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CHAPTER-1

CRYSTAL STRUCTURE AND BINDING

Crystal structure is one of the most important aspect of material science and engineering, as many properties of materials depends on their crystal structures. The basic principles of many material characterization techniques such as x-ray diffraction, Transmission electron microscopy are based on crystallography. Therefore, understanding the basics of crystal structures is of paramount importance.

Symmetry elements in a crystal

The symmetries possessed by crystals are described by crystals' symmetry operations. A symmetry operation is that which transforms the crystals to itself i.e. a crystal remains invariant under a symmetry operation. These symmetry operations are:

- Translation
- Rotation
- Reflection
- Inversion

Rotation, reflection and inversion are point operations and their combinations give crystal symmetry elements which collectively determine the symmetry of crystal around a point. The group of such symmetry operations at a point is called a point group. There are 32 point groups in a 3D lattice. The group of all the symmetry elements of a crystal structure is called a space group. There are 230 distinct space groups in 3D lattice exhibited by crystals.

Inversion Symmetry

This symmetry element implies that each point located at $\vec{x}$ relative to a lattice point has an identical point $-\vec{x}$ relative to the same lattice point.

In other words, it means that the lattice possesses the centre of inversion or centre of symmetry.

Reflection Symmetry

A lattice is said to possess reflection symmetry if there exists a plane in the lattice which divides it into two identical halves which are mirror images of each other. In other words, a crystal is said to possess reflection symmetry about a plane if it is left unchanged in every way after being reflected by the plane.

Rotation Symmetry

A lattice is said to possess the rotation symmetry if its rotation by an angle θ about an axis transforms the lattice to itself. Since the lattice always remains invariant by a rotation of 2π, the angle 2π must be an integral multiple of θ.

$$n\theta = 2\pi$$
$$\Rightarrow \theta = \frac{2\pi}{n}$$

The factor n takes integral values and is known as multiplicity of rotation axis. Only one, two, three, four and six fold rotation axes of symmetry are possible in a crystal lattice.

Two fold rotation — 180° rotation — Diad axis
Three fold rotation — 120° rotation — Triad axis
Four fold rotation — 90° rotation — Tetrad axis
Six fold rotation — 60° rotation — Hexad axis

Translation Symmetry

In the translation symmetry operation, the first point is repeated at equal distances along a line by a translation nT. Here, T is the translation vector and n is an integer. The translation symmetry elements exhibited by the crystals are screw axis and glide planes.

- When a rotation corresponding to 2-, 3-, 4- or 6-fold axis combines with a translation parallel to the rotation axis, then the symmetry element is called the _screw axis_. In general, a screw axis is represented by the symbol n_m. This is performed by a rotation of $\frac{2\pi}{n}$ and translation of $\frac{m}{n}$ times the translation vector parallel to the rotation axis.

- The operation in a _glide plane_ involves a translation $t/2$ parallel to a reflection plane followed by reflection across the plane. 't' denotes the distance between the successive atoms. Glide planes are divided into 3 types. They are axial glides, diagonal glides and diamond glides.

Types of Space lattices

Two dimensional lattice types

There are five distinct lattice types in 2 dimensions, the ~~oblique lattice and the four special lattices. The four~~ special lattices are the result of four distinct types of restrictions. The distinct lattice types are commonly known as the Bravais lattices.

Lattices	Restrictions.
Square lattice	$\lvert a_1 \rvert = \lvert a_2 \rvert$, $\phi = 90°$
Hexagonal lattice	$\lvert a_1 \rvert = \lvert a_2 \rvert$, $\phi = 120°$
Rectangular lattice	$\lvert a_1 \rvert \neq \lvert a_2 \rvert$, $\phi = 90°$
Centered Rectangular lattice	$\lvert a_1 \rvert \neq \lvert a_2 \rvert$, $\phi = 90°$

So, we can say there are five Bravais lattices in 2 dimensions.

Three dimensional lattice types

The point symmetry groups in 3 dimensions require 14 different lattice types. These are grouped into seven systems. The division into systems is expressed in the table in terms of the axial relations that describe the c[...]

System	No: of lattices	Restrictions
Triclinic	1	$\alpha \neq \beta \neq \gamma$ $a_1 \neq a_2 \neq a_3$
Monoclinic	2	$\alpha = \gamma = 90°, \neq \beta$ $a_1 \neq a_2 \neq a_3$
Orthorhombic	4	$\alpha = \beta = \gamma = 90°$ $a_1 \neq a_2 \neq a_3$
Tetragonal	2	$\alpha = \beta = \gamma = 90°$ $a_1 = a_2 \neq a_3$
Cubic	3	$\alpha = \beta = \gamma = 90°$ $a_1 = a_2 = a_3$
Trigonal	1	$\alpha = \beta = \gamma \angle 120, \neq 90$ $a_1 = a_2 = a_3$
Hexagonal	1	$\alpha = \beta = 90°, \gamma = 120°$ $a_1 = a_2 \neq a_3$

Miller Indices

Miller Indices may be defined as the reciprocals of the intercepts made by the plane on the crystallographic axes when reduced to smallest numbers. Following are the steps involved in the determination of Miller Indices of a plane.

(1) Find the intercepts of the plane on the crystallographic axes.

(2) Take reciprocals of these intercepts.

(3) Simplify to remove fractions, if any, and enclose the numbers obtained in paranthesis ( ).

Eg :- Consider the plane ABCD of a cubic crystal.

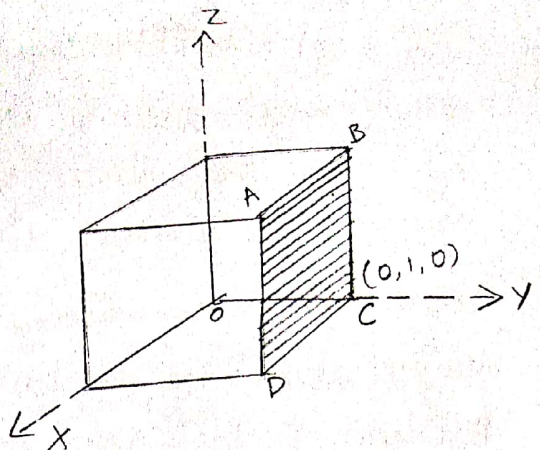The plane cuts the x-axis at infinity, y-axis at 1 and z-axis at infinity.

∴ The coordinates of the intercepts are

$$\infty, 1, \infty$$

Taking the reciprocals,

$$\frac{1}{\infty}, 1, \frac{1}{\infty}$$

or 0, 1, 0

Hence (0 1 0) are the Miller Indices of plane ABCD. The direction $\overline{OC}$ is given by [0 1 0].

Body centred Cubic Structure

In this structure of unit cell, there are 8 atoms at the corners and another atom at the body centre.

Coordination Number - 8

No: of atoms in the unit cell - 2

Packing factor - 68%

Eg :- Li, Na, K, Cr

Face Centred Cubic Structure

In this structure there are eight atoms at eight corners of the unit cell and six atoms at the centres of six faces.

Coordination Number - 12

No: of atoms in the unit cell - 4

Packing factor - 74%

Eg :- Copper, Aluminium, Lead, Silver.

Hexagonal Close Packed structure

The hcp structure has the shape of hexagon. The unit cell of this contains one atom at each corner, one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell.
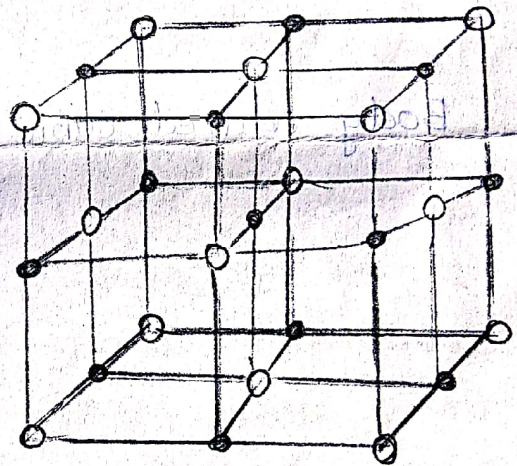
Coordination number – 12

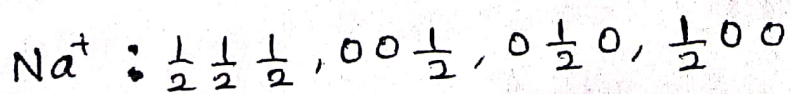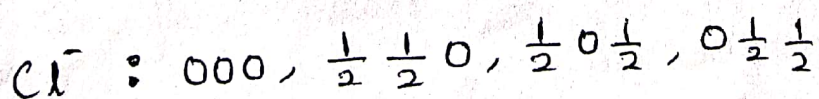No: of atoms in the unit cell – 6

Packing factor – 74 %

Eg :- Magnesium, Zince, Cadmium.

Sodium Chloride Structure

The sodium Chloride, NaCl is shown in the figure. The Bravais lattice of sodium chloride structure is face centred cubic. The basis consists of one Na^+ ion and one Cl^- separated by one half the body diagonal of the unit cube.


A unit cell of NaCl comprises of four molecules.

In this structure, each ion is surrounded by six neighbours of the opposite kind. Therefore, the coordination number is six. The various positions of ions in the unit cell are as follows:

$$Cl^- : 000, \tfrac{1}{2}\tfrac{1}{2}0, \tfrac{1}{2}0\tfrac{1}{2}, 0\tfrac{1}{2}\tfrac{1}{2}$$

$$Na^+ : \tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}, 00\tfrac{1}{2}, 0\tfrac{1}{2}0, \tfrac{1}{2}00$$

Diamond Structure

The space lattice of diamond is face centred cube. The primitive basis of the diamond structure has 2 identical atoms at coordinates 000 and $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ associated with each point of the fcc lattice. The diamond structure contains 8 atoms.
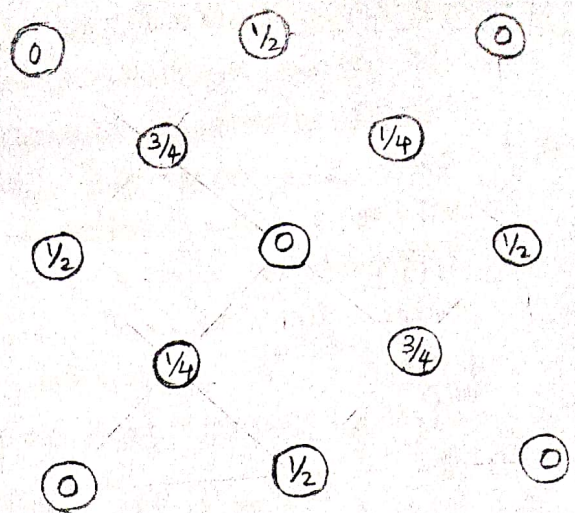
Each atom has 4 nearest neighbours and 12 nearest neighbors. The diamond structure is relatively empty. The packing factor of the dc structure is only 34%. The diamond structure is an example of the directional covalent bonding found in column IV of the periodic table of elements. Carbon, Silicon, Germanium and tin can crystallize in the diamond structure.

The figure shows the atomic positions in the cubic cell of the diamond structure projected on a cube face; fractions denote height above the base in units of a cube edge. The points at 0 and ½ are on the fcc lattice; those at ¼ and 3/4 are on a similar lattice displaced along the body diagonal by one-fourth of its length. With a fcc space lattice, the basis consists of two identical atoms at 000 and ¼ ¼ ¼.

X-ray diffraction

x-rays interact with the electron cloud of the atom. Because of their shorter wavelength, x-rays are scattered by adjacent atoms in crystals, which can interfere and give rise to diffraction effects. When x-rays enter into a crystal, each atom acts as a diffraction centre and crystal as a whole acts like a three dimensional diffraction grating. The diffraction pattern so produced can tell us much about the internal arrangement of atoms in crystals.

Consider two incoming x-rays OE and O'A inclined at an angle θ with the top most plane of the crystal and are scattered in the directions AP and EP', also at an angle θ with that plane. Since the pathlength of x-rays OEP' and O'AP are same, they arrive at P and P' respectively in phase with each other and again form a common wavefront. This is the condition for scattering in phase by one plane of the crystal.

Now, consider the effect of an adjacent plane. Consider the incoming beam OC and scattered ray CP''. If EB and ED are parallel to the incident and scattered wavefronts respectively,

The total path length = BCD

$$= 2 BC$$
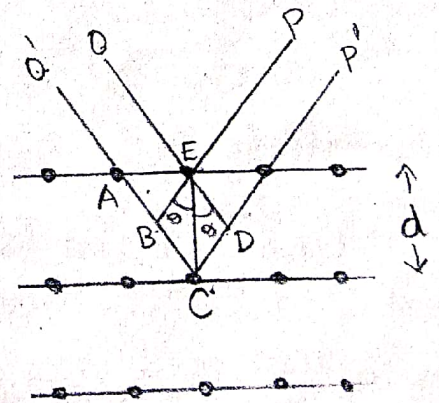
We have, $BC = d\sin\theta$

$\Rightarrow$ path difference $= 2d\sin\theta$.

If the 2 planes scatter inphase with each other,

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

$n = 0, 1, 2 \ldots$ gives the order of reflection. The above equation is known as Bragg's law.

Ewald Construction

Bragg's diffraction condition has been obtained from the assumption that a crystal is made up of a large number of equidistant parallel planes. The integer n in the expression gives the order of diffraction. If we incorporate n with d,

$$\lambda = 2\frac{d}{n}\sin\theta \qquad\qquad (1)$$

It is possible to assign the indices to some imaginary planes whose spacing is d_{hkl}/n. The modified form of Bragg's law is

$$\lambda = 2 d_{hkl} \sin\theta_{hkl}$$

which indicates the diffraction by the specific planes $(h\,k\,l)$ or at a particular angle θ_{hkl} corresponding to a particular plane $(h\,k\,l)$.

$$\therefore \quad \sin\theta_{hkl} = \frac{\lambda/2}{d_{hkl}} = \frac{1/d_{hkl}}{2/\lambda} \qquad\qquad (2)$$

We know that a triangle inscribed inside a circle is a right angled triangle when the diameter of the circle is taken as the hypotenuse of the triangle. We construct a circle whose diameter is $2/\lambda$ and inscribe a triangle satisfying (2). The perpendicular component is $1/d_{hkl}$ and the opposite angle is θ_{hkl}. This is simply a graphical representation of Bragg's law.

The crystal is placed at the centre, C of the circle. of radius $1/\lambda$. Point O, where direct x-ray beam leaves the circle after passing through the crystal is the origin of the reciprocal lattice net.
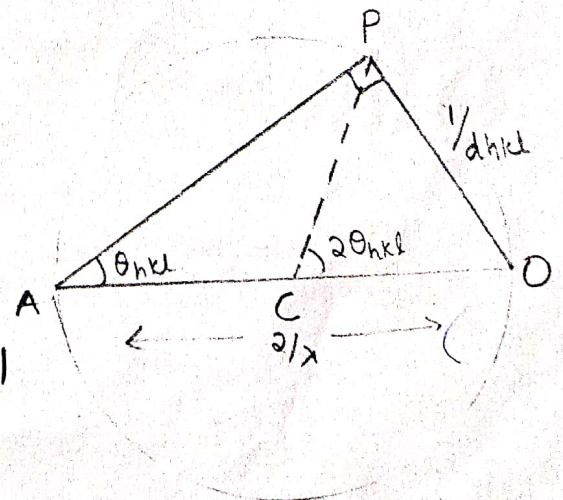
Whenever a reciprocal lattice vector intersect the circle (2) is satisfied, then a diffracted beam passes through point of intersection and hence the x-ray diffraction becomes possible. The locus of a point where the diffracted beam and reciprocal lattice point intersect a circle of radius $1/\lambda$ is called **Ewald sphere** or sphere of reflection. Here, 2 possibilities may arise. They are:

① If the circle doesnot pass through any reciprocal lattice point, it will indicate that the particular wavelength in question will not be diffracted by the crystal in that orientation, and a reorientation of the crystal has to be made.

② If the circle passes through a reciprocal lattice point P, then OP is a reciprocal lattice vector normal to some set of lattice planes.

$$OP = |G| = 1/d$$

Let k and k' be the incident and reflected wave vectors. Then,

$$k' = k + G \underline{\hspace{2cm}} (3)$$

This equation shows that the scattering changes only the direction of k and the scattered wave differ from the incident wave by a reciprocal lattice vector G.

$$|k| = |k'| = \frac{2\pi}{\lambda} \underline{\hspace{2cm}} (4)$$

On squaring (3),

$$k'^2 = (k+G)^2 = k^2 + G^2 + 2k \cdot G$$

From (4),

$$\boxed{G^2 + 2k \cdot G = 0}$$

This is the **Bragg's law in vector form**

[* Description of x-ray diffraction using reciprocal lattice
→ Ewald construction]

The Reciprocal Lattice

A crystal lattice may be considered as an assembly of various different sets of equidistant parallel planes. Consider a real crystal lattice and apply the following:

1) From a common origin, draw a normal to each crystal plane.

2) Set the length of each normal equal to 2π times the reciprocal of the interplanar spacing d_{hkl}.

3) Mark a point at the end of each normal which represents the crystal plane.

A collection of points obtained in this way corresponding to various crystal planes form a lattice array and is known as reciprocal lattice. Similar to the translation vector in the direct lattice, the reciprocal lattice vector may be defined as

$$G = n_1 \cdot a^* + n_2 \cdot b^*$$

For a general lattice, if the angle between a and b is θ,

$$a^* = \frac{2\pi}{a\sin\theta} \quad , \quad b^* = \frac{2\pi}{b\sin\theta}$$

In a three dimensional case, consider a direct crystal lattice whose unit cell is defined by the vectors a, b and c. If the area of bc plane is A, then the volume of the unit cell V is given by

$$V = \text{Area of bc-plane} \times \text{height}$$

$$= A \times d_{100}$$

So that, $a^* = \dfrac{2\pi}{d_{100}} = \dfrac{2\pi A}{V}$

We know that $A = b \times c$

$$V = a \cdot (b \times c)$$

Therefore,

$$a^* = \frac{2\pi}{d_{100}} = \frac{2\pi\,(b \times c)}{a \cdot (b \times c)}$$

Similarly,

$$b^* = \frac{2\pi}{d_{010}} = \frac{2\pi\,(c \times a)}{a \cdot (b \times c)}$$

$$c^* = \frac{2\pi}{d_{001}} = \frac{2\pi\,(a \times b)}{a \cdot (b \times c)}$$

Properties of the Reciprocal lattice.

- Every reciprocal lattice vector G is normal to the plane of the crystal lattice (hkl).
- The interplanar spacing d_{hkl} in a real crystal lattice is equal to $1/|G|$.
- The reciprocal of a reciprocal lattice is a real lattice.
- Volume of the unit cell of the reciprocal lattice is inversely proportional to that of corresponding real lattice.

Reciprocal lattice to sc lattice.

The primitive translation vectors of a simple cubic lattice is

$$a = a\hat{i}, \quad b = a\hat{j}, \quad c = a\hat{k}$$

The volume of the unit cell is $V = a \cdot b \times c = a^3$

The primitive translation vectors of the reciprocal lattice of the simple cubic lattice is

$$a^* = \frac{2\pi\,b \times c}{a \cdot (b \times c)} = \frac{2\pi}{a}\hat{i}$$

$$b^* = \frac{2\pi\,(c \times a)}{a \cdot (b \times c)} = \frac{2\pi}{a}\hat{j}$$

$$c^* = \frac{2\pi\,(a \times b)}{a \cdot (b \times c)} = \frac{2\pi}{a}\hat{k}$$

Reciprocal lattice is itself a simple cubic lattice with a lattice constant $2\pi/a$.

Reciprocal lattice to Bcc lattice

The primitive translation vectors of the bcc lattice are given by

$$a' = \frac{a}{2}(-\hat{i} + \hat{j} + \hat{k})$$

$$b' = \frac{a}{2}(\hat{i} - \hat{j} + \hat{k})$$

$$c' = \frac{a}{2}(\hat{i} + \hat{j} - \hat{k})$$

The volume of the primitive unit cell, $V = |a' \cdot b' \times c'| = a^3/2$

The primitive translation vectors of the reciprocal lattice are defined by

$$a^* = 2\pi \frac{b' \times c'}{a' \cdot b' \times c'} = \frac{2\pi \times \frac{a^2}{4}(\hat{i} - \hat{j} + \hat{k}) \times (\hat{i} + \hat{j} - \hat{k})}{a^3/2}$$

$$= \frac{2\pi}{a}(\hat{j} + \hat{k})$$

Similarly, $\quad b^* = \frac{2\pi}{a}(\hat{i} + \hat{k})$

$$c^* = \frac{2\pi}{a}(\hat{i} + \hat{j})$$

These are the primitive vectors of the fcc lattice. Thus, the fcc lattice is the reciprocal of the bcc lattice.

Reciprocal lattice to fcc lattice

The primitive translation vectors of fcc lattice are.

$$a' = \frac{a}{2}(\hat{j} + \hat{k}) \quad , \quad b' = \frac{a}{2}(\hat{i} + \hat{k}) \quad , \quad c' = \frac{a}{2}(\hat{i} + \hat{j})$$

Volume of the primitive cell, $V = a^3/4$.

Now, $\quad a^* = 2\pi \frac{b' \times c'}{a' \cdot (b' \times c')} = 2\pi \frac{\frac{a^2}{4}(\hat{i} + \hat{k}) \times (\hat{i} + \hat{j})}{a^3/4} = \frac{2\pi}{a}(-\hat{i} + \hat{j} + \hat{k})$

Similarly, $b^* = \frac{2\pi}{a}(\hat{i} - \hat{j} + \hat{k}), \quad c^* = \frac{2\pi}{a}(\hat{i} + \hat{j} - \hat{k})$.

These are the translation vectors of bcc lattice. So, the bcc lattice is the reciprocal lattice of the fcc lattice.

Wigner-Seitz Primitive Cell

1) Draw lines to connect a given lattice point to all neighboring lattice points.

2) At the midpoints and normals to these lines, draw new lines or planes.

3) The smallest volume enclosed in this way is the Wigner-Seitz primitive cell.
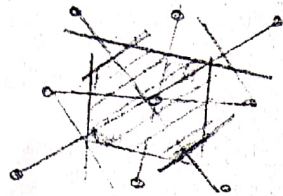
Brillouin Zones

A Brillouin zone is defined as a Wigner-Seitz primitive cell in the reciprocal lattice. The Brillouin zone gives a vivid geometrical interpretation of the diffraction condition

$$2k \cdot G = G^2$$

Dividing both sides by 4,

$$k \cdot (G/2) = (G/2)^2$$

Select a vector G from the origin to a reciprocal lattice point. Construct a plane normal to this vector G at its midpoint. This plane forms a part of a zone boundary. An x-ray beam in the crystal will be diffracted if its wave vector k has the magnitude and direction required by the above equation. The diffracted beam will then be in the direction $k-G$ with $\Delta k = -G$. Thus, the brillouin construction exhibits all the wave vectors k which can be Bragg reflected by the crystal. The first Brillouin zone is the smallest volume entirely enclosed by the planes that are perpendicular bisectors of the reciprocal lattice vectors drawn from the origin.

Simple Cubic Lattice

The boundaries of the first Brillouin zones are the planes normal to the six reciprocal lattice vectors

$$\pm \frac{1}{2} a^* = \pm \frac{\pi}{a} \hat{\imath}$$

$$\pm \frac{1}{2} b^* = \pm \frac{\pi}{a} \hat{\jmath}$$

$$\pm \frac{1}{2} c^* = \pm \frac{\pi}{a} \hat{k}$$

The six planes bound a cube of edge $2\pi/a$ and of volume $(2\pi/a)^3$ This is the first Brillouin zone.

BCC Lattice

The primitive translation vectors

$$\pm a^* = \frac{2\pi}{a} (\pm \hat{k} \pm \hat{\jmath})$$

$$\pm b^* = \frac{2\pi}{a} (\pm \hat{\imath} \pm \hat{k})$$

$$\pm c^* = \frac{2\pi}{a} (\pm \hat{\imath} \pm \hat{\jmath})$$

This zone is bounded by the planes normal to the 12 vectors at their midpoints. The zone is a regular 12 faced solid-rhombic dodecahedron.

FCC Lattice

The shortest G's are the eight vectors

$$\frac{2\pi}{a} (\pm \hat{\imath} \pm \hat{\jmath} \pm \hat{k})$$

The first Brillouin zone is a truncated octahedron.

Crystals of Inert Gases

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

> 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 cha
  in the free atom is spherically symmetric.
> In the crystal, the inert gas atoms pack together
  as closely as possible.

Vander Waals Interaction

It is the principal attractive interaction in crystals of
inert gases. It is also known as the London interaction
or the induced dipole-dipole interaction.

Consider two identical inert gas atoms at a
separation R large in comparison with the radii of the
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 cancelled outside a neutral atom
by electrostatic potential of the charge on the nucleus.
Thus 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 atoms.

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 & x_2
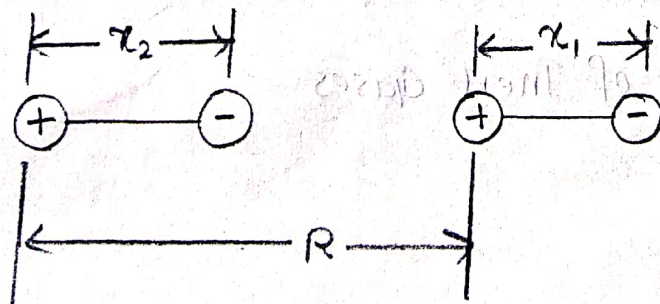
The particles oscillate along the x-axis. Let P_1 and P_2 denote the momenta. The force constant is C. Then the Hamiltonian of the unperturbed system is

$$\mathcal{H}_0 = \frac{P_1^2}{2m} + \frac{1}{2}Cx_1^2 + \frac{P_2^2}{2m} + \frac{1}{2}Cx_2^2 \quad\quad\text{①}$$

Each uncoupled oscillator is assumed to have the frequency w_0 of the strongest absorption line of the atom.

Thus, $C = mw_0^2$

Let $\mathcal{H}_1$ be the coulomb interaction energy of the 2 oscillators,

$$\mathcal{H}_1 = \frac{e^2}{R} + \frac{e^2}{R+x_1-x_2} - \frac{e^2}{R+x_1} - \frac{e^2}{R-x_2} \quad\quad\text{②}$$

In the approximation, $|x_1|, |x_2| \ll R$,

$$\mathcal{H}_1 \cong \frac{-2e^2 x_1 x_2}{R^3} \quad\quad\text{③}$$

The total Hamiltonian with the approximate form ③ for $\mathcal{H}_1$ can be diagonalised by the normal mode transformation

$$\left.\begin{array}{l} x_s = \frac{1}{\sqrt{2}}(x_1+x_2) \\ x_a = \frac{1}{\sqrt{2}}(x_1-x_2) \end{array}\right\} \quad\quad\text{④}$$

Solving for x_1 and x_2,

$$\left.\begin{array}{l} x_1 = \frac{1}{\sqrt{2}}(x_s+x_a) \\ x_2 = \frac{1}{\sqrt{2}}(x_s-x_a) \end{array}\right\} \quad\quad\text{⑤}$$

s and a represents symmetric and antisymmetric modes of motion. The momenta P_s and P_a associated with the modes are

$$P_1 = \frac{1}{\sqrt{2}} (P_s + P_a)$$
$$P_2 = \frac{1}{\sqrt{2}} (P_s - P_a)$$ ⑥

The total Hamiltonian $\mathcal{H}_0 + \mathcal{H}_1$ after the transformation ⑤ and ⑥

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$$

$$= \frac{P_1^2}{2m} + \frac{1}{2} C x_1^2 + \frac{P_2^2}{2m} + \frac{1}{2} C x_2^2 - \frac{2 e^2 x_1 x_2}{R^3}$$

$$= \frac{1}{4m} \left[(P_s + P_a)^2 + (P_s - P_a)^2 \right] + \frac{C}{4} \left[(x_s + x_a)^2 + (x_s - x_a)^2 \right]$$

$$- \frac{e^2}{R^3} (x_s^2 - x_a^2)$$

$$= \frac{P_s^2}{2m} + \frac{P_a^2}{2m} + \frac{C}{2} x_s^2 + \frac{C}{2} x_a^2 - \frac{e^2 x_s^2}{R^3} + \frac{e^2 x_a^2}{R^3}$$

$$\therefore \mathcal{H} = \left[\frac{1}{2m} P_s^2 + \frac{1}{2} \left(C - \frac{2e^2}{R^3} \right) x_s^2 \right] + \left[\frac{1}{2m} P_a^2 + \frac{1}{2} \left(C + \frac{2e^2}{R^3} \right) x_a^2 \right]$$ ⑦

The two frequencies of the coupled oscillators are found by the inspection of ⑦,

$$\omega = \left[\left(C \pm \frac{2e^2}{R^3} \right) / m \right]^{1/2}$$

$$= \omega_0 \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{CR^3} \right) - \frac{1}{8} \left(\frac{2e^2}{CR^3} \right)^2 + \cdots \right]$$ ⑧

where, $\omega_0 = \sqrt{C/m}$

The zero point energy of the system is $\frac{1}{2}\hbar(\omega_s + \omega_a)$. Because of the interaction, the sum is lowered from the uncoupled value by

$$\Delta U = \frac{1}{2} \hbar (\Delta \omega_s + \Delta \omega_a)$$

$$\Delta W_s = W_s - W_0$$

$$= \sqrt{(C + \tfrac{2e^2}{R^3})/m} - \sqrt{C/m}$$

$$= W_0 \left[\frac{e^2}{CR^3} - \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 \right]$$

$$\Delta W_a = W_a - W_0$$

$$= W_0 \left[\frac{-e^2}{CR^3} - \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 \right]$$

$$\therefore \Delta W_s + \Delta W_a = -W_0 \left[\frac{1}{4}\left(\frac{2e^2}{CR^3}\right)^2 \right]$$

$$\Rightarrow \Delta U = \frac{-\hbar}{2}\left(\frac{W_0}{4}\right)\left(\frac{2e^2}{CR^3}\right)^2$$

$$= -\hbar W_0 \cdot \frac{1}{8}\left(\frac{2e^2}{CR^3}\right)^2 = \frac{-A}{R^6} \qquad\qquad ⑨$$

This attractive interaction varies as the minus sixth power of the separation of the 2 oscillators. This is called the vander waals interaction. The interaction is a quantum effect in the sense that $\Delta U \to 0$ as $\hbar \to 0$. Thus the zero point energy is lowered by the dipole-dipole coupling.

An approximate value of the constant A in ⑨ is for identical atoms is given by $\hbar W_0 \alpha^2$, where $\hbar W_0$ is the energy of the strongest optical absorption line and α is the electronic polarizability.

Cohesive energy of inert gas crystals:

The energy required to pull the crystal apart into a set of free atoms is called cohesive energy.

When two atoms are brought together, their charge distributions gradually overlap. When the charge distributions of 2 atoms overlap, there is a tendency for electrons from atom B to occupy in part states of atom A already occupied by electrons of atom A and vice versa. 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 B/R^{12}, where B is a positive constant, when used together with a long range attractive potential of the form

$$\Delta U = - A/_{R^6} \quad \text{———} \quad ①$$

constants A and B are empirical parameters determined from independent measurements made in the gas phase. We can write the potential energy of 2 atoms at separation R as

$$U(R) = 4 \varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^{6} \right] \quad \text{———} \quad ②$$

where ε and σ are the new parameters with $A = 4 \varepsilon \sigma^6$ and $B = 4 \varepsilon \sigma^{12}$

The potential ② is known as the Lennard-Jones potential.

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 ② over all pairs of atoms in the crystal. If there are N atoms in the crystal, the total potential energy is

$$U_{tot} = \frac{1}{2} N (4\varepsilon) \left[\sum_{j} \left(\frac{\sigma}{P_{ij} R} \right)^{12} - \sum_{j} \left(\frac{\sigma}{P_{ij} R} \right)^{6} \right] \qquad ③$$

where, $P_{ij} R$ is the distance between reference atom i and any other atom j, expressed in terms of the nearest neighbors distance R. The factor $\frac{1}{2}$ occurs with the N to compensate for counting twice each pair of atoms.

For the FCC structure,

$$\sum_{j} P_{ij}^{-12} = 12.13188, \qquad \sum_{j} P_{ij}^{-6} = 14.45392 \qquad ④$$

If we take U_{tot} in ③ as the total energy of the crystal, the equilibrium value R_0 is given by taking that U_{tot} be a minimum w.r.t variations in the nearest-neighbor distance R.

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

Then, $\frac{R_0}{\sigma} = 1.09 \qquad ⑤$

This value is same for all elements with an fcc structure.

- A slight departure of R_0/σ for the lighter atoms from the universal value 1.09 predicted for inert gases can be explained by zero point quantum effects.

The cohesive energy of inert gas crystals at absolute zero and at zero pressure is obtained by substituting ④ and ⑤ in ③,

$$U_{tot}(R) = 2N\epsilon \left[(12.13)\left(\frac{\sigma}{R}\right)^{12} - (14.45)\left(\frac{\sigma}{R}\right)^6\right] \quad \text{——⑥}$$

And at $R = R_0$,

$$U_{tot}(R_0) = -(2.15)\,4\,N\epsilon \quad \text{——⑦}$$

This is same for all inert gases. This is the calculated cohesive energy when the atoms are at rest.

Quantum mechanical corrections act to reduce the binding by 28, 10, 6 and 4 percent of ⑦ for Ne, Ar, Kr and Xe respectively. The heavier the atom, the smaller the quantum correction.

Covalent Crystals

The covalent bond is formed from 2 electrons, one from each atom participating in the bond.

The binding of molecular hydrogen is a simple example of a covalent bond. The strongest binding occurs when the spins of the two electrons are antiparallel. The binding depends on the relative spin orientation because the Pauli principle modifies the distribution of charge according to the spin orientation. This spin dependent coulomb

energy is called the exchange interaction. The Pauli principle gives a strong repulsive interaction between atoms with filled shells. If the atoms are not filled, electron overlap can be accommodated without excitation of electrons to high energy states and the bond will be shorter.

Metallic Bonding

Metals are characterized by high electrical conductivity and a large number of electrons in a metal are free to move about. These electrons are called conduction electrons. The characteristic feature of metallic binding is the lowering of the energy of the valence electrons in the metal as compared with the free atom.

Metals tend to crystallize in relatively close packed structures and not in loosely packed structures. In the transition metals there is additional binding from inner electron shells.

Hydrogen Bonding

Because neutral hydrogen has only one electron, it should form a covalent bond with only one other atom. But under certain conditions, an atom of hydrogen is attracted by rather strong forces to two atoms. This type of bonding is called the hydrogen bonding.

Hydrogen bond is rather ionic in character, being formed only between the most electronegative atoms. Hydrogen bond is an important part of the interaction between H_2O molecules and is responsible for the physical properties of water and ice. It is important in certain ferroelectric crystals and in DNA

Ionic Crystals

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 are sodium chloride and the cesium chloride. The electronic configurations of all ions of a simple ionic crystal correspond to closed electronic shells, as in the inert gas atoms.

Madelung Interaction - Cohesive Energy
of Ionic Crystals

The long range interaction between ions with charge $\pm q$ is the electrostatic interaction, 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 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 percent. The main contribution to the binding energy of ionic crystals is electrostatic and is called the _Madelung Energy_.

If U_{ij} is the interaction energy between ions i and j, U_i which includes all interactions involving the ion i,

$$U_i = \sum_j U_{ij} \qquad\qquad ①$$

U_{ij} may be written as the sum of a central field repulsive potential of the form $\lambda \exp(-r/\rho)$ and a coulomb potential $\pm q^2/r$. Here λ and ρ are empirical parameters.

$$U_{ij} = \lambda \exp(-r_{ij}/\rho) \pm q^2/r_{ij} \qquad\qquad ②$$

The repulsive term describes the fact that each ion result overlap with the electron distributions of neighboring ions. In the NaCl structure, the value of U doesnot depend on whether the reference ion is a positive or negative ion. Hence the total lattice energy U_{tot} of a crystal composed of N molecules as $U_{tot} = N U_i$

The total lattice energy is defined as the energy required to separate the crystal into individual ions at an infinite distance apart. Also $r_{ij} = P_{ij} R$, where R is the nearest neighbor separation in the crystal. If we include only the repulsive interaction only among the nearest neighbors.

$$U_{ij} = \begin{cases} \lambda \exp(-R/\rho) - \dfrac{q^2}{R} & \longrightarrow \text{Nearst neighbour.} \\ \\ \pm \dfrac{1}{P_{ij}} \dfrac{q^2}{R} & \longrightarrow \text{Otherwise} \end{cases}$$

③

Thus, $U_{tot} = N U_i$

$$U_{tot} = N \left(z\lambda e^{-R/\rho} - \frac{\alpha q^2}{R} \right) \quad\text{——— ④}$$

where z is the number of nearest neighbours of any ion. and

$$\alpha = \sum_j \frac{(\pm)}{P_{ij}} = \text{Madelung constant} \quad\text{——— ⑤}$$

If we take the reference ion as a negative charge, the '+' sign will apply to positive ions and '−' sign to negative ions.

At the equilibrium seperation,

$$\frac{dU_{tot}}{dR} = 0$$

$$\Rightarrow \quad N\frac{dU_i}{dR} = -\frac{N z \lambda}{\rho} \exp(-R/\rho) + \frac{N \alpha q^2}{R^2} = 0$$

or,
$$R_o^2 \exp(-R_o/\rho) = \rho \alpha q^2 / z \lambda \qquad \text{(7)}$$

This determines the equilibrium separation R_o if the parameters ρ, λ of repulsive interaction are known. Using ④ and ⑦,

$$U_{tot} = \frac{N \rho \alpha q^2}{R_o^2} - \frac{\alpha q^2 N}{R_o}$$

$$\therefore \quad U_{tot} = -\frac{N \alpha q^2}{R_o}\left[1 - \rho/R_o \right] \qquad \text{(8)}$$

Here, the term $-\frac{N \alpha q^2}{R_o}$ is the Madelung energy. ρ is the order of $0.1 R_o$, so that the repulsive interaction has a very short range.

We can compute the Madelung constant for the infinite line of ions of alternating signs.

Reference ion

$\oplus \quad \ominus \quad \oplus \quad \ominus \quad \oplus \quad \ominus \quad \oplus$

$\leftarrow R \rightarrow$
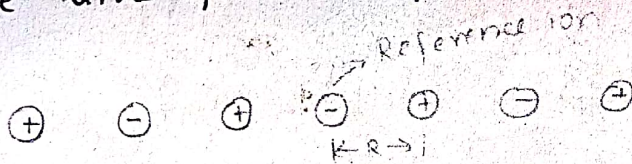
Then, $\quad \dfrac{\alpha}{R} = \sum_J \dfrac{(\pm)}{r_{ij}}$

r_{ij} is the distance of the jth ion from the reference ion.

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

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

We sum this series by taking the expansion

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

$\therefore$ For one dimensional chain, $\quad \alpha = 2\ln 2.$