

FERROMAGNETISM ANTIFERROMAGNETISM, AND FERRIMAGNETISM

FERROMAGNETISM

- 93^o (Saturation magnetisation in paramagnetic materials occurs at very low temperatures and at high applied magnetic fields. In ferromagnetic materials, the saturation magnetisation is achieved at ordinary temperatures and at ordinary values of the applied magnetic field. Ferromagnetic materials possess spontaneous magnetisation i.e. magnetisation even in absence of an external magnetic field below a certain temperature, called the Curie temperature. Above this temperature, the behaviour of the material becomes paramagnetic.)
- Well above the Curie temp, the susceptibility follows the Curie-Weiss law,

$$\chi = C/(T-\theta) \quad \dots \dots \dots \quad (1)$$

where C is the Curie constant; the temperature θ is called the paramagnetic Curie temperature and is usually some degrees higher than 0°C .

In ferromagnetic materials the magnetisation vs. magnetic field relationship exhibits hysteresis.

Of the elements, only Fe, Ni, Co, Gd, and Dy are ferromagnetic, although there are a relatively large number of ferromagnetic alloys and oxides.

The theory of ferromagnetism depends on the following two hypothesis:

- i) A ferromagnetic specimen of macroscopic dimensions contains, in general, a number of small regions (domains) which are spontaneously magnetized; the magnitude of the spontaneous magnetization of the specimen is determined by the vector sum of the magnetic moments of the individual domains.
- ii) Within each domain the spontaneous magnetization is due to the existence of a "molecular field" which tends to produce a parallel alignment of the atomic dipoles.

The Weiss Molecular Field

Spontaneous magnetisation implies cooperation between the atomic dipoles in a domain, i.e., there must be a kind of interaction between the atomic dipoles due to which they are parallelly oriented.

Weiss proposed that the "molecular-field" acting on a given dipole can be written as

$$H_m = H + \gamma M \quad \dots \dots \dots (2)$$

where $H_m \rightarrow$ Molecular field

$H \rightarrow$ Applied field

$M \rightarrow$ Magnetisation constant
and $\gamma \rightarrow$ molecular field, Weiss constant

Clearly, the term γM provides the co-operative effect.

Now we shall use the quantum theory of magnetization rather than the classical Langevin theory. ~~weakly~~ Weiss theory.

- ① We consider a solid containing N atoms per unit volume, each with a total angular momentum quantum numbers J (which includes the total orbital contribution L and total spin contribution s). We know the magnetisation

$$M = N g_{\mu_B} J B_J(x) \quad \dots \dots \dots (3)$$

when $J \rightarrow \infty$ $B_J(x) \rightarrow L_J^{(n)}$

Quantum model to
classical model

where $B_J(x) \rightarrow$ Brillouin function

$$\text{and } x = \frac{g_{\mu_B} H}{kT} = \alpha x \quad \dots \dots \dots (4)$$

for paramagnetic solids.

- ② In the case of Ferromagnetic material we will replace 'H' by H_m in the above equation

$$x = \frac{g_{\mu_B} H_m}{kT} = \frac{g_{\mu_B} (H + \gamma M)}{kT} \quad \dots \dots \dots (5)$$

As we are interested on spontaneous magnetisation, so we make applied mag. field, $H=0$

$$\therefore x = \frac{g_{\mu_B} \gamma M}{kT} \quad \dots \dots \dots (6)$$

Therefore, magnetisation

$$M = \frac{\alpha x kT}{g_{\mu_B} \gamma} \quad \dots \dots \dots (7)$$

$\alpha \rightarrow x$

If we plot M vs x , the eq(7) represents a straight line having the slope $(\frac{kT}{g_{\mu_B} \gamma})$. As from Eq(3) and eq(7), so for a given temp. T , the

value of 'M' is obtained by the point of intersection between the straight line from Eq.(7) and the curve from Eq.(3). From Fig. it follows that for $T < \theta_f$, one obtains a nonvanishing value for M, although the external field $H=0$. Hence for $T < \theta_f$, the spontaneous magnetisation results. For $T = \theta_f$, the slope of the straight line represented by Eq.(7) and is equal to that of tangent of curve from Eq.(3) at the origin. Thus, for $T > \theta_f$, the spontaneous

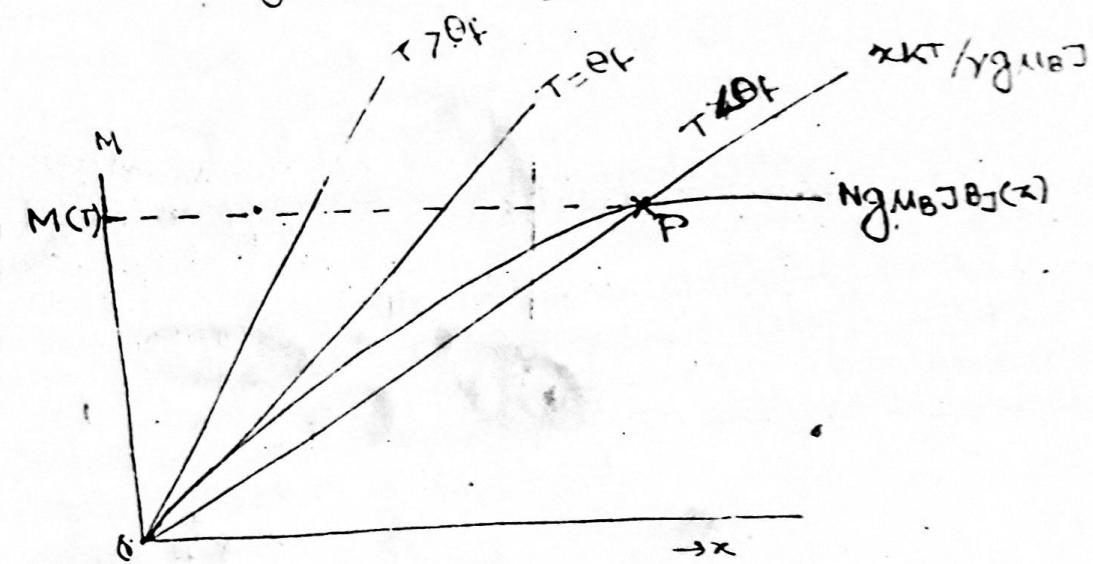


Fig.

magnetization vanishes.

Now it will be evident that there must exist a relation between the Curie temperature θ_f and the molecular field constant γ . We expect that θ_f increases with the increase of γ because the tendency for parallel alignment increases as γ becomes larger. This relation can be established by the following way,

We consider that $x \ll 1$, then Brillouin function is given by

$$B_J(x) \approx \frac{(J+1)x}{3J} \quad (8)$$

Putting this value in Eq.(5) we get

$$M = N g M_B \frac{(J+1)x}{3J} = N g M_B \frac{(J+1)x}{3} \quad (9)$$

So the slope of the tangent of the curve by the eq.(9) is $\frac{N g M_B (J+1)}{3}$.

Now, when $T = \theta_f$, then the above slope is equal to the slope of the straight line given by eq.(7).

$$\therefore \frac{Ng\mu_B(J+1)}{3} = \frac{\nu\theta_f}{g\mu_B Y J} \quad [\because T = \theta_f]$$

$$\frac{3k\theta_f}{Y} - Ng^v\mu_B^v J(J+1) = N\mu_J^v \quad \dots \dots \quad (10)$$

[∴ we have $\mu_{eff}^v = \mu_J^v = [g^v\mu_B^v J(J+1)]$]
 $\mu_f \rightarrow$ total mag moment per atom.

$$\therefore \theta_f \propto Y \quad [\text{proved}] \quad \checkmark$$

Hence θ_f is proportional to the molecular field constant.

Let us now consider the susceptibility in the region well above the ferromagnetic Curie temp. i.e. $T > \theta_f$. In this region there is no spontaneous magnetisation and magnetisation occurs only when an external field H is applied.

Thus when $H \neq 0$,

$$\chi = \frac{g\mu_B^v J(H + YM)}{KT}$$

Again from Eq. (9)

$$\begin{aligned} M &= Ng\mu_B^v J(J+1) \frac{\chi}{3} = Ng\mu_B^v J(J+1) \frac{g\mu_B^v J(H + YM)}{3KT} \\ &= \frac{Ng^v\mu_B^v J(J+1)(H + YM)}{3KT} \quad , \quad (\text{Putting the value of } \chi) \\ &= \frac{Ng^v\mu_B^v J(J+1)H}{3KT} + \frac{Ng^v\mu_B^v J(J+1)YM}{3KT} \\ &= \frac{N\mu_J^v H}{3KT} + \frac{N\mu_J^v YM}{3KT} \quad (\because \mu_J^v = g\mu_B^v J^*) \end{aligned}$$

$$\therefore M(1 - \frac{N\mu_J^v YM}{3KT}) = \frac{N\mu_J^v H}{3KT}$$

$$\therefore \frac{M}{H} = \chi = \frac{(N\mu_J^v / 3KT)}{\left(1 - \frac{N\mu_J^v YM}{3KT}\right)} = \frac{N\mu_J^v / 3K}{\left(T - \frac{N\mu_J^v YM}{3K}\right)} \quad \dots \dots \quad (11)$$

Again from Curie-Weiss law, we know

$$\chi = C/(T - \theta)$$

Comparing eq(11) and eq(12), we get

$$C = \frac{N\mu_J^v}{3K}$$

$$\text{and } \theta = \frac{N\mu_J^v}{3K} \gamma = CY \quad . \quad (12)$$

$$\text{Now from (10), we get } \theta_f = \frac{N\mu_J^v YM}{3KT} \quad . \quad (13)$$

Thus, θ (paramagnetic Curie temp.)

= θ_f (Ferromagnetic Curie temp.)

but it is not possible

$$\Theta = \Theta_f$$

(15)

Thus Weiss theory cannot distinguish between Θ and Θ_f .

Comparison of the Weiss theory with experiment

i) Temperature dependence of spontaneous magnetisation: The maximum component of an atomic dipole associated with a quantum number J in any given direction is $g\mu_B J$. Hence the maximum value of the spontaneous magnetisation is given by $N g \mu_B J$, (where N is the number of atoms per unit volume)

when $x \rightarrow \infty$, and $B_J(x) \rightarrow 1$.

Now from M vs x plot we can say at $T=0$, spontaneous magnetisation $M(0)$ is maximum.

$$M(0) = N g \mu_B J \quad \dots \dots \quad (16)$$

Again $M(T) = N g \mu_B J B_J(x) \Rightarrow$ Spontaneous Magnetisation at temp 'T'.

$$\therefore \frac{M(T)}{M(0)} = B_J(x) \quad \dots \dots \quad (17)$$

Again,

$$\chi = \frac{g \mu_B H_m J}{kT} = \frac{g \mu_B (H + \gamma M)}{kT}$$

When $H = 0$, then $\chi = g \mu_B \gamma M / kT$

$$\therefore M(T) = \frac{\chi kT}{g \mu_B \gamma J} \quad \text{from eq.(7).}$$

$$\begin{aligned} \therefore \frac{M(T)}{M(0)} &= \frac{\chi kT}{g \mu_B \gamma J} \times \frac{1}{N g \mu_B J} \\ &= \frac{\chi kT}{N g \mu_B^2 \gamma J} = \frac{\chi kT}{N g \mu_B^2 J \gamma} \\ &= \frac{\chi kT (J+1)}{N g \mu_B^2 J \gamma} = \frac{\chi kT (J+1)}{3 k \beta_f J} \end{aligned}$$

$$\begin{aligned} \therefore M_J &= g \mu_B J (J+1) \\ \therefore g \mu_B^2 J &= \frac{M_J}{(J+1)} \end{aligned}$$

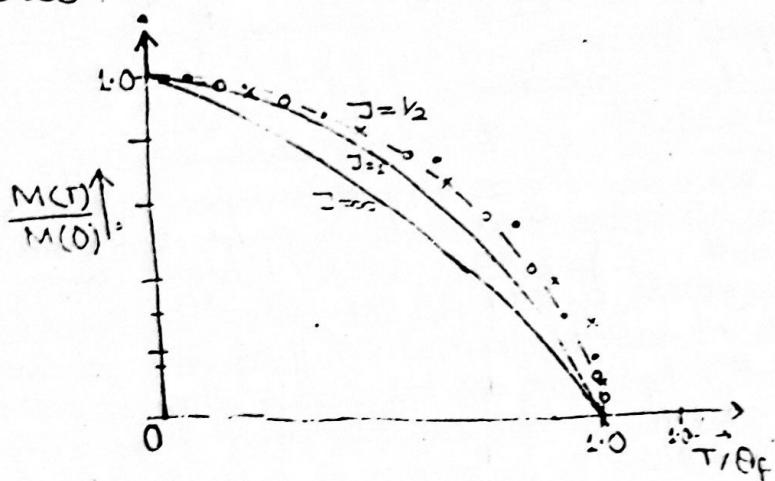
$$\text{Now, } \Theta_f = \frac{N M_J}{3k} \gamma$$

$$N M_J \gamma = 3k \Theta_f$$

$$\therefore \frac{M(T)}{M(0)} = \frac{\chi k T (J+1)}{3 \beta_f J} \quad \dots \dots \quad (18)$$

Thus eq(17) and eq(18) are same. Hence by intersection method we can determine the value of $M(T)/M(0)$.

If now we plot $M(T)/M(0)$ vs. T/θ_f graph for a given value of 'J', then we get the different curves for the different values of 'J' (i.e. for $J=\infty$, $J=1$, $J=\frac{1}{2}$). Among them $J=\frac{1}{2}$ curve best fits with experimental data so we can conclude that the spontaneous magnetisation is mainly due to the electron spin since that the orbital momentum of them. For $J=\infty$, the spontaneous magnetisation is due to freely rotating magnetic dipoles.



The above conclusion can be confirmed by the gyroscopic experiments. In such experiments, one rotates the magnetization of a given standard specimen and observe the resulting rotation (Einstein-de Haas method) or one rotates the specimen and observes the resulting magnetization (Bennett method). By these two methods, the value of g (gyromagnetic ratio) i.e. the ratio of magnetic moment to ang. momentum as $g=2$ for electron spin and $g=1$ for orbital motion of electron. Results of such experiments show that the magnetization is largely due to the electron spin.

The effective number of Bohr magnetons per atom:

From the saturation magnetization at $T=0$ and the number of atoms per unit volume, one can calculate the effective no. of Bohr magnetons m_{eff} per atom.

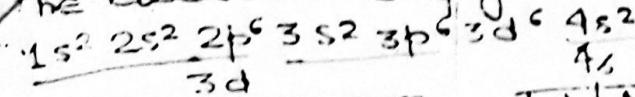
$$\text{We know. } M_J^2 = M_0 g^2 J(J+1)$$

$$\therefore M_J = M_0 g \sqrt{J(J+1)}$$

described by the following equation.

For 'Fe': $Z = 26$

The electronic configuration is



3d

$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow	\uparrow
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$\uparrow\downarrow$

\checkmark Fe²⁶

3d shell can have maximum 10 electrons. But here 6 electrons are present. So, 4 unpaired electrons are present.

∴ No. of Bohr magneton = 4 ∴ $n_{eff} = 2.2$

b) For Co: $Z=27$ Electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^1$

$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow	\uparrow
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$\uparrow\downarrow$

so no. of unpaired electrons = 3

∴ No. of Bohr magneton = 3 ∴ $n_{eff} = 1.79$

c) For Ni: $Z=28$ Electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

Electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$

$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	\uparrow	\uparrow
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$\uparrow\downarrow$

so no. of unpaired electrons = 2

∴ No. of Bohr magneton = 2 ∴ $n_{eff} = 0.606$

Thus in the above three cases we see that n_{eff} is nonintegral. Mott and Slater gave an explanation of the nonintegral values for n_{eff} on the basis of a wide 4s band overlapping with a narrow 3d band.

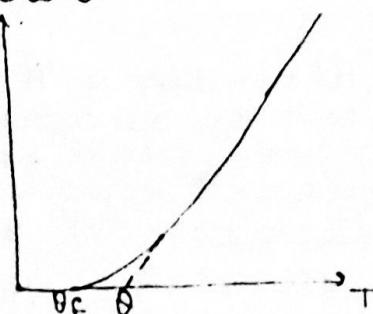
In case of Fe, $n_{eff} = 2.2$ indicates that there are 5 electrons with parallel spin and $(5-2.2)=2.8$ electrons with antiparallel spins. Hence total of 8 electrons, 3d band contains $(5+2.8)=7.8$ electrons and 4s band contains $(8-7.8)=0.2$ electrons.

i) The paramagnetic region: From Curie-Weiss law we know, $\chi = C/(T-\theta)$ or, $\frac{1}{\chi} = \frac{C(T-\theta)}{C}$

If we plot $\frac{1}{\chi}$ vs. T graph then we get straight line with intercept on T axis is equal to θ .

But near Curie point i.e. at $T=C_0$ (Paramagnetic Curie Temp), this straight line nature of the curve does not hold good. Here it becomes concave in nature. So, $C_f \neq 0$

Experimentally, we get the following observations.

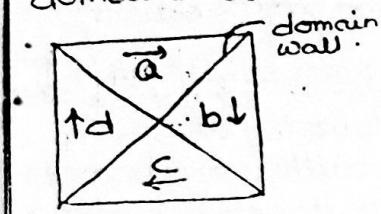


For	Fe	Ni
θ_f (Kok)	1093	631
θ (Kok)	1093	650

Qualitative remarks about domains

In order to explain the fact that a piece of ferromagnetic material may exist in the nonmagnetized state and to explain the hysteresis in the B-H curve, Weiss postulated that the material contains a large no. of small regions called domains. The size of a domain is about 10^{-6} m or larger and the material within each domain is magnetised to its full value. The spontaneous magnetization occurs due to the molecular field ' H_m ' and this produces the parallel orientation of the atomic magnetic dipoles within each domain. The total spontaneous magnetisation of the specimen is the vector sum of the magnetic moment vectors of individual domains.

Now when no external magnetic field is applied then the atomic dipoles are oriented randomly within the domain. So the size, shape and the directions of the domains are such that the net magnetization is zero.



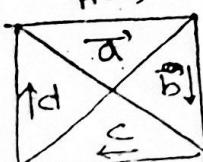
when no mag. field is applied.

Now when the external field is applied, then the ferromagnetic specimen is magnetised and this can take place by the two processes

i) Magnetization due to Wall motion or Displacement process

and ii) Magnetization due to rotation of domain vectors.

i) Displacement process:



Magnetic field H is applied in the direction shown in Fig. Here we see that all the domain vectors make some angles with the direction of H excepting a domain vector. The vector of which

domain makes the least angle with the direction of H . With the increase of H , the size of that domain will increase and consequently the sizes of other domains decreases. The vector of the domain which makes the greatest angle with the direction of H , the shape of this domain decreases more than the other domain with the increase of H . So the size of 'a' domain increases and the size of the other domains decreases until the size of 'c' domain becomes smallest.

H



The direction of H is called the Easy direction.

With the increase of H , the shape of 'a' domain increases more and the size of the other domains decrease more. This process will continue until

Fig. Magnetisation due to wall motion

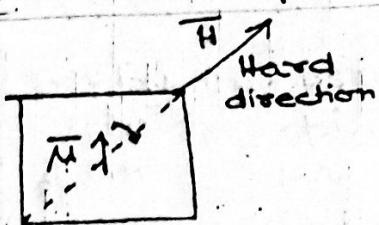
The domain α takes the size of the whole specimen. This is known process is known as the Wall motion of the domain. This configuration is much more stable and the magnetic energy of the system then decreases to minimum value.

ii) Rotation of domain vectors process

Now the total specimen is covered by the domain α'

α'

Then if the magnetic field \vec{H} is applied along hard direction, then there is an angle between the direction of domain vector (\vec{u}') and the direction of \vec{H} shown in figure.



with the increase of H along this direction the magnetisation increases and \vec{u}' moves towards the direction of \vec{H} . And finally \vec{u}' goes to the direction of \vec{H} i.e.

$\vec{u}' \parallel \vec{H}$ for a certain value of H . Then the saturation magnetisation reaches.

The thickness and energy of the Bloch Wall :-

The separation between two successive domains within a ferromagnetic specimen is called "Bloch Wall". According to Bloch, the spin direction during going from one domain to another domain through Bloch wall does not change suddenly but gradually as shown in Fig.

Consider two successive domains - one has up spin and the other has down spin. Then the movement of spin direction from one domain to other domain is shown below.

The reason for this gradual change of spin direction rather than the abrupt change is discussed below

Consider two electrons with parallel spins. Then the exchange energy between them = $-2Jes^2$
 $= -2Jes^2 \cos 0^\circ$
 $= -2Jes^2$, where $J_e \rightarrow$ exchange integral.

If there is an angle ϕ between the two spin directions of two electrons, their exchange energy between them is given by, $-2Jes^2 \cos \phi = -2Jes^2(1 - \phi^2/2)$

[For small ϕ]

So by this process of changing the angle between two successive spins from 0 to ϕ , the exchange energy between them increases by an amount $= 2Jes^2 \phi^2/2 = J_e s^2 \phi^2$

Now consider a Bloch wall with a single row of $(n+1)$ no. of spins separating two domains of which the magnetisation directions make an angle ϕ_0 . Then the angle between two successive spins $= \phi = \phi_0/N$

Then the total exchange energy of all the spins in Bloch wall $= E_x = J_e s^2 \phi_0^2 N = J_e s^2 \frac{\phi_0^2}{N^2} N = J_e s^2 \frac{\phi_0^2}{N}$.. (1)

So with increase of N , E_x decreases.

Now consider a Bloch wall of 1 cm^2 area and a^2 thickness, where a is the lattice constant. So then the total energy of Bloch wall / cm^2 area

$$\sigma = [\sigma_{\text{exchange}} + \sigma_{\text{anisotropy}}]$$

To get the "σ" exchange for the Bloch wall we have to multiply eq.(1) with the number of rows of spin within $1/\text{cm}^2$ area of Bloch wall i.e. $1/a^2$

$$\therefore \sigma_{\text{exchange}} = \frac{J_e s^2 \phi_0^2}{Na^2} \quad \text{and} \quad \sigma_{\text{anisotropy}} = KNa$$

where K = anisotropy constant.

∴ Total energy of Bloch wall per cm^2 is given by,

$$\sigma = \frac{J_e s^2 \phi_0^2}{Na^2} + KNa \quad \dots \dots \dots \quad (2)$$

The equilibrium value of N may be obtained by minimizing σ with respect to N . Hence, putting $d\sigma/dN = 0$, we get $-\frac{J_e s^2 \phi_0^2}{N^2 a^2} + Ka = 0$

$$\text{or, } N^2 = \frac{J_e s^2 \phi_0^2}{Ka^2}$$

$$\therefore N = \frac{s \phi_0}{a} \sqrt{\frac{J_e}{Ka}} \quad \checkmark \quad (3)$$

For Iron, putting $J_e = \frac{k_0 F}{3}$, $s = 1/2$, $k = 10^5 \text{ erg/c.c.}$, $\phi_0 = \pi$ we get $N \approx 300$ and thickness of Bloch wall $t = 1000 \text{ Å}$

Now putting the value of N from eq.(3) to eq.(2), we get total energy of Bloch wall per cm^2 as,

$$\sigma = \left[\frac{J_e s^2 \phi_0^2}{a^2} \frac{a}{s \phi_0} \sqrt{\frac{Ka}{J_e}} + Ka s \phi_0 \right] \frac{J_e}{Ka}$$

$$= \sigma \frac{4}{3} \sqrt{\frac{kT_e}{a}} + \sigma \frac{4}{3} \sqrt{\frac{kT_e}{a}}$$

$$\therefore \sigma = 2 \cdot \frac{4}{3} \sqrt{\frac{kT_e}{a}} \quad (1)$$

which is of order of 10^8 g/cm^2 for Fe.

[The above treatment is rather crude; for example, due to anisotropy, the angle between successive spins is not constant throughout the Bloch wall]

Antiferromagnetism

(Ferromagnetic behaviour was explained by Heisenberg who showed that quantum mechanical exchange interactions produce large internal fields and the neighbouring dipoles have a tendency to align in the same direction. However, it can be proved quantum mechanically that when the separation between the interacting dipoles is very small, the exchange forces produce a tendency for antiparallel alignment of the spin dipole moments of the neighbouring atoms. Such material are termed antiferromagnetic materials.)

Theoretical investigations of antiferromagnetic materials were first made by Neel and Bitter. After this discovery many materials, such as MnO_2 , MnF_2 , FeO etc., were found to show antiferromagnetic properties.

The most characteristic feature of an antiferromagnetic material is that its susceptibility versus temperature curve shows a sharp maximum at a temperature known as the Neel temperature, T_N (Fig.). The significance of the Neel temperature is that above this temperature the material behaves paramagnetic. The susceptibility χ is given by

$$\chi = \frac{C}{T+\theta}$$

for $T > T_N$, where C is the Curie constant and θ is the paramagnetic Curie temperature.

The two sublattice model

We assume that the nearest neighbours of A atom are B atoms and vice versa. Beside antiferromagnetic AB interaction, there must be antiferromagnetic AA and BB interactions. The molecular fields of A site and B site can be given as,

$$H_{ma} = H - \alpha M_a - \beta M_b$$

$$H_{mb} = H - \beta M_a - \alpha M_b$$

(2)

where $H \rightarrow$ Applied magnetic field

$M_A \rightarrow$ Magnetisation of A lattice

$M_B \rightarrow$ Magnetisation of B lattice

$\alpha, \beta \rightarrow$ Positive Weiss constants

Now we consider the two cases,

Case I: When $T > T_w$ (i.e. $T > m_f$)

Then the magnetisation for A lattice is given as

$$M_A = \left(\frac{N\mu^2}{3kT} \right) H_{ma}$$

$$\text{where } \mu^2 = \mu_0 \gamma J(J+1)$$

$$M = \frac{N\mu^2}{3kT} H_m$$

where $N = \text{No. of A atoms per unit volume}$

If the dipoles of A lattice are identical to those of B lattice and the equal no. of A and B sites are present,

$$\text{then } M_B = \left(\frac{N\mu^2}{3kT} \right) H_{mb}$$

$$\begin{aligned} \therefore \text{Total magnetisation: } M &= M_A + M_B = \left(\frac{N\mu^2}{3kT} \right) [H_{ma} + H_{mb}] \\ - \left(\frac{N\mu^2}{3kT} \right) [2H - (\alpha + \beta) M_A - (\alpha + \beta) M_B] &= \frac{N\mu^2}{3kT} [2H - (\alpha + \beta)(M_A + M_B)] \\ = \frac{N\mu^2}{3kT} [2H - (\alpha + \beta) M] \\ \therefore M \left[1 + \frac{N\mu^2}{3kT} (\alpha + \beta) \right] &= \frac{2N\mu^2}{3kT} H \end{aligned}$$

$$\therefore X = \frac{M}{H} = \frac{2N\mu^2/3k}{[T + N\mu^2/3k(\alpha + \beta)]} \quad \dots \dots \quad (2)$$

Eq.(2) can be written in the form

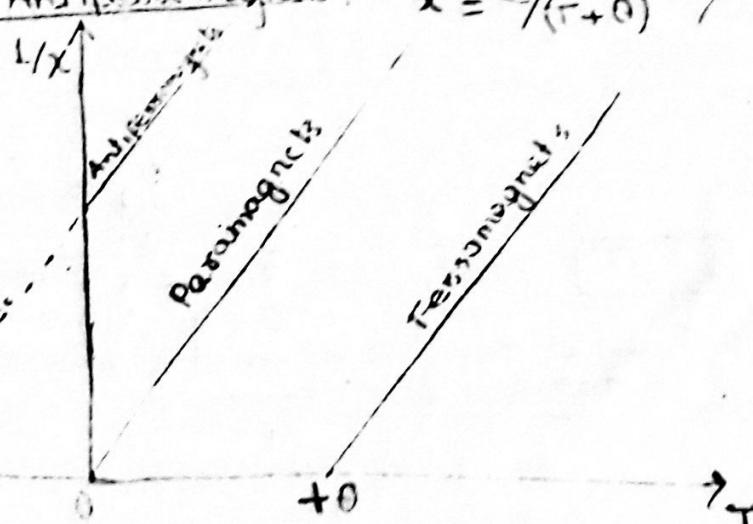
$$X = C/(\tau + \theta) \quad \dots \dots \quad (3)$$

$$\text{If } C = 2N\mu^2/3k \quad \text{and} \quad \theta = \frac{N\mu^2}{3k} (\alpha + \beta) = \frac{C}{2} (\alpha + \beta)$$

so, for paramagnets: $X = C/\tau$

for Ferro-magnets: $X = C/(\tau - \theta)$

for Antiferromagnets: $X = C/(\tau + \theta)$



Case II

Consider the region for which $T < T_N$.
Then we consider the external magnetic field,

$$H = 0$$

$$H_{Ma} = -\alpha M_a - \beta M_b$$

$$H_{Mb} = -\beta M_a - \alpha M_b$$

$$\therefore M_a = \left(\frac{N\mu^2}{3kT_N} \right) (-\alpha M_a - \beta M_b) \quad \dots \dots \dots (4)$$

$$M_b = \left(\frac{N\mu^2}{3kT_N} \right) (-\beta M_a - \alpha M_b) \quad \dots \dots \dots (5)$$

From eq(1) and (5) we get respectively,

$$M_a \left[1 + \frac{N\mu^2 \alpha}{3kT_N} \right] + \frac{N\mu^2 \beta}{3kT_N} M_b = 0 \quad \dots \dots \dots (6)$$

and

$$M_b \left[1 + \frac{N\mu^2 \alpha}{3kT_N} \right] + \frac{N\mu^2 \beta}{3kT_N} M_a = 0 \quad \dots \dots \dots (7)$$

From eq.(6) and eq.(7), equating the determinant of the coefficients of 'M_a' and 'M_b' to zero we get,

$$\begin{vmatrix} \left(1 + \frac{N\mu^2 \alpha}{3kT_N} \right) & \frac{N\mu^2 \beta}{3kT_N} \\ \frac{N\mu^2 \beta}{3kT_N} & \left(1 + \frac{N\mu^2 \alpha}{3kT_N} \right) \end{vmatrix} = 0$$

$$\therefore \left(1 + \frac{N\mu^2 \alpha}{3kT_N} \right)^2 - \left(\frac{N\mu^2 \beta}{3kT_N} \right)^2 = 0$$

$$\text{or, } \left(1 + \frac{N\mu^2 \alpha}{3kT_N} \right) = \frac{N\mu^2 \beta}{3kT_N}$$

$$\text{or, } 3kT_N + N\mu^2 \alpha = N\mu^2 \beta$$

$$\therefore T_N = \frac{N\mu^2 (\beta - \alpha)}{3k} = \frac{C}{2} (\beta - \alpha) \quad \dots \dots \dots (8)$$

$$\text{as } C = \frac{2N\mu^2}{3k}$$

Eq. (8) shows that T_N increases with strong antiferromagnetic AB interaction i.e. β and decreases with increase of antiferromagnetic AA' and BB' interactions i.e. α .

$$\text{Now, } \frac{T_N}{\theta} = \frac{\frac{1}{2} (\beta - \alpha)}{\theta} = \frac{\beta - \alpha}{\alpha + \beta} \quad \dots \dots \dots (9)$$

Experimental results show that $T_N < \theta$.

$$\therefore \alpha > 0$$

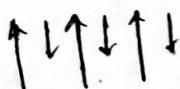
So this gives the evidence that the antiferromagnetic AA and BB interactions are present.

Ferrimagnetism

In ferrimagnetic materials, the alignment of the neighbouring dipoles is antiparallel, but the adjacent dipoles are of unequal magnitude. Ferrites are the nonmetallic ferrimagnetic materials and are of great importance from the electronic and electrical engineering point of view. They form a class of solid oxides of first point of view. The general chemical formula of ferrites may be written as $\text{Me}^{2+}\text{Fe}_2^{3+}\text{O}_4$, where Me^{2+} represents a suitable divalent metal ion such as Mn, Ni, Co, Mg, Cu, Cd or Zn. Ni for Me gives Nickel Ferrite. $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$ is ferrous ferrite, also commonly known as magnetite (Fe_3O_4). Magnetite is the oldest ferrimagnetic material known to mankind.

A complicated class of ferrites, termed mixed ferrites, is formed when Me²⁺ is replaced by a mixture of ions. Mixed ferrites have established their technical importance under the trade name Ferroxcubé. Mn-Zn ferrites (Ferroxcubé IV) are the most important examples of mixed ferrites. Mixed ferrites give higher saturation magnetisation than simple ferrites.

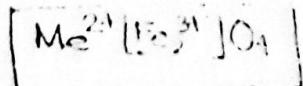
Most of the ferrites possess magnetic properties similar to those of metallic ferromagnetics. For example, they show hysteresis, spontaneous magnetisation and related phenomena. The most important property of ferrites is that their dc resistivity is 10^3 to 10^11 times as great as that of iron. As a result, the power losses due to eddy currents in ferrites are much reduced and hence they are well suited for high frequency applications, such as, in high-frequency transformers and high frequency generators.



| These are three types of structures of Ferrimagnetics
i) NORMAL SPINEL STRUCTURE

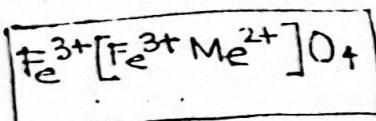
$\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$, here the divalent Fe²⁺ ion is replaced by divalent metal ion say, Ni, Cu, Cr, Mn etc. We denote this divalent metal ion as, Me²⁺.

So the normal spinel structure is



Here 8 divalent ions occupy the tetrahedral positions. And 16 trivalent ions occupy the octahedral positions.

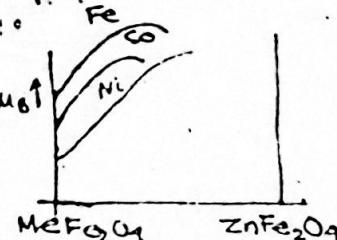
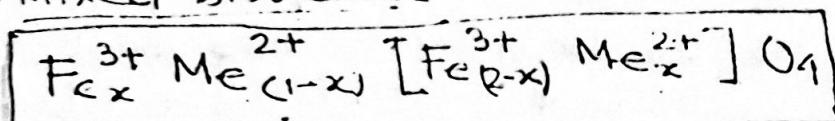
ii) Inverse Spinel Structure



B divalent ions occupy 8 positions of octahedral

and 16 Fe^{3+} ions are equally distributed among 8 octahedral positions and tetrahedral positions.

iii) Mixed structure



NEEL THEORY

In order to explain the magnetic properties of Ferrite, Neel put forward a hypothesis. According to him there is a strong and negative interaction between the ions on the tetrahedral sites (A sites) and the octahedral site (B sites). This produces the antiparallel alignment between those A and B ions.

Consider, the magnetisation of A site = M_a
and the " " of B site = M_b

$$\begin{aligned} \text{Susceptibility of A site} &= \chi_a \\ \text{of B site} &= \chi_b \end{aligned}$$

$$\therefore \text{Total susceptibility} : \chi = (\chi_a + \chi_b)$$

$$= \frac{M}{H}$$

$$\boxed{\chi = \frac{(M_a + M_b)}{H}} \quad (10)$$

Now, molecular field of A site and B site are given below, respectively,

$$\begin{aligned} H_{ma} &= H - \beta M_b \\ H_{mb} &= H - \beta M_a \end{aligned}$$

$$. (11)$$

Now,

$$\boxed{\chi_a = \frac{C_a}{T} = \frac{M_a}{H_{ma}} = \frac{M_a}{(H - \beta M_b)}} \quad (12)$$

and

$$\boxed{\chi_b = \frac{C_b}{T} = \frac{M_b}{H_{mb}} = \frac{M_b}{(H - \beta M_a)}} \quad (13)$$

Case I

Consider, the case $T = T_c$ = Ferrimagnetic Curie temp
then $H = 0$

$$\therefore \text{Then, } X_a = \frac{C_a}{T_c} = \frac{M_a}{-\beta M_b} \quad \dots \quad (14)$$

$$\text{and } X_b = \frac{C_b}{T_c} = \frac{M_b}{-\beta M_a} \quad \dots \quad (15)$$

So from the equation (1) and (15), we get

$$M_a T_c = -\beta C_a M_b \quad \therefore M_a = -\beta C_a M_b / T_c$$

$$\text{and } M_b T_c = -\beta C_b M_a \quad \therefore M_b = -\beta C_b M_a / T_c$$

Putting the value of 'M_b' in 'M_a' we get

$$M_a = \frac{\beta C_a}{T_c} \left(\frac{\beta C_b M_a}{T_c} \right) = \frac{\beta^2 C_a C_b M_a}{T_c^2}$$

$$\text{or, } M_a \left[1 - \frac{\beta^2 C_a C_b}{T_c^2} \right] = 0 \quad \therefore M_a = 0 \quad \left[1 - \frac{\beta^2 C_a C_b}{T_c^2} \right] = 0$$

$$\therefore T_c^2 = \beta^2 C_a C_b$$

$$\therefore T_c = \beta \sqrt{C_a C_b} \quad \checkmark \quad \dots \quad (6)$$

Case II

Now consider the case when $T > T_c$

Then H=H

$$X_a = \frac{C_a}{T} = \frac{M_a}{H M_a} = \frac{M_a}{(H - \beta M_b)} \quad \dots \quad (7)$$

$$X_b = \frac{C_b}{T} = \frac{M_b}{H \cdot c} = \frac{M_b}{(H - \beta M_a)} \quad \dots \quad (8)$$

∴ From (7) and (8), we get

$$M_a T = C_a H - C_a \beta M_b \quad \dots \quad (9)$$

$$\text{and } M_b T = C_b H - C_b \beta M_a \quad \dots \quad (10)$$

$$\text{From Eq(10), } M_b = \frac{C_b H - C_b \beta M_a}{T}$$

Putting this value of 'M_b' in equation (9), we get

$$M_a T = C_a H - C_a \beta \left[\frac{C_b H - C_b \beta M_a}{T} \right]$$

$$= C_a H - \frac{C_a C_b \beta H}{T} + \frac{C_a C_b \beta^2 M_a}{T}$$

$$\text{or, } M_a \left[T - \frac{C_a C_b \beta^2}{T} \right] = C_a H - \frac{C_a C_b \beta H}{T}$$

$$\text{or, } M_a \left[T^2 - C_a C_b \beta^2 \right] = C_a H T - C_a C_b \beta H$$

$$\text{or, } \frac{M_a}{H} = \frac{C_a T - C_a C_b \beta}{T^2 - C_a C_b \beta^2} = \frac{C_a T - C_a C_b \beta}{T^2 - T_c^2}$$

$$\text{and similarly } \frac{M_b}{H} = \frac{C_b T - C_a C_b \beta}{T^2 - T_c^2}$$

$$\text{From Eq(10), } X = \frac{M_a + M_b}{H} = \frac{(C_a + C_b) T - 2 C_a C_b \beta}{(T^2 - T_c^2)} \quad \dots \quad (21) \quad 95$$

$$\text{If } C_a = C_b = c,$$

then $T_c = \beta c$, which is similar as in case of antiferromagnetism.

∴ Antiferromagnetism is a special case of ferrimagnetism.

Magnetic Resonance

Nuclear Magnetic Moments

Atomic nuclei have the magnetic moment associated with total angular momentum.

Now we consider the nuclear spin = I .

Then the total angular momentum of nucleus
 $= Ma = \hbar [I(I+1)]^{1/2}$

The possible components of total angular momentum in the direction of applied field H (i.e. in the Z direction) is determined by the magnetic quantum no ' m_I ' associated with I .

m_I can have the values :-

$$[I, (I-1), (I-2), \dots, 0, \dots, -(I-2), -(I-1), -I]$$

Now the magnetic moment μ associated with ' Ma ' is given by,

$$\boxed{\mu = g \frac{e}{2M_p c} Ma}$$

where M_p = Mass of the nucleus

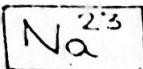
• Z component of ' μ ' (μ_z) along H direction,

$$\boxed{\mu_z = g \frac{e}{2M_p c} I \hbar = g \frac{e \hbar}{2M_p c} I = g \mu_n I}$$

∴ Z component of Ma is ' $I\hbar$ '

where μ_n = Nuclear magneton $= \frac{e\hbar}{2M_p c}$.

Consider now the example :-



$$I = \frac{3}{2}$$

∴ No. of possible m_I values are $(2I+1) = (3+1) = 4$

∴ Possible m_I values are

$$(-\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2})$$

So the difference between two successive ' m_I ' values is $\frac{1}{2}$.

∴ Energy difference between two successive levels indicated by different m_I is ' $\mu_z H$ ' i.e. ' $g \mu_n H$ '.

93 Comparative Study Of NMR And E.S.R.

In the both processes the static magnetic field H is applied in Z -direction and a oscillatory weak perturbing field with amplitude ' H_0 ' is applied in perpendicular direction to H . Now in the two processes the absorption of

e.m. energy occurs from the oscillatory field when the resonance condition occurs.

Consider the ESR process:-

We consider electron spin = $\frac{1}{2}$

Then each magnetic state is represented by ' M_s '.

The values of ' M_s ' are —

$$[s, (s-1), (s-2), \dots, 0, -(s-2), -(s-1), -s]$$

So the mag. moment component along the direction of H i.e. along z-direction is $= M_z = g \frac{e \hbar}{2mc} \tau_s = g \mu_B s$

Here,

$$\boxed{\mu_B = \frac{e \hbar}{2mc} = \text{Bohr Magneton}} \\ = 9.27 \times 10^{-21} \text{ erg/cscsted}$$

where m = mass of an ele

So the potential energy of the magnetic state

$$= E = M_z H = g \mu_B s H$$

So difference in potential energy of the two successive magnetic states $= \Delta E = g \mu_B \Delta s H$

$$\text{Now, } \Delta s = \Delta M_s = \pm 1$$

$$\therefore \boxed{\Delta E = g \mu_B H}$$

Now if ' ω_e ' be the angular frequency of the oscillating field, then the resonance condition occurs, when,

$$\boxed{h \omega_e = g \mu_B H}$$

$$\therefore \frac{h}{2\pi} \cdot 2\pi \nu_e = g \mu_B H$$

$$\therefore \boxed{\nu_e = \frac{g \mu_B H}{h}} \quad [g (\text{for electron spin}) = 2]$$

Resonance frequency of oscillatory field is :-

$$\nu_e = \frac{g \mu_B H}{h} = \frac{2 \times 9.27 \times 10^{-21}}{6.626 \times 10^{-34}} \text{ H} \quad \text{Hz} \\ = 2.798 \times 10^6 \text{ Hz} \\ \approx \underline{2.8 \text{ Hz MHz}}$$

2.8 Hz MHz

Consider the NMR process

We consider the nuclear spin ' I ? Then each magnetic state is represented by ' M_I '. The values of ' M_I ' should be

$$[I, (I-1), (I-2), \dots, 0, \dots, -(I-2), -(I-1), -I]$$

The magnetic moment component along z-direction

$$= M_z = g \frac{e \hbar}{2mc} \tau_I = g \mu_N I$$

$$\text{here, } \left[\mu_n = \frac{e\hbar}{2Mpc} \Rightarrow \text{Nuclear Magneton} \right. \\ \left. = 5.05 \times 10^{-21} \text{ erg/oested} \right] \quad 5.05 \times 10^{-21} \text{ J/T}$$

now, the potential energy of the magnetic state
 $= E = \mu_n H = g \mu_n H$

The difference in potential energy of the two successive magnetic states $= \Delta E = g \mu_n \Delta I H$

Now, $\Delta I = \Delta M_I = \pm 1$

$$\therefore [\Delta E = g \mu_n H]$$

If we say, the angular frequency of oscillatory field is ' ω_n ', then the resonance condition occurs when $[\hbar \omega_n = g \mu_n H]$ (g for nuclear spin = 5.586)

$$\text{or, } \hbar \omega_n = g \mu_n H$$

or, the resonance frequency of oscillatory field is given by,

$$\checkmark \left[\omega_n = \frac{g \mu_n H}{\hbar} \right] = \frac{5.586 \times 5.05 \times 10^{-24}}{6.626 \times 10^{-34}} H \text{ Hz.} \quad (\text{g for proton } 5.586)$$

$$= 4.26 \text{ kHz.} \quad (\omega_n = 4.26 \text{ kHz})$$

X Diamagnetism

In diamagnetic materials the magnetisation M is proportional to the applied magnetic field intensity H but the susceptibility χ is negative. Materials in which the atoms or molecules have no permanent magnetic moment exhibit this diamagnetic behaviour. In such materials, the number and spatial arrangement of the electron orbits of an atom are such that the vector sum of their magnetic moments is zero.

The basic principle of diamagnetic behaviour may be understood with reference to Lenz's law as given below:

Consider an electron moving around the nucleus in a circular orbit of radius r . Suppose that the angular velocity of the electron is ω_0 in the absence of the magnetic field. Due to the application of an external magnetic field, the magnetic flux through the orbit will change. As a result, a current will be induced which will produce a magnetic field in a direction opposite to that of the applied field. The induced current will alter the fo. of motion of the electron and will persist without change in magnitude as long as the external field is present. Obviously then, any atomic orbit will give a negative contribution to magnetic susceptibility.

In the absence of the external magnetic field, the centrifugal force is balanced by the Coulomb force of attraction between the nucleus and revolving electron. Thus, we have

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\epsilon_0 r^2}$$

$$\text{or, } m\omega^2 r = \frac{Ze^2}{4\pi\epsilon_0 r^2} \quad (i)$$

where Ze represents the charge of the nucleus, e electronic charge, m the mass of the electron and ϵ_0 the permittivity of free space.

When a magnetic field is applied perpendicular to the plane of the orbit, an additional Lorentz force acts on the electron. This extra radial force may be inward or outward depending on the direction of the applied magnetic field. Assuming that this force merely accelerates or decelerates the electron without altering the radius of the orbit we can write the new balanced equation

$$m\omega^2 r = \frac{Ze^2}{4\pi\epsilon_0 r^2} \pm e\omega B \quad (ii)$$

where ω represents the new angular velocity and B

the applied magnetic flux density.

From Eq(ii) we obtain with the help of Eq(iii)

$$\omega = \omega_0 \pm \frac{eB}{m} \omega \quad (\text{iii})$$

Now, $\omega_0 \approx 10^{19}$ to 10^{15} rad/s. The magnetic field (B) generally used in the laboratory is of the order of 1T. Therefore, the quantity eB/m is much smaller than ω_0 . Hence we can write

$$\omega = \omega_0 \left(1 \pm \frac{eB}{m\omega_0} \frac{\omega}{\omega_0} \right)^{1/2} \approx \omega_0 \pm \omega_L \frac{\omega}{\omega_0} \quad (\text{iv})$$

where $\omega_L (= \frac{eB}{2m})$ is the Larmes frequency.

Solving (iv), we get

$$\omega = \frac{\omega_0}{1 \mp \frac{\omega_L}{\omega_0}} \approx \omega_0 \left(1 \pm \frac{\omega_L}{\omega_0} \right) = \omega_0 \pm \omega_L$$

The frequency change ω_L produces the induced magnetic moment

$$\vec{M}_{\text{ind}} = -\frac{1}{2} e \vec{r} \vec{\omega}_L = -\frac{e^2}{4m} \vec{r}^2 \vec{B} \quad (\text{v})$$

If the orbit is not perpendicular to the applied magnetic field it precesses about \vec{B} with the Larmes frequency. In this case the induced magnetic moment will have a component opposite to the direction of the field \vec{B} . This component is given by

$$\vec{M}_{\text{ind}} = -\frac{e^2}{4m} \vec{B} \langle \vec{r}^2 \rangle$$

where $\langle \vec{r}^2 \rangle$ gives the mean square radius of the projection of the orbit on a plane perpendicular to \vec{B} . If n' number of electrons of an atom revolve in orbits which are coincident in various directions, the total induced moment in the atom is given by

$$\vec{M}_{\text{ind}} = -\frac{e^2}{4m} \vec{B} \sum_{i=1}^{n'} \langle \vec{r}^2 \rangle \quad (\text{vi})$$

Considering cartesian co-ordinate axes Ox, Oy and Oz , where the origin (O) coincides with the centre of the circular orbits we can write

$$\vec{r}^2 = x^2 + y^2 + z^2$$

where x, y, z represent the co-ordinates of any point on an orbit of radius r . If Oz coincide with the direction of \vec{B} , then

$$\vec{r}^2 = x^2 + y^2$$

Since $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$ we get

$$\langle \vec{r}^2 \rangle = \frac{2}{3} \langle r^2 \rangle$$

Here $\langle \rho^2 \rangle$ is the mean sq. distance of an arbitrary electron from the nucleus. Therefore

$$\text{Mind} = -\frac{e^2}{6m} B \sum_{l=1}^{n'} \langle \rho^2 \rangle \quad (\text{vi})$$

If the solid contains N atoms per unit volume, then the magnetic moment per unit volume, i.e., magnetization M is given by

$$\begin{aligned} M &= -\frac{e^2 N}{6m} B \sum_{l=1}^{n'} \langle \rho^2 \rangle \\ &= -\frac{e^2 N \mu_0 M_r}{6m} H \sum_{l=1}^{n'} \langle \rho^2 \rangle \end{aligned} \quad (\text{vii})$$

where the relationship $B = \mu_0 M_r H$ has been used. The diamagnetic susceptibility χ_{dia} is therefore

$$\chi_{\text{dia}} = \frac{M}{H} = -\frac{e^2 N \mu_0 M_r}{6m} \sum_{l=1}^{n'} \langle \rho^2 \rangle \quad (\text{viii})$$

where M_r may be considered as unity. Eq (viii) is known as Langsdorf equation.

An atom having permanent dipole moment will also have the diamagnetic effect. In this case, however, the permanent magnetic moment will tend to rotate into the direction of the applied magnetic field yielding paramagnetic property. This will mask the diamagnetic action.

The examples of diamagnetic materials are Cu, Au, Ge, Si, NaCl, Al₂O₃ etc.

Quantum theory of diamagnetism

X

The Lagrangian in generalised coordinate is

$$L = \frac{1}{2} M \dot{q}^2 - Q \phi(q) + \frac{Q}{c} \dot{q} A(q) \quad (\text{1})$$

In Cartesian co-ordinate, the Lagrange equation of motion is

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) - \frac{\partial L}{\partial x} = 0 \quad (2)$$

The equations for y and z can be written in similar manner.

$$\frac{\partial L}{\partial z} = -Q \frac{\partial \phi}{\partial z} + \frac{Q}{c} \left(x \frac{\partial A_z}{\partial x} + y \frac{\partial A_y}{\partial x} + z \frac{\partial A_x}{\partial x} \right) \quad (3)$$

$$\frac{\partial L}{\partial x} = M \ddot{x} + \frac{Q}{c} \frac{dA_x}{dt} = M \ddot{x} + \frac{Q}{c} \left(\frac{\partial A_x}{\partial t} + \dot{x} \frac{\partial A_x}{\partial x} + \dot{y} \frac{\partial A_y}{\partial x} + \dot{z} \frac{\partial A_z}{\partial x} \right) \quad (4)$$

$$\frac{d}{dt} \left(\frac{\partial L}{\partial \dot{x}} \right) = M \ddot{x} + \frac{Q}{c} \frac{dA_x}{dt} = M \ddot{x} + \frac{Q}{c} \left(\frac{\partial A_x}{\partial t} + \dot{x} \frac{\partial A_x}{\partial x} + \dot{y} \frac{\partial A_y}{\partial x} + \dot{z} \frac{\partial A_z}{\partial x} \right) \quad (5)$$

This (2) becomes

$$M\ddot{x} + Q \frac{\partial \phi}{\partial x} + \frac{Q}{c} \left[\frac{\partial A_x}{\partial t} + \dot{y} \left(\frac{\partial A_x}{\partial y} - \frac{\partial A_y}{\partial x} \right) + \dot{z} \left(\frac{\partial A_z}{\partial z} - \frac{\partial A_x}{\partial z} \right) \right] = 0 \quad (5)$$

or, $M \frac{d^2x}{dt^2} = QEx + \frac{Q}{c} [\vec{v} \times \vec{B}]_x \quad (6)$

where $Ex = -\frac{\partial \phi}{\partial x} - \frac{1}{c} \frac{\partial A_x}{\partial t} \quad (7)$

and $\vec{B} = \vec{\nabla} \times \vec{A} \quad (8)$

Eq(6) is the Lorentz force equation.

The momentum \vec{p} is defined in terms of the Lagrangian as

$$\vec{p} = \frac{\partial L}{\partial \dot{q}} = M\vec{q} + \frac{Q}{c}\vec{A} \quad (9)$$

The Hamiltonian $H(p, q)$ is defined as

$$H(p, q) = p \cdot \dot{q} - L \quad (10)$$

$$\text{or, } H = M\dot{q}_x^2 + \frac{Q}{c}\dot{q}_y\vec{A} - \frac{1}{2}M\dot{q}_z^2 + Q\phi - \frac{Q}{c}\dot{q}_z\vec{A} \\ = \frac{1}{2M}(\vec{p} - \frac{Q}{c}\vec{A})^2 + Q\phi \quad (11)$$

which is hamiltonian of a particle in a magnetic field.

Now, $p \rightarrow -i\hbar\nu$

$$\therefore H = \frac{1}{2M} \left[i\hbar\nu - \frac{Q}{c}\vec{A} \right]^2 + Q\phi(x) \\ = \frac{1}{2M} \left[-i\hbar \left(\hat{i} \frac{\partial}{\partial x} + \hat{j} \frac{\partial}{\partial y} + \hat{k} \frac{\partial}{\partial z} \right) - \frac{Q}{c} (\hat{i}A_x + \hat{j}A_y + \hat{k}A_z) \right]^2 \\ + Q\phi(x) \\ = \frac{1}{2M} \left[\hat{i} \left(-i\hbar \frac{\partial}{\partial x} - \frac{Q}{c}A_x \right) + \hat{j} \left(-i\hbar \frac{\partial}{\partial y} - \frac{Q}{c}A_y \right) \right. \\ \left. + \hat{k} \left(-i\hbar \frac{\partial}{\partial z} - \frac{Q}{c}A_z \right) \right]^2 + Q\phi$$

Considering only x component of H

Now,

$$H \Psi = \left(-i\hbar \frac{\partial}{\partial x} - \frac{Q}{c}A_x \right) \left(-i\hbar \frac{\partial}{\partial x} - \frac{Q}{c}A_x \right) \Psi \\ = \left(-i\hbar \frac{\partial}{\partial x} - \frac{Q}{c}A_x \right) \left(-i\hbar \frac{\partial\Psi}{\partial x} - \frac{Q}{c}A_x \Psi \right) \\ = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} + i\hbar \frac{Q}{c} \frac{\partial}{\partial x} (A_x \Psi) + i\hbar \frac{Q}{c} A_x \frac{\partial \Psi}{\partial x} + \frac{Q^2}{c^2} A_x^2 \Psi \\ = -\hbar^2 \frac{\partial^2 \Psi}{\partial x^2} + i\hbar \frac{Q}{c} \left[\Psi \frac{\partial A_x}{\partial x} + A_x \frac{\partial \Psi}{\partial x} \right] + i\hbar \frac{Q}{c} A_x \frac{\partial \Psi}{\partial x} + \frac{Q^2}{c^2} A_x^2 \Psi$$

In 3-D, and taking $q = -e$ i.e. the electronic charge if

$$\frac{1}{i\hbar} H = -\frac{\hbar^2}{2M} \nabla^2 - i\hbar \frac{e}{c} \nabla A - i\frac{e\hbar}{Mc} A \cdot \nabla + \frac{e^2}{2mc^2} A^2 - cf$$

$$\text{Now, } \nabla \cdot A = \frac{1}{c} \frac{\partial A}{\partial t} = 0 \quad \text{and } B = \nabla \times \vec{A}$$

$$\therefore H = -\frac{\hbar^2}{2M} \nabla^2 - i\frac{e\hbar}{Mc} A \cdot \nabla + \frac{e^2}{2mc^2} A^2 - cf.$$

Considering the effect of a uniform magnetic field in the $-z$ direction, we may write

$$Ax = -\frac{1}{2} y B \quad Ay = \frac{1}{2} x B \quad Az = 0$$

$$A^2 = \frac{1}{4} B^2 (x^2 + y^2)$$

$$H = -\frac{\hbar^2}{2M} \nabla^2 - i\frac{e\hbar}{2Mc} B (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x}) + \frac{e^2}{2mc^2} \frac{B^2}{4} (x^2 + y^2) - cf$$

Extra terms in H due to presence of B

$$= \underbrace{-\frac{i\hbar e}{2Mc} B (x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x})}_{1^{\text{st}}} + \underbrace{\frac{e^2 B^2}{8Mc^2} (x^2 + y^2)}_{2^{\text{nd}}}.$$

The first term on the right is proportional to the orbital angular momentum component L_z if it is measured from the nucleus. In mononuclear system this term gives rise only to paramagnetism. The 2nd term gives for a spherically symmetric system a contribution

$$E' = \frac{e^2 B^2}{12mc^2} \langle \sigma^2 \rangle \quad \text{by first order perturbation}$$

theory. The associated magnetic moment is diamagnetic.

$$\mu = -\frac{\partial E'}{\partial B} = -\frac{e^2 \langle \sigma^2 \rangle}{6Mc^2} B$$

in agreement with the classical result.

For ZnO, of

$$\chi = \frac{N_A Z}{B}$$

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Heisenberg Exchange (The interpretation of Weiss field)

Apart from certain details, the Weiss field describes the observations satisfactorily. So far, however, we have not touched upon the problem of the origin of this field. We shall limit the discussion here to the interpretation that given by Heisenberg.

In 1928 Heisenberg showed that the large molecular field may be explained in terms of the so-called exchange interaction between the electrons. We have now consider the hydrogen molecule. Let the nuclei be denoted by a and b , the atomic wave functions by Ψ_a and Ψ_b , the electrons by 1 and 2. The interaction potential between two atoms then,

$$V_{ab} = e^2 \left(\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{ba}} - \frac{1}{r_{21}} \right) \quad (1)$$

The Heitler-London theory of chemical binding ^{gives} knows that the energy of the system may be written as

$$E = K \pm J_e \quad (2)$$

where K is the Coulomb interaction energy, which does not concern us here

and

J_e = the exchange integral

$$= \int \Psi_a^*(1) \Psi_b^*(2) V_{ab} \Psi_a(2) \Psi_b(1) d\tau_1 d\tau_2$$

The plus sign in eq(2) refers to the nonmagnetic state of the molecule in which the two electronic spins are antiparallel. The minus sign corresponds to the case in which the two spins are parallel i.e to the magnetic state. From the eq(2), it is evident that for magnetic state J_e is positive, because then $(K - J_e) < (K + J_e)$

Considering the relative orientations of two spins, eq(2) can be written as

$$E = \text{const} - 2J_e \vec{S}_1 \cdot \vec{S}_2 \quad (3)$$

In other words, the exchange energy appears in the total energy as if there exists a direct coupling J_e .

between the two spins. The exchange interaction is fundamentally electrostatic and that the spin enters into the energy expression as a consequence of the Pauli exclusion principle.

We shall thus assume & that for two atoms i and j, the effective coupling between the spins due to exchange interaction is equivalent with $-2J_{ij} \vec{S}_i \cdot \vec{S}_j$, in the energy expression J_{ij} is the exchange integral for the two atoms.

We shall now assume that the exchange integral is negligible & except for nearest neighbours and that its value is J_e for all neighbouring pairs. From eq.(3) we may write for the exchange energy of a given atom i with its neighbours

$$V = -2J_e \sum \vec{S}_i \cdot \vec{S}_j \quad (4)$$

where the summation is over the near neighbours of atom i. The essential assumption is that the instantaneous values of the neighbouring spins may be replaced by their time averages. Thus, for the ~~nearest~~^{near} neighbours, we have

$$V = -2zJ_e (S_{xi}\langle S_{xj} \rangle + S_{yi}\langle S_{yj} \rangle + S_{zi}\langle S_{zj} \rangle) \quad (5)$$

Assuming that the magnetization M is along the z-direction, we may write

$$\langle S_{xj} \rangle = \langle S_{yj} \rangle = 0 \text{ and } \langle S_{zj} \rangle = M/g_{UB}N \quad (6)$$

According to (5) and (6),

$$V = -2zJ_e S_{zi}M/g_{UB}N \quad (7)$$

Now the above expression should be equal to the potential energy of spin i in Weiss field γM . i.e;

$$\begin{aligned} P.E. &= -\mu \cdot H = fM/g_{UB}N H = -\frac{M}{g_{UB}N} g_{UB} N \\ &= -g_{UB} S_{zi} \gamma M \end{aligned} \quad (8)$$

Equating,

From (7) and (8), we get

$$\begin{bmatrix} \mu = g_{UB} S_{zi} \\ H = \gamma M \end{bmatrix}$$

$$-2zJ_e S_{zi}M/g_{UB}N = -g_{UB} S_{zi} \gamma M$$

$$\text{or, } \boxed{\gamma = \frac{2zJ_e}{g^* M_B N}} \quad (9)$$

Eq.(9) is the relation between exchange integral J_e and Weiss constant γ .

$$TdS = dE + M dH = \left(\frac{\partial E}{\partial T}\right)_H dT + \left[\left(\frac{\partial E}{\partial H}\right)_T + M\right] dH$$

Because dS is a total differential, it follows that

$$\frac{1}{T} \left[\left(\frac{\partial E}{\partial H}\right)_T + M \right] = \left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \quad \therefore dS = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_H dT + \left(\frac{\partial M}{\partial T}\right)_H dH$$

where the last equality follows from one of the Maxwell relations.

For an isothermal process (B to C) one may thus write

$$dS = \left(\frac{\partial M}{\partial T}\right)_H dH \quad \text{or, } S = S_{H=0} + \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$$

In the curie region

$$X = \frac{M}{H} = N g^* J(J+1) \mu_B^* / 3kT$$

$$\text{and } p_{eff} = g [J(J+1)]^{1/2}$$

$$\therefore M = N p_{eff} \mu_B^* H / 3kT \quad \therefore \left(\frac{\partial M}{\partial T}\right)_H = - \frac{N p_{eff} \mu_B^* H}{3kT^2}$$

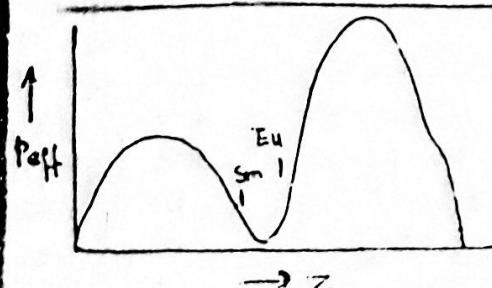
so that then

$$S = S_{H=0} - N \mu_B^* p_{eff} H^2 / 6kT^2$$

Comparison of theory and experiment for paramagnetic salts.

Paramagnetism requires the existence of partly filled electronic shells. Thus paramagnetic compounds are essentially those containing transition group elements. Of these, the rare earth group (incomplete 4f shell) and the iron group (incomplete 3d shell) have been investigated most extensively.

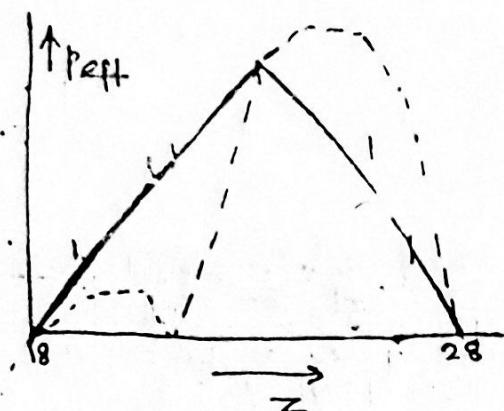
The rare earth ions:



The quantum theory describes the behaviour of most of these salts quite well. This may be seen from the Fig., where the effective no. of Bohr magnetons calculated by van Vleck from expression $p_{eff} = g [J(J+1)]^{1/2}$, the

J values and g 's were obtained from Hund's rules and from Lande's formula. Theoretical The ions Sm^{3+} and Eu^{3+} evidently do not obey the simple theory. However, it has been shown by van Vleck and Frank that these discrepancies can be explained satisfactorily if one considers the special situation with regard to the energy levels of these ions.

The iron group ions: If one calculates the effective no. of Bohr magnetons for the ions of the iron group from expression $P_{eff} = g [J(J+1)]^{1/2}$, the results do not agree at all with the ~~explore~~ experimental values obtained from the Curie law. This may be seen from Fig where the vertical lines represent experimental values and the dashed curve represents $P_{eff} = g [J(J+1)]^{1/2}$. However if one assumes that only the electron spins contribute to the magnetization, i.e., if one replaced $P_{eff} = g [J(J+1)]^{1/2}$



by $P_{eff} = 2[S(S+1)]^{1/2}$ one obtains quite good agreement with experiment (full curve). Thus the iron group ions behaves as if the orbital magnetic moment does not contribute at all. One speaks in this case of quenching of the orbital momentum. The quenching is not necessarily complete, it may be partial.

Quenching of the orbital angular momentum

Crystal Field Splitting

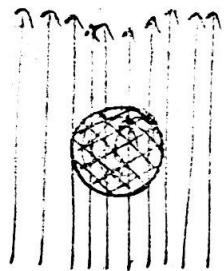
The difference in behavior of the rare earth and the iron group salts is that the 4f shell responsible for paramagnetism in the rare earth ions lies deep inside the ions, within the 5s and 5p shells, whereas in the iron gr. ions the 3d shell responsible for paramagnetism is the outermost shell. The 3d shell experiences the intense inhomogeneous electric field produced by neighbouring ions. This inhomogeneous electric field is called the crystal field. The interaction of the paramagnetic ions with the crystal field has two major effects; the coupling of L and S vectors is largely broken up, so that the states are no longer specified by their J values; further, the $2L+1$ sublevels belonging to a given L which are degenerate in free ion may now be split by the crystal field. This splitting diminishes the contribution of the orbital motion to the magnetic moment.

SUPERCONDUCTIVITY

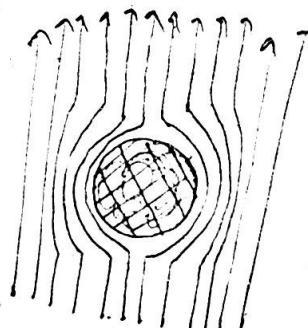
Describe Meissner effect in type I superconductors.
Briefly draw London equation and show how it leads to Meissner effect.

Meissner effect :-

When a specimen is placed in a magnetic field and is then cooled through the transition temperature for super conductivity, the magnetic flux originally present is ejected from the specimen. This is called the Meissner effect.



Normal state



Superconducting State

A bulk specimen of superconductor behaves in an external magnetic field H as if

$$B = H + 4\pi M = 0$$

$$\therefore \frac{M}{H} = \infty = -\frac{1}{4\pi} \quad \text{--- (1)}$$

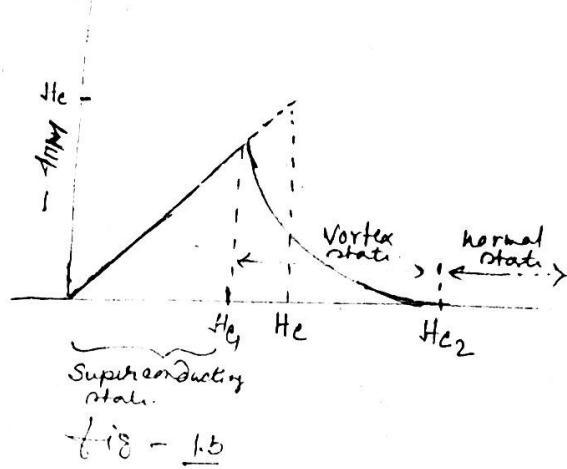
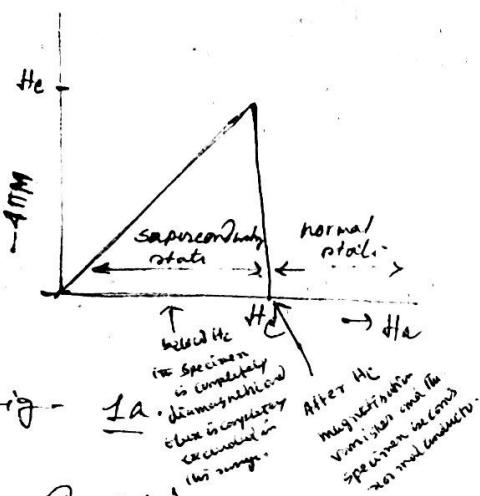
$\infty \rightarrow$ magnetic non-susceptibility. Since $\infty = -ve$, this shows that the superconducting substance is a diamagnetic material.

There are two types of superconductors viz. type-I superconductor and type-II superconductor.

Type-I S.C

The magnetization curve expected for a s.c under the conditions of Meissner-Ochsenfeld (eqn. ①) is

sketched in fig 1.a. This applies quantitatively to a specimen in the form of a long solid cylinder placed in a longitudinal magnetic field. Such specimens of many materials exhibit this behavior; they are called type I. S.C or soft s.c. The values of applied magnetic critical field H_c are always too low for type I s.c. to have any useful technical application in coils for superconducting magnets.

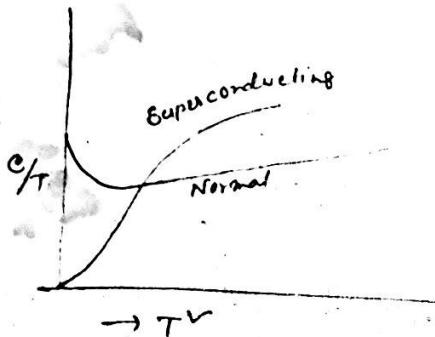


Type II - s.c

for the other group of s.c. the magnetization curve is of the type of II. s.c. for this gr., for applied fields below H_c , the specimen is diamagnetic and hence no flux is completely excluded in this range of field. H_c is called lower critical field. At H_c , the flux begins to penetrate the specimen, and the penetration increases until H_{c2} (upper critical field) is reached. At H_{c2} the magnetization vanishes and the specimen becomes normal conductor. (fig - 1.b)

The magnetization of this group vanishes gradually as the field is increased rather than suddenly as for type I s.c. They are completely superconducting for all field below H_{c2} . They tend to be alloys or transition metals with high electrical resistivity in the normal state. This type of s.c. is called type II s.c. or hard s.c.

The heat capacity of gallium is plotted in fig (a) compares the normal and superconducting states; fig (b)



$$C = AT + BT^{-3}$$

Fig - a

$$\Rightarrow \frac{C}{T} = A + BT^{-\nu}$$

$$\text{For Ga} \rightarrow \frac{C}{T} = 0.596 + 0.588T^{-\nu}$$

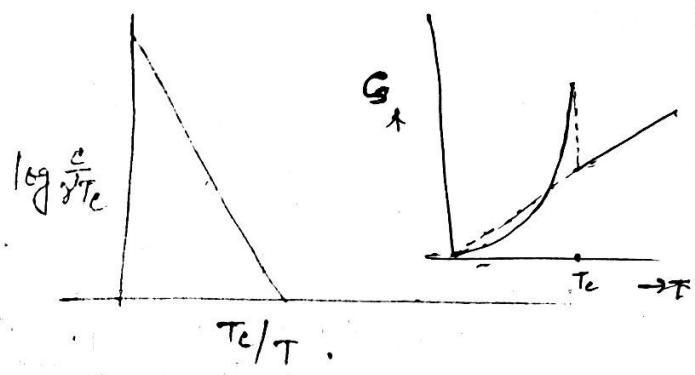


Fig - b

Fig (b) shows that the electronic contribution to the heat capacity in the superconducting state is an exponential form with an argument proportional to $-\frac{1}{T}$, suggesting the excitation of electrons across an energy gap.

i) Isotopic effect :-

It has been observed that the critical temperature of superconductors varies with isotopic mass. In mercury (Hg) T_c varies from 4.185 K to 4.156 K as the average atomic mass M varies from 199.5 to 203.1 atomic mass units. The transition temp. changes smoothly when we mix different isotopes of the same element. In this way, we get a relation $M^\alpha T_c = \text{const.}$; $\alpha = \text{const.}$

From the dependence of T_c on the isotopic mass we learn that lattice vibrations and hence electron-lattice interaction are deeply involved in superconductivity. There is no other reason for the superconducting transition temp. to depend on the number of nucleons in the nucleus. The original B.C.S model gave the result $T_c \propto \Delta E_{\text{gap}} \propto M^{-1/2}$. So that $T_c \propto \frac{1}{M^{1/2}}$, but the Coulomb interactions b/w the electrons changes the relation.

Thermodynamics of the superconducting Transition

The transition betw. the normal and superconducting states is thermodynamically reversible, just as the transition betw. liquid and vapour phases of a substance is reversible.

For that, we apply thermodynamics relation to get entropy difference betw. normal and superconducting states in terms of the critical field curve H_c versus T . At absolute zero, if the magnetic field (applied) is zero, then the heat capacity difference betw. normal and superconducting states gives the stabilization energy.

No work done due to application of dH_a is

$$dS = dE + M dH_a$$

$$\therefore dW = T dS - \tilde{M} \cdot d\tilde{H}_a$$

$$= T dS + \frac{H_a dH_a}{4\pi}$$

$$\therefore 4\pi \tilde{M} = \tilde{H}_a$$

$$\therefore M = \frac{H_a}{4\pi}$$

$$\text{At } T = 0, dU = \frac{H_a dH_a}{4\pi}$$

i.e. the increase in the energy density of the S.C. is

$$U_s(B_a) - U_s(0) = \int_{0}^{B_a} \frac{1}{4\pi} H_a dH_a$$

$$= \frac{1}{8\pi} B_a^2$$

B_a = critical field.

At the critical pt. $B_a = B_{ac}$.

$$\therefore \Delta U_s = \frac{B_{ac}^2}{8\pi} \text{ gives the stabilization energy.}$$

~~Let's~~ down London eqn. and show how it leads to Meissner effect. :-

London assume that in the superconducting state, the current density \vec{j} is directly proportional to the vector potential \vec{A} of the local magnetic field.

$$\vec{j} \propto \vec{A}$$

$$\text{i.e., } \vec{j} = -\frac{c}{4\pi\lambda_L^2} \vec{A}.$$

Now this is the London eqn., where c is the velocity of light and λ_L is a const. with the dimension of length.

$$\begin{aligned} \text{Now } \nabla \times \vec{j} &= -\frac{c}{4\pi\lambda_L^2} \nabla \times \vec{A} \\ &= -\frac{c}{4\pi\lambda_L^2} \vec{B} \quad \text{--- (2) } [\because \nabla \times \vec{A} = \vec{B}]. \end{aligned}$$

~~Now~~ ~~Maxwell~~ ~~eqn~~ ~~=~~ ~~0~~

From a ~~Maxwell~~ eqn., we can write

$$\nabla \times \vec{B} = \frac{4\pi}{c} \vec{j}$$

$$\Rightarrow \nabla \times (\nabla \times \vec{B}) = \frac{4\pi}{c} \nabla \times \vec{j} = -\nabla^2 \vec{B}$$

$$\text{Now, } \nabla^2 \vec{B} = \frac{4\pi}{c} \cdot \frac{c}{4\pi\lambda_L^2} \vec{B} \quad \text{using (2).}$$

$$\Rightarrow \boxed{\nabla^2 \vec{B} = \frac{1}{\lambda_L^2} \vec{B}} \quad \text{--- (3)}$$

This ~~eqn~~ accounts for the Meissner effect because it does not allow a mag. uniform in space, so that a mag. field cannot exist in a superconductor. That is, $\vec{B}(r) = \vec{B}_0 = \text{const.}$ is not a soln. of (3), unless the const. field \vec{B}_0 is identically zero. The result follows because $\nabla^2 \vec{B}_0$ is always zero, but \vec{B}_0/λ_L^2 is not zero unless \vec{B}_0 is zero. Eqn. (3)

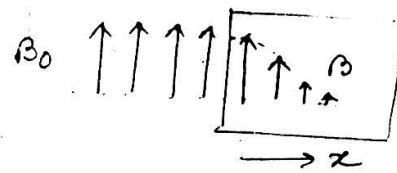
ensures that $\vec{J} = 0$ whenever $\vec{B} = 0$.

In the pure superconducting state the only field is exponentially damped as we go in from an external surface. Let a semi-infinite s.c. occupy the space on the +ve side of the x -axis as in Fig ②. Therefore the soln. of eq. ③ is

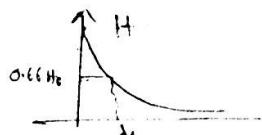
$$\vec{B} = B_0 \exp\left(-\frac{x}{\lambda_L}\right) - ④$$

$B_0 \rightarrow$ field inside the sample.

$B_0 \rightarrow$ mag. field.



Thus we see λ_L measures the depth of penetration of the magnetic field; it is known as the London Penetration depth.

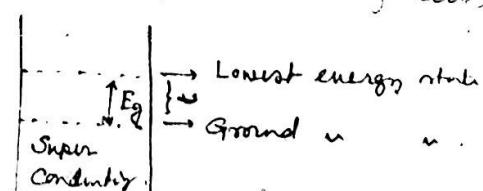
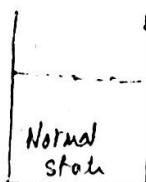


$$\text{Now, } \frac{B}{B_0} = \frac{1}{e} \quad \text{at } x = \lambda_L \quad \boxed{\lambda_L = \left(\frac{mc^2}{4\pi neV}\right)^{1/2}}$$

B.C.S theory :-

When the temp is sufficiently lowered ($\sim 1-10^\circ K$) the lattice vibration decreases and some of the electrons on the fermi surface in perfect coherence with lattice vibration form pairs, called Cooper pairs.

With appropriate attractive interaction between electrons in the pairs, a new ground stat. is formed which is super conducting and the energy gap E_g is $\sim 10^{-4} eV$. The thermal properties, the critical field, and most of the e.m. properties are natural consequences of this energy gap.



The penetration depth and coherence length can also be derived from B.C.S assumptions.

The London eqn is obtained for magnetic field that varies slowly in space - explains the Meissner effect, is also derived from B.C.S theory

According to this theory, the superconducting temp T_c is given by

$$T_c = 1.41 \theta e^{-\frac{1}{UD(\ell_F)}}$$

where $\theta \rightarrow$ Debye temp;

$U \rightarrow$ electron-lattice interaction energy.

$D(\ell_F) \rightarrow$ electron density at ℓ_F .

This T_c gives qualitative agreement with practical experiment.

Magnetic flux through a superconducting ring is quantized and the effective unit of charge is $2e$ than e .

Flux Quantization in a Superconducting Ring :-

Let us consider a S.C. ring.

According to B.C.S theory, probability for $\psi = n^{1/2} e^{i\theta(n)}$.

Such that the pair concentration

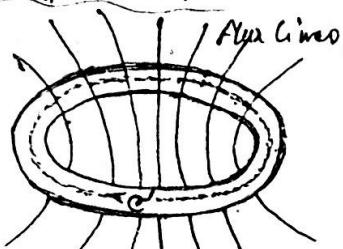
$$n = N^* \psi = \text{const.}$$

The velocity of such a Cooper pair is

$$\vec{v} = \frac{1}{m} [\vec{p} - \frac{q}{c} \vec{A}]$$

$$= \frac{1}{m} (-i\hbar \vec{v} - \frac{q}{c} \vec{A}) \quad \text{using quantum theory.}$$

$$\therefore \text{the particle flux} = N^* \vec{v} \cdot \vec{\psi} = \frac{n}{m} (\hbar \vec{v} \theta - \frac{q}{c} \vec{A})$$



At absolute zero (n) is the limit of the concentration of electrons in the conduction band, the n right to pair.

So that the electric current density is

$$\vec{j} = q \vec{v} \times \vec{B} = \frac{nq}{m} \left[\vec{\nabla} \phi - \frac{q}{c} \vec{A} \right] \quad \text{--- 5.Q}$$

$$\Rightarrow \vec{\nabla} \times \vec{j} = - \frac{n}{m} \frac{q^2}{c} \vec{B} \quad [\vec{\nabla} \times \vec{\nabla} \phi = 0]$$

--- 5.b. $\vec{\nabla} \times \vec{A} = \vec{B}$

But from London eqn.

$$\vec{\nabla} \times \vec{j} = - \frac{c}{4\pi \mu_L^2} \vec{\nabla} \times \vec{A} = - \frac{c}{4\pi \mu_L^2} \vec{B} \quad \text{--- 6.}$$

From 5.Q & 6. Comparing 5.b. and 6., we get

$$\mu_L^2 = \frac{mc^2}{4\pi nq^2} \quad \text{--- 7.}$$

If $\vec{j} = 0$, $\vec{\nabla} \phi - \frac{q}{c} \vec{A} = 0$.

$$\Rightarrow \vec{\nabla} \phi = \frac{q}{c} \vec{A}$$

For a closed loop δ' ,

$$\oint_{\delta'} \vec{\nabla} \phi \cdot d\vec{l} = q \oint_{\delta'} \vec{A} \cdot d\vec{l}$$

According to Wilson-Sommerfeld g. condition

$$\oint_{\delta'} \vec{\nabla} \phi \cdot d\vec{l} = 2\pi s, \quad s=1, 2, 3, \dots$$

$$\begin{aligned} \text{or, } \oint_{\delta'} \vec{\nabla} \phi \cdot d\vec{l} &= q \oint_{\delta'} \vec{A} \cdot d\vec{l} \\ &= q \oint_{\delta'} (\vec{\nabla} \times \vec{A}) \cdot d\vec{l} \quad (\text{Stokes' Law}) \\ &= q \oint_{\delta'} \vec{B} \cdot d\vec{l} \end{aligned}$$

$$\text{total flux } \Phi = \frac{(2\pi \hbar c)}{q} s$$

\rightarrow the total flux is quantized.

The quantum B flux in a superconductor is

$$\Phi_0 = \frac{2\pi \hbar c}{q} \Rightarrow \frac{2\pi \hbar c}{2e} = 2.0878 \times 10^{-7} \text{ gauss-cm}^2$$

Josephson Superconductor Tunneling

Under suitable conditions we observe remarkable effects associated with the tunneling of superconducting pairs from a superconductor through a layer of an insulator into another superconductor. Such a junction is called a weak link. There are two types of Josephson effect.

① dc Josephson effect

② ac in $\propto \sin \omega t$

DC Josephson effect :-

In absence of any electric or magnetic field, some Cooper pairs pass through the insulating barrier (weak link) which results a flow of d.c supercurrent.

Let A and B are two identical superconductor bars probability amplitudes

$$\psi_1 = n_1^{1/2} e^{i\theta_1(r)} \quad (i)$$

$$\text{and } \psi_2 = n_2^{1/2} e^{i\theta_2(r)} \quad (ii) \text{ respectively.}$$

The time-dependent Schrödinger eqn $i\hbar \frac{\partial \psi}{\partial t} = H\psi$ applied to the two amplitudes gives

$$i\hbar \frac{\partial \psi_1}{\partial t} = -T \psi_2 \quad (1)$$

$$i\hbar \frac{\partial \psi_2}{\partial t} = T \psi_1 \quad (2), \quad T \rightarrow \text{transmission coeff.}$$

$$\Rightarrow \frac{\partial \psi}{\partial t} = \frac{1}{2} n_1^{-1/2} e^{i\theta_1(r)} \frac{\partial n_1}{\partial t} + i \psi_1 \frac{\partial \theta_1}{\partial t} = -i T \psi_2 \quad (3)$$

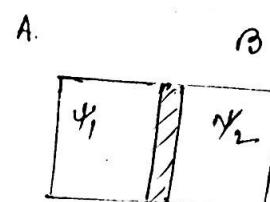
from one end to the other end.

$$\text{and } \frac{\partial \psi_2}{\partial t} = \frac{1}{2} n_2^{-1/2} e^{i\theta_2(r)} \frac{\partial n_2}{\partial t} + i \psi_2 \frac{\partial \theta_2}{\partial t} = -i T \psi_1 \quad (4)$$

Multiplying (3) by ψ_1^* and (4) by ψ_2^* , we get

$$\begin{aligned} \frac{1}{2} \frac{\partial n_1}{\partial t} + i n_1 \frac{\partial \theta_1}{\partial t} &= -i T (n_1 n_2)^{1/2} e^{i(\theta_2 - \theta_1)} \\ &= -i T (n_1 n_2)^{1/2} e^{i\delta} \quad (5) \end{aligned}$$

$\therefore \delta = \theta_2 - \theta_1$



Similarly, multiplying ④ by η_2^* , we get

$$\frac{1}{2} \frac{\partial n_2}{\partial z} + i \eta_2 \frac{\partial \theta_2}{\partial z} = -iT(n_1 n_2)^{1/2} e^{-i\delta} \quad \text{--- ⑤}$$

$\eta_1 = \text{constant}$

Equating real and imaginary parts of eq ③ and ⑤,
we get

$$\frac{\partial n_1}{\partial z} = 2T(n_1 n_2)^{1/2} \sin \delta; \quad \frac{\partial n_2}{\partial z} = -2T(n_1 n_2)^{1/2} \cos \delta \quad \text{--- ⑥}$$

$$\text{and } \frac{\partial \theta_1}{\partial z} = -T(\frac{\eta_2}{\eta_1})^{1/2} \cos \delta; \quad \frac{\partial \theta_2}{\partial z} = -T(\frac{\eta_1}{\eta_2})^{1/2} \cos \delta \quad \text{--- ⑦}$$

For identical superconductors A and B, $n_1 \approx n_2$.

∴ we get from ⑥ and ⑦,

$$\frac{\partial \theta_1}{\partial z} = \frac{\partial \theta_2}{\partial z} \Rightarrow \frac{\partial}{\partial z} (\theta_2 - \theta_1) = 0 = \frac{\partial \delta}{\partial z} \quad \text{--- ⑧}$$

$J_0 = \text{constant}$
a phase diff = const.

$$\text{and } \frac{\partial n_2}{\partial z} = -\frac{\partial n_1}{\partial z}. \quad \text{--- ⑨}$$

The current flow from A to B is proportional to $\frac{\partial n_2}{\partial z}$
or, same being $-\frac{\partial n_1}{\partial z}$.

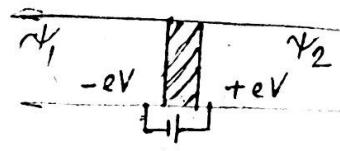
• The current ~~flow~~ J of superconductor pairs across the j_h depends on the phase difference δ as

$$J = J_0 \sin \delta = J_0 \sin (\theta_2 - \theta_1) \quad \text{from ⑧.}$$

AC Josephson effect

A dc voltage applied across the j_h causes rf current oscillations across the j_h . Further an rf voltage applied with the dc voltage can even cause a dc current across the j_h .

Let a voltage V be applied across the j_h . We can do this because the j_h is an insulator. An electron pair experiences a potential difference of V on passing across the



function., where $q = -2e$. We can say that a pair on one side is at potential energy $-eV$ and a pair on the other side is at eV . The eqn of motion

$$\text{if } \frac{\partial \psi_1}{\partial t} = \hbar T \psi_2 - eV \psi_1, \quad \dots \quad (1) \quad \psi_1 = u_1^{1/2} e^{i\theta_1}$$

$$\text{and if } \frac{\partial \psi_2}{\partial t} = \hbar T \psi_1 + eV \psi_2. \quad \dots \quad (2) \quad \psi_2 = u_2^{1/2} e^{i\theta_2}.$$

~~assuming~~, \therefore Now,

$$\frac{\partial \psi_1}{\partial t} = \frac{1}{2} u_1^{-1/2} e^{-i\theta_1} \frac{\partial u_1}{\partial t} + i u_1^{1/2} e^{-i\theta_1} \frac{\partial \theta_1}{\partial t}$$

$$\Rightarrow \frac{1}{2} u_1^{-1/2} e^{-i\theta_1} \frac{\partial u_1}{\partial t} + i \psi_1 \frac{\partial \theta_1}{\partial t} = -i T \psi_2 + i eV \psi_1 \cdot \hbar^{-1}$$

Multiplying (1) by ψ_1^* , we get $\dots \quad (3)$.

$$\frac{1}{2} \frac{\partial u_1}{\partial t} + i u_1 \frac{\partial \theta_1}{\partial t} = i eV u_1 \hbar^{-1} - i T (u_1 u_2)^{1/2} e^{i\delta}$$

Similarly from (2), we get

$$\frac{1}{2} \frac{\partial u_2}{\partial t} + i u_2 \frac{\partial \theta_2}{\partial t} = -i eV u_2 \hbar^{-1} - i T (u_1 u_2)^{1/2} e^{-i\delta}.$$

From above two eqns, we get

$$\frac{\partial u_1}{\partial t} = 2T(u_1 u_2)^{1/2} \sin \delta; \quad \frac{\partial u_2}{\partial t} = -2T(u_1 u_2)^{1/2} \sin \delta$$

$$\text{and } \frac{\partial \theta_1}{\partial t} = \frac{eV}{\hbar} - T(u_1/u_2)^{1/2} \cos \delta;$$

$$\frac{\partial \theta_2}{\partial t} = -\frac{eV}{\hbar} - T(u_1/u_2)^{1/2} \cos \delta$$

For identical superconductors, $u_1 \approx u_2$.

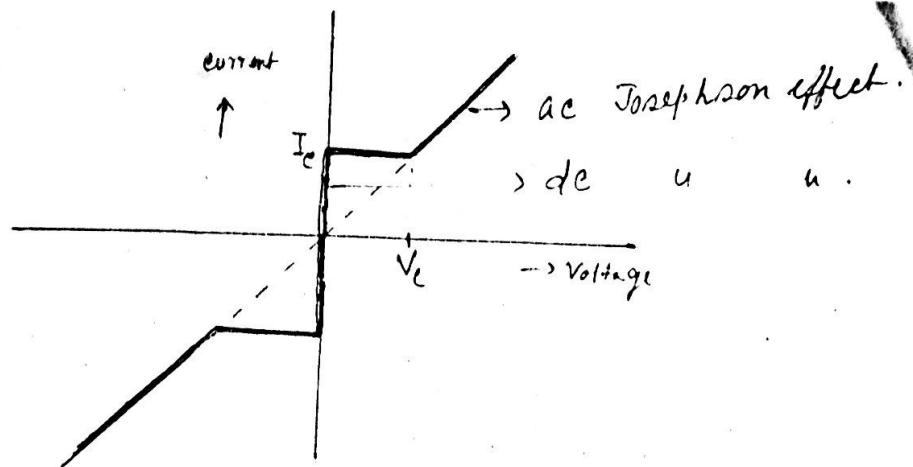
$$\therefore \frac{\partial(\theta_2 - \theta_1)}{\partial t} = \frac{\partial \delta}{\partial t} = -\frac{2eV}{\hbar}; \Rightarrow \delta = \delta(0) - \frac{2eV}{\hbar} t.$$

$$\text{and } \frac{\partial u_1}{\partial t} = -\frac{\partial u_2}{\partial t}.$$

As current is flowing but phase dependence const. will less.

$$\text{So, } \vec{J} = J_0 \sin (\delta(0) - \frac{2eV}{\hbar} t).$$

The current oscillates with frequency $\omega = \frac{2eV}{\hbar}$.



Current-voltage characteristic of a Josephson j.b. The voltage V_c is the critical voltage under zero applied voltage up to a critical current I_c ; this is the dc Josephson effect.

At voltages above V_c the j.b. has a finite resistance, but the current has an oscillatory comp. of freq. $\omega = 2eV/\hbar$; this is the ac Josephson effect.

Q.2 Give brief description in —

i) destruction of external mag. field.

ii) thermodynamic trans. and

iii) isotopic effect in connection with superconductivity

iv) Heat Capacity.

In all superconductors the entropy (S) decreases markedly on cooling below the critical temp. T_c . The decrease in entropy ~~tells us that~~ ^{between} the normal state and superconducting state tells us that superconducting state is more ordered than the normal state,

for the entropy is a measure of the disorder of a system. Some or all of the electrons thermally excited in the normal stat. are ~~condensed~~ in the superconducting stat.

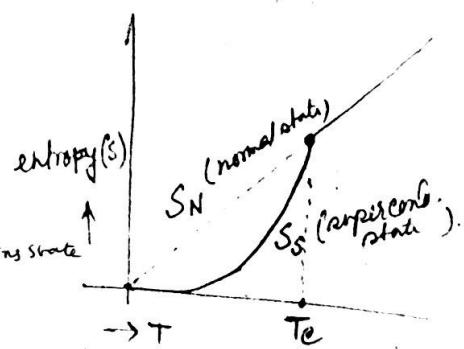


Fig for 11.