

# Notes on Modern Physics

*Under preparation by Arani Chakravarti,*

*Visva Bharati*

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# Chapter 1

## Discharge of electricity through gases :

### 1.1 Under normal temperature and pressure

Gases are normally good insulators:-

If all precautions are taken to stop leakage from electroscopes, still the leaves collapse slowly. C.T.R. Wilson in 1900 showed the conductivity of air  $\propto$  to amount of air enclosed so air must be the conducting medium.

Enhanced conductivity is shown by

1. Combustion gases
2. UV, X-rays irradiation
3. After the passage of sparks
4. Radio active substances. Even the walls of the room contain radio active materials!

This enhanced conductivity drops if the influence is removed.

Ionisation  $\rightarrow$  In gases at NTP the detached electrons quickly attach themselves to other atoms to form (+)ve and (-)ve ion pairs. Townsend has shown that  $\sim$  one out of  $10^8$  are ionised per second even with strong ionisation. As electrons are light, (+)ve and (-)ve gas ions are of almost the same mass and mobility. At low pressures free electrons may exist with much higher speeds.

#### 1.1.1 Ionisation Current

It is measured with electrometers as it is too small to measure with galvanometers.

#### 1.1.2 I-V Characteristics

The current for a particular voltage depends on the amount of gas present. Thus it depends on the pressure also!

If  $q$  is the no. of ion pairs produced in unit vol per unit time then  $a(\text{area of the plate}) \times l(\text{gap})$  is the volume and the number available for conduction  $=qal$  Ohm's law is approximately followed in a region corresponding to the saturation region of a transistor.  $I_{sat} = qale$  if 'e' is the charge of an ion.

Note : Provided the voltage is such as to maintain a state of saturation throughout, increasing 'l' will increase  $I_{sat}$  (opposite to that of conductors). But of course the voltage has to be already higher than what is required for saturation with the smaller gap! As the gap increases,

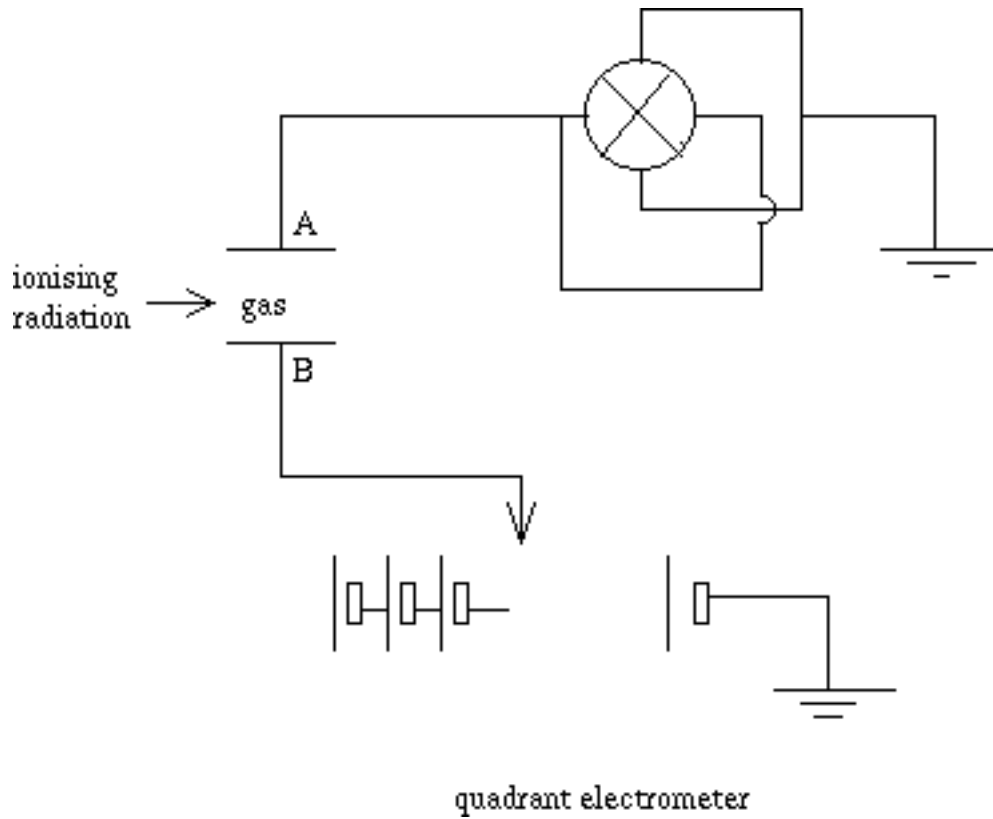


Figure 1.1: Schematic of a quadrant electrometer. If  $V = K\theta$ , where  $K \equiv \text{const.}$  of the meter and  $\theta \equiv \text{deflection}$ ,  $I = KC \frac{\theta}{t}$  ( $C$  is the capacity of  $AB$  and the electrometer)

Note: Why is the exponential charging expression not important?  $\rightarrow$  Electrometer charges to a much lower voltages than that supplied -so  $V/I \sim \text{const.}$  for this arrangement.

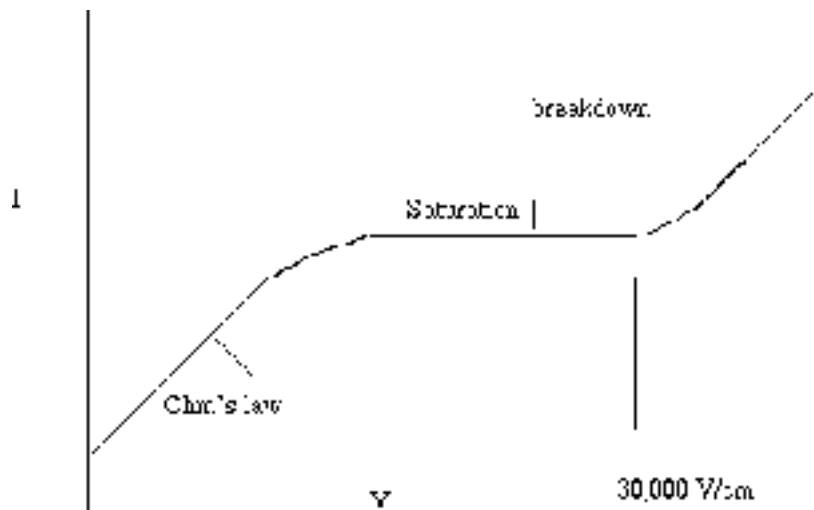


Figure 1.2: I-V characteristics. Shows breakdown

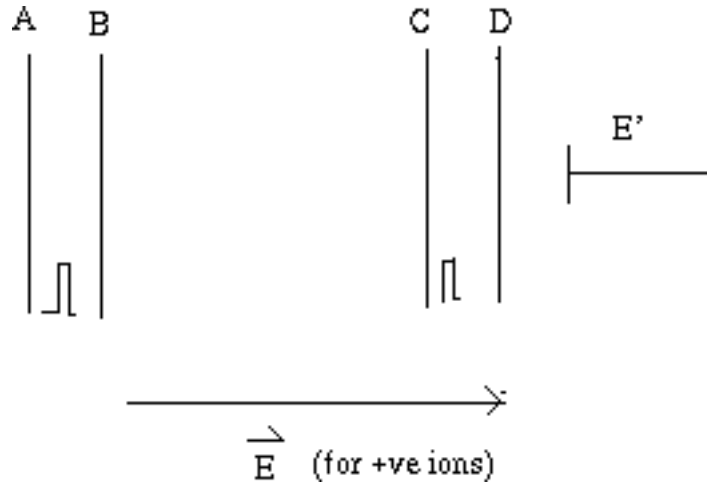


Figure 1.3: Tyndall's apparatus for measuring ionic mobilities.

the resistance due to collisions increases as expected, but the voltage is already large enough to overcompensate that.

Note : In all the cases the applied p.d. is not responsible for causing ionisations.

The high p.d. region -> ionisation by collision and spark discharge occur.

### 1.1.3 Mobilities of Ions

(Tolansky - Int. at. phys.)

$e$  → charge of ion,

$m$  → mass of ion,

$E$  → field applied

hence, force =  $Ee$  and  $acc^n = \frac{Ee}{m}$

let  $t$  ≡ time required to travel over one mean free path. The mean free path can be ascertained from kinetic theory.

After  $t$  it collides and since the other gas atoms move about randomly, the drift velocity is killed. Hence the velocity at the end of the mean free path =  $\frac{Ee}{m}t$  (uniform acceleration)

This is repeated and since the  $v - t$  curve is linear, the average drift velocity =  $\frac{Ee}{2m} \equiv \underbrace{\kappa}_{\left(\frac{et}{2m}\right)} E$ ,

where  $\kappa \equiv \frac{et}{2m}$  = constant for a gas, called the ionic mobility.

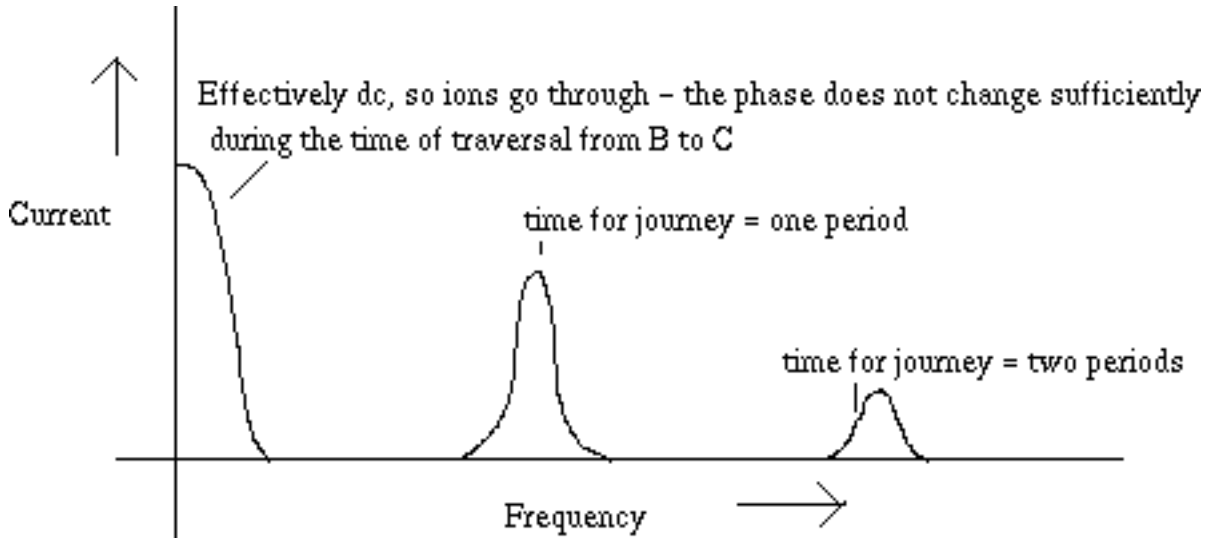
## 1.2 Tyndalls' method of measuring ionic mobilities

Steady field  $\vec{E}$  draws ions from left to right. Oscillating field between A-B allows bursts of ions into space BC. They travel to C under the influence of  $\vec{E}$ . ac signal in phase with that between A-B is applied to C

D (Note: simply connecting A-C, B-D won't do - the potential difference must be there for the ions to move from AB to CD. Probably two transformer secondaries would be used to provide oscillating fields in synchronism while keeping the mean values of the fields different.) By varying the frequency a condition is attained when the ions reach C just when the field is ready to pull them through CD and onto E'.

For only one kind of ion, the  $i - \nu$  plot is given by figure (1.4)

If there is a mixture of ions, then each component produces its own peak. So from frequency time is known, and since  $\vec{E}$  is known, the mobility may be calculated. By making the pulse narrow the spatial spread of the ions beyond B can be made very small and high resolution achieved.

Figure 1.4:  $i-\nu$  plot from Tyndall's apparatus

### 1.2.1 Ageing and cluster formation

Chiefly when polar molecules are present, they stick to the ions and quickly form clusters. Mobility decreases steadily for about two seconds even if small amounts of impurity are present. The mobility of both kinds of ions are the same initially but due to different clustering (why? related to prevalence of a particular shape among common polar molecules?) the (-)ve ions soon show higher mobility. At very high purity and relatively lower pressures, cluster formation is inhibited and both (+)ve and (-)ve ions show a large increase in the mobility. Bare electrons tend to appear and the (-) mobility seems to go up even more (but of course the masses will be different). The cluster phenomenon was shown up in the following way.  $v = \frac{Eet}{2m}$ , now the gap between molecules is inversely proportional to the pressure (Boyle's law). So is the time 't'. Thus  $\frac{vp}{E}$  should be a const. This was found to be substantially true and was used to determine the mass of the ions. In all cases the mass was found to be more, suggesting the existence of clusters. On applying pressure,  $v = AE/p$  where  $A$  is a constant. This is true as long as the drift velocity is small compared with the thermal velocity. If the two are comparable, the expression to use is (empirical):  $v = A \left(\frac{E}{p}\right) + B \left(\frac{E}{p}\right)^2$ . The smaller the ionic mass,  $E/P$  has to be higher for this form to become necessary (Rajam).

### 1.2.2 Effect of impurity :

$\frac{vp}{E}$  should be const.  $\Rightarrow v$  vs.  $E/P$  curve should be a straight line. Positive dry air and negative damp air both obey this  $\rightarrow$  showing that the cluster structure remains even with reduced pressure. But (-)ve dry air becomes non-linearly mobile, necessitating the acceptance of diminishing mass with reduced pressure (free electrons are being formed!). The reduction in mobility due to addition of polar molecules increases with increasing impurity concentration. Longer chains (in aliphatic alcohols) also mean lower mobility because longer chains  $\Rightarrow$  greater radius  $\Rightarrow$  smaller mean free path (Why not also larger mass?). It is considered probable that each cluster is in a dynamic state, continuously losing and capturing molecules.

### 1.2.3 Ionic mass and mobility

$$\text{mobility} \propto \left(1 + \frac{m}{M}\right)^{\frac{1}{2}}$$

$M \equiv$  mass of ion



$m \equiv$  mass of carrier gas molecules  
This formula is well obeyed.

### 1.2.3.1 Effect of temperature

$k(\text{mobility}) = \frac{BT^{\frac{1}{2}}}{C+T}$  (empirical relation), B,C are constants; T=absolute temperature

Similar in form to the effect of temperature on the viscosity of a gas. Maximum value is reached at the room temperature for (+)ve ions, and at 40° for (-)ve ions.

### 1.2.4 Recombination of ions (Rajam)

Let 'q'=no. of ions of each kind per unit volume per unit time

Let n (-)ve and n (+)ve ions be present at time t. Now, no. of collisions  $\propto n^2$ . Each collision results in a recombination (Rajam got this wrong!).

Hence, No. of recombinations =  $\alpha n^2$ , where,  $\alpha \equiv$  co-efficient of recombination

Now rate of increase of ion = rate of generation i.e. rate of recombination

Hence,  $\frac{dn}{dt} = q - \alpha n^2$ . At a constant ionisation rate, n increases till  $\frac{dn}{dt} = 0 \Rightarrow q = \alpha n^2$

Now, let V be the applied p.d. and  $v_+$  and  $v_-$  be the mobilities of the +ve and -ve ions, l=distance between the points of the applied p.d.

Hence, field =  $\frac{v}{l}$

considering area 'a' perpendicular to the current,

$$I = ane(v_+ + v_-) \frac{v}{l}$$

but,  $\sqrt{\frac{q}{\alpha}}$

$$\frac{I}{I_s} = \frac{(v_+ + v_-) * v}{\sqrt{q\alpha} * l^2} \quad \text{Ohms Law Like}$$

If ionizing agency is removed,  $q=0$

$$\frac{dn}{dt} = -\alpha n^2$$

$$\frac{dn}{n^2} = -\alpha dt \Rightarrow -\frac{1}{n} = -\alpha t + c$$

Boundary Condition  $\rightarrow$  at  $t=0, n=n_0$

$$\Rightarrow c = -\frac{1}{n_0}, \text{ hence}$$

$$-\frac{1}{n} = -\alpha t - \frac{1}{n_0} \Rightarrow \frac{1}{n} - \frac{1}{n_0} = \alpha t \Rightarrow n = \frac{n_0}{1 + n_0 \alpha t}$$

(Rutherford verified this relation)

$$\text{At time } T = \frac{1}{n_0 \alpha}, n = n_0/2$$

$\alpha \approx 1.6 \times 10^{-6} \rightarrow$  depends on nature and pressure in a complicated way not fully understood.

## 1.3 Millikan's oil drop experiment (1913)

The schematic of the apparatus is shown in figure (1.5). Drops of low vapour pressure oil get charged by friction and can be made to move up, down or remain stationary by varying the electric field.

From Stoke's law ,

$$6\pi\eta av = \frac{4}{3}\pi a^3(\rho - \sigma)g, \text{ where } \rho \equiv \text{density of oil, } \sigma \equiv \text{density of air, } a \equiv \text{radius}$$

hence,

$$m = \frac{4}{3}\pi \left[ \frac{9}{2} \frac{\eta v}{(\rho - \sigma)g} \right]^{\frac{3}{2}} \rho$$

$$\text{(since, } m = \frac{4}{3}\pi a^3 \rho \text{ and } a^3 = \frac{6\pi\eta av \times 3}{4\pi(\rho - \sigma)g} \Rightarrow a^2 = \frac{9}{2} \frac{\eta v}{(\rho - \sigma)g} \text{)}$$

Repeated observation show mass of the same drop remains const. over the experimental interval. Now v is proportional to the force (F).

if  $v_1 \equiv$  velocity without field and  $v_2 \equiv$  velocity with field (upwards)

then  $\frac{v_1}{v_2} = \frac{F}{En - F}$ , where  $E \equiv$  field, and  $n \equiv$  no. of charges

X-rays ionise gas and cause sudden velocity change to  $v_2'$

hence,  $\frac{v_1}{v_2'} = \frac{F}{En' - F}$ , where  $n' \equiv$  new no of charges

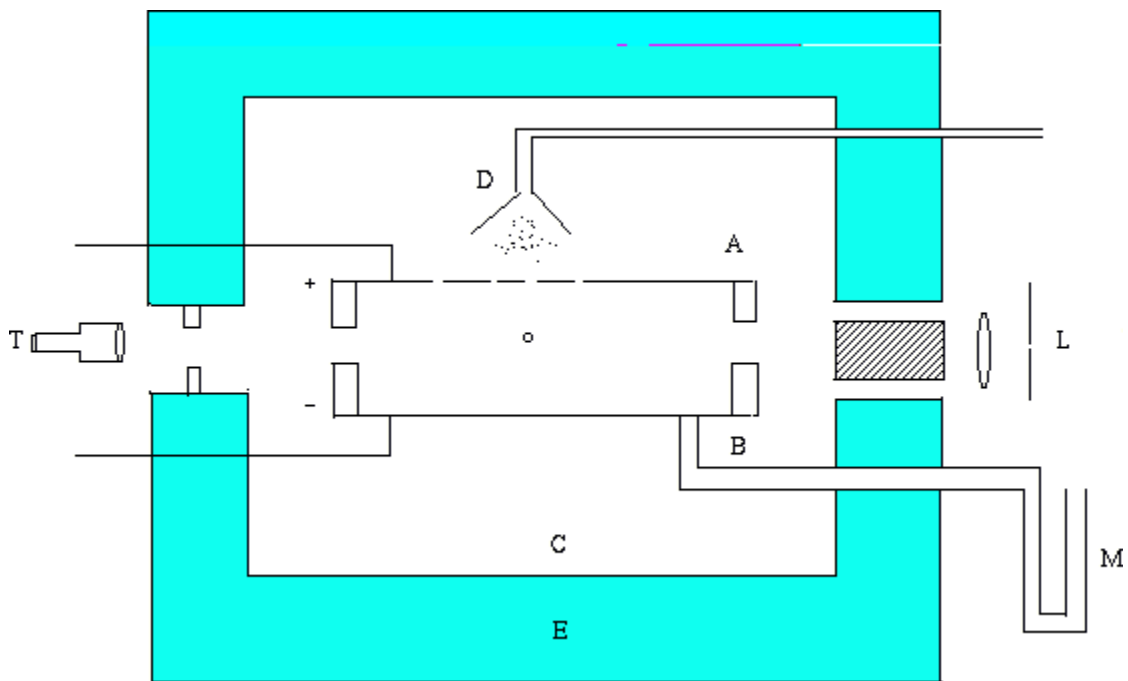
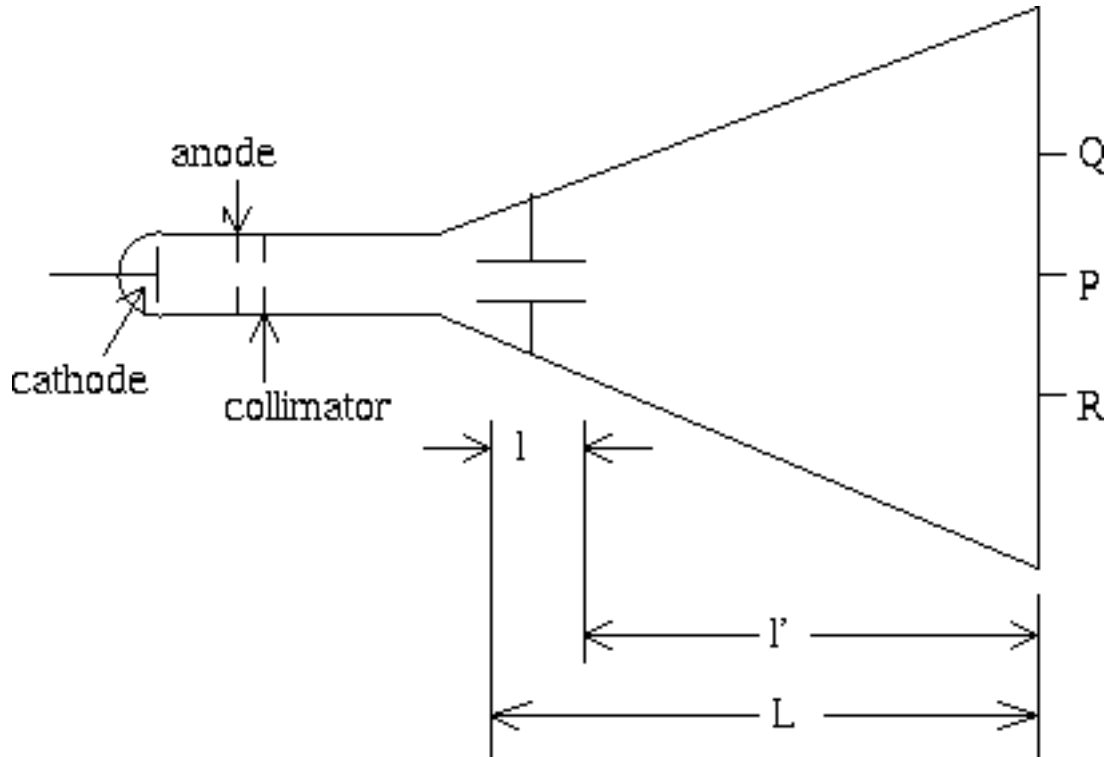


Figure 1.5:

Millikan's apparatus for measuring the charge of the electron. A and B are optically plane metallic disks about 20 cm in dia and 1.6 cm apart. They are supported perfectly parallel. E is a constant temperature oil bath. D is a spray atomiser. Heavy non-volatile oil is used. L is an arc with the heat rays filtered by water cells. T is a telescope with a graduated eye-piece. M is a manometer to measure the pressure of the inner chamber?

Figure 1.6: Thomson's setup for measuring  $e/m$  of the electron

and,  $\frac{v_2}{v_1} = \frac{Een-F}{F}$

hence,  $\frac{v_2-v_1}{v_1} = \frac{Ee(n'-n)}{F}$

minimum value of  $(n' - n) = 1$ , so after a large no. of measurements,  $e$  can be found from the smallest value of  $(n' - n)$  i.e.  $(v_2 - v_1)$ . The change in the charge was always found to be an integral multiple of  $e$ .

**correction:**  $e$  comes out to be larger for smaller drops! Stokes law needs to be modified for small droplets. Instead of  $F = 6\pi\eta av$  we should use  $F = 6\pi\eta av(1 + \beta\lambda/a)$ , where  $\beta \equiv \text{constant}$  and  $\lambda \equiv \text{mean free path}$ .  $\beta$  is found by plotting  $e$  with  $a$ .

Millikan made thousands of measurements with oil, glycerine, mercury etc., air, hydrogen etc., of different sizes of droplets. From these observations  $e$  came out to be  $1.6 \times 10^{-20}$  e.m.u. or  $1.6 \times 10^{-19}$  coulomb.

## 1.4 Thomson's $e/m$ measurement

The apparatus is shown in figure (1.6).

Magnetic and electric fields act over the same length path  $l$ . Let upper plate be (+)ve and the point shift to Q

$$F = Ec, \text{ acceleration} = \frac{Ee}{m},$$

hence  $x \equiv \text{deflection at the boundary of } l = \frac{1}{2} \frac{Ee}{m} \left(\frac{l}{v}\right)^2$  where  $\frac{l}{v} \equiv \text{time in } l$ ,  
hence

$$v_{tan} = \frac{Ee l}{m v}$$

hence,

$$QP = \frac{Eel'}{mv v} + \frac{1}{2} \frac{Eel}{mv^2} \cdot l = \frac{Eel}{mv^2} \left( l' + \frac{1}{2}l \right) = \frac{EelL}{mv^2} \quad (1.1)$$

Now let only magnetic field be applied,  
hence

$$Hev = \frac{mv^2}{l}$$

$$PR = l' \tan\theta + y$$

now,  $l = r \sin\theta \implies \sin\theta = \frac{l}{r}$ . Since  $\theta$  is small,  $\sin\theta \simeq \tan\theta$   
hence,

$$PR = l' \frac{l}{r} + y$$

now

$$l^2 + (r - y)^2 = r^2$$

$$\text{or, } l^2 = y(2r - y) = 2yr - y^2 \simeq 2yr$$

hence,

$$y = \frac{l^2}{2r}$$

$$PR = l' \frac{l}{r} + l \frac{l}{2r} = \frac{l}{r} \left( l' + \frac{l}{2} \right) = \frac{lL}{r} = lL \frac{He}{mv} \quad (1.2)$$

Now if both are applied and spot brought back to P ,

$$Ee = Hev \implies v = \frac{E}{H} \quad (1.3)$$

using this  $v$ , from 1.1,

$$QP = \frac{eElL}{mv^2}$$

from which we have

$$\frac{e}{m} = \frac{QP v^2}{ElL} = \frac{QP E}{lLH^2}$$

Similarly, from 1.2

$$PR = \frac{lLHe}{mv}$$

from which we have,

$$\frac{e}{m} = \frac{PRv}{lLH} = \frac{PRE}{lLH^2}$$

so, apply  $E$  or  $H$  alone, measure deflection, bring back to P by applying  $H$  or  $E$ .

# Chapter 2

## X-Rays

### 2.1 Production:

In the Gas tubes, to produce X-rays platinum, molybdenum or tungsten is used as the target which is placed at the cathode's focus. Generally 30,000 to 50,000 volt is used across the cathode and the anode. [see figure (2.1)].

#### 2.1.0.1 Limitations of gas tubes

- Electrons constituting the cathode ray stream are produced by ionisation of the gas in the tube and collisions of these ions with the cathode. The applied voltage depends in a critical manner on the pressure of the gas, which changes very sharply at low pressures. So it is not easy to maintain both the *intensity* and *quality* of the X-rays for any length of time.
- The wall of the tube gradually absorb the residual gas and so the number of electrons produced by ionisation decreases with time. This is called *hardening* of the tube.
- To produce *hard* X-rays (i.e. of small wavelength), it is desirable to remove all gas from the tube, but then, who will produce the electrons?

#### 2.1.1 Coolidge Tube:

A modern Coolidge tube is shown in figure (). The cathode is a filament of tungsten heated by passing current from a low-tension supply. Thermionic emission produces electrons which are accelerated as usual. The tube is evacuated to very high vacuum (0.0001 mm or better), because the presence of gas is no longer necessary for the process of production of electrons. Usually the cathode is placed inside a metal cup which helps to focus the electrons. A copper rod cooled by water is thermally connected to the target to act as a heat sink.

##### 2.1.1.1 Advantages and disadvantages

- The intensity of emission can be varied independently of the voltage applied, and hence the frequency, by simply varying the current through the filament and hence its temperature.
- The quality of the X-rays can be controlled very accurately by varying the accelerating voltage as the possibility of collisions with residual gas atoms is very small.
- As there is no hardening, the accelerating potential can be kept constant and need not be varied just to keep the tube functioning.
- A disadvantage is the not-too-good focussing of the X-rays, as a result of which the whole surface of the target becomes the source of X-rays.

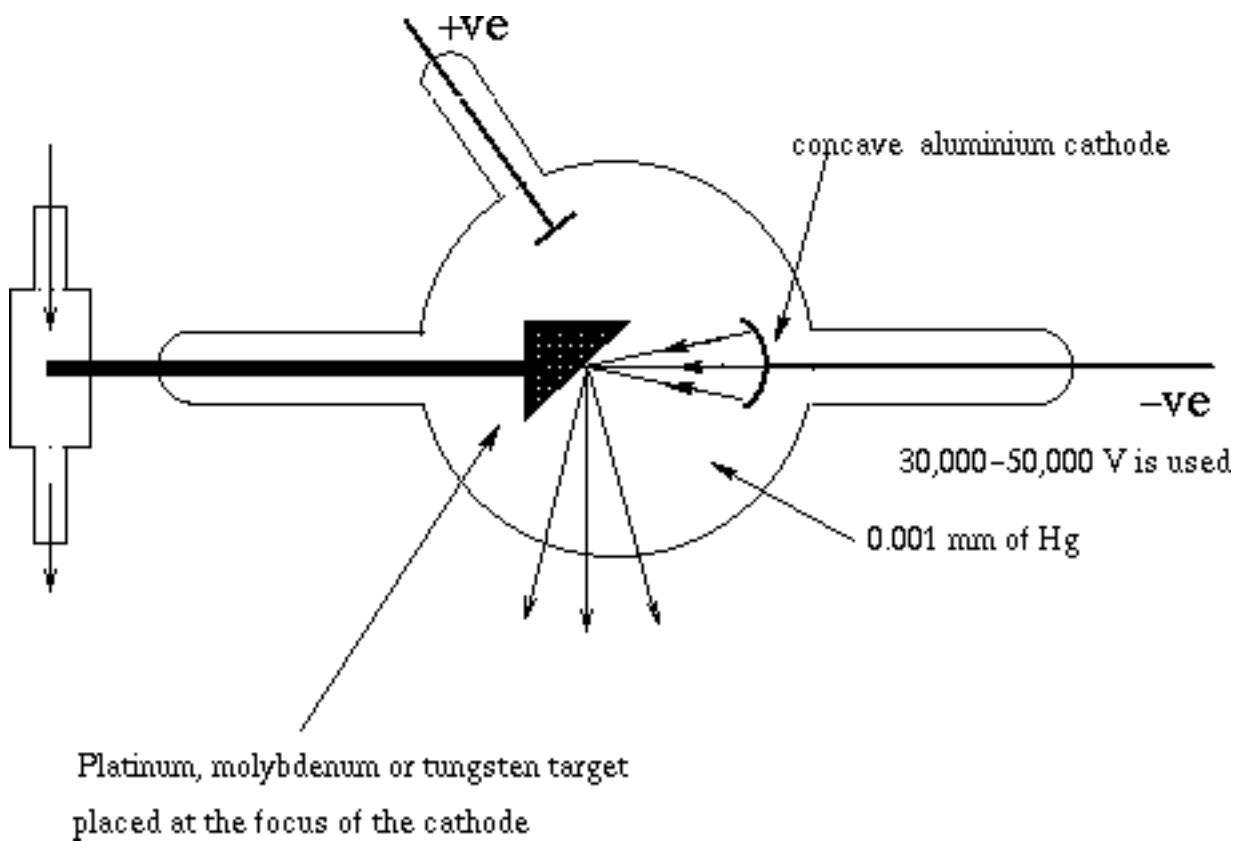


Figure 2.1: Gas tube. It is a simple cathode ray discharge tube. The front surface of the target is at  $45^\circ$  to the direction of the incident cathode ray beam.

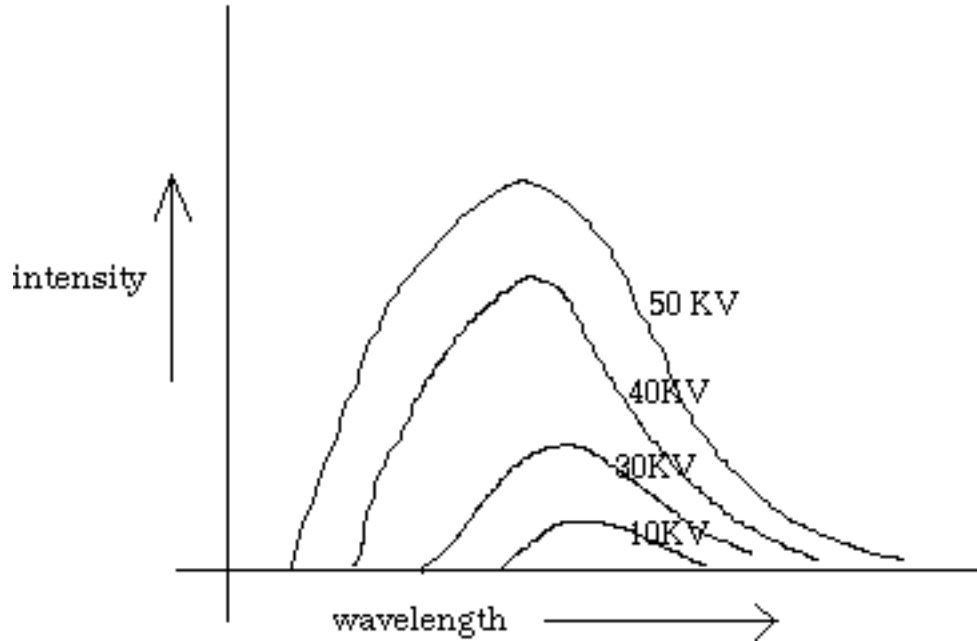


Figure 2.2: continuous X-ray spectrum

### 2.1.2 Betatron:

This is called a *betatron*. A transformer arrangement is used as shown in figure (1). The electric field induced by changing a magnetic field is utilised for the acceleration of the electrons. A toroidal vacuum tube is arranged between the pole pieces of an electromagnet which is fed with ac of high voltage adjusted to a convenient frequency (about 60 to 600 Hz). Electrons are injected from a heated filament by an arrangement of suitable grids and injector shields. The alternating magnetic field acts parallel to the axis of the toroid. As a result, an electric field is set up along the circular electron path in the toroid which serves to accelerate the electrons. This field also supplies the radially directed (inwards) Lorentz force which keeps the electrons from straying out of their circular orbits. The orbit is maintained at constant radius by a suitable combination of solenoids and timing. The electrons make several hundred thousand revolutions during a quarter cycle of the magnetic field, i.e., during the quarter of the cycle when the magnetic field increases. At the end of the quarter cycle, when the intensity is at its maximum, the magnetic field is distorted by discharging capacitors through suitable placed coils and the electrons are deflected onto the target, which is often just the back of the injector shield. X-rays (mainly  $\gamma$  rays) are produced. Nearly 500 MeV beams may be produced. The X-rays produced are highly monochromatic.

## 2.2 Continuous X-ray spectrum

The nature of the continuous X-ray spectrum is shown in the figure (2.2). Short wavelength limit  $eV = h\nu_{max}$  - **Duane and Hunt's law** ( $\nu_{max}$  occurs when all the energy is dissipated in a single collision. It enables the direct measurement of  $h$ .)

Called 'white radiation' - Total amount is

1.  $\propto$  to the atomic weight of the anti-cathode material, wavelength independent of material.
2.  $\propto$  square of the applied voltage.

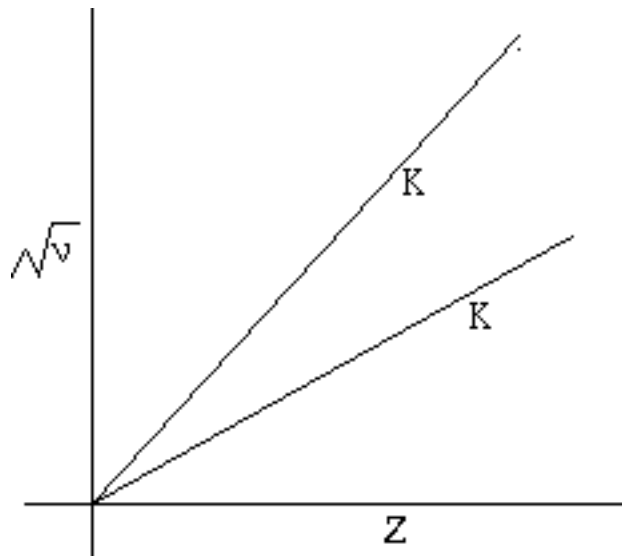


Figure 2.3: Moseley diagram

## 2.3 Characteristic spectrum

Above a certain voltage only continuous spectrum is seen at all voltages. The characteristic spectrum is superposed on the continuous spectrum.

Lines are characteristic of the anti-cathode. Two main lines are k-lines. Softer L, M lines also. Two methods of production.

1. Use material as target
2. Hard X-rays made to fall on a target whose characteristic X-rays are softer.

Common targets (use by Bragg)  $\rightarrow$  Platinum, Osmium, Palladium, Rhodium

## 2.4 Moseley's law

Crystal X-ray photographic method  $\rightarrow$  potassium ferrocyanide crystal for diffracting X-rays. Vacuum camera .  $0.4 \text{ \AA}^\circ$  . to  $8 \text{ \AA}^\circ$  , using 38 different elements.

1. Spectral lines in two groups - K and L series
2. Simple spectra of same type for all elements. Corresponding lines occur at shorter wavelength for larger atomic weight.
3. **Mosley's law**
4.  $\nu = a(Z - b)^2$  for a particular line, where a,b=characteristic constants [see figure(2.3)]  
Shows that at. no. and not at. wt. was important.

### Results

1. Removal of discrepancy in the order of elements in the periodic table, e.g.  $_{18}A^{40}$  comes before  $_{19}K^{39}$  ,  $_{27}Co^{58.9}$  comes before  $_{28}Ni^{58.7}$  . According to at.wts.,this should be wrong !
2. gases in the Moseley diagram showed up new elements -hafnium(72), illinium(61), masrium(43), rhenium(75)



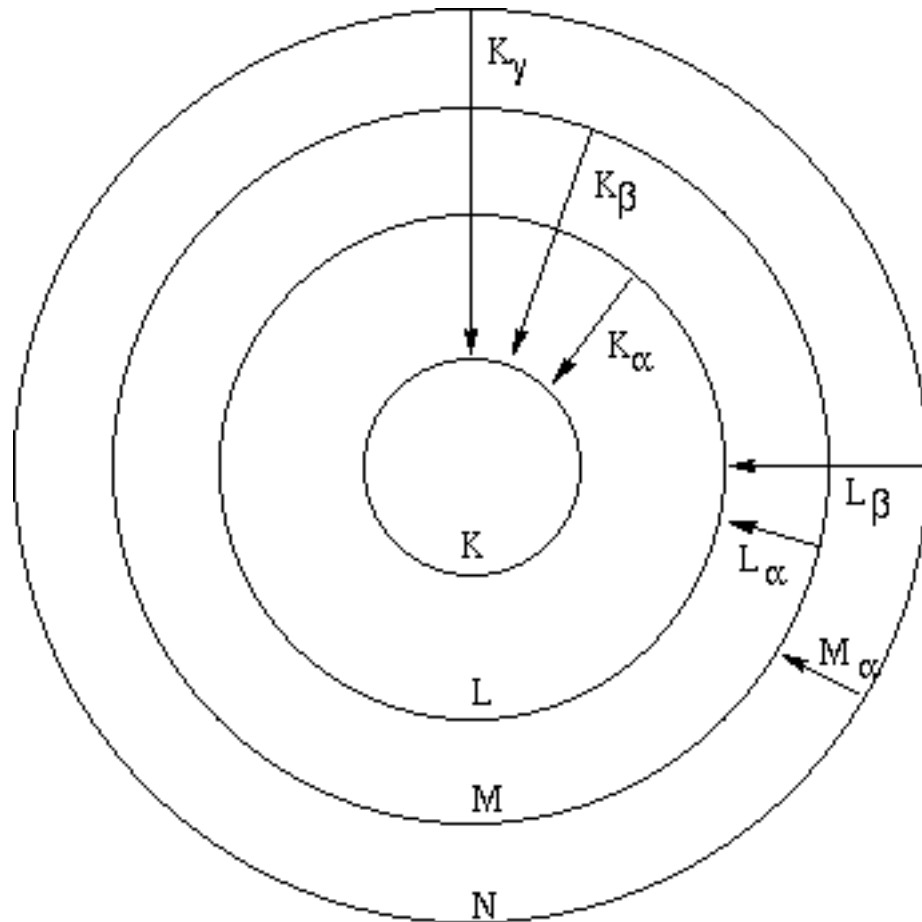


Figure 2.4: Kossel diagram

3. Determination of at.wt. of rare earths.

K-single group, L-3 subgroups, M-5 subgroups, N-7 subgroups.

#### **Kossel diagram**

In the case of light elements (H, He), the optical spectra observed are the 'X-rays' of these elements. In H, Lyman  $\rightarrow$  K, Balmer  $\rightarrow$  L, Paschen  $\rightarrow$  M.

## 2.5 X-ray energy level diagram

Transition to the normal state means capture of a free electron of negligible kinetic energy. Spark spectrum is a limiting case of the X-ray spectra, belonging to ionised atoms  $\rightarrow$  visible and ultra-violet.

## 2.6 Explanation of Moseley's law from Bohr's theory

Circular orbit of radius  $a$

Therefore, attraction =  $\frac{Ze^2}{a^2}$

Centrifugal force =  $\frac{mv^2}{a}$

Therefore,

$$\frac{Ze^2}{a^2} = \frac{mv^2}{a} \Rightarrow v^2 = \frac{Ze^2}{am} \quad (2.1)$$

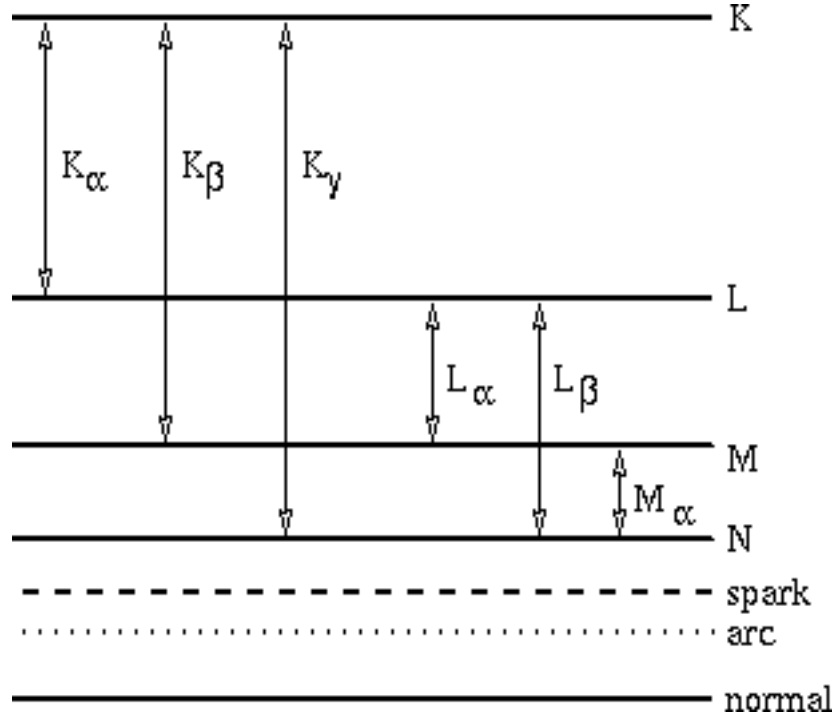


Figure 2.5: X-ray energy level diagram

Bohr's condition :  $I\omega = n\hbar$

But  $I\omega = ma^2\omega$  (circular)  $= ma^2\frac{v}{a} = mav = n\hbar$

$$\Rightarrow v = \frac{n\hbar}{am} \quad (2.2)$$

Dividing (2.1) by (2.2),

$$v = \frac{Ze^2 am}{am n\hbar} = \frac{Ze^2}{n\hbar} \quad (2.3)$$

From (2.1)

$$K.E. = \frac{1}{2}mv^2 = \frac{Ze^2}{2a}$$

$$P.E. = -\frac{Ze^2}{a}$$

Therefore,

$$W = \frac{Ze^2}{2a} - \frac{Ze^2}{a} = -\frac{Ze^2}{2a} \quad (2.4)$$

Here  $W$  represents the total energy. From (2.2),

$$a = \frac{n\hbar}{vm}$$

put  $v$  from (2.3)

$$a = \frac{n^2\hbar^2}{mZe^2} \quad (2.5)$$

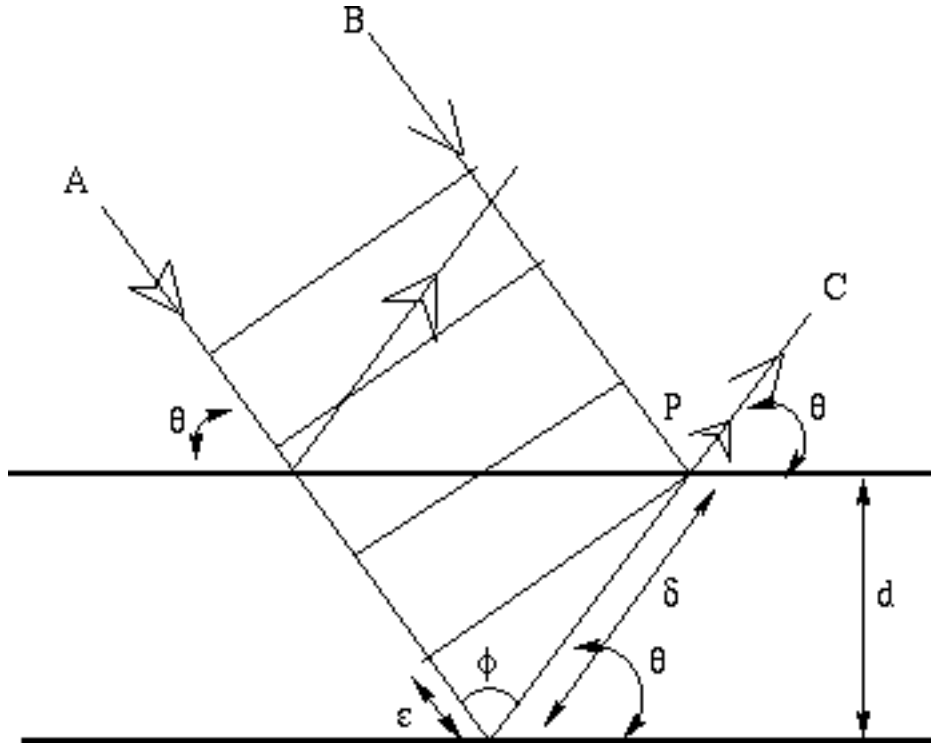


Figure 2.6: Ray diagram when a X-ray falls on a crystal surface

put in (2.4)

$$W = -\frac{Ze^2}{2a} = \frac{Ze^2 m Ze^2}{2n^2 \hbar^2} = \frac{Z^2 e^4 m}{2n^2 \hbar^2} \quad (2.6)$$

Thus energy is proportional to  $Z^2$ .

## 2.7 Bragg's law

Ray A will emerge along ray C after reflection at the lower plane. ray B will emerge along C after reflection at the upper plane. at the moment when B is at P , A will be at Q. Thus the extra path traversed will be  $\epsilon + \delta$

now

$$\frac{d}{\delta} = \sin\theta \implies \delta = \frac{d}{\sin\theta}$$

Again,

$$\epsilon = \delta \cos\phi = \frac{d}{\sin\theta} \cos(180 - 2\theta) = \frac{d}{\sin\theta} (-\cos 2\theta) = -\frac{d}{\sin\theta} (1 - 2\sin^2\theta)$$

hence total path difference,

$$\epsilon + \delta = \frac{d}{\sin\theta} - \frac{d}{\sin\theta} (1 - 2\sin^2\theta) = 2d \sin\theta$$

for constructive interference  $2d \sin\theta = n\lambda$

## 2.8 Bravais lattice

### Definitions

1. A Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the point the array is viewed.
2. A 3D Bravais lattice consists of all points with position vectors  $\vec{R}$  of the form

$$\vec{R} = n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$$

where  $\vec{a}_i$ s are any 3 vectors not all in the same plane, and  $n_1, n_2, n_3$  range through all integer values.  $\vec{a}_i$ s are called primitive vectors and are said to span or generate the lattice. Simple cubic - equal length and mutually perpendicular

**Counterexample** The vertices of a 2D honeycomb do not form a Bravais lattice because even though the structure is periodic, but orientationally the page has to be rotated through  $180^\circ$  each time you move through one link.

Note that the lattice, being an abstract construct, is essentially infinite, but when it is 'fleshed out' with real ions, it forms a finite crystal.

There are infinitely many possible choices of primitive vectors.

bcc  $\rightarrow$  If each centre point is considered a corner point of another simple cubic array then the original corner points becomes the central points. So identical surrounding for each point i.e. it is a Bravais lattice.

Let original cubic lattice have primitive vectors  $a\hat{x}, a\hat{y}, a\hat{z}$ . Then the bcc lattice primitives are  $\vec{a}_1 = a\hat{x}, \vec{a}_2 = a\hat{y}, \vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$ . We can choose a more symmetric set  $\vec{a}_1 = \frac{a}{2}(\hat{y} + \hat{z} - \hat{x}), \vec{a}_2 = \frac{a}{2}(\hat{z} + \hat{x} - \hat{y}), \vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y} - \hat{z})$ . This is the set of vectors from a corner to the central points outside the cube.

### fcc

Why Bravais lattice? See how all the points are equivalent.

Symmetric set:

$$\vec{a}_1 = \frac{a}{2}(\hat{y} + \hat{z}), \quad \vec{a}_2 = \frac{a}{2}(\hat{z} + \hat{x}), \quad \vec{a}_3 = \frac{a}{2}(\hat{x} + \hat{y})$$

fcc  $\rightarrow$  Ag, Al

bcc  $\rightarrow$  Ba, Cr

Simple cubic  $\rightarrow$  under normal conditions, only  $\alpha$  phase of polonium. The vectors joining any two points to all others is also called a Bravais lattice. The translations defined by these vectors is also called so.

### Good definition

A Bravais lattice is a discrete set of vectors not all in a plane, closed under vector addition and subtraction.

**Coordination Number** - Number of nearest neighbours.

- Simple cubic - 6
- bcc - 8
- fcc - 12

### 2.8.1 Primitive unit cell

A volume of space, which, when translated through **all** the vectors of a Bravais lattice, fills **all** of space. There must not be any voids or overlap. Only common surfaces are allowed. There is no unique choice of primitive unit cells.

There can be only one lattice point per primitive unit cell. This can be seen as follows:- if there are more than one point per primitive unit cell then the smallest translations, i.e. from one of these points to the other (which is a valid lattice translation) will move the primitive unit cell halfway, i.e. will cause an overlap with the next cell. Similarly, voids will be left if the no. of points is less than one. Note that here a Bravais lattice point is a point of translational symmetry; there may be more than one **ion** in a primitive unit cell (which defines the basis) but in that case translations from the position of one ion to the other will not be valid lattice translations. Thus if  $n \equiv$  no. of points per unit volume and  $v \equiv$  volume of the unit cell, then  $nv = 1 \Rightarrow v = 1/n$ . Thus all primitive unit cells have the same volume. *Given any two primitive unit cells of arbitrary shape, it is possible to cut the first into pieces, which, when translated through appropriate lattice vectors, can be reassembled to give the second.* The set of all points  $\vec{r}$  of the form

$$\vec{r} = x_1\vec{a}_1 + x_2\vec{a}_2 + x_3\vec{a}_3, \quad 0 \leq x_i \leq 1$$

where the primitive vectors are  $\vec{a}_1, \vec{a}_2, \vec{a}_3$  form an example of a primitive cell, which is the parallelepiped formed by  $\vec{a}_1, \vec{a}_2, \vec{a}_3$ . Such a choice does not necessarily show the symmetry of the system.

### 2.8.2 Conventional unit cell

A region that fills up all space without overlapping when translated through some *subset* of the vectors of a Bravais lattice. It has the required symmetry but may be larger than the primitive.

Bcc cubic unit cell has two points per cell, i.e. volume is double that of the primitive cell -> eight corners each shared by eight cells each + 1 central point. In the case of fcc -> 4-> eight corners each by 8-> so 1 and six faces each by 2 so 3, total - 4.

Numbers specifying the size of a unit cell are called **lattice constants**.

### 2.8.3 Wigner-Seitz primitive cell

This prescription results in a primitive cell with the full symmetry of the Bravais lattice. The Wigner-Seitz cell about a lattice point in the region in space that is closer to that point than to any other lattice point. If such a set is defined for a set of points not forming a Bravais lattice then it is called a Voronoy polyhedron and its shape and orientation will depend on the choice of points.

Because of the translational symmetry of the Bravais lattice, the Wigner-Seitz cell about any point will be taken into the Wigner-Seitz cell about any other, when translated through the lattice vector joining the two points.

Since there is nothing in the definition of a wigner\_seitz cell that refers to any particular choice of primitive vectors, the Wigner-Seitz cell will be as symmetrical as the Bravais lattice.

**Prescription:** Draw lines connecting a particular point to all other points in the lattice bisect each line with a perpendicular plane and take the smallest closed polyhedron about that point.

In 2-d , if the lattice is not rectangular the w-s cell is always a hexagon.

### 2.8.4 Basis

A crystal structure consists of identical copies of the same physical unit, called the **basis** located at all the points of a Bravais lattice or translated through all the vectors of a Bravais lattice. The basis is a set of points which get translated as a whole to the lattice points through the lattice vectors. Vertices of a two dimensional honey comb (by itself not Bravais) is a 2-d triangular Bravais lattice with a two point basis.

### 2.8.4.1 Non-primitive unit cells:

bcc described as a simple cubic lattice with two point basis.  $0, \frac{a}{2}(\vec{x} + \vec{y} + \vec{z})$

fcc simple cubic with four point basis.  $0, \frac{a}{2}(\vec{x} + \vec{y}), \frac{a}{2}(\vec{y} + \vec{z}), \frac{a}{2}(\vec{z} + \vec{x})$

### 2.8.4.2 NaCl crystal

Equal no. of Na & Cl placed at alternate points of a simple cubic lattice in such a way that each ion has six of the other kind as nearest neighbours. fcc - Bravais with basis consisting of Na at 0 and Cl at  $\frac{a}{2}(\hat{x} + \hat{y} + \hat{z})$  i.e. at the centre of the conventional cubic cell.

## 2.9 Reciprocal Lattice

Let vectors  $\vec{R}$  define a Bravais lattice. If a plane wave  $e^{i(\vec{k} \cdot \vec{R})}$  has the same periodicity, then the set of all such  $\vec{K}$  forms the reciprocal lattice.

This means,  $e^{i\vec{k} \cdot (\vec{r} + \vec{R})} = e^{i\vec{k} \cdot \vec{r}}$  for arbitrary  $\vec{r}$

i.e.  $e^{i\vec{k} \cdot \vec{r}} \times e^{i\vec{k} \cdot \vec{R}} = e^{i\vec{k} \cdot \vec{r}} \Rightarrow e^{i\vec{k} \cdot \vec{R}} = 1$ . Thus, find  $\vec{k}$  for all the  $\vec{R}$ s and you have the reciprocal lattice. As a result, the reciprocal lattice is defined with respect to a particular Bravais lattice. That Bravais lattice is called the **direct lattice**. ( $e^{ikr} = \cos kr + i \sin kr = 1 \Rightarrow kr = \text{integer} \times 2\pi$ )

### 2.9.1 Prescription for construction

Let  $\vec{a}_1, \vec{a}_2, \vec{a}_3$  be the set of primitive vectors for the direct lattice. Then reciprocal lattice is generated by

$$\begin{aligned} b_1 &= 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\ b_2 &= 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \\ b_3 &= 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)} \end{aligned}$$

$[\vec{b}_i \cdot \vec{a}_j = 2\pi\delta_{ij}, \text{ Use } \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) = \vec{a}_2 \cdot (\vec{a}_3 \times \vec{a}_1) = \vec{a}_3 \cdot (\vec{a}_1 \times \vec{a}_2)]$

Now any vector in the reciprocal lattice can be expressed as

$$\vec{k} = k_1 \vec{b}_1 + k_2 \vec{b}_2 + k_3 \vec{b}_3 \quad (2.7)$$

Again

$$\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$$

Therefore

$$\vec{k} \cdot \vec{R} = 2\pi(k_1 n_1 + k_2 n_2 + k_3 n_3)$$

Now for  $e^{i\vec{k} \cdot \vec{R}}$  to be equal to 1 for all  $\vec{k}$ ,  $\vec{k} \cdot \vec{R} = 2\pi \times \text{integer}$  for any choice of  $n_i$ . Thus  $k_i$  have to be integers - that is the only condition. The condition that  $\vec{k}$  be a reciprocal lattice vector is satisfied by just those vectors that are linear combination of the  $\vec{b}_i$  with integral coefficients. Thus (2.7) defines a Bravais lattice with primitive vectors given by  $\vec{b}_i$ . The reciprocal of the reciprocal lattice is the original (direct) lattice.

### Examples

1. *Simple cubic* Bravais lattice,  $\vec{a}_1 = a\hat{x}$ ,  $\vec{a}_2 = a\hat{y}$ ,  $\vec{a}_3 = a\hat{z}$ . Reciprocal lattice is given by :  $\vec{b}_1 = \frac{2\pi}{a}\hat{x}$ ,  $\vec{b}_2 = \frac{2\pi}{a}\hat{y}$ ,  $\vec{b}_3 = \frac{2\pi}{a}\hat{z}$
2. *Fcc cubic* Bravais lattice. Reciprocal lattice:  $\vec{b}_1 = \frac{4\pi}{a} \cdot \frac{1}{2}(\hat{y} + \hat{z} - \hat{x})$ ,  $\vec{b}_2 = \frac{4\pi}{a} \cdot \frac{1}{2}(\hat{z} + \hat{x} - \hat{y})$ ,  $\vec{b}_3 = \frac{4\pi}{a} \cdot \frac{1}{2}(\hat{x} + \hat{y} - \hat{z})$ . It is a bcc lattice with conventional cubic cell of side  $\frac{4\pi}{a}$ .

3. *bcc lattice*. The reciprocal lattice is fcc with conventional cubic cell of side  $\frac{4\pi}{a}$

If  $v$  is the volume of a primitive cell in the direct lattice, then the primitive cell of the reciprocal lattice has a volume  $\frac{(2\pi)^3}{v}$ .

### Examples:

1. Prove that the reciprocal lattice primitive vectors satisfy

$$\vec{b}_1 \cdot (\vec{b}_2 \times \vec{b}_3) = \frac{(2\pi)^3}{\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3)}$$

2. Prove directly that the reciprocal of reciprocal is direct (use  $\vec{A} \times (\vec{B} \times \vec{C}) = \vec{B}(\vec{A} \cdot \vec{C}) - \vec{C}(\vec{A} \cdot \vec{B})$ )

3. Prove that the volume of a Bravais lattice primitive cell is given by

$$v = | \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) |$$

## 2.10 Lattice Planes

Given a particular Bravais lattice, a lattice plane is defined to be any plane containing at least three non-collinear Bravais lattice points, The infinity of points, on such a plane will form a two-dimensional Bravais lattice within the plane.

### 2.10.1 Family of lattice planes

A set of parallel, equally spaced lattice planes. They together contain all the lattice points.

### 2.10.2 Theorem

For any family of lattice planes separated by a distance 'd' there are reciprocal lattice vectors perpendicular to the planes, the shortest of which have a length of  $\frac{2\pi}{d}$ . OR, if  $\frac{2\pi}{d}$  is the length of the shortest reciprocal lattice vector parallel to any reciprocal lattice vector  $\vec{k}$ , then there is a family of lattice planes normal to  $\vec{k}$  separated by a distance  $d$ . The proof comes from:

1. Reciprocal lattice vectors are wave vectors of plane waves that are unity at all lattice sites.
2. Plane wave has same value at all points lying in a family of planes that are perpendicular to its wave vector and separated by an integral number of wavelengths.

Let  $\hat{n}$  be a unit vector normal to a family of lattice planes. Let  $\vec{k} = 2\pi\hat{n}/d$ . Now  $\lambda = 2\pi/k = d$  for a wave given by  $e^{i\vec{k}\cdot\vec{r}}$ . Thus  $e^{i\vec{k}\cdot\vec{r}}$  is constant in planes perpendicular to  $\vec{k}$  and has the same value on all the planes. Since one of the planes contain  $\vec{r} = 0$ ,  $e^{i\vec{k}\cdot\vec{r}} = 1$  and has to be unity for any point in any of the planes. Since the planes contain all the Bravais lattice points  $\vec{R}$ ,  $\vec{k}$  is a reciprocal lattice vector. Again  $\vec{k}$  is the shortest reciprocal lattice vector perpendicular to the planes, because any wave vector  $< \vec{k}$  will give a plane wave with  $\lambda > d \rightarrow$  cannot have the same value on all planes in the family.

**Converse** Let  $\vec{k}$  be the shortest parallel reciprocal lattice vector. Consider the set of real space planes on which  $e^{i\vec{k}\cdot\vec{r}} = 1$ . They are perpendicular to  $\vec{k}$  and separated by  $d = 2\pi/k$ . Since direct lattice vectors  $\vec{R}$  all satisfy  $e^{i\vec{k}\cdot\vec{R}} = 1$  for any reciprocal lattice vector  $\vec{k}$ , they must all lie within these planes i.e. the family of space planes as defined above must contain within it a family of lattice planes. Again, the spacing between the planes is  $d$  and not a multiple because if every  $n^{th}$  plane in the family contained Bravais lattice points, the vector  $\vec{k}/n$  i.e. of length  $\frac{2\pi}{nd}$  would be a reciprocal lattice vector, but shorter than  $\vec{k}$ .

### 2.10.3 Miller Indices:

They are used to specify the orientation of a plane by specifying a vector normal to the plane. So choose a reciprocal lattice vector. Choose the **shortest**. Miller indices of a lattice plane are the coordinates of the shortest reciprocal lattice vector normal to that plane, with respect to a specified set of primitive reciprocal lattice vectors. Thus a plane with miller indices  $h, k, l$  is normal to the reciprocal lattice vector  $h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ . They have to be integers because any reciprocal lattice vector is a linear combination of primitives with integral coefficients. Since the shortest vector is chosen,  $h, k, l$  can have no common factor. Miller indices depends on particular choice.

In cubic lattices the reciprocal is also cubic and so, the Miller indices are the coordinates of a normal to the particular lattice plane.

#### 2.10.3.1 In terms of the direct lattice:

A lattice plane  $(h, k, l)$  is perpendicular to the reciprocal lattice vector  $\vec{k} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$ . It will be contained in the continuous plane  $\vec{k} \cdot \vec{r} = A$  for suitable constant  $A$ . This plane intersects the axes (direct) at  $x_1\vec{a}_1, x_2\vec{a}_2, x_3\vec{a}_3$ . The  $x_i$  are determined by the condition that  $x_i\vec{a}_i$  satisfy the equation of the plane  $\vec{k} \cdot (x_i\vec{a}_i) = A$ , since  $x_1\vec{a}_1$  is also a point on the plane and follows  $\vec{k} \cdot \vec{r} = A$ . Since  $\vec{k} \cdot \vec{a}_1 = 2\pi h, \vec{k} \cdot \vec{a}_2 = 2\pi k$  and  $\vec{k} \cdot \vec{a}_3 = 2\pi l$ ,

$$x_1 = \frac{A}{2\pi h}, x_2 = \frac{A}{2\pi k}, x_3 = \frac{A}{2\pi l}$$

Therefore intercepts with the crystal axes of a lattice plane are inversely proportional to the Miller indices of the plane.

#### 2.10.3.2 Crystallographic definition:

Define Miller indices as a set of integers with no common factors, inversely proportional to the intercepts of the crystal plane along the crystal axes:

$$h : k : l = \frac{1}{x_1} : \frac{1}{x_2} : \frac{1}{x_3} \quad (\text{note that this is actually saying the same thing!})$$

#### 2.10.3.3 Notations

##### Miller indices

$(hkl) \rightarrow$  Put  $\vec{k}$  for  $(-)$ ve

##### Directions in direct lattice

$[n_1 n_2 n_3]$  direction of  $n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$

$(100), (010), (001)$  are equivalent in cubic crystal due to symmetry. Use  $\{ \}$  to denote such a set of Miller indices and  $\langle \rangle$  for a set of equivalent directions.

## 2.11 Von Laue Formulation of X-ray Diffraction

In this formulation, there is no particular sectioning of the crystal into lattice planes and no assumption of specular reflection has been made. The crystal is assumed to consist of identical microscopic objects placed at the sites  $\vec{R}$  of a Bravais lattice, each of which can radiate the incident radiation in **all** directions. We illustrate the process with the help of the schematic figure (2.7).

X-ray of wavelength  $\lambda$  is incident along the direction  $\hat{n}$  and gets scattered in all directions. Let us observe the radiation scattered along the direction  $\hat{n}'$ . Incident wave vector is  $\vec{k} = \frac{2\pi\hat{n}}{\lambda}$  and the scattered wave vector is  $\vec{k}' = \frac{2\pi\hat{n}'}{\lambda}$ . The path difference between the two rays has to be an integral multiple of the wavelength for constructive interference to occur. Thus

$$d\cos\theta + d\cos\theta' = \vec{d} \cdot (\hat{n} - \hat{n}') = m\lambda$$



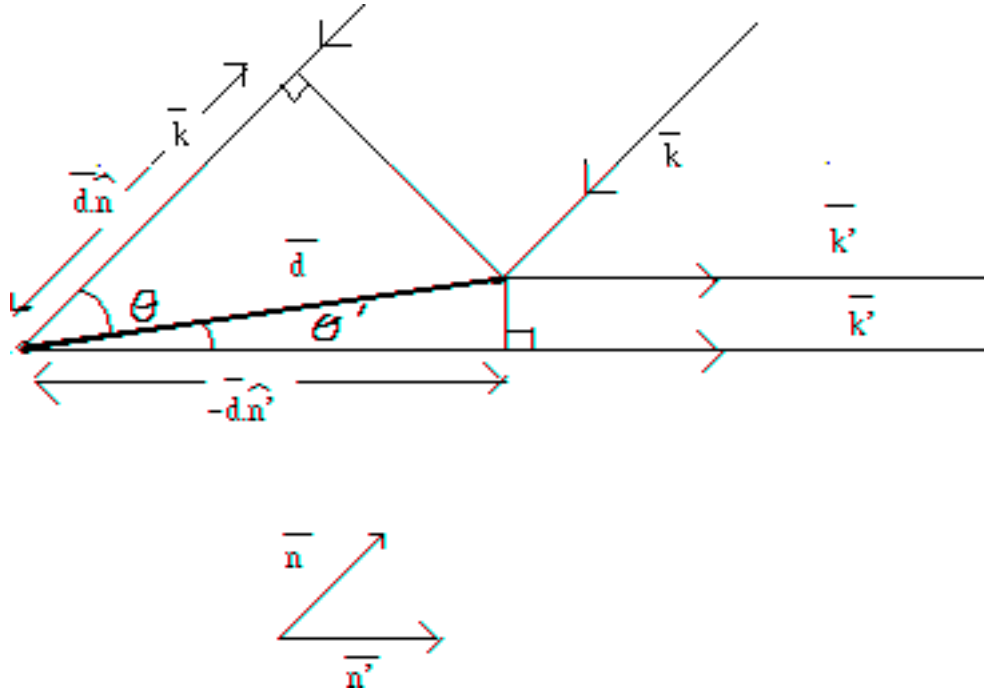


Figure 2.7: Laue scattering from two scatterers separated by the vector  $\vec{d}$ . The incident radiation is along the direction specified by the unit vector  $\hat{n}$  and the scattered ray leaves along the direction  $\hat{n}'$ .  $\vec{k}$  and  $\vec{k}'$  are the incident and scattered wave vectors.

Multiplying both sides by  $\frac{2\pi}{\lambda}$ , we get

$$\vec{d} \cdot (\vec{k} - \vec{k}') = 2\pi m \quad (\text{integral } m) \quad (2.8)$$

For an array (Bravais lattice) the sites are displaced from each other by Bravais lattice vectors  $\vec{R}$ . The above equation has to hold simultaneously for all values of  $\vec{d}$  that are lattice vectors. Thus equation (2.8) has to hold simultaneously for all values of  $\vec{d}$  that are Bravais lattice vectors.

$$\begin{aligned} \vec{R} \cdot (\vec{k} - \vec{k}') &= 2\pi m \\ \Rightarrow e^{i(\vec{k}' - \vec{k}) \cdot \vec{R}} &= 1 \\ \Rightarrow \text{Cos}(\vec{k}' - \vec{k}) \cdot \vec{R} + i \text{Sin}(\vec{k}' - \vec{k}) \cdot \vec{R} &= 1 \\ \Rightarrow \text{Cos}(\vec{k}' - \vec{k}) \cdot \vec{R} &= 1 \\ \Rightarrow (\vec{k}' - \vec{k}) \cdot \vec{R} &= 2\pi m \end{aligned}$$

Compare this with the definition of reciprocal lattice.

### 2.11.1 Laue condition

Constructive interference will occur provided the change in wave vector  $\vec{K} = \vec{k} - \vec{k}'$  is a vector of the reciprocal lattice. **Alternative** If  $\vec{K}' - \vec{k}$  belongs to the reciprocal lattice, so does  $\vec{k} - \vec{k}'$ . Let  $\vec{K} = \vec{k} - \vec{k}'$ . Now  $\vec{k}$  and  $\vec{k}'$  have the same magnitude (as  $\lambda$  is the same). Therefore  $\vec{k}' = \vec{k} - \vec{K}$ . But the magnitude of  $\vec{k}'$  and  $\vec{k}$  is the same. Thus  $\vec{k} = |\vec{k} - \vec{K}|$ . Squaring both sides, we get

$$\begin{aligned} k^2 &= (\vec{k} - \vec{K}) \cdot (\vec{k} - \vec{K}) \\ &= \vec{k} \cdot \vec{k} - \vec{K} \cdot \vec{k} - \vec{k} \cdot \vec{K} + K^2 \\ &= k^2 - 2\vec{K} \cdot \vec{k} + K^2 \\ \Rightarrow \vec{k} \cdot \vec{K} &= \frac{1}{2}K^2 \Rightarrow \vec{k} \cdot \frac{\vec{K}}{K} = \frac{1}{2}K \Rightarrow \vec{k} \cdot \hat{K} = \frac{1}{2}K \end{aligned}$$

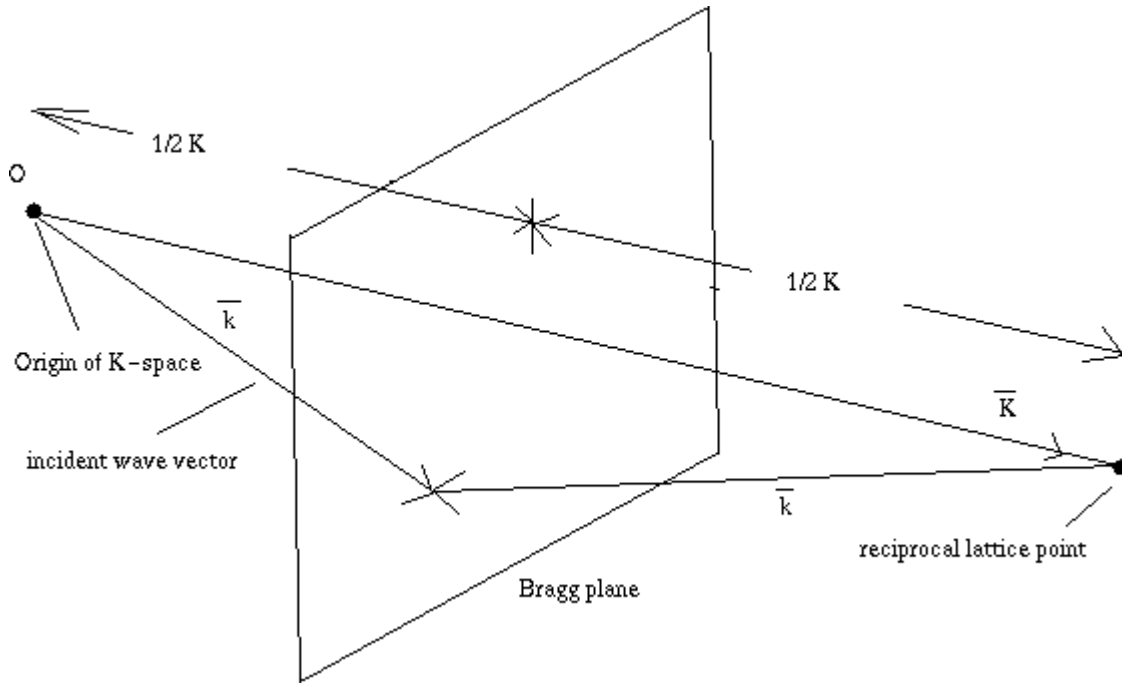


Figure 2.8: The Laue condition and Bragg planes

Therefore component of incident wave vector  $\vec{k}$  along the reciprocal lattice vector  $\vec{K}$  must be half the length of  $\vec{K}$ . Thus, incident wave vector  $\vec{k}$  will satisfy the Laue condition if and only if the tip of the vector lies in a plane that is the perpendicular bisector of a line joining the origin of  $k$ -space to a reciprocal lattice point  $\vec{K}$ . These planes are called the Bragg planes figure (2.8).

### 2.11.2 Ewald construction

In general the tip of  $\vec{k}$  will not lie on a Bragg plane and there will be no constructive interference. Experimentally one has to vary the wavelength or the direction (i.e. orientation of the crystal with respect to the incident direction).

Figure (2.9) shows an Ewald construction. Draw in  $K$ -space a sphere centred on the tip of the incident wave vector  $\vec{k}$  of radius  $|\vec{k}|$ . The surface of that sphere will pass through the origin. If some reciprocal lattice point also lies on the surface of that sphere, only then the Laue condition will be satisfied and we will get a peak.

## 2.12 Methods of X-ray diffraction

### 2.12.1 Laue method

Here we use a fixed orientation (single crystal) and fixed incident direction  $\hat{n}$ . A range of wavelengths,  $\lambda$ , from  $\lambda_1$  to  $\lambda_0$  is also used. The Ewald sphere will expand between the two spheres defined by  $\vec{k}_0 = \frac{2\pi\hat{n}}{\lambda_0}$  and  $\vec{k}_1 = \frac{2\pi\hat{n}}{\lambda_1}$ . Note that the origin of both the vectors is the same. The situation is shown in figure (2.10). The reciprocal lattice points lying within the shaded region will give Bragg peaks. By making the spread in the wavelength large enough, some peaks may always be observed and by not making it too large, the number of peaks can be kept manageable. The Laue method is most suitable for determining the orientation of a single crystal specimen of known structure. If the incident direction lies along a symmetry axis, the pattern of spots will have the same symmetry.

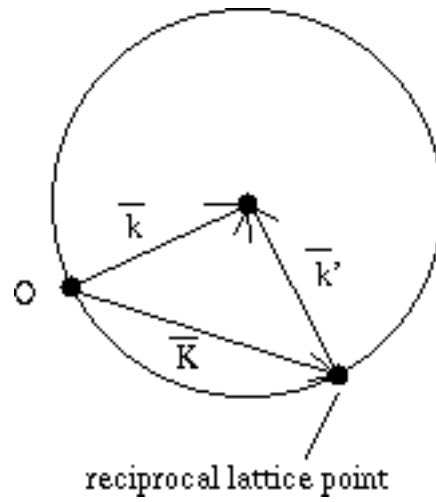


Figure 2.9: Ewald construction.  $|\bar{k}| = |\bar{k}'|$  for all  $\bar{k}'$  with tip at the centre and tail on the surface. If that tail happens to touch a reciprocal lattice point, there will be a diffraction peak.

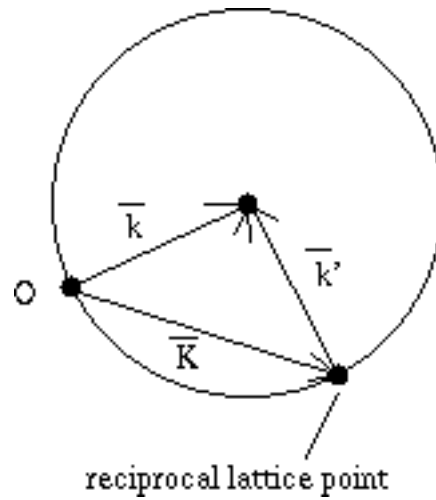


Figure 2.10: Ewald construction for the Laue method. The shaded region represents the spread in the wavelengths used. Reciprocal lattice points lying within the shaded region will give rise to Bragg peaks.

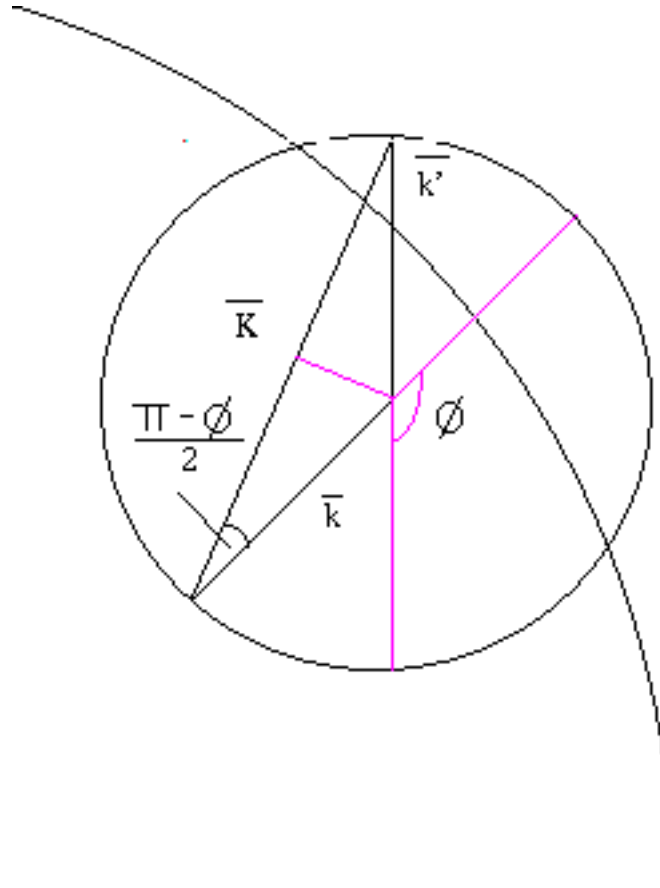


Figure 2.11: Ewald construction for the Debye-Scherrer method

### 2.12.2 Rotating crystal method

Monochromatic X-rays are used in this method. The crystal is rotated about a fixed axis and the pattern recorded on films or detectors. The reciprocal axis rotates about the same axis. Since the frequency and direction of the incident radiation is fixed, the Ewald sphere is fixed and the entire reciprocal lattice rotates. Each reciprocal lattice point traverses a circle about the rotation axis and a Bragg reflection occurs whenever this circle intersects the Ewald sphere. (diagram from Ashcroft-Mermin).

### 2.12.3 Debye-Scherrer or powder method

This is equivalent to a rotating crystal experiment in which, in addition, the axis of rotation is varied over all possible orientations. Isotropic averaging of incident direction occurs because the powdered or polycrystalline sample is like a collection of crystals with all kinds of orientations. The individual grains of the powder are still large enough to cause diffraction. The Ewald sphere is fixed as the wavelength and incident direction are the same. Now, instead of a circle, each reciprocal lattice point generates a sphere of radius  $K$  (sphere because there is no fixed axis of rotation). The intersection with the Ewald sphere is a circle provided  $|K|$  is less than  $2|k|$ . The vector joining any point on such a circle with the tip of the incident  $k$  is a wave vector  $k'$  for which scattered radiation will be observed. Thus each reciprocal lattice vector of length  $< 2k$  generates a cone of scattered radiation at an angle  $\phi$  [figure(2.11)] to the forward direction. Then  $K = 2k \sin \frac{1}{2} \phi$ . By measuring the angles  $\phi$  at which Bragg reflections are observed, the length of all reciprocal lattice vectors shorter than  $2k$  can be estimated. From this information the reciprocal

lattice can often be constructed.

### 2.12.4 Diffraction by monatomic lattice with basis

Carbon in the diamond structure or hexagonal close-packed beryllium where  $n = 2$ . The basis is required to bet the requisite symmetry. The contents of each primitive cell can be analysed into a set of identical scatterers at positions  $\vec{d}_1, \vec{d}_2, \dots, \vec{d}_n$  etc. *within the cell*.

If the Bragg peak is associated with change in wavevector  $\vec{K} = \vec{k}' - \vec{k}$ , then the phase difference between scattered at  $\vec{d}_i$  and  $\vec{d}_j = \vec{K} \cdot (\vec{d}_i - \vec{d}_j)$  and the amplitudes (at addition) will differ by a factor  $e^{i\vec{K} \cdot (\vec{d}_i - \vec{d}_j)}$ . Thus the amplitudes are in the ratios  $e^{i\vec{K} \cdot \vec{d}_1}, \dots, e^{i\vec{K} \cdot \vec{d}_n}$ . The net ray from the entire primitive cell is the sum and the amplitude will have the factor  $S_{\vec{K}} = \sum_{j=1}^{j=n} e^{i\vec{K} \cdot \vec{d}_j}$ .  $S_{\vec{K}}$  is called the **geometrical structure factor** and expresses the extent to which interference inside a cell can diminish the intensity associated with the reciprocal lattice vector  $\vec{K}$ . The intensity  $\propto |S_{\vec{K}}|^2$ .

## 2.13 Thomson Scattering of X-rays

### 2.13.1 Electromagnetic radiation by accelerated charges:

Coulomb's law  $\rightarrow \vec{E} = \frac{q}{r^2} \left( \frac{\vec{r}}{r} \right)$

$\rightarrow$  Gaussian units

Energy stored in the electric field per unit volume is :

$$\rho = \frac{E^2}{8\pi}$$

For a uniformly moving charge, electric field ( $\vec{E}$ ) moves along with it and a magnetic field ( $\vec{H}$ ) also develops, but even though the field is now non-static, there is no radiation away from the charge. For such a charge,

$$\rho = \frac{1}{8\pi} (E^2 + H^2)$$

For an accelerated charge-

- At rest at "t"
- Constant acceleration "a" to the right during "t" to "t' "
- Continuously moving with constant final velocity

At a later instant "t'' ", we consider the system from a frame moving with the final velocity. All times are measured in the frame.

$\rightarrow$

Beyond a radius  $c(t-t')$  from the original position, there is no upgradation of information. So lines still radiate from the original position.

$\Rightarrow$

Within a radius of  $c(t'' - t')$ , all the information has been updated and the lines of force are radially directed outward from the present position.

$\rightarrow$

As a result there are breaks in the lines of force contained between a sphere centred on the initial position and of radius  $c(t'' - t)$  and another sphere centred on the present position and of radius  $c(t'' - t')$ . As  $t''$  increases this region expands outwards with velocity  $c$ . So both longitudinal and transverse components appear. The longitudinal components die out rapidly as with Coulomb's law but for the transverse components the gap between the lines of force does not increase that rapidly and these components survive at greater distances.

Detailed calculations show : (at large distances)

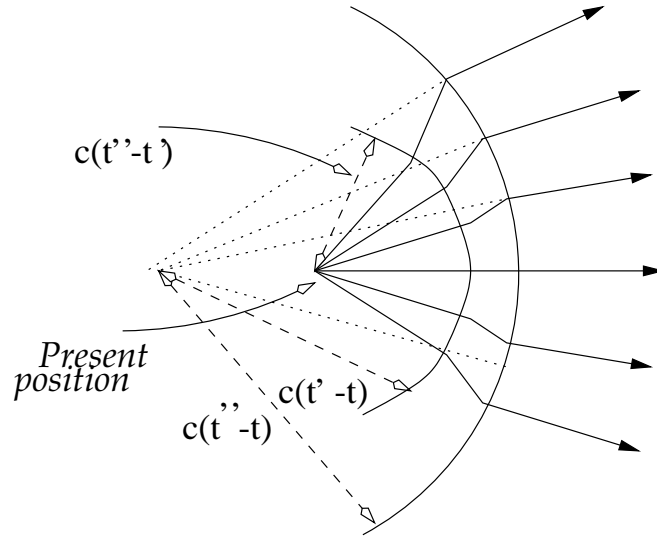


Figure 2.12: Radiation from an accelerated charge

$$E_{\perp} = \frac{qa \sin \theta}{c^2 r}$$

$r = c(t - t')$  → magnitude of the vector  $\vec{r}$  from the region at which acceleration  $\vec{a}$  occurred to the point at which the transverse field is being measured.  $\theta$  is the angle between  $\vec{r}$  &  $\vec{a}$ . A transverse magnetic field will also be generated, which (for unit permeability) is :

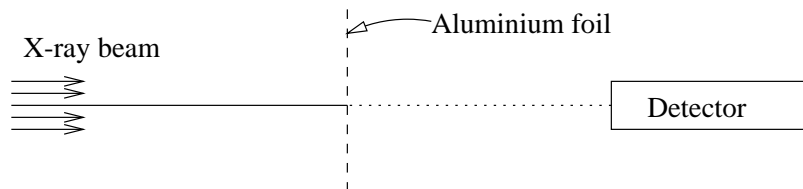
$$H_{\perp} = \frac{qa \sin \theta}{c^2 r}$$

Therefore,  $E_{\perp} = H_{\perp}$  and the energy density of radiation is :

$$\rho = \frac{1}{8\pi} (E_{\perp} + H_{\perp}) = \frac{E_{\perp}}{4\pi} \rho = \frac{E_{\perp}}{4\pi}$$

These are valid only if the dimensions of the region in which the acceleration took place is small compared to "c" times the period of it's direction.

### 2.13.2 Thomson Scattering



Attenuation will be due to both absorption and scattering. By varying the angle subtended by the detector, the attenuations due to i) scattering and ii) absorption may be separated. Alternatively, only the scattered X-rays may be detected in a separate experiment.

Assumptions

1.  $\lambda \ll 10^{-8}$  cm  $\rightarrow$  characteristic atomic direction.
2. Energy of an X-ray quantum is large compared to the binding energy of atomic electrons.

$$h\nu \gg \text{Binding Energy}(B.E.)$$

3. X-ray quantum energy is small compared to the rest mass of an electron.

$$h\nu \ll mc^2$$

Why ??

1. Interference effects are ruled out due to incoherent radiation ( any  $e^-$  will do )
2. Consider electrons to be free
3. Compton effect can be ignored as there is no change in wavelength.

We consider electrons interaction with sinusoidal electric field. Magnetic field has negligible effect. The intensity  $I = \rho c$ , i.e., the energy contained within a parallelepiped with 1 sq. cm. base and length that light travels in 1 cm.

$$I(\theta) = \frac{E_{\perp}^2 c}{4\pi} = \frac{q^2 a^2 \sin^2 \theta}{4\pi c^3 r^2}$$

Thus the intensity follows the inverse square law - otherwise conservation of energy.

(Discuss how it means that the energy had to be associated with the square of the field)

Total energy - integrate  $I(\theta)$  over surface of an arbitrary radius.

$$\begin{aligned} R &= \int I(\theta) d\theta \\ &= \int_0^{\pi} \underbrace{2\pi r \sin \theta}_{\text{circumference}} \times \underbrace{r d\theta}_{\text{shell width}} \\ &= \int_0^{\pi} I(\theta) 2\pi r^2 \sin \theta d\theta \end{aligned}$$

Evaluate to get  $R = \frac{2}{3} \frac{q^2 a^2}{c^3}$

Therefore force =  $-eE$

Acceleration is :

$$\frac{\vec{F}}{m} = \frac{-eE}{m} \quad (2.9)$$

$\vec{E}, \vec{F}, \vec{a}$  all oscillate sinusoidally with the frequency  $\nu$  of the incident wave. The electron also oscillates sinusoidally with a frequency  $\nu$  and emits electromagnetic waves of the same frequency.

Rate of scattering,  $S$  is

$$S = \frac{2}{3} \frac{e^2 a^2}{c^3} \quad (2.10)$$

$$S = \frac{2}{3} e^2 \frac{\left(\frac{-eE}{m}\right)^2}{c^3} \quad (2.11)$$

$$S = \frac{2}{3} \frac{e^4 E^2}{m^2 c^3} \quad (2.12)$$

Take time average,

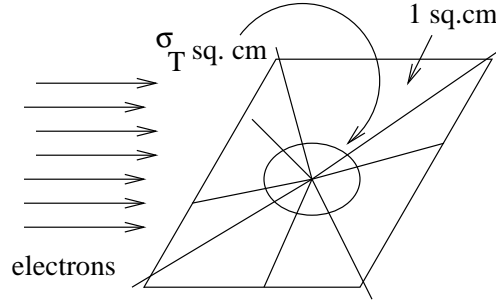


Figure 2.13: Angular distribution

$$\bar{S} = \frac{2 e^4 \overline{E^2}}{3 m^2 c^3} = \frac{2 e^4 \overline{E^2}}{3 m^2 c^3} \quad (2.13)$$

(because only "E" varies with time). Let  $\bar{I} \equiv$  energy of the incident radiation.

$$\bar{I} = \bar{\rho}c = \frac{c\overline{E^2}}{4\pi} \quad (2.14)$$

Comparing eqn (2.13) and eqn (2.14), we see that both are proportional to  $\overline{E^2}$ .

$$\begin{aligned} \bar{s} &= \sigma_T \bar{I} \\ \sigma_T &= \frac{8\pi}{3} \left( \frac{e^2}{2mc} \right)^2 \\ \sigma_T &= 6.66 \times 10^{-25} \text{ cm}^2 \end{aligned} \quad (2.15)$$

where  $\sigma_T$  is the Thomson scattering cross-section. It describes a characteristic property of a free electron.

This should not be taken literally! There is no sharp cut-off distance beyond which there is no scattering and within which everything gets scattered!

### Why is it called a Cross-section ??

Imagine the electron at the centre of a disc of area  $\sigma_T \text{ cm}^2$  oriented normal to the beam direction. Average energy incident per second per unit area is  $\bar{I}$ . Now if all the radiation hitting the disc is scattered, then  $\bar{S} = \sigma_T \bar{I}$ !

### 2.13.3 Angular Distribution

Now  $I(\theta) \propto \sin^2 \theta$  where  $\theta$  is the angle between direction of acceleration and direction of emission. We wrote the distribution in term of the angle  $\Theta$  between  $\vec{r}$  and  $\vec{i}$  and the azimuthal orientation of  $\vec{E}$  to consider the cone of an unpolarized beam.

Let  $\hat{I}$  define the z direction and  $\hat{r}$  lies in the xz plane. Let  $\hat{a}$  have an azimuthal angle of  $\phi$ .



$$\begin{aligned}
 \hat{r} &= \sin \Theta \hat{i} + \cos \Theta \hat{k} \\
 \hat{a} &= \cos \phi \hat{i} + \sin \phi \hat{j} \\
 \hat{a} \cdot \hat{r} &= (\cos \phi \hat{i} + \sin \phi \hat{j}) \cdot (\sin \Theta \hat{i} + \cos \Theta \hat{k}) \\
 &= \cos \phi \sin \Theta = \cos \theta \\
 \sin^2 \theta &= 1 - \cos^2 \phi \sin^2 \Theta \\
 \bar{S}(\Theta) &\propto \int_0^{2\Pi} (1 - \cos^2 \phi \sin^2 \Theta) d\phi \\
 &= \phi \Big|_0^{2\Pi} - \sin^2 \Theta \int_0^{2\Pi} \cos^2 \phi d\phi \\
 &= 2\Pi - \Pi \sin^2 \Theta \\
 \bar{S}(\Theta) &\propto (2 - \sin^2 \Theta)
 \end{aligned}$$

Here  $\bar{S}(\Theta) \equiv$  the average energy emitted per second per unit solid angle at the angle  $\Theta$ . i.e., we scale  $\bar{S}(\Theta)$  Therefore,  $\bar{S}(\Theta) = k(2 - \sin^2 \Theta)$  (some  $k$ ) accordingly-

We have to evaluate  $\bar{S} = \int \bar{S}(\Theta) d\Omega$

Area of the shaded region is 
$$\begin{aligned}
 Area &= 2\Pi r \sin \Theta r d\Theta \\
 &= 2\Pi r^2 \sin \Theta d\Theta
 \end{aligned}$$

$$\begin{aligned}
 d\Omega &= \frac{2\Pi r^2 \sin \Theta d\Theta}{r^2} \\
 \text{Therefore Solid angle} &= 2\Pi \sin \Theta d\Theta
 \end{aligned}$$

$$\text{or, } \bar{S} = 2\Pi k \int_0^\Pi (2 - \sin^2 \Theta) \sin \Theta d\Theta$$

But from our previous discussions,  $\bar{S} = \frac{8\Pi}{3} \left(\frac{e^2}{mc^2}\right)^2 \bar{I}$

Carry out the integration and equate the two to evaluate "k" and get  $\bar{S} = \frac{1}{2} \left(\frac{e^2}{mc^2}\right)^2 (2 - \sin^2 \Theta) \bar{I}$ .

Define the symbol  $\frac{dG}{d\Omega} = \frac{1}{2} \left(\frac{e^2}{mc^2}\right)^2 (2 - \sin^2 \Theta)$ . Then  $\bar{S} = \frac{d\sigma_T}{d\Omega} \bar{I}$ .

This quantity " $\frac{d\sigma_T}{d\Omega}$ " is called the differential scattering cross-section  $\rightarrow$  has dimensions of sq. cm.

It tells, what fraction of the intensity of a beam of X-rays is scattered in a Thomson scattering process by a free electron into a unit solid angle at the angle  $\Theta$ .

### 2.13.4 Scattering by an atom

For the assumptions given above, all the "Z" electrons of the atom scatter independently and  $\bar{S} = Z\sigma_T \bar{I}$ . Define  $\sigma_{sa} = Z\sigma_T$ .  $\bar{S} = \sigma_{sa} \bar{I}$ .

where,  $\sigma_{sa}$  is the scattering cross-section per atom.

Similarly, the differential scattering cross-section per atom is:  $\frac{d\sigma_{sa}}{d\Omega} = Z \frac{d\sigma_T}{d\Omega}$ .



# Chapter 3

## Free-electron theory of metals

### 3.1 Classical free-electron theory - Drude model

#### 3.1.1 Assumptions

1. Between collisions the interaction of a given electron, both with the others and with the ions, is neglected. Thus in the absence of externally applied electromagnetic fields each electron is taken to move uniformly in a straight line. In the presence of externally applied fields each electron is taken to move as determined by Newton's laws of motion in the presence of those fields, but neglecting the additional complicated fields produced by the other electrons and ions. The neglect of electron-electron interactions between collisions is the independent-electron approximation. The corresponding neglect of electron-ion interactions is known as the free-electron approximation.
2. The collisions are instantaneous. Drude attributed this to the electrons bouncing off the impenetrable cores. Electron-electron scattering is considered much less important. This is different from gases where the main scattering mechanism is that due to collisions between the molecules themselves. Actually, only a scattering mechanism is required, the exact mechanism is not that important.
3. Electrons experience collisions with a probability per unit time given by  $\frac{1}{\tau}$  where  $\tau$  is called the *relaxation time, collision time or mean free time*.  $\tau$  is considered independent of position and velocity. This is reasonable because the scattering is mainly due to the thermal velocity of the carriers and that is much greater than any additional drift velocity that applied fields may produce.
4. Electrons achieve thermal equilibrium with surroundings only through collisions, i.e. all information regarding previous velocity is lost immediately after a collision. Only speed appropriate to the local temperature remains.

#### 3.1.2 Dc conductivity

If  $\vec{j}$  is the current density,  $\vec{v}$  the drift velocity and  $n$  the number density of carriers, then  $\vec{j} = -ne\vec{v}$  and the acceleration is given by  $-\frac{e\vec{E}}{m}$ . If  $\tau$  is the average time elapsed between the last collision and the 'present' moment, then the average drift velocity is given by  $v_{av} = -\frac{e\vec{E}\tau}{m}$ . Thus

$$\vec{j} = -ne \times \frac{-e\vec{E}\tau}{m} = \frac{ne^2\tau}{m} \vec{E}$$

Putting  $\vec{j} = \sigma \vec{E}$ ,

$$\sigma = \frac{ne^2\tau}{m} \tag{3.1}$$

Thus linearity with  $E$  is shown. (Note: the idea of free particle between collisions is coming into play here!) From the resistivity, the relaxation time  $\tau$  may be estimated.

$$\tau = \frac{m}{\rho n e^2} = \left( \frac{0.22}{\rho_\mu} \right) \left( \frac{r_s}{a_0} \right)^3 \times 10^{-14} s \quad (3.2)$$

where  $\rho_\mu$  is the resistivity in micro-ohm-cm.

At room temperature  $\tau \sim 10^{-14} - 10^{-15} s$ . Mean free path  $\lambda = v_0 \tau$  where  $v_0$  represents the average electronic speed.

From classical equipartition,  $\frac{1}{2} m v_0^2 = \frac{3}{2} k_B T$ .  $v_0 \sim 10^7 cm/s$  for an electron from this. The mean free path turns out to be from  $1 \text{ \AA}$  to  $10 \text{ \AA}$ . This is comparable with the interatomic spacing, and so it is apparently consistent.

Actually,  $v_0$  is about 100 times larger at room temperatures. Again the mean free path  $\lambda \sim 10^3 \text{ \AA}$  at low temperatures. So the idea of the carriers bumping off the immobile cores is wrong. This is because this system cannot be described by classical physics. However, expressions that do not explicitly involve the relaxation time can still be used.

### 3.1.3 DC conductivity in presence of spatially uniform static magnetic field

At time  $t$  average electronic velocity  $\vec{v}$  is  $\frac{\vec{p}(t)}{m}$  where  $\vec{p}$  is the total momentum per electron. So,

$$j = \frac{-ne\vec{p}(t)}{m} \quad (3.3)$$

An electron taken at random at  $t$  will have a collision within a time  $dt$  with probability  $\frac{dt}{\tau}$ . So, the probability of no collision between  $t$  and  $t + dt$  is  $1 - \frac{dt}{\tau}$ . But if there is no collision it will acquire an additional momentum of  $\vec{f}(t)dt + \vec{O}(dt)^2$ . (just Taylor expansion upto second term). The contribution of all those electrons that do not collide between  $t$  and  $t + dt$  to the momentum per electron is the fraction  $(1 - \frac{dt}{\tau})$  that they constitute of all electrons, times their average per electron  $\vec{p}(t) + \vec{f}(t)dt + \vec{O}(dt)^2$ . Neglecting those electrons that do have a collision within  $dt$ , (The fraction of such electrons is  $\frac{dt}{\tau}$ . The random velocity part averages out and only momentum acquired during  $dt$  equal to  $f(t)dt$  is relevant. So the term is of the order  $dt^2$ .)

$$\begin{aligned} \vec{p}(t + dt) &= \left(1 - \frac{dt}{\tau}\right) [\vec{p}(t) + \vec{f}(t)dt + \vec{O}(dt)^2] \\ &= \vec{p}(t) - \left(\frac{dt}{\tau}\right) \vec{p}(t) + \vec{f}(t)dt + \vec{O}(dt)^2 \end{aligned}$$

Neglecting higher order terms

$$\begin{aligned} \vec{p}(t + dt) - \vec{p}(t) &= -\left(\frac{dt}{\tau}\right) \vec{p}(t) + \vec{f}(t)dt + \vec{O}(dt)^2 \\ S_o \frac{d\vec{p}(t)}{dt} &= -\left(\frac{t}{\tau}\right) + (\vec{t}) \end{aligned} \quad (3.4)$$

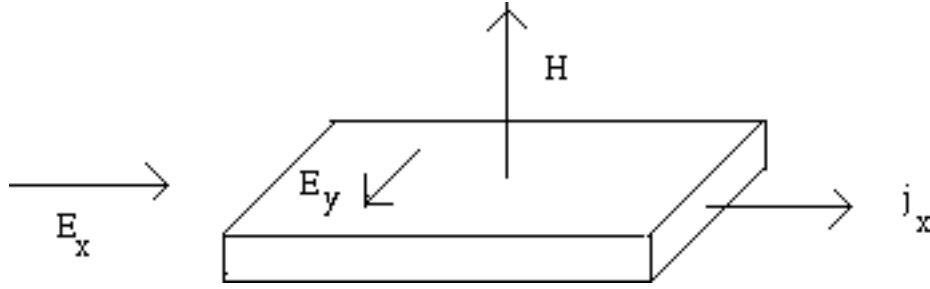
Thus the effect of collision is to introduce a frictional damping term into the equation of motion for the momentum per electron.

## 3.2 Hall effect

The Hall effect makes it possible to determine experimentally some of the microscopic properties of the conductors and semiconductors. A wire is placed in mutually perpendicular electric and magnetic fields. If the electric field is in the  $x$  direction a current density  $j_x$  is established along the  $x$  direction. Now, a magnetic field pointing in the positive  $z$  direction exerts a Lorentz force

$$-\frac{e}{c} \vec{v} \times \vec{H}$$

(for unit permeability  $H = B$ ) on the moving electrons in the negative  $y$  direction (the electron's drift velocity is opposite to the current flow) This causes the electrons to accumulate at the lower

Figure 3.1: Hall effect, The applied magnetic field is along the  $z$  axis

face of the wire and as a result of this an electric field builds up in the  $y$  direction that opposes further transverse migration of the electrons. In equilibrium this Hall field  $E_y$  balances the Lorentz force. In this context, a quantity known as the Hall coefficient is defined by the relation

$$R_H = \frac{E_y}{j_x H} \quad (3.5)$$

Now, to calculate the Hall coefficient, the current densities  $j_x, j_y$  in the presence of an electric field with arbitrary components  $E_x$  and  $E_y$  and a magnetic field along the  $z$  axis are to be obtained. For this purpose equation (3.4) is to be used with

$$\vec{f} = -e(\vec{E} + \vec{v} \times \frac{\vec{H}}{c}) \quad (3.6)$$

So

$$\frac{d\vec{p}}{dt} = -e(\vec{E} + \frac{\vec{p}}{mc} \times \vec{H})S \quad (3.7)$$

In the steady state the current is independent of time. So the  $x$  and the  $y$  components of equation (3.7) become

$$\begin{aligned} 0 &= -eE_x - w_c p_y - \frac{p_x}{\tau} \\ 0 &= -eE_y + w_c p_x - \frac{p_y}{\tau} \end{aligned} \quad (3.8)$$

where

$$w_c = \frac{eH}{mc} \text{ (cyclotron frequency)}$$

Multiplying by  $\frac{-ne\tau}{m}$  and using  $\vec{j} = -ne\vec{v}$ ,  $\sigma_0 = \frac{ne^2\tau}{m}$  (Drude model DC conductivity in the absence of a magnetic field) we get

$$\begin{aligned} \sigma_0 E_x &= w_c \tau j_y + j_x \\ \sigma_0 E_y &= -w_c \tau j_x + j_y \end{aligned} \quad (3.9)$$

The Hall field  $E_y$  is determined by setting  $j_y$  to zero in the second equation of (3.9). Thus

$$\begin{aligned} E_y &= -\left(\frac{w_c \tau}{\sigma_0}\right) j_x \\ &= -\left(\frac{eH}{mc} \times \frac{m}{ne^2\tau} \times \tau\right) j_x \\ &= -\left(\frac{H}{nec}\right) j_x \end{aligned}$$

So from equation (3.5)

$$R_H = -\frac{1}{nec} \quad (3.10)$$

So, the Hall coefficient depends on no parameters of the metal except the density of carriers. From this relation we can see that by measuring the resistivity of the material it is possible to find the number of electrons per unit volume participating in the conduction process. But, here a problem arises due to the fact that contrary to the prediction of (3.10) the Hall coefficient does depend on the magnetic field, temperature and on the care with which the sample has been prepared. However

at very low temperatures in very pure samples, and at very high fields the measured Hall coefficients approach a limiting value which is precisely the simple Drude result given by (3.10). Another fact of great importance is the fact that the measurement on the Hall field determines the sign of the charge carriers. If the charge carriers were positive the sign of their  $x$  velocity would have been reversed and so the Lorentz force on them would be along the same direction as that on the electrons. As a consequence the sign of  $E_y$  would be reversed. In the case of semiconductors this direction of  $E_y$  indicates whether the material is of an n-type or a p-type semiconductor.

In the general case, when  $\vec{j}$  is at an angle  $\phi$  to  $\vec{E}$ , the equations give  $\tan\phi = \omega_c\tau$ . The cyclotron frequency  $\omega_c$  is the angular frequency of a free electron in the magnetic field.

### 3.2.0.1 Order estimate

Putting  $\omega_c = 2\pi\nu_c$ , as  $\nu_c$  (in  $10^9$  Hz) =  $2.8 \times H$  (in kGauss)

### 3.2.1 Ac conductivity

An ac electric field is given by  $\vec{E}(t) = \text{Re} \vec{E}(\omega)e^{-i\omega t}$  and the corresponding equation of motion is

$$\frac{d\vec{p}}{dt} = -\frac{\vec{p}}{\tau} - eE \quad (3.11)$$

We use trial solution  $\vec{p}(t) = \text{Re}(\vec{p}(\omega)e^{-i\omega t})$ . Substitute complex  $\vec{p}$  and  $\vec{E}$  into (3.11) to get

$$-i\omega\vec{p}(\omega) = -\frac{\vec{p}(\omega)}{\tau} - e\vec{E}(\omega)$$

But  $\vec{j} = -ne\vec{p}/m$ . Thus

$$\begin{aligned} \vec{j}(t) &= \text{Re}(\vec{j}(\omega)e^{-i\omega t}) \\ \Rightarrow \vec{j}(\omega) &= -\frac{ne\vec{p}(\omega)}{m} \\ &= \frac{(ne^2/m)\vec{E}(\omega)}{(1/\tau) - i\omega} \Rightarrow \vec{j}(\omega) = \sigma(\omega)\vec{E}(\omega) \end{aligned}$$

Using  $\sigma_0 = \frac{ne^2\tau}{m}$  we can write the ac conductivity as

$$\sigma(\omega) = \frac{\sigma_0}{1 - i\omega\tau} \quad (3.12)$$

which goes to the Drude result as  $\omega \rightarrow 0$ .

### 3.2.2 Propagation of electromagnetic radiation in a metal

1. The electric field of a wave is accompanied by a corresponding magnetic field. But the force due to the magnetic field,  $-e\vec{p}/mc \times \vec{H}$  is small by a factor of  $\frac{v}{c}$  with respect to the force due to the electric field. But  $v \sim 0.1$  cm/s. So the contribution from the magnetic field can be neglected.
2. The field are varying in space and time whereas till now we have assumed uniform fields. However, since the field does not vary much over a mean free path, the approximation is valid.

Thus, the relation

$$\vec{j}(\vec{r}, \omega) = \sigma(\omega)\vec{E}(\vec{r}, \omega) \quad (3.13)$$

is valid whenever the wavelength of the incident radiation is much greater than the mean free path.

From Maxwell's equations:

1.  $\vec{\nabla} \cdot \vec{E} = 0$  since in the case of small-amplitude electromagnetic waves, the induced charge density vanishes in a sufficiently large conductor. We just get currents and no real build-up of charge.
2.  $\vec{\nabla} \cdot \vec{H} = 0$  which is identically true.
3.  $\vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{H}}{\partial t}$
4.  $\vec{\nabla} \times \vec{H} = \frac{4\pi}{c} \vec{j} + \frac{1}{c} \frac{\partial \vec{E}}{\partial t}$

We look for a solution with  $e^{-i\omega t}$  time dependence. Now,

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{E}) = \vec{\nabla}(\vec{\nabla} \cdot \vec{E}) - \nabla^2 \vec{E} = -\nabla^2 \vec{E}$$

from simple vector identity and using  $\vec{\nabla} \cdot \vec{E} = 0$ . Again

$$\begin{aligned} \vec{\nabla} \times (\vec{\nabla} \times \vec{E}) &= \vec{\nabla} \times \left( -\frac{1}{c} \frac{\partial \vec{H}}{\partial t} \right) \\ &= \vec{\nabla} \times \left( \frac{i\omega}{c} \vec{H} \right) \text{ since } \vec{H} \sim e^{-i\omega t} \\ &= \frac{i\omega}{c} \vec{\nabla} \times \vec{H} \\ &= \frac{i\omega}{c} \left( \underbrace{\frac{4\pi\sigma}{c} \vec{E}}_{= \frac{4\pi}{c} \vec{j}} - \underbrace{\frac{i\omega}{c} \vec{E}}_{= \frac{\partial \vec{E}}{\partial t}} \right) \end{aligned}$$

Equating the two we get

$$-\nabla^2 \vec{E} = \frac{\omega^2}{c^2} \left( 1 + \frac{4\pi i\sigma}{\omega} \right) \vec{E}$$

Putting

$$\epsilon(\omega) = 1 + \frac{4\pi i\sigma}{\omega} \tag{3.14}$$

we get,

$$-\nabla^2 \vec{E} = \frac{\omega^2}{c^2} \epsilon(\omega) \vec{E}$$

This is a wave equation with a complex dielectric constant. If the frequency is high,  $\omega\tau \gg 1$ , and we can use (3.12) and (3.14) to get

$$\begin{aligned} \epsilon(\omega) &= 1 + 4\pi i \left( \frac{\sigma_0}{1-i\omega\tau} \right) \frac{1}{\omega} \\ &= 1 + 4\pi i \left( \frac{ne^2\tau}{m(1-i\omega\tau)} \right) \frac{1}{\omega} \text{ (Drude conductivity)} \\ &\approx 1 - 4\pi i \left( \frac{ne^2\tau}{im\omega^2\tau} \right) \\ &= 1 - \frac{4\pi ne^2}{m\omega^2} \end{aligned}$$

Defining the **plasma frequency** as

$$\omega_p^2 = \frac{4\pi ne^2}{m} \tag{3.15}$$

we get

$$\epsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

If  $\epsilon$  is real and negative ( $\omega < \omega_p$ ) we get an exponential decay of  $\vec{E}$  as we move into the metal, i.e., there is no propagation. If  $\epsilon$  is positive, ( $\omega > \omega_p$ ), we get oscillatory solutions and the metal becomes transparent. If we use (3.2) and (3.15) to get

$$\omega_p \tau = 1.6 \times 10^2 \left( \frac{r_s}{a_0} \right) \left( \frac{1}{\rho_\mu} \right)$$

Since the resistivity in microhm centimeters,  $\rho_\mu$ , is of the order of unity and since  $\left( \frac{r_s}{a_0} \right)$  is in the range from 2 to 6, the high frequency condition  $\omega \tau \gg 1$  is well satisfied at the plasma frequency. The alkali metals actually become transparent in the ultraviolet region.

### 3.2.2.1 Plasmons

This time we allow  $\rho$ , the charge density, to vary, i.e. we do not deal only with currents, but allow some capacitor-like charging of different regions of the metal as well. We use the equation of continuity

$$\vec{\nabla} \cdot \vec{j} = -\frac{\partial \rho}{\partial t} \Rightarrow \vec{\nabla} \cdot \vec{j}(\omega) = i\omega \rho(\omega)$$

if  $\rho$  has an oscillatory dependence of  $e^{-i\omega t}$ . Again

$$\vec{\nabla} \cdot \vec{E}(\omega) = 4\pi \rho(\omega) \text{ (Gaus' law)}$$

Use  $\vec{j}(\vec{r}, \omega) = \sigma(\omega) \vec{E}(\vec{r}, \omega)$ . Thus

$$i\omega \rho(\omega) = 4\pi \sigma(\omega) \rho(\omega)$$

This can be solved if

$$1 + \frac{4\pi i \sigma(\omega)}{\omega} = 0$$

This is the same condition as for the onset of propagation. Then a **charge density wave**, called a **plasma oscillation** or **plasmon** can propagate. It is as if the whole electron gas is displaced (through  $d$ ) with respect to the positive background of ions. The field produced will be  $4\pi\sigma$  where  $\sigma$  is the charge per unit area at either end of the slab. Then

$$Nm\ddot{d} = -Ne |4\pi\sigma| = -Ne(4\pi nde) = -4\pi ne^2 Nd$$

So we get oscillations at the plasma frequency.

### 3.2.3 Wiedemann - Franz law

This law states that the ratio  $\frac{K}{\sigma}$  of thermal to electrical conductivity is directly proportional to the temperature  $T$  with a proportionality constant that is the same for all metals.  $\frac{K}{\sigma T}$  is called the **Lorentz number**.

Assume that the bulk of the thermal current is carried by the conduction electrons in a metal. Let the thermal current density be denoted by  $\vec{j}^q$ . from Fourier's law of heat conduction,  $\vec{j}^q = -K \vec{\nabla} T$ . After each collision the electron forgets about its previous history and emerges with a speed appropriate to the local temperature.

#### 3.2.3.1 1-D model

Assume that the electrons move only along the  $x$ -axis. At a point  $x$  half the electrons come from the high temperature side and the other half from the low temperature side. If  $\epsilon(T)$  is the thermal energy per electron at equilibrium with the metal at  $T$ , then an electron which has collided last at  $x'$  will have energy  $\epsilon(T[x'])$ . An electron arriving at  $x$  from the high temperature side will have



its last collision at  $x - v\tau$ . Then  $\epsilon(T[x - v\tau])$  is the energy carried by such an electron. The contribution to the thermal current density at  $x$  will be given by

$$\underbrace{\frac{n}{2}}_{\text{No. of such electrons per vol.}} \times v \times \text{energy} = \frac{n}{2} v \epsilon(T[x - v\tau])$$

For the electrons from the low temperature side, a similar relation holds for the contribution to the thermal current density  $\rightarrow \left(\frac{n}{2}\right) (-v) \epsilon(T[x + v\tau])$  (note that the velocity is in the other direction). Adding the two contributions we get

$$j^q = \frac{1}{2} n v [\epsilon(T[x - v\tau]) - \epsilon(T[x + v\tau])]$$

If variation of  $T$  over a mean free path is small, expand about  $x$  to get

$$j^q = n v^2 \tau \frac{d\epsilon}{dT} \left( -\frac{dT}{dx} \right)$$

For the three dimensional case, in analogy with the above,

$$v \equiv v_x \text{ and } \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3} v^2$$

Again,

$$n \frac{d\epsilon}{dT} = \left( \frac{N}{V} \right) \frac{d\epsilon}{dT} = \frac{N d\epsilon}{dT V} = c_v \text{ (electronic)}$$

Thus

$$\vec{j}^q = \frac{1}{3} v^2 \tau c_v (-\vec{\nabla} T) \Rightarrow K = \frac{1}{3} v^2 \tau c_v = \frac{1}{3} \lambda v c_v$$

where  $v^2 \equiv$  mean squared electronic speed. Therefore

$$\frac{K}{\sigma} = \frac{\frac{1}{3} c_v v^2 \tau m}{n e^2 \tau} = \frac{1}{3} \frac{c_v m v^2}{n e^2}$$

Assuming classical equipartition,  $c_v = \frac{3}{2} n k_B$  and  $\frac{1}{2} m v^2 = \frac{3}{2} k_B T$ . Therefore

$$\frac{K}{\sigma} = \frac{3}{2} \left( \frac{k_B}{e} \right)^2 T \propto T$$

which is the Wiedemann-Franz law. The Lorentz number is

$$\begin{aligned} \frac{K}{\sigma T} &= \frac{3}{2} \left( \frac{k_B}{e} \right)^2 = 1.24 \times 10^{-13} \text{ (erg/esu - K)}^2 \\ &= 1.11 \times 10^{-8} \text{ watt - ohm/K}^2 \end{aligned}$$

This is about half that seen in experiments. Drude made a further mistake which gave him a factor of two and extraordinary agreement was found.

At room temperature, electronic specific heat is actually hundred times smaller, but the mean square electronic speed is about hundred times larger. This is the reason why this model, which is completely inapplicable in the case of electrons, still gave some astounding results!

### 3.2.4 Thermopower

Along with the thermal energy, the velocity also depends on the position of the last collision. In the above derivation we have neglected it. Now we have to consider it. A mean velocity will exist from the high temperature to the low temperature region but this will cause a build-up of charge

at one side of the sample and an opposing field will build up till equilibrium is restored. In this way, the thermal gradient-induced pressure is balanced by the thermoelectric field set up in the sample. This is the origin of the **Seebeck effect**.

$$\vec{E} = S\vec{\nabla}T$$

Mean electronic velocity at  $x$

$$\begin{aligned} v_s &= \frac{1}{2}[v(x - v\tau) - v(x + v\tau)] \\ &= -\tau v \frac{dv}{dx} \\ &= -\tau \frac{d}{dx} \left( \frac{v^2}{2} \right) \end{aligned}$$

In three dimensions

$$\begin{aligned} v \equiv v_x \text{ and } \langle v_x^2 \rangle &= \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3}v^2 \\ \Rightarrow \vec{v}_s &= -\frac{\tau}{6} \frac{dv^2}{dT} (\vec{\nabla}T) \end{aligned}$$

The mean velocity due to the field (drift) =  $-\frac{e\vec{E}T}{m} = \vec{v}_E$ . For equilibrium, where the mean velocity vanishes,

$$\begin{aligned} \vec{v}_s + \vec{v}_E &= 0 \\ \Rightarrow -\frac{\tau}{6} \frac{dv^2}{dT} (\vec{\nabla}T) - \frac{e\vec{E}\tau}{m} &= 0 \end{aligned}$$

Use  $\vec{\nabla}T = \frac{\vec{E}}{T}$  to get, using magnitudes

$$\begin{aligned} \frac{\tau}{6} \frac{dv^2}{dT} \frac{E}{S} - \frac{eE\tau}{m} &= 0 \\ \Rightarrow -\frac{1}{6} \frac{dv^2}{dT} \frac{E}{S} &= \frac{eE}{m} \\ \Rightarrow S &= -\frac{dv^2}{dT} \frac{E}{6} \frac{m}{eE} \\ \Rightarrow S &= -\left(\frac{1}{3e}\right) \frac{d}{dT} \frac{mv^2}{2} = -\frac{c_v}{3ne} \end{aligned}$$

Putting  $c_v = 3nk_B/2$ , the value of  $S$  comes out to be  $-0.43 \times 10^{-4} \text{ V/K}$ , which is about hundred times more than the actual result. Here the fortuitous cancellation has not occurred and the Drude theory's limitations are clearly revealed. This shows that a quantum mechanical description is not only better, but absolutely necessary in this case.

### 3.3 Free-electron Theory - Quantum

#### 3.3.1 The Born-von Karman boundary conditions and consequences

A single electron can be described by a wave function  $\Psi(\vec{r})$  and the specification of which of two possible orientations its spin possesses. For a free electron of energy  $\epsilon$ :

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi(\vec{r}) = \epsilon \Psi(\vec{r})$$

The boundary conditions corresponding to the problem is simply that the particle has to be confined to the volume  $V$ . So we use a cube with length  $L = V^{1/3}$ . If we use the most obvious condition that  $\Psi = 0$  at the boundary, we get standing wave solutions (like the case of a particle in an infinite square well). It is not easy to describe transport of charge and energy with such solutions, travelling waves are more suitable. The conditions used are called **Born-von Karman** or **periodic** boundary conditions. The opposite faces of the cube are considered joined, so that an electron leaving from one face is equivalent to its entering from the other face. This keeps the

electron confined within  $V$ , but makes the surface inconsequential. The one-dimensional analogy is a circular ring of metal, but in  $3 - D$ , the arrangement cannot be visualised. Analytically,

$$\begin{aligned}\Psi(x, y, z + L) &= \Psi(x, y, z) \\ \Psi(x, y + L, z) &= \Psi(x, y, z) \\ \Psi(x + L, y, z) &= \Psi(x, y, z)\end{aligned}$$

The solution of this equation is  $\Psi_{\vec{k}}(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\cdot\vec{r}}$ , where  $\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$ . Here, the normalisation condition  $\int d\vec{r} |\Psi(\vec{r})|^2 = 1$  has been used to get the  $\frac{1}{\sqrt{V}}$  constant.  $\vec{k}$  is any position-independent vector. The momentum operator is given by  $\vec{p} = -i\hbar\vec{\nabla}$ . Now,  $-i\hbar\vec{\nabla} e^{i\vec{k}\cdot\vec{r}} = \hbar\vec{k} e^{i\vec{k}\cdot\vec{r}}$ . Thus  $\Psi$  is an eigenfunction of the momentum operator with eigenvalue  $\hbar\vec{k}$ . So a definite momentum is there with value  $\hbar\vec{k}$ . Then the velocity  $\vec{v} = \frac{\hbar\vec{k}}{m}$ . Again, the energy  $\epsilon = \frac{\hbar^2 k^2}{2m}$ . So we can write the energy in the familiar classical form

$$\epsilon = \frac{p^2}{2m} = \frac{1}{2} m v^2$$

Note that here this form of writing the energy, which seems to be obvious from classical mechanics, is valid only because of the form of the wave function, and may not be generally true. We have chosen the free particle wave function, where the spatial spread is infinite and hence, the momentum is definitely known. If, due to some other form of the wavefunction, the eigenvalue of the momentum operator was different, the momentum would be different. Again, due to the form of the wave function, the vector  $\vec{k}$  may be interpreted as the wave vector of a wave with wavelength  $\lambda = \frac{2\pi}{k}$ . This gives us the idea of a **de Broglie wavelength**.

The periodic boundary condition will be satisfied only if

$$e^{ik_x L} = e^{ik_y L} = e^{ik_z L} = 1$$

Now  $e^z = 1 \Rightarrow z = 2\pi i n$  ( $n \rightarrow \text{integer}$ ). Thus

$$k_x = \frac{2\pi n_x}{L}, \quad k_y = \frac{2\pi n_y}{L}, \quad k_z = \frac{2\pi n_z}{L} \quad n_x, n_y, n_z \rightarrow \text{integers}$$

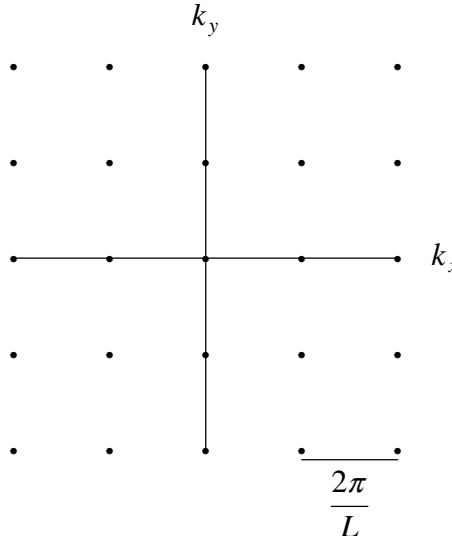
Therefore, in  $\vec{k}$ -space, the allowed wave vectors are those whose coordinates along the three axes are given by integral multiples of  $\frac{2\pi}{L}$ . For the two-dimensional case, a schematic representation is shown in figure (3.2)

The dots in the figure represent allowed values of the 2-dimensional  $\vec{k}$ -vector. The other values of  $\vec{k}$  that fall between the dots are allowed by the plane wave solution, but they do not correspond to solutions that keep the electron confined within the sample volume. Note also that as the gap between the dots is  $\frac{2\pi}{L}$ , as the volume increases, more and more of the empty  $\vec{k}$ -space becomes available (other points appear between the dots) and in the limit of infinite volume, where the particle is free, all of the  $\vec{k}$ -space becomes available. Thus, the smaller the volume, more constrained is the electron and fewer are the allowed values. This is a typical example of how ultimately the boundary conditions give rise to the granular quantum behaviour.

For a large  $\vec{k}$ -space region, the volume divided by the volume per  $\vec{k}$ -space point gives the number of allowed values of  $\vec{k}$ . In analogy with figure (3.2), we can see that each point is unique in a volume  $(\frac{2\pi}{L})^3$  of the  $\vec{k}$ -space. Thus a volume  $\Omega$  will contain  $\frac{\Omega}{(2\pi/L)^3} = \frac{\Omega V}{8\pi^3}$  allowed values of  $\vec{k}$ .

The number of allowed  $\vec{k}$  values per unit volume of  $\vec{k}$ -space ( $\vec{k}$ -space **density of levels**) is then  $\frac{V}{8\pi^3}$ . Assuming non-interacting electrons, the  $N$ -electron ground states can be built up by putting electrons into the one-electron levels in accordance with the Pauli exclusion principle. So, taking account of spin, two states exist per  $\vec{k}$ -value. For large  $N$ , as the energy is proportional to  $k^2$ , the  $\vec{k}$ -space volume upto a certain energy becomes a sphere of radius  $k_F$  (in the ground state). Thus the number of allowed values of  $\vec{k}$  within a certain energy is given by

$$\left(\frac{4}{3}\pi k_F^3\right) \left(\frac{V}{8\pi^3}\right) = \frac{k_F^3}{6\pi^2} V$$

Figure 3.2: The  $\vec{k}$ -space in two dimensions

Thus the number of allowed electrons is  $N = \frac{k_F^3}{3\pi^2}V$ , and the number per unit volume of the sample (this time the real volume, not the volume of  $\vec{k}$ -space!) is given by

$$n = \frac{k_F^3}{3\pi^2} \quad (3.16)$$

$\vec{k}_F$  is called the **Fermi wave vector**, the sphere is called the **Fermi sphere**, the surface of the sphere is the **Fermi surface**,  $\hbar k_F \equiv p_F$  is the **Fermi momentum**,  $\epsilon_F = \frac{\hbar^2 k_F^2}{2m}$  is the **Fermi energy**, and  $v_F = \frac{p_F}{m}$  is called the **Fermi velocity**, which is analogous with the thermal velocity  $\left(\frac{3k_B T}{m}\right)^{\frac{1}{2}}$  in a classical gas.

Using the ratio  $\frac{r_s}{a_0}$  (varies from 2 to 6 in metals), where  $r_s$  is the radius of the sphere whose volume is equal to the volume per conduction electron and  $a_0$  the Bohr radius ( $= \frac{\hbar^2}{me^2} = 0.529 \times 10^{-8} \text{ cm}$ ), we can express the quantities in the following way. Now,  $\frac{V}{N} = \frac{1}{n} = \frac{4\pi r_s^3}{3} \Rightarrow r_s = \left(\frac{3}{4\pi n}\right)^{\frac{1}{3}}$ . Using this and (3.16), we get

$$k_F = \frac{(9\pi/4)^{\frac{1}{3}}}{r_s} = \frac{1.92}{r_s} \Rightarrow k_F = \frac{3.36}{r_s/a_0} \text{ \AA}^{-1}$$

Thus the de Broglie wavelength for the most energetic electrons is of the order of angstroms. Again

$$v_F = \frac{\hbar}{m} k_F = \frac{4.20}{(r_s/a_0)} \times 10^8 \text{ cm/s}$$

is of the order of one percent of the velocity of light. Classically, at  $T = 0$  (ground state)  $v = 0$ . Even at room temperature, the classical thermal velocity is only of the order of  $10^7 \text{ cm/s}$ .

The Fermi energy,

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m} = \left(\frac{e^2}{2a_0}\right) (k_F a_0)^2$$

using  $a_0 = \frac{\hbar^2}{mc^2}$ . Now  $\frac{e^2}{2a_0}$  is the Rydberg ( $Ry$ ), the ground state binding energy of the hydrogen atom under the assumption of infinite proton mass i.e  $13.6 \text{ eV}$ . Thus the Fermi energy has a magnitude near the typical binding energy of the atom.

$$\epsilon_F = \frac{50.1}{(r_s/a_0)} \text{ eV} \longrightarrow 1.5 - 15 \text{ eV}$$

To calculate the ground-state energy of a system of  $N$  electrons in a volume  $V$ , add the energies of all the electrons inside the Fermi sphere:

$$E = \underbrace{2}_{spin} \sum_{k < k_F} \left( \frac{\hbar^2}{2m} \right) k^2$$

Now volume of  $\vec{k}$ -space per allowed value of  $\vec{k} \equiv \Delta\vec{k} = \frac{8\pi^3}{V}$ . The summation over different values of  $\vec{k}$  is in this case the same as a summation over each volume element in the case of a smooth function

$$\sum_{\vec{k}} F(\vec{k}) = \frac{V}{8\pi^3} \sum_{\vec{k}} F(\vec{k}) \Delta\vec{k}$$

Now in the limit of large volume and low granularity, i.e., a large number of allowed points in  $\vec{k}$ -space, the summation can be replaced by an integration

$$\underbrace{lim}_{V \rightarrow \infty} \frac{1}{V} \sum_{\vec{k}} F(\vec{k}) = \int \frac{d\vec{k}}{8\pi^3} F(\vec{k})$$

Thus

$$\begin{aligned} \frac{E}{V} &= \frac{1}{4\pi^3} \int_{k < k_F} d\vec{k} \frac{\hbar^2 k^2}{2m} \\ &= \frac{1}{4\pi^3} \int 4\pi k^2 dk \frac{\hbar^2 k^2}{2m} \quad (\text{spherical shell}) \\ &= \frac{1}{4\pi^3} \int \frac{4\pi \hbar^2}{2m} k^4 dk \\ &= \frac{1}{\pi^2} \frac{\hbar^2}{2m} \int k^4 dk \\ &= \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m} \end{aligned}$$

To find the energy per electron, we have to divide this number by  $\frac{N}{V} = \frac{k_F^3}{3\pi^2}$  (3.16). Thus

$$\frac{E}{N} = \frac{3}{10} \frac{\hbar^2 k_F^2}{m} = \frac{3}{5} \epsilon_F$$

This is the average over all values of  $k_F$ . We now define the **Fermi temperature**  $T_F$  as  $\frac{\epsilon_F}{k_B} = \frac{58.2}{(r_s/a_0)^2} \times 10^4 K$ . Thus  $\frac{E}{N} = \frac{3}{5} k_B T_F$ . In the case of a classical gas the energy is given by  $\frac{3}{2} k_B T_F$  which tends to zero as the temperature goes to zero. Such a value is approached by a classical gas only at around  $T = \frac{2}{5} T_F \approx 10^4 K$ . Thus the Pauli exclusion principle and the granularity of the allowed states in  $\vec{k}$ -space causes the electrons to have energies which would have been attained by classical gases only at very high temperatures.

The pressure exerted by the electron gas is given by  $-\left(\frac{\partial E}{\partial V}\right)_N$ . But  $E = \frac{3}{5} N \epsilon_F$  and  $\epsilon_F \propto k_F^2$ . But

$$k_F = \left(\frac{N}{V} \times 3\pi^2\right)^{\frac{1}{3}} \Rightarrow \epsilon_F \propto \left(\frac{N}{V}\right)^{\frac{2}{3}}. \text{ From this it can be shown that } P = \frac{2}{3} \frac{E}{V}.$$

The bulk modulus  $B = \frac{1}{K} = -V \frac{\partial P}{\partial V} \longrightarrow \left(\frac{6.13}{r_s/a_0}\right)^5 \times 10^{10} \text{ dynes/cm}^2$ . Thus the free electron gas pressure is an important part of the bulk modulus of a metal.

### 3.3.2 Sommerfield theory of conduction in metals

We consider a small volume element  $d\vec{k}$  of  $\vec{k}$ -space about the point  $\vec{k}$ . Since two spins are possible, number of 1-electron levels in this volume is  $\left(\frac{V}{4\pi^3}\right) d\vec{k}$ . The probability of each level being occupied is  $f(\epsilon(\vec{k}))$  where  $f(\epsilon)$  is the **Fermi function** given by

$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

Now the total number of electrons in the  $\vec{k}$ -space volume element (expectation number) is equal to  $\frac{V}{4\pi^3} f(\epsilon(\vec{k})) d\vec{k}$ , where  $\epsilon(\vec{k}) = \frac{\hbar^2 k^2}{2m}$ . Now the velocity of the free electron  $\equiv \vec{v} = \hbar \vec{k}/m$ . Therefore

the number of electrons in an element of volume  $d\vec{v}$  about  $\vec{v}$  is equal to the number in an element  $d\vec{k} = (m/\hbar)^3 d\vec{v}$  about  $\vec{k} = m\vec{v}/\hbar$ . Then the number of electrons per unit volume of **real** space in a velocity space element of volume  $d\vec{v}$  about  $\vec{v}$  is  $f(\vec{v})d\vec{v}$ , where

$$f(\vec{v}) = \frac{(m/\hbar)^3}{4\pi^3} \frac{1}{e^{(\frac{1}{2}mv^2 - \mu)/k_B T} + 1}$$

This is different from the classical case, where

$$f_B(\vec{v}) = n \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-mv^2/2k_B T}$$

Now we apply the Fermi-Dirac distribution to the classical Drude model. This can be justified if and only if the position and momentum of the electrons can both be specified with sufficient accuracy. A typical electron in a metal has a momentum  $\sim \hbar k_F$ . Thus  $\Delta\vec{p}$  must be small compared to this for a reasonably good classical description. Now  $k_F = \frac{1.92}{r_s}$  i.e.  $k_F \sim \frac{1}{r_s}$ . Thus

$$\Delta x \sim \frac{\hbar}{\Delta p} \gg \frac{1}{k_F} \sim r_s$$

Now  $r_s$  is of the order of Angstroms. Therefore the classical description will fail if the electrons are localized to within atomic distances. But the electron can wander through the bulk of the metal and so  $\Delta x$  is large and  $\vec{p}$  is sufficiently well known and there is no problem as far as the momentum is concerned.

How accurately do we need to know the position with respect to the Drude model?

1. Spatial variation of fields or temperatures should be of larger range than the uncertainty in position. For visible light,  $\lambda \sim 10^3 \text{ \AA}$ . This is much larger than the atomic distances and as a result, the uniform field approximation is valid. There is enough margin.
2. An implicit assumption is made in the Drude model that the electron can be localized to much less than the mean free path. Quantum mechanically the mean free path is of the order of  $100 \text{ \AA}$  at room temperature. So there is no problem.

Thus the classical description is applicable. Only the distribution function needs to be changed in accordance with quantum mechanical requirements.

### 3.3.2.1 Mean free path

We use  $v_F$  as a measure of the typical electronic speed. Again, the relaxation time  $\tau$  is a measure of the time between collisions. From the Drude model,

$$\begin{aligned} v_F &= \frac{4.20}{r_s/a_0} \times 10^8 \text{ cm/s} \\ \tau &= \left( \frac{0.22}{\rho_\mu} \right) \left( \frac{r_s}{a_0} \right)^3 \times 10^{-14} \text{ s} \\ \lambda = v_F \tau &= \frac{(r_s/a_0)^2}{\rho_\mu} \times 92 \text{ \AA} \end{aligned}$$

where  $\rho_\mu$  is the resistivity in  $\mu\Omega - cm$ . We can use the Drude conductivity because of the 100/100 cancellation of errors in the original model. So only  $\lambda$  changes in response to the change in  $v$ .  $\lambda \sim 100 \text{ \AA}$ , as  $\rho_\mu \sim 1$  to 100, and  $r_s/a_0 \sim 2$  to 6.

**3.3.2.2** Thermal conductivity

We use the same old  $K = \frac{1}{3}v^2\tau c_v$ . Put  $v_F^2 = 2\epsilon_F/m$ , use  $\sigma = \frac{ne^2\tau}{m}$  and eliminate the relaxation time to get

$$\frac{K}{\sigma T} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = 2.44 \times 10^{-8} \text{ Watt} - \text{Ohm}/K^2$$

Here we use the correct value for the electronic specific heat and get a good value of the Lorentz number (Note: the electronic specific heat derivation needs to be included here).





# Chapter 4

## Band Theory of solids :-

### 4.1 Introduction :-

#### 4.1.1 Diffraction of electrons :-

Atoms are close together - no valence electrons constitute a single system of electrons common to the entire crystal. As many separate levels as atoms in the crystal -> each atomic electronic level splits up into these.

The de Broglie wavelength of free electrons is :-  $\lambda = \frac{h}{p}$

Unbound, low energy electrons have large  $\lambda$  -> they can move freely inside the crystal. Those with energy near  $\varepsilon_F$  have  $\lambda \simeq a$ , and diffract like X-rays. So, from the atomic planes in a crystal,

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

Put  $k = \frac{2\pi}{\lambda}$ ,

$$\Rightarrow \text{Again, } \left. \begin{aligned} k &= \frac{n\pi}{a \sin \theta} \\ k_x &= k \sin \theta \\ &= \frac{n\pi}{a} \end{aligned} \right\}$$

If  $k < \frac{\pi}{a}$  -> Electrons can move freely through the lattice in any direction.

If  $k = \frac{\pi}{a}$  -> Electrons are diffracted, they can't move in x or y direction.

Considering a 2-dimensional square lattice,

$$\Rightarrow \begin{aligned} x \rightarrow \theta &= 90^\circ, & \text{Electron gets reflected back} \\ y \rightarrow \theta &= 0^\circ, & \text{It gets reflected back from the } \perp r \text{ plane} \end{aligned}$$

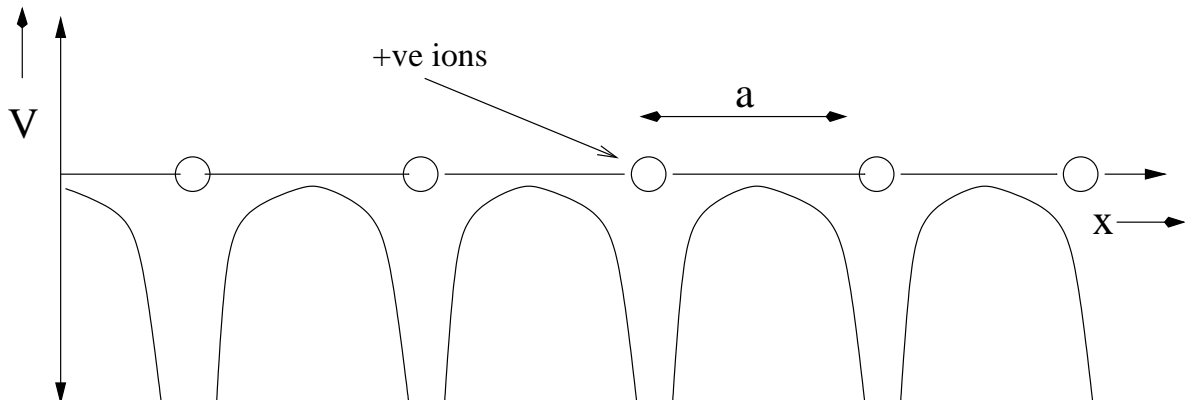


Figure 4.1: Periodic potential inside a crystal, when diffraction occurs.

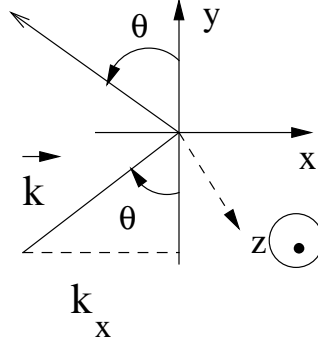


Figure 4.2: Bragg's reflection condition

The more  $k \gg \frac{\pi}{a}$ , it becomes more limited. At

$$k = \frac{\pi}{(a \sin 45^\circ)} = \frac{\sqrt{2}\pi}{a} \quad (4.1)$$

even diagonally moving electrons are reflected back.

#### 4.1.2 Brillouin zone :-

Region in  $\vec{k}$  space that low  $k$  electrons can occupy without being diffracted is 1<sup>st</sup> Brillouin zone.

The second one has  $k > \left(\frac{\pi}{a}\right)$  but cannot be diffracted by diagonal planes. For electrons moving in the  $\pm x$  or  $\pm y$  directions respectively, the range of  $\vec{k}$  is :-

$$\frac{\pi}{a} \leq k \leq \frac{\pi}{2a}$$

with possible range of  $k$  values narrowing as the diagonal directions are approached.

i.e., the electrons in the second Brillouin zone have sufficiently small  $\vec{k}$  to avoid diffraction by the diagonal planes .

Now,

$$E = \frac{\hbar^2 k^2}{2m} \quad (4.2)$$

i.e., according to eqn.4.1 ,45° incidence on the x-y planes will cause reflection and so also will the diagonal planes reflect them back, considering the incidence to be normal to the incidence planes. So in that direction (point P in the fig.4.3) the two zones merge. Now, for a free electron, E is as in eqn.4.2

This is the case for  $k \ll \frac{\pi}{a}$ , when there is very little interaction with the lattice. The contour lines of constant energy in 2-D  $\vec{k}$  space are circles of constant "k". As "k" increases, due to the  $k^2$  dependance of "E"(in eqn.4.2), the lines become closer together (if the contours represent constant "E" lines with a fixed "E" separation). Again the closer an electron is to a Brillouin zone boundary, the greater is it's probability for diffraction by the real lattice. As the electron's energy is affected, the contour lines become distorted (i.e., they are no longer circular as in fig.4.5).

Now consider electrons moving in the x-direction. When  $k = \frac{\pi}{a}$ , the waves are <sup>\*\*</sup>Bragg Reflected back & forth, so that the solutions of the Schrödinger equation allowed are standing waves with the periodicity of the lattice.

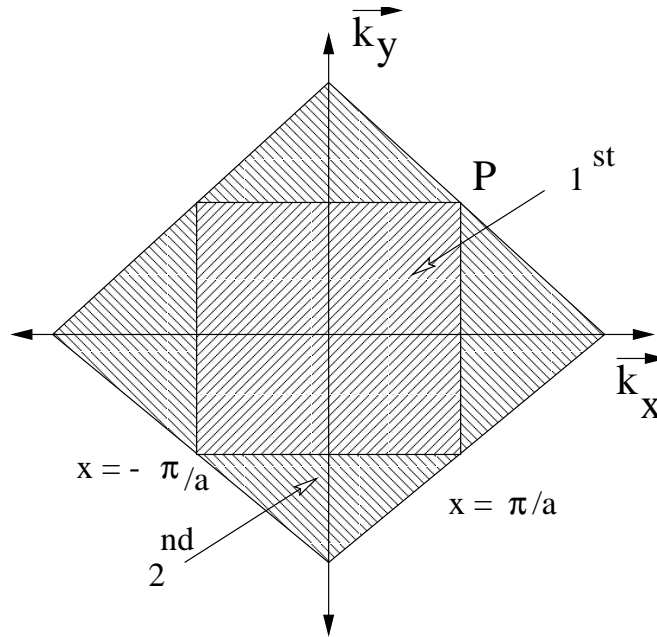


Figure 4.3: Brillouin zones

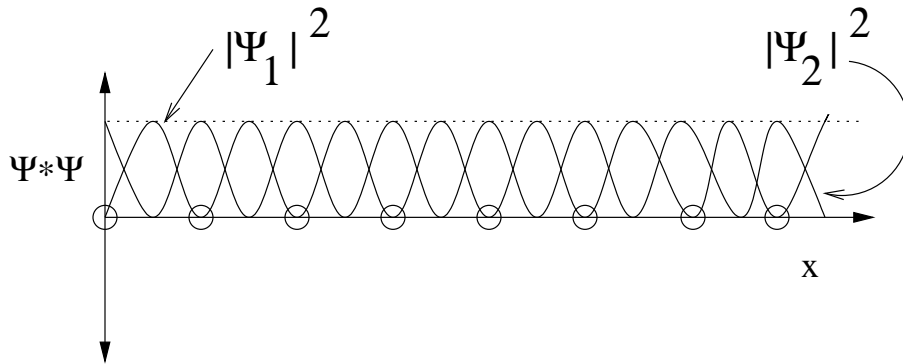


Figure 4.4: Electron position vs Probability plot

For  $n = 1$ ,

$$or, \left. \begin{aligned} \Psi_1 &= A \sin \frac{\pi x}{a} \\ \Psi_2 &= A \cos \frac{\pi x}{a} \end{aligned} \right\} \quad (4.3)$$

Here,  $|\Psi_1|^2$  has minima at the "+ve" ion sites,  $|\Psi_2|^2$  has maxima. Now charge density corresponding to an electron wave function  $\Psi$  is  $e |\Psi|^2$

$\Psi_1$  charge concentrated between the positive ions.

$\Psi_2$  charge concentrated at the positive ions.

So two energies  $E_1$  and  $E_2 \rightarrow (E_1 > E_2)$ . No other solutions at  $k = \pm \frac{\pi}{a}$  and so no energy is possible between  $E_1$  and  $E_2$ . We get the forms below, with free forbidden gaps.

### 4.1.3 Distribution of electron energies :-

At low  $\vec{k}$ , large  $\lambda \rightarrow$  free electron-like.

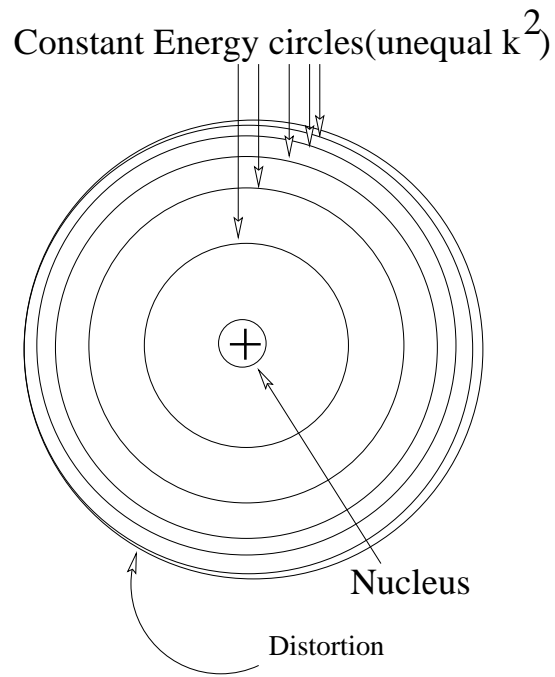


Figure 4.5: Distortion in energy due to the " $k^2$ " term

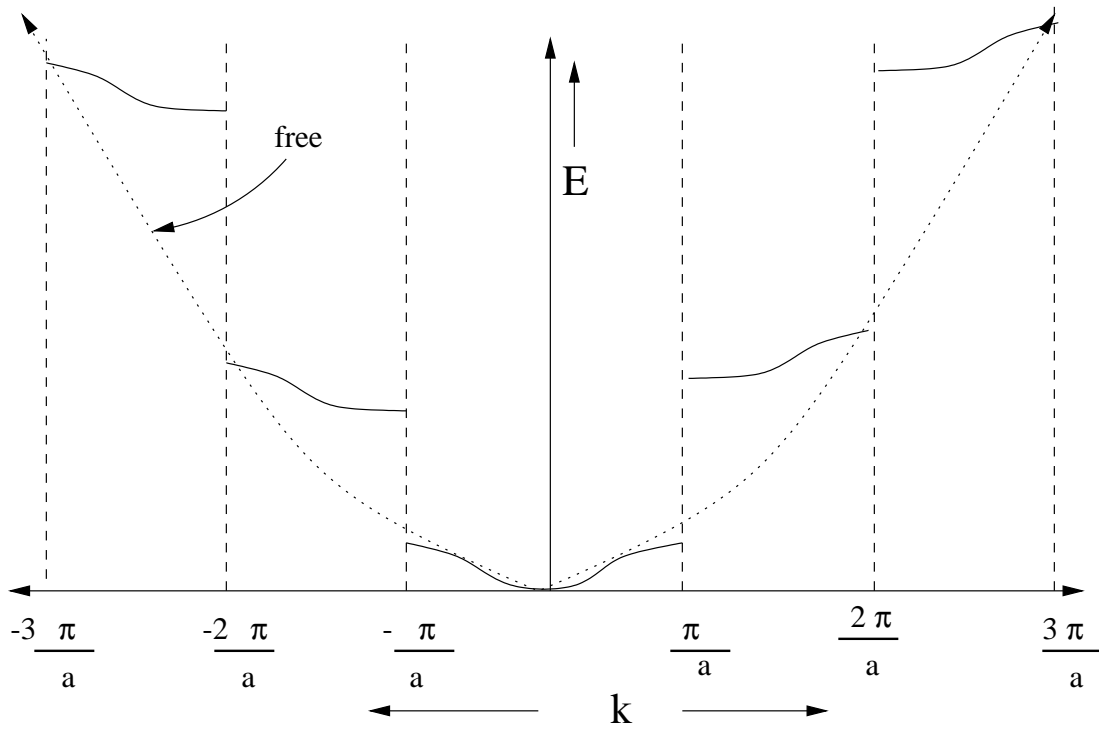
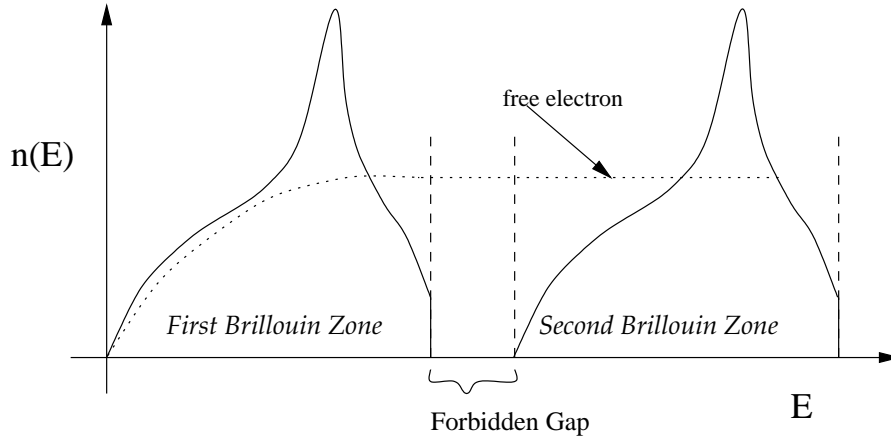


Figure 4.6:  $\vec{k}$  vs  $\vec{E}$  graph

Figure 4.7:  $E$  versus  $n(E)$  graph

At larger  $E$ , number of available energy states goes beyond that of the free-electron  $\rightarrow$  due to distortion, more different  $\vec{k}$  values for each energy.

At  $k = \pm \frac{\pi}{a}$ , electrons in  $k$  and  $k_y$  directions cannot have higher energy but other directions are still permitted. At higher energies, a point is reached where,  $n(E) = 0$ . So forbidden bounds occur.

Although there must be an energy gap between successive Brillouin zones, in any one direction, the various gaps may overlap permitted energies in other directions. Such a crystal as a whole may be such as to have no forbidden gap at all.

#### 4.1.4 For an insulator :-

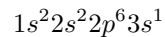
1. Must have even number of valence electrons per structural unit, because then the highest energy band may be completely filled. (Each energy level splits into as many levels in the band as the number of electrons.
2. The band with the highest energy electrons must be separated from the next allowed band above it by energy gap quite larger than  $k_B T$ . So none can reach the gap to reach the unfilled states.

Alkali metals, with odd number of valence electrons per structural unit (one per atom) are conductors. Divalent metals like Mg and Zn have overlapping energy bands,  $\rightarrow$  they conduct also.

If the forbidden gap is narrow or the amount of overlap small,  $\rightarrow$  *Semiconductors*.

##### 4.1.4.1 Sodium :-

In Sodium (Na), as the atoms are brought closer, the energy levels begin to spread into bands.



So even with forbidden gaps, Na conducts!

So the first occupied level to spread out is the  $3s$ . The average energy of the  $3p$  and  $3s$  bands drops, showing attractive forces. The observed inter nuclear distance corresponds to the lowest energy.

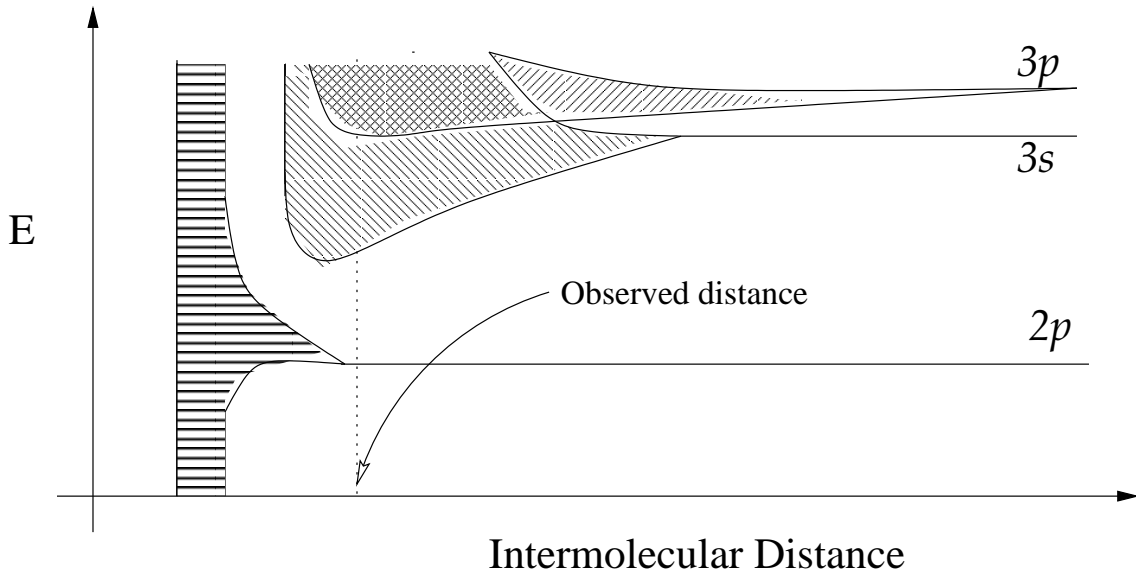


Figure 4.8: Overlapping bands

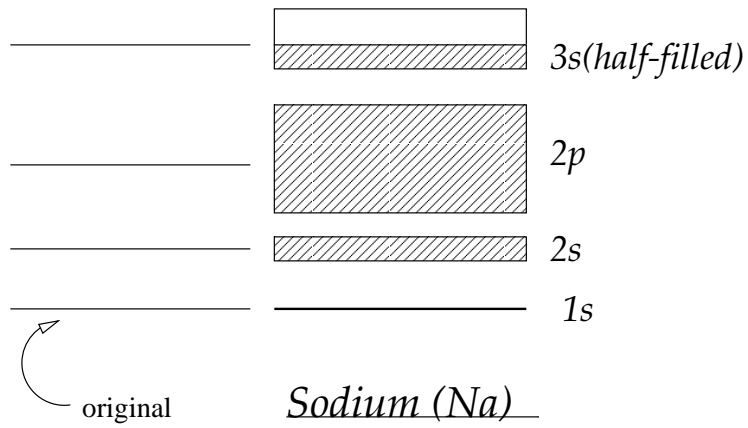
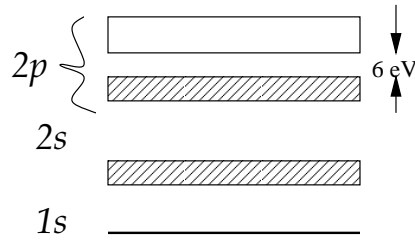


Figure 4.9: Sodium energy levels



Diamond

Figure 4.10: Diamond

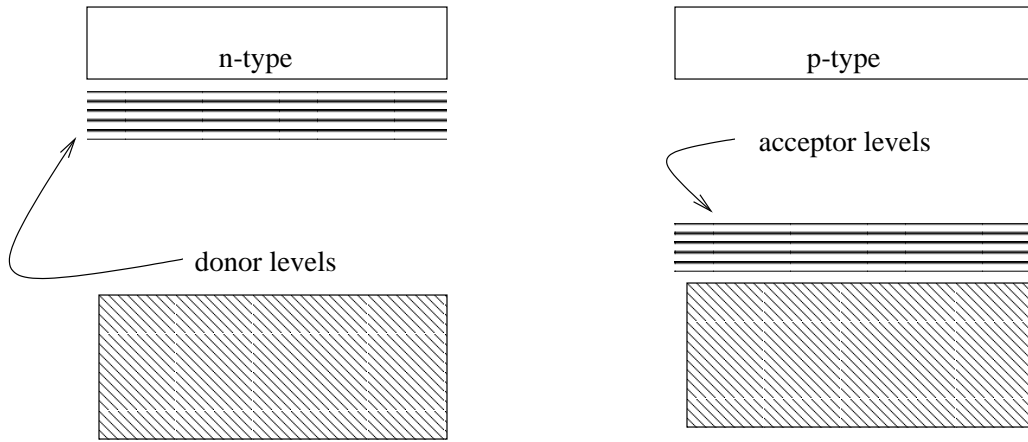


Figure 4.11: Doping in n-type & p-type semiconductors

**4.1.4.2 Diamond :-**

The Brillouin zone boundary crosses in the middle of the 2p band, causing 6eV gap.  $\lambda = 10^{-8}m$  (mean free path). So  $6 \times 10^8 V/m$  is required to make diamond conduct.

**4.1.5 Semiconductors doped :-**

In Beryllium (Be), Zinc (Zn) and Cadmium (Cd)  $\rightarrow$  the overlap of the Fermi surface into the highest band is small. So some holes may be formed in the lower band as in fig4.11 . They are the main carriers.