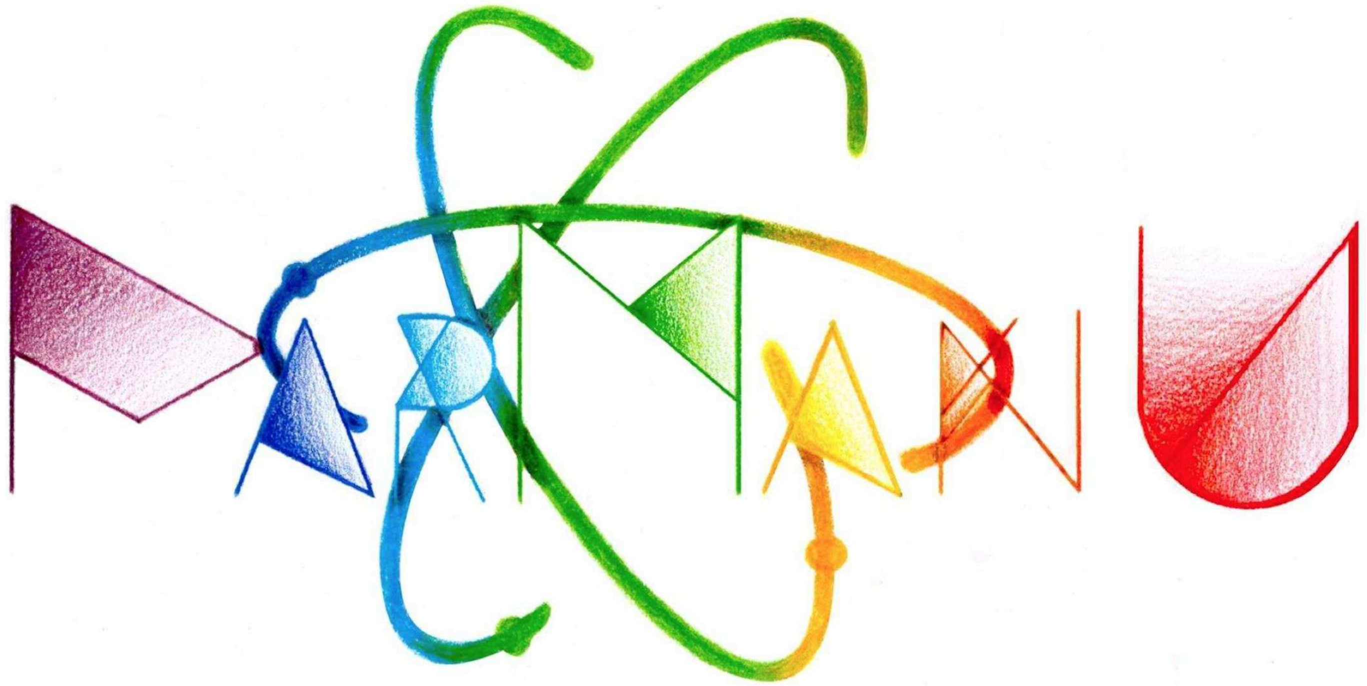
Diamagnetism & Paramagnetism

Dr.D.V. Kala

PARMANU

Physics Association for Revolutionary Methods of Advancement and Understanding.

Scanned by CamScanner



Physics Association for Revolutionary Methods of Advancement
& Understanding

Scanned by CamScanner

DIAMAGNETISM AND PARAMAGNETISM

The magnetic moment of a free atom has got three principal sources :-

(1) The spin with which the electrons are endowed.
(2) Their orbital angular momentum about the nucleus.
(3) Change in the orbital moment induced by an external magnetic field.

The first two effects give paramagnetic contributions to the magnetization and third gives riseto diamagnetism.

Atoms with filled electrons shells have zero spin and zero orbital moment. The moments we talk in this chapter are associated with unfilled shells in total magnetic field exists when the atoms have unfilled shells.

Any substance if in a magnetic field gets magnetized, then its extent of magnetization is measured by a parameter (M) called as Magnetization, and is defined as 'Magnetic moment per unit volume. Then there is a parameter 'χ' which is associated with substance which is magnetised and is defined as 'magnetic susceptibility'.

$$\chi = \frac{M}{B} \qquad \text{(C.G.S. unit)}$$

$$\chi = \mu_0 \frac{M}{B} \qquad \text{(S.I. unit)}$$

'χ' is dimensionless. It is +ve for paramagnet & -ve for diamagnet.

Scanned by CamScanner

χ_M is quite frequently defined susceptibilit and it is molar susceptibility and magnetic moment per gram is symbolised as 'σ' (sigm

Ordered arrays of magnetic moment may give rise to Ferromagnetic, Ferrimagnetic, Antiferromagnetic and Antiferrimagnetic substan

We all know, nucleus is positively charged and it also spins about its axis, hence it has g its own magnetic moment known as 'Nuclear magnetic moment'. Because of its slower spin magnetic moments of nuclei are of the order o 10^{-3} times smaller than the magnetic moment of the electrons.

The usual treatment of the diamagnetism of atoms and ions employs the Larmor Theorem:

In a magnetic field the motion of the electr around central nucleus is, to the first order i B, the same as a possible motion in the absen of B, except for the superposition of a precessio of the electrons with angular frequency.

$$\omega = \frac{eB}{2mc} \qquad (C.G.S.)$$

$$\omega = e\frac{B}{2m} \qquad (S.I.) \qquad \ldots (1)$$

If the field is applied slowly, the motion in the rotating reference system will be the same as the original motion in the rest system before the application of the field.

Scanned by CamScanner

If the average electron current around the nucleus is zero, initially the application of the magnetic field will cause a finite current around the nucleus. The current is equivalent to a magnetic moment opposite to the applied field. It is assumed that the Larmor frequency is much lower than the frequency of the original motion in the central field. This condition is not satisfied in free carrier cyclotron resonance, and the cyclotron frequency is twice the frequency.

The Larmor precession of Z electrons is equivalent to an electric current,

I = (charge) (revolutions per unit time) =

$$(-Ze)\left(\frac{1}{2\pi} \cdot \frac{eB}{2m}\right) \quad (S.I.) \quad \ldots \quad (2)$$

The magnetic moment μ of a current loop is given by the product,

(current) X (area of the loop).

The area of the loop of radius 'r' is πr^2.

$$(S.I.) \quad \mu = \frac{Ze^2 B}{4m} r^2$$

$$(C.G.S.) \quad \mu = \frac{Ze^2 B}{4mc^2} r^2$$

Scanned by CamScanner

Langerin Diamagnetic Equation.

Diamagnetism is a property when magnetic field of the induced current is opposite to the applie field. Mathematically, diamagnetism can be disscus using Larmor's Theorem. According to the theory, in the presence of magnetic field the motion of t electron around the nucleus in the presence of external magnetic field is similar to as in the case of absence of magnetic field except for the superposition of precession of the electron with angular frequency

$$(CGS)\quad \omega = \frac{eB}{2mc} \quad ; \quad (SI)\quad \omega = \frac{eB}{2m} \quad \cdots ①$$

If the average electron current around the nucleus is zero initially; the application of the magnetic field will cause a finite current around t nucleus, however, the current is equivalent to a magnetic moment opposite to the applied field.

This characteristic is called Diamagnetism.

The Larmor precession of Z electrons is equivale to an electric current.

$$(SI),\ I = (\text{charge})(\text{revolutions per unit } \cancel{\text{volume}}\ \text{time})$$

$$= (-Ze)\left(\frac{1}{2\pi} \cdot \frac{eB}{2m}\right) \quad \cdots ②$$

The magnetic moment μ of a current loop is given by the product (current) X (area of the loop

Scanned by CamScanner

The area of a loop of radius ρ is $\pi\rho^2$.
We get,

$$(SI) \quad \mu = -\frac{Ze^2B}{4m}\langle\rho^2\rangle;$$

$$(CGS) \quad \mu = -\frac{Ze^2B}{4mc^2}\langle\rho^2\rangle \quad \ldots ③$$

Here, $\langle\rho^2\rangle = \langle x^2\rangle + \langle y^2\rangle$ is the mean square of the perpendicular distance of the electron from the field axis through the nucleus. The mean square distance of the electrons from the nucleus is $\langle r^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle$. For a spherically symmetrical distribution of charge we have,

$\langle x^2\rangle = \langle y^2\rangle = \langle z^2\rangle$, so that,

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

From ③, the diamagnetic susceptibility per unit volume is, if N is the number of atoms per unit volume,

$$(CGS) \quad \chi = \frac{N\mu}{B} = -\frac{NZe^2}{6mc^2}\langle r^2\rangle; \quad \ldots ④$$

$$(SI) \quad \chi = \frac{\mu_0 N\mu}{B} = -\frac{\mu_0 NZe^2}{6m}\langle r^2\rangle$$

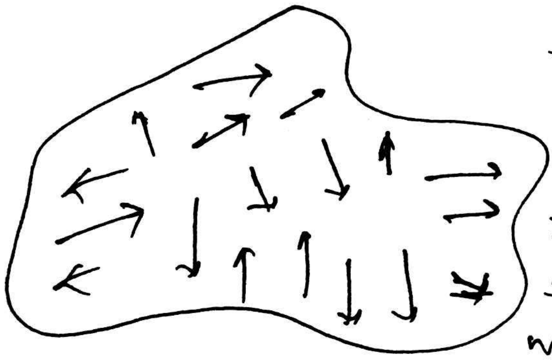
This is the classical Langerin result.
The negative sign of (χ) shows that the induced magnetic field is opposite to the applied magnetic field.

Scanned by CamScanner

Typical experimental values of the molar susceptibility of inert gases are as follows:-

Elements	χ_M in CGS in 10^{-6} cm^3/mole
He	-1.9
Ne	-7.2
Ar	-19.4
Kr	-28.0
Xe	-43.0

• Paramagnetism.



Unlike, in a diamagnetic substance where, the net contribution by the atom toward magnetic field is zero. In a paramagnetic substance, each atom contri magnetic moment (may be because of orbital motion of electrons, spin of electi or combination of both). However, in a substanc all magnetic moments are randomly oriented, s net magnetic field is zero. When external fiel is applied, initially some of them and then mo of them (depending on the strength of the fie applied) get alligned in the direction of external magnetic field i.e. the induced field add up with the applied field and the net field is stronger. This property of a substance to induce a magn field in the direction of external magnetic fi is known as Paramagnetism.

Scanned by CamScanner

① Paramagnetism is found in atoms, molecules, and lattice defects possesing an odd number of electrons. As here, the total spin of the system cannot be zero. For example :- Free Sodium (Na II) atoms, Gases Nitricoxide, organic free radicals, etc.

② Free atoms and ions with partially filled inner shells (transition elements); ions isoelectronic with transition elements; rare earth and actinide elements

③ Few compounds with an even number of electrons including molecular oxygen and organic biradicals.

④ Metals.

• Quantum Theory Of Paramagnetism.

The magnetic moment of an atom or an ion in free space is given by,

$$\vec{\mu} = \gamma \hbar \vec{J} \qquad \ldots ①$$

where,

$$\vec{J} = \vec{L} + \vec{S} \qquad \ldots ②$$

and,

γ = ratio of magnetic moment to the angular momentum.

And is defined as 'Gyro magnetic ratio' or 'Magnetogyric ratio.'

In spectroscopic splitting we define Lande 'g' factor, expressible as,

Scanned by CamScanner

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \quad \cdots ③$$

and is related to r as below:-

$$r = \frac{-g\mu_B}{\hbar} \quad \cdots ④$$

Using eq^n ④ in eq^n ①, we get,

$$\vec{\mu} = \frac{-g\mu_B \cancel{\hbar}\vec{J}}{\cancel{\hbar}}$$

i.e, $\vec{\mu} = -g\mu_B\vec{J} \quad \cdots ⑤$

μ_B ; Bohr magneton is defined as,

$$\mu_B = \frac{e\hbar}{2mc} \quad \cdots ⑥$$

The energy levels of a system in a magnetic field are,

(scalar)

$$U = -\vec{\mu}\cdot\vec{B} \quad \cdots ⑦$$

$$\therefore \quad U = m_J g\mu_B B \quad \cdots ⑧$$

where, m_J = azimuthal Quantum number & values from $-J$ .... to $+J$.

Scanned by CamScanner

With a single spin with no orbital moment,

$m_J = J = L + S$ (for this case, $L = 0$ & $S = \pm 1/2$). . . . ⑨

$\therefore m_J = \pm \frac{1}{2}$ . . . ⑩

And, $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

$\because$ $L = 0$, J is, $J = L + S$; $\therefore J = S$ as $L = 0$

The above equation is modified to,

$$g = 1 + \frac{S(S+1) + S(S+1) - 0(0+1)}{2S(S+1)}$$

$\therefore g = 2$ . . . ⑪

As a result eq^n ⑧ reduces to,

$U = \pm \mu_B B$ . . . ⑫

As in the diagram below,

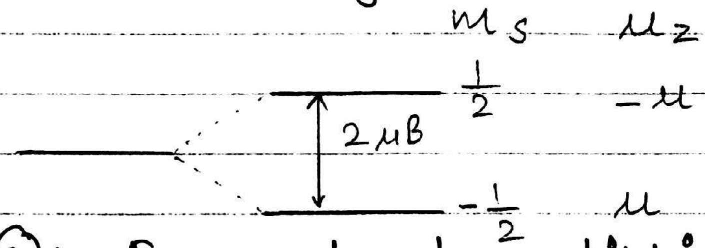


Fig ⓐ:- Energy levels splitting for one electron in a magnetic field B.

Scanned by CamScanner

If a system has only two levels the equilibrium populations are, with $\tau \equiv k_B T$,

$$\frac{N_1}{N} = \frac{\exp(\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)} \quad \cdots (13)$$

$$\frac{N_2}{N} = \frac{\exp(-\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)} \quad \cdots (14)$$

here N_1, N_2 are the populations of the lower & upper levels, and $N = N_1 + N_2$.

The resultant magnetization for 'N' atoms per unit volume is expressible as,

$$M = (N_1 - N_2)\mu = \mu\left\{\left[\frac{N \cdot \exp(\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)}\right] - \left[\frac{N \cdot \exp(-\mu B/\tau)}{\exp(\mu B/\tau) + \exp(-\mu B/\tau)}\right]\right\} \cdots$$

(Let, $x = \mu B/k_B T$
$= \mu B/\tau$)

$$M = N\mu \cdot \left[\frac{e^{x} - e^{-x}}{e^{x} + e^{-x}}\right] = N\mu . \tanh x \quad \cdots (16)$$

$$M = N\mu \cdot \tanh x \quad \cdots (17)$$

Let's consider the case when $x \ll 1$

Hence, $\tanh x \rightarrow x$

Expression (17) reduces to,

$$M \cong N\mu \cdot \left(\frac{\mu B}{k_B T}\right) \quad \cdots (18)$$

Expression ⑱ can be redefined as, $p = g\sqrt{J(J+1)}$

$$M = NgJ\mu_B B_J(x) \quad \ldots ⑲$$

where, $$x \equiv \frac{gJ\mu_B B}{k_B T} \quad \ldots ⑳$$

where the Brillouin function B_J is defined by,

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh}\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \operatorname{ctnh}\left(\frac{x}{2J}\right) \quad \ldots ㉑$$

Equation ⑯ is a special case of eq^n ㉑ for, $J = 1/2$. For $x \ll 1$, we get,

$$\operatorname{ctnh} x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \ldots, \quad \ldots ㉒$$

and the susceptibility is,

$$\frac{M}{B} \cong \frac{NJ(J+1)g^2\mu_B^2}{3k_B T} = \frac{Np^2\mu_B^2}{3k_B T} = \frac{C}{T} \quad \ldots ㉓$$

Here, 'p' is the effective number of Bohr magnetons, defined as,

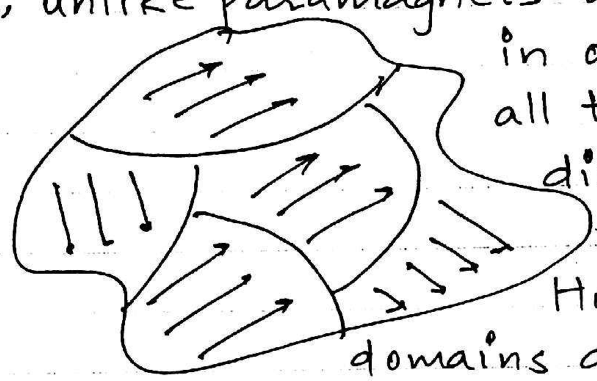
$$p \equiv g[J(J+1)]^{1/2} \quad \ldots ㉔$$

The constant C is known as the Curie constant. Eq^n ㉓ is known as Curie Law.

Scanned by CamScanner

Ferromagnetism (Magnetic Ordering)

Ferromagnets are enhanced version of paramagnets where, unlike paramagnets there are many dip in one direction, and all the dipoles in one direction forms a regio called as 'domain'. However, since, the domains are also randomly oriented the net magnetic field is zero.



Ferromagnetic Order :- A ferromagnet has a spontaneous magnetic moment – a magnetic moment even in zero applied magnetic field. A spontaneous moment suggests that electron spins and magnetic moments are arranged in a regular manner.

Curie Point and the Exchange Integral.

Consider a paramagnet with a concentrati of N ions of spin S. Given an internal interaction tending to line up the magnetic moments parall to each other, we shall have a ferromagnet. Let us postulate such an interaction and call it th 'exchange field'. The orienting effect of the exchange field is opposed by thermal agitation, and at elevated temperatures the spin order is destroyed.

We treat the exchange field as equivalent to a magnetic field $\vec{B}_E$. The magnitude of the exchange field may be as high as 10^7 gauss.

Scanned by CamScanner

We assume that $\vec{B_E}$ is proportional to the magnetization $\vec{M}$. The magnetization is defined as the magnetic moment per unit volume; unless otherwise specified it is understood to be the value in thermal equilibrium at the temperature T. If domains (regions magnetized in different directions) are present, the magnetization refers to the value with a domain. In the mean field approximation we assume each magnetic atom experiences a field proportional to the magnetization:

$$\vec{B_E} = \lambda \vec{M} \quad \dots \text{①}$$

where, $\vec{B_E}$ = magnetic field
$\vec{M}$ = magnetization.

Exchange field is also called 'Molecular field' or the 'Weiss field'.

where, λ in eq^n ① is proportionality constant and is independent of temperature.

With reference to ferromagnetic substance, we define a temperature known as 'Curie Temperature' (T_c). It is a temp. above which the spontaneous magnetization vanishes; it separates the disordered paramagnetic phase at $T > T_c$ from the ordered ferromagnetic phase at $T < T_c$. We can find T_c in terms of λ.

Consider the paramagnetic phase and a field 'B_a' is applied will cause a finite magnetization and will cause a finite exchange field 'B_E'

$$(\text{CGS}) \quad M = \chi_p (B_a + B_E) \quad \dots \text{②}$$

$$(\mathrm{SI}) \qquad \mu_0 M = \chi_P (B_a + B_E) \quad \cdots \quad \text{②}'$$

The paramagnetic susceptibility is given by the Curie Law,

$$\chi_P = \frac{C}{T} \quad \cdots \quad \text{③}$$

where, C = Curie constant.

Using equations ①, ② & ③, we get,

$$MT = C(B_a + \lambda M) \quad \cdots \quad \text{④}$$

$$(\mathrm{CGS}) \qquad \chi = \frac{M}{B_a} = \frac{C}{(T - C\lambda)} \quad \cdots \quad \text{⑤}$$

The above expression can be modified as,

$$\chi = \frac{C}{T - T_c} \ ; \quad T_c = C\lambda \quad \cdots \quad \text{⑥}$$

This is known as Curie-Weiss Law.

According to experimental results,

$$\chi \propto \frac{1}{(T - T_c)^{1.33}} \quad \cdots \quad \text{⑦}$$

The relation between Curie constant (C) & λ is also expressible as,

$$\lambda = \frac{T_c}{C} = \frac{3 k_B T_c}{N g^2 S(S+1) \mu_B^2} \quad \cdots \quad \text{⑧}$$

Scanned by CamScanner

Diamagnetism and Paramagnetism.

- Rare Earth Ions.

Ans. These are set of seventeen chemical elements in the periodic table, specifically the fifteen Lanthanides plus Scandium and yttrium. Scandium and yttrium are considered rare earth elements since they tend to occur in the same ore deposit as the lanthanides and exhibit similar chemical properties.

Experiments on rare earth ions in crystals show that they obey the Curie law. The effecti number of magnetons agrees well with the theor of spin-orbit interaction. In these ions, the angular momenta L & S are strongly coupled & the moment of the ion can respond freely to the external field.

In these ions the 4f shells is incompletely filled. The outer 5p shell is completely filled while the 5d & 6s shells which are still further out are stripped of their electrons to form the ionic crystal. Thus the only incomplete shell is 4f in which the magnetic behaviour occurs. The electrons in this shell are screened by the outer 5p and 5d shells, crystals field interaction becomes minimum and the magnetically it behaves as a free ion.

Scanned by CamScanner

In lanthanum just before the rare earth group begins, the 4f shell is empty. At cerium, one 4f electron exists and the number of 4f electr increases steadily through the group till at Yttrium $4f^{13}$ and the filled shell $4f^{14}$ at lutecium.

→ Lanthanide contraction is a term used to describe the greater than expected decrease in ionic radii of the elements in the lanthanide ser from atomic number 57, lanthanum, to 71, lutetiu which results in smaller than otherwise expecte ionic radii for the subsequent elements startin with 72, hafnium.

- Iron Group Ions.

A- Iron group ions behave magnetically as if $J = S$ that is only the spin moment can contribute to magnetization. The magnetic properties of this group of elements are due to the electrons in the incomplete 3d shell.

Since, electrons in this outermost shell interac strongly with neighbouring ions, the orbital motion i essentially destroyed or quenched, leaving only th spin moment to contribute to magnetization.

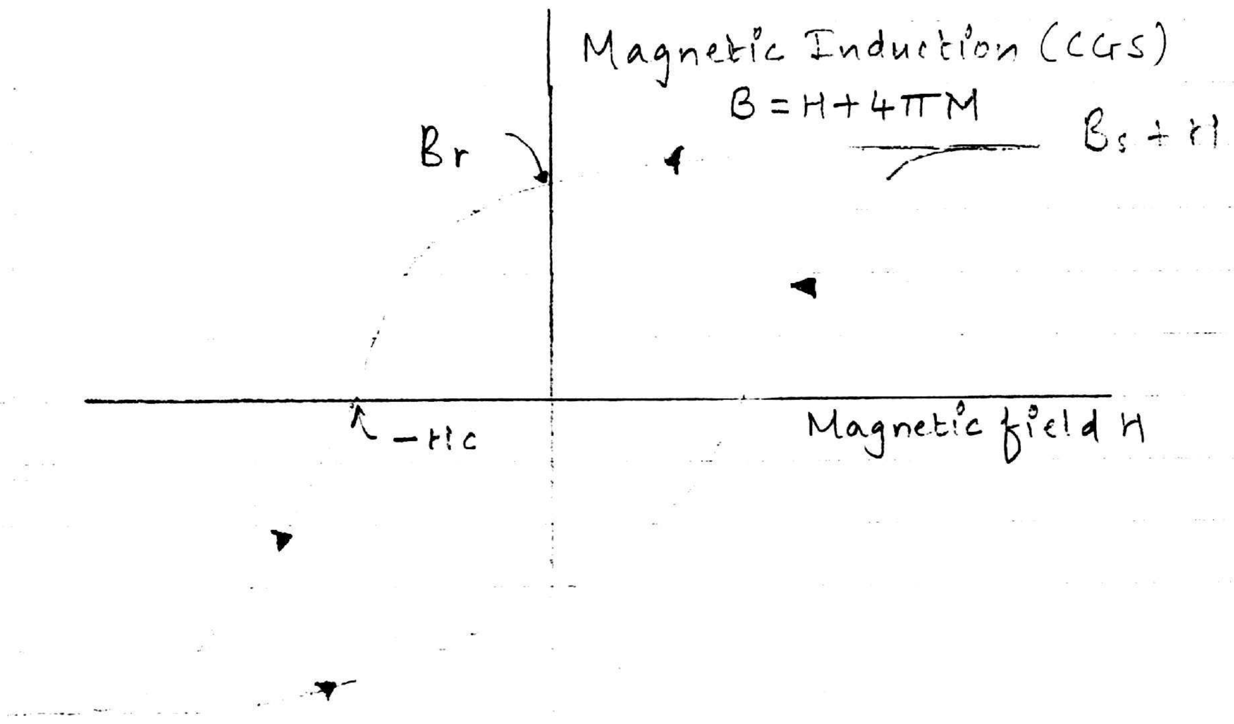
- Crystal Field Splitting.

→ The difference in behaviour of the rare earth & the iron group salts is that the 4f shell responsib for paramagnetism in the rare earths lays deep inside the ion, within the 5s & 5p shells. Whereas i the iron group ions the 3d shell responcible for the paramagnetism is the outermost shell. This 3d shell experiences the intense inhomogeneous electric field produced by the 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 $\vec{L}$ and $\vec{S}$ 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 the free ion may now be split by the crystal field, this splitting diminishes the contribution of the orbital motion to the magnetic moment.

Scanned by CamScanner

→ Coercive force and Hysteresis



Refer the diagram above; is for the hysteresis cur for a given ferromagnetic substance.

Coercive force is the reverse field Hc required to redu the induction zero, is the most sensitive property of a ferromagnetic material. The coercive force may range from value of 600 G in a loudspeaker permanen magnet and 20,000 G in a special high stability magn to 0.5 G in a commercial power transformer or 0.004 G in a pulse transformer.

In a transformer low hysteresis is desired; th means a low coercive force. The coercive force decreases as the impurity content decreases and also as interna strains are removed by annealing. Alloys that contai a precipitated phase may have a high coercivity. The high coercivity of materials composed of very small grains or fine powders. A sufficiently small particle, with diameter less than 10^{-5} or 10^{-6} cm,

Scanned by CamScanner

is always magnetized to saturation as a single domain because the formation of a flux-closure configuration is energetically unfavourable.

In a sufficiently small single domain particle it will not be possible for magnetization reversal to take place by means of the process of boundary displacement, which usually requires relatively weak fields. Instead the magnetization of the particle must rotate as a whole, a process that may require large fields depending on the anisotropy energy of the material and the shape of the particle. The coercive force of fine iron particles is expected theoretically to be about 500 gauss on the basis of rotation opposed by the crystalline anisotropy energy: and this is of the order of the value

→ Ferromagnetic Domains.

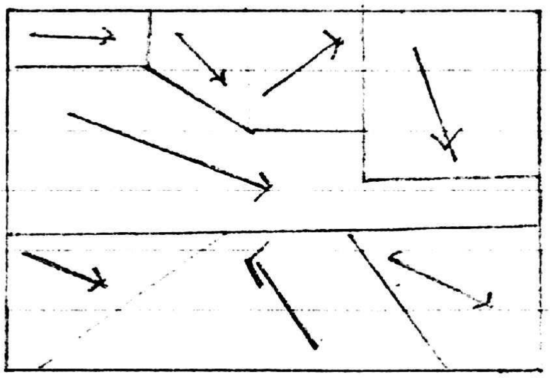


Fig:- Ferromagnetic domain pattern on a single crystal platelet of nickel.
The domain boundaries are made visible by the Bitter technique.
The direction of magnetization within a domain is determined by observing growth or contraction of the domain in a magnetic field.

Scanned by CamScanner