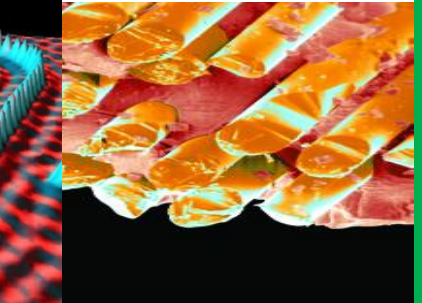
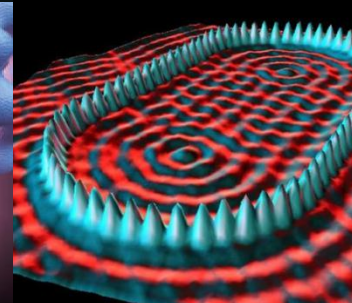
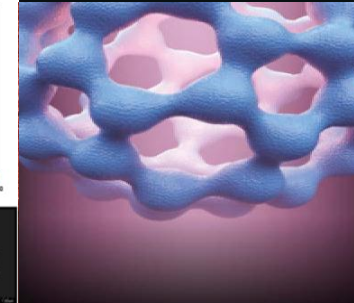
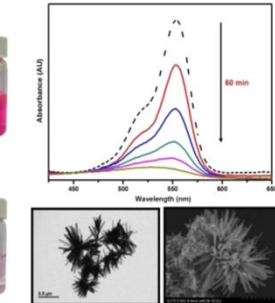
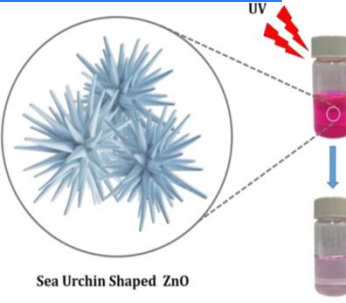
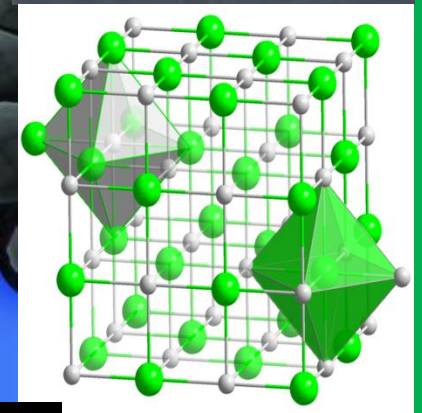
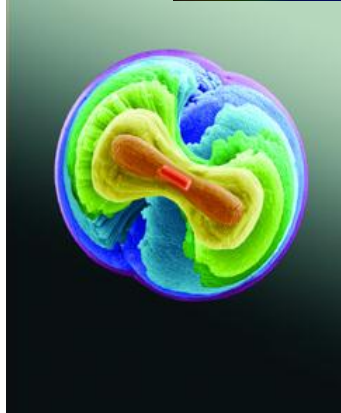
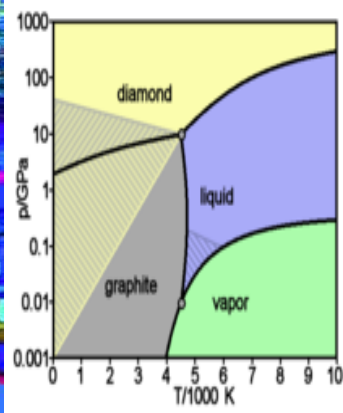
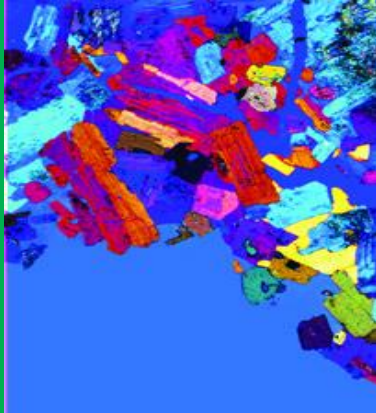
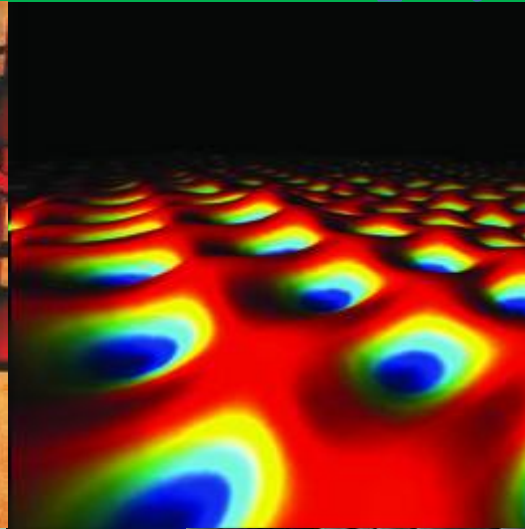
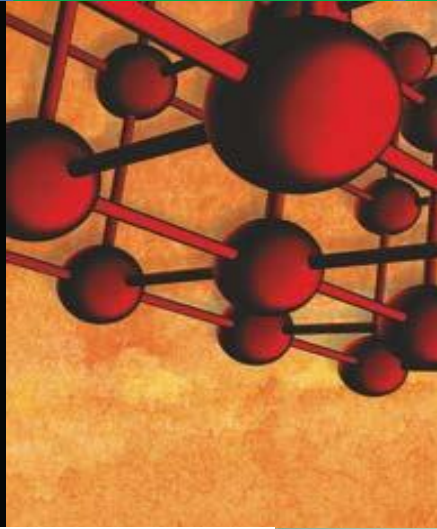
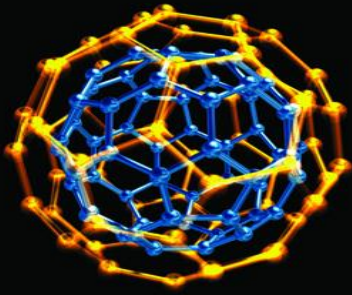


JIMMA UNIVERSITY
College of Natural science
Department of physics

Solid state physics I
Year II
Stream BSc

PRESENTED BY GIZACHEW DIGA
(MSc in solid state physics)

Various applications of solid state physics



Introduction to Solid State Physics

Chapter one

The concept of crystal structure

Introduction

Solid State Physics: definitions

- ❑ What is solid state physics?
- ❑ Why study solid state physics?
- ❑ What is condensed matter physics?
- ❑ Why study condensed matter physics?

❖ Solids are of two types

I. Crystalline solid:

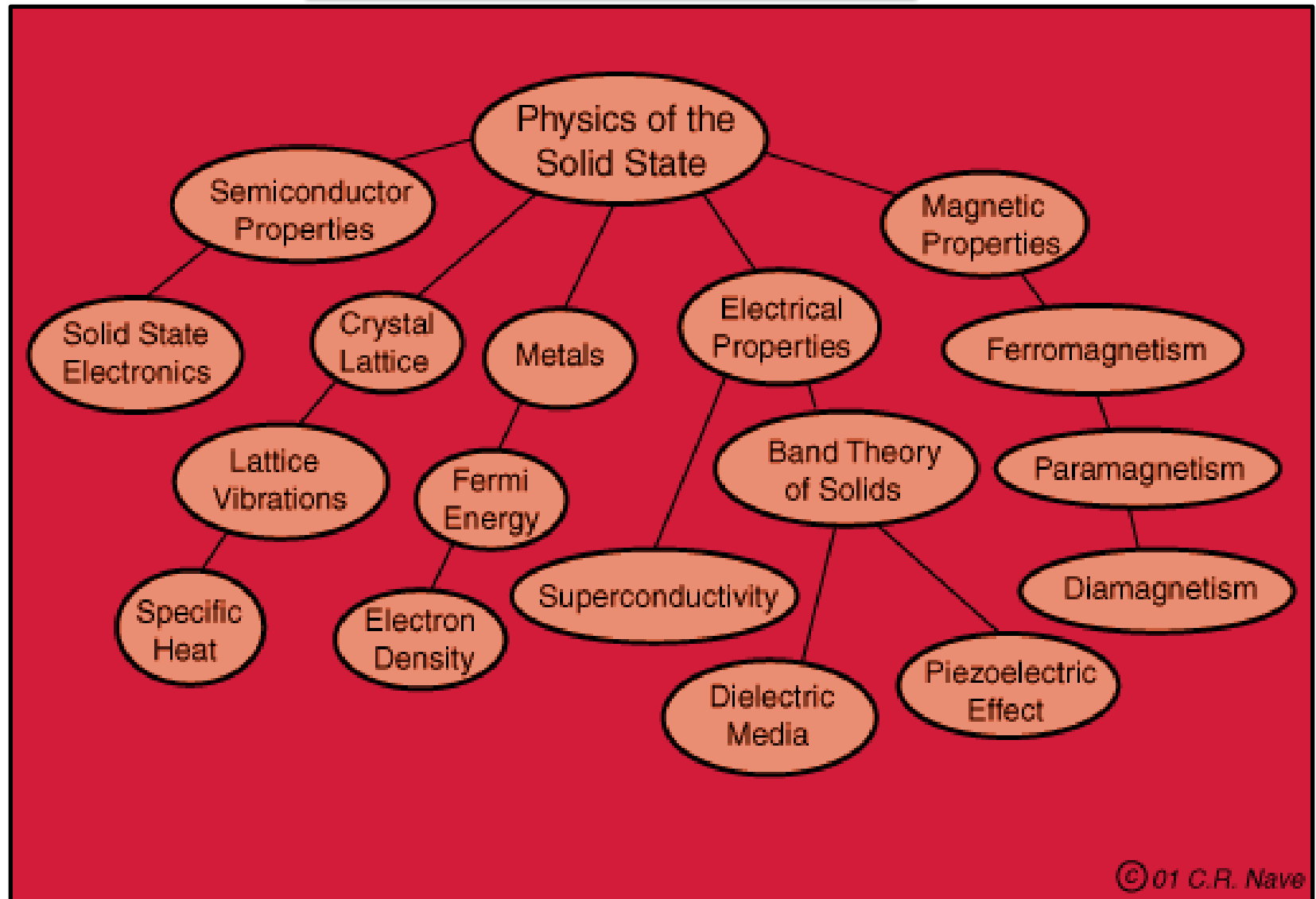
- ◆ have definite repetition pattern.
- ◆ have periodic arrangement.
- ◆ Example SiO_2 (quartz)

- ❖ The periodicity of atoms in crystalline solid can be described by a lattice.
- ❖ lattice is a network of points in space lattice.

II. Amorphous solids:

- ◆ have no definite repetition pattern
- ◆ characterized by random arrangement of atoms. E.g: SiO_2 (glass).

Solid state Physics



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Fig 1: Tree diagram of Solid State Physics

Periodic array of atoms

- ❖ A serious study of solid state physics (SSP) begin after the discovery of x-ray and theoretical calculations of properties of crystals & electrons.
- ❖ **Why crystalline solids rather than non crystalline solids?**
 - √ The electronic properties of solids are best expressed in crystals.
 - √ The properties of the most important semiconductors depend on the crystalline structure of the host).
 - √ Because electrons have short wavelength components that respond dramatically to the regular periodic atomic order of the specimen.
- ❖ Non crystalline materials, notably glasses, are important for optical propagation because light *waves* have a longer wavelength than electrons and see an average over the order, and not the less regular local order itself.

- ❖ A crystal is formed by adding atoms in a constant environment, usually in a solution.
- ❖ The first crystal discovered was **quartz grown** from silicate solution in a slow geological process.
- ❖ **The crystal form develops as identical building blocks are added continuously.**
- ❖ The building blocks here are atoms or groups of atoms.
- ❖ The crystal thus, formed is a **3D periodic array of identical building blocks**, apart from any imperfections and impurities.

Exercise

1. Discuss the influence of imperfections and impurities for crystal formations and growth?

- ❖ The original experimental evidence for the periodicity of the structure rests on the discovery by mineralogists that the index numbers that define the orientations of the faces of a crystal are exact integers.
- ❖ This evidence was supported by the discovery in **1912** of x-ray diffraction by crystals, when Laue developed the theory of x-ray diffraction by a periodic array, and his coworkers reported the first experimental observation of x-ray diffraction by crystals.
- ❖ X-rays are important for this task b/c they are waves and have a wavelength comparable with the length of a building block of the structure.
- ❖ Such analysis can also be done "With neutron diffraction and with electron diffraction, but x-rays are usually the tool of choice.

- ❑ The result of diffraction is that crystals are built of a periodic array of atoms or groups of atoms.
- ❑ With the atomic model of a crystal, physicists could think much further.
- ❑ And the *development* of quantum *theory* was of great importance to the birth of solid state physics.

EXERCISE

1. Explain the difference between crystalline & Amorphous solids.
2. Explain Amorphous solids and quantum fluids.

❖ **Amorphous \Rightarrow Non-crystalline solids**

Symmetry operations

❖ Four types of symmetry operations

⇒ Translations,

⇒ Reflections

⇒ Rotations &

⇒ Inversion.

Lattice translation vectors

- ❖ An ideal crystal is constructed by the infinite repetition of identical groups of atoms (Fig. 2).
- ❖ A group is called the **basis**.
- ❖ The set of mathematical points to which this basis is attached is called the **lattice**.
- ❖ The lattice in three dimensions may be defined by three translation vectors a_1, a_2 , **and** a_3 such that the arrangement of atoms in the crystal looks the same when viewed from the point \mathbf{r} as when viewed from every point \mathbf{r}' translated by an integral multiple of the a 's:

$$\mathbf{r}' = \mathbf{r} + u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3 \quad (1)$$

where, u_1, u_2 , and u_3 are integers.

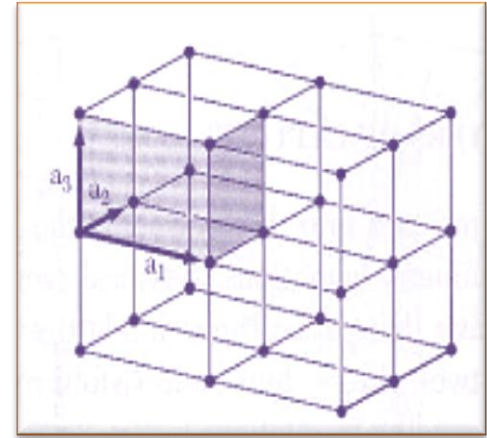
- ❖ The set of points \mathbf{r}' defined by (1) for all u_1, u_2, u_3 defines the lattice.
- ❖ The lattice is said to be **primitive** if any two points from which the atomic arrangement looks the same always satisfy (1) with a suitable choice of the integers u_1 .

Primitive translation vectors, a_i

- ❖ There is no cell of smaller volume than primitive cell,

$$V_0 = a_1 \cdot a_2 \times a_3$$

that can serve as a building block for the crystal structure.



- ❖ Primitive translation vectors define the **crystal axes**, which form three adjacent edges of the primitive parallelepiped.
- ❖ No primitive axis are often used as crystal axes when they have a simple relation to the symmetry of the structure.

Basis and crystal structure

- ❖ A crystal is made by adding a basis to every lattice point.
- ❖ Lattice points themselves are mathematical constructions.
- ❖ Every basis in a given crystal is identical to every other in composition, arrangement, and orientation.
- ✚ The number of atoms in the basis may be one, or it may be more than one.
- ✚ The position of the center of an atom j of the basis relative to the associated lattice point is

$$\mathbf{r}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3 \quad (2)$$

- ✚ We may arrange the origin, which we have called the associated lattice point, so that $0 \leq x_j, y_j, z_j \leq 1$.

Primitive lattice cell

- ❑ The parallelepiped defined by primitive axes a_1 , a_2 and a_3 is called a primitive cell (Fig. 3b). (Pag-5).
- ✓ A primitive cell *is* a type of cell or unit cell .
- ✓ A cell will fill all space by the repetition of suitable crystal translation operations.
- ✓ A primitive cell *is* a minimum volume cell.

Ways of choosing the primitive axes and primitive cell for a given lattice

- ✚ The number of atoms in a primitive cell or primitive basis is always the same for a given **crystal structure**.
- ✚ There is always one lattice point per primitive cell.
- ✚ If the primitive cell is a parallelepiped with lattice points at each of the eight corners, each lattice point is shared among eight cells, so that the total number of lattice points in the cell is one: $8 \times \frac{1}{8} = 1$.
- ✚ The volume of a parallelepiped with axes $a_1 > a_2, a_3$ is;

$$V_c = |a_1 \cdot a_2 \times a_3| \quad (3)$$

- ❖ The basis associated with a primitive cell is called a **primitive basis**.
- ❖ No basis contains fewer atoms than a primitive basis contains.
- ❖ Another way of choosing a primitive cell is known to physicists as a **Wigner-Seitz cell**.

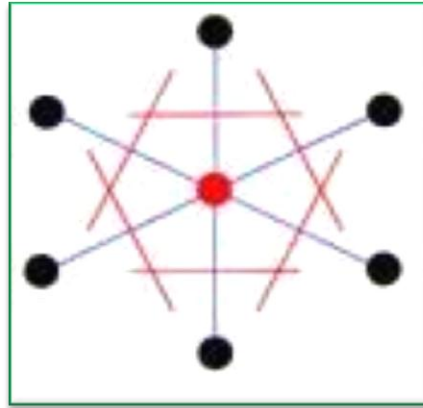


Fig 4: Wigner Seitz Cell

Steps for the construction of Wigner Seitz Cell

- ❖ Draw lines to connect a given lattice point to all nearby lattice points
- ❖ At the midpoint and normal to these lines draw new lines or planes
- ❖ The smallest volume enclosed in this way is **Wigner- Seitz primitive cell**.

FUNDAMENTAL TYPES OF LATTICES

- ❖ Crystal lattices can be carried or mapped into themselves by the lattice translations, T and by various other symmetry operations.
- ❖ A typical symmetry operation is that of rotation about an axis that passes through a lattice point.
- ❖ Lattices can be found such that one, two, three, four, and six fold rotation axes carry the lattice into itself, corresponding to rotations by 2π , $\frac{2\pi}{2}$, $\frac{2\pi}{3}$, $\frac{2\pi}{4}$, and $\frac{2\pi}{6}$ radians and by integral multiples of these rotations.
- ❖ The rotation *axes* are denoted by the symbols 1, 2, 3, 4, and 6.
- ❖ We cannot find a lattice that goes into itself under other rotations, such as by $\frac{2\pi}{7}$ radians or $\frac{2\pi}{5}$ radians.
- ❖ A single molecule properly designed can have any degree of rotational symmetry, but an infinite periodic lattice cannot.
- ❖ A crystal can be formed from molecules that individually have a fivefold rotation axis, but we should not expect the lattice to have a fivefold rotation axis.

- ❖ By lattice point group we mean the collection of symmetry operations which, applied about a lattice point, carry the lattice into itself.
- ❖ The possible rotations have been listed.
- ❖ We can have mirror reflections m about a plane through a lattice point.
- ❖ The inversion operation is composed of a rotation of π followed by reflection in a plane normal to the rotation axis; the total effect is to replace r by $-r$.

Two-Dimensional Lattice Types

- ❖ Oblique lattice is a general lattice that is invariant only under rotation of π and 2π about any lattice point.
- ❖ But special lattices of the oblique type can be invariant under rotation of $\frac{2\pi}{3}$, $\frac{2\pi}{4}$, & $\frac{2\pi}{6}$, or under mirror reflection.
- ❖ We must impose restrictive conditions on a_1 and a_2 if we want to construct a lattice that will be invariant under one *or* more of these new operations.
- ❖ There are four distinct types of restriction, and each leads to what we may call a special lattice type.
- ❖ Thus there are five distinct lattice types in two dimensions, the oblique Lattice and the four special lattices shown in Fig. 7.
- ❖ **Bravais lattice** is the common phrase for a distinct lattice type; we say that there are five Bravais lattices in two dimensions.

2D Bravais lattice

❖ In 2D, there are 5 lattice

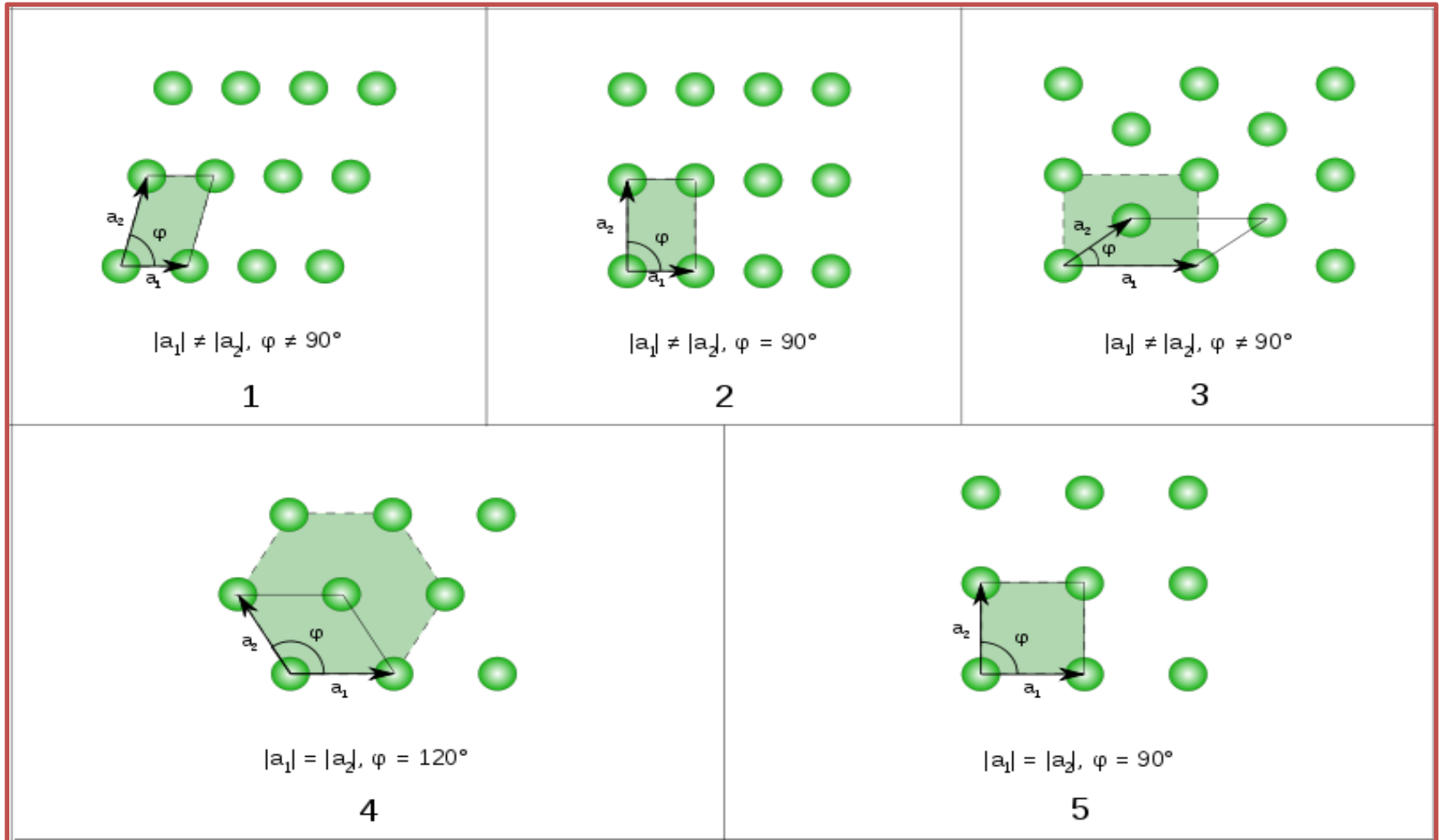


Figure -7

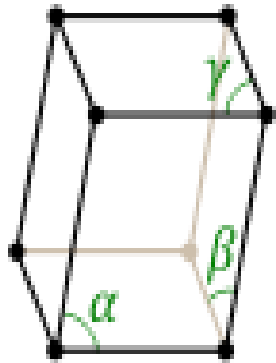
Three dimensional lattice types

- ❖ The point symmetry groups in three dimensions require the 14 different lattice types.
- ❖ The general lattice is triclinic, and there are 13 special lattices.
- ❖ These are grouped for convenience into systems classified according to seven types of cells, which are triclinic, monoclinic, orthorhombic, tetragonal, cubic, trigonal, and hexagonal.
- ❖ The division into systems is expressed in the table in terms of the axial relations that describe the cells.
- ❖ The cells in Fig. 8 are conventional cells: of these only the Sc is a primitive cell.
- ❖ Often a non primitive cell has a more obvious relation with the point symmetry operations than has a primitive cell.
- ❖ There are three lattices in the cubic system: the simple cubic (Sc) lattice, the body-centered cubic (bcc) lattice, and the face-centered cubic (fcc) lattice.

3-D lattice types

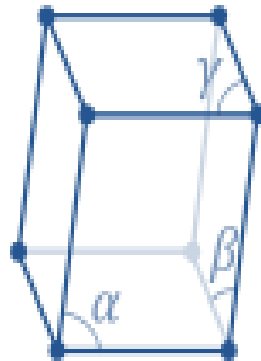
Triclinic

$$\alpha, \beta, \gamma \neq 90^\circ$$



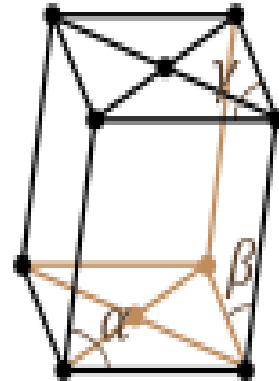
Monoclinic

$$\alpha \neq 90^\circ$$
$$\beta, \gamma = 90^\circ$$



Simple

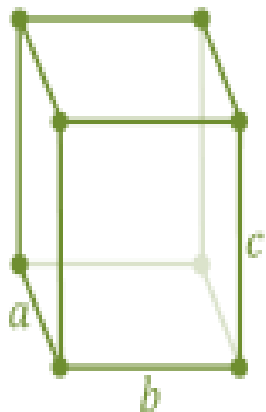
$$\alpha \neq 90^\circ$$
$$\beta, \gamma = 90^\circ$$



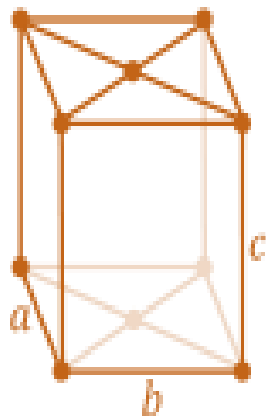
Base-Centered

Orthorhombic

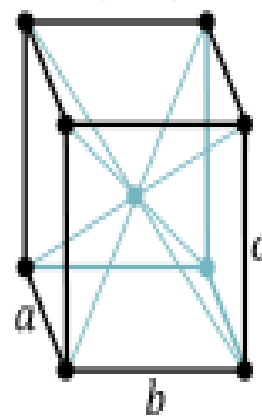
$$a \neq b \neq c$$



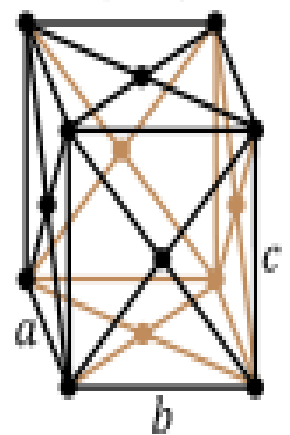
$$a \neq b \neq c$$



$$a \neq b \neq c$$

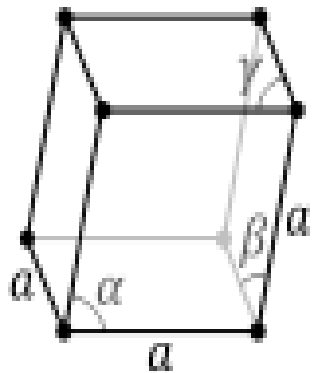


$$a \neq b \neq c$$

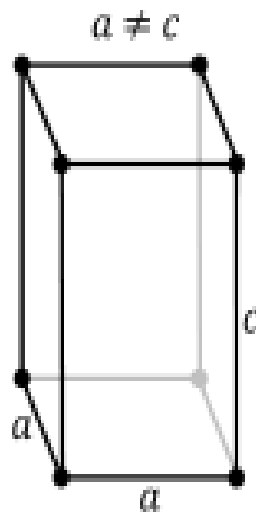


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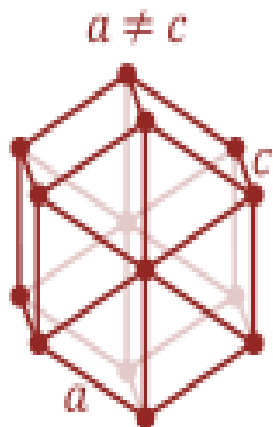
$\alpha, \beta, \gamma \neq 90^\circ$



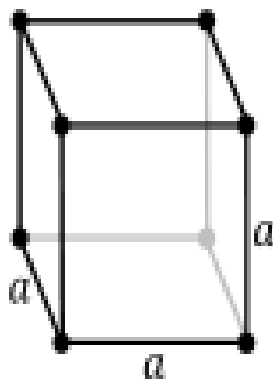
Hexagonal



Simple

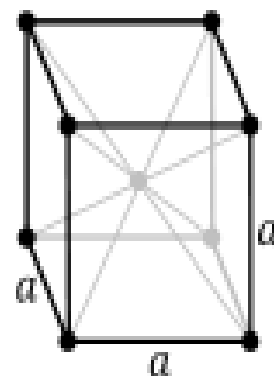


Cubic

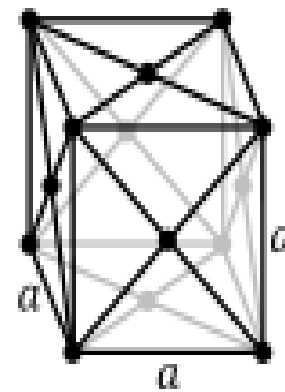


Simple

Body-Centered



Body-Centered



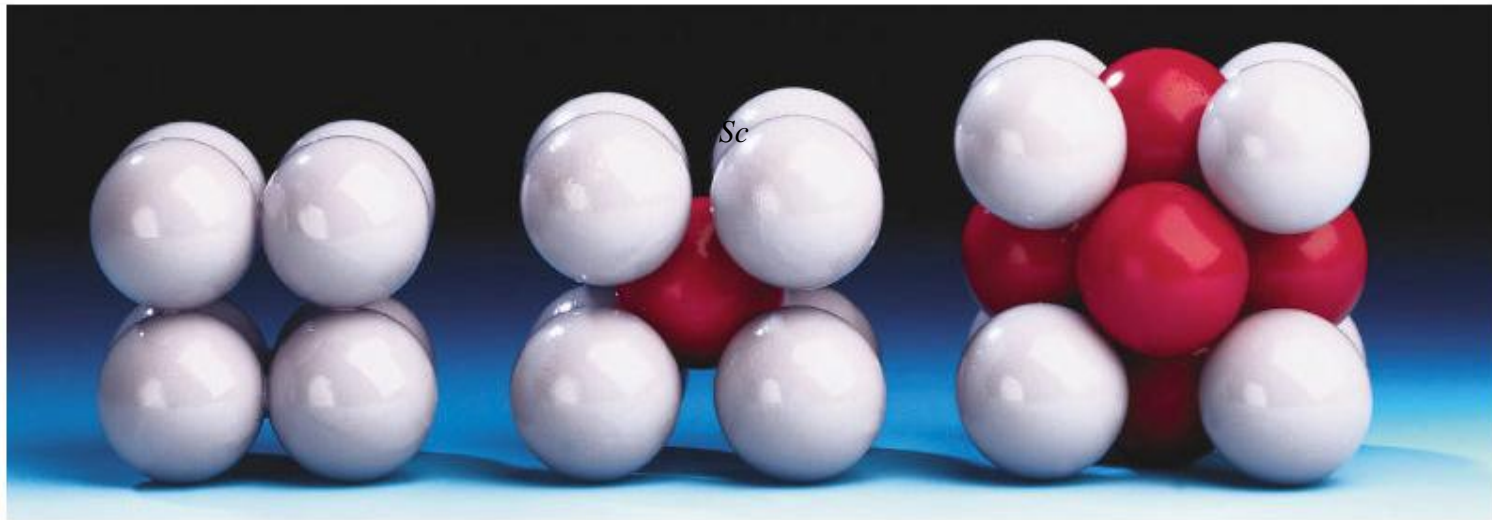
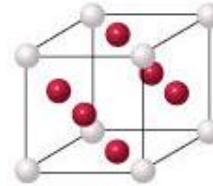
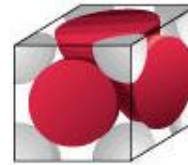
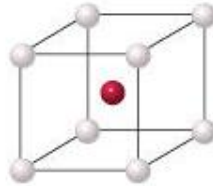
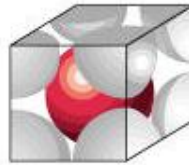
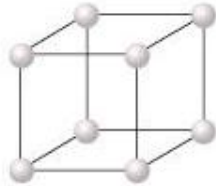
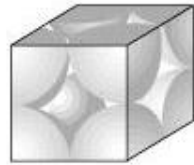
Face-Centered

The Six Crystal axis

System	Type	Edge - Angle Relations	Symmetry
Triclinic	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	$\bar{1}$
Monoclinic	P (b = twofold axis) C	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ \neq \beta$	2/m
	P (c = two fold axis) C	$a \neq b \neq c$ $\alpha \neq \beta = 90^\circ \neq \gamma$	
Orthorhombic	P C (or A, B) b F	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	mmm
Tetragonal	P b	$a_1 = a_2 \neq c$ $\alpha = \beta = \gamma = 90^\circ$	4/mmm
Hexagonal	R P	$a_1 = a_2 \neq c$ $\alpha = \beta = 90^\circ, \gamma = 120^\circ$	m 6/mmm
Cubic	P b F	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma = 90^\circ$	m3m

P = Primitive F = Face Centered b = Body Centered C = Centered on opposing faces

Cubic crystal systems



(a)

Sc

(b)

Bcc

(c)

Fcc

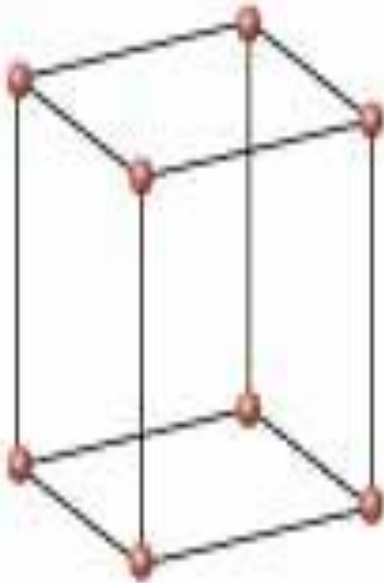
Coordination Number

❖ It is equal to the number of nearest neighbor that surrounds each atom.

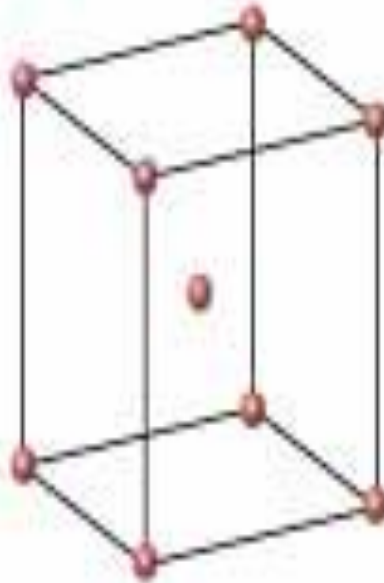
◆ Simple Cubic - 6

◆ Body Centered Cubic – 8

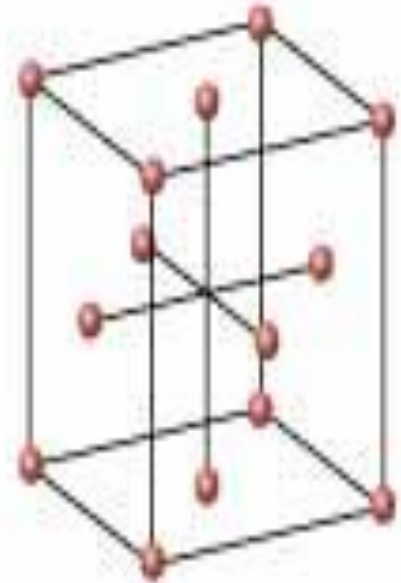
◆ Face Centered Cubic - 12



Primitive cubic



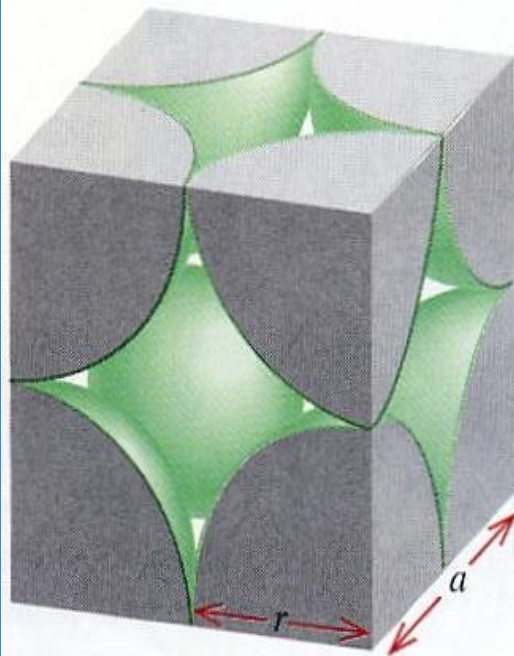
Body-centered cubic



Face-centered cubic

Cubic crystal structures

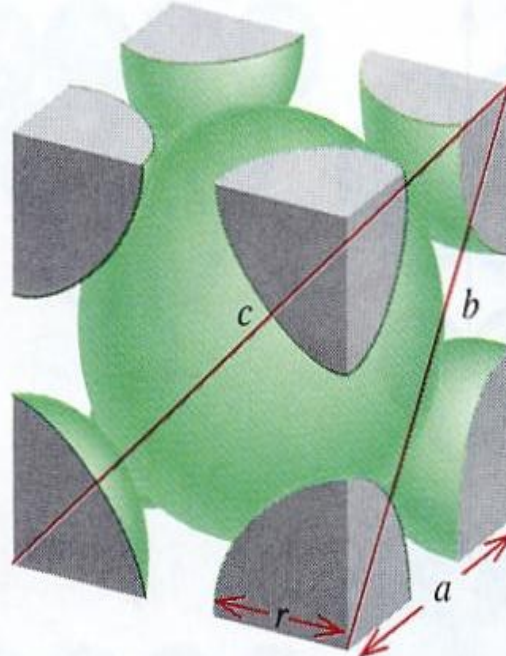
Sc



scc

$$a = 2r$$

Bcc



bcc

$$b^2 = a^2 + a^2$$

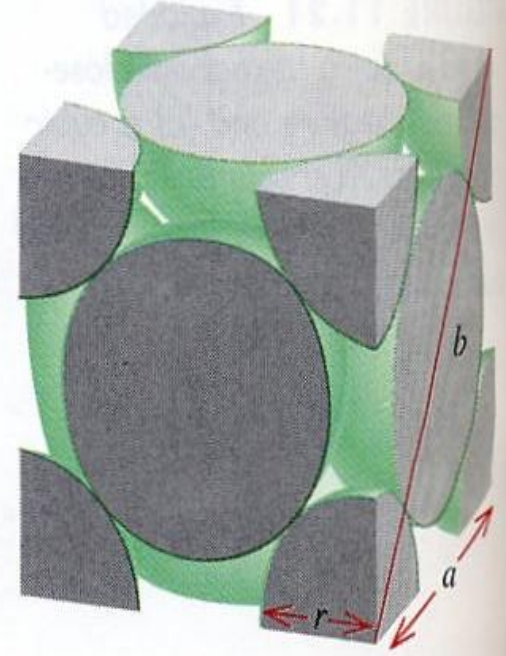
$$c^2 = a^2 + b^2$$

$$= 3a^2$$

$$c = \sqrt{3}a = 4r$$

$$a = \frac{4r}{\sqrt{3}}$$

Fcc



fcc

$$b = 4r$$

$$b^2 = a^2 + a^2$$

$$16r^2 = 2a^2$$

$$a = \sqrt{8}r$$

Figure 8 The relationship between the edge length (a) and radius (r) of atoms in the simple cubic cell, body-centered cubic cell, and face-centered cubic cell.

Atomic packing factor

❑ The packing fraction is the maximum proportion of the available volume *that* can be filled with hard spheres.

✚ The atomic packing factor is given by $= \frac{\text{volume of atom in a unit cell}}{\text{volume of the unit cell}}$

✚ For simple cubic crystal is given

$$\text{A.p.f} = 1 \frac{\left(\frac{4\pi}{3}r^3\right)}{a^3} = 1 \frac{\left(\frac{4\pi}{3}\left(\frac{a}{2}\right)^3\right)}{a^3} = \frac{\pi}{6} = \mathbf{0.524} \quad (4)$$

✚ For body centered cubic

$$\text{A.p.f} = 2 \frac{\left(\frac{4\pi}{3}r^3\right)}{a^3} = 2 \frac{\left(\frac{4\pi}{3}\left(\frac{\sqrt{3}}{4}a\right)^3\right)}{a^3} = \frac{\sqrt{3}\pi}{8} = \mathbf{0.680} \quad (5)$$

✚ For face centered cubic

$$\text{A.p.f} = 4 \frac{\left(\frac{4\pi}{3}r^3\right)}{a^3} = 4 \frac{\left(\frac{4\pi}{3}\left(\frac{\sqrt{2}}{4}a\right)^3\right)}{a^3} = \frac{\sqrt{2}\pi}{6} = \mathbf{0.740} \quad (6)$$

Figure 9 Body-centered cubic lattice, showing a primitive cell.

- ❖ The primitive cell shown is a rhombohedron of edge $\frac{1}{2}\sqrt{3}a$, and the angle between adjacent edges is $109^\circ 28'$.

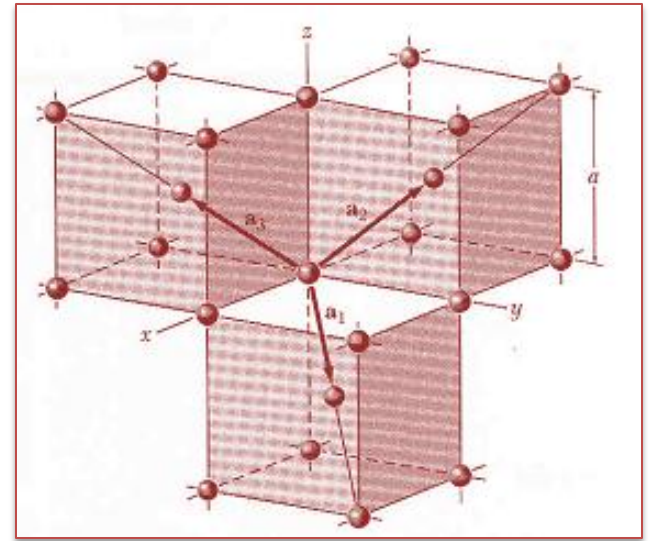
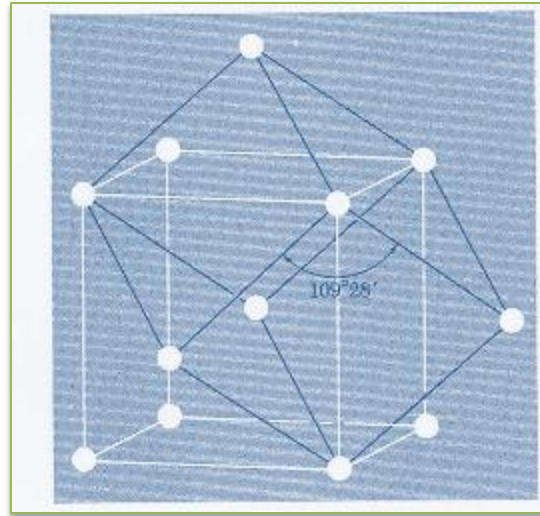


Figure 10 Primitive translation vectors of the body centered cubic lattice; these vectors connect the lattice point at the origin to lattice points at the body centers. The primitive cell is obtained on completing the rhombohedron.

- ❖ In terms of the cube edge a , the primitive translation vectors are

$$\mathbf{a}_1 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z}) \quad (7a)$$

$$\mathbf{a}_2 = \frac{a}{2}(-\hat{x} + \hat{y} + \hat{z}) \quad (7b)$$

$$\mathbf{a}_3 = \frac{a}{2}(\hat{x} - \hat{y} + \hat{z}) \quad (7c)$$

Here \hat{x} , \hat{y} , and \hat{z} are the Cartesian unit vectors.

- ❖ The characteristics of the three cubic lattices are summarized in Table 2.
- ❖ A primitive cell of the bcc lattice is shown in Fig. 9, and the primitive translation vectors are shown in Fig. 10.
- ❖ The primitive translation vectors of the fcc lattice are shown in Fig. 11.
- ❖ Primitive cells contain only **one lattice point**.
- ❖ However, the conventional bcc cell contains two lattice points, and the fcc *cell* contains four lattice points.

Characteristics of cubic systems

№		Simple cubic	Body centered	Face centered
1	Volume of conventional cell	a^3	a^3	a^3
2	Lattice points per cell	1	2	4
3	Volume of primitive cell	a^3	$\frac{1}{2a^3}$	$\frac{1}{4a^3}$
4	Lattice points per cell	$\frac{1}{a^3}$	$\frac{2}{a^3}$	$\frac{4}{a^3}$
5	Coordination number	6	8	12
6	Nearest neighbor distance	a	$\frac{\sqrt{3}a}{2} = 0.866$	$\frac{a}{\sqrt{2}} = 0.707$
7	№ of next nearest neighbor	12	6	6
8	Next neighbor distance	$\sqrt{2}a$	a	a
9	Packing fraction	$\frac{1}{6}\pi = 0.54$	$\frac{\sqrt{3}\pi}{8} = 0.68$	$\frac{\sqrt{2}}{6}\pi = 0.74$

The Nearest distance for Sc, Bcc & Fcc

❖ For sc the nearest distance is a .

❖ For bcc the nearest distance is

$$r = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \frac{\sqrt{3}}{2} a = 0.866a$$

❖ For Fcc, the nearest distance is

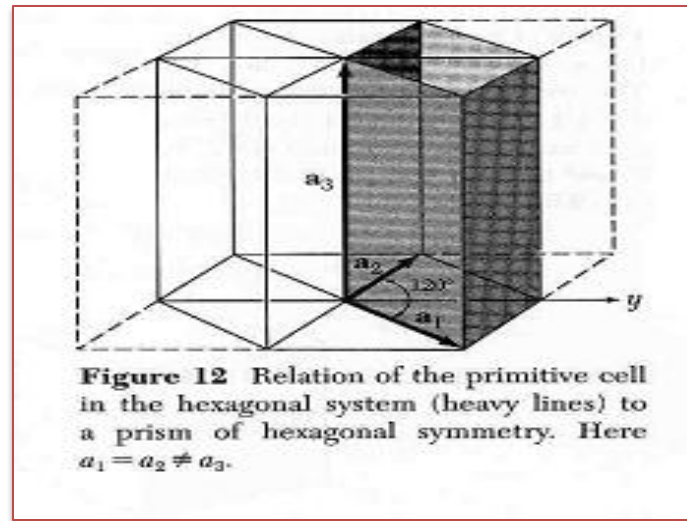
$$r = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + (0)^2} = \frac{\sqrt{2}}{2} a = 0.707a$$

$$a_1 = \frac{1}{2}a(\hat{x} + \hat{y})$$

$$a_2 = \frac{1}{2}a(\hat{y} + \hat{z})$$

$$a_3 = \frac{1}{2}a(\hat{z} + \hat{x})$$

The angles between the axes are 120° .



- ❖ The position of a point in a cell is specified by (2) in terms of the atomic coordinates x, y, z .
- ❖ Here each coordinate is a fraction of the axial length $a_1 > a_2 > a_3$ in the direction of the coordinate axis, with the origin taken at *one* corner of the cell.
- ❖ Thus the coordinates of the body center of a cell are $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ and the face centers include $\frac{1}{2} \frac{1}{2} 0, 0 \frac{1}{2} \frac{1}{2}$ and $\frac{1}{2} 0 \frac{1}{2}$.
- ❖ In the hexagonal system the primitive cell is a right prism based on a rhombus with an included angle of 120° .
- ❖ Figure 12 shows the relationship of the rhombic cell to a hexagonal prism.

Index system for crystal planes

- ❖ The orientation of a crystal plane is determined by 3 - points in the plane, which are not collinear.
- ❖ If each point lay on a different crystal axis, the plane could be specified by giving the coordinates of the points in terms of the lattice constants a_1 , a_2 , a_3 .
- ❖ However, it turns out to be more useful for structure analysis to specify the orientation of a plane by the indices determined by the following rules (Fig. 13).
- ❖ Find the intercepts on the axes in terms of the lattice constants a_1 , a_2 , a_3 .
- ❖ The axes may be those of a **primitive** or **non primitive** cell.

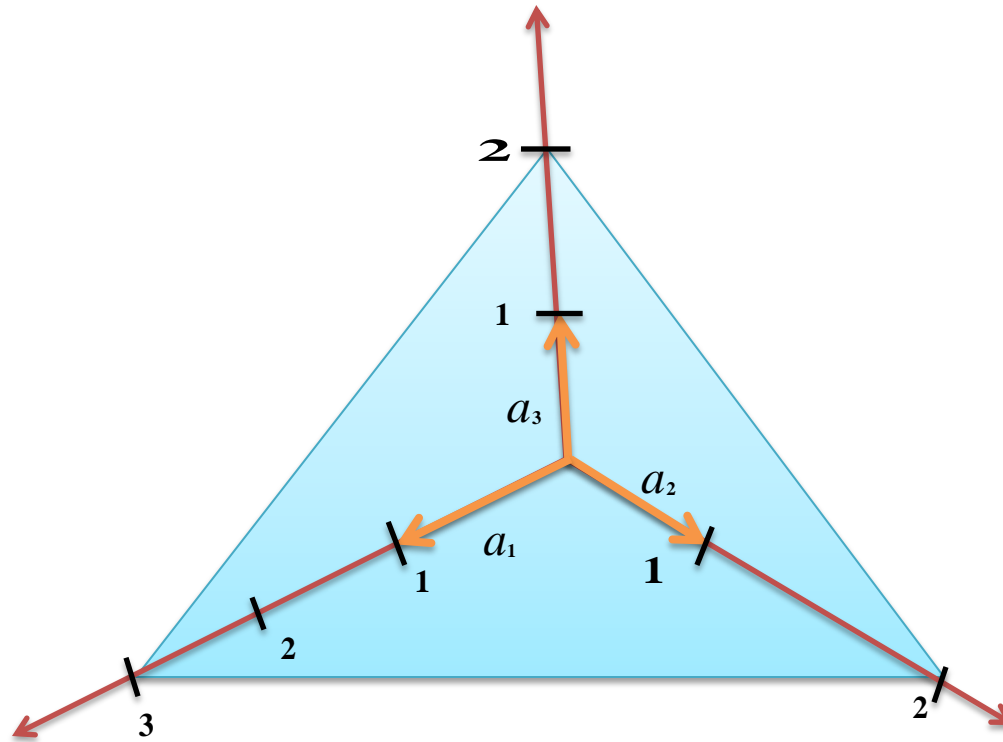


Figure 13. This plane intercepts the a_1, a_2, a_3 axes at the $3a_1, 2a_2, 2a_3$.

The reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$.

The smallest three integers having the same ratio are 2, 3, 3, and

thus, the indices of the plane are (233).

❖ Take the reciprocal of these numbers and then reduce to three integers having the same ratio, usually the three small integers, the result enclosed in parenthesis, (hkl) are the index of the plane.

- ❖ For the plane whose intercepts are 4, 1, 2, the reciprocals are $\frac{1}{4}$, **1**, and $\frac{1}{2}$.
- ❖ The smallest three integers having the same ratio are (142).
- ❖ For an intercepts at infinity, the corresponding index is zero.
- ❖ The indices of some important planes in a cubic crystal are illustrated by Fig. **14**.
- ❖ The indices (hkl) may denote a **single plane** or a **set of parallel planes**.
- ❖ If a plane cuts an axis on the negative side of the origin, the corresponding index is negative, indicated by placing a minus sign above the index: ($h\hat{k}l$).
- ❖ The cube faces of a cubic crystal are (100), (010), (001), ($\bar{1}00$), ($0\bar{1}0$), and ($00\bar{1}$).
- ❖ Planes equivalent by symmetry may be denoted by curly brackets (braces) around indices; the set of cube faces is {100}.

- ❖ When we speak of the (200) plane we mean a plane parallel to (100) but cutting the a_1 axis at $\frac{1}{2}a$.
- ❖ The indices $[uvw]$ of a direction in a crystal are the set of the smallest integers that have the ratio of the components of a vector in the desired direction, defined to the axes.
- ❖ The a_1 axis is the $[100]$ direction; the $-a_2$ axis is the $[0\bar{1}0]$ direction.
- ❖ In cubic crystals the direction $[hkl]$ is perpendicular to a plane (hkl) having the same indices, but this is not generally true in other crystal systems.

➤ **h, k, l are Miller indices**

➤ **a, b, c are unit cell distances**

➤ **α, β, γ are angles between the lattice directions.**

❑ Complexity of calculations is dependent on the symmetry of the crystal system.

Table 1-2. Values of the Interplanar Spacing (d_{hkl}) in the Six Crystal Systems

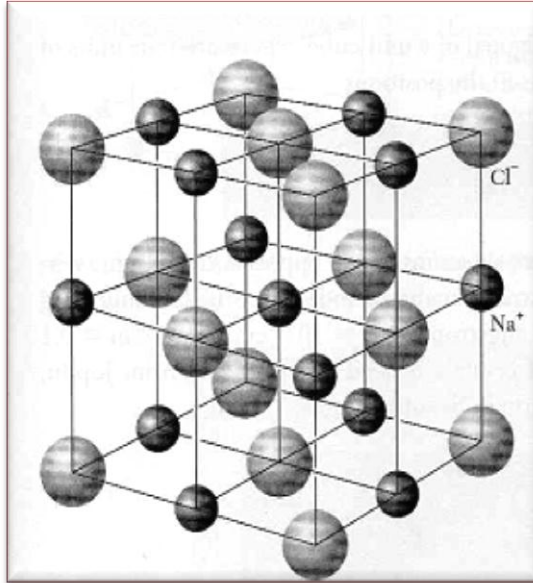
System	d_{hkl}
Cubic	$\left[\frac{1}{a^2} (h^2 + k^2 + l^2) \right]^{-1/2}$
Tetragonal	$\left[\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right]^{-1/2}$
Orthorhombic	$\left[\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right]^{-1/2}$
Hexagonal	$\left\{ \left[\frac{4}{3a^2} (h^2 + hk + k^2) + \frac{l^2}{c^2} \right]^{-1/2} \right.$ hexagonal indexing
	$\left. \left[\frac{1}{a^2} \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + lh)(\cos^2 \alpha - \cos \alpha)}{1 - 2 \cos^3 \alpha + 3 \cos^2 \alpha} \right]^{-1/2} \right.$ rhombohedral indexing
Monoclinic	$\left[\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} + \frac{k^2}{b^2} \right]^{-1/2}$
Triclinic	$\left[\frac{h^2}{a^2} \sin^2 \alpha + \frac{k^2}{b^2} \sin^2 \beta + \frac{l^2}{c^2} \sin^2 \gamma + \frac{2hk}{ab} (\cos \alpha \cos \beta - \cos \gamma) \right. \\ \left. + \frac{2kl}{bc} (\cos \beta \cos \gamma - \cos \alpha) + \frac{2lh}{ca} (\cos \gamma \cos \alpha - \cos \beta) \right. \\ \left. \frac{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma}{1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma} \right]^{-1/2}$

Miller Index

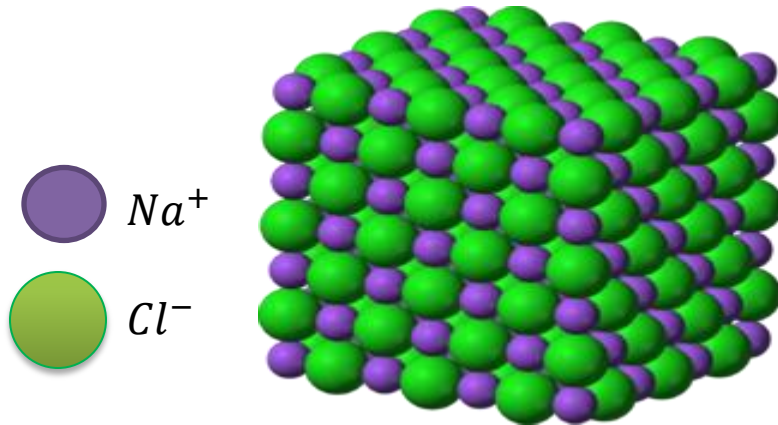
- Miller indices describes the directions & planes.
- The directions and planes could be in lattice or in crystals.
 - ♥ In 1-D ; there is one index
 - ♥ In 2-D; there are two indices
 - ♥ In 3-D; there are three indices
- Note: In the case of miller- Bravais indices for **hexagonal** a third index is added to three redundant index (hki).
- ❖ Where, **i** – is the redundant index.
- ❖ The **redundant index** is added to show the symmetry of the structure.

Simple Crystal Structures

- ❖ We focus simple crystal structures such as NaCl, CsCl, HcP, Diamond, & cubic ZnS structures.



- ✓ Na^+ ions form a face-centered cubic lattice.
- ✓ Cl^- ions are located between each two neighboring Na^+ ions. Or,
- ✓ Cl^- ions form a face-centered cubic lattice
- ✓ Na^+ ions are located between each two neighboring Cl^- ions.

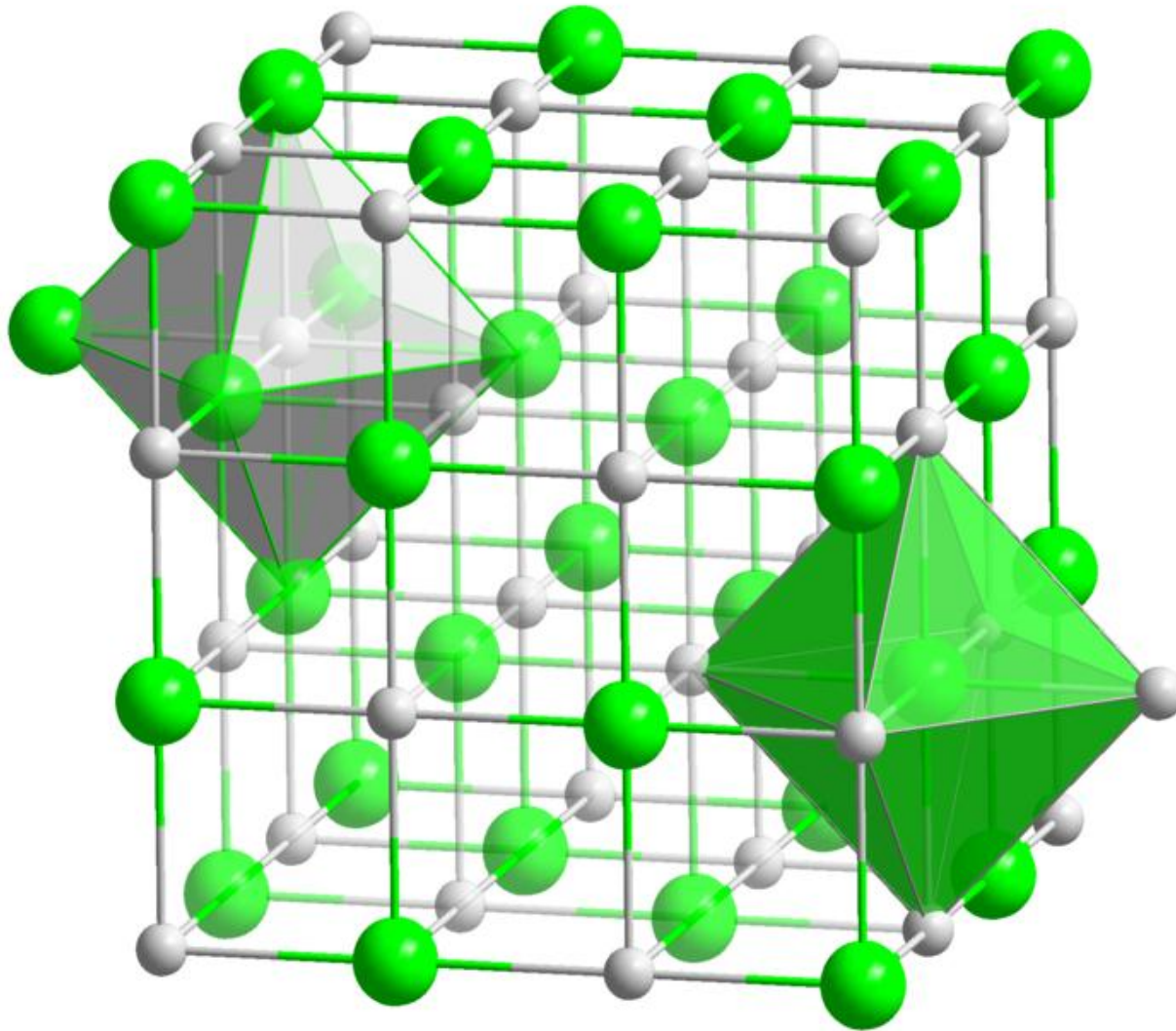


Cl:	000;	$\frac{1}{2}\frac{1}{2}0$,	$\frac{1}{2}0\frac{1}{2}$	$0\frac{1}{2}\frac{1}{2}$
Na:	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$,	$00\frac{1}{2}$;	$0\frac{1}{2}0$;	$\frac{1}{2}00$

NaCl structure

- ❖ Fig -16: Models of NaCl. The Na ions are smaller than chlorine ions. (Courtesy of A. N. Holden and P. Singer.)

NaCl primitive cell



Primitive
cell

NaCl

NaCl

Group → ↓ Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
Lanthanides				57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides				89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- ❖ The lattice is face-centered cubic; the basis consists of one Na^+ ions and one Cl^- ion separated by one-half the body diagonal of a unit cube.
- ❖ There are four units of NaCl in each unit cube, with atoms in the positions.

$$\begin{array}{l} \text{Cl: } 0\ 0\ 0, \quad \frac{1}{2}\frac{1}{2}\frac{1}{2}, \quad \frac{1}{2}0\frac{1}{2}, \quad 0\frac{1}{2}\frac{1}{2} \\ \text{Na: } \frac{1}{2}\frac{1}{2}\frac{1}{2}, \quad 0\ 0\ \frac{1}{2}; \quad 0\frac{1}{2}\ 0; \quad \frac{1}{2}\ 0\ 0 \end{array}$$

- ❖ Each atom has as nearest neighbors *six atoms of the opposite* kind.
- ❖ Representative crystals having the NaCl arrangement include those in the following table.
- ❖ The cube edge a is *given in angstrom*; $1\text{\AA} = 10^{-8}\text{cm} = 10^{-10}\text{m} = 0.1\text{nm}$.

(See for PbS)

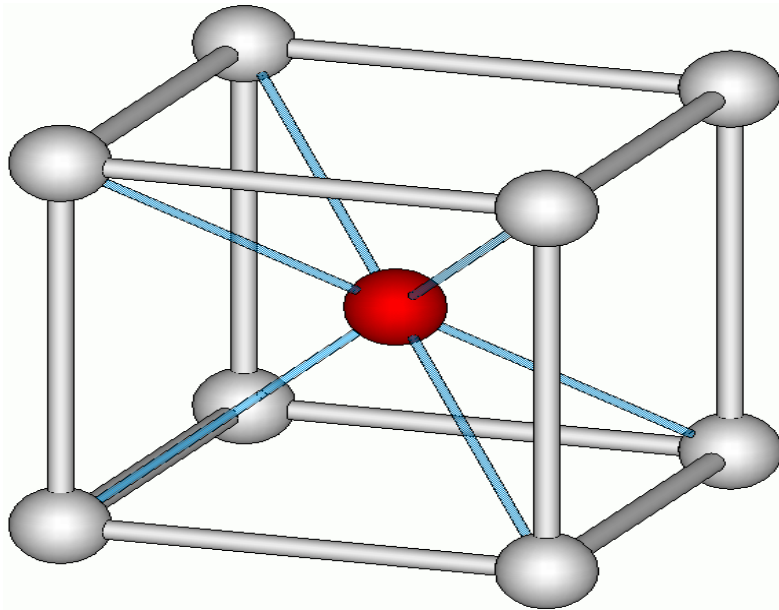
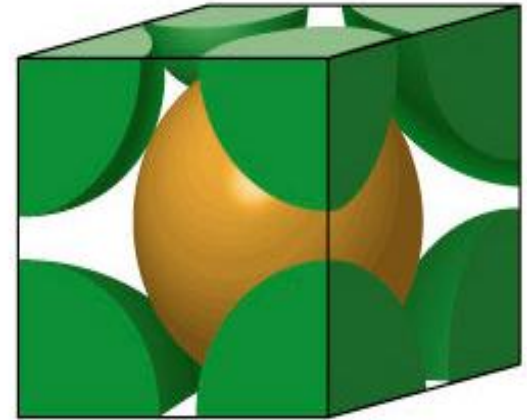
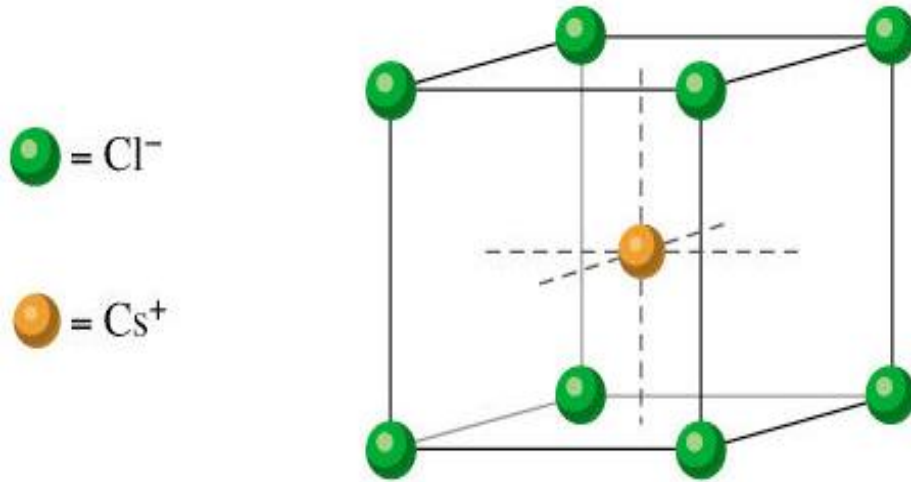
Crystal	a	crystal	a
LiH	4.08Å	AgBr	5.77Å
MgO	4.20Å	PbS	5.92Å
MnO	4.43Å	KCl	6.29Å
NaCl	4.63Å	KBr	6.59Å

Cesium Chloride Structure

- ❖ The cesium chloride structure is shown in Fig. 18.
- ❖ There is one molecule per primitive cell, with atoms at the corners 000 and body centered *positions* $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ of the simple cubic space lattice.
- ❖ Each atom may be viewed as at the center of a cube of atoms of the opposite kind, so that the number of nearest neighbors or coordination number is eight.

Crystal	a	crystal	a
BeCu	2.70Å	LiHg	3.29Å
AlNi	2.88Å	NH ₄ Cl	3.87Å
CuZn(β-brass)	2.94Å	TlBr	3.97Å
CuPb	2.99Å	CsCl	4.11Å
AgMg	2.38Å	TlI	4.20Å

CsCl structure



❖ **Simple cubic lattice**

Cs^+ ions form a cubic lattice

Cl^- ions are located at the center of each cube

❖ Equivalently, we can say that

Cl^- ions form a cubic lattice

Cs^+ ions are located at the center of each cube

Coordinates:

Cs: 000

Cl: $\frac{1}{2} \frac{1}{2} \frac{1}{2}$

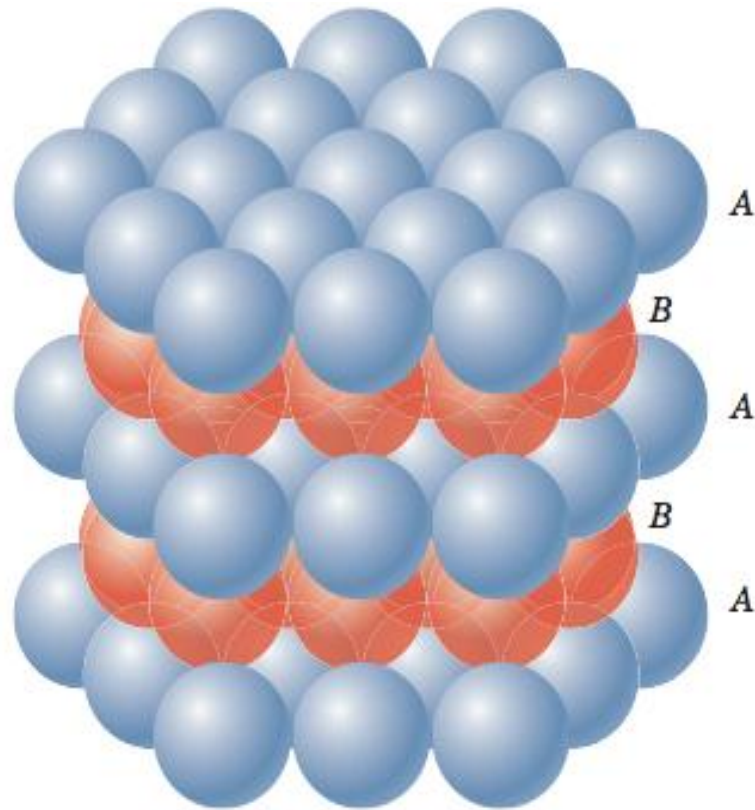
❖ Notice that this is a simple cubic lattice.

Fig:18

Hexagonal close packed structure

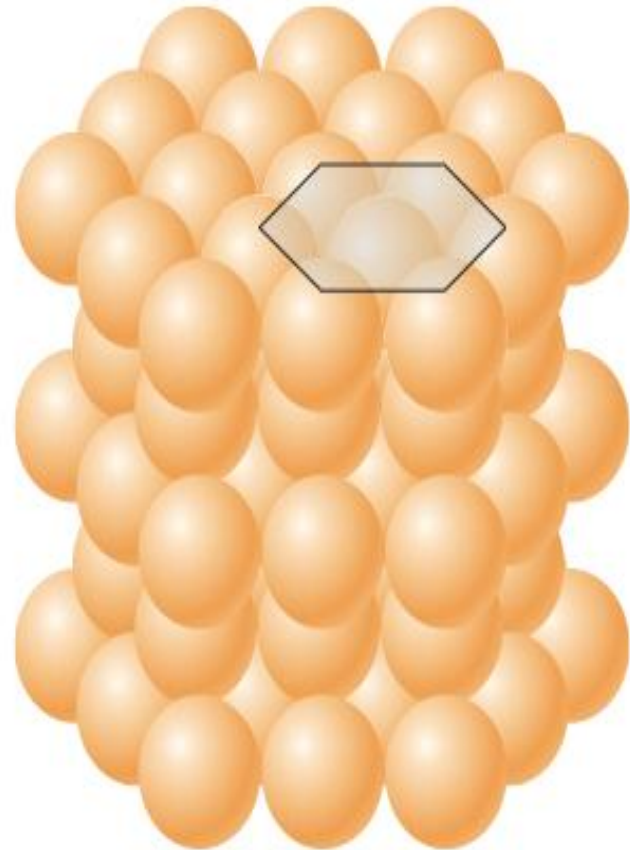
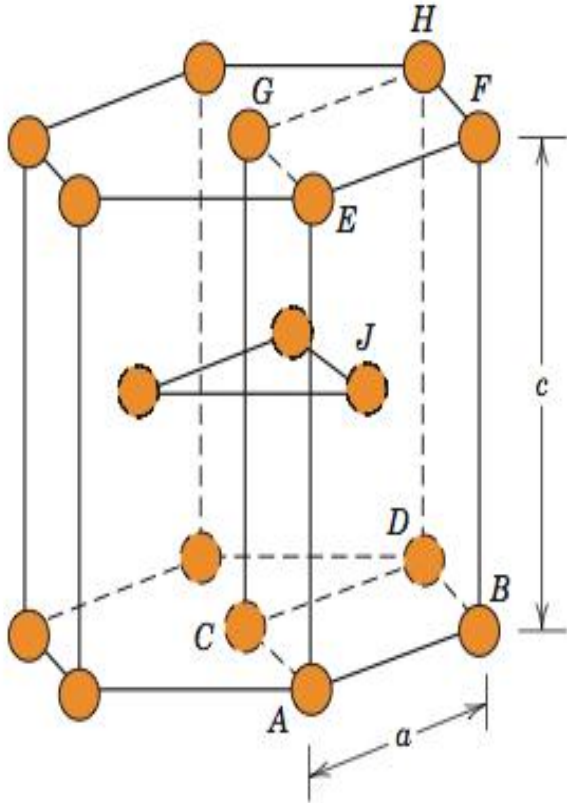
- ❖ There are an infinite number of ways of arranging identical spheres in a regular array that maximizes the packing fraction (Fig. 19) .
- ❖ One is the face centered cubic structure; another is the hexagonal close-packed structure (Fig. 20).
- ❖ The fraction of the total volume occupied by the spheres is 0.74 for both structures.
- ❖ No structure, regular or not, has denser packing.
- ❖ There are an infinite number of ways of arranging identical spheres in a regular array that maximizes the packing fraction.

HCP structure



Hexagonal close packed structure

HCP unit cell



Hexagonal close packed structure unit cell

The Diamond structure

- ❖ The diamond structure is the structure of the semiconductors silicon and germanium and is related to the structure of several important semiconductor binary compounds.
- ❖ The space lattice of diamond is face-centered cubic.
- ❖ The primitive basis of the diamond structure has two identical atoms at coordinates 000 and $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ associated with each point of the fcc lattice, as shown in Fig. 22.
- ❖ Because the conventional unit cube of the fcc lattice contains 4 lattice points, it *follows* that the conventional unit cube of the diamond structure contains $2 \times 4 = 8$ atoms.
- ❖ There is no way to choose a primitive cell such that the basis of diamond contains only one atom.

Diamond structure: is **non Bravais lattice**

- ❖ The diamond structure allows a center-of-inversion symmetry operation at the midpoint of every line between nearest-neighbor atoms.
- ❖ The inversion operation carries an atom at \mathbf{r} into an atom at $-\mathbf{r}$.

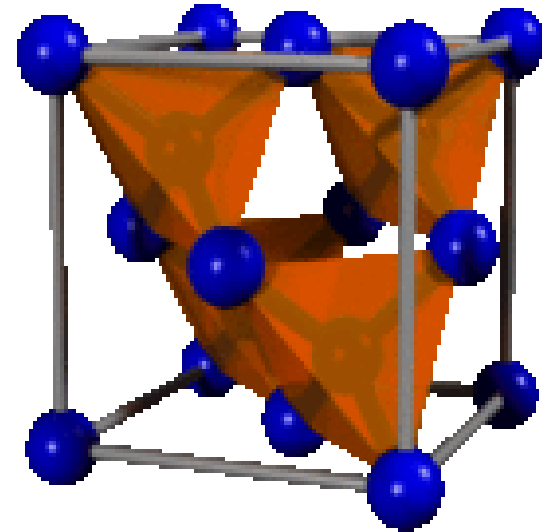
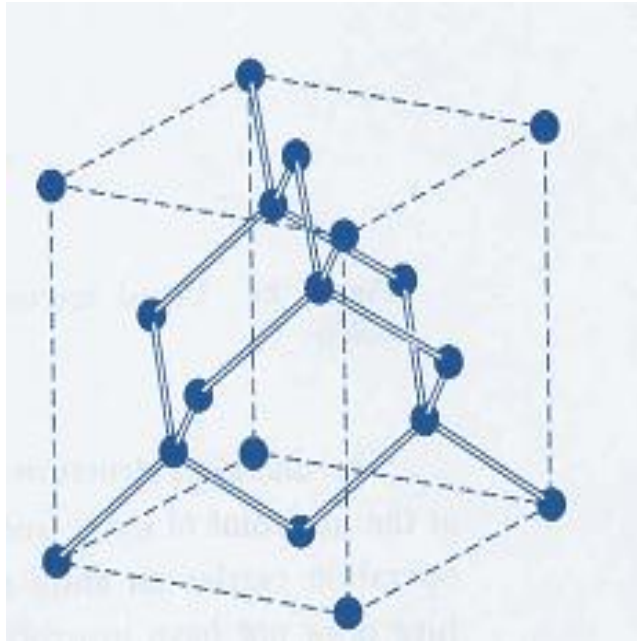
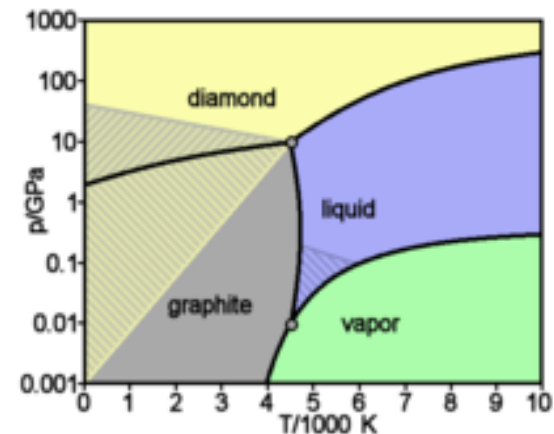


fig 23. Diamond structure



- ✚ Each atom has 4 nearest neighbors and 12 next nearest neighbors.
- ✚ The diamond structure is relatively empty: the maximum proportion of the available volume which may be filled by hard spheres is only 0.34, which is 46 percent of the filling factor for a closest-packed structure such as fcc or hcp.
- ✚ The diamond structure is an example of the directional covalent bonding found in column IV of the periodic table of elements.
- ✚ Carbon, silicon, germanium, and tin can crystallize in the diamond structure, with lattice constants $a = 3.567, 5.430, 5.658, \text{ and } 6.49 \text{ \AA}$, respectively.
- ✚ Here a is the edge of the conventional cubic cell.

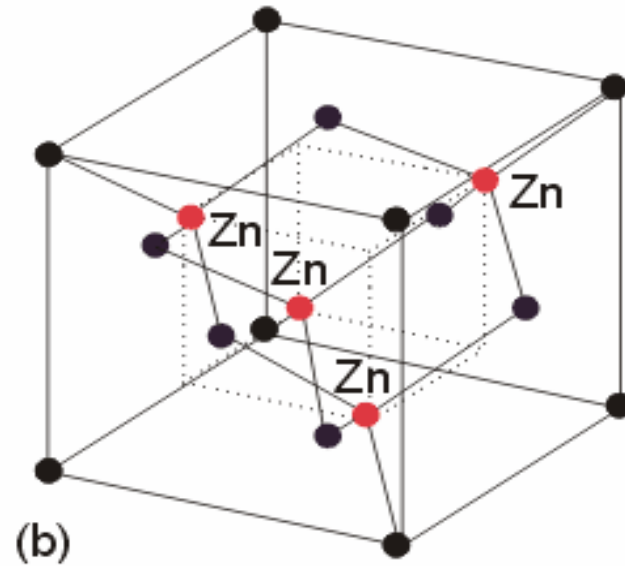
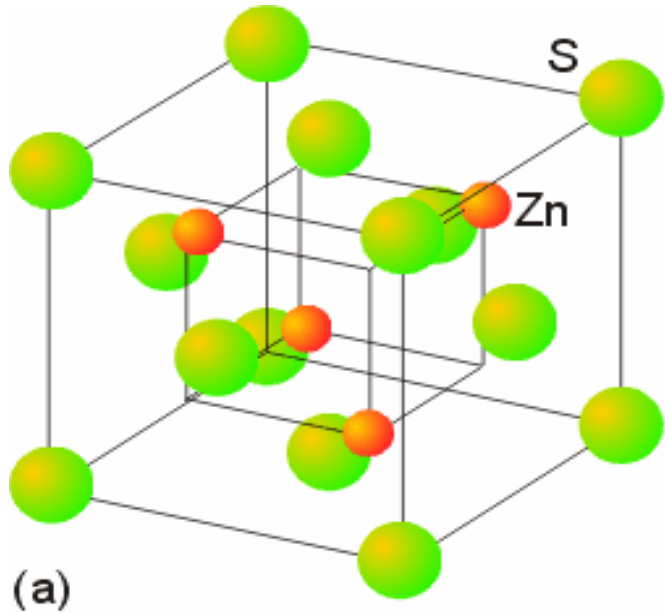
ZnS cubic structure

- ❖ The cubic ZnS structure does not have **inversion symmetry**.
- ❖ Examples of the cubic zinc sulfide structure are

Crystal	a	Crystal	a
SiC	4.35Å	ZnSe	5.56Å
ZnS	5.41Å	GaAs	5.56Å
AlP	5.45Å	AlAs	5.66Å
GaP	5.45Å	InSb	6.46Å

- ❖ The close equality of the lattice constants of several pairs, notably (Al, Ga)P and (Al, Ga)As, makes possible the construction of semiconductor hetero-junctions (Chapter 19).

ZnS structure



Coord No: $Zn^{2+} 4$, $S^{2-} 4$

Atomic unit cell

$Zn:S = 4:4 = 1:1 = ZnS$

S^{2-} at Fcc

Zn^{2+} at $\frac{1}{2}$ Td holes

Chapter 2

Wave diffraction & reciprocal lattice vector

Bragg-law:

- Diffraction of wave depends on
 - ⇒ Crystal structure &
 - ⇒ Wavelength
- An optical wave length such as 5000Å, the superposition of waves scattered by the individual atoms of a crystals results in ordinary optical refraction.
- Diffraction occurs when the wavelength is equal or smaller than the lattice constant.

$$\lambda \leq a \quad (1)$$

- Bragg presented a simple explanations of the diffracted beams by the crystals.
- The **Bragg** deviations is simple & convincing only because it reproduce correct result.

- **Elastic scattering** is treated b/c in elastic scattering, energy of the x-ray is not changed on reflection.
- We consider parallel lattice planes spaced 'd' apart.
- The path difference for rays reflected from the adjacent plane is $2d\sin\theta$.
- ❖ The angle, θ – is measured from the plane.
- ❖ **Constructive interference** occur when the path difference is an integral multiple of wave length.

$$2d\sin\theta = n\lambda \quad (2)$$

,provided that $\lambda \leq 2d$.

- ❖ The Bragg law in equ (2) is the consequence of the periodicity of the lattice.
- ❖ The Bragg law does not depend on the **composition of the basis** associated with the lattice point.

Fourier analysis

- We have seen that a crystal is invariant under any translations of the form;

$$\mathbf{T} = u_1 \mathbf{a}_1 + u_2 \mathbf{a}_2 + u_3 \mathbf{a}_3 \quad (3)$$

Where, u_1, u_2 , & u_3 are integers and a_1, a_2 , & a_3 are the crystal axis

- Any local physical property of crystal such as
 - ◆ Charge concentrations,
 - ◆ Electron number density, &
 - ◆ Magnetic moment density are invariant under translation, \mathbf{T} .
- The most important quantity here is that the electron number density is a periodic function of \mathbf{V} , with periods; a_1, a_2 , & a_3 in the direction of 3-crystal axis.

$$\begin{aligned}
 n(x + a) &= n_o + \sum \left[c_p \cos \left(\frac{2\pi p x}{a} + 2\pi p \right) + s_p \sin \left(\frac{2\pi p x}{a} + 2\pi p \right) \right] \\
 &= n_o + \sum \left[c_p \cos \left(\frac{2\pi p x}{a} \right) + s_p \sin \left(\frac{2\pi p x}{a} \right) \right] \\
 &= n(x)
 \end{aligned} \tag{4}$$

- ❖ $\frac{2\pi p}{a}$ - is the point in the reciprocal lattice or Fourier space of the crystal.
- ❖ The **reciprocal lattice points** describes the allowed terms in the Fourier series.
- ❖ The term is allowed if it is constant with the periodicity of the crystal.

$$n(r + T) = n(r)$$

- ❖ Such periodicity creates an ideal situations for Fourier analysis.
- ❖ The most interesting properties of crystals are directly related to the Fourier component of the electron number density.
- ❖ We might expand $n(x)$ in a Fourier's sine's & cosines series.

□ We might expand $n(x)$ in a Fourier series sine's & cosines.

$$n(x) = n_o + \sum_{p>0} \left[c_p \cos\left(\frac{2\pi p x}{a}\right) + s_p \sin\left(\frac{2\pi p x}{a}\right) \right]$$

- ❖ Where p 's are positive integers and c_p & s_p are real constants called the Fourier coefficient of expansions.
- ❖ The factor $\frac{2\pi}{a}$ in the argument ensures that $n(x)$ has the period a .
- ❖ Other points in the reciprocal lattice are not allowed in the Fourier expansion of a periodic functions.
- ❖ It is convenient to write the series (4) in the compact form as

$$n(x) = \sum_p n_p \exp\left(\frac{i2\pi p x}{a}\right) \tag{5}$$

- ❖ Where the sum is over all integers, p , positive, negative or zero. The coefficient n_p are complex numbers.

➤ To ensure that $n(x)$ is a real function we require that

$$n_{-p}^* = n_p \quad (6)$$

➤ For the sum of the terms in p and $-p$ to be real, equ(6) must be satisfied.

➤ The asterisk in n_p^* denotes the complex conjugate.

$\phi = \frac{2\pi p x}{a}$, the sum in

$$n_p(\cos\phi + i\sin\phi) + n_{-p}(\cos\phi - i\sin\phi) = (n_p + n_{-p})\cos\phi + i(n_p - n_{-p})\sin\phi \quad (7)$$

Which in turn is equal to the real function.

$$2\text{Re}\{n_p\}\cos\phi - 2\text{Im}\{n_p\}\sin\phi \quad (8)$$

➤ Here, $\text{Re}\{n_p\}$ & $\text{Im}\{n_p\}$ denotes the real and imaginary parts of the n_p .

➤ In three dimensions, $n(x)$ is extended to $n(r)$, where $r = x_i + y_j + z_{\hat{k}}$.

❖ We must find a set of vector G such that

$$n(r) = \sum_G n_G \exp(iG \cdot r) \quad (9)$$

❖ Which is invariant under all crystal translations, T that leave the crystal invariant.

Exercise

1. Discuss the difference between direct lattice and reciprocal lattice vectors.

Inversion of Fourier series

➤ We now that the Fourier coefficient in equ (5) is given by

$$n_p = \frac{1}{a} \int_0^a dx n(x) \exp\left(\frac{-i2\pi p x}{a}\right) \quad (10)$$

□ By substituting equ(5) in to equation (10) to obtain

$$n_p = \frac{1}{a} \int_0^a dx n(x) \exp\left(i2\pi(p' - p) \frac{x}{a}\right) \quad (11)$$

□ If $p' \neq p$ the value of the integrals is

$$\frac{a}{i2\pi(p' - p)} \exp(i2\pi(p' - p) - 1) = 0 \text{ and } \exp(i2\pi) = 1$$

➤ For the term $P' = P$, the integrand $\exp(0) = 1$ and the value of the integral is a . So, that

$$n_p = \frac{1}{a} n_p a = n_p.$$

□ Which is an identity so that equ(10) is also an identity. As in (10) the inversion (9) gives

$$n_G = \frac{1}{V_c} \int_{cell} dv n(r) \exp(-iG \cdot r) \quad (12)$$

Where V_c is the volume of the cell of the crystal.

Reciprocal lattice vectors

- ❖ To describe more about Fourier analysis of the electron concentration, we need to find a vector G of the Fourier sum, $\sum n_G \exp(iG \cdot r)$ as in (9).
- ❖ The powerful tool to describe Fourier analysis is the use of the axis vectors, b_1 , b_2 , & b_3 of the reciprocal lattice.

$$\left. \begin{aligned} b_1 &= 2\pi \frac{a_2 \times a_3}{a_1 \cdot a_2 \times a_3} \\ b_2 &= 2\pi \frac{a_3 \times a_1}{a_1 \cdot a_2 \times a_3} \\ b_3 &= 2\pi \frac{a_1 \times a_2}{a_1 \cdot a_2 \times a_3} \end{aligned} \right\} \quad (13)$$

- ❖ The factors 2π are not used by the crystallographer but is convenient in solid state physics.
- ❖ a_1, a_2 & a_3 are the primitive vectors of the crystal(direct) lattice and b_1, b_2 & b_3 are the primitive vectors of the reciprocal lattice.

❖ Each vectors defined by (13) is orthogonal to two axis vectors of the crystal lattice.

❖ b_1, b_2 & b_3 have the prosperity that

$$b_i \cdot a_j = 2\pi \delta_{ij} \quad (14)$$

❖ Where

$$\left| \begin{array}{l} \delta_{ij} = 1, \text{ if } i = j \\ \delta_{ij} = 0, \text{ if } i \neq j \end{array} \right.$$

❖ Points in the reciprocal lattice are mapped by the set of the vectors, G such that

$$G = v_1 b_1 + v_2 b_2 + v_3 b_3 \quad (15)$$

Where, v_1, v_2 & v_3 are integers

❖ The vector G of this form is called the reciprocal lattice.

□ In the Fourier series representations, electron number density is invariant under crystal translations.

$$T = u_1 a_1 + u_2 a_2 + u_3 a_3$$

❖ Thus, the electron number density has the property;

$$n(r + T) = \sum_G n_G \exp(iG \cdot r) \exp(iG \cdot T) \quad (16)$$

❖ But $\exp(iG \cdot T) = \exp(i2\pi n) = 1$

Since,

$$\begin{aligned} \exp(iG \cdot T) &= \exp(i(v_1 b_1 + v_2 b_2 + v_3 b_3)(u_1 a_1 + u_2 a_2 + u_3 a_3)) \\ &= \exp((i2\pi)v_1 u_1 + v_2 u_2 + v_3 u_3) \\ &= \exp(i2\pi n) = 1 \end{aligned} \quad (17)$$

❖ The argument of the exponential has the form $2\pi I$ times an integer, $n = (v_1 u_1 + v_2 u_2 + v_3 u_3)$.

➤ Thus, by equation (9) we have desired invariance.

$$n(r + T) = n(r) = \sum_G n_G \exp(iG \cdot r)$$

- ❑ Every crystal structure has two lattice associated with it.

1. Crystal(direct) lattice &

2. Reciprocal lattice.

- ❑ A **diffraction pattern** of a crystal is a map of the reciprocal lattice of the crystal.
- ❑ A microscopic image if it could be resolved on a fine enough scale is a map of crystal structure in real space.
- ❑ The two lattice are related by the equation (13).
- ❑ When we rotate a crystal, we rotate both the **direct lattice** & **reciprocal lattice**.
- ❖ Vectors in the crystal(direct) lattice has a dimension of $[length]$.
- ❖ Vectors in the reciprocal lattice has a dimension of $\left[\frac{1}{length}\right]$.
- ❖ A reciprocal lattice is a lattice in Fourier space associated with the crystal.

Diffraction conditions

□ **Theorem:** The set of reciprocal lattice vectors G determines possible x-ray diffractions.

□ As shown in fig - 6 diffractions in the phase factors is $\exp[i(k - k').r]$

❖ K & k' are the wavevectors of incoming & out going beams of light.

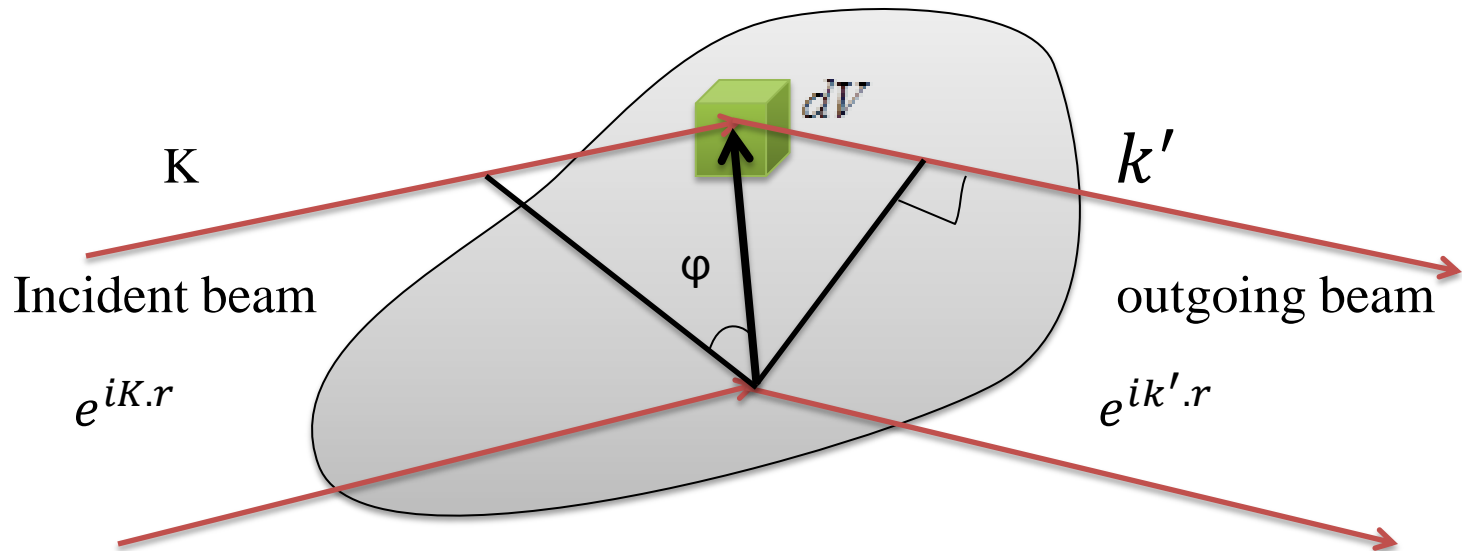


Fig 6.

- The difference in the path length of the incident wave k at point, O , r is $r \sin \phi$.
- And the difference in phase angle is $\frac{2\pi r \sin \phi}{\lambda}$ which is equal to $k.r$.
- For the diffracted wave the difference in phase angle is $-k'.r$.
- The total difference in phase angle is $(k - k').r$
- The wave scattered from dv at r has the phase factor $\exp(i(k - k').r)$ relative to the wave scattered from the volume element at the origin, O .

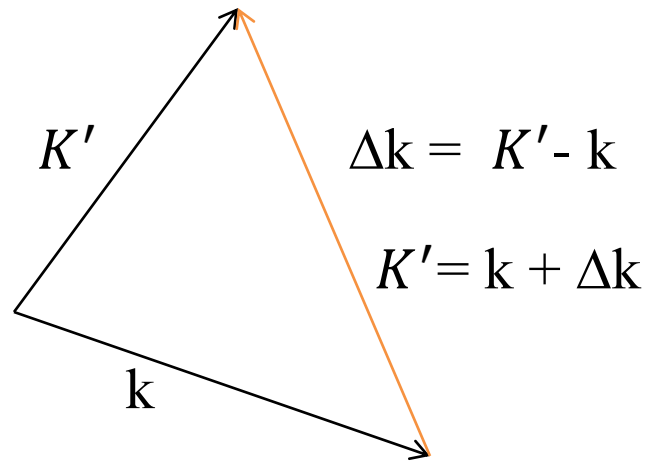


Fig 7: Definition of scattering vector Δk such that $k + \Delta k = k'$

- ❖ In elastic scattering the magnitude satisfies, $K' = k$.
- ❖ Furthermore, in Bragg's scattering from a periodic lattice any allowed Δk must equal some reciprocal lattice vectors, G .
- ❖ We suppose that the amplitude of the wave scattered from the volume element is proportional to the **local electron concentration**, $n(r)$.

$$F \sim n(r)$$

- ❖ The total amplitude of the scattered wave in the direction of \mathbf{k}' is proportional to integral over the crystal of $\mathbf{n}(\mathbf{r})d\mathbf{v}$ times the phase factor, $\exp(i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r})$.
- ❖ In other words the amplitude of the electric or magnetic vectors in the scattered electromagnetic wave is proportional to the scattering amplitude, F .

$$\begin{aligned}
 F &= \int d\mathbf{v} n(\mathbf{r}) \exp(i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{r}) \\
 &= \int d\mathbf{v} n(\mathbf{r}) \exp(-i\Delta\mathbf{k} \cdot \mathbf{r})
 \end{aligned} \tag{18}$$

Where, $\mathbf{k} - \mathbf{k}' = \Delta\mathbf{k}$; or $\mathbf{k} + \Delta\mathbf{k} = \mathbf{k}'$

- ❖ $\Delta\mathbf{k}$ measures the change in the wave vector, and called the scattering vector.
- ❖ In order to find the wave vector of the scattered beam, we add, $\Delta\mathbf{k}$ to \mathbf{k}' .
- ❖ To find the scattering amplitude, we substitute equation (18) in to equ(9). The resulting scattering amplitude is;

$$F = \sum_G \int d\mathbf{v} n_G \exp[i(\mathbf{G} - \Delta\mathbf{k}) \cdot \mathbf{r}] \tag{19}$$

- ❖ When the scattering amplitude is equal to a particular reciprocal lattice,

$$\Delta\mathbf{k} = \mathbf{G} \tag{20}$$

- The argument of the exponential vanishes and the scattering amplitude reduces to

$$F = Vn_G \quad (21)$$

- It is simple exercise to show that F is negligibly small when Δk differs significantly from any reciprocal lattice vectors.

- ❖ In elastic scattering of photons its energy $\hbar\omega$ is conserved so that the frequency

$$\omega = ck' \quad (22)$$

- ❖ Of the emergent beam is equal to the frequency of the incident beam. Thus, the magnitude k & k' .

- ❖ Therefore, $k^2 = k'^2$, a result that holds for elastic scattering of electrons and neutrons beams.

$$\Delta k = G \text{ or } k + G = k'$$

So that the diffraction condition is obtained from

$$(k + G)^2 = k^2$$

$$2kG + G^2 = 0 \quad (23)$$

- ❖ This is the central result of the theory of elastic scattering of waves in a periodic lattice.

□ If \mathbf{G} is a reciprocal lattice vectors so is $-\mathbf{G}$ and with this substitutions we can rewrite equation (22) as

$$2\mathbf{K} \cdot \mathbf{G} = G^2 \quad (24)$$

- ❖ This particular expression is often used as the conditions for diffraction.
- ❖ Equ(23) is another statement of the Bragg's diffractions conditions.
- ❖ The result of problem 1 is that the spacing d_{hkl} between parallel planes that is normal to the

direction of $\mathbf{G} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$ is $d_{hkl} = \frac{2\pi}{G}$

Thus , the result $2\mathbf{k} \cdot \mathbf{G} = G^2$ might be written as $2\left(\frac{2\pi}{\lambda}\right)\sin\theta = \frac{2\pi}{d_{hkl}}$

Or $2d_{hkl}\sin\theta = \lambda$

θ is the angle between the incident beam and the crystal planes.

$$2d\sin\theta = n\lambda \quad (25)$$

d - is the spacing between adjacent parallel planes with indices, $\frac{h}{n}$, $\frac{k}{n}$, and $\frac{l}{n}$.

Brillouin zone

Brillouin zone: is defined as a Wigner Seitz primitive cell in the reciprocal lattice.

- It gives a statement of diffraction condition.
- ❖ It describe electron energy band theory & elementary excitations such as photons, phonons, Magnons, Plasmon's, etc.
- ❖ It gives vivid geometrical interpretation of diffraction condition

$$2K \cdot G = G^2 \quad (26)$$

- are not an essential part of the X-ray diffraction in the analysis of crystal structure, but it is part of the analysis of the electronic energy band structure of the crystals.
- A reciprocal space is a space of k 's & G 's so that the diffracted beam is in the direction of $K-G$.

Reciprocal lattice to SC lattice

□ The primitive translation vectors of sc lattice are

$$a_1 = a\hat{x}$$

$$a_2 = a\hat{y} \tag{27a}$$

$$a_3 = a\hat{z}$$

□ Here, \hat{x}, \hat{y} & \hat{z} are orthogonal vectors of unit length. The volume of the cell is $v_c = a_1 \cdot a_2 \times a_3 = a^3$.

➤ The primitive translations vectors of the reciprocal lattice are found

$$b_1 = \left(\frac{2\pi}{a}\right)\hat{x}$$

$$b_2 = \left(\frac{2\pi}{a}\right)\hat{y} \tag{27b}$$

$$b_3 = \left(\frac{2\pi}{a}\right)\hat{z}$$

❖ Here, a reciprocal lattice is itself a simple cubic lattice with lattice constant $\frac{2\pi}{a}$.

- ❖ The boundaries of the FBZ are planes normal to the six reciprocal lattice vectors, $\pm b_1$, $\pm b_2$ & $\pm b_3$ at their mid points.

$$\pm b_1 = \pm \left(\frac{\pi}{a} \right) \hat{x}$$

$$\pm b_2 = \pm \left(\frac{\pi}{a} \right) \hat{y} \text{ ----- (28)}$$

$$\pm b_3 = \pm \left(\frac{\pi}{a} \right) \hat{z}$$

- ❖ The six planes bound a cube of edge $\frac{2\pi}{a}$ & a volume of $\left(\frac{2\pi}{a} \right)^3$.
- ❖ This cube is the first Brillouin zone of the **sc** crystal lattice.

Reciprocal lattice to bcc lattice

□ The primitive translation vectors of the bcc lattice are

$$a_1 = \frac{1}{2a}(-\hat{x} + \hat{y} + \hat{z})$$

$$a_2 = \frac{1}{2a}(\hat{x} - \hat{y} + \hat{z}) \quad (29)$$

$$a_3 = \frac{1}{2a}(\hat{x} + \hat{y} - \hat{z})$$

❖ Where a - is the side of conventional cube and \hat{x} , \hat{y} & \hat{z} are orthogonal unit vectors parallel to the cubic edges. The volume of the primitive cell is

$$V_c = |a_1 \cdot a_2 \times a_3| = \frac{1}{2}a^3 \quad (30)$$

□ The primitive translations of reciprocal lattice are defined by (13). Thus, we have

$$b_1 = \frac{2\pi}{a}(\hat{y} + \hat{z})$$

$$b_2 = \frac{2\pi}{a}(\hat{x} + \hat{z}) \quad (31)$$

$$b_3 = \frac{2\pi}{a}(\hat{x} + \hat{y})$$

□ By comparison with fig -14 (p.37) these are just the primitive vectors of an fcc lattice. So that an fcc lattice is the reciprocal lattice of the bcc lattice.

□ In general the reciprocal lattice vectors for integral v_1, v_2 & v_3 .

$$\mathbf{G} = v_1 \mathbf{b}_1 + v_2 \mathbf{b}_2 + v_3 \mathbf{b}_3$$

$$= \left(\frac{2\pi}{a}\right) [(v_2 + v_3)\hat{x} + (v_1 + v_3)\hat{y} + (v_1 + v_2)\hat{z}]$$

□ The shortest \mathbf{G} 's are the 12 vectors whose all choice of sign are independent.

$$b_1 = \frac{2\pi}{a}(\pm \hat{y} \pm \hat{z})$$

$$b_2 = \frac{2\pi}{a}(\pm \hat{x} \pm \hat{z}) \tag{33}$$

$$b_3 = \frac{2\pi}{a}(\pm \hat{x} \pm \hat{y})$$

❑ One primitive cell of reciprocal lattice is the parallelepiped described by b_1 , b_2 & b_3 . The volume of this cell in the reciprocal lattice is

$$V_c = |b_1 \cdot b_2 \times b_3| = 2\left(\frac{2\pi}{a}\right)^3 \tag{34}$$

❑ The cell contains one reciprocal lattice point because each of the eight corners point is shared eight parallelepiped.

❑ Each parallelepiped contains one eighth of each of the eight corners points.

❑ An other primitive cell the central (Wigner Seitz cell) of the reciprocal lattice which FBZ.

❑ Each cell contains one lattice point at the central point of a cell.

❑ This zone for bcc lattice is bounded by the plane normal to 12 vectors of equ(33) at their mid point.

❑ The zone is a regular 12-faced solid , a rhombo dodecadron.

Reciprocal lattice to fcc

- ❑ The primitive translation vectors of fcc lattice are

$$a_1 = \frac{1}{2}a(\hat{y} + \hat{z})$$

$$a_2 = \frac{1}{2}a(\hat{x} + \hat{z}) \text{ ----- (35)}$$

$$a_3 = \frac{1}{2}a(\hat{x} + \hat{y})$$

- ❑ The volume of the primitive cell is

$$V_c = |a_1 \cdot a_2 \times a_3| = \frac{1}{4}a^3 \text{ ----- (36)}$$

- ❑ The primitive translation vectors of the lattice reciprocal to the fcc lattice are

$$b_1 = \frac{2\pi}{a}(-\hat{x} + \hat{y} + \hat{z})$$

$$b_2 = \frac{2\pi}{a}(\hat{x} - \hat{y} + \hat{z}) \text{ ----- (37)}$$

$$b_3 = \frac{2\pi}{a}(\hat{x} + \hat{y} - \hat{z})$$

- ❖ Equation (36) describes the primitive translation vectors of bcc lattice.

- Thus the bcc lattice is reciprocal to fcc lattice.
- The volume of the primitive cell of reciprocal lattice of fcc lattice is

$$V_c = 4 \left(\frac{2\pi}{a} \right)^3 = 32 \left(\frac{\pi}{a} \right)^3$$

- ❖ the shortest G's are the eight lattice vectors

$$\mathbf{G} = \left(\frac{2\pi}{a} \right) (\pm \hat{x} \pm \hat{y} \pm \hat{z}) \quad (38)$$

- ❖ The boundaries of the central cell are determined for the most part by eight planes normal to these vectors at their mid point.
- ❖ The corner of the octahedral thus, formed are cut by the perpendicular bisector of six other reciprocal lattice;

$$\left(\frac{2\pi}{a} \right) (\pm 2\hat{x})$$

$$\left(\frac{2\pi}{a} \right) (\pm 2\hat{y}) \quad (39)$$

$$\left(\frac{2\pi}{a} \right) (\pm 2\hat{z})$$

□ The 1st Brillouin zone is the smallest bounded volume about the origin. (see fig 15)

□ The six planes bound a cube of edge $\frac{4\pi}{a}$ & volume of $\left(\frac{4\pi}{a}\right)^3$.

Chapter 3

Properties of Ionic crystals

❑ What holds a crystal together?

- ❖ The attractive electrostatic interaction between the negative charges of the electrons and the positive charges of the nuclei is entirely responsible for the cohesion of solids.
- ❖ Magnetic forces have *only a weak effect on cohesion* and gravitational forces are negligible.
- ❖ Specialized terms categorize distinctive situations: exchange energies, vander Waals forces, and covalent bonds.
- ❖ The observed differences between the forms of condensed matter are caused in the final analysis by differences in the distribution of the outermost electrons and the ion cores.

3.1 Cohesive energy

- ❖ The **cohesive energy** of a crystal is the energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation, with the same electronic configuration.
- ❖ **Lattice energy** the energy that must be added to the crystal to separate its component ions into free ions at rest *at infinite separation*.
- ❖ It is used in the discussion of ionic crystals.
- ❖ The inert gas crystals are weakly bound, with cohesive energies less than a few percent of the cohesive energies of the elements in the C, Si, Ge ... column.
- ❖ The alkali metal crystals have intermediate values of the cohesive energy.
- ❖ The transition element metals (in the middle columns) are quite strongly bound.

- ❖ The melting temperatures and bulk moduli vary roughly as the cohesive energies.

CRYSTALS OF INERT GASES

- ❖ The inert gases form the simplest crystals.
- ❖ The electron distribution is very close to that of the free atoms.

Properties at absolute zero

- ❖ The crystals are;
 - ◆ **transparent insulators, weakly bound, with**
 - ◆ **low melting temperatures.**
 - ◆ **The atoms have very high ionization energies.**
- ❖ The outermost electron shells of the atoms are completely filled, and the distribution of electron charge in the free atom is spherically symmetric.

Cohesive energy

- ❖ The crystal structures in (Fig. 2) are all cubic close-packed (fcc), except He^3 and He^4 .
- ❖ **What holds an inert gas crystal together?** The electron distribution in the crystal is not significantly distorted from the electron distribution around the free atoms because not much energy is available to distort the free atom charge distributions.
- ❖ The cohesive energy of an atom in the crystal is only 1% or less of the ionization energy of an atomic electron.
- ❖ Part of this distortion gives the **Van der Waals interaction**.

Exercise

1. **What holds an inert gas crystal together?**(Van der Waals interaction or London interaction).
2. **Explain the nature of crystal structures in He^3 and He^4 .**

Van der Waals - London interaction

- ❖ Consider two identical inert gas atoms at a separation R *large in comparison* with the radii of the atoms.
- ❖ What interactions exist between the two neutral atoms?
- ❖ If the charge distributions on the atoms were rigid, the interaction between atoms would be zero, because the electrostatic potential of a spherical distribution of electronic charge is canceled outside a neutral atom by the electrostatic potential of the charge on the nucleus.
- ❖ Then the inert gas atoms could show no cohesion and could not condense.
- ❖ But the atoms induce dipole moments in each other, and the induced moments cause an attractive interaction between the atoms.

Exercise

1. What interactions exist between the two neutral atoms? (ans. attractive interactions due to induced dipole moment).

- ❖ As a model, we consider two identical linear harmonic oscillators 1 and 2 Separated by R .
- ❖ *Each oscillator bears charges $\pm e$ with separations x_1 and x_2 as in fig. 3.*
- ❖ The particles oscillate along the x axis.
- ❖ Let p_1 and p_2 denotes the momenta .The force constant is C .
- ❖ Then the Hamiltonian of the unperturbed system is

$$H_o = \frac{p_1^2}{2m} + \frac{1}{2} C x_1^2 + \frac{p_2^2}{2m} + \frac{1}{2} C x_2^2 \quad (3.1)$$

- ❖ Each uncoupled oscillator is assumed to have a frequency of ω_o of the strong optical absorption line or the atom.

thus, $C = m\omega_o^2$

- ❖ Let H_1 be the coulomb interaction of the two oscillators, and the internuclear coordinate is R .

$$\textcolor{blue}{H}_1 = \frac{e^2}{R} + \frac{e^2}{R+X_1-X_2} + \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2} \quad (3.2)$$

❖ In the limit, $|x_1|, |x_2| \ll R$, we expand 3.2 in to obtain in lowest order,

$$H_1 \cong - \frac{2e^2 x_1 x_2}{R^3} \quad (3.3)$$

❖ The total Hamiltonian with approximate form in (3.3) for H_1 can be diagonalized by the normal mode transformations by the normal mode transformation.

$$x_s = \frac{1}{\sqrt{2}} (x_1 + x_2)$$

$$x_a = \frac{1}{\sqrt{2}} (x_1 - x_2) \quad (3.4)$$

On solving for x_1 and x_2

$$x_1 = \frac{1}{\sqrt{2}} (x_s + x_a); x_2 = \frac{1}{\sqrt{2}} (x_s - x_a) \quad (3.5)$$

❖ The subscripts *s* and *a* denote *symmetric* and *antisymmetric* modes of motion.

❖ The momenta p_1 and p_2 associated with the two modes are

$$p_1 = \frac{1}{\sqrt{2}} (p_s + p_a); p_2 = \frac{1}{\sqrt{2}} (p_s - p_a) \quad (3.6)$$

➤ The total Hamiltonian H_0 and H_1 after the transformations (5) and (6) is

$$H = \left[\frac{P_s^2}{2m} + \frac{1}{2} \left(C - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[\frac{P_a^2}{2m} + \frac{1}{2} \left(C + \frac{2e^2}{R^3} \right) x_a^2 \right] \quad (3.7)$$

➤ The two frequencies of the coupled oscillators are found by inspection of (3.7) to be.

❖ The two frequencies of the coupled oscillators are found by inspection of (7) to be

$$\omega = \left[\left(c \pm \frac{2e^2}{R^3} \right) / m \right]^{1/2} = \omega_o \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{cR^3} \right) - \frac{1}{8} \left(\frac{2e^2}{cR^3} \right)^2 + \dots \right] \quad (3.8)$$

❖ With ω_o given by $\left(\frac{c}{m} \right)^{1/2}$

❖ The zero point energy of the system is $\frac{1}{2} \hbar (\omega_s + \omega_a)$; because of the interactions, the sum is reduced from uncoupled value $2 \cdot \frac{1}{2} \hbar \omega_o$ by

$$\Delta U = \frac{1}{2} \hbar (\Delta \omega_s + \omega_a) = \frac{1}{2} \hbar \omega_o \cdot \frac{1}{8} \left(\frac{2e^2}{cR^3} \right)^2 = \frac{-A}{R^3} \quad (3.9)$$

❖ This attractive interaction varies as the minus sixth power of the separation of the two oscillators.

- ✚ This is called the van der Waals interaction, known also as the London interaction or the induced dipole-dipole interaction.
- ✚ It is the principal attractive interaction in crystals of inert gases and also in crystals of many organic molecules.
- ✚ The interaction is a quantum effect, in the sense that $\Delta U \sim 0$ as $\hbar \sim 0$.
- ✚ Thus, the zero point energy of the system is lowered by the dipole-dipole coupling of Eq. (3).
- ❖ The van der Waals interaction does not depend for its existence on any overlap of the charge densities of the two atoms.
- ❖ An approximate value of the constant A in (9) for identical atoms is given by $\hbar\omega_o\alpha^2$ where $\hbar\omega_o$ is the energy of the strongest optical absorption line and α is the electronic polarizability.

Repulsive interactions

- ✚ As the two atoms are brought together, their charge distributions gradually decrease there by changing the electrostatic energy.
- ✚ As close separations, the overlap energy is repulsive in large part because of Pauli exclusion principle.
- ✚ Accordingly, two electrons can not have all their same quantum numbers equal.
- ✚ The Pauli principle prevents multiple occupancy, and electron distributions of atoms with closed shells can overlap only if accompanied by the partial promotion of electrons to unoccupied high energy states of the atoms.
- ✚ Thus the electron overlap increases the total energy of the system and gives a repulsive contribution to the interaction.
- ✚ Experimental data on the inert gases can be fitted well by an empirical repulsive potential of the form $\frac{B}{R^{12}}$, where B is a positive constant, when used together with a long-range attractive potential of the form of (9).

➤ The constants A and B are empirical parameters determined from independent measurements made in the gas phase; the data used include the virial coefficients and the viscosity.

➤ It is usual to write the total potential energy of two atoms at separation R as

$$U(R) = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \quad (3.10)$$

❖ The σ and ε are the new parameters and are related through,

$$A = 4\varepsilon\sigma^6 \text{ and } B = 4\varepsilon\sigma^{12}$$

❖ The potential (3.10) is known as the **Lennard-Jones potential**.

❖ The force between the two atoms is given by, $\frac{-dU}{dR}$.

❖ Values of ε and σ given in Table 4 can be obtained from gas-phase data, so that calculations on properties of the solid do not involve disposable parameters.

❖ Other empirical forms for the repulsive interaction are widely used, in particular the exponential form $\lambda \exp(\frac{-R}{\rho})$, where ρ is a measure of the range of the interaction.

Equilibrium lattice constants

- ❖ If we neglect the kinetic energy of the inert gas atoms, the cohesive energy of an inert gas crystal is given by summing the Lennard -Jones potential (3.10) over all pairs of atoms in the crystal.
- ❖ If there are N atoms in the crystal the total potential energy is $p_{ij}R$

$$U_{tot} = \frac{1}{2}N(4\epsilon) \left[\sum_j' \left(\frac{\sigma}{p_{ij}R} \right)^{12} - \sum_j' \left(\frac{\sigma}{p_{ij}R} \right)^6 \right] \quad (3.11)$$

- ❖ Where, $p_{ij}R$ is the distance between the reference atom i & any other atom j expressed in terms of the nearest neighbor distance, R .
- ❖ The factor $\frac{1}{2}$ occurs with N compensate twice for counting of each atoms.

$$\sum_j' (p_{ij})^{-12} = 12.13889 \text{ \& } \sum_j' (p_{ij})^{-6} = 14.45392$$

- ❖ There are 12 nearest neighbor sites in the fcc structures; the series are rapidly converging and is closer to 12.
- ❖ The nearest neighbors contribute most of the interaction energy of inert gas crystals.

- ❖ The corresponding sums for the hcp structure are 12.13229 and 14.45489.
- ❖ If we take U_{tot} in (11) as the total energy of the crystal, the equilibrium value R_o is given by requiring that U_{tol} be a minimum with respect to variations in the nearest-neighbor distance R ;

$$\frac{dU_{tol}}{dR} = 0 = -2N\varepsilon \left[12(12.13) \frac{\sigma^{12}}{R^{13}} - 6(14.45) \frac{\sigma^6}{R^7} \right] \quad (3.13)$$

$$\frac{R_o}{\sigma} = 1.09 \quad (3.14)$$

, which is the same for all elements with an fcc structure.

- ❖ The observed values of $\frac{R_o}{\sigma}$ using independent determined values are given in table

	Ne	Ar	Kr	Xe
$\frac{R_o}{\sigma}$	1.14	1.11	1.10	1.09

- ❖ The slight departure of $\frac{R_o}{\sigma}$ lighter atoms from the universal value 1.09 predicted for inert gases can be explained by zero-point quantum effects.

Cohesive energy cont'

- ❖ The cohesive energy of inert gas crystals at absolute zero and at zero pressure is obtained by substituting (12) and (14) in (11):

$$U_{tot}(R) = -2N\varepsilon \left[(12.13) \frac{\sigma^{12}}{R^{13}} - (14.45) \frac{\sigma^6}{R^7} \right] \quad (3.15)$$

And at $R = R_o$

$$U_{tot}(R) = -2.15(4N\varepsilon) \quad (3.16)$$

,Which is the same for inert gases.

- ❖ This is the calculated cohesive energy when atoms are at rest.
- ❖ Quantum-mechanical corrections act to reduce the binding by 28, 10, 6, and 4 percent of Eq. (16) for Ne, Ar, Kr, and Xe, respectively.
- ❖ The heavier the atom, the smaller the quantum correction.
- ❖ We can understand the origin of the quantum correction by consideration of a simple model in which an atom is confined by fixed boundaries.

- ✚ If the particle has the quantum wavelength λ , where λ is determined by the boundaries, then the particle has kinetic energy $\frac{p^2}{2m}$ with the de Broglie relation $p = \frac{h}{\lambda}$ the connection between the momentum and the wavelength of a particle.
- ✚ On this model the quantum zero-point correction to the energy is inversely proportional to the mass.
- ✚ One consequence of the quantum kinetic energy is that a crystal of the isotope Ne^{20} is observed to have a larger lattice constant than a crystal of Ne^{22} .
- ✚ The higher quantum kinetic energy of the lighter isotope expands the lattice because the kinetic energy is reduced by expansion.
- ✚ The observed lattice constants (extrapolated to absolute zero from 2.5K) are

$$Ne^{20} = 4.4644\text{\AA} \text{ and}$$

$$Ne^{22} = 4.4559\text{\AA}$$

3.2 Ionic bonding

- ❖ Ionic crystals are made up of positive and negative ions.
- ❖ The ionic bond results from the electrostatic interaction of oppositely charged ions.
- ❖ Two common crystal structures found for ionic crystals, the NaCl and the CsCl structures.
- ❖ The electronic configurations of all ions of a simple ionic crystal correspond to closed electronic shells, as in the inert gas atoms.
- ❖ The electronic configuration of Lithium fluoride is



- ❖ And the singly charged ions have of lithium fluoride has and electronic configurations of



- ❖ As for helium and neon respectively.
- ❖ Inert gas atoms have closed shells, and the charge distributions are spherically symmetric.

- ✚ We expect that the charge distributions on each ion in an ionic crystal will have approximately spherical symmetry, with some distortion near the region of contact with neighboring atoms.
- ✚ This picture is confirmed by x-ray studies of electron distributions (fig 3.7).
- ✚ The distance between a positive ion and the nearest negative ion in crystalline NaCl is 2.81×10^{-8} cm, and
- ✚ The attractive coulomb part of the potential energy of the two ions by themselves is 5.1 eV.
- ✚ This value may be compared (Fig. 8) with the experimental value of 7.9 eV per molecular unit for the lattice energy of crystalline NaCl with respect to separated Na^+ and Cl^- ions.

Exercise

1. Ionic compounds are usually poor conductors of electricity. Why?

Electrostatic or Madelung Energy

- ❖ The long-range interaction between ions with charge $\pm q$ is *the electrostatic interaction $\frac{\pm q^2}{r}$ attractive between ions of opposite charge and repulsive between ions of the same charge.*
- ❖ The ions arrange themselves in whatever crystal structure gives the strongest attractive interaction compatible with the repulsive interaction at short distances between ion cores.
- ❖ The repulsive interactions between ions with inert gas configurations are similar to those between inert gas atoms.
- ❖ The van der Waals part of the attractive interaction in ionic crystals makes a relatively small contribution to the cohesive energy in ionic crystals, of the order of 1 or 2%.
- ❖ The main contribution to the binding energy of ionic crystals is **electrostatic** and is called the **Madelung energy**.

- ❖ If U_{ij} is the energy between ions i & j we define a sum U_i w/c include all interactions involving, ions, i .

$$U_i = \sum_j' u_{ij} \quad (3.17)$$

- ❖ the summation includes all ions except, $i = j$.
- ❖ U_{ij} may be written as the sum central field repulsive potential that as the form of $\lambda \exp(\frac{-r}{\rho})$, where λ and ρ are empirical parameter.

- ❖ The electrostatic force, $\frac{\pm q^2}{r}$.

❖ *Thus,*

$$U_{ij} = \lambda \exp(\frac{-r_{ij}}{\rho}) \pm \frac{q^2}{r_{ij}} \quad (3.18)$$

In SI units the coulomb interaction is written as

$$\text{❖} \quad F_c = \frac{\pm q^2}{4\pi\epsilon_0 r} \quad \text{and in CGS it is } \frac{\pm q^2}{r}$$

- ❖ The repulsive part describes the fact that ions resist the overlap with the electron distributions of neighboring atoms.
- ❖ The strength, λ and range ρ are constants to be determined from the observed values of lattice constant & compressibility.
- ❖ we have used exponential form of the empirical repulsive potential instead of R^{-12} for noble gases.
- ❖ The change is made because it may give better representations of the repulsive potential.
- ❖ For the ions, we do don't have gas phase data available to permit the independent determinations of λ and ρ .
- ❖ **ρ is the measure of the range of repulsive interaction.**
- ❖ **For $r = \rho$, the repulsive interaction is reduced to $\frac{1}{e}$ of the value at $r = 0$.**
- ❖ In the NaCl, the value of U_i does not depend on whether the reference ion is positive or negative.

- ❖ We can neglect the surface effects and write the total lattice energy U_{tot} of crystal composed of N molecules or 2N ions.

$$U = NU_i$$

- ❖ Here, N rather than 2N occurs since we count each pairs of interactions or each bond only once.
- ❖ the total lattice energy U_{tot} is defined as the energy required to separate the crystal in to individual ions at infinite distance apart.
- ❖ Here, we introduce the quantity, ρ_{ij} such that $r_{ij} = \rho_{ij}R$
- ❖ Where R is the nearest neighbor separations in the crystal.
- ❖ If we include the repulsive interactions to only nearest neighbors we have,

$$U_{ij} = \begin{cases} \lambda \exp\left(\frac{-R}{\rho}\right) - \frac{q^2}{R} & \text{for nearest neighbor} \\ \frac{\pm 1}{\rho_{ij}} \frac{q^2}{R} & \text{otherwise} \end{cases} \quad (3.19)$$

$$U = NU_i = N \left(z \lambda e^{\frac{-R}{\rho}} - \frac{\alpha q^2}{R} \right) \quad (3.20)$$

Where z is the number of nearest neighbor of any atom.

- ❖ The madelung constant, α is given by

$$\alpha = \sum_j' \frac{\pm 1}{\rho_{ij}} \quad (3.21)$$

- ❖ The sum should include the nearest neighbor separation , z.
- ❖ The madelung constant is of central importance for the theory of ionic crystals.
- ❖ At the equilibrium separation, $\frac{dU_{tot}}{dR} = 0$, so that,

$$\frac{dU_{tot}}{dR} = \frac{Nz\lambda}{\rho} \exp\left(\frac{-R}{\rho}\right) + \frac{N\alpha q^2}{R^2} = 0 \quad (3.22)$$

$$R_o^2 \exp\left(\frac{-R}{\rho}\right) = \frac{N\rho\alpha q^2}{\lambda z} \quad (3.23)$$

- ❖ This determines the equilibrium separations, R_o if the parameters, λ and ρ of repulsive interactions are known.
- ❖ Calculations from 3.19 through 3.23 are made in CGS systems.
- ❖ For SI systems q^2 is replaced by $\frac{q^2}{4\pi\epsilon_0}$.

- ❖ The total lattice energy of the crystal of $2N$ ion at their equilibrium separation R_0 is written using equations 3.20 and 3.23.

$$U_{tot} = -\frac{N\alpha q^2}{R_0} \left(1 - \frac{\rho}{R_0}\right) \quad (3.24)$$

- ❖ The term $-\frac{N\alpha q^2}{R_0}$ is the madelung energy.
- ❖ It is approximated that ρ is of the order of R_0 so that the repulsive interaction has very short range.

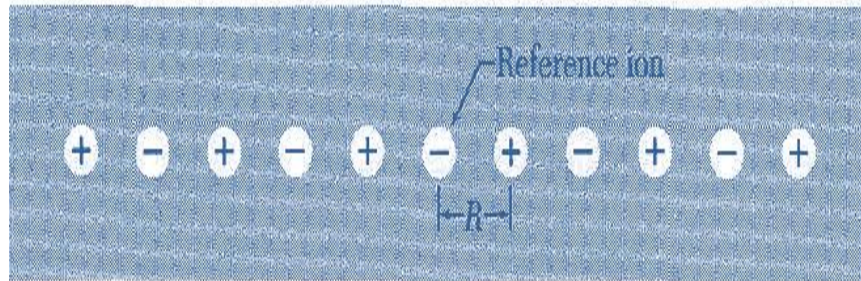


Fig-9 line of ions of alternating signs with distance r between ions

Evaluation of Madelung constant, α

- The 1st calculation of the coulomb energy constant, α was made by madelung.
- It is given by $\alpha = \sum_j' \frac{\pm}{p_{ij}}$
- For equation (20) to be constant, α should be positive.
- If we take the reference ion as negative charge, the plus sign we apply to positive ions and the minus ions for negative ions.
- Equivalently, α can be defined as

$$\frac{\alpha}{R} = \sum_j' \frac{(\pm)}{r_j} \quad (3.25)$$

Where, r_j is the distance of the jth ion from the reference ion & R is the nearest neighbor distance.

- ❖ The value of α depends on **nearest neighbor distance**, R and **lattice parameter**, a or in terms of some other relevant length.
- ❖ Taking the negative ion as a reference, letting R the distance between the adjacent ion;

$$\frac{\alpha}{R} = 2 \left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + \dots \right]$$

$$\alpha = 2 \left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right]$$

- ❖ The factor 2 occur because there are two ions, one to the right and other to the left, at equal distance, r_j .
- ❖ Summing this series by expansion,

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

□ Thus, the madelung constant for one - dimensional chain is

$$\alpha = 2\ln 2$$

- In 3D, the series presents a greater difficulty.
- Thus, the series doesn't converge unless the successive terms in the series are arranged so that the contributions from positive to negative ions cancel in the series.

Structure	α
NaCl	1.747565
CsCl	1.762675
ZnS	1.6381

3.2 Covalent bonding

- ❖ The covalent bond is the classical electron pair or homopolar bond of organic chemistry.
- ❖ It is a strong bond; the bond between the 2- carbon atoms in a diamond.
- ❖ The electrons forming the bond will tends to be partly localized in the region between the two atoms joined by bonds.
- ❖ **The spins of two electrons in the bond are antiparallel.**
- ❖ **The covalent bond has a strong directional properties.**

Properties:

- ✓ Formed by a system of continuous covalent bonds
- ✓ Non conductive LATTICES both in the solid and in the molten state
- ✓ Diamond, boron nitride, quartz (SiO_2), graphite and silicon carbide (SiC)
- ✓ Their arrangement thus, forms low filling factor, 0.34 compared to 0.78 of hcp.
- ✓ Have 4- NN and tetrahedral angles.

- # The tetrahedral bond has 4-nearest neighbors where as hcp has 12 nearest neighbors.
- # The binding of molecular hydrogen is a simple example of covalent bonding.
- # The strong binding occurs when the spins of two electrons are antiparallel.
- # The binding depends on the relative spin orientations.
- # However, it doesn't depends on the strong magnetic dipole force between spins.
- # But Pauli principle modifies the distributions of charge according to the spin orientations.
- # This spin dependent coulomb interaction is the **exchange integrations**.

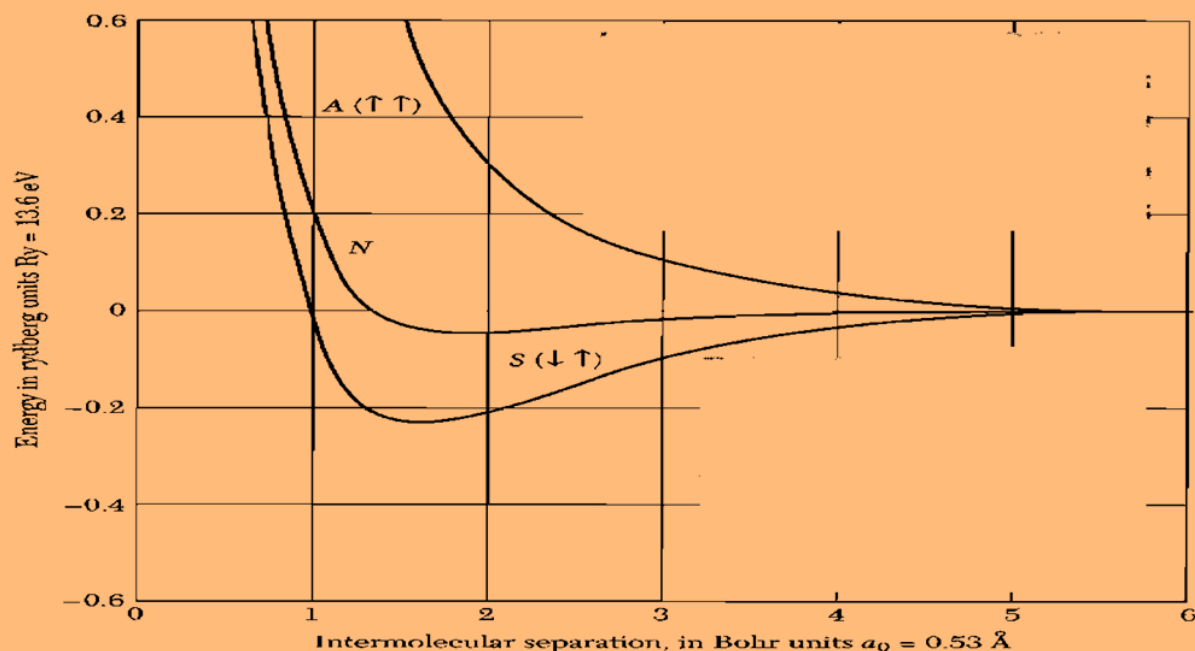


Figure 12 Energy of molecular hydrogen (H_2) referred to separated neutral atoms. A negative energy corresponds to binding. The curve N refers to a classical calculation with free atom charge densities; A is the result for parallel electron spins, taking the Pauli exclusion principle into account, and S (the stable state) for antiparallel spins. The density of charge is represented by contour lines for the states A and S .

The Pauli principle gives a strong repulsive interaction between atoms with filled shells. If the shells are not filled, electron overlap can be accommodated without excitation of electrons to high energy states and the bond will be shorter. Compare the bond length (2 \AA) of Cl_2 with the interatomic distance (3.76 \AA) of Ar in solid Ar; also compare the cohesive energies given in Table 1. The difference between Cl_2 and Ar_2 is that the Cl atom has five electrons in the $3p$ shell and the Ar atom has six, filling the shell, so that the repulsive interaction is stronger in Ar than in Cl.

The elements C, Si, and Ge lack four electrons with respect to filled shells, and thus these elements (for example) can have an attractive interaction associated with charge overlap. The electron configuration of carbon is $1s^2 2s^2 2p^2$. To form a tetrahedral system of covalent bonds the carbon atom must first be promoted to the electronic configuration $1s^2 2s^2 2p^3$. This promotion from the ground state requires 4 eV, an amount more than regained when the bonds are formed.

Fractional Ionic character of bonds in binary crystals

Crystal	Fractional ionic character	Crystal	Fractional ionic character
Si	0.00	GaAs	0.31
SiC	0.18	GaSb	0.26
Ge	0.00	AgCl	0.86
ZnO	0.62	AgBr	0.85
ZnS	0.62	AgI	0.77
ZnSe	0.63	MgO	0.84
ZnTe	0.61	MgS	0.79
CdO	0.79	MgSe	0.79
CdS	0.69	LiF	0.92
CdSe	0.70	NaCl	0.94
CdTe	0.67	RbF	0.96
InP	0.42		
InAs	0.36		
InSb	0.32		

After, J.C Philips, bonds and bands in semiconductors

3.4 Metallic bonding

- ❖ Metals are characterized by high electrical conductivity and; a large number of electrons in a metals are free to move about.
- ❖ These free electrons are referred as conduction electrons.
- ❖ The valence electrons of the atom become the conduction electrons.
- ❖ In some metals the interactions of ionic cores with conduction electrons always makes a large contributions to binding energy.
- ❖ The characteristic features of metallic binding;
 - ⇒ **Energy of the valence electrons is lower than energy of free atoms.**
- ❖ The binding energy of alkali metals crystal is less than alkali metal halides crystals.
- ❖ The bond formed by conduction electron is not very strong.

- ❖ The interatomic distances are relatively large in the alkali metals b/c the kinetic energy of the conduction electron is lower at large interatomic distance.
- ❖ This lead to weak binding.
- ❖ **The strength of a metallic bond depends on three things:**
 - i. The number of electrons that become delocalized from the metal.
 - ii. The charge of the cation (metal).
 - iii. The size of the cation.

- ❖ In general, metallic bonding is due to delocalization of electrons.
- ❖ Metals tend to crystallize in relatively closed packed structures, hcp, fcc, bcc but not in loosely packed structures such as diamond.
- ❖ In the transition metals there is additional binding from inner electron shells.

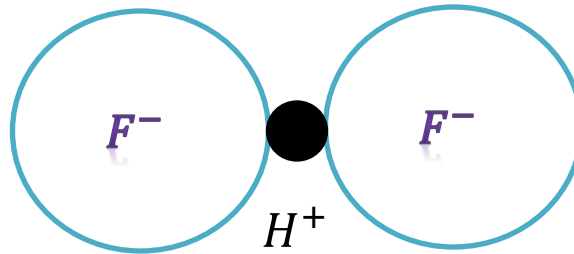
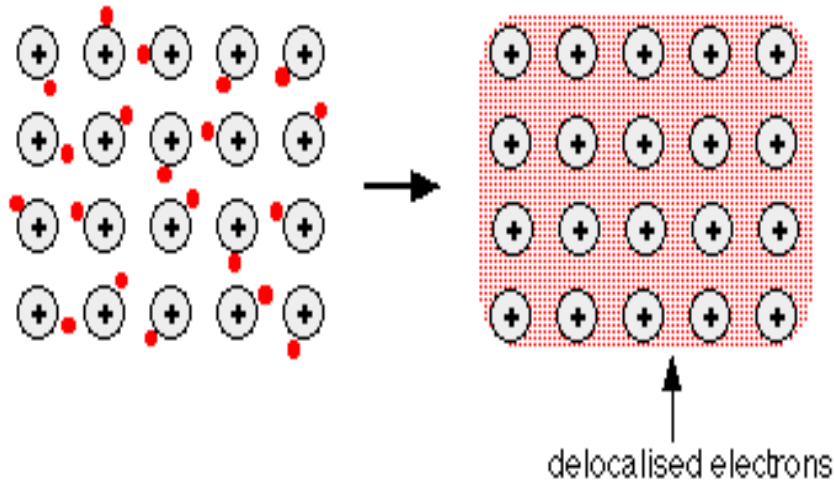


Fig. Hydrogen fluoride, HF_2^-
is stabilized by hydrogen bond.

- ❖ Transition metals and metals following these metals have large d-electron shells and are characterized by high binding energy.

3.5 Characteristics of Metallic crystals

- ❖ The delocalized electrons are free to move about the metallic lattice.
- ❖ This is sometimes described as "an array of positive ions in a sea of electrons".



- ❖ Each positive center in the diagram represents all the rest of the atom apart from the outer electron, but that electron hasn't been lost.
- ❖ It may no longer have an attachment to a particular atom, but those electrons are still there in the structure.

- ❖ Metals are generally ductile and malleable.
- ❖ They are conductive and not very hard.
- ❖ They are highly symmetric because metallic bonds are nondirectional.

Exercise

1. Using the Lenard-Jones potential, calculate the ratio of the cohesive energies of neon in the bcc and fcc structures. Use the lattice sums for bcc structures be molecule as a sphere.

$$\sum_j' p_{ij}^{-12} = 9.11418 \text{ and } \sum_j' p_{ij}^{-6} = 12.2533$$

(Ans. 0.958).

2. Using the values λ and ρ , and madelung constant calculate the cohesive energy of KCl in the ZnS structure and compare the value calculated for the KCl in the CsCl structure.

3. Explain how ion core interaction with conduction electron produce a larger binding energy?

Chapter 4

4.1 Vibrations of crystals

Vibrations of crystals with monoatomic basis

- We consider the elastic vibrations of the crystal with one atom in the primitive cell.
- ❖ We want to find the frequency of an elastic wave in terms of the wave vector that describe a wave and in terms of elastic constant.
- ❖ The mathematical solution is simple in $[100]$, $[110]$, and $[111]$ propagation directions in cubic crystal.
- ❖ These are the directions of cub edge, face diagonal, & body diagonal.
- ❖ When a wave propagate along one of these directions entire plane of atoms move in a phase with displacement either parallel or perpendicular to the direction of wavevector.

- ❑ We can describe with a single coordinate u_s , the displacement of a plane, s from its equilibrium positions.
- The problem is now one dimensional.
- For each wave vector, there are three modes as a solutions for u_s ; one longitudinal polarizations & two transverse polarizations fig-2 & 3 respectively.
- ❖ We assume that the elastic response of a crystal is a linear function of force.
- ❖ This is equivalent to the assumption that elastic energy is quadratic function of relative displacement of any two points in the crystal.
- ❖ Terms in the energy that are linear in displacement will vanishes in equilibrium.
- ♠ Moreover, cubic and higher terms may be neglected for sufficiently small elastic deformations.
- ♠ we assume that the force on the plane, s caused by the displacement of the plane $s + p$ is proportional to the difference , $u_{s+p} - u_s$ of their displacement.

□ For brevity, we consider only nearest-neighbor interactions with $p = \pm 1$

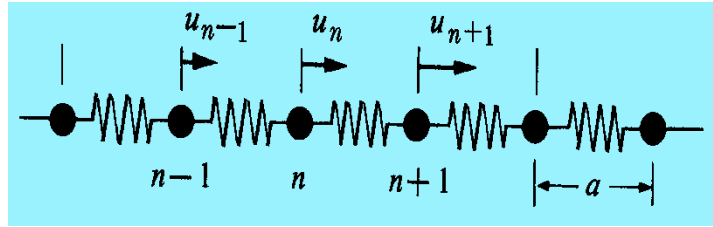


Fig 4.1 Spring Model

❖ Here $n = s$. The total force on plane s from $s \pm 1$ is

$$F_s = c(u_{s+1} - u_s) + c(u_{s-1} - u_s) \quad (1)$$

- This expression is linear in displacement and is of the form of Hook's law.
- The constant, c is the force constant between nearest neighbor planes and will differ for longitudinal and transverse waves.
- Here, c is defined for one atom & F_s is the force on one atom in a plane s .

❑ The equation of motion of an atom in the plane s is

$$M \frac{d^2 u_s}{dt^2} = c(u_{s+1} + u_{s-1} - 2u_s) \quad (2)$$

Where M is the mass of an atom.

❖ We look for solutions with all displacements having the time dependency, $e^{-i\omega t}$.

Then $\frac{d^2 u_s}{dt^2} = -\omega^2 u_s$.

❖ Equation (2) becomes

$$-M\omega^2 u_s = c(u_{s+1} + u_{s-1} - 2u_s) \quad (3)$$

❖ This is a differential equations and have a solution of travelling wave solution of as in (4).

❖ From the equations

$$U_{s\pm 1} = u_0 \exp(iska) \exp(\pm ika) \quad (4)$$

where a is the spacing between the planes and k is the wave vector.

❖ The choice of α - depends on the direction of wave vector k . Using equations (4) and (3)

$$-\omega^2 m u \exp(iska) = C u \{ \exp(i(s+1)ka) + \exp(i(s-1)ka) - 2 \exp(iska) \} \quad (5)$$

❖ We can cancel out $u \exp(iska)$ from both sides.

$$\omega^2 m = C \{ \exp(ika) + \exp(-ika) - 2 \}$$

$$\omega^2 m = -C \{ 2 \cos ka - 2 \}$$

$$\omega^2 = \frac{2c}{M} \{ 1 - \cos ka \} \quad (6)$$

□ The boundary of the first Brillouin zone lies in the region, $\frac{\pm\pi}{a}$.

□ We show from (6) that the stop ω versus k is zero at the zone boundary.

$$\frac{d\omega^2}{dk} = \left(\frac{2ca}{M}\right) \sin ka = 0 \quad (7)$$

□ At $k = \frac{\pm\pi}{a}$, for here $\sin ka = \sin(\pm\pi) = 0$.

□ The special significance of the phonon wave vector that lie on the zone boundary is developed in (11) below.

□ By trigonometric identity with equation (6) may be written as

$$\omega^2 = \left(\frac{4c}{M}\right) \sin^2 \left(\frac{1}{2} ka\right)$$
$$\omega = \left(\frac{4c}{M}\right)^{\frac{1}{2}} \left| \sin \frac{1}{2} ka \right| \quad (8)$$

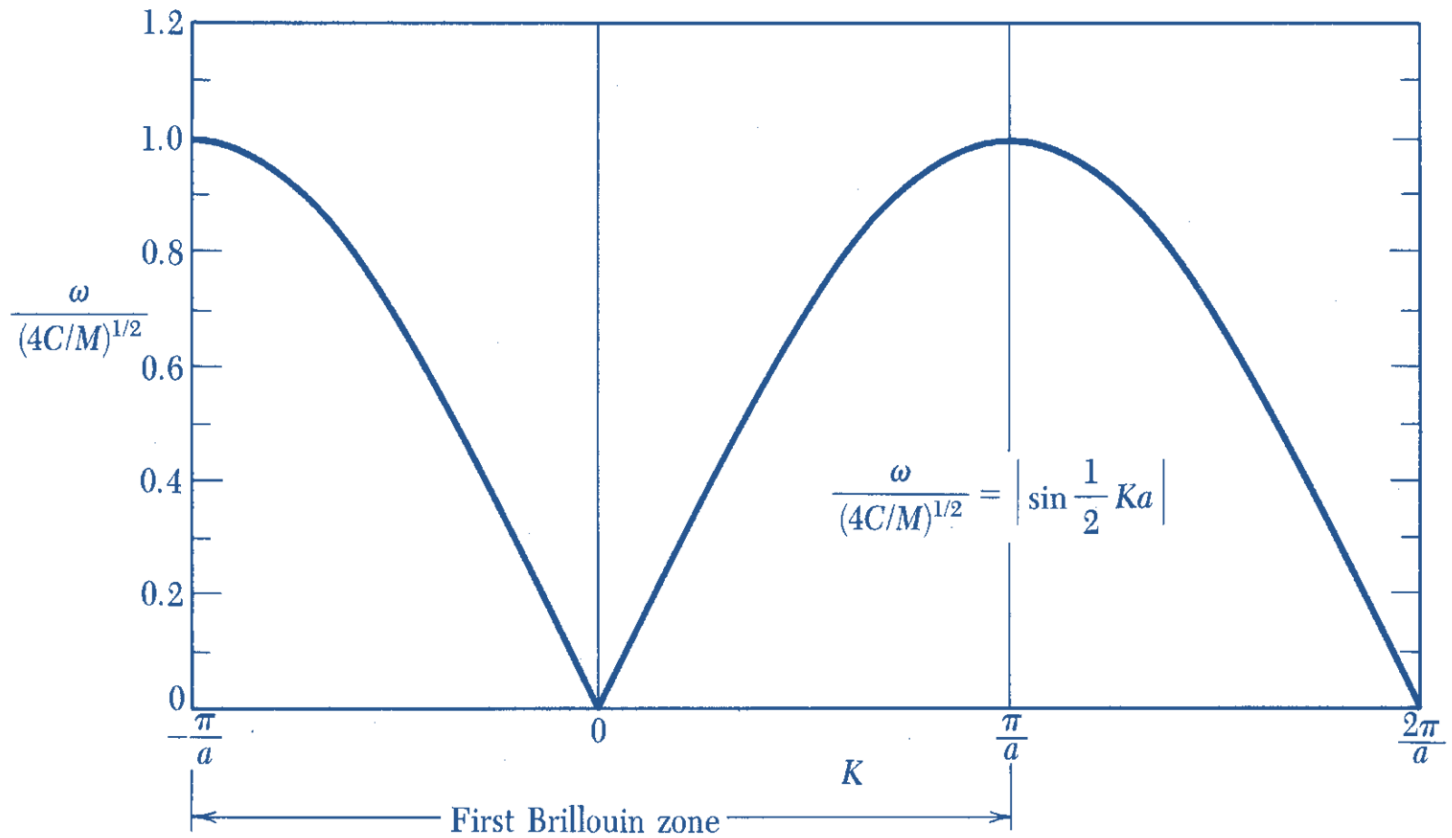


Fig 4.2 Phonon dispersion relation

- Fig- 4 a plot of ω versus K .
- The region of $k \ll \frac{1}{a}$ or $\lambda \gg a$ corresponds to the continuum approximations.
- Here $\omega \sim k$.

First Brillouin Zone

- ❖ What range of k is physically significant for elastic waves?
- ❖ From equation (4), the ratio of the displacements of two successive planes is given by

$$\frac{u_{s+1}}{u_s} = \frac{ue^{(i(s+1)ka)}}{ue^{(iska)}} = e^{ika} \quad (9)$$

- The range from $-\pi$ to $+\pi$ for the plane ka covers all independent values of the exponential.

- ❑ The range of the independent values of k is specified by

$$-\pi < ka < \pi$$

Or

$$\frac{-\pi}{a} < k < \frac{\pi}{a}$$

- ❑ The extreme values are $k_{max} = \pm \frac{\pi}{a}$.
- ❑ The values of k outside Brillouin zone (**Fig - 5**) merely reproduce lattice motion described by values within the limit of $\pm \frac{\pi}{a}$.
- ❑ We may treat the value of k outside this limit by substituting the integral multiple of $\frac{2\pi}{a}$ that will give a value inside this limit.
- ❑ Suppose k lies outside the FBZ, but related wave vector, k' defined
- ❑ $k' = k - \frac{2\pi n}{a}$ lies within the first Brillouin Zone, where n is an integer.

□ The displacement ratio, (10) becomes

$$\frac{u_{s+1}}{u_s} = e^{(i2\pi n)} e^{(i(k'a - 2\pi a))}$$

$$\frac{u_{s+1}}{u_s} = e^{(ik'a)} = e^{(ika)} \quad (10)$$

Where,

$$e^{(i2\pi n)} = 1$$

□ Thus, the displacement can always be described by wave vector within the first Brillouin zone.

□ We note that $\frac{2\pi n}{a}$ is always a reciprocal lattice vector because $\frac{2\pi}{a}$ is a reciprocal lattice vector.

□ Thus, by subtracting an appropriate reciprocal lattice vector from k , we always obtain an equivalent wave vector in the FBZ.

□ At the boundaries, $K_{max} = \pm \frac{\pi}{a}$ of the Brillouin zone, the solution is $u_s = u e^{iska}$, which does not represent a travelling wave but a standing wave.

- ❑ At the zone boundaries, $sk_{max}a = \pm s\pi$, when

$$u_s = u \exp(\pm is\pi) = u(-1)^s \quad (11)$$

- ❑ This is a standing waves.
- ❑ Alternate atoms oscillates in opposite phase because $u_s = \pm 1$ according to whether s is an even integer or an odd one.
- ❑ The wave moves neither to right nor to the left. This condition is equivalent to the Braggs – reflections of x-rays, when the Bragg condition is satisfied.
- ❑ A travelling waves can not propagates through the lattice but through the successive **reflections back and forth**, a standing wave is set up.
- ❑ The critical value, $k_{max} = \pm \frac{\pi}{a}$ found here satisfies the Bragg conditions, $2d \sin \theta = n\lambda$.

Where, $\theta = \frac{\pi}{2}$, $n = 1$, so that $\lambda = 2a$.

$$d = a, \quad k = \frac{2\pi}{a}.$$

Standing waves

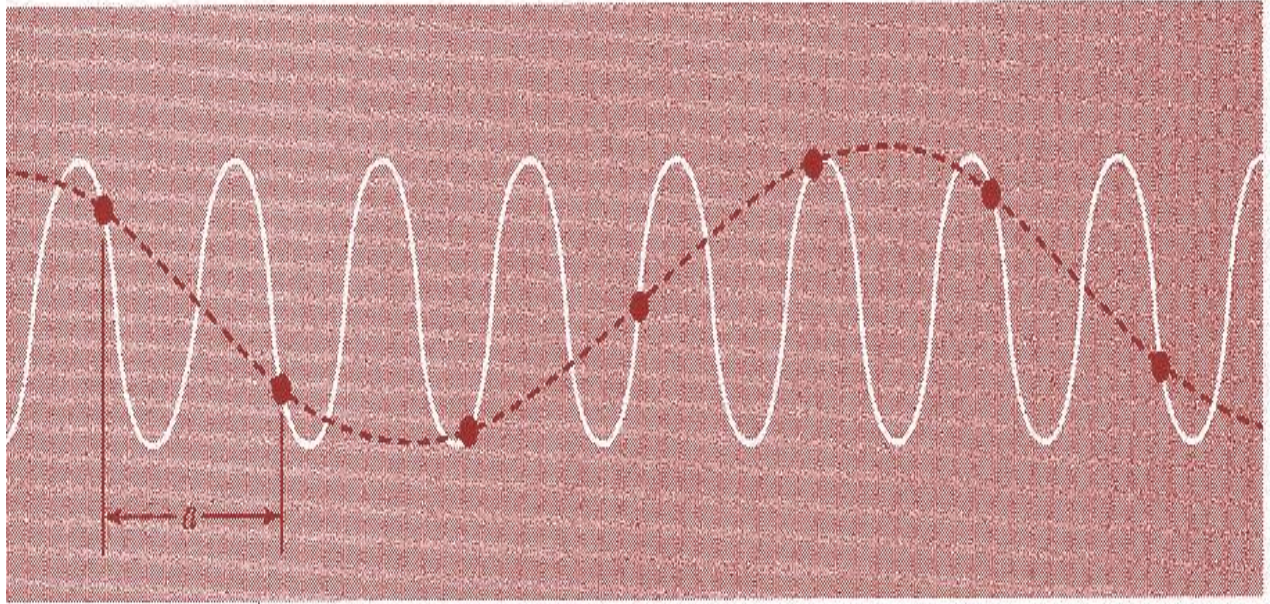


Figure 3. The wave represented by solid curve conveys no information given by the dashed line. Only wavelengths longer than $2a$ *are needed to represent the , motion.*

□ Within X- rays we have $n =$ other integers besides unity because the amplitude of the EMW has meaning in space between atoms but the displacement amplitude of an elastic wave has meaning only at the atoms themselves.

Group velocity

- ❑ Group velocity is a **transmission velocity** of a wave packet.
- ❑ It is the derivative of angular frequency, ω as a function of wave vector, k .

$$V_g = \frac{d\omega}{dk}$$

$$V_g = \text{grad}\omega(k)$$

$$V_g = \nabla_k \omega(k) \quad (12)$$

- ❑ group velocity is the velocity of the energy in the medium of propagation.
- ❑ With particle dispersion relation, the group velocity is given by

$$V_g = \left(\frac{ca^2}{M}\right)^{\frac{1}{2}} \cos\frac{1}{2}ka \quad (13)$$

- ❖ This is zero at the edge of the zone boundary where, $\mathbf{k} = \frac{\pi}{a}$.

❑ Here, the wave is a standing wave as in equation(11) & expect zero net transmission velocity for a standing wave.

❑ Now we might consider the long wavelength & short wavelength limit.

1. Long wave length limit:

when $ka \ll 1$, we expand, $\cos ka = 1 - \frac{1}{2}(ka)^2$, so that the dispersion relation (6) becomes

$$\omega^2 = \left(\frac{c}{M}\right) k^2 a^2$$

$$\omega = \sqrt{\frac{c}{M}} ka \quad (14)$$

➤ This shows that angular frequency is directly proportional to the wave vector at long wavelength limit.

□ According to equation (15), the velocity of sound is independent of frequency in long wave length limit.

□ Thus, $v = \frac{\omega}{k}$, exactly in the continuum theory of elastic waves.

□ In the continuum limit, $ka \ll 1$.

Force constant from exp't.

- ❑ In metals, the effective force may be quite long ranged, & are carried from ion to ion through the conduction electrons. Interactions have been found between planes of atoms and separated by many plans ~ 20 planes.
- ❑ The range of force may be estimated from the experiment on dispersion relation for ω .
- ❑ The generalization of the dispersion relation in (6) to p - nearest neighbor planes is easily found to be

$$\omega^2 = \left(\frac{2}{M}\right) \sum_{p>0} C_p (1 - \cos pka) \quad (15a)$$

We solve for the interplanar force constants, c_p by multiplying both sides by $\cos rka$, where r is an integer & integrating over the range of independent values of k;

$$\begin{aligned} M \int_{-\frac{\pi}{a}}^{+\frac{\pi}{a}} dk \omega_k^2 \cos rka &= 2 \sum_{p>0} C_p \int_{-\frac{\pi}{a}}^{+\frac{\pi}{a}} dk (1 - \cos pka) \cos rka \\ &= -2\pi \frac{C_r}{a} \end{aligned} \quad (15b)$$

❑ The integral vanishes except for $p = r$.

❑ Thus,

$$C_p = \frac{-Ma}{2\pi} \int_{\frac{\pi}{a}}^{\frac{\pi}{a}} d\omega_k^2 \cos pka \quad (16)$$

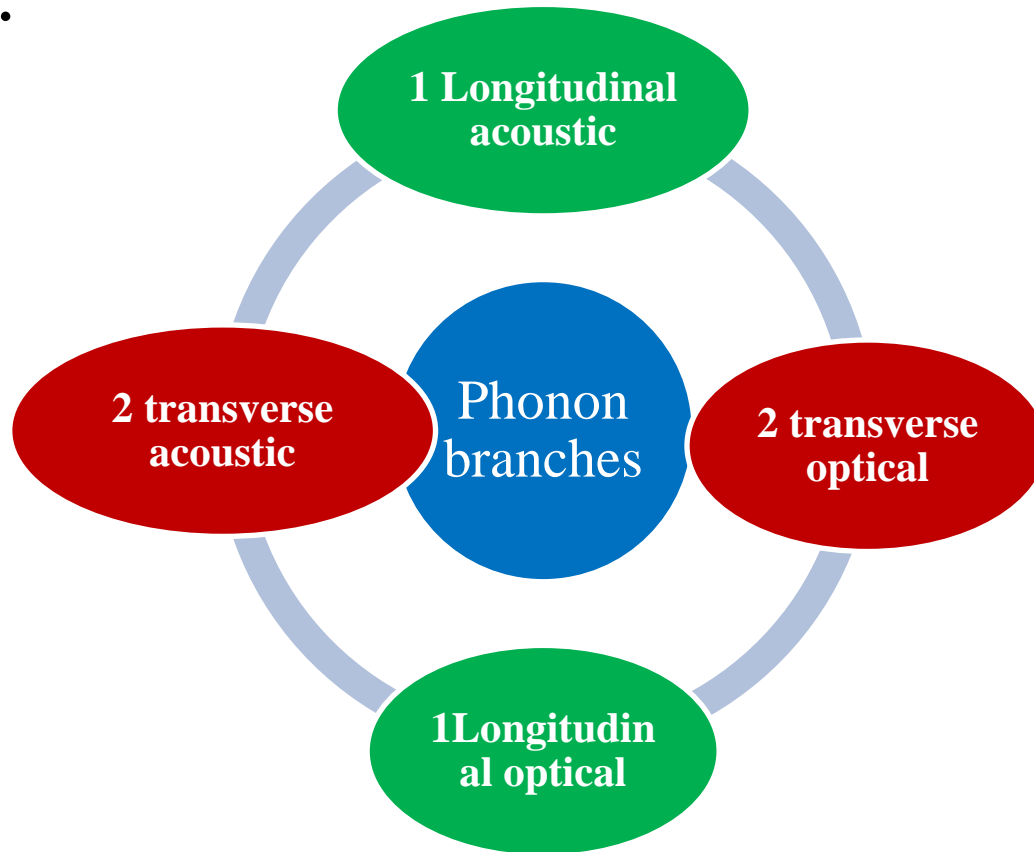
- Equation (17) gives the force constant at a range, pa for a structure in the monoatomic basis.
- LA & TA branches have a total of $3N$ modes accounting a total of $3N$ degree of freedom.
- The remaining $(3p - 3)N$ is accommodated by the optical phonon.
- We consider a cubic crystal where atoms of masses M_1 lie on a set of planes and atoms of masses M_2 lie on the interleaved between those set of fig-9.

- ❑ It is not essential that the masses be d/t but either the force constant or the mass may will be different if the two atoms of the basis are in non-equivalent sites α in the direction of normal to the lattice plane.
- ❑ We treat waves that propagate in the symmetry direction such that a single crystal contains only a single type of atoms.. Such directions are [111] in NaCl plane & [100] in CsCl structure.
- ❑ We write the equations of motion under assumption that each plane interacts with its nearest neighbor planes.
- ❑ And the force constants are identical between all pairs of nearest neighbor planes.

Two atoms per primitive basis

- ❑ The phonon dispersion relation shows new features in the crystal with two or more atoms per primitive basis.
- ❑ Consider for example: NaCl or diamond structure with atoms in the primitive cell.
- ❑ For the polarization mode in a given propagation direction, the dispersion relation ω vs k , develops two types of phonons, namely;
 - i) **the acoustic branch** &
 - ii) **optical phonon branch.**
- ❑ We have longitudinal acoustic, LA , transverse acoustic, TA, longitudinal optical , LO and transverse optical , TO branches.
- ❑ If there are p –atoms in the primitive cell, there are
 - ⇒ **3p acoustic branch** &
 - ⇒ **3p - 3 optical branches.**
- ❑ Thus, germanium (fig 8a) and KBr in (fig 8b) each with two atoms in a primitive cell have six branches.

- Thus, germanium (fig 8a) and KBr in (fig 8b) each with two atoms in a primitive cell have six branches.



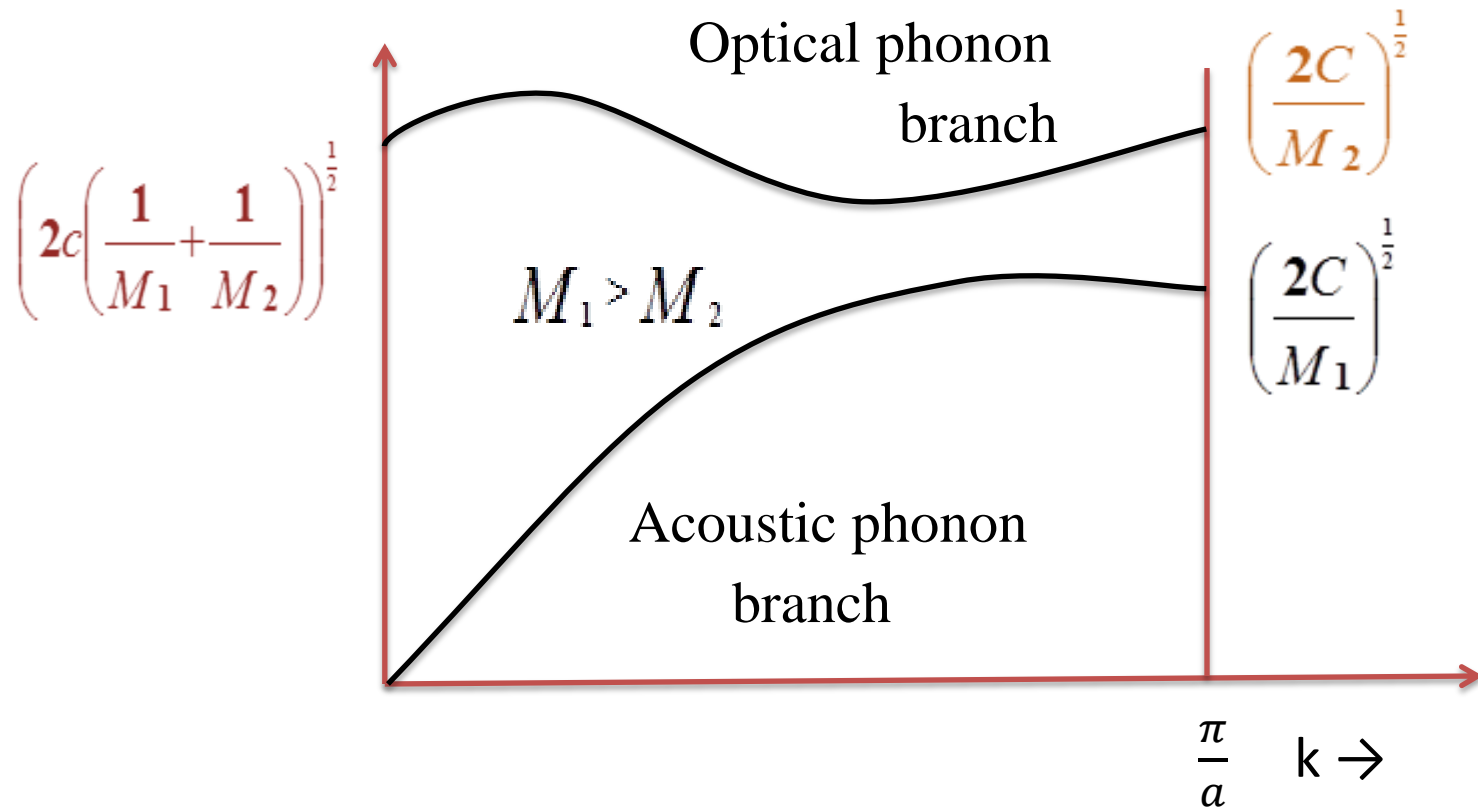


Fig:6b Optical and acoustic branches of phonon dispersion relation for diatomic linear lattice showing limiting frequency at $k = 0$ and

$$k = k_{max} = \frac{\pi}{a}.$$

❖ The lattice constant is a .

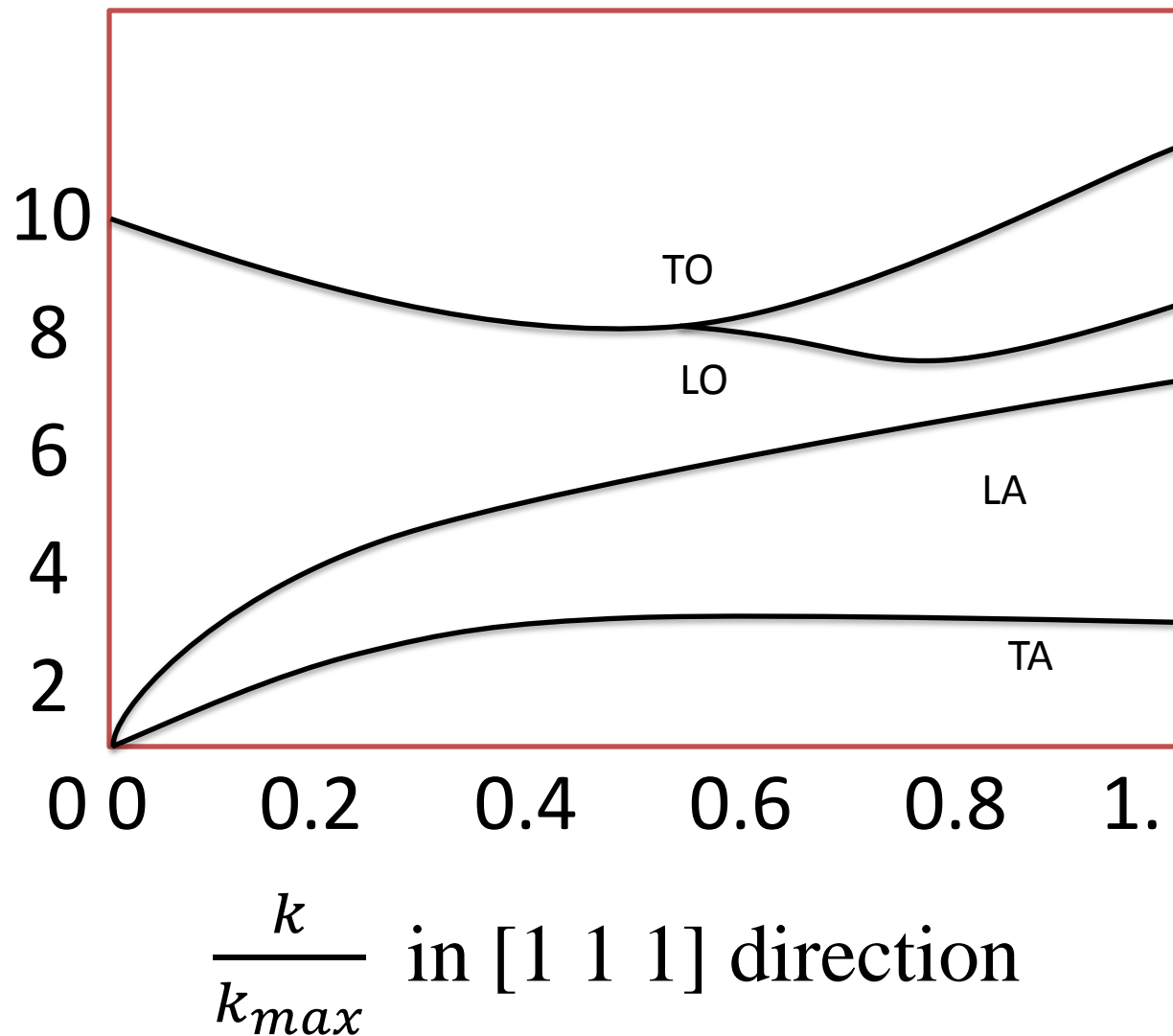


Fig 6a: Phonon dispersion relation in [111] direction in germanium at 80K.

□ From fig 8a we notice that

- Two TA phonon branches are horizontal at the zone boundary position,

$$K_{max} = \left(\frac{2\pi}{a} \right) \left(\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right)$$

- The LO and TO branches coincide at $k = 0$. This is the consequence of the critical symmetry of the Ge.
- The results were obtained with neutron inelastic scattering by G. Nilsson & G. Neftin.
- The numerology of the branches follows from the number of the degree of freedom.
- With p-atoms in the primitive cell & N- primitive cell there are PN atoms.
- Each atom has 3 - degree of freedom one for each of the x, y, & z directions making a total of 3PN degree of freedom for the crystals.
- The number of allowed k- values in a single branch is just N-times for one Brillouin zone.

□ thus,

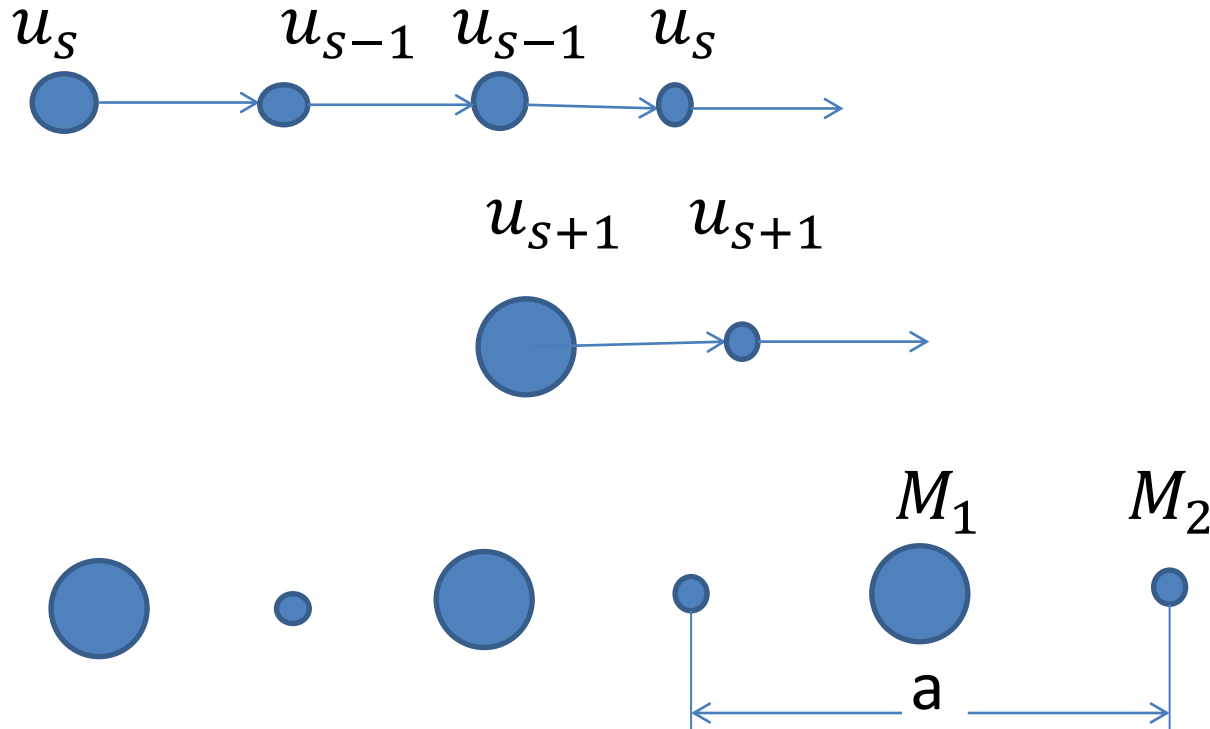


Fig-7 A diatomic crystal structure with masses M_1 & M_2 connected by a force constant c between adjacent planes. The displacement of atoms m_1 are denoted by u_{s-1} , u_s & u_{s+1} .

- And the displacement of atoms M_2 is given by

$$u_{s-1}, u_s \text{ \& } u_{s+1}.$$

- The repeats distance is a in the direction of wave vector K .
- The atoms are shown in undisturbed positions.
- LA & TA branches a total of $3N$ modes there by accounting for $3N$ degree of freedom.
- The remaining $(3p - 3)$ degree of freedom are accommodated by optical branches.
- We treat waves that propagate in a symmetry direction such that a single plane contains only a single type of cells.
- Such directions are $[111]$ for NaCl & $[100]$ for CsCl.

- We write the equation of motion under assumption that each plane interacts only with its nearest neighbor.
- By referring fig-9 we can write the equation of motion.

$$M_1 \frac{d^2 u_s}{dt^2} = c(v_s + v_{s-1} - 2u_s)$$

$$M_1 \frac{d^2 V_s}{dt^2} = c(u_{s+1} + u_s - 2v_s) \quad (17)$$

- We use the solution of the travelling waves with different amplitude, u and v on alternate plane.

$$u_s = u_0 \exp(iska) \exp(-i\omega t)$$

$$V_s = v_0 \exp(iska) \exp(-i\omega t) \quad (18)$$

- We define a - the distance between nearest identical planes not nearest neighbor plane.

□ Up on substitution of equation (18) in to equation (17) we obtain

$$-\omega^2 M_1 u = cv[1 + \exp(-ika)] - 2cu$$

$$-\omega^2 M_2 v = cu[\exp(ika) + 1] - 2cv$$

□ The homogenous linear solution equations have a solution only if the determinant of the coefficient u & v vanishes.

$$\begin{vmatrix} 2c - M_1 \omega^2 & -c(1 + \exp(ika)) \\ -c(1 + \exp(ika)) & 2c - M_2 \omega^2 \end{vmatrix} = 0 \quad (20)$$

This implies

$$M_1 M_2 \omega^4 - 2c(M_1 + M_2)\omega^2 + 2c^2(1 - \cos ka) = 0 \quad (21)$$

■ We can solve this equation exactly for ω^2 ; but it is a simple to examine equ (18) for the limiting cases.

i) If $ka \ll 1$ & $Ka = \pm \frac{\pi}{a}$ at the zone boundaries.

□ For small ka , we have $\cos ka = 1 - \frac{1}{2}k^2a^2$ and the roots are ;

$$\omega^2 = 2c\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \quad (22)$$

equation (23) is for the optical branch

$$\omega^2 = \frac{\frac{1}{2}c}{M_1 + M_2} k^2 a^2 \quad (23)$$

□ And equation (23) is for the acoustic branch, provided that the extent of first Brillouin zone is

$\pm \frac{\pi}{a} \leq k \leq \frac{\pi}{a}$, Where a is the repeat distance in equation (19).

At $k_{max} = \pm \frac{\pi}{a}$, so that the roots are

$$\omega^2 = \frac{2C}{M_1} \text{ \& } \omega^2 = \frac{2C}{M_2} \quad (24)$$

- ❑ The dependency of ω on k is shown in (fig- 4.7, Kittel) for $M_1 > M_2$.
- ❑ The particle displacement in the transverse acoustic (TA) & transverse optical (TO) branch are shown below.
- ❑ For optical branches at $k = 0$, we find the substitution of (22) in (19).

$$\frac{u}{v} = \frac{-M_2}{M_1} \quad (25)$$

- ❑ The atoms vibrate against each other, but their centre of mass is fixed.
- ❑ If this atoms carry opposite charges as in (fig 4.10, Kittel) we may excite the motion of this problem.

Exercise

1. If there are 3 atoms in the primitive cell, then what are the total number of acoustic & optical phonon branches respectively?
2. Explain the difference between acoustic phonon branch & optical phonon branch.

Chapter 5

Phonon heat capacity

- ❑ By heat capacity we mean either heat capacity at constant pressure or heat capacity at constant volume.
- ❑ However, heat capacity at constant volume is more fundamental one.

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad (1)$$

Where,

U – is the energy

T – is the temperature.

c_v -is the heat capacity at constant volume

- ❑ The contribution of phonon to the heat capacity of crystals is called **lattice heat capacity** C_{latt} .

- The total energy of phonon at a temperature $\tau = (k_B T)$ may be written as a sum of the energies of all phonon modes, here indexed by the wave vector k , and polarization index, p .

$$U_{lat} = \sum_k \sum_p \langle n_{k,p} \rangle \hbar \omega_{k,p} \quad (2)$$

Where,

$\langle n_{k,p} \rangle$ - is the thermal equilibrium occupancy of phonons of wave vector k and polarization, p .

- The form of $\langle n_{k,p} \rangle$ is given by the Planck distribution function.

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\hbar \omega}{k_B T}\right) - 1} \quad (3)$$

Here, $\langle \dots \rangle$ the average of thermal equilibrium.

Planck distributions

- ◆ We consider a set of harmonic oscillators in thermal equilibrium.
- ◆ The ratio of number of oscillators in the $(n + 1)^{th}$ quantum state of excitations to the number in the n^{th} quantum state is given by

$$\frac{N_{n+1}}{N_n} = \exp\left(\frac{-\hbar\omega}{\tau}\right) \quad (4)$$

Where $\tau = K_B T$

- ◆ The fraction of the total number of oscillators in the n^{th} quantum state is

$$\frac{N_n}{\sum_{s=0}^{\infty} N_s} = \frac{\exp\left(\frac{-n\hbar\omega}{\tau}\right)}{\sum_{s=0}^{\infty} \exp\left(\frac{-s\hbar\omega}{\tau}\right)} \quad (5)$$

- ◆ We see that the average excitations quantum number of an oscillator is

$$\langle n \rangle = \frac{\sum_s s \exp\left(\frac{-s\hbar\omega}{\tau}\right)}{\sum_s \exp\left(\frac{-s\hbar\omega}{\tau}\right)} \quad (6)$$

□ The summations in (6) are

$$\sum_s s^s = \frac{1}{1-x} \quad (7)$$

$$\sum_s s x^s = x \frac{d}{dx} \sum_s x^s = \frac{x}{(1-x)^2}$$

Where

$$X = \exp\left(\frac{-\hbar\omega}{\tau}\right)$$

Thus, we may rewrite (6) as the Planck distributions.

$$\langle n \rangle = \frac{x}{1-x} = \frac{1}{\exp\left(\frac{\hbar\omega}{\tau}\right) - 1} \quad (8)$$

Normal mode enumerations

- The energy of a collections of oscillators of frequency, $\omega_{k,p}$, in thermal equilibrium is found in (1) and (2).

$$U = \sum_k \sum_p \frac{\hbar \omega_{k,p}}{e^{\left(\frac{\hbar \omega_{k,p}}{\tau}\right)} - 1} \quad (8)$$

- It is usually convenient to replace the summations over k by an integral.
- Suppose that the crystal has $D_p(\omega)d\omega$ mode of a given polarization, p in the frequency ω to $\omega + d\omega$. Then, the energy is

$$U = \sum_p \int d\omega D_p(\omega) \frac{\hbar \omega}{e^{\left(\frac{\hbar \omega}{\tau}\right)} - 1} \quad (9)$$

- The lattice heat capacity is found by differentiating lattice energy with respect to temperature.

□ letting , $x = \frac{\hbar\omega}{\tau}$ then

$$C_v = \frac{\partial U}{\partial T} = K_B \sum_p \int d\omega D_p(\omega) \frac{x^2 e^x}{(e^x - 1)^2} \quad (10)$$

- The central problem is to find $D(\omega)$, the number of modes per unit frequency range.
- This function is called the density of modes or more often density of states.
- Consider the boundary value problem for vibrations of a one dimensional line of length, L carrying $N+1$ particles of separations, a .

Density of States

- Consider the boundary value problem for vibrations of a one dimensional line of length, L carrying $N+1$ particles of separations, a .

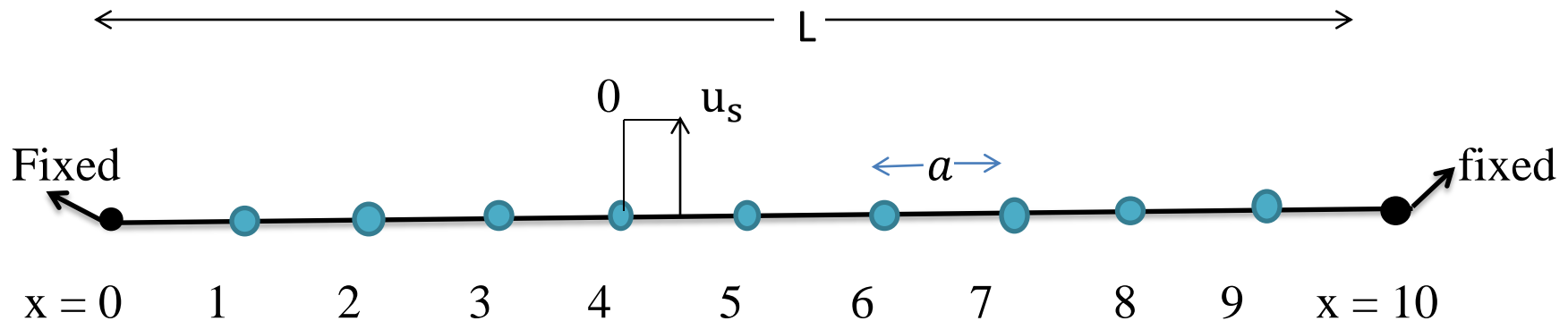


Fig 2: Elastic line of $N+1$ atoms, with $N = 0$ for boundary conditions that the end of atoms $s = 0$ and $s = 10$ are fixed. The particle displacement in the normal modes for either longitudinal or transverse displacement are of the form $u_s \sim \sin ksa$. This form is automatically zero for atoms at the ends, $s = 0$. We choose k - to make the displacement zero at the ends, $s = 10$.

$$K = 0, \frac{\pm 2\pi}{L}, \frac{\pm 4\pi}{L}, \frac{\pm 6\pi}{L}, \dots, \frac{N\pi}{l}.$$

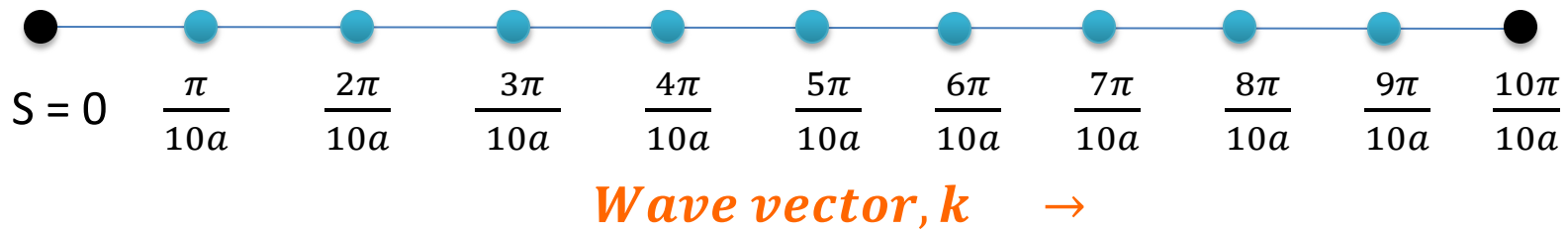


Figure 3. The boundary condition $\sin sKa = 0$ for $s = 10$ can be satisfied by choosing values of $S = 0, \frac{\pi}{10a}, \frac{2\pi}{10a}, \frac{3\pi}{10a}, \frac{4\pi}{10a}, \frac{5\pi}{10a}, \frac{6\pi}{10a}, \frac{7\pi}{10a}, \frac{8\pi}{10a}, \frac{9\pi}{10a}$ where $10a$ is the length L of the line. The present figure is in K space.

- ❖ The dots are not atoms but are the allowed values of K .
- ❖ Of the $N + 1$ particles on the line, only $N - 1$ are allowed to move, and their most general motion can be expressed in terms of the $N - 1$ allowed values of K .
- ❖ This quantization of K has nothing to do with quantum mechanics but follows classically from the boundary conditions that the end atoms be fixed.

- ❑ Suppose that the particle at $s = 0$ and $s = N$, at the ends of the line are held fixed.
- ❑ Each normal vibration mode of polarizations ,p has the form of a standing wave where u_s is the displacement of the particle s.

$$u_s = u_0 \exp(-\omega_{k,p} t) \sin k s a \quad (11)$$

$\omega_{k,p}$ - is related to the k by the dispersion relation. K is fixed by the end boundary conditions,

$$k = \frac{\pi}{L}, \frac{2\pi}{L}, \frac{3\pi}{L}, \dots, \frac{(N-1)\pi}{L} \quad (12)$$

- ❑ The solution for $k = \frac{\pi}{L}$ has the solutions of

$$u_s \sim \sin\left(\frac{s\pi a}{L}\right) \quad (13)$$

And vanishes for $s = 0$ and $s = N$ as required.

- ❑ The solutions for $K = \frac{N\pi}{L} = \frac{\pi}{a} = K_{max}$ has $U_s \sim \sin s\pi a$. This allows no motion of any atom because $\sin s\pi$ vanishes at each atom.
- ❑ There are N-1 allowed independent values of K in (12). This number is equal to the № of particles allowed to move.

☐ Each allowed value of K is associated with a standing wave.

☐ For the one dimensional line there is one mode for each interval;

☐ $\Delta k = \frac{\pi}{L}$ So, that the number of modes per unit a range of k is $\left| \begin{array}{l} \frac{l}{\pi}, \text{ for } k \leq \frac{\pi}{a} \\ 0, \text{ for } k > \frac{\pi}{a} \end{array} \right|$

☐ There are three polarizations, p for each value of k .

☐ In 2-D two of these are transverse and one is the longitudinal.

☐ In three dimensions the polarizations are simple only for a wave vector in certain special crystal direction.

☐ An other device for enumerating mode is equally valid. We consider the medium as unbounded, but requires that the solutions be periodic over large distance, L so that $U(sa) = U(sa + L)$.

☐ The method of periodic boundary conditions does not change the physics of the problem in any essential respect for large system.

❖ In the running wave solutions,

$$u_s = U(o)e^{i(ska - \omega_k t)} \quad (14)$$

The allowed values of k are

$$K = 0, \frac{\pm 2\pi}{L}, \frac{\pm 4\pi}{L}, \frac{\pm 6\pi}{L}, \dots, \frac{N\pi}{L}$$

❖ This method of enumeration gives the same number of mode (one per mobile atom) as in (12).

❖ The change in wavevector between successive values of k is, $\Delta k = \frac{2\pi}{l}$.

❖ For periodic boundary conditions, the number of modes per unit range of k is, $\frac{L}{2\pi}$ for

$$\frac{-\pi}{a} \leq k \leq \frac{+\pi}{a} \text{ and } 0 \text{ otherwise.}$$

❖ We need to know the $D(\omega)$ the number of modes per unit frequency range for a given polarizations.

Fig:4 For N atoms constrained to slide in a circular ring.

❖ The particles oscillate if connected by elastic springs.

❖ In normal mode the displacement u_s of the atom s will be of the form $\sin(ska)$ or $\cos(ska)$ which are independent modes.

❖ By the geometrical periodicity of the ring

❖ Boundary condition is $u_{s+1} = u_s$ for all s .

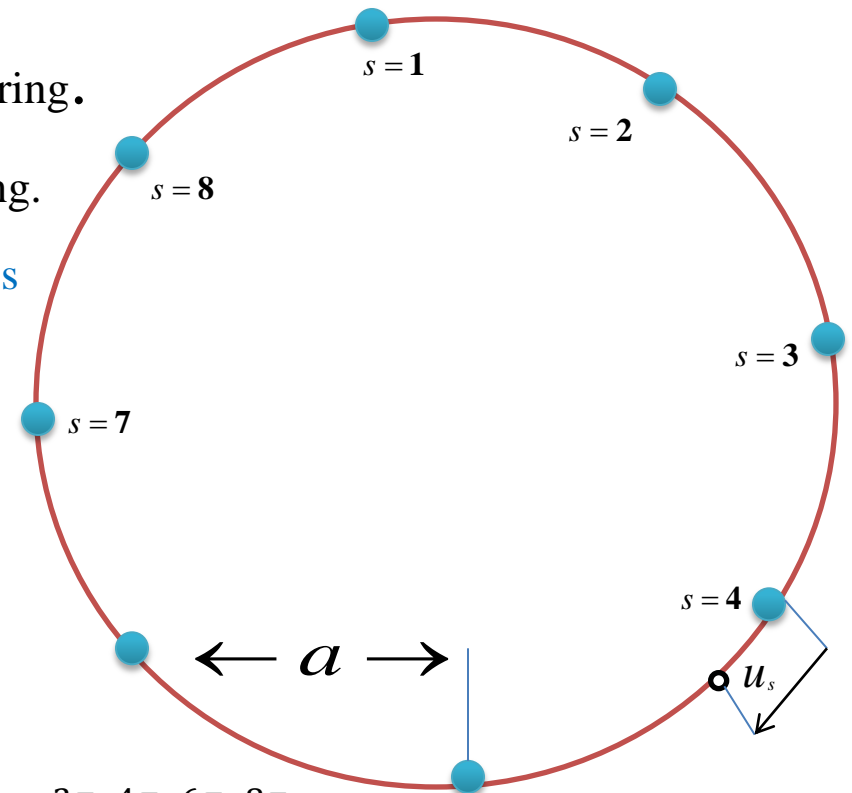
❖ So, Nka must be an integral multiple of 2π .

❖ For $N=8$, the allowed independent values of k are $0, \frac{2\pi}{8a}, \frac{4\pi}{8a}, \frac{6\pi}{8a}, \frac{8\pi}{8a}$.

❖ The value $k=0$ & the value $k=\frac{8\pi}{8a}$ is meaningless for sine form and has meaning for cosine term.

❖ The 3 other values of k are allowed for both sine & cosine term.

❖ Therefore, the periodic boundary conditions lead to one mode per particle exactly as for two fixed end boundary conditions in fig-3.



□ The number of modes $D(\omega)d\omega$ in $d\omega$ at ω is given in one dimension by

$$D(\omega)d\omega = \frac{L}{\pi} \frac{dk}{d\omega} \cdot d\omega$$

$$= \frac{L}{\pi} \frac{d\omega}{d\omega/dk}$$

With, $\frac{d\omega}{dk} = v_g$

$$D(\omega)d\omega = \frac{Ld\omega}{\pi v_g} \quad (15)$$

V_g - is the group velocity.

□ We can also obtain the group velocity from the dispersion relation.

□ There is a singularity in $D(\omega)$ when ever the dispersion relation $\omega(k)$ is horizontal, at $V_g = 0$.

The Debye Model

- ❖ From dispersion relation the density of state $g(\omega)$ obtained by integrating over the Brillion zone.
- ❖ The number allowed values are the number of unit cells (N) in the crystals.
- ❖ In the Debye model, define a cutoff ω_D

$$N = \int_0^{\omega_D} g(\omega) d\omega \quad (16)$$

Where, N is the number of unit cells in the crystal, and $g(\omega)$ is the density of states in one phonon branch.

- ❖ For each mode the density of state is given by

$$g(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{v^3}$$

$$N = \int_0^{\omega_D} \frac{V}{2\pi^2} \frac{\omega^2}{v^3} d\omega = \frac{V}{6\pi^2} \frac{\omega_D^3}{v^3}$$

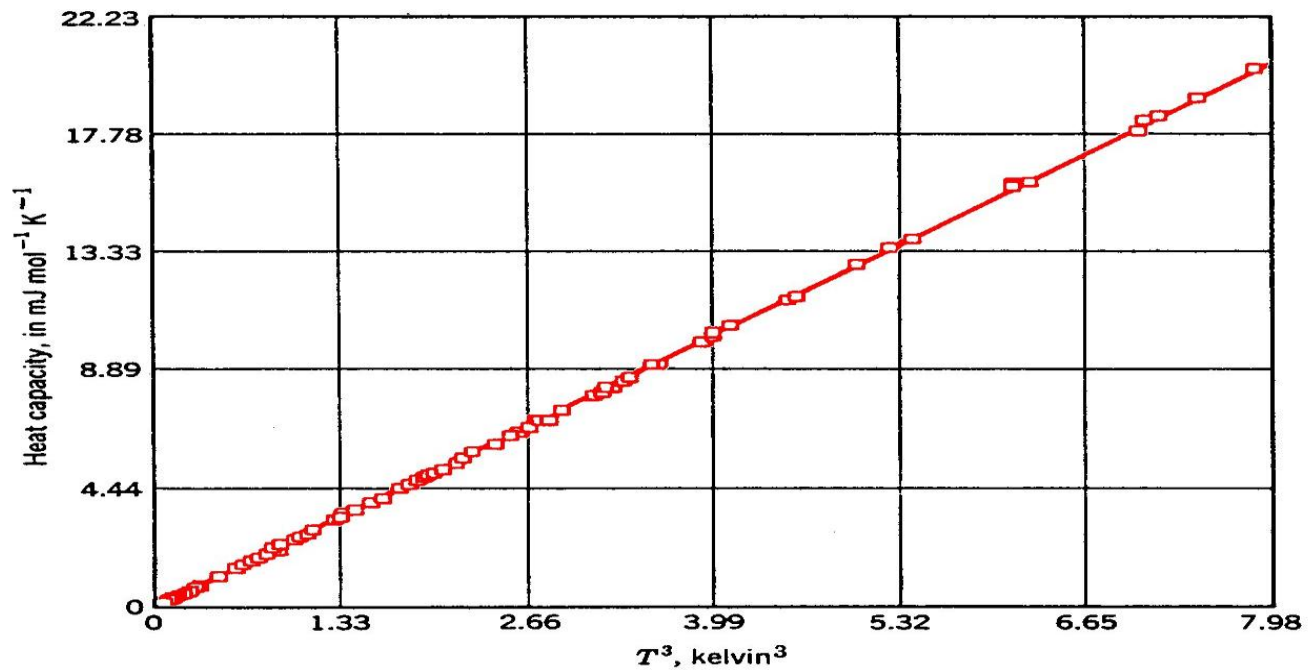
✚ Hence, the Debye cutoff frequency is given by

$$\omega_D^3 = \frac{6N\pi^2}{V} \nu^3 \quad (17)$$

❖ Equivalently the Debye temperature, θ_D is given by

$$\theta_D = \frac{\hbar\omega}{K_B T} \quad (18)$$

✚ In the Debye model the specific heat capacity is given by combining the Debye density of states with the Bose-Einstein distribution.



The low-temperature heat capacity of solid argon compared with the Debye T^3 prediction with $\Theta_D = 92$ K (solid line).

Fig 5. Debye's T^3 law for Argon

❖ The internal energy and the specific heat capacity's are given by

$$U = \sum_{i=1}^{n=3} \frac{V}{2\pi^2 v^2} \int_0^{\omega_D} d\omega \omega^2 \frac{\hbar\omega}{e^{\frac{\hbar\omega}{K_B T}} - 1} \quad (19)$$

with $x = \frac{\hbar\omega}{K_B T} = \frac{\theta}{T}$, $\omega = \frac{K_B T x}{\hbar}$, and $\omega_D = \frac{K_B \theta_D x}{\hbar}$

$$U = \frac{3V}{2\pi^2 v^2} \hbar \left(\frac{K_B T}{\hbar} \right)^4 \int_0^{x_D} dx \frac{x^3}{e^x - 1}$$

$$U = 9NK_B T \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} \quad (20)$$

Hence from table of integration, $\int_0^{x_D} dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$ as $T \sim 0$, $x_D \sim \infty$

$$C_v = \frac{\partial U}{\partial T} = \frac{12\pi^4}{5} NK_B \left(\frac{T}{\theta} \right)^3$$

$$C_v = 234 NK_B \left(\frac{T}{\theta} \right)^3 \quad (21)$$

Einstein Model

✚ According to Einstein's Model the heat capacity of oscillator is given by

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v = Nk_B \left(\frac{\hbar\omega}{\tau} \right)^2 \frac{e^{\frac{\hbar\omega}{\tau}}}{\left(e^{\frac{\hbar\omega}{\tau}} - 1 \right)^2} \quad (22)$$

✚ This expresses the Einstein (1907) result for the contribution of N identical oscillators to the heat capacity of a solid.

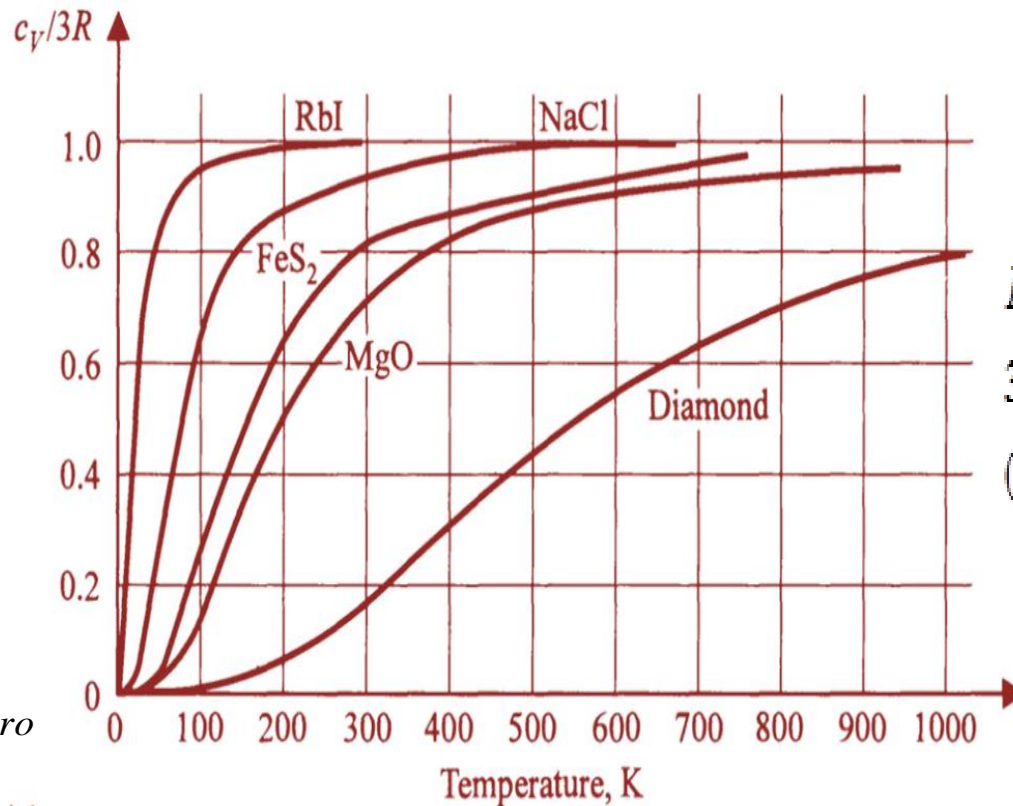
✚ In three dimensions N is replaced by 3N, there being three modes per oscillator.

✚ At high temperature limit, C_v becomes $3NK_B$, which is known as the Dulong and Petit law.

✚ At low temperatures (22) decreases as $e^{-\frac{\hbar\omega}{\tau}}$, whereas the experimental form of the phonon contribution is known to be T^3 as accounted for by the Debye model treated above.

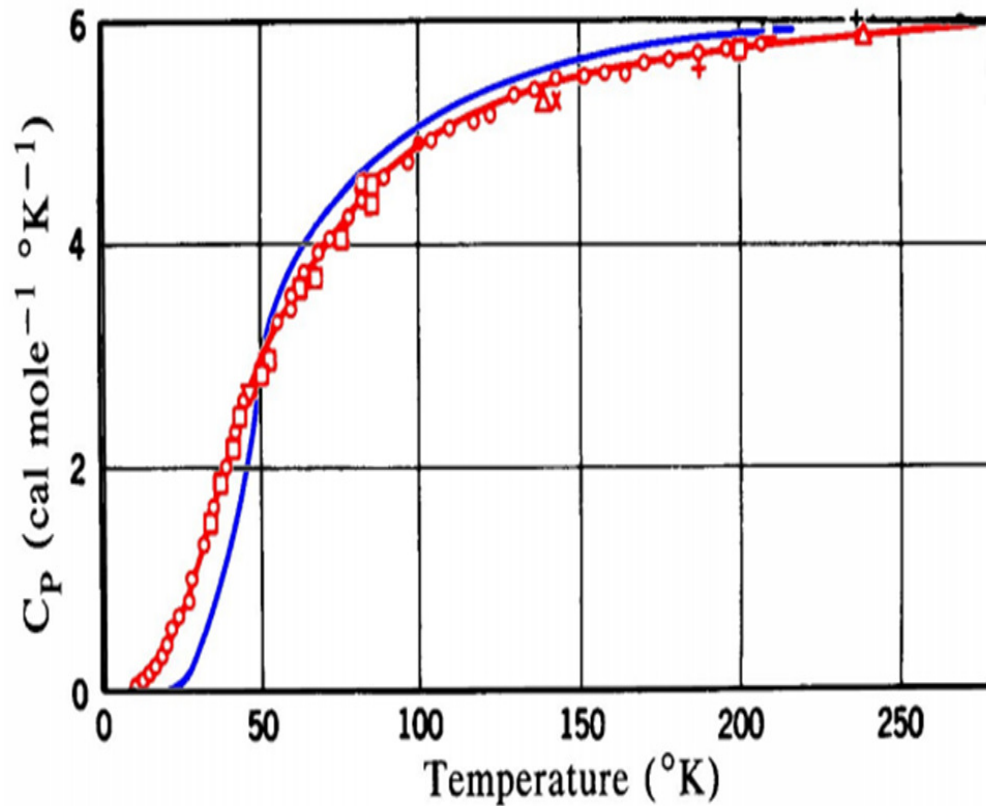
✚ The Einstein model, however, is often used to approximate the optical phonon part of the phonon spectrum.

Heat capacities for different compounds



Heat Capacity drops zero at low temperature

Heat Capacity approaches $3R$ ($25J/K$) at high temperature (Dulong and Peteit law)



At low T , Debye's curve drops slowly because long wavelength vibration can still be excited.

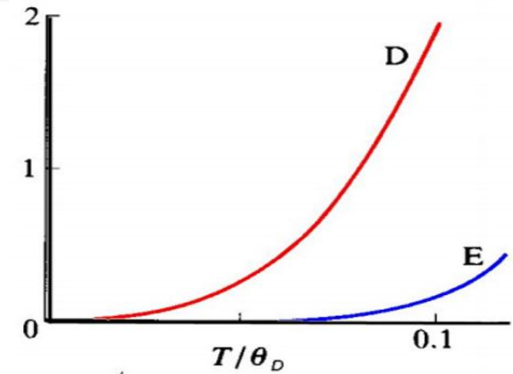


Fig -7 Heat capacity of silver at ($\theta_D = 215\text{K}$)

✚ **Einstein model**: at low temperature, the heat capacity decrease as

$$\exp\left(\frac{-\hbar\omega}{\tau}\right).$$

❖ At high temperature, $C_v = 3NK_B$, the case of Dulong and Peteit law.

➤ **Debye Model**; at low temperature, $C_v = 234NK_B \left(\frac{T}{\theta}\right)^3$.

➤ This means, $C_v \sim T^3$ and $\theta = \frac{\hbar\omega}{k_B}$ is the characteristic temperature.

➤ And at high temperature, $C_v = 3NK_B$.

Thermal conductivity

- ❖ The thermal conductivity coefficient , K of solid is defined by

$$j_v = -K \frac{dT}{dx} \quad (23)$$

Where, j_v is flux of thermal energy or energy transmitted across per unit area per time, and $\frac{dT}{dx}$ is temperature gradient.

- ❖ Thermal energy transfer is random. This random nature of conductivity brings temperature gradient.
- ❖ From kinetic theory of gas, the thermal conductivity is given by

$$k = \frac{1}{3} C v \ell \quad (24)$$

Where, C –is specific heat capacity, v – is the average particle velocity, and ℓ is the mean free path of the particle.

- ❖ This result was first applied by Debye to describe the thermal conductivity in dielectric solids.

Exercise

1. Most of the time Phonons on a lattice do not carry momentum.

Why?

2. Show that the thermal conductivity coefficient, K is given by

$$k = \frac{1}{3} C v \ell.$$



Good Luck!!!