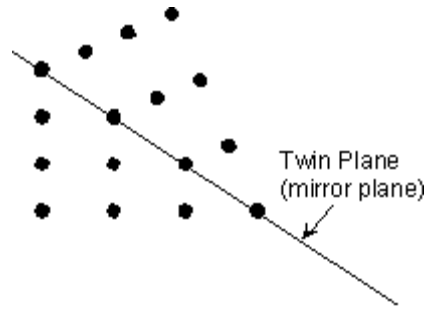
Twinned crystals – may be described by the symmetry operation to bring one in coincidence with the other.

One kind involves a 180° rotation about an axis called the twin axis, the other involves a reflection across a plane called the twin plane.

The plane where the two parts of the twinned crystal unite is called the composition plane.

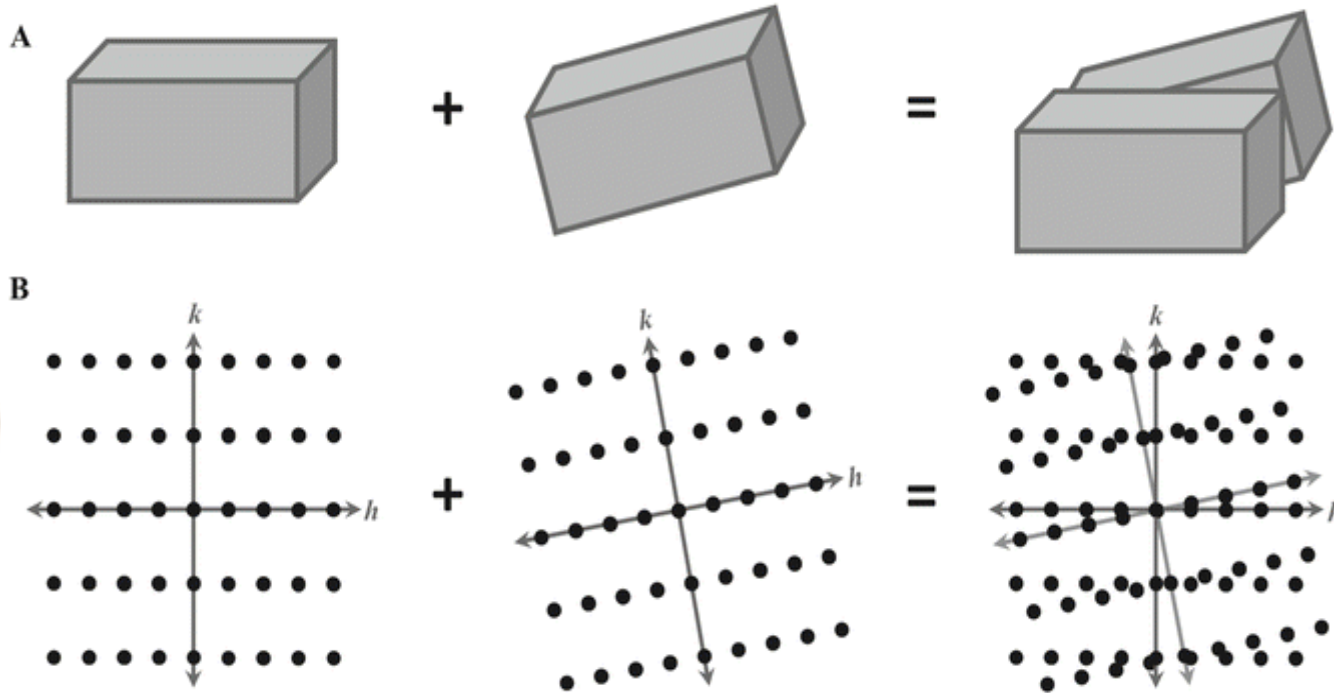
Crystallography

Geometry and the structure of crystals



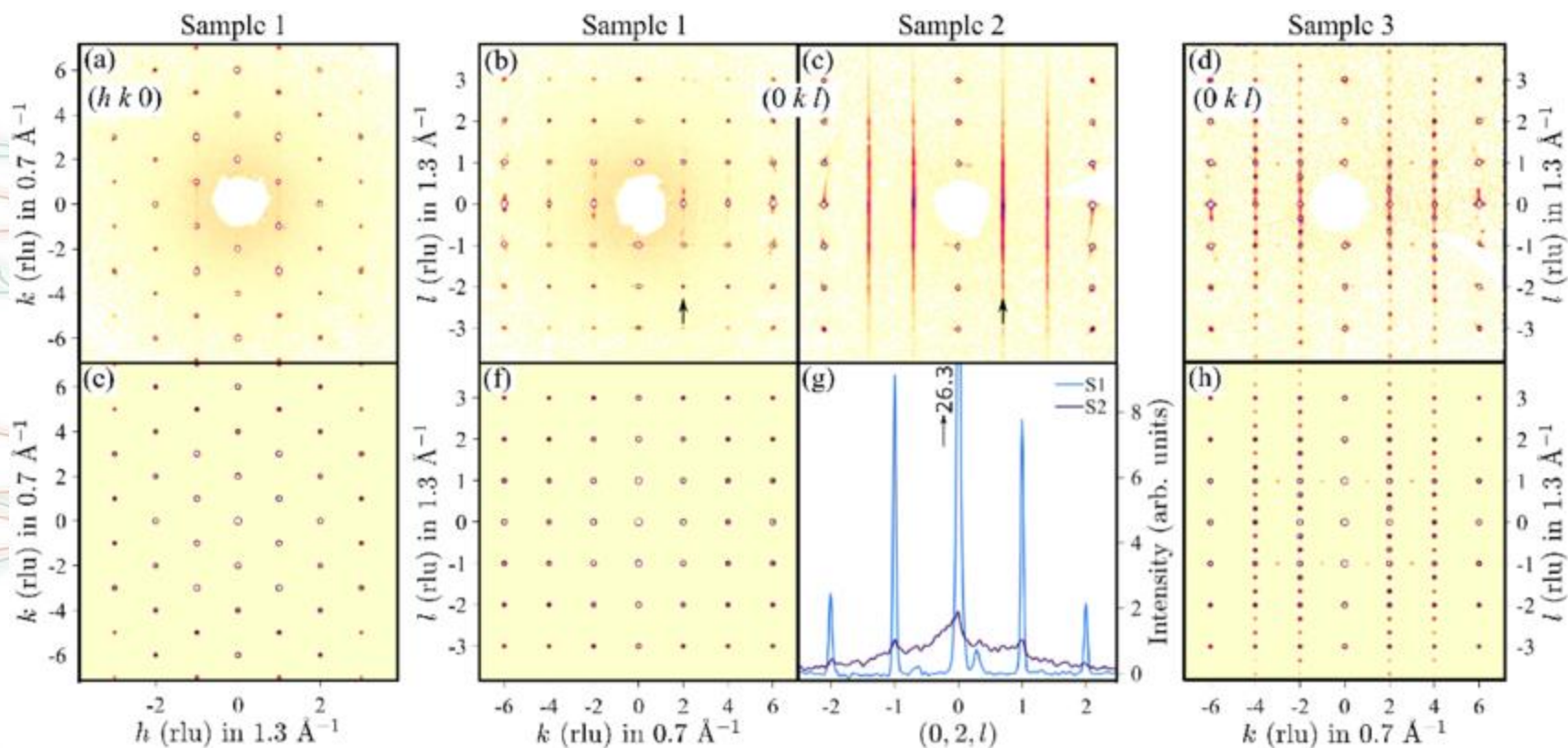
Crystallography

Geometry and the structure of crystals



Crystallography

Geometry and the structure of crystals



Crystallography

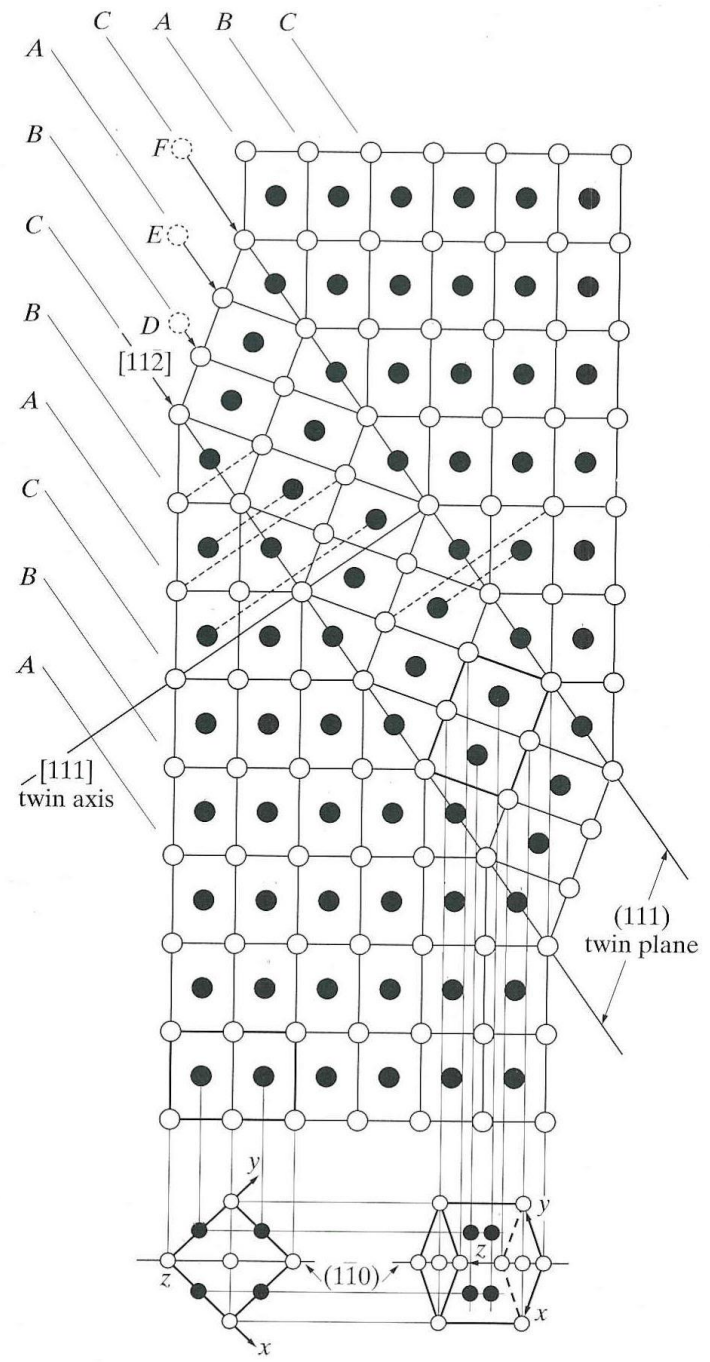
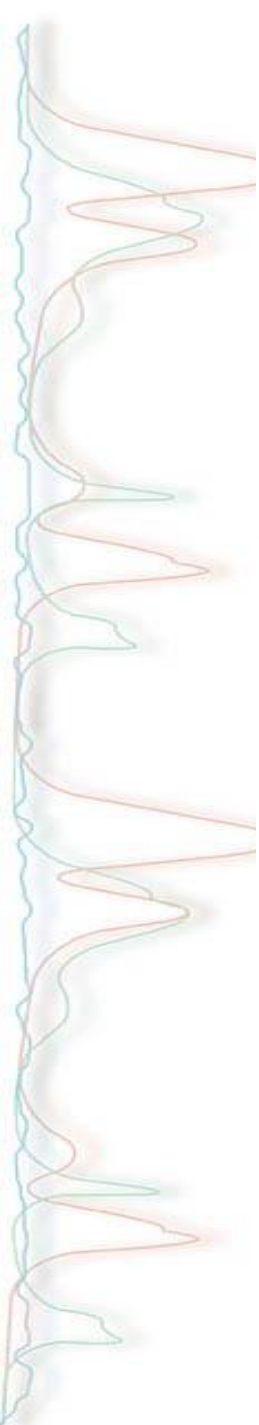
Geometry and the structure of crystals

D. Vectors and Planes

Crystal Defects

Kinds of twins:

1. Annealing twins – occur in fcc metals and alloys which have been cold worked and then annealed to cause recrystallization. (Cu, Ni, α -brass, Al,...)
2. Deformation twins – occur in deformed hcp metals (Zn, Mg, Be,...) and bcc metals. (α -Fe, W,...)



PLAN OF CRYSTAL

PLAN OF TWIN

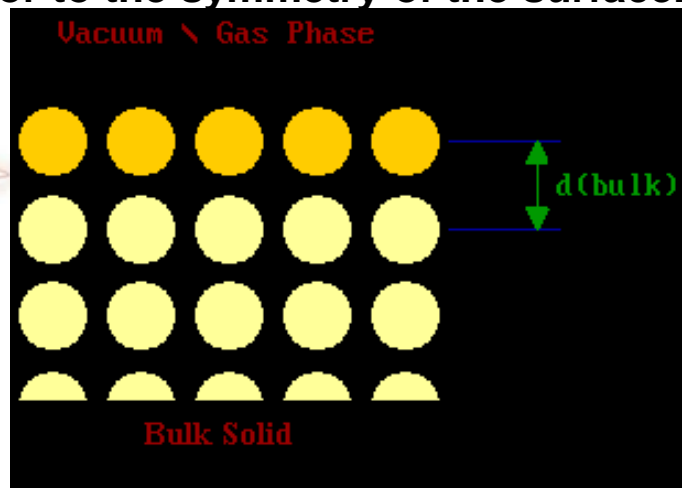
Crystallography

Geometry and the structure of crystals

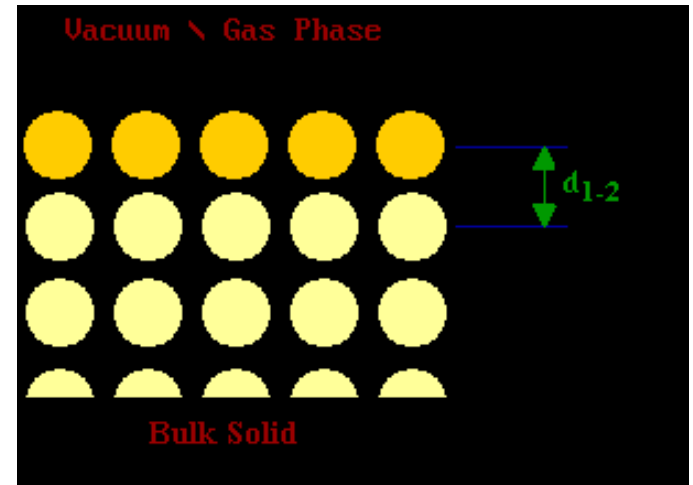
D. Vectors and Planes

Surface Crystal Defects

Relaxation is a small and subtle rearrangement of the surface layers which may nevertheless be significant energetically, and seems to be commonplace for metal surfaces. It involves adjustments in the layer spacings perpendicular to the surface, there is no change either in the periodicity parallel to the surface or to the symmetry of the surface.



Unrelaxed Surface



Relaxed Surface ($d_{1-2} < d_{\text{bulk}}$)

Crystallography

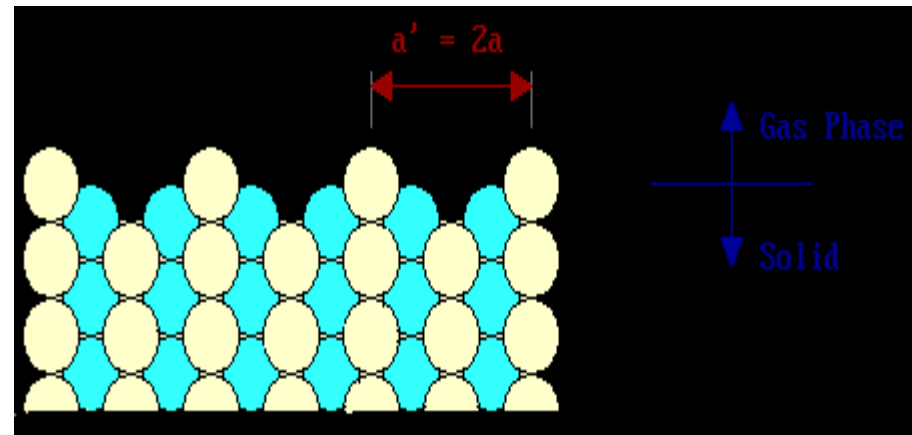
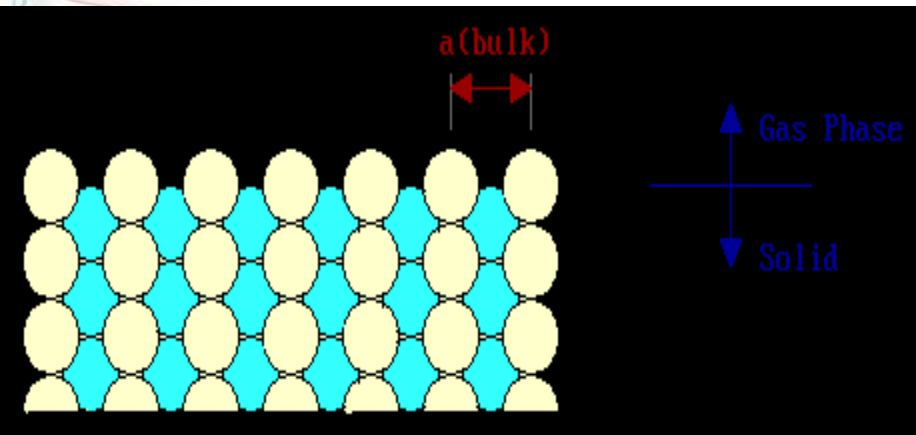
Geometry and the structure of crystals

D. Vectors and Planes

Surface Crystal Defects

The Reconstruction of surfaces involves larger (yet still atomic scale) displacements of the surface atoms. It occurs with many of the less stable metal surfaces (e.g. it is frequently observed on fcc(110) surfaces), but is much more prevalent on semiconductor surfaces.

Unlike relaxation, the phenomenon of reconstruction involves a change in the periodicity of the surface structure - the diagram below shows a surface, viewed from the side, which corresponds to an unreconstructed termination of the bulk structure.



Crystallography

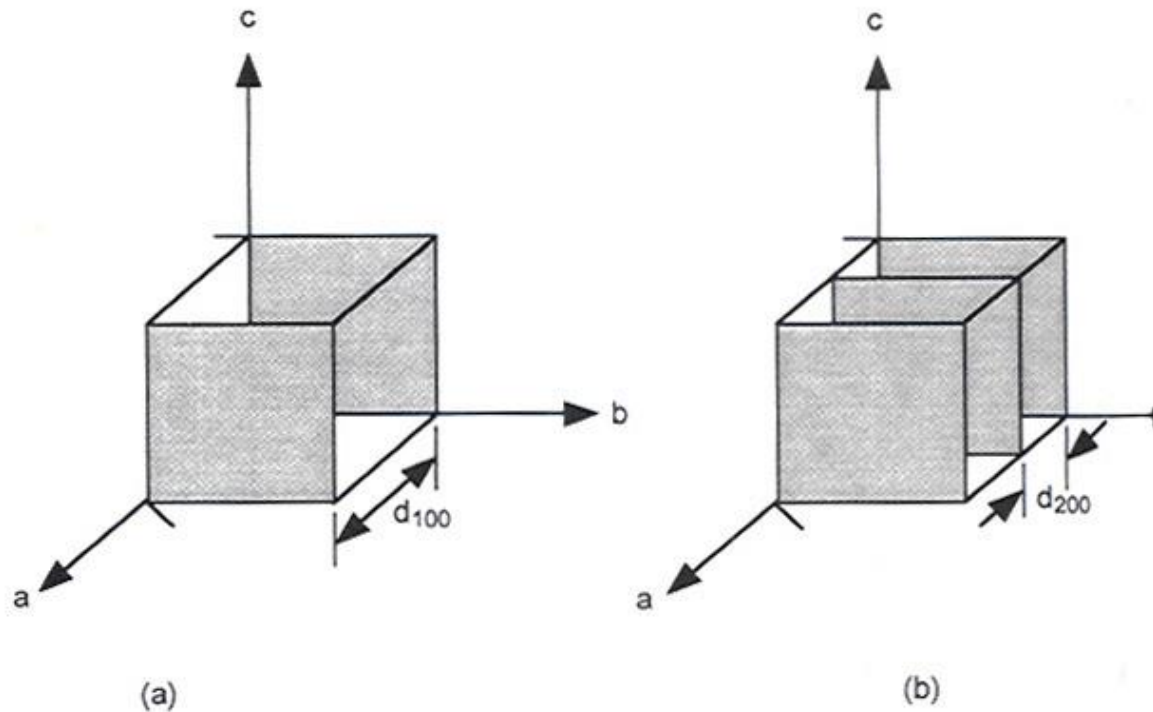
Geometry and the structure of crystals

E. Interplanar Spacings

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

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, α , β , γ).

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



The d_{hkl} interplanar spacing.

For a cubic system:

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

Crystallography

Geometry and the structure of crystals

E. 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 $a = 3\text{\AA}$, $b = 4\text{\AA}$, and $c = 5\text{\AA}$ if the reflections are 001, 010, 100, 011 and 101?

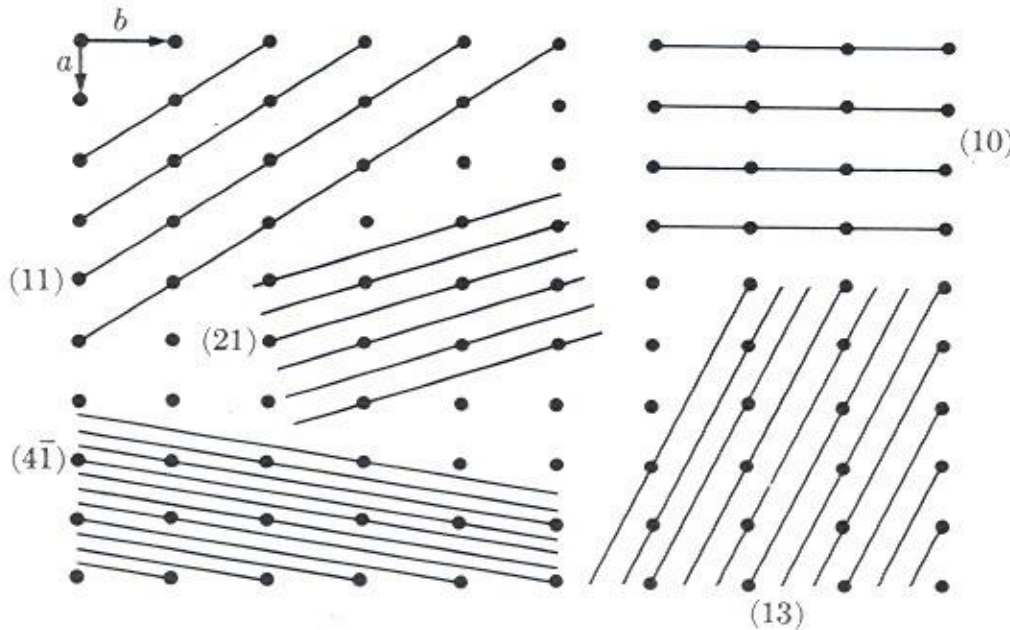
001	5
010	4
100	3
011	3.12
101	2.57

Crystallography

Geometry and the structure of crystals

E. 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

E. 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

E. Interplanar Spacings

$$\begin{aligned}\text{Density} &= \text{mass/volume} \\ &= \text{formula weight/molar volume} \\ &= \text{FW}/(\text{volume of unit cell})N \\ &= (\text{FW} \times Z) / (V \times N)\end{aligned}$$

Z = # of formula units per unit cell

Crystallography

Geometry and the structure of crystals

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?

Crystallography

Read Chapter 2 from textbooks:

- X-ray Diffraction, A Practical Approach by Norton
- Introduction to X-ray powder Diffractometry by Jenkins and Synder
- Elements of X-ray Diffraction by Cullity and Stock

Homework 2: Due next Tuesday

Define the fcc cell. What is N? Draw the crystal and planar representation.

Define the diamond cubic structure cell. What is N? Draw the crystal and planar representation.

Homework 3: Due next Thursday

Exam 1: Tuesday Sept 17th. Lectures 1-6

If you find any websites not using outdated java, that have some cool interacting software for crystal structures, or miller indices, or etc.. please send to me for xtra credit.



Group Assignments:

Group 1:

Group 2:

Group 3:

Group 4:

Crystallography

Lab Assignment:

Lab 1: Safety and Sample Preparation

Tuesday, Sept. 8:00 am

Group 1

Tuesday, Sept. 8:30 am

Group 2

Thursday Sept. 8:00 am

Group 3

Thursday Sept. 8:30 am

Group 4