Solid State

1st Law of Crystallography

In 1669, Niels Stensen (Steno), Professor of Anatomy at Copenhagen and Vicar Apostolic of the North, compared the interfacial angles in various specimens of quartz rock crystals. An interfacial angle may be defined as the angle between lines drawn perpendicular to two faces.

Steno found that the corresponding angles (in different crystals) were always equal.

After the invention of the contact goniometer in 1780, this conclusion was checked and extended to other substances, and the constancy of interfacial angles has been called the "first law of crystallography."

Second Law of Crystallography

The real foundations of crystallography may be said to date from the work of the Abbe Rene Just Hϋay, Professor of the Humanities at the University of Paris.
In 1784, he proposed that the regular external form of crystals was a reflection of an inner regularity in the arrangement of their constituent building units. These units were believed to be little cubes or polyhedral.

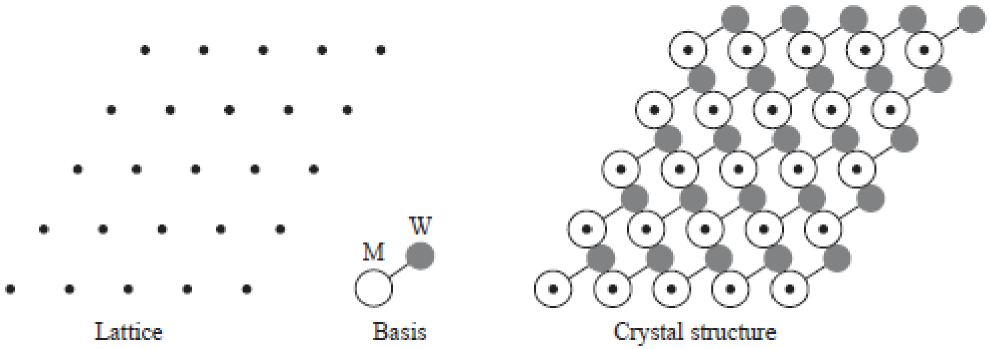
The Basis and Lattice Points

Structural unit of a crystal called the **basis** (or *motif*). The crystal structure is generated by repeating the basis in three dimensions. The basis may be a single atom or molecule, or it may be a small group of atoms, molecules, or ions. Each repeated basis group has the same structure and the same spatial orientation as every other basis group in the crystal.

The environment of each repeated unit is the same throughout the crystal (neglecting surface effects).

For KCl the basis consists of one K^+ and one Cl^- ion whereas for Cu the basis is Cu atoms.

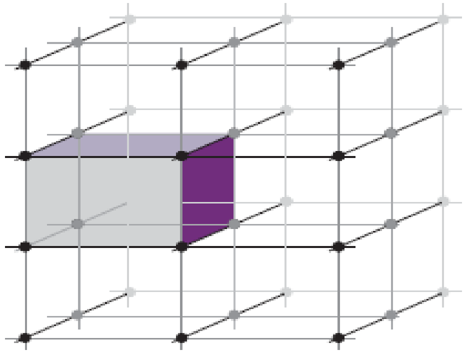
Space Lattice is a three dimensional array of points, called lattice points, representing the location of the basis. Each of the points is surrounded identically by its neighbours.



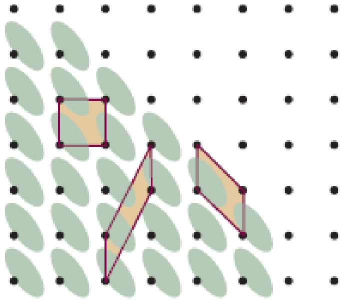
The crystal structure is generated by associating a basis group with each lattice point.

Unit cell

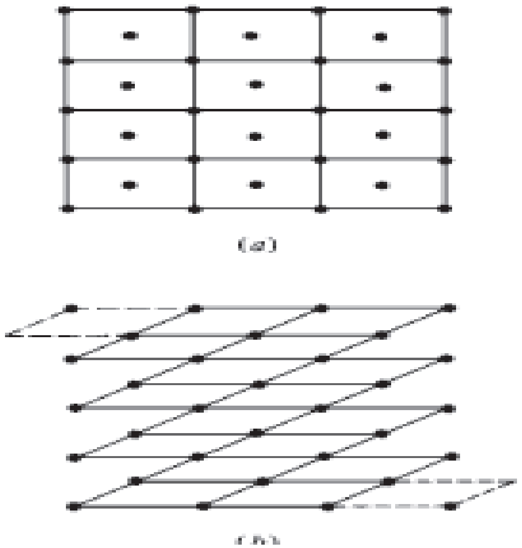
A *unit cell* is the smallest array of atoms (or molecules) in the crystal such that the translational replication of which in three dimensions generates the entire crystal. In other words, the crystal can be defined by a repeating pattern of unit cells.



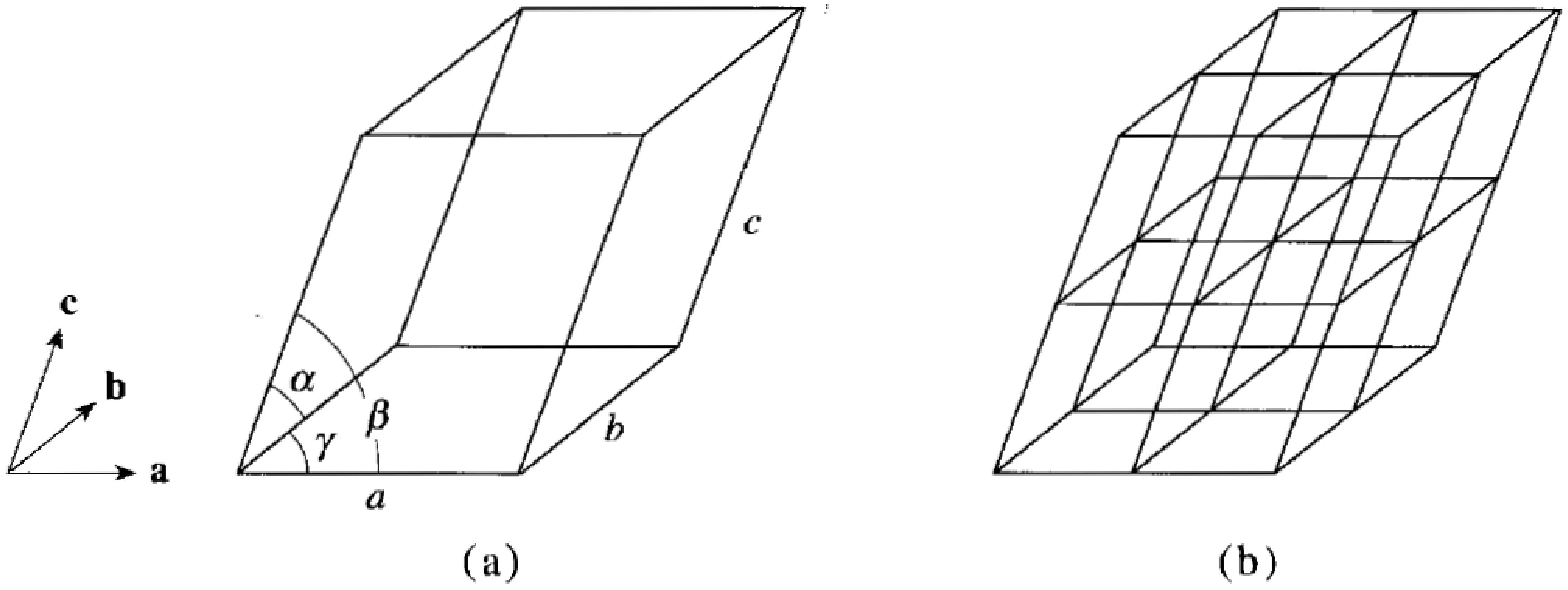
A unit cell is a parallepiped (but not necessarily rectangular) figure from which the entire crystal structure can be constructed by using only translations (not reflections, rotations, or inversions).



A unit cell can be chosen in a variety of ways, as shown here. It is conventional to choose the cell that represents the full symmetry of the lattice. In this rectangular lattice, the rectangular unit cell would normally be adopted

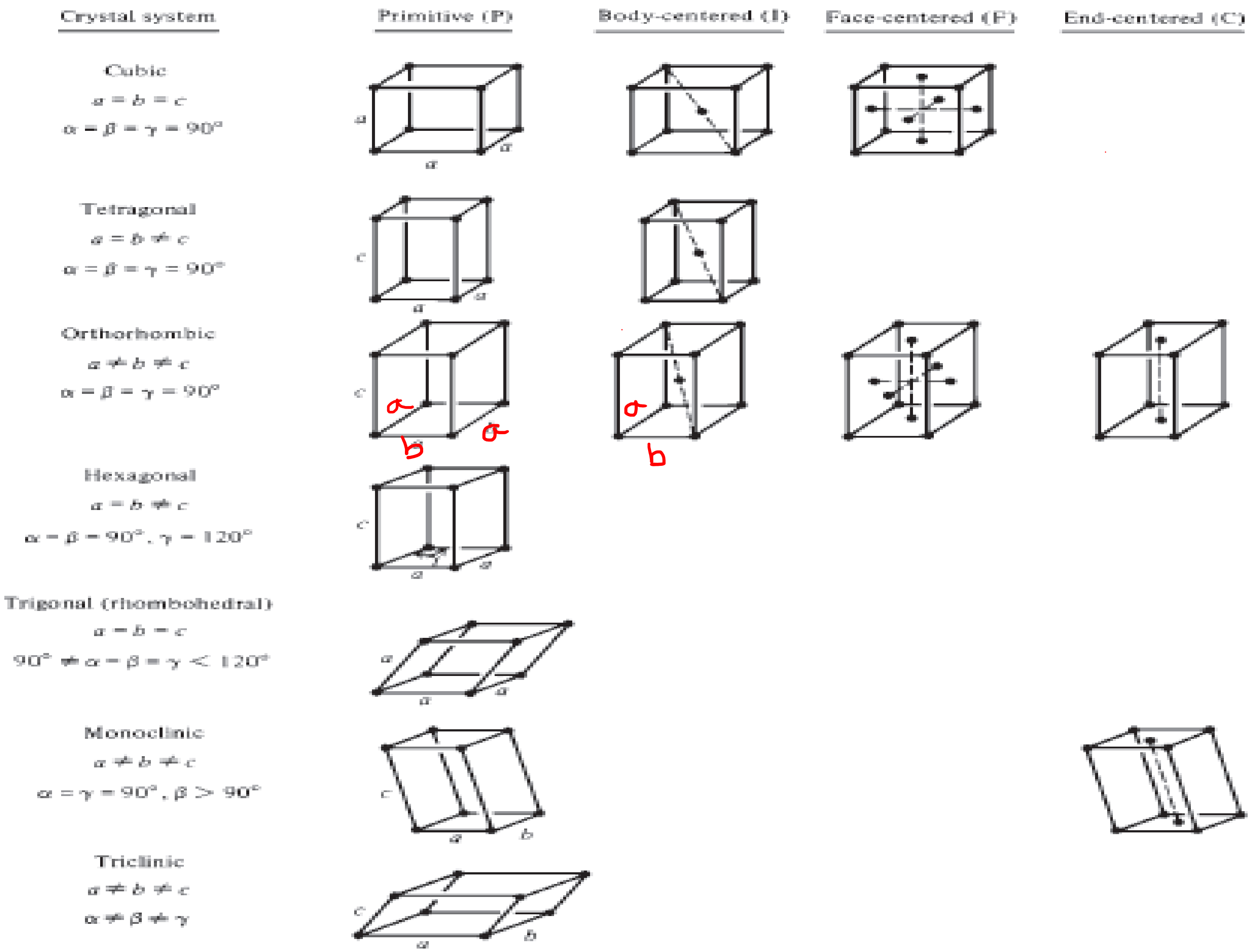


(*a*) A two-dimensional centered lattice. (*b*) The same lattice divided into primitive unit cells.

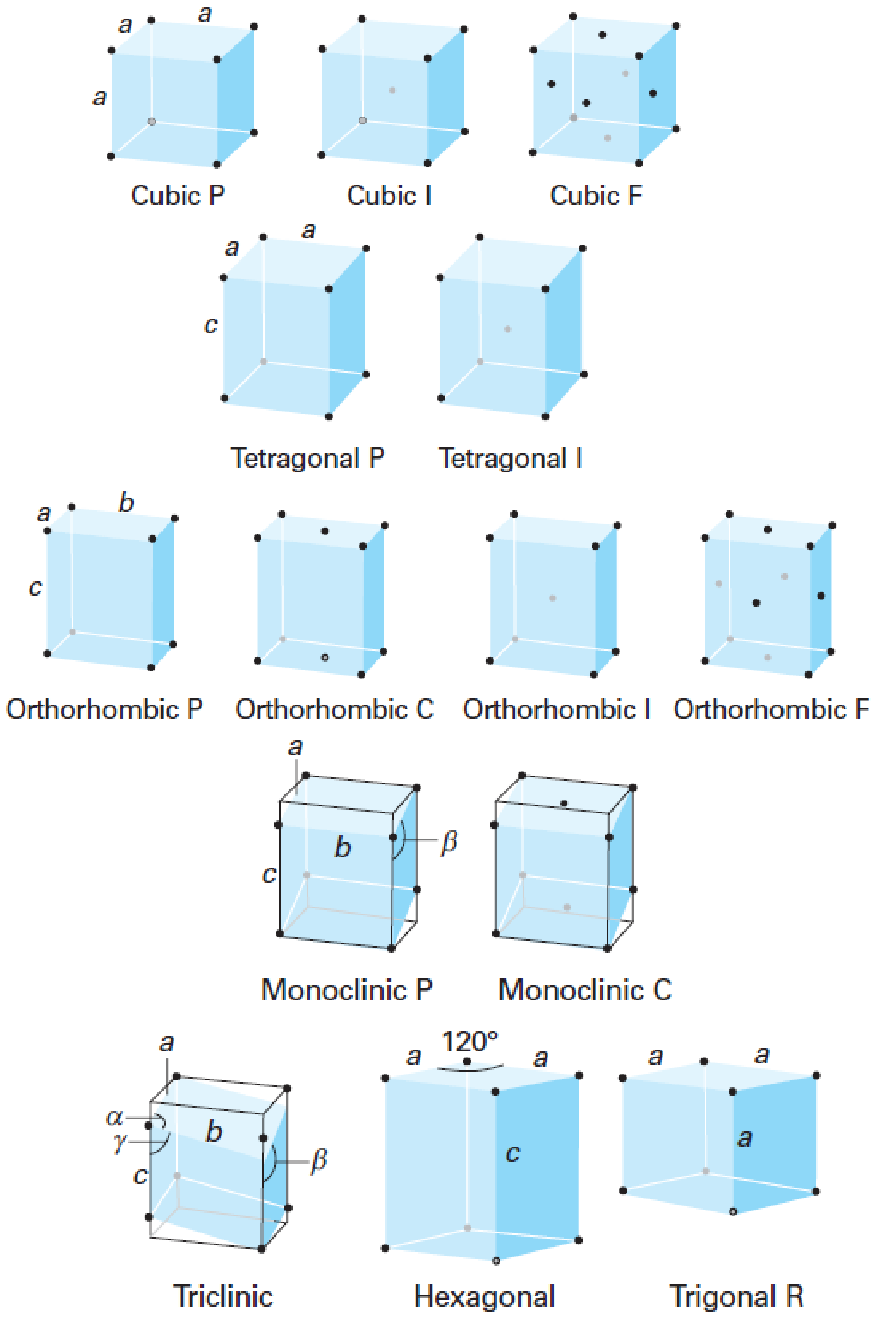


(a) The general shape of a unit cell. We take the bottom left corner of the unit cell to be the origin of the **a**, **b**, **c** coordinate system. The unit cell is defined by a, b, and c, its length along the **a**, **b**, and **c** axes, respectively, and the angles α, β, and γ between pairs of axes. (b) By replicating the unit cell in three dimensions, a crystal lattice is generated.

Unit cells of 14 Bravais Lattices



Crystal system	Primitive (P)	Body-centered (I)	Face-centered (F)	End-centered (C)
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90^\circ$				
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$				
Hexagonal $a = b \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$				
Trigonal (rhombohedral) $a = b = c$ $90^\circ \neq \alpha = \beta = \gamma < 120^\circ$				
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90^\circ, \beta > 90^\circ$				
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$				



Cubic P Cubic I Cubic F

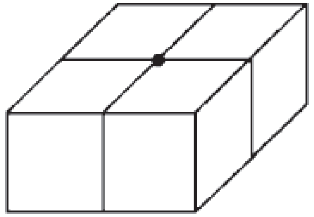
Tetragonal P Tetragonal I

Orthorhombic P Orthorhombic C Orthorhombic I Orthorhombic F

Monoclinic P Monoclinic C

Triclinic Hexagonal Trigonal R

Fig. 20.8 The fourteen Bravais lattices. The points are lattice points, and are not necessarily occupied by atoms. P denotes a primitive unit cell (R is used for a trigonal lattice), I a body-centred unit cell, F a face-centred unit cell, and C (or A or B) a cell with lattice points on two opposite faces.



The lattice point shown is shared by four unit cells at the same level and four more unit cells (not shown) immediately above.

Unit Cell	Lattice Points
Primitive	$1\left(\frac{1}{8}\times 8\right)$
Body Centered Lattice	$2\left(\frac{1}{8}\times 8+1\right)$
Face Centered Lattice	$4\left(\frac{1}{8}\times 8+\frac{1}{2}\times 6\right)$

Miller Indices: Description of The Orientation of a Lattice Plane

Because of the periodicity of the crystal lattice, we can view the lattice as being comprised of sets of equally spaced parallel planes containing lattice points Although this particular description of the crystal lattice may seem to be just another arbitrary way of looking at the crystal structure, it is important for understanding X-ray diffraction patterns and relating these patterns to the distances and angles between atoms and molecules in the crystal.

The orientation of a crystal plane is described by its **Miller indices** (*hkl*), which are obtained by the following steps:
(1) finding the intercepts of the plane on the *a*, *b*, *c* axes in terms of multiples of the unit-cell lengths *a*, *b*, *c*;
(2) taking the reciprocals of these numbers;
(3) if fractions are obtained in step 2, multiplying the three numbers by the smallest integer that will give whole numbers.
If an intercept is negative, one indicates this by a bar over the corresponding Miller index.

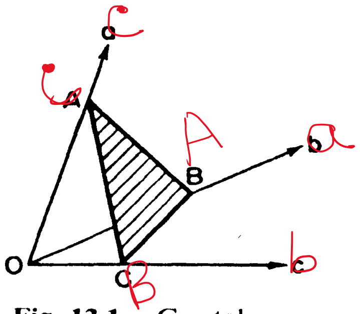


Fig. 13.1. Crystal axes.

Intercept on a axis=$\frac{\overline{OA}}{a}$

Intercept on b axis =$\frac{\overline{OB}}{b}$

Intercept on c axis=$\frac{\overline{OC}}{c}$

$$\frac{a}{\overline{OA}} = h, \quad \frac{b}{\overline{OB}} = k, \quad \frac{c}{\overline{OC}} = l$$

The shaded plane labeled *r* intercepts the *a* axis at *a*/2 and the *b* axis at *b*/2 and lies parallel to the *c* axis (intercept at ∞).

Step 1 gives 1/2, 1/2 , ∞

Step 2 gives 2, 2, 0. Hence the Miller indices are (220).

The plane labeled *s* has Miller indices (110).

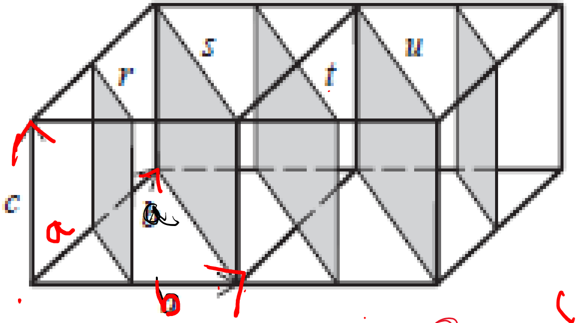
The plane labeled *t* has intercepts 3*a*/2, 3b/2, ∞; , Intercepts , $\frac{3a/2}{a}$, $\frac{3b/2}{b}$, $\frac{\infty c}{c}$

step 2 gives 2/3 ,2/3 ,0, and the Miller indices are (220).

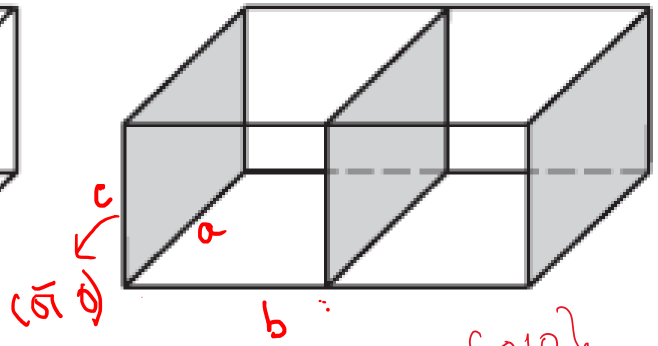
Plane *u* has intercepts 2*a*, 2*b*, ∞, so step 2 gives ½ , ½, 0, and step 3 gives (110).

Also shown are a (111) plane and (100) planes. The higher the value of the Miller index *h* of a plane, the closer to the origin is the *a* intercept of the plane.

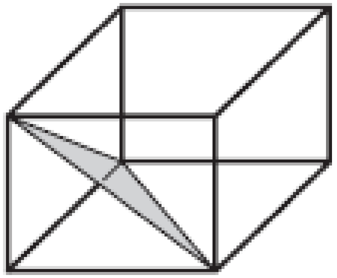
The Miller indices are associated with a family of parallel planes separated by a distance *a* /*h* along the **a** axis, *b/k* along the **b** axis, and *c/l* along the c axis. In determining the Miller indices of a set of parallel equally spaced planes, one looks at the intercepts of the plane closest to the origin but not containing the origin. {220} represent a set of equally spaced parallel planes (220) along with planes (110) midway between them.



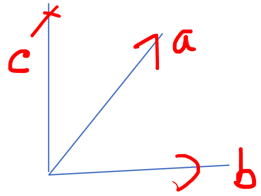
(*a*) (220) planes {220}

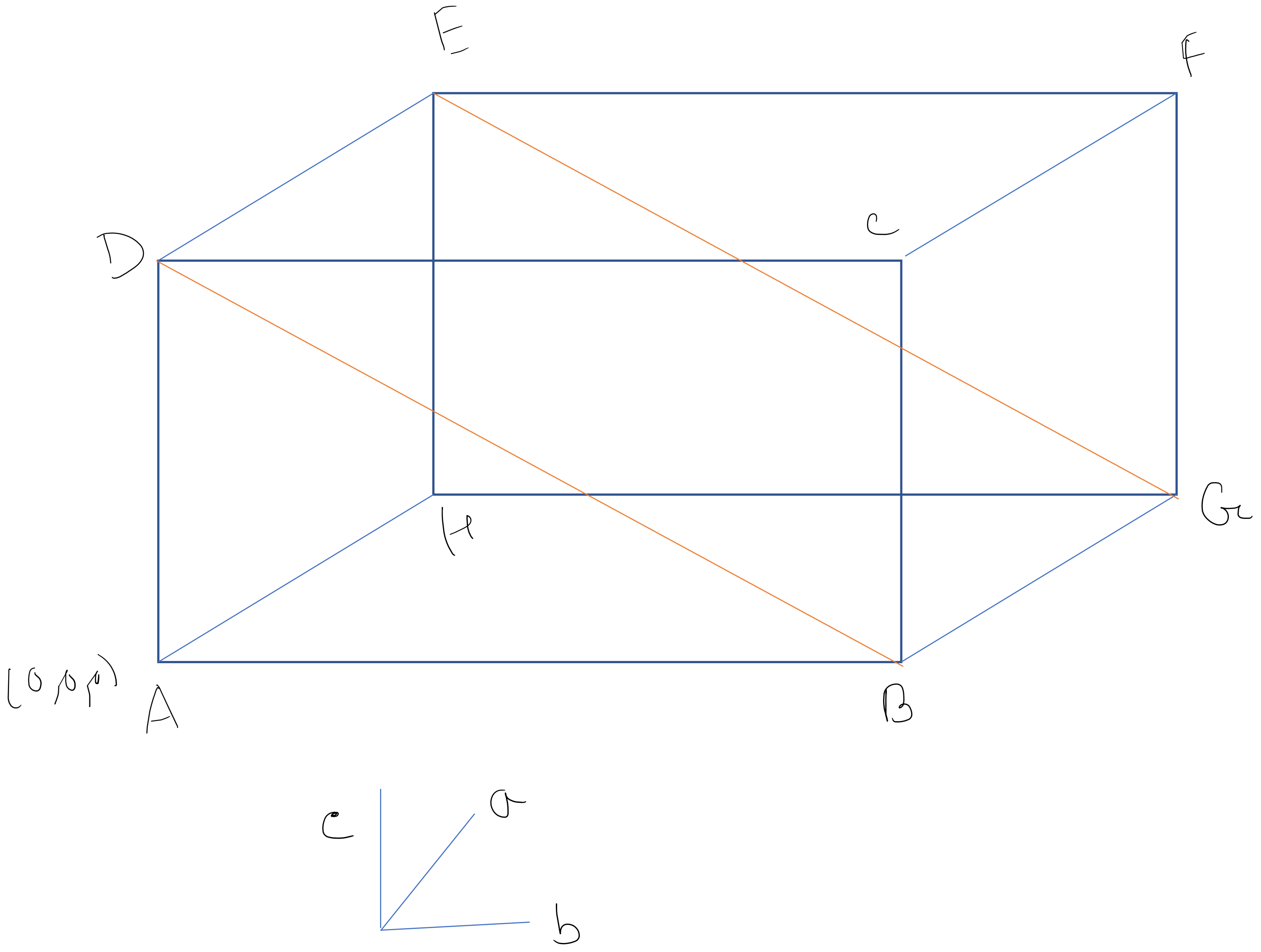


(*b*) (~~100~~) planes {010}

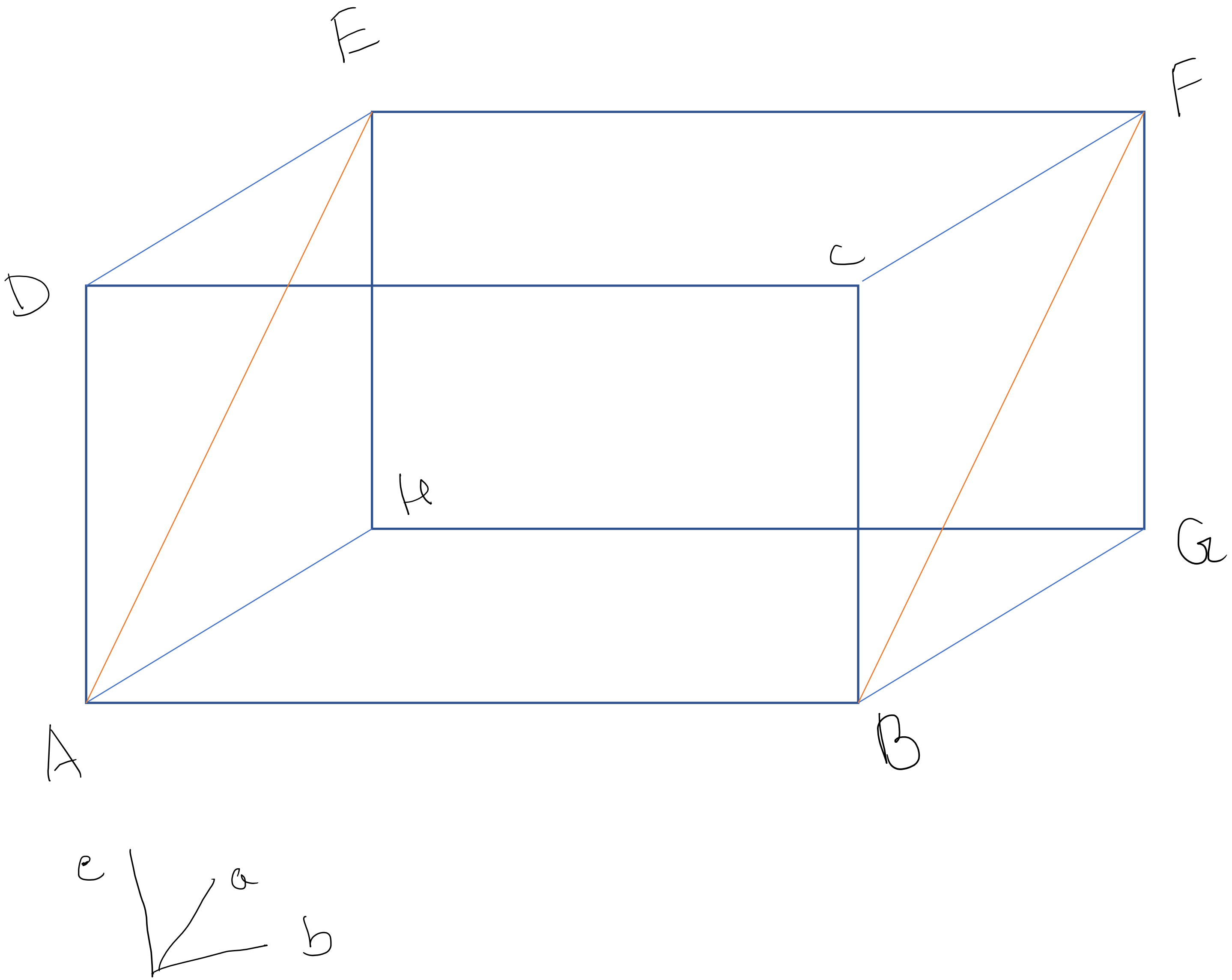


(*c*) (111) plane





BGED (0 11)



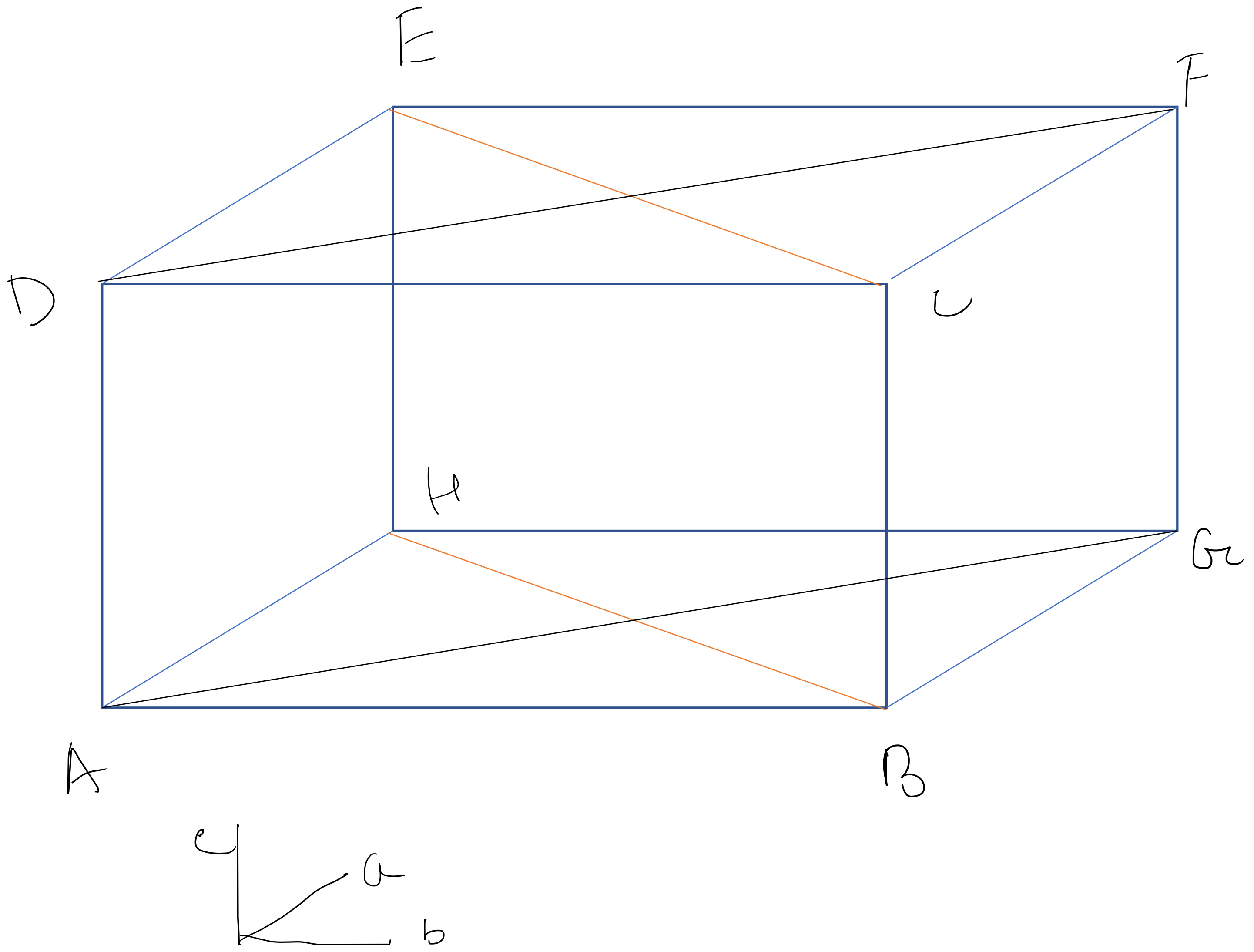
Shift origin along
a axis towards H

intercepts:

along a axis = $-a$
along b axis = ∞
along c axis = c

Thus,

ABFE $(\bar{1}01)$

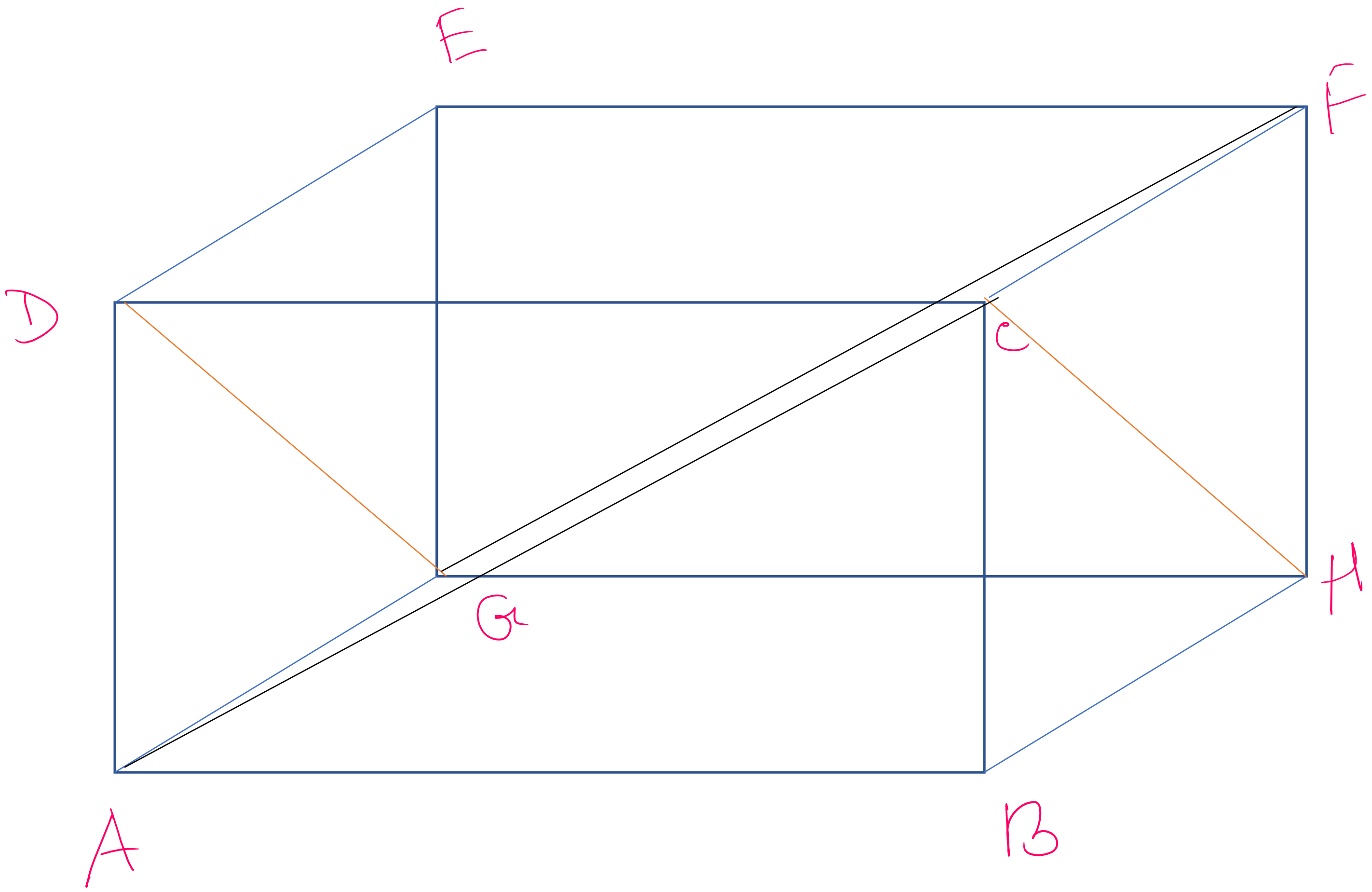


ECBH (110)

To describe Miller indices of AGFD shift origin along a axis or b axis.

Shifting origin along a axis towards H gives
AGFD $(\bar{1}10)$

Shifting origin along b axis gives
AGFD $(1\bar{1}0)$

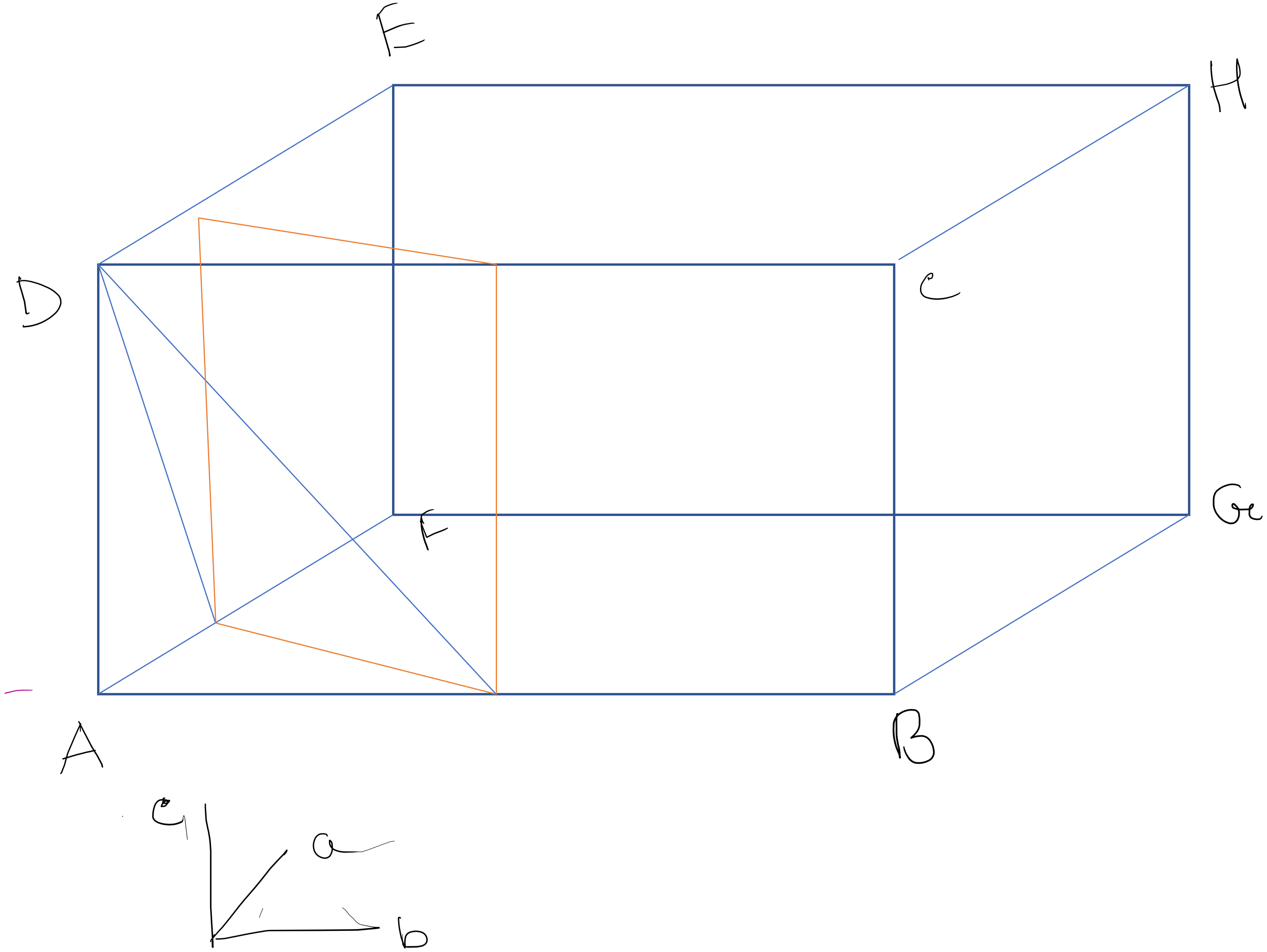


HCDG (101)

For ACFG

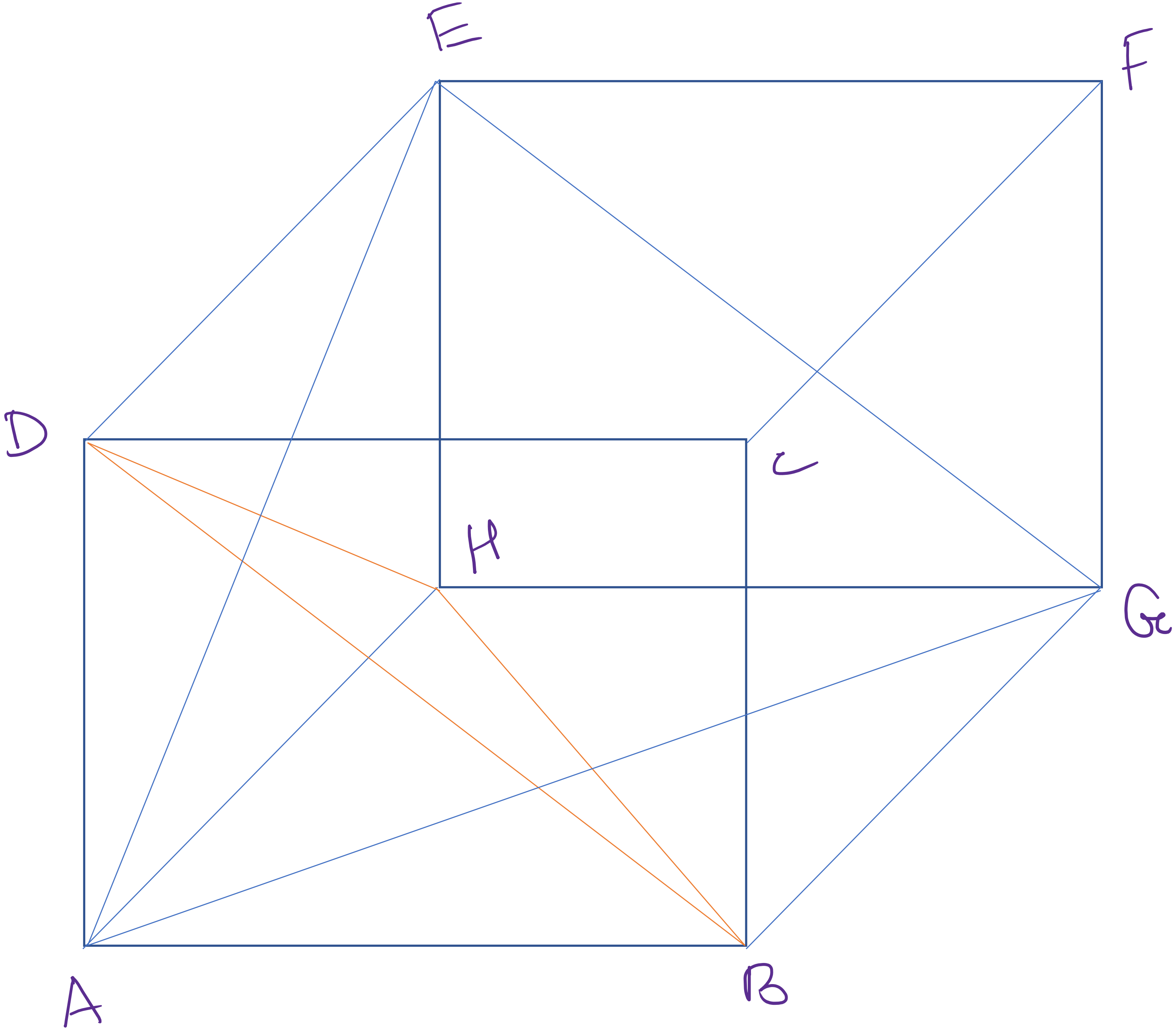
Shifting along b axis towards B gives $(0\bar{1}1)$

Shifting along c axis towards D gives $(01\bar{1})$



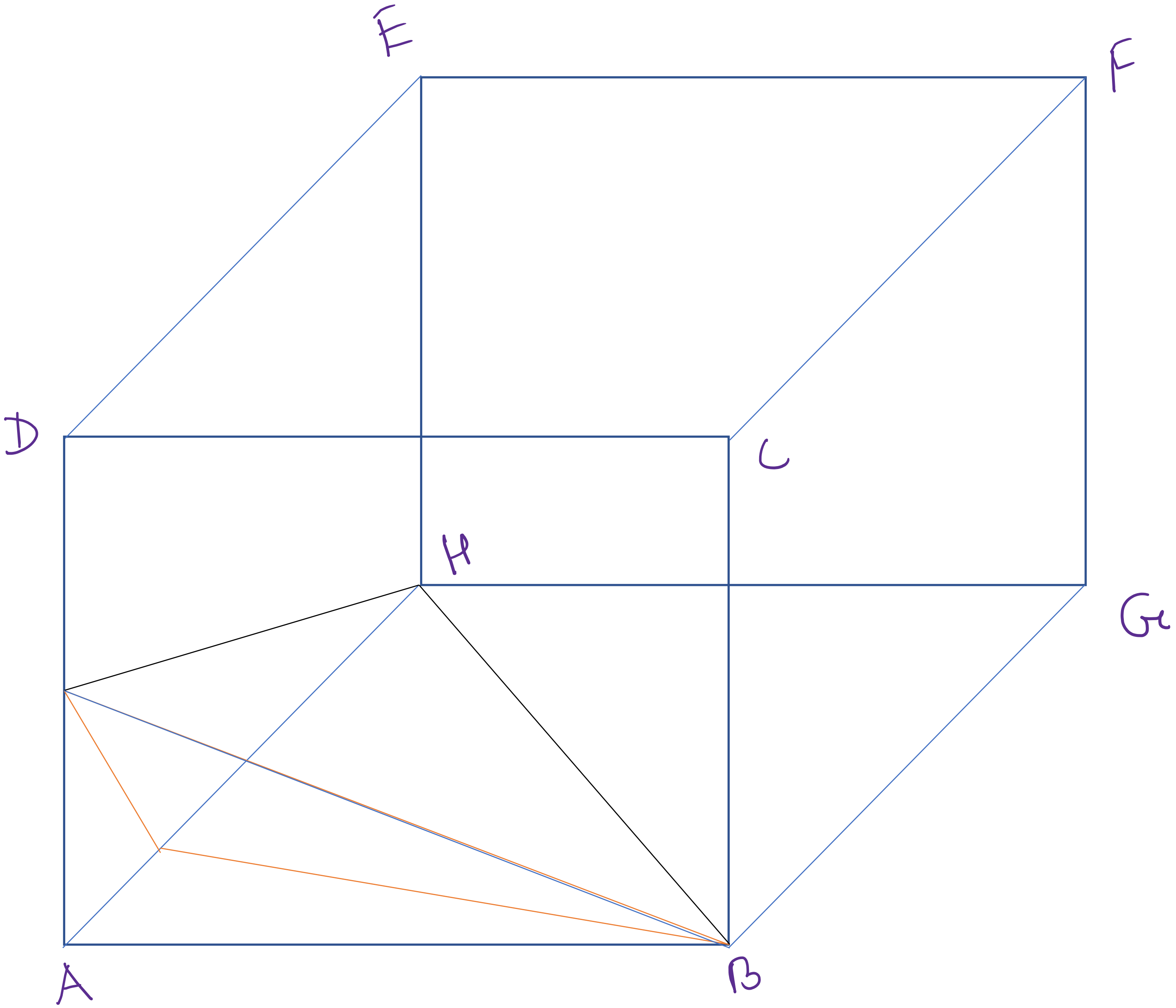
(3 2 1)

(3 2 0)



(111)

$(\bar{1}11)$

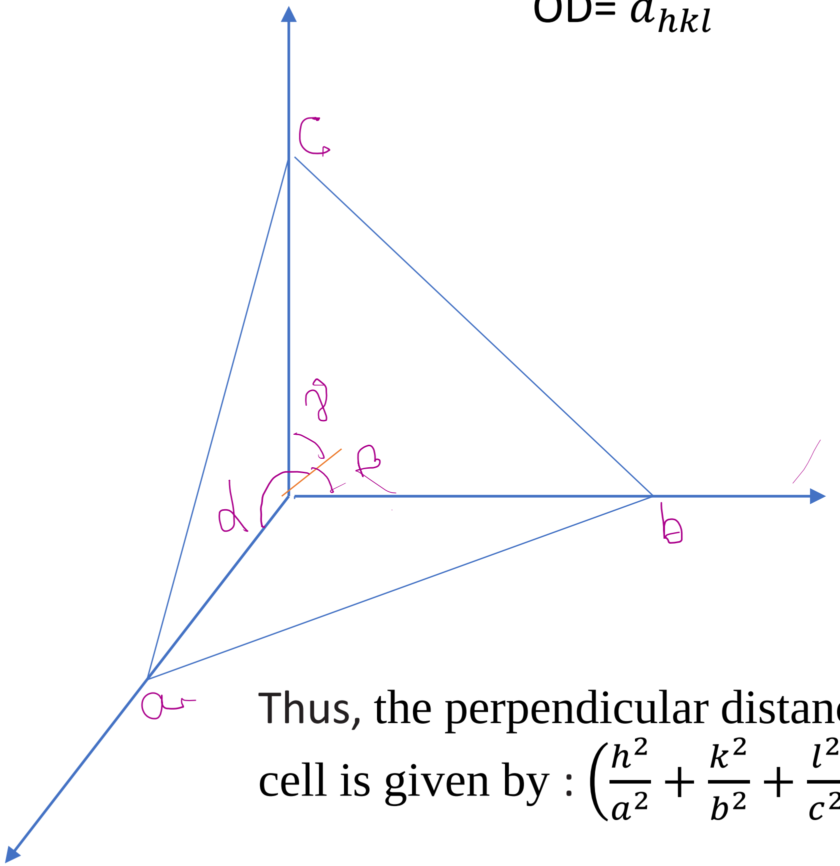


(312)

(112)

The Separation between the Planes

OD= d_{hkl}



$$\frac{a}{h}\,cos\alpha = d_{hkl}$$

$$\frac{b}{k}\,cos\beta = d_{hkl}$$

$$\frac{c}{l}\,cos\gamma = d_{hkl}$$

$$\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$$

$$or, d_{hkl}^2\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)=1$$

Thus, the perpendicular distance between adjacent *hkl* planes for a orthorhombic unit cell is given by : $\left(\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right)=\frac{1}{d_{hkl}^2}$

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

Consider an orthorhombic unit cell with dimensions $a = 487$ pm, $b = 646$ pm, and $c = 415$ pm. Calculate the perpendicular distance between (a) the 110 planes and (b) the 222 planes of this crystal.

Density of a Solid

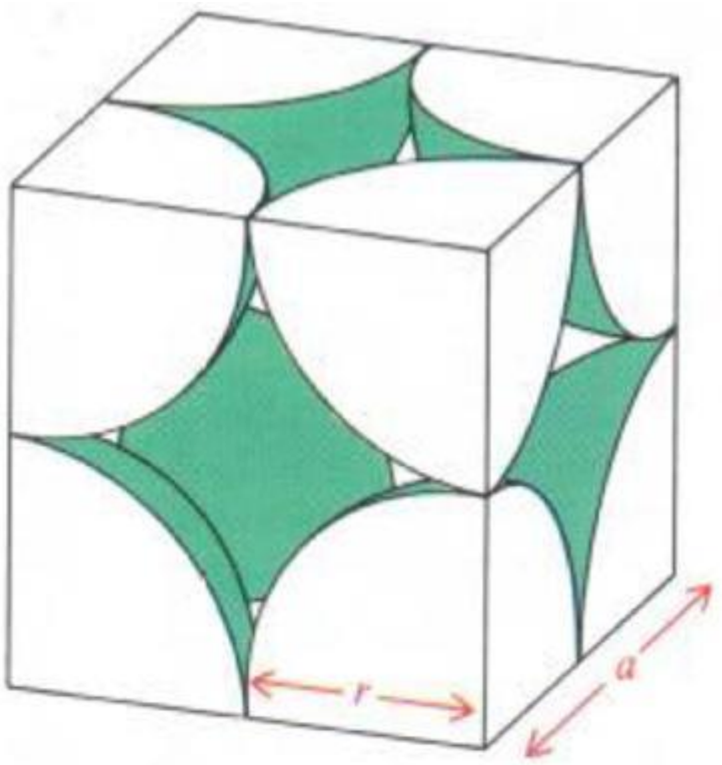
Let a substance crystallizes in a cubic system with *a* being the distance between two lattice points.

Volume of the cube = a^3 (If *a*, *b* and *c* are the lengths of its edges of the cuboid then V=*abc*)

If *z* is the number of lattice points in the unit cell then volume occupied by each point =$\frac{a^3}{z}$

Thus, volume occupied by Avogadro no of points = $\frac{N_A a^3}{z}$

If molecular weight is M then $\rho = \frac{M}{V} = \frac{Mz}{N_A a^3}$



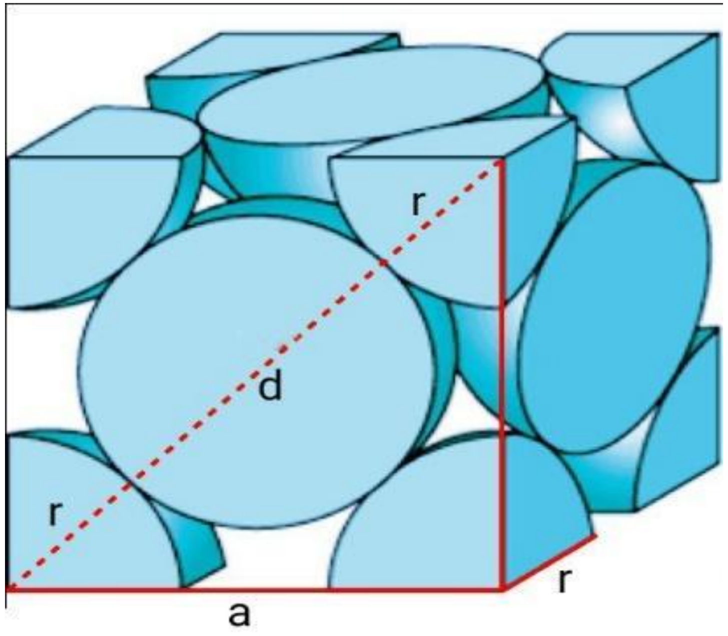
$$a = 2r, r = radius$$

Volume of cube=a^3

Volume of one particle=$\frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{a}{2}\right)^3$

The fraction of volume occupied=

$=\frac{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3}{a^3}$=0.526



$$\sqrt{2}a = 4r, r = radius$$

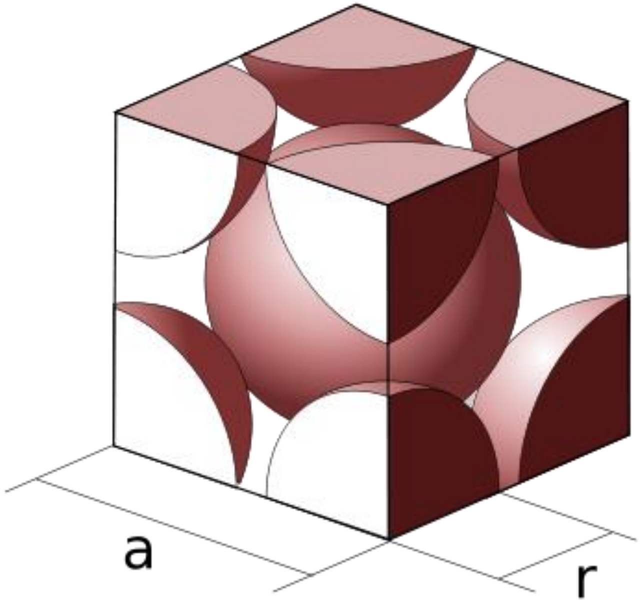
Volume of cube=a^3

Volume of one particle=$\frac{4}{3}\pi r^3$

$$= \frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3$$

The fraction of volume occupied=

$=\frac{\frac{4}{3}\pi\left(\frac{\sqrt{2}a}{4}\right)^3 \times 4}{a^3}$=0.741



$$\sqrt{3}a = 4r, r = radius$$

Volume of cube=a^3

Volume of one particle=$\frac{4}{3}\pi r^3$

$$= \frac{4}{3}\pi\left(\frac{\sqrt{3}a}{4}\right)^3$$

The fraction of volume occupied=

$=\frac{\frac{4}{3}\pi\left(\frac{\sqrt{3}a}{4}\right)^3 \times 2}{a^3}$=0.68

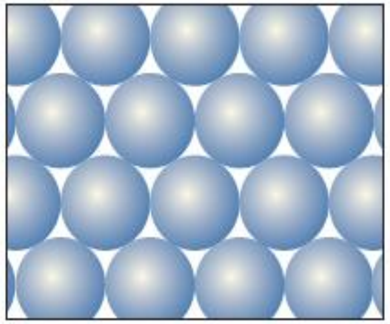


Fig. 20.32 The first layer of close-packed spheres used to build a three-dimensional close-packed structure.

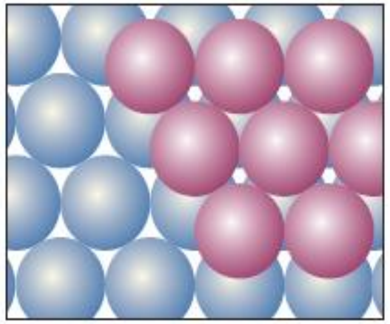


Fig. 20.33 The second layer of close-packed spheres occupies the dips of the first layer. The two layers are the AB component of the close-packed structure.

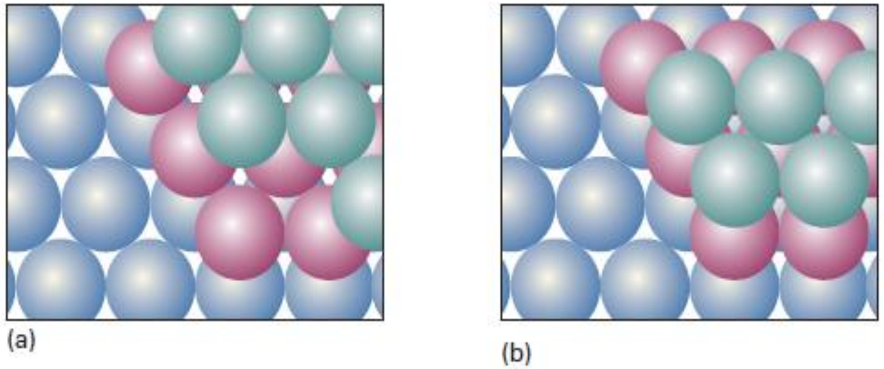


Fig. 20.34 (a) The third layer of close-packed spheres might occupy the dips lying directly above the spheres in the first layer, resulting in an ABA structure, which corresponds to hexagonal close-packing. (b) Alternatively, the third layer might lie in the dips that are not above the spheres in the first layer, resulting in an ABC structure, which corresponds to cubic close-packing

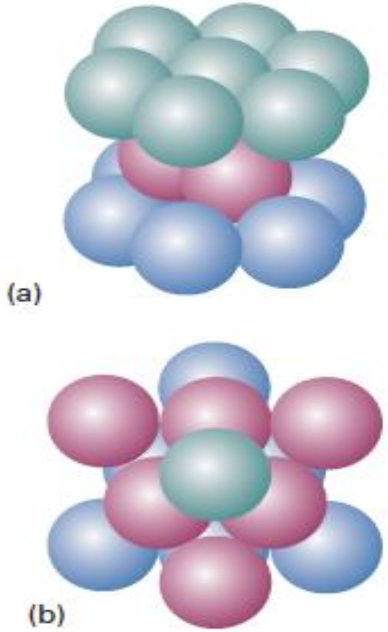
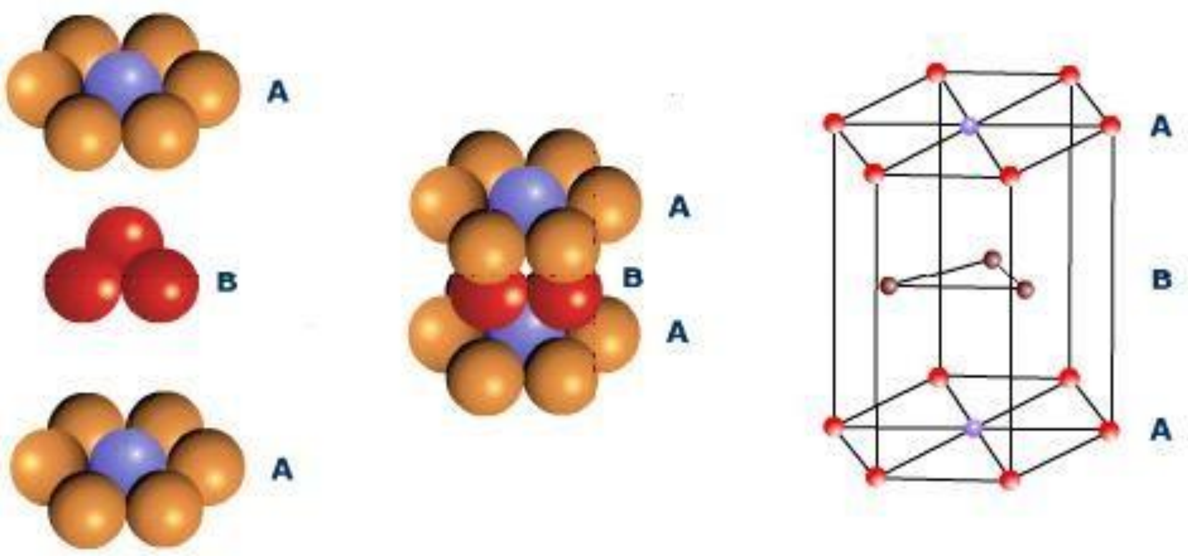
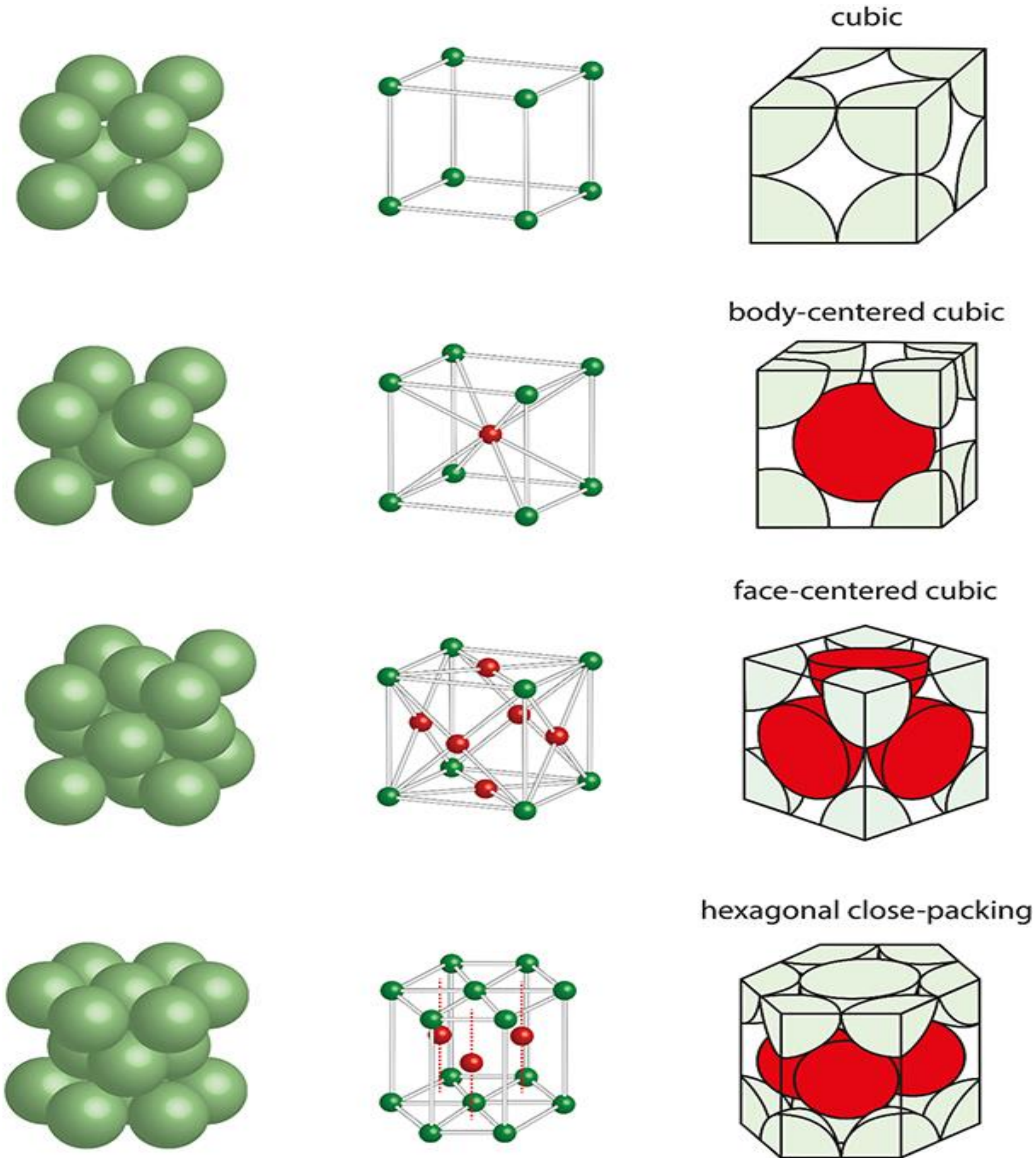


Fig. 20.35 A fragment of the structure shown in Fig. 20.34 revealing the (a) hexagonal (b) cubic symmetry. The tints on the spheres are the same as for the layers in Fig. 20.34.

Hexagonal Close Packing

[Hexagonal Closed Packed Structure 3D Animation - YouTube]





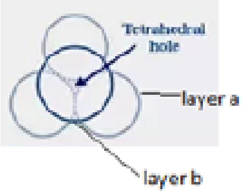
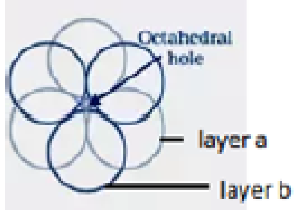
Coordination Number

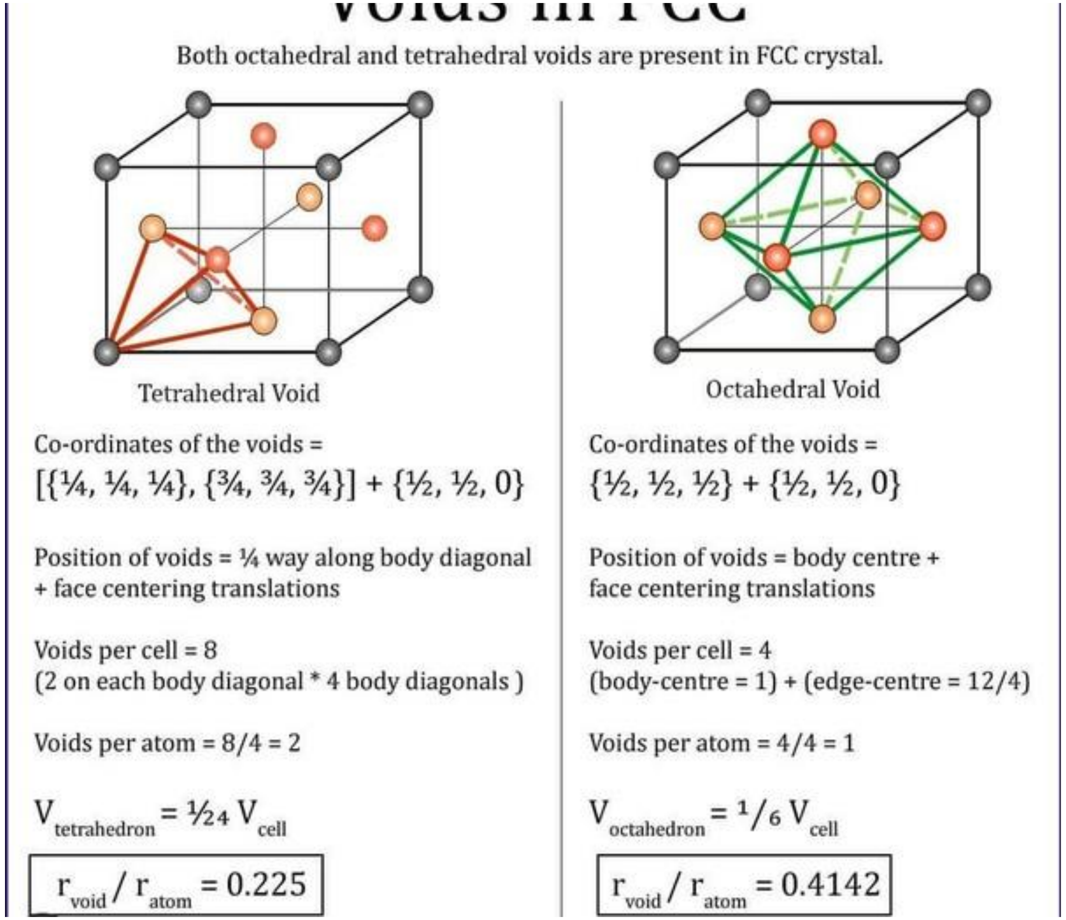
6

8

12

12

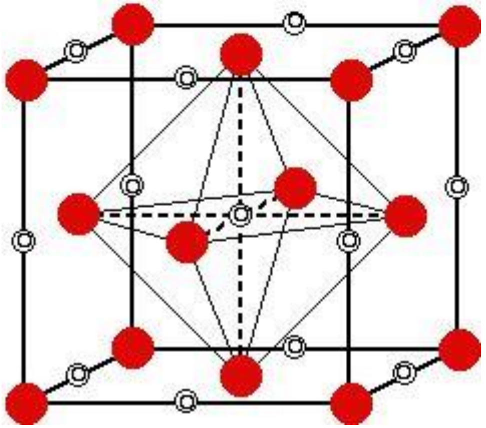
S.NO	TETRAHEDRAL VOIDS	OCTAHEDRAL VOIDS
1	When a sphere of second layer (b) is above the void in the first layer (a), tetrahedral void is formed  	When a sphere of second layer (b) partially covers the void in the first layer (a), octahedral void is formed 
2	If the number of close packed spheres be 'n' then, the number of tetrahedral voids generated is equal to 2n.	If the number of close packed spheres be 'n' then, the number of octahedral voids generated is equal to n
3	This constitutes four spheres, three in the lower layer (a) and one in the upper layer (b).	This constitutes six spheres, three in the lower layer (a) and three in the upper layer (b)
4	When the centers of these four spheres are joined, a tetrahedron is formed.	When the centers of these six spheres are joined, an octahedron is formed.

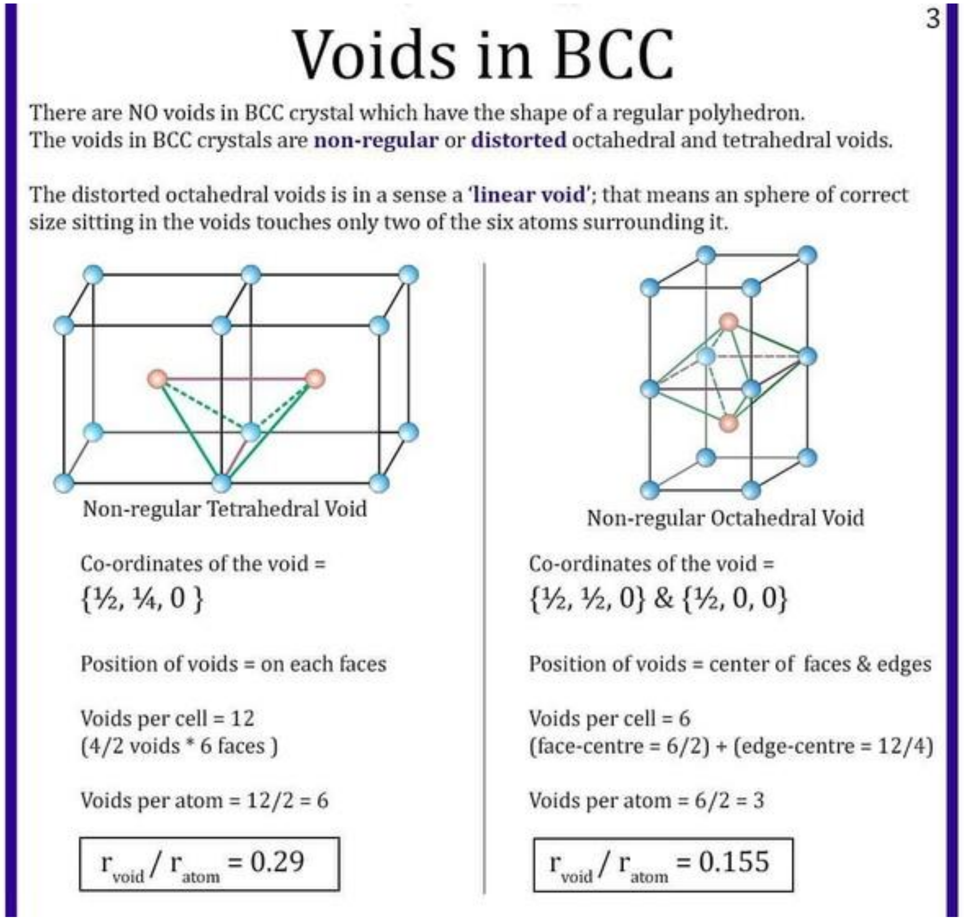


Voids in FCC

Both octahedral and tetrahedral voids are present in FCC crystal.

Tetrahedral Void	Octahedral Void
Co-ordinates of the voids = $[\{\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{4}\}, \{\tfrac{3}{4}, \tfrac{3}{4}, \tfrac{3}{4}\}] + \{\tfrac{1}{2}, \tfrac{1}{2}, 0\}$	Co-ordinates of the voids = $\{\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}\} + \{\tfrac{1}{2}, \tfrac{1}{2}, 0\}$
Position of voids = ¼ way along body diagonal + face centering translations	Position of voids = body centre + face centering translations
Voids per cell = 8 (2 on each body diagonal * 4 body diagonals)	Voids per cell = 4 (body-centre = 1) + (edge-centre = 12/4)
Voids per atom = 8/4 = 2	Voids per atom = 4/4 = 1
$V_{tetrahedron} = \tfrac{1}{24} V_{cell}$	$V_{octahedron} = {}^{1}/_{6}\, V_{cell}$
$\boxed{r_{void} / r_{atom} = 0.225}$	$\boxed{r_{void} / r_{atom} = 0.4142}$



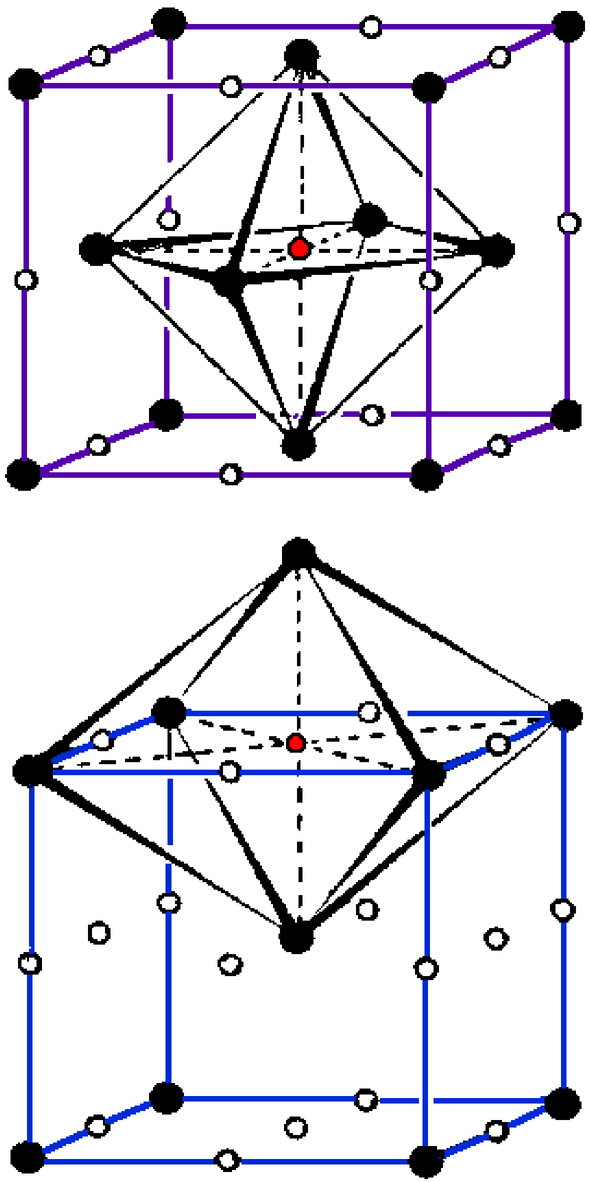


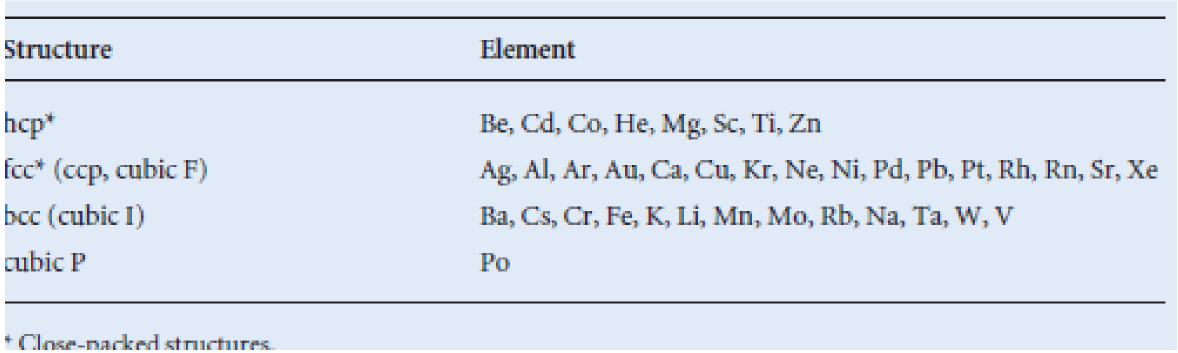
Voids in BCC

There are NO voids in BCC crystal which have the shape of a regular polyhedron.
The voids in BCC crystals are **non-regular** or **distorted** octahedral and tetrahedral voids.

The distorted octahedral voids is in a sense a '**linear void**'; that means an sphere of correct size sitting in the voids touches only two of the six atoms surrounding it.

Non-regular Tetrahedral Void	Non-regular Octahedral Void
Co-ordinates of the void = {½, ¼, 0 }	Co-ordinates of the void = {½, ½, 0} & {½, 0, 0}
Position of voids = on each faces	Position of voids = center of faces & edges
Voids per cell = 12 (4/2 voids * 6 faces)	Voids per cell = 6 (face-centre = 6/2) + (edge-centre = 12/4)
Voids per atom = 12/2 = 6	Voids per atom = 6/2 = 3
$\boxed{r_{void} / r_{atom} = 0.29}$	$\boxed{r_{void} / r_{atom} = 0.155}$





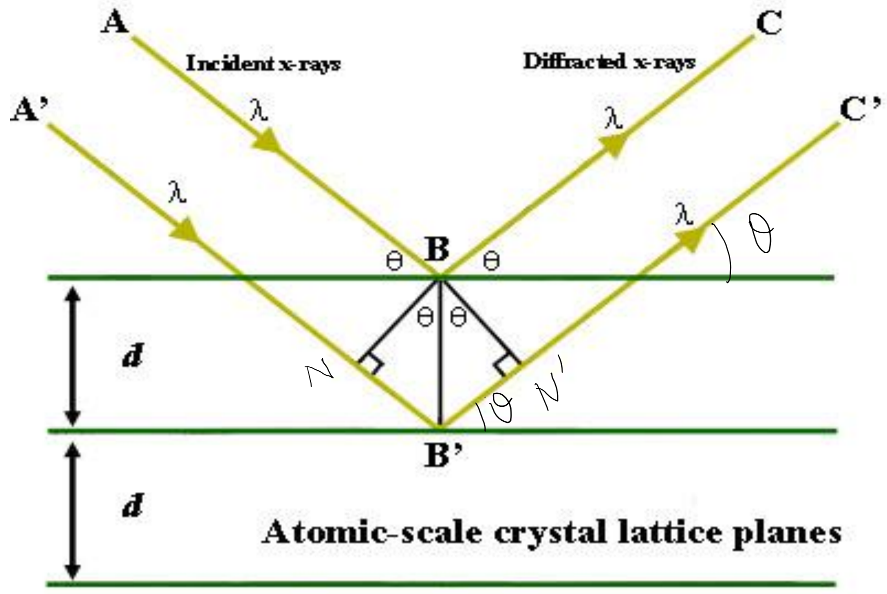
Structure	Element
hcp*	Be, Cd, Co, He, Mg, Sc, Ti, Zn
fcc* (ccp, cubic F)	Ag, Al, Ar, Au, Ca, Cu, Kr, Ne, Ni, Pd, Pb, Pt, Rh, Rn, Sr, Xe
bcc (cubic I)	Ba, Cs, Cr, Fe, K, Li, Mn, Mo, Rb, Na, Ta, W, V
cubic P	Po

* Close-packed structures.

X-Ray Diffraction and Bragg’sLaw

The structure of a crystal can be determined using the technique of X-ray diffraction. The wavelength of X-ray (~1 Å) is of the order of the distance between the constituting atoms or molecules . Hence, crystals act as diffraction gratings for x-rays. This was first realized by von Laue in 1912.

The method developed by the Braggs (William and his son Lawrence, who later jointly won the Nobel Prize) is the foundation of almost all modern work in X-ray crystallography.



NB=N´B´ , θ= glancing angle

NB= N´B´= d sinθ
The path difference between the two incident rays =
NB+N´B´= 2 d sinθ

If the path difference between them is integral multiple of λ
then we will get constructive interference and a bright spot.
2 d sinθ= n λ
Reflections with *n* = 2, 3, . . . are called second-order, third-order, and so on;

For a set of planes to give a diffracted beam intense enough to be observed, each plane of the set must have a high density of electrons. This requires a high density of atoms, so each plane must have a high density of lattice points. Because the number of sets of such planes is limited, the number of values of d_{hkl} is limited and the Bragg condition will be met only for certain values of θ.

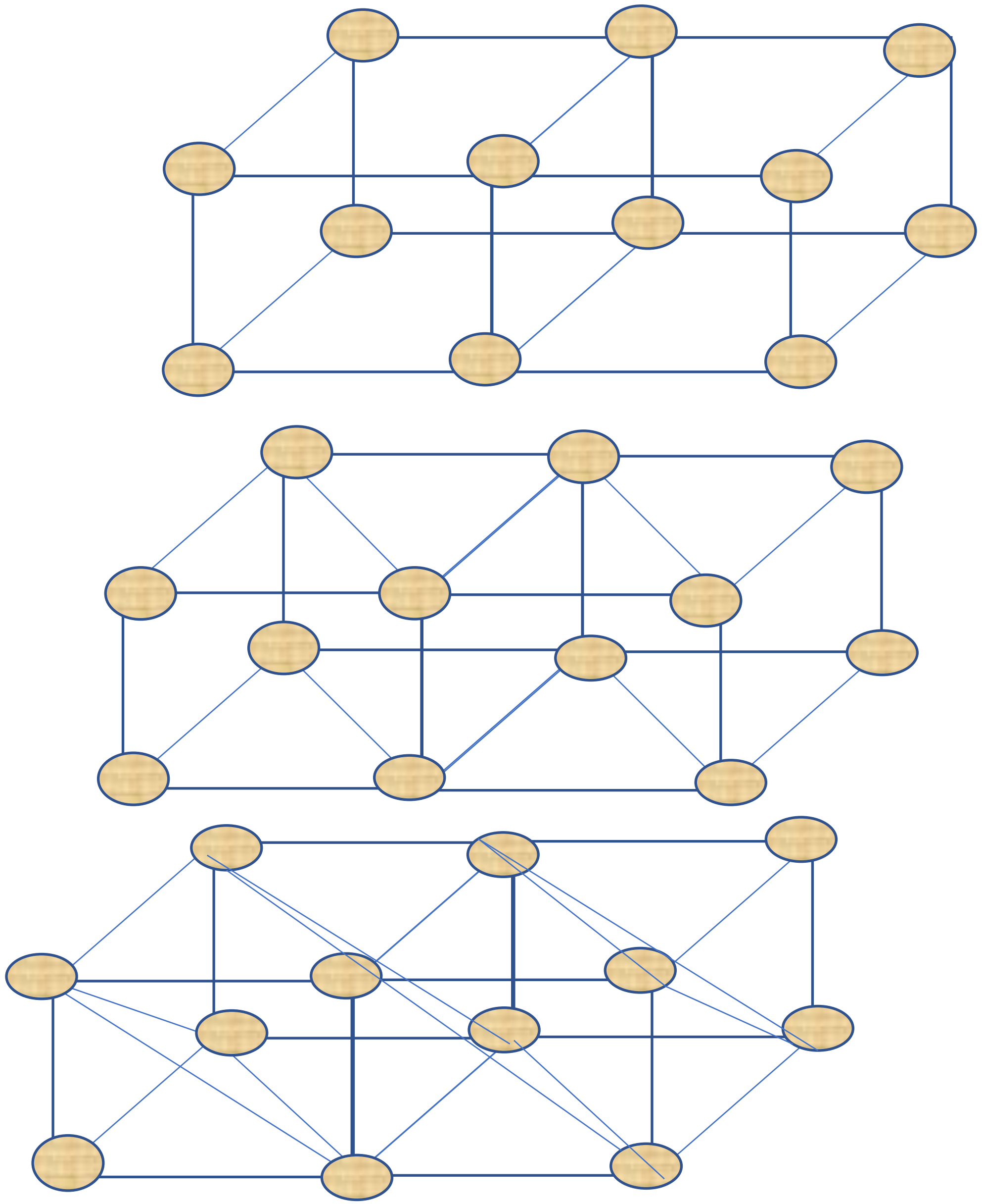
X-ray crystallographers prefer to write Bragg's equation in the form

$$2d_{nh,nk,nl} sin\theta = \lambda$$

For example, for a primitive cubic lattice, the n =2 diffracted beam from the (100) set of planes is considered to be the n =1 diffracted beam from the (200) planes, whose spacing d_{200} is half that of the (100) planes. Similarly, the n =3 diffracted beam for the (100) planes is considered to be the n = 1 diffracted beam for the (300) planes.

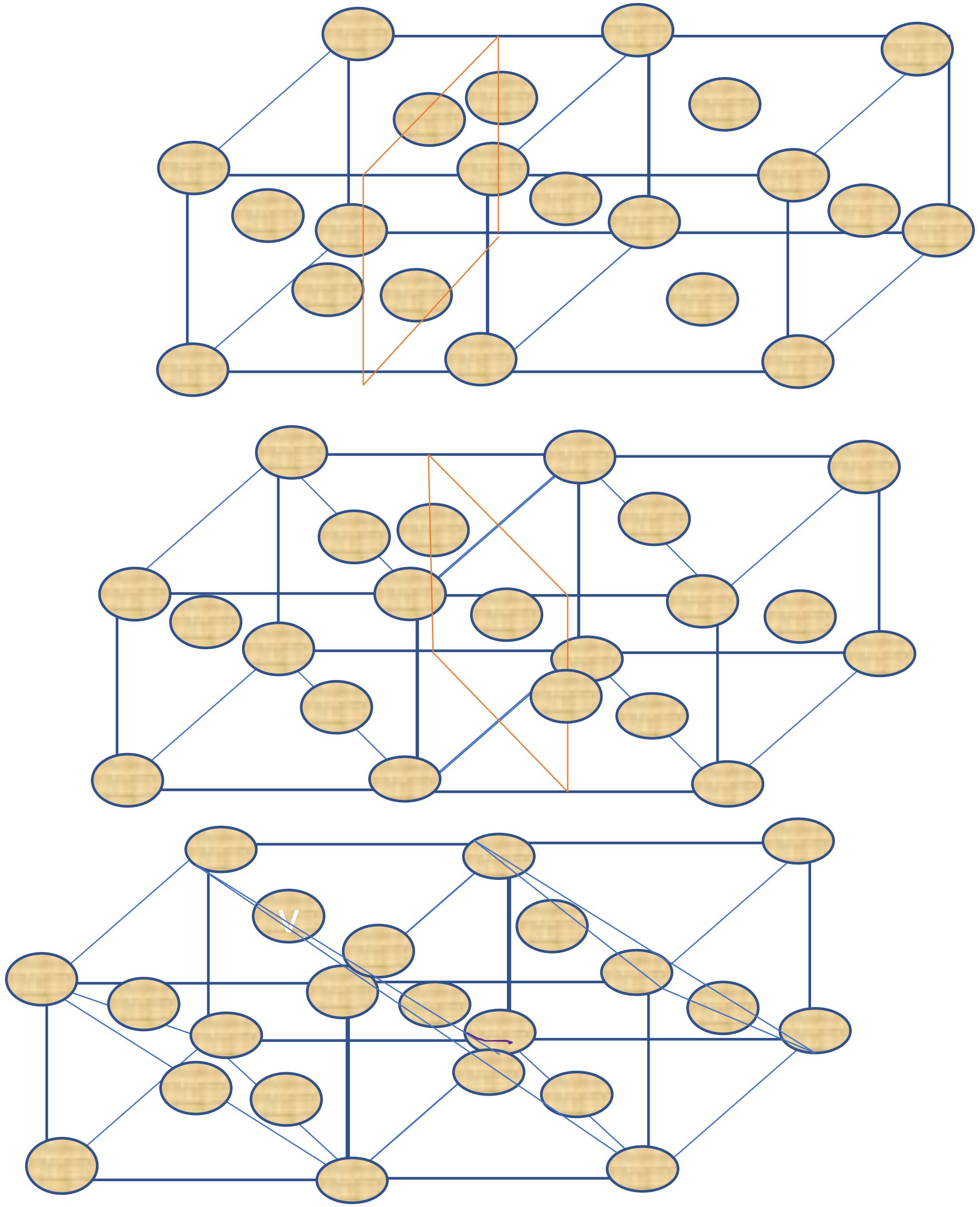
And $2d_{nh,nk,nl} \gg \lambda$

Primitive Lattices



$$d_{100}:d_{110}:d_{111} = a:\frac{a}{\sqrt{2}}:\frac{a}{\sqrt{3}} = 1:0.707:0.577$$

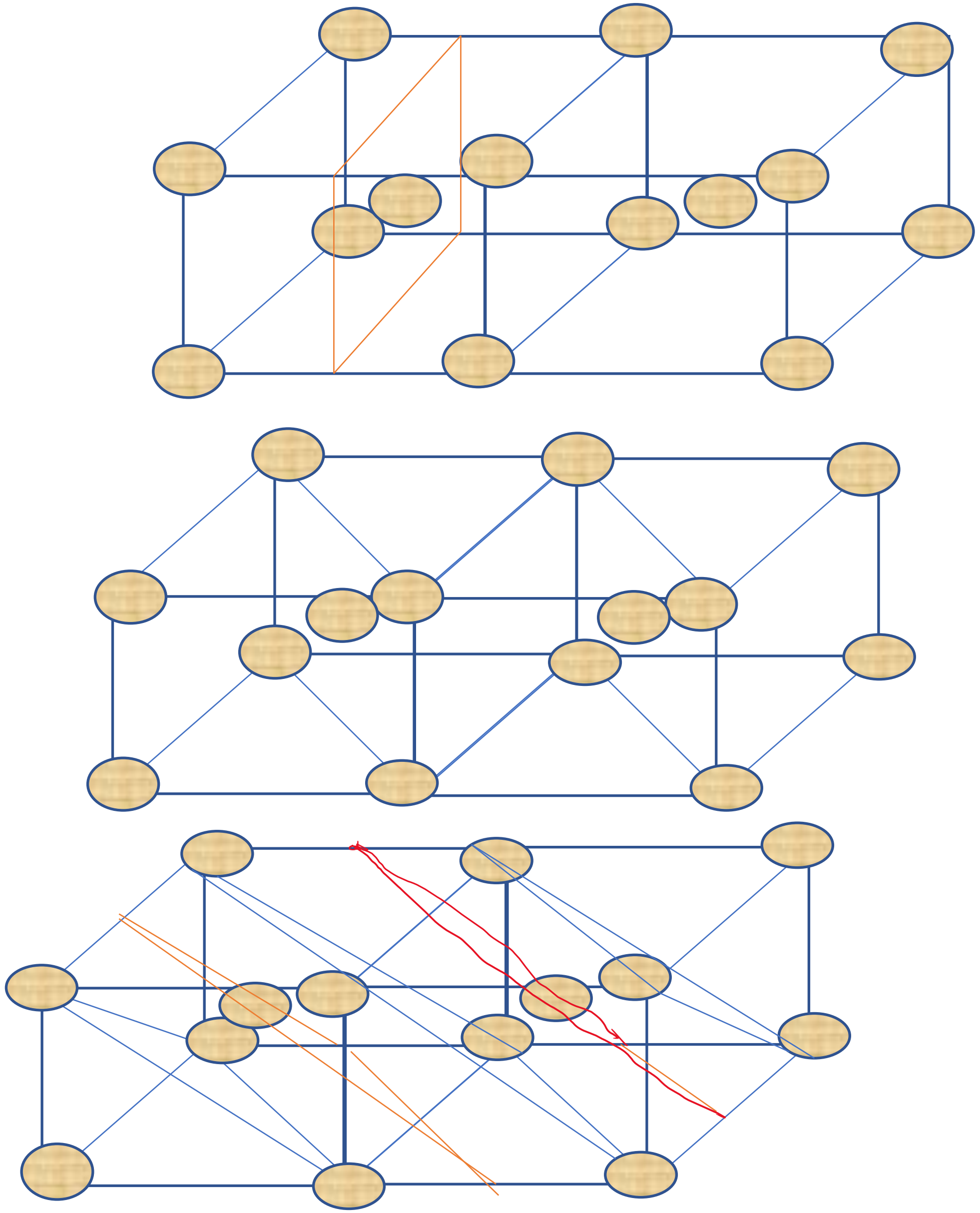
Face Centered Lattices



For n =1 and {010} planes, the x-rays reflected from adjacent (010) planes have a path difference of one wavelength. But the path difference between x-rays reflected from the (020) plane and x-rays reflected from (020) plane is one-half wavelength. These waves are out of phase and cancel. The cancellation is exact, because the number of lattice points in plane (020) of the unit cell is the same as the number of lattice points in plane (010) of the unit cell. For n =2, the path difference between x-rays reflected from two parallel (020) planes is 2λ and between x-rays reflected from two adjacent (020) and (020) planes is λ; hence, no cancellation occurs. Putting n 3, 4, . . . , we see that, a face-centered lattice gives 200, 400, 600, . . . reflections, but not 100, 300, 500, . . . reflections. These missing reflections are called **extinctions** or **systematic absences.**

$$d_{200}:d_{220}:d_{111} = \frac{a}{2}:\frac{a}{2\sqrt{2}}:\frac{a}{\sqrt{3}} = 1:0.707:1.154$$

Body centered Lattices



$$d_{200}:d_{110}:d_{222} = \frac{a}{2}:\frac{a}{\sqrt{2}}:\frac{a}{2\sqrt{3}} = 1:1.414:0.577$$

1. For a primitive lattice there are no extinctions.

2. For a face-centered lattice, the only reflections that occur are those whose three indices are either all even numbers or all odd numbers. h, k, l are all odd or even

3. For a body-centered lattice, the only reflections that occur are those for which the sum of the indices is even. h+k+l should be even.

In order to find out the types of cubic lattice the angles at which first, second and third order reflections take place are studied

$$d_{100}:d_{110}:d_{111} = \frac{n\lambda}{2sin\theta_1}:\frac{n\lambda}{2sin\theta_2}:\frac{n\lambda}{2sin\theta_3} = \frac{1}{sin\theta_1}:\frac{1}{sin\theta_2}:\frac{1}{sin\theta_3}$$

The intensity of diffracted beams depend ypon

i) The number of extra nuclear electrons

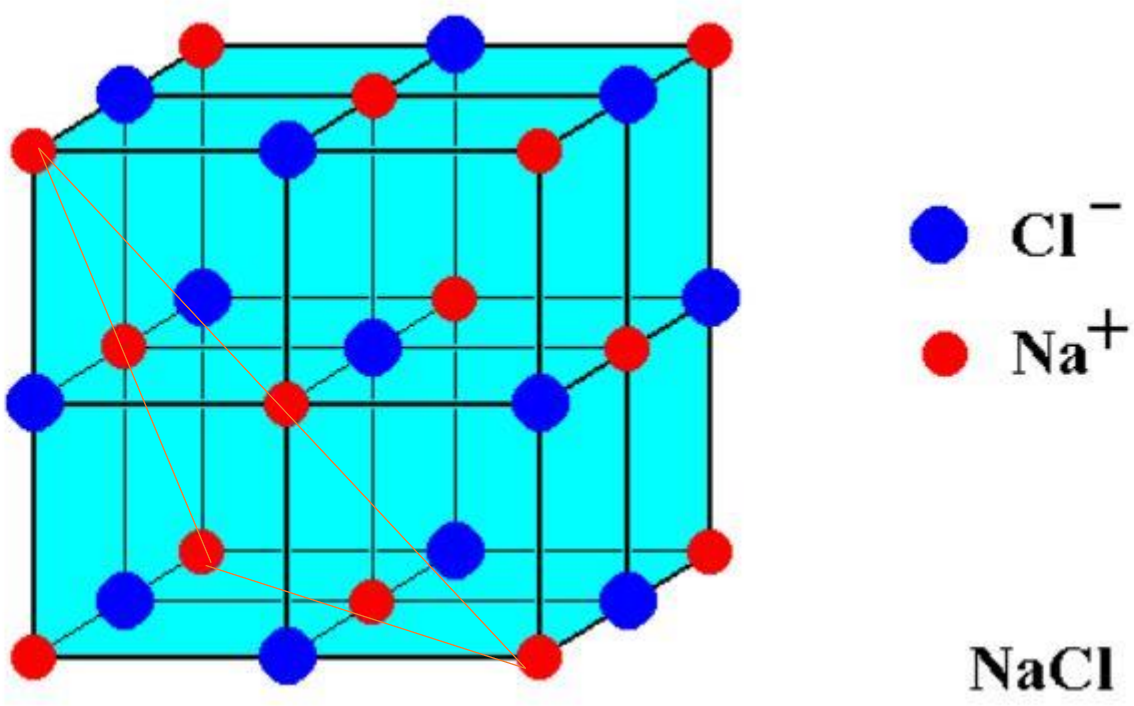
ii) Order of diffraction

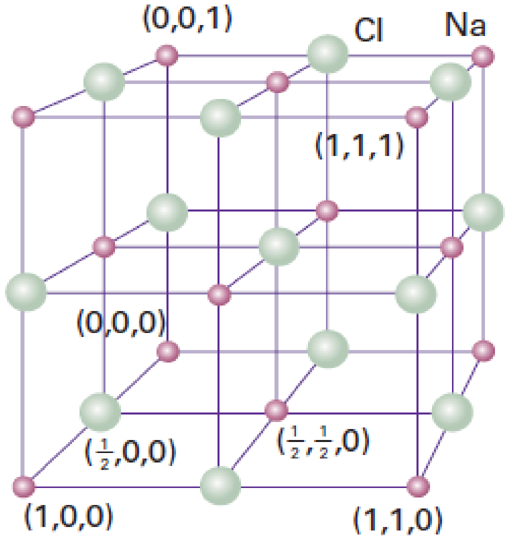
NaCl Crystal

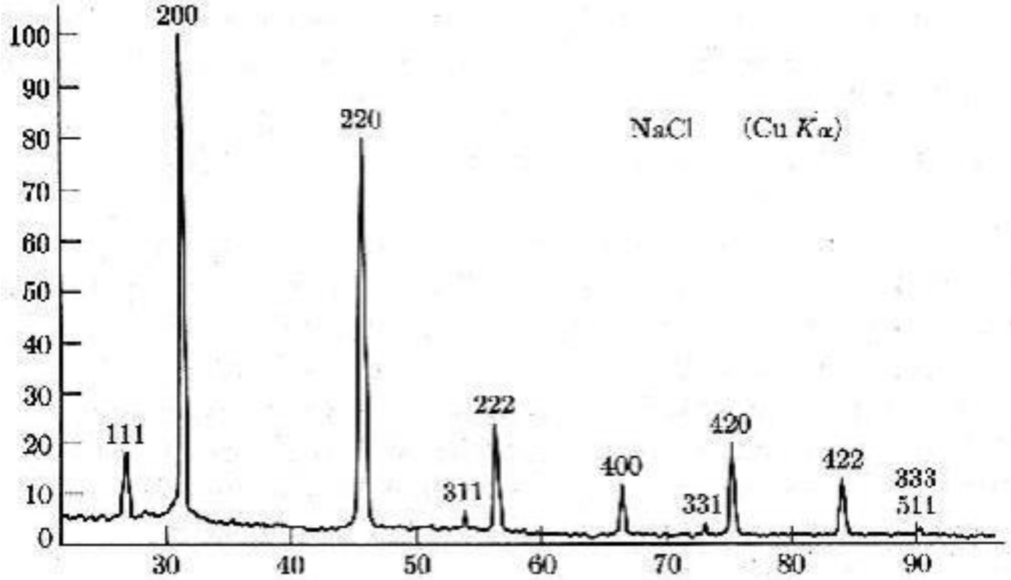
Two interpenetrating close-packed (fcc) lattices constitutes the crystal NaCl. The positions of one lattice are occupied by positive ions, while those of the other are occupied by negative ions. In this lattice there are 14 Na^+ ions and 13 Cl^- ions. However in each unit cell their Individual no is 4. Each Cl^- is surrounded by 6 Cl^- ions and 12 Na^+ ions.

For first order reflection, $\boldsymbol{d_{200}:d_{220}:d_{111} = \frac{a}{2}:\frac{a}{2\sqrt{2}}:\frac{a}{\sqrt{3}} = 1:0.707:1.154}$

Since, the intensities of diffracted beam depends on number of electrons in the outermost shell and intensities increases alternately with order for(111) plane but never can totally cancel each other. Hence the planes must alternately consists of Na^+ and Cl^- ions.






NaCl (Cu $K\alpha$)
200
220
111
311
222
400
331
420
422
333
511
0
10
20
30
40
50
60
70
80
90
100
30
40
50
60
70
80
90

KCl Crystal

KCl reveals itself as primitive cubic lattice with d=a/2 instead of face centered cubic lattice with edge length a. K^+ and Cl^- are isoelectronic. Hence they have same electrons in the outermost shell and thus same diffracting power. So diffraction from (111) plane containing only K^+ ions completely cancel that from the same plane containing only Cl^- ions. So we get diffraction from (222) plane instead of (111) plane. Thus,

$$d_{200} : d_{220} : d_{222} = \frac{a}{2} : \frac{a}{2\sqrt{2}} : \frac{a}{2\sqrt{3}} = 1 : 0.707 : 0.577$$