

Physics

Solid State Physics

M. Sc. (Sem. - III) (PHCT - 232) (Paper-II)

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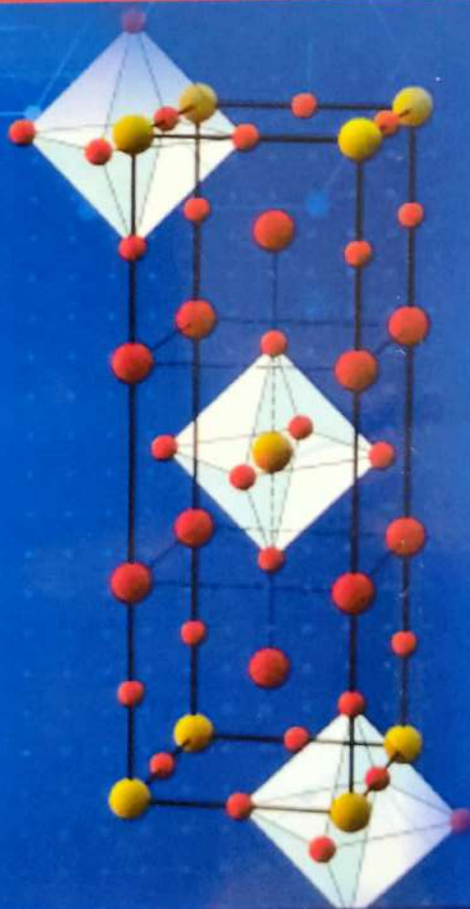
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Solid State Physics

(PHCT-232)

M. Sc. (Sem. - III) (Paper-II)

**(According to New Syllabus of Savitribai Phule Pune University
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Diamagnetism and Paramagnetism

UNIT

2

- 2.1 Introduction
- 2.2 Classical theory of Diamagnetism
- 2.3 Langevin theory of Paramagnetism
- 2.4 Quantum theory of Paramagnetism
- 2.5 Paramagnetic susceptibility of conduction electron
- 2.6 Magnetic properties of rare earth ions and iron group ions with graphical representation
- 2.7 Crystal field splitting
- 2.8 Quenching of orbital angular momentum

2.1 Introduction :

Magnetic materials fascinated human beings for over 4000 years. Magnetism is a phenomenon through which materials assert an attractive or repulsive force or influence on other materials. In the modern concept all materials are said to exhibit magnetism, though of different nature.

When a substance is placed in a magnetic field \vec{H} substance get magnetized. The magnetic dipole moment per unit volume \vec{M} is produced inside the substance is called magnetization. The relation between magnetization and magnetic field is given by the equation

$$\vec{M} = \chi \vec{H}$$

The constant χ is called magnetic susceptibility of the material. It is defined as the ratio of magnetization M to the magnetic field intensity H . The value of χ for vacuum or free space is zero because there is no magnetism in vacuum.

In this unit we shall discuss temperature dependence of susceptibility using Langevin's function for diamagnetic and paramagnetic materials. We shall also discuss crystal field splitting and quenching of orbital angular momentum.

2.2 Classical Theory of Diamagnetism :

Diamagnetic materials are those materials in which number of electrons in the outermost shell is two. These two electrons revolve around the nucleus in a definite path called orbit of electron with same angular velocity ω but in opposite direction.

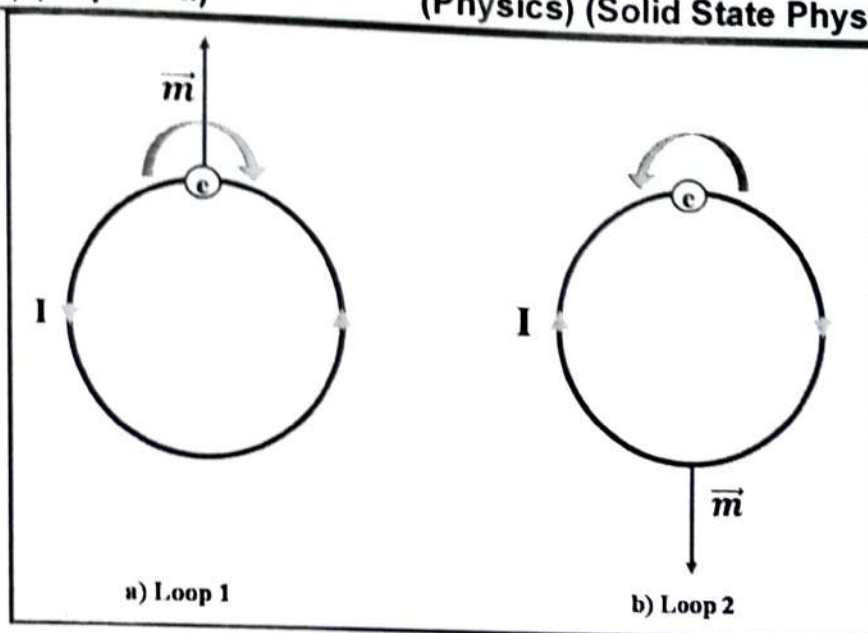


Fig. 2.1: The orbit of electron in the absence of external magnetic field (\vec{B})

The electron revolving around the nucleus is equivalent to tiny current loop and thereby having magnetic dipole moment \vec{m} . The magnetic dipole moment of loop 1 is directed upwards whereas that of loop 2 is directed inwards as shown in Figure 2.1.

In the absence of external magnetic field (\vec{B}), the magnetic dipole moments of two loops being equal and opposite to each other and will cancel out. So, net magnetic dipole moment will be zero.

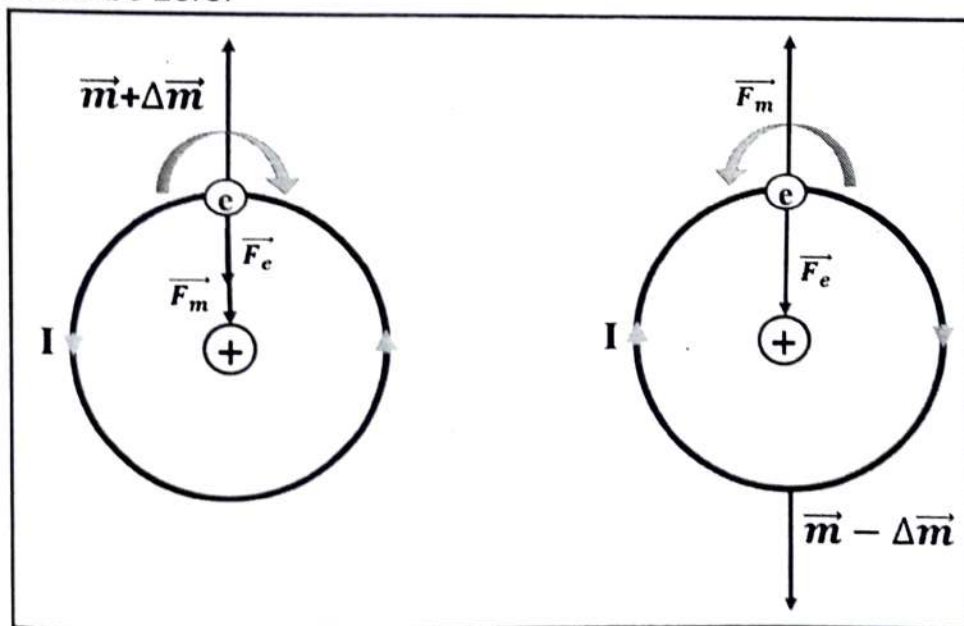


Fig. 2.2: The orbit of electron in the presence of external magnetic field (\vec{B})

When an external magnetic field is applied to a diamagnetic atom (see Figure 2.2), the two electrons orbiting in opposite directions has different values of magnetic dipole moment as

$$(\vec{m} + \Delta\vec{m}) - (\vec{m} - \Delta\vec{m}) = 2 \Delta\vec{m}$$

Since there are large number of atoms in any given diamagnetic material, magnetic dipole moments due to all the atoms add up and net magnetization is obtained in a direction opposite to that of applied magnetic field.

Examples of diamagnetic materials are bismuth, antimony, gold, mercury, copper etc.

Let magnetic field \vec{B} is applied perpendicular to the plane of paper. The magnetic flux associated with loop is

$$\phi = BA = B(\pi r^2) \quad (1)$$

Where ϕ is magnetic flux having SI unit as weber (Wb) and A is the area of circular loop. According to Faraday's law of electromagnetic induction, due to changing magnetic flux in loop, an induced emf is developed in the loop.

$$e = -\frac{d\phi}{dt} \quad (2)$$

According to Lenz's law, negative sign indicates that induced emf opposes the applied magnetic field.

Using (1) in (2) we have

$$e = -\frac{d(B\pi r^2)}{dt} = -\pi r^2 \frac{dB}{dt} \quad (3)$$

As emf is induced, there will be electric field.

$$E = \frac{V}{d}$$

Where V is applied potential which is emf induced and d is the total distance covered by electron while revolving in circular path which is circumference of the circle.

$$E = \frac{e}{2\pi r} \quad \text{here } V = e \quad (4)$$

Using (3) in (4) we get

$$E = \frac{1}{2\pi r} \left(-\pi r^2 \frac{dB}{dt} \right) = -\frac{r}{2} \frac{dB}{dt} \quad (5)$$

Due to electric field E , electron in orbit will experience force is given by

$$F = -eE$$

$$ma = -eE \quad (\because F = ma) \quad (6)$$

Using (5) in (6) we get

$$ma = -e \left(-\frac{r}{2} \frac{dB}{dt} \right) = \frac{er}{2} \frac{dB}{dt}$$

$$m \frac{dv}{dt} = \frac{er}{2} \frac{dB}{dt}$$

$$dv = \frac{er}{2m} dB$$

Integrating both sides we have

$$\int_{v_1}^{v_2} dv = \frac{er}{2m} \int_0^B dB$$

$$v_2 - v_1 = \Delta v = \frac{er}{2m} B \quad (7)$$

Where v_1 is initial velocity and v_2 is final velocity. Applied magnetic field which is gradually increases from 0 to B .

The corresponding change in dipole moment of current loop due to revolution of an electron is given by

$$\Delta m = IA$$

$$\Delta m = \frac{q}{T} A \quad (\because I = \frac{q}{T})$$

$$\text{But } T = \frac{2\pi r}{\Delta v} \quad (\because \text{Time} = \frac{\text{distance}}{\text{speed}})$$

$$\Delta m = -\frac{e\pi r^2}{\frac{2\pi r}{\Delta v}} = -\frac{e\Delta v r}{2} \quad (\text{here } q = -e) \quad (8)$$

Using (7) in (8) we get

$$\Delta m = -\frac{e}{2} \left(\frac{er}{2m} B \right) r = -\frac{e^2 r^2}{4m} B \quad (9)$$

This change in magnetic moment is for one electron. On summing overall electrons in the atom, the induced magnetic moment per atom becomes

$$\Delta m = -\frac{e^2 B}{4m} \sum r^2 \quad (10)$$

Where summation extends overall Z orbital electrons in the atom. Since the core electrons have different radii, we may write

$$\sum r^2 = Z \langle r^2 \rangle \quad (11)$$

Where $\sqrt{\langle r^2 \rangle}$ is the average radius of the electron from the field axis (i.e. Z axis). If the orbit lies in the xy plane, then

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$$

If $\langle r_0^2 \rangle$ represents the average distance of the electron from the nucleus then

$$\langle r_0^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$$

When the atom has spherical symmetry

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle$$

$$\text{Therefore } \langle r^2 \rangle = 2 \langle x^2 \rangle$$

$$\text{and } \langle r_0^2 \rangle = 3 \langle x^2 \rangle$$

$$\frac{\langle r^2 \rangle}{\langle r_0^2 \rangle} = \frac{2}{3}$$

$$\langle r^2 \rangle = \frac{2}{3} \langle r_0^2 \rangle \quad (12)$$

Using (11) and (12) in (10) we get

$$\Delta m = -\frac{e^2 B Z}{4m} \left(\frac{2}{3} \langle r_0^2 \rangle \right)$$

$$\Delta m = -\frac{Z e^2 B}{6m} \langle r_0^2 \rangle$$

If there are N number of atoms per unit volume then magnetic dipole moment per unit volume of the substance is

$$M = \frac{\Delta m}{V} = -\frac{NZe^2B}{6m} \langle r_0^2 \rangle$$

Since $B = \mu_0 H$ we have

$$M = -\frac{NZe^2\mu_0 H}{6m} \langle r_0^2 \rangle \tag{13}$$

Now magnetic susceptibility is given by

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

From equation (13) magnetic susceptibility for diamagnetic substances is

$$\chi_{dia} = -\frac{NZe^2\mu_0}{6m} \langle r_0^2 \rangle \tag{14}$$

Equation (14) is Langevin's formula for the susceptibility of diamagnetism of core electrons. It shows that for diamagnetic substances $\chi_{dia} < 0$ and it is independent of temperature. χ_{dia} for most diamagnetic materials is of the order of 10^{-6} which is found true experimentally.

2.3 Langevin Theory of Paramagnetism :

In some materials, the permanent magnetic moments of the atoms or ions are acted upon individually with no mutual interaction among them (randomly distributed), this effect is called paramagnetism. The examples of paramagnetic substances are aluminium, platinum, manganese, oxygen, tungsten etc.

The atoms of paramagnetic substances possess permanent magnetic dipoles. In the absence of external magnetic field (see Figure 2.3, $\vec{B} = 0$) the atomic dipoles are distributed randomly throughout the paramagnetic material. Therefore magnetic dipole moments of individual atomic dipoles cancel each other. Thus, paramagnetic substances do not exhibit any magnetic properties in the absence of external magnetic field.

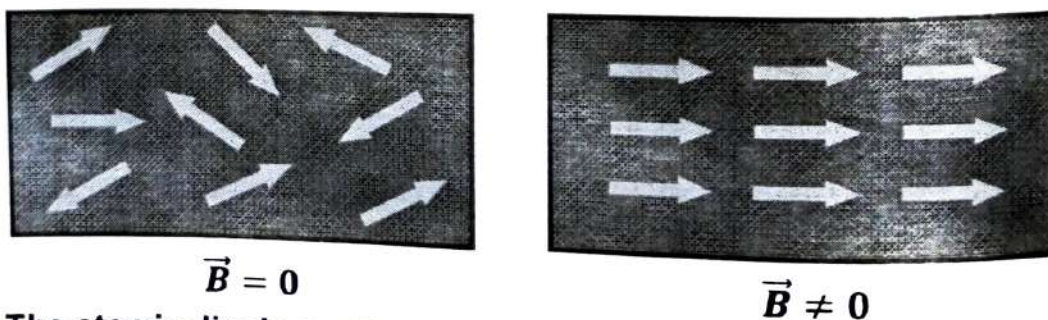


Fig. 2.3: The atomic dipole configuration for a paramagnetic material without and with magnetic field.

Now when substance is subjected to an external magnetic field \vec{B} (see Figure 2.3, $\vec{B} \neq 0$), each of the atomic dipole experiences a torque as shown in Figure 2.4. Due to torque, the atomic dipole rotates and align themselves along the direction of \vec{B} and some net magnetic dipole moment is produced in the substance in the presence of external magnetic field \vec{B} .

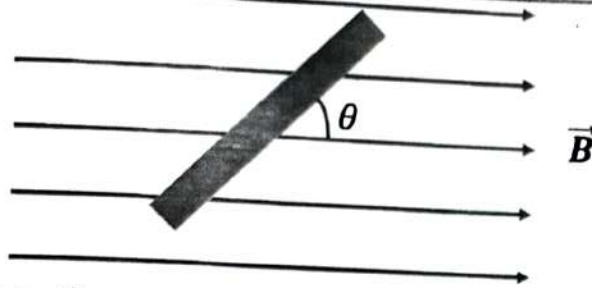


Fig. 2.4: Torque acting on a dipole in presence of magnetic field (\vec{B})

At room temperature if we go increasing \vec{B} , the total magnetic dipole moment also increases till the magnetic moment becomes maximum and the paramagnetism is maximum. At this stage, all the atomic dipoles align themselves along the direction of \vec{B} . If the temperature of substance is further increased, the orientation of atomic dipoles is opposed due to the thermal agitation of the atoms (as atoms acquires high K.E.) and the paramagnetism decreases. Thus alignment of atomic dipoles predominates over thermal agitation at low temperature and stronger \vec{B} .

Langevin explained features of paramagnetism purely on classical considerations. This theory treats paramagnetic solid as a paramagnetic gas in which every particle is assumed to have permanent magnetic dipole moment $\vec{\mu}_m$.

Let number of particles in unit volume of gas is N . When external field \vec{B} is applied to the system then potential energy of a particle whose magnetic axis makes an angle θ with \vec{B} is

$$E = -\mu_m B \cos \theta \quad (15)$$

$$dE = \mu_m B \sin \theta d\theta \quad (16)$$

Let dN out of total N number of particles have their magnetic axes inclined at an angle θ with \vec{B} . Then according to Maxwell-Boltzmann distribution law, number of particles in the energy range E to $E + dE$ is given by

$$dN = e^{(-E/kT)} dE \quad (17)$$

Where k is the Boltzmann constant having value of $1.38 \times 10^{-23} \frac{J}{K}$.

Using (15) and (16) in (17) we get

$$dN = \mu_m B e^{(\mu_m B/kT) \cos \theta} \sin \theta d\theta \quad (18)$$

$$dN = C e^{\alpha \cos \theta} \sin \theta d\theta \quad (19)$$

Where

$$C = \mu_m B \quad (20)$$

$$\alpha = \frac{\mu_m B}{kT} \quad (20)$$

Let N is the total number of particles having inclination between 0 to π then

$$N = \int_0^\pi dN \quad (21)$$

Using (18) in (21) we have

$$N = \int_0^\pi C e^{\alpha \cos \theta} \sin \theta d\theta$$

Let $\cos \theta = x \Rightarrow -\sin \theta d\theta = dx$
 When $\theta = 0, x = 1$ and $\theta = \pi, x = -1$

$$N = C \int_1^{-1} e^{\alpha x} (-dx)$$

By using property of definite integrals we have

$$N = C \int_{-1}^1 e^{\alpha x} dx = C \left[\frac{e^{\alpha x}}{\alpha} \right]_{-1}^1 = \frac{C}{\alpha} [(e^{\alpha} - e^{-\alpha})]$$

$$C = \frac{\alpha N}{(e^{\alpha} - e^{-\alpha})} \quad (22)$$

The component of $\vec{\mu}_m$ along \vec{B} is $\mu_m \cos \theta$. So, total magnetic dipole moment due to all the N particles per unit volume is called magnetization M is given by

$$M = \int_0^{\pi} \mu_m \cos \theta dN \quad (23)$$

Using (18) in (23) we have

$$M = \int_0^{\pi} \mu_m \cos \theta C e^{\alpha \cos \theta} \sin \theta d\theta$$

$$M = C \mu_m \int_0^{\pi} e^{\alpha \cos \theta} \cos \theta \sin \theta d\theta$$

Let $\cos \theta = t \Rightarrow -\sin \theta d\theta = dt$
 When $\theta = 0, t = 1$ and $\theta = \pi, t = -1$

$$M = C \mu_m \int_1^{-1} e^{\alpha t} t (-dt)$$

By using property of definite integrals we have

$$M = C \mu_m \int_{-1}^1 t e^{\alpha t} dt$$

Above integration can be solved by integration by parts formula.

$$\left[\text{Integration by parts formula: } \int uv dx = u \int v dx - \int \left(\frac{du}{dx} \int v dx \right) dx \right]$$

$$M = C \mu_m \left\{ t \int_{-1}^1 e^{\alpha t} dt - \int_{-1}^1 \left[\frac{d}{dt}(t) \int e^{\alpha t} dt \right] dt \right\}$$

$$= C \mu_m \left\{ \left[t \frac{e^{\alpha t}}{\alpha} \right]_{-1}^1 - \int_{-1}^1 \frac{e^{\alpha t}}{\alpha} dt \right\}$$

$$= C \mu_m \left\{ \left(\frac{1}{\alpha} (e^{\alpha} + e^{-\alpha}) \right) - \frac{1}{\alpha} \left[\frac{e^{\alpha t}}{\alpha} \right]_{-1}^1 \right\}$$

$$= C \mu_m \left\{ \left(\frac{e^{\alpha} + e^{-\alpha}}{\alpha} \right) - \frac{1}{\alpha^2} (e^{\alpha} - e^{-\alpha}) \right\}$$

Substituting the value of the constant C from equation (22) one gets

$$M = \frac{\alpha N \mu_m}{(e^\alpha - e^{-\alpha})} \left\{ \left(\frac{e^\alpha + e^{-\alpha}}{\alpha} \right) - \left(\frac{e^\alpha - e^{-\alpha}}{\alpha^2} \right) \right\}$$

$$M = N \mu_m \left\{ \left(\frac{e^\alpha + e^{-\alpha}}{e^\alpha - e^{-\alpha}} \right) - \frac{1}{\alpha} \right\}$$

$$M = N \mu_m \left\{ \coth \alpha - \frac{1}{\alpha} \right\} \quad \text{where } \coth \alpha = \left(\frac{e^\alpha + e^{-\alpha}}{e^\alpha - e^{-\alpha}} \right)$$

$$M = M_s L(\alpha) \tag{24}$$

Where $M_s = N \mu_m$ is a constant called as saturation magnetization when all the spins are aligned in the direction of applied magnetic field.

The term $L(\alpha) = \left\{ \coth \alpha - \frac{1}{\alpha} \right\}$ is known as Langevin function. The plot of $L(\alpha)$ with α is shown in Figure 2.5.

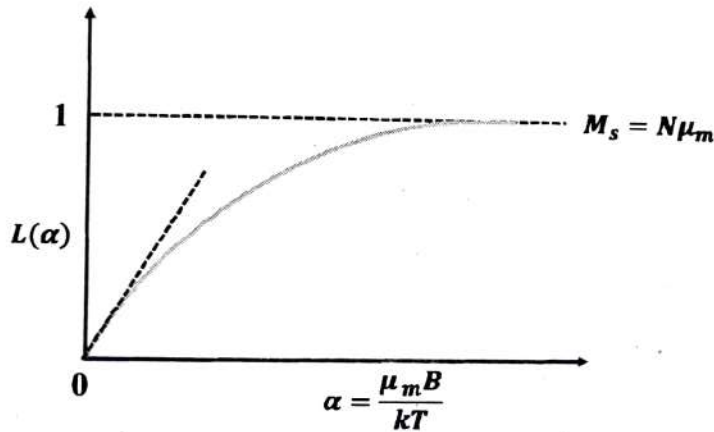


Fig. 2.5: Variation of normalized magnetization with $\alpha = \frac{\mu_m B}{kT}$

The curve indicates that for large value of $\alpha = \frac{\mu_m B}{kT}$ that is for large B and low T , $L(\alpha)$ tends to unity i.e. $M = M_s$. It is the curve when all the atomic dipoles align themselves in field direction and magnetization is maximum.

As

$$M = M_s \left\{ \coth \alpha - \frac{1}{\alpha} \right\}$$

$$M = M_s \left\{ \left(\frac{1}{\alpha} + \frac{\alpha}{3} - \frac{\alpha^3}{45} + \dots \right) - \frac{1}{\alpha} \right\}$$

$$M = M_s \left\{ \left(\frac{\alpha}{3} - \frac{\alpha^3}{45} + \dots \right) \right\}$$

For small value of α , i.e. $\alpha \ll 1$ we can write

$$M = M_s \left(\frac{\alpha}{3} \right)$$

As $\chi = \frac{M}{H}$, magnetic susceptibility for paramagnetic substances is

$$\chi_{para} = \frac{M}{H} = \frac{M_s \left(\frac{\alpha}{3} \right)}{H}$$

$$\chi_{para} = \frac{M_s \left(\frac{\mu_m B}{3 kT} \right)}{H}$$

$$\chi_{para} = \frac{M_s \mu_m B}{3HkT}$$

Since $B = \mu_0 H$ and by putting value of M_s back in above equation we have

$$\chi_{para} = \frac{N \mu_m^2 \mu_0}{3kT}$$

$$\chi_{para} = \left(\frac{N \mu_m^2 \mu_0}{3k} \right) \frac{1}{T} \tag{25}$$

This can be written in a simplified way

$$\chi_{para} = \frac{C}{T} \text{ which is known as Curie law.}$$

Where $C = \frac{N \mu_m^2 \mu_0}{3k}$ is constant called as Curie constant. Equation (25) shows that for paramagnetic substance χ_{para} is positive and varies inversely with absolute temperature as shown in Figure 2.6.

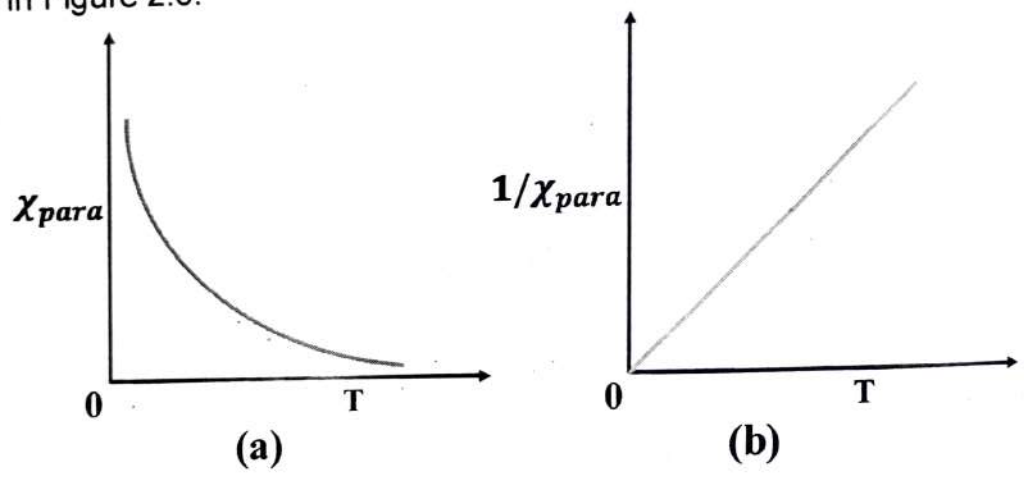


Fig. 2.6: Variation (a) χ_{para} and (b) $1/\chi_{para}$ with temperature T for a paramagnetic material illustrating Curie law, $\chi_{para} = \frac{C}{T}$

2.4 Quantum Theory of Paramagnetism :

The classical theory assumes that the permanent magnetic dipole moment ($\vec{\mu}$) of atom can possess any orientation with respect to the applied magnetic field (\vec{B}). But according to quantum theory $\vec{\mu}$ can only have finite set of orientations with applied magnetic field. The magnetic dipole moment of an atom is given by

$$\vec{\mu} = -g \mu_B \vec{J} \tag{26}$$

Where g is Lande factor given by $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$ and $\mu_B = \frac{eh}{4\pi m}$ is called as Bohr Magneton which has a value of $9.27 \times 10^{-24} \text{ Am}^2$. It is the quantum of orbital magnetic moment and is accepted as one unit for measuring the magnetic moments of atomic systems. \vec{J} is the total angular momentum given by $\vec{J} = \vec{L} + \vec{S}$, where \vec{L} is the orbital angular momentum and \vec{S} is the spin angular momentum.

The potential energy of a magnetic dipole in a uniform magnetic field is given by

$$U = -\vec{\mu} \cdot \vec{B} = -\mu B \cos \theta \tag{27}$$

Using magnitude of $\vec{\mu}$ from equation (26) in (27) we get

$$U = g\mu_B B J \cos \theta$$

$$U = g\mu_B B m_J \tag{28}$$

Where $m_J = J \cos \theta$ is the projection of \vec{J} on magnetic field \vec{B} (see Figure 2.7) and known as magnetic quantum number. It takes values $+J, J - 1, \dots, 0, \dots, -J$ i.e. $(2J + 1)$ values.

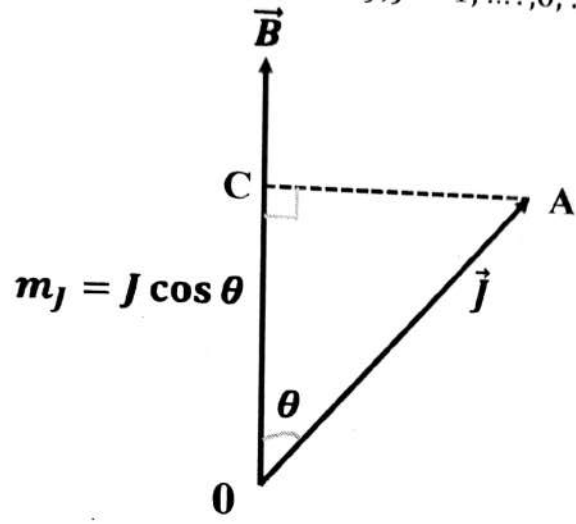


Fig. 2.7: Projection of \vec{J} on magnetic field \vec{B}

For 1s electron, $L = 0, S = \frac{1}{2} \Rightarrow J = 0 + \frac{1}{2} = \frac{1}{2}$

$m_J = 2\left(\frac{1}{2}\right) + 1 = 2 \Rightarrow m_J = -\frac{1}{2}$ or $+\frac{1}{2}$.

From Lande factor formula we get $g = 2$. From equation (28) we get values of U as follows

For $m_J = \frac{1}{2}, g = 2$ we get $U = \mu_B B$ and

For $m_J = -\frac{1}{2}, g = 2$ we get $U = -\mu_B B$

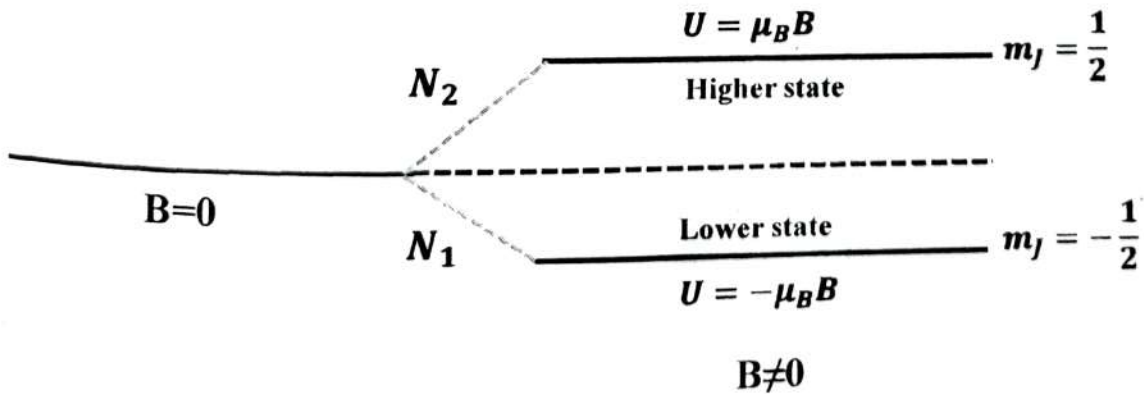


Fig. 2.8: Splitting of an energy level for an electron with spin $\frac{1}{2}$ and zero orbital momentum in a magnetic field

Let N be the number of atoms per unit volume of paramagnetic substance (29)

$$N = N_1 + N_2$$

Where $N_1 =$ Number of atoms in lower state, $N_2 =$ Number of atoms in higher state.

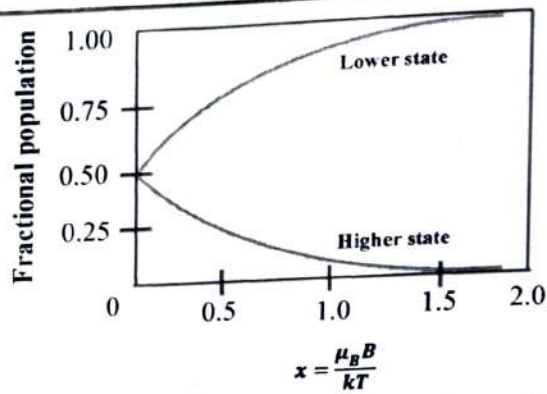


Fig. 2.9: Fractional populations of a two level system in thermal equilibrium at temperature T in a magnetic field B . The magnetic moment is proportional to the difference between the two curves.

According to Maxwell-Boltzmann law,

$$N_1 \propto e^{-U/kT} \propto e^{-(-\mu_B B)/kT} = N_0 e^{\mu_B B/kT} \quad (30)$$

$$N_2 \propto e^{-U/kT} \propto e^{-(\mu_B B)/kT} = N_0 e^{-\mu_B B/kT} \quad (31)$$

Let
$$\frac{\mu_B B}{kT} = x \quad (32)$$

Using (32) in (30) and (31) we get

$$N_1 = N_0 e^x \quad (33)$$

$$N_2 = N_0 e^{-x} \quad (34)$$

Using (33) and (34) equation (29) becomes

$$N = N_0 e^x + N_0 e^{-x} = N_0 (e^x + e^{-x}) \quad (35)$$

Fractional population in lower state is given by

$$\frac{N_1}{N} = \frac{N_0 e^x}{N_0 (e^x + e^{-x})} = \frac{e^x}{(e^x + e^{-x})} \quad (36)$$

Fractional population in higher state is given by

$$\frac{N_2}{N} = \frac{N_0 e^{-x}}{N_0 (e^x + e^{-x})} = \frac{e^{-x}}{(e^x + e^{-x})} \quad (37)$$

At $x = 0$, $\frac{N_1}{N} = \frac{1}{2}$ and $\frac{N_2}{N} = \frac{1}{2}$

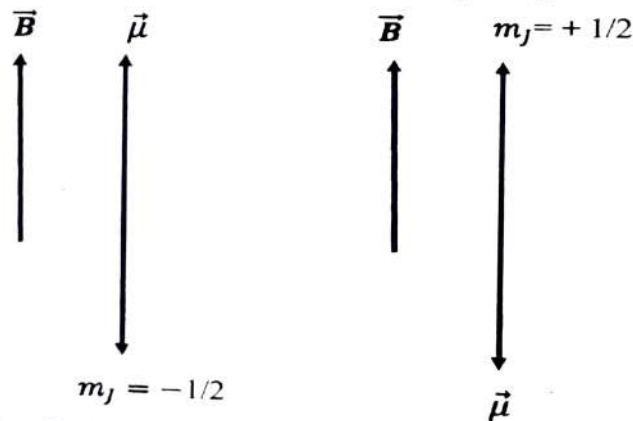


Fig. 2.10: Spin quantization of an electron

Net magnetization is given by (See Figure 2.10)

$$\vec{M} = N_1 \vec{\mu} - N_2 \vec{\mu}$$

Using (36) and (37) we have

$$\begin{aligned} \vec{M} &= N\vec{\mu} \left(\frac{N_1}{N} - \frac{N_2}{N} \right) \\ &= N\vec{\mu} \left(\frac{e^x}{(e^x+e^{-x})} - \frac{e^{-x}}{(e^x+e^{-x})} \right) \\ &= N\vec{\mu} \left(\frac{e^x - e^{-x}}{e^x + e^{-x}} \right) \\ &= N\vec{\mu} \tanh x \end{aligned}$$

The magnitude of net magnetization is

$$M = N\mu \tanh x \quad (38)$$

If $x \ll 1$, i.e. $\frac{\mu_B B}{kT} \ll 1$ then $\tanh x \approx x$ (39)

Using (39) in (38) we get

$$M = N\mu x$$

For $1s$ e^- system, $g = 2, J = \frac{1}{2} \Rightarrow \mu = \mu_B$ ($\because \vec{\mu} = -g\mu_B \vec{J}$ and taking its magnitude)

Therefore,

$$M = N\mu_B x$$

$$M = N\mu_B \frac{\mu_B B}{kT} = \frac{N\mu_B^2 B}{kT} = \frac{N\mu_B^2 \mu_0 H}{kT}$$

Now

$$\chi_{para} = \frac{M}{H} = \frac{N\mu_B^2 \mu_0}{kT}$$

This result is for $1s$ e^- system.

In general each level will split into $(2J + 1)$ energy levels. So, instead of $\tanh x$ in equation (38) we get another function which is $B_J(x)$ called as Brillouin function and it describes the variation of induced magnetization with J , temperature and magnetic field.

$$M = N\mu B_J(x) \quad (40)$$

Where, $B_J(x) = \left[\frac{2J+1}{2J} \right] \coth \left[\frac{(2J+1)x}{2J} \right] - \left[\frac{1}{2J} \right] \coth \left[\frac{x}{2J} \right]$ (41)

For $x \ll 1$, i.e. $\frac{\mu_B B}{kT} \ll 1$ then $\coth x \approx \frac{1}{x} + \frac{x}{3}$ (42)

Using (42) in (41) we get

$$B_J(x) = \left[\frac{2J+1}{2J} \right] \left[\frac{2J}{(2J+1)x} + \frac{(2J+1)x}{6J} \right] - \left[\frac{1}{2J} \right] \left[\frac{2J}{x} + \frac{x}{6J} \right]$$

By solving above equation we get

$$B_J(x) = \frac{(J+1)x}{3J} \quad (43)$$

Using (43) in (40) we have

$$\begin{aligned} M &= N\mu \frac{(J+1)x}{3J} = N\mu \frac{(J+1)\mu_B B}{3J kT} = \frac{N\mu^2 (J+1)B}{3JkT} \quad (\because \mu_B \approx \mu) \\ M &= \frac{Ng^2 \mu_B^2 J^2 (J+1)B}{3JkT} = \frac{NB\mu_B^2 J(J+1)g^2}{3kT} = \frac{NB\mu_B^2 P_{eff}^2}{3kT} \end{aligned}$$

Where $P_{eff} = g\sqrt{J(J+1)}$ (44)

and is called effective number of Bohr magneton.

Since $B = \mu_0 H$

$$M = \frac{N\mu_0 H \mu_B^2 P_{eff}^2}{3kT}$$

$$\chi_{para} = \frac{N\mu_0 \mu_B^2 P_{eff}^2}{3kT} = \left(\frac{N\mu_0 \mu_B^2 P_{eff}^2}{3k} \right) \frac{1}{T} \quad (45)$$

This can be written as $\chi_{para} = \frac{C}{T}$ which is Curie law.

Where,

$C = \frac{N\mu_0\mu_B^2 P_{eff}^2}{3k}$ is constant known as Curie Constant.

The equation (45) when compared with equation (25), is found to be quite identical with classical result with a difference that in quantum result $\mu_B P_{eff}$ replaces μ_m .

2.5 Paramagnetic Susceptibility of Conduction Electron:

In some simple metals like sodium or aluminium, the valence electrons are no longer attached to any particular atom. As a result, although the metal ions do not contribute to the magnetic moment, the moving electrons produce a non-zero magnetic moment.

This free electron Paramagnetism is a weak phenomenon and is often referred to as Pauli Paramagnetism or Paramagnetism of conduction electrons. Most metals show paramagnetic behaviour. It is rather small and independent of temperature and is quite different from the Curie law behaviour of a normal paramagnetic ion.

The cause of the weak Paramagnetism was explained by W. Pauli (1927) in terms of the Fermi-Dirac statistics of electrons in solids. It is known as Pauli Paramagnetism. A metal is defined according to the Drude-Lorentz model as an ionic lattice embedded in a sea of electron gas (gas, because electrons are not supposed to interact with each other). The electron gas in metals may be treated as quantum mechanical particles while the atoms or ions in paramagnetic materials behave as classical particles. With the help of the uncertainty principle ($\Delta x \Delta p \approx \hbar$), we can show that the electrons should be treated as quantum particles if kept below a certain temperature and molecules should be treated as classical particles at all the temperatures. The temperature below which particles should be treated as quantum particles is given by T_q (Where, $T_q = \frac{\hbar^2 N^{2/3}}{3km}$). For the electron gas, all temperatures are below T_q , and hence we take a limiting temperature T equal to absolute zero for our discussion.

In order to understand the existence of Pauli Paramagnetism, let us recall the distribution between densities of states versus energy at absolute zero of temperature. That curve may be split into two parts with spins pointing in the positive Z-direction and other with spin in the opposite direction as shown in Figure 2.11 (a).

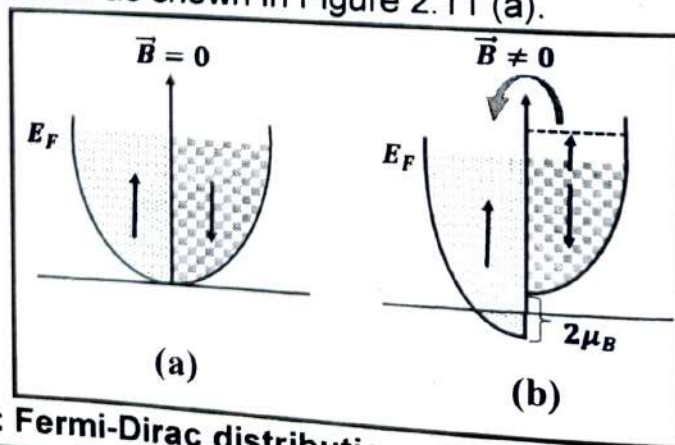


Fig. 2.11: Fermi-Dirac distribution at (a) $B = 0$ and (b) $B \neq 0$

In absence of an external magnetic field, the distribution of electrons with spins parallel to the Z -direction is equal to the number of electrons with opposite spins and hence the net magnetic moment of the electron gas is zero.

When a field is applied along the Z -direction, the energy of the spins aligned parallel to B is lowered by the amount μ_B , while the energy of the spins opposite to B is raised by the same amount as shown in Figure 2.11 (b). As a result of this, the Fermi level for the two spin distributions shift with respect to each other and give rise to energetically unstable situation. In order to acquire the stable configuration, the electrons lying near the Fermi level with antiparallel spins flip into the region of parallel spins until the two Fermi levels become equal again as shown in Figure 2.11 (b).

The number of electrons which effectively change their direction is equal to the density of states at the energy level in one of the spin distribution times the change in energy, i.e.

$$N_{eff} = \frac{1}{2} g(E_F) \mu_B B \quad (46)$$

Where the factor $\frac{1}{2}$ is due to the fact that the density of states of one spin distribution is half of the total density of states. Thus after the application of the field, the number of electrons with spins parallel to the field is greater than the electrons with opposite spin by N_{eff} , leading to a net magnetization. Since each flip increases the magnetization by $2\mu_B$ (from $-\mu_B$ to $+\mu_B$), the net magnetization is given by

$$M = N_{eff} \times 2\mu_B = g(E_F) \mu_B^2 B \quad (47)$$

And hence the Pauli spin susceptibility of the electron pair is

$$\chi_{Pauli} \approx \mu_0 \mu_B^2 g(E_F) \quad (48)$$

According to equation (48), χ_{Pauli} is essentially temperature independent. This is clear from the fact that temperature has a very small effect on the Fermi-Dirac distribution of the electrons. Now density of states per unit volume is given by

$$g(E_F) = \frac{3N}{2E_F} \text{ where } E_F \text{ is the Fermi energy.}$$

So that

$$\frac{3\mu_0 N \mu_B^2}{2E_F} = \frac{3\mu_0 N \mu_B^2}{2kT_F} \quad (49)$$

Where, $E_F = kT_F$ and T_F is the Fermi temperature.

Equation (49) is known as Pauli Paramagnetism formula. This equation can be rewritten in terms of the classical susceptibility as

$$\chi_{Pauli} = \frac{3}{2} \chi_c \frac{T}{T_F} \quad (50)$$

Where, $\chi_c = \frac{\mu_0 N \mu_B^2}{kT}$ is the classical susceptibility for $J = \frac{1}{2}$. Since T_F is normally very high, χ_{Pauli} is smaller than χ_c by about two orders of magnitude, which is in agreement with the experimental results.

2.6 Magnetic Properties of Rare Earth Ions and Iron Group Ions with Graphical Representation :

It was noted in section 2.4 that paramagnetism requires the existence of partly filled electronic shells. Thus paramagnetic compounds are essentially 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 palladium group (4d), the platinum (5d), and the uranium group (5f-6d) have received relatively little attention.

2.6.1 The Rare Earth Ions :

The theory outlined in section 2.4 describes the behaviour of most of the rare earth salts quite well. This may be seen from Figure 2.12, where the full curve represents the effective number of Bohr magnetons calculated by van Vleck from expression $P_{eff} = g\sqrt{J(J+1)}$. The J values and g were obtained from Hund's rules and from Lande factor formula as outlined in section 2.4. The vertical lines correspond to observed values of P_{eff} , obtained from measurements of the temperature dependence of χ_m (see equation 45). 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.

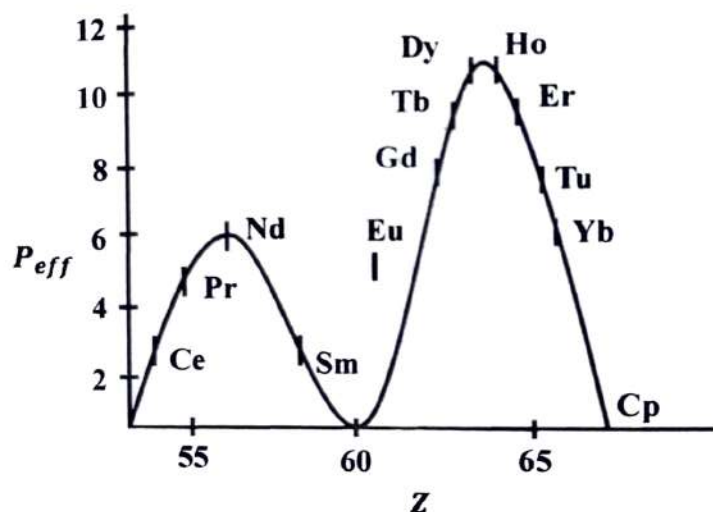


Fig. 2.12: The effective moment in Bohr magnetons as function of the number of the number of electrons for the trivalent positive rare earth ions. The full curve represents the values calculated from expression (44) ; the vertical lines represent the range of experimental values. (After Bates, Modern Magnetism, Cambridge, 1951, p.148)

2.6.2 The Iron Group Ions :

If one calculates the effective number of Bohr Magnetons for the ions of the iron group from expression (44), the results do not agree at all with the experimental values obtained from the Curie law. This may be seen from figure 2.13 where the vertical lines represent experimental values and dashed curve represents expression (44). However, if one assumes that only the electron spins contribute to the magnetization i.e. if one replaces J by S from expression of P_{eff} one obtains quite good agreement with experiment (full curve in Figure 2.12). Thus the iron group ions behave 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. Stoner suggested the following explanation for the different behaviour of the rare earth and iron groups in this respect.

In the solid state, the paramagnetic ions find themselves in strong electric fields produced by neighbouring diamagnetic ions. In the iron group, the paramagnetic 3d electrons are the outermost electrons and these are therefore fully exposed to the crystalline field. Consequently, the orbital motion is locked into the field of the neighbours and cannot orient itself in an external magnetic field. The electron spin has no direct interaction with the electrostatic field and thus orients itself freely in an external magnetic field.

In the rare earth group, on the other hand, the paramagnetic 4f electrons lie relatively deep inside the ions, because the outer electrons occupy 5s and 5p levels. The screening of the 4f electrons from the crystalline field thus leaves the orbits of the 4f electrons practically the same as in the free ion.

Further experimental evidence for the idea of quenching of the orbital momentum in the iron group salts has been obtained from studies of the anisotropy of the susceptibility in single crystals. The crystalline fields distort the orbits in particular directions and thus the magnetic field associated with these orbits has directional properties. The spin magnetic moment orients itself along the resultant of the external field plus the field associated with the orbits, and anisotropy results.

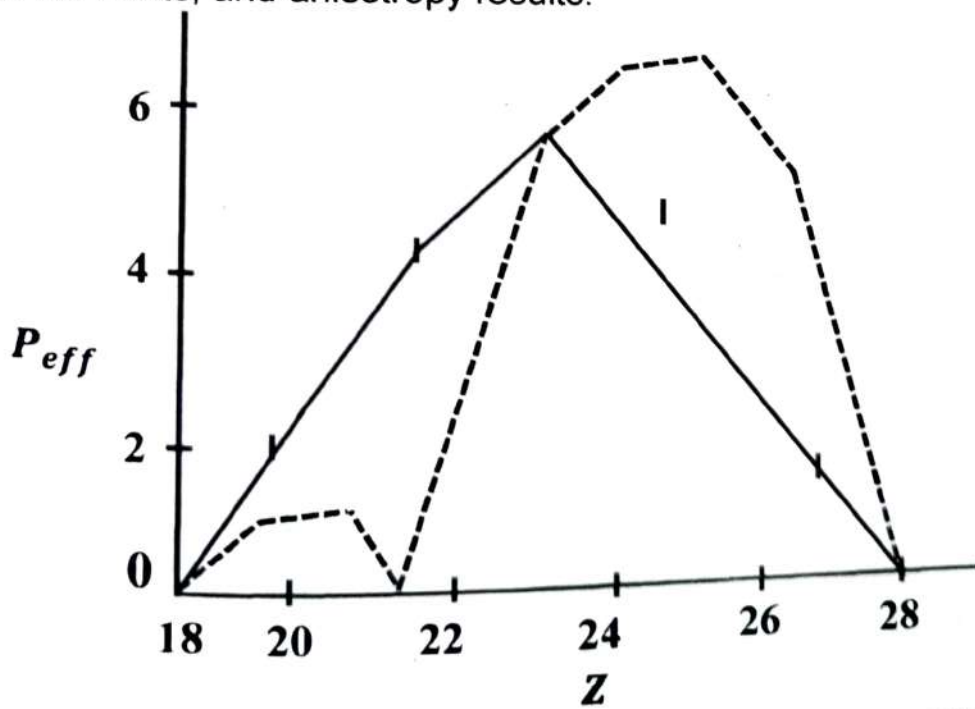


Fig. 2.13 The effective moment in Bohr Magnetons for the iron group as function of the number of electrons Z in the ions. The dashed curve represents the values calculated from expression (44) ; the full curve refers to formula $P_{eff} = g\sqrt{S(S+1)}$. The vertical lines represent the ranges of experimental values. (After Bates, Modern Magnetism, Cambridge, 1951, p.152)

2.7 Crystal Field Splitting :

The equation (45) fits well for many paramagnetic crystals including the materials consisting ions of rare earth group. Deviations do occur, however, these are due to the fact that energy level system and states of an ion in a crystal are not necessarily the same as those for a free ion. The main reason for this is that in a crystal, a paramagnetic ion is surrounded by other ions with which it will interact. In particular, the neighbouring ions whether magnetic or not, will still be electrically charged and these create an inhomogeneous electric field in the neighbourhood of the paramagnetic ions which we are considering. This is often called *crystal field*. The interaction of the paramagnetic ions with the crystal field has two major consequences: The coupling \vec{L} and \vec{S} is largely broken up, so that the states are no longer specified by their \vec{J} values; further, the $(2L + 1)$ sublevels belonging to a given L which are degenerate in the free ion may now split up by the crystal field. The splitting decreases the contribution of the orbital motion of the magnetic moment.

Crystal field splitting is unimportant for rare earth ions, because their partially filled $4f$ shells lie deep inside the ions (beneath filled $5s$ and $5p$ shells). In contrast to this, the partially filled d -shells are subject to non-negligible electric fields that do not have spherical symmetry, but only the symmetry of the crystalline site at which the ion is located. As a result, the basis for Hund's rules is partially invalidated. As it turns out, the first two of Hund's rules can be retained, even in the crystalline environment. The crystal field must, however, be introduced as a perturbation on the $(2S + 1)(2L + 1)$ fold set of states determined by the first two rules. This perturbation acts in addition to the spin-orbit coupling. Therefore Hund's third rule (which resulted from the action of the spin-orbit coupling alone) must be modified.

In case of the transition metal ions from the iron group (partially filled $3d$ shells) the crystal field is very much larger than the spin-orbit coupling, so that to a first approximation a new version of Hund's third rule can be constructed in which the perturbation of spin-orbit coupling is ignored altogether, in favour of the crystal field perturbation. This latter perturbation will not split the spin degeneracy, since it depends only on spatial variables and therefore commutes with S , but it can completely lift the degeneracy of the orbital L -multiplet, if it is sufficiently asymmetric. The result will then be a ground state multiplet in which the mean value of every component of \vec{L} vanishes (even though \vec{L}^2 still has the mean value $L(L + 1)$). One can interpret this classically as arising from a precession of the orbital angular momentum in the crystal field, so that although its magnitude is unchanged, all its components average to zero.

2.8 Quenching of the Orbital Angular Momentum :

In an electric field directed toward a fixed nucleus, the plane of a classical orbit is fixed in space, so that all the orbital angular momentum components L_x, L_y, L_z are constant. In quantum theory one angular momentum component, usually takes as L_z , and the square of the total orbital angular momentum L^2 are constant in a central field. In a non-

central field the plane of the orbit will move about; the angular momentum components are no longer constant and may average to zero. In a crystal L_z will no longer be a constant of the motion, although to a good approximation L^2 may continue to be constant. When L_z averages to zero, the orbital angular momentum is said to be quenched. The magnetic moment of a state is given by the average value of the magnetic moment operator $\mu_B(\vec{L} + 2\vec{S})$. In a magnetic field along the Z-direction the orbital contribution to the magnetic moment is proportional to the quantum expectation value of L_z ; the orbital magnetic moment is quenched if the mechanical moment L_z is quenched.

Solved Problems

Problem 1:

Estimate the order of the diamagnetic susceptibility of copper by assuming that only one electron per atom makes the contribution. The radius of the copper atom is 1\AA and the lattice parameter is 3.608\AA .

Solution:

Given: $r = 1\text{\AA} = 10^{-10}m$, $a = 3.608 \times 10^{-10}m$, $\chi_{dia} = ?$

We know that copper is a face centred cubic crystal, so it has 4 atoms per unit cell. The number of electrons per unit volume can be found as

$$N = \frac{n}{a^3} = \frac{4}{(3.608 \times 10^{-10})^3} = 8.5 \times 10^{28}/m^3$$

Now making use of eq. (14) and substituting all values, we obtain

$$\chi_{dia} = -\frac{NZe^2\mu_0}{6m} \langle r_0^2 \rangle = \frac{4\pi \times 10^{-7} \times 8.5 \times 10^{28} \times (1.6 \times 10^{-19})^2 \times 10^{-20}}{6 \times 9.1 \times 10^{-31}} = -5 \times 10^{-6}$$

Problem 2:

Approximately how large must be the magnetic induction for the orientation energy to be comparable to the thermal energy at room temperature? Assume $\mu_m = 5\mu_B$.

Solution:

Given: $\mu_m = 5\mu_B$, $T = 300K$, $B = ?$

Here, the magnetic energy = $\mu_m B$ and thermal energy = kT . Now, according to the question $\mu_m B = kT$

$$\text{So that } B = \frac{kT}{\mu_m} = \frac{kT}{5\mu_B} = \frac{1.38 \times 10^{-23} \times 300}{5 \times 9.27 \times 10^{-24}} = 89.32 \frac{W}{m^2} \approx 10^2 \frac{W}{m^2}$$

Problem 3:

A paramagnetic salt contains $10^{28} \frac{\text{ions}}{m^3}$ with magnetic moment of one Bohr magneton. Calculate the paramagnetic susceptibility and the magnetization produced in a uniform magnetic field of $10^6 \frac{A}{m}$, at room temperature.

Solution:

Given: $= 10^{28} \frac{\text{ions}}{\text{m}^3}$, $\mu_m = \mu_B = 9.27 \times 10^{-24} \text{ Am}^2$, $H = 10^6 \frac{\text{A}}{\text{m}}$, $T = 300\text{K}$, $\chi_{\text{para}} = ?$, $M = ?$
 From eq. (25), we know that the paramagnetic susceptibility is given by

$$\chi_{\text{para}} = \frac{N\mu_m^2\mu_0}{3kT} = \frac{10^{28} \times (9.27 \times 10^{-24})^2 \times 4\pi \times 10^{-7}}{3 \times 1.38 \times 10^{-23} \times 300} = 0.87 \times 10^{-4}$$

Further, the magnetization is given by

$$M = \chi H = \chi_{\text{para}} H \text{ here for paramagnetic material } \chi = \chi_{\text{para}}$$

$$M = 0.87 \times 10^{-4} \times 10^6 = 87 \frac{\text{A}}{\text{m}}$$

Problem 4:

The applied magnetic field in copper is $10^6 \frac{\text{A}}{\text{m}}$. If the magnetic susceptibility of copper is -0.8×10^{-5} , calculate the flux density and the magnetization in copper.

Solution:

Given: $H = 10^6 \frac{\text{A}}{\text{m}}$, $\chi = -0.8 \times 10^{-5}$, $\mu_0 = 4\pi \times 10^{-7} \frac{\text{H}}{\text{m}}$, $B = ?$, $M = ?$

Using equation $M = \chi H$ we have

$$M = -0.8 \times 10^{-5} \times 10^6 = -8 \frac{\text{A}}{\text{m}}$$

Further the relation between B , H and M is given by $B = \mu_0(H + M)$.

Therefore, $B = \mu_0(H + M) = 4\pi \times 10^{-7}(-8 + 10^6) = 1.256 T$

Problem 5:

A magnetic field $10^4 \frac{\text{A}}{\text{m}}$ produces a magnetic induction of $4\pi \frac{\text{Wb}}{\text{m}^2}$ in an iron rod. Calculate the susceptibility.

Solution:

Given: $H = 10^4 \frac{\text{A}}{\text{m}}$, $B = 4\pi \frac{\text{Wb}}{\text{m}^2}$, $\chi = ?$

The relative permeability is given by $\mu_r = 1 + \chi = \frac{B}{\mu_0 H}$

$$\chi = \frac{B}{\mu_0 H} - 1 = \frac{4\pi}{4\pi \times 10^{-7} \times 10^4} - 1 = 999$$

Problem 6:

The magnetic moment of the magnet weighing 0.062 kg is $6 \times 10^{-6} \text{ Am}^2$. If its density is $6200 \frac{\text{kg}}{\text{m}^3}$, calculate the intensity of magnetization.

Solution:

Given: $W = 0.062 \text{ kg}$, $m = 6 \times 10^{-6} \text{ Am}^2$, $\rho = 6200 \frac{\text{kg}}{\text{m}^3}$, $M = ?$

$$\text{Volume } V = \frac{W}{\rho} = \frac{0.062}{6200} = 10^{-5} \text{ m}^3$$

Now intensity of magnetization is given by

$$M = \frac{m}{V} = \frac{6 \times 10^{-6}}{10^{-5}} = 0.6 \frac{A}{m}$$

Problem 7:

The magnetic field of intensity $1600 \frac{A}{m}$ produces a magnetic flux of $4 \times 10^{-4} \text{ Wb}$ in an iron bar of area of cross-section 4 cm^2 . Calculate the magnetic permeability and susceptibility of the specimen.

Solution:

Given: $H = 1600 \frac{A}{m}$, $\phi = 4 \times 10^{-4} \text{ Wb}$, $A = 4 \text{ cm}^2 = 4 \times 10^{-4} \text{ m}^2$, $\chi = ?$, $\mu = ?$

$$\text{We have } \phi = BA \Rightarrow B = \frac{\phi}{A} = \frac{4 \times 10^{-4}}{4 \times 10^{-4}} = 1 \frac{\text{Wb}}{\text{m}^2}$$

$$\mu = \frac{B}{H} = \frac{\phi}{AH} = \frac{1}{1600} = 6.25 \times 10^{-4} \frac{H}{m}$$

If χ is the susceptibility, then

$$\chi = (\mu_r - 1) = \frac{\mu}{\mu_0} - 1 = \frac{6.25 \times 10^{-4}}{4\pi \times 10^{-7}} - 1 = 496.6$$

Problem 8:

A magnetic material has a magnetization of $2300 \frac{A}{m}$ and produces a flux density of $0.00314 \frac{\text{Wb}}{\text{m}^2}$. Calculate the magnetizing force and relative permeability of the material.

Solution:

Given: $B = 0.00314 \frac{\text{Wb}}{\text{m}^2}$, $M = 2300 \frac{A}{m}$, $H = ?$, $\mu_r = ?$

As we have $B = \mu_0(H + M)$ then

$$H = \frac{B}{\mu_0} - M = \frac{0.00314}{4\pi \times 10^{-7}} - 2300 = 198 \frac{A}{m}$$

But $B = \mu H = \mu_r \mu_0 H$ implies that

$$\mu_r = \frac{B}{\mu_0 H} = \frac{0.00314}{4\pi \times 10^{-7} \times 198} = 12.56$$

**Exercise****Q. 1. Short Answer Questions:**

- 1) What is the relation between magnetic field and magnetic flux associated with the current carrying loop?
- 2) Give the relation between magnetic susceptibility, magnetization and magnetic field.
- 3) What is Bohr magneton? Give its value along with SI unit.
- 4) What is the order of the susceptibility of a diamagnetic material?

- 5) Give the SI unit of magnetic flux, magnetic field, magnetic susceptibility and relative permeability.
- 6) Write the formula for magnetic susceptibility of diamagnetic substances obtained by Langevin theory of diamagnetism.
- 7) What is Pauli paramagnetism? Write expression for Pauli paramagnetism.
- 8) What do you mean by crystal field splitting?
- 9) Write expression for paramagnetic susceptibility obtained by Langevin theory as well as quantum theory.
- 10) Write formula for effective number of Bohr magneton in terms of J and S also.
- 11) What is the relation between magnetic moment and current?
- 12) Give the formula for the Lande g factor.
- 13) What is the relation between total angular momentum \vec{J} , orbital angular momentum \vec{L} and spin angular momentum \vec{S} ?
- 14) What do you mean by quenching of orbital angular momentum?
- 15) Write relation between the Fermi energy and the Fermi temperature.

Q. 2. Long Answer Type Questions:

- 1) Show that the magnetic susceptibility for diamagnetic substances is negative and independent of temperature.
- 2) Explain the paramagnetic phenomenon. Derive an expression for paramagnetic susceptibility using Langevin theory of paramagnetism.
- 3) Derive an expression of Curie law for paramagnetic substances using quantum theory of paramagnetism.
- 4) Obtain an expression for paramagnetic susceptibility of conduction or free electrons i.e. Pauli paramagnetism.
- 5) Explain magnetic properties of rare earth ions and iron group ions with graphical representation.
- 6) Explain in detail the term Crystal Field Splitting.
- 7) Explain the paramagnetism in rare earth ions and iron group ions on the basis of quenching of orbital angular momentum.
- 8) Show that the magnetic susceptibility for paramagnetic substances varies inversely with temperature. Also plot the curve of paramagnetic susceptibility with temperature illustrating Curie law.

Q. 3. Unsolved Problems:

- 1) A magnetic material has a magnetization of $3300 \frac{A}{m}$ and produces a flux density of $0.0044 \frac{Wb}{m^2}$. Calculate the magnetizing force.
Ans : $201 \frac{A}{m}$
- 2) The applied magnetic field in a piece of ferric oxide is $10^6 \frac{A}{m}$. If the magnetic susceptibility of material at room temperature is 1.5×10^{-3} , calculate the flux density and the magnetization of the material.

Ans : $1.5 \times 10^{-3} \frac{A}{m}$, 1.259 T

- 3) The magnetic susceptibility of copper is -0.5×10^{-5} . Calculate the magnetic moment per unit volume in copper when it is subjected to a field of $10^4 \frac{A}{m}$.

Ans : $-0.05 \frac{A}{m}$

- 4) A paramagnetic material which has $10^{28} \frac{\text{atoms}}{m^3}$. The magnetic moment of each atom is $1.8 \times 10^{-23} Am^2$. Calculate the paramagnetic susceptibility at 300 K. What would be the dipole moment of a bar of this material 0.1m long and 1 sq cm cross-section placed in a field of $8 \times 10^4 \frac{A}{m}$.

Ans : 3.28×10^{-4} , $2.62 \times 10^{-4} Am^2$

- 5) The magnetic susceptibility of a material is 1000. If this material is placed in a magnetic field of strength $1000 \frac{A}{m}$, what will be value of magnetic induction?

Ans : $0.4\pi \frac{Wb}{m^2}$

- 6) The magnetic susceptibility of silicon is -0.4×10^{-5} . What is the flux density and magnetization in a magnetic field of intensity $10^5 \frac{A}{m}$?

Ans : $0.124 \frac{Wb}{m^2}$, $-0.4 \frac{A}{m}$

- 7) A circular loop conductor having a diameter of 50 cm carries a current of 100 mA. The loop is placed in a magnetic field having a uniform flux density of $0.05 \frac{Wb}{m^2}$ with its axis inclined at 60° to the direction of the field. Calculate the values of magnetic dipole moment and torque experienced by the current loop.

Ans : $0.0196 Am^2$, $0.0025 Nm$

- 8) Given that magnetic permeability of free space $\mu_0 = 4\pi \times 10^{-7} \frac{H}{m}$, mass of an electron $e = 1.6 \times 10^{-19} C$, Planck's constant $h = 6.625 \times 10^{-34} Js$ and mass of an electron $m_e = 9.1 \times 10^{-31} kg$. Compute Bohr magneton.

Ans : $9.27 \times 10^{-24} Am^2$




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