MAGNETIC PROPERTIES

Diamagnetic, Paramagnetic, ferromagnetic, ferrimagnetic and Antiferromagnetic substances ⇒

Charge particle ⟶ In motion ⟶ generates a magnetic field.

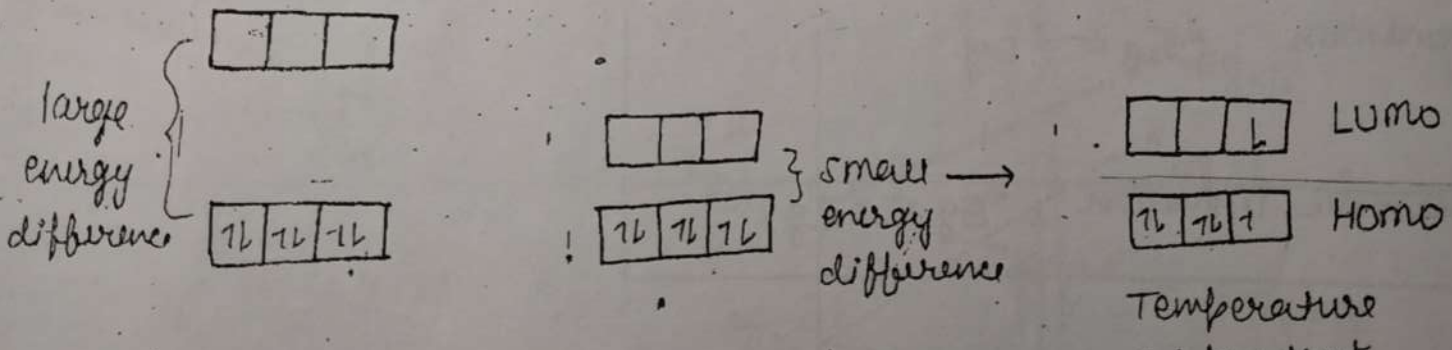
Diamagnetic substances ⇒

⇒ Magnetic moment, $\mu = 0$

⇒ All e^-s paired.

Applied magnetic field ⟶

induced magnetic field ⟵



Temperature independent paramagnetic (TIP) occurs at room T.

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A complex may has-

① All paired electrons. d^6 (LS) — eg, t2g ← diamagnetic

② unpaired electrons with paired e's. — d^7 (HS) — eg, t2g ← paramagnetic

③ All unpaired electrons only — d^5 (HS) — eg, t2g ← paramagnetic

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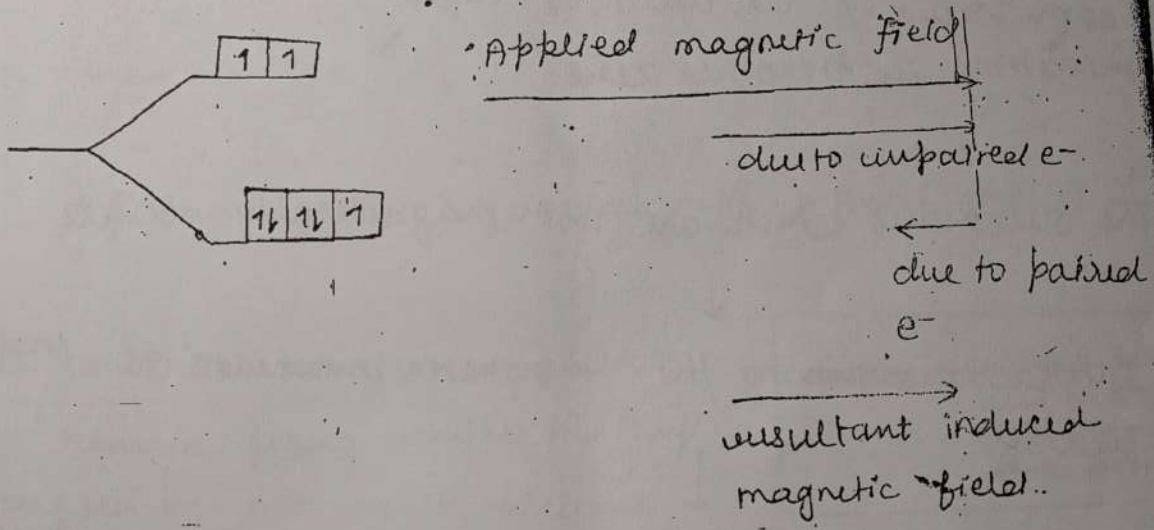

In case of magnetically dilute substances.

↓

No interaction among the magnetic moments of individual atoms, ions or molecules of a substance.

↓

Substances are always paramagnetic whether the tem is low or high.

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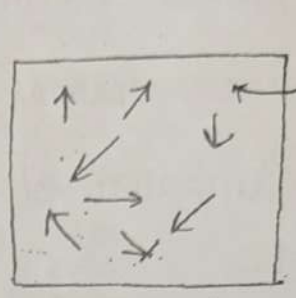
magnetic moment of paramagnetic substances ($\vec{M}=0$)

paramagnetism $\propto \frac{1}{\text{Temperature}}$



magnetic moment is of a particular ion or atom not of whole substance.

At low temp^r randomisation decreases, therefore there will be some value of $\vec{M}$ while at high T due to more randomisation $\vec{M}$ becomes zero.

The substances which are not magnetically dilute

↓

Interaction among the magnetic moments of individual particle.

↓

Paramagnetic substances may converted into ferromagnetic ferrimagnetic or Antiferromagnetic substances

↓

Occurs below critical temp^r

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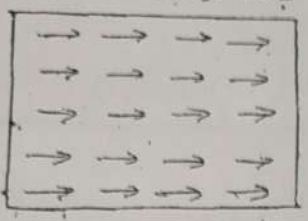
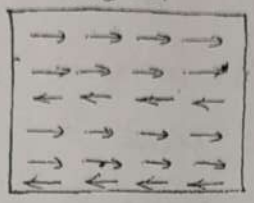
Ex:- Fe, CO, Ni, CrO_2



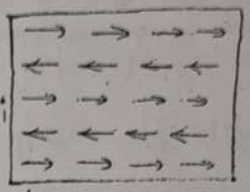
Ferromagnetic

Fe_3O_4



Ferrimagnetic

MnO



Antiferromagnetic

↓

below critical temp^r called as Curie's Temp^r (T_c)

below critical temp^r called Neel's temp^r.

magnetic moment-

ferromagnetic > ferrimagnetic > Antiferromagnetic

Iron once converted into ferromagnetic will be remain ferro. whether the temp^r is increased or not. i.e it becomes permanent magnet.

[redacted] → Na thiosulfate used in photography to make photos from -ve

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Magnetic susceptibility ⇒

H = Applied magnetic field

B = induced magnetic field in the sample

$$\boxed{\Delta H = B - H} \quad \text{—(1)}$$

for diamagnetic substances $B < H$

" paramagnetic " $B > H$

ΔH = -ve for diamagnetic substances

ΔH = +ve for paramagnetic "

difference between B and H is measured in terms of intensity magnetisation (I).

$$4\pi I = B - H \quad \text{—(2)}$$

or

$$4\pi \frac{I}{H} = \frac{B}{H} - 1 \quad \text{—(3)}$$

$\frac{B}{H}$ = magnetic permeability

$\frac{I}{H}$ = magnetic susceptibility per unit volume (K)

(Kappa)

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$$K = \frac{I}{H} \quad -(4)$$

magnetic susceptibility ⇒ Tendency of a substance to be magnetised

if volume → m.s. per unit volume

if moles – " " " moles

$$\chi = \frac{K \cdot (v)}{d(v) \text{ mass}} = \frac{K}{d \text{ mass}} \quad -(5)$$

Specific magnetic susceptibility i.e. magnetic susceptibility per unit mass.

$$\chi_m = \chi \cdot M \quad -(6)$$

M ↖ molar mass

χ_m ↑ molar magnetic susceptibility

↑ magnetic susceptibility per mole → degree to which one mole of a substance interacts with extend magnetic field

From classical theory-

$$\chi_m = \frac{N^2 \mu^2}{3RT} \quad -(7)$$

N → Avogadro no.

μ → magnetic moment (B.M.)

R – gas const.

$$\mu = \left(\frac{\chi_m \cdot 3RT}{N^2}\right)^{1/2} \quad -(8)$$

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$$\chi_m^p \text{ corrected} = (\chi_m^p - \chi_m^d)$$

(χ_m^p ← paramagnetic, χ_m^d ← diamagnetic)

↑ very small

↑ can be neglected

$$\mu = 2.84 (\chi_m \cdot T)^{1/2} \quad \text{—⑨}$$

from eqn ⑦ :-

$$\chi_m = \frac{C}{T}$$

C = Curie's constant

$$= \frac{N^2 \mu^2}{3R}$$

Paramagnetic susceptibility $\propto \frac{1}{T}$

For ferromagnetic, ferrimagnetic or antiferromagnetic substances :-

$$\chi_m = \frac{C}{(T-\theta)}$$

θ = an empirical constant and has the unit of temp^r

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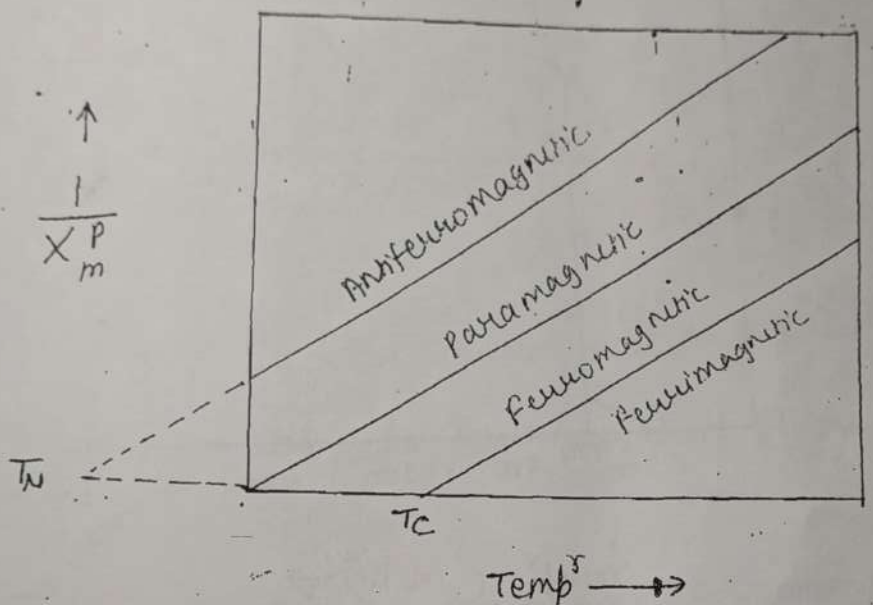
θ = +ve → Ferromagnetic or Ferrimagnetic

θ = -ve → Antiferromagnetic



V.V.I.

High spin and low spin equilibrium ⇒

d^4, d^5, d^6 and d^7 — HS → weak ligand; LS → strong ligand

$[Fe(Phen)_2(NCS)_2]$ ← exist both as HS & LS equilibrium at 174K

$Fe^{2+} \rightarrow d^6$

only known compound which exist both in HS & LS

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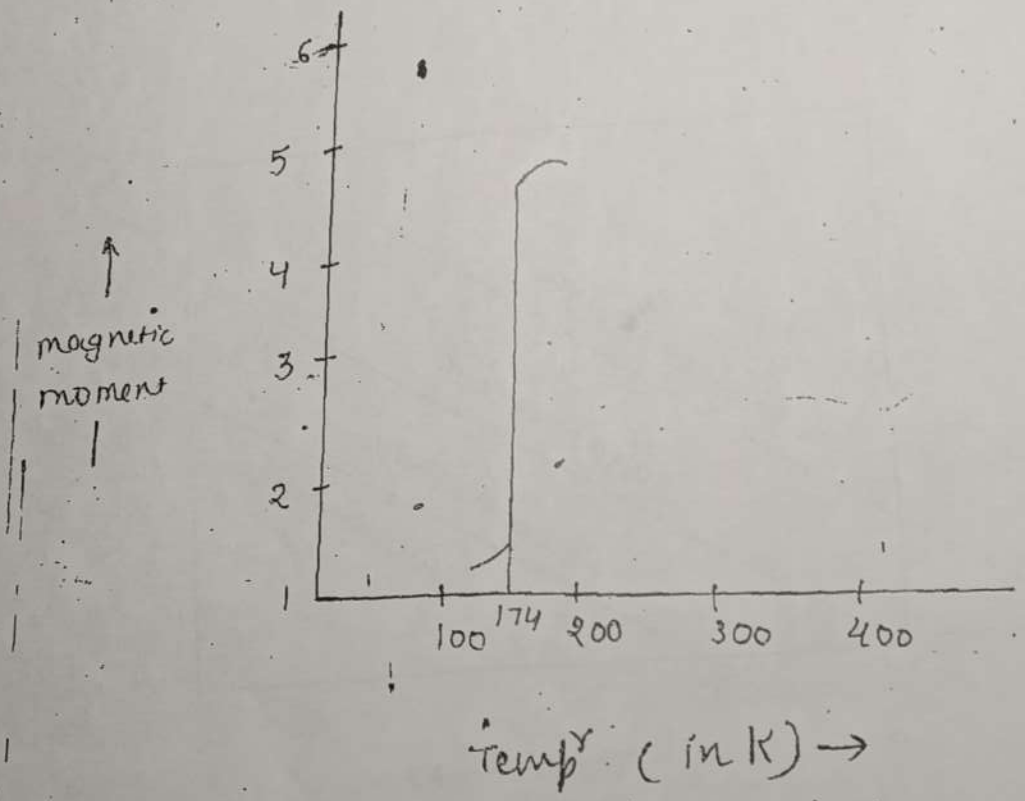

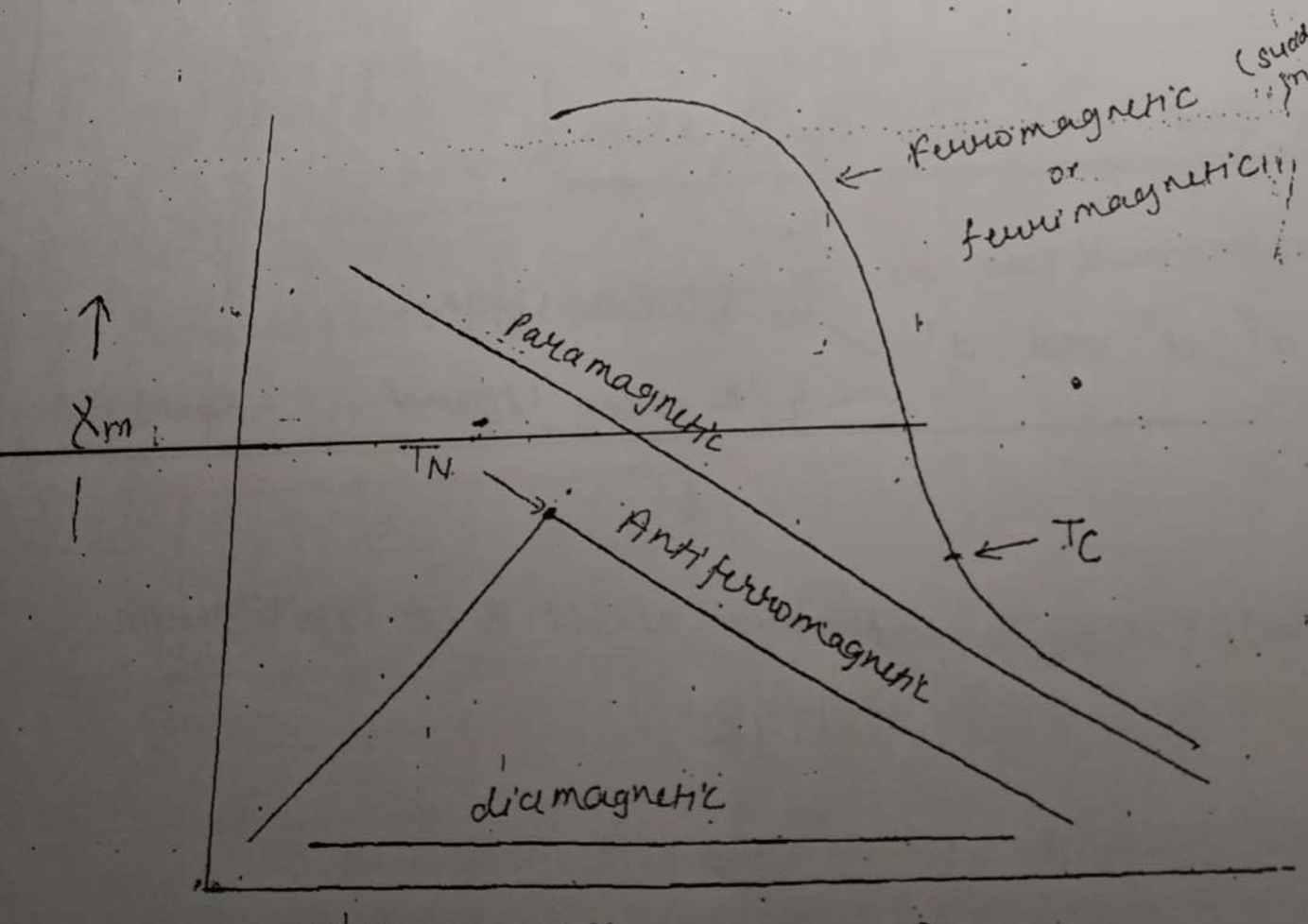

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Magnetic Moment ⇒

due to orbital motion and spin motion

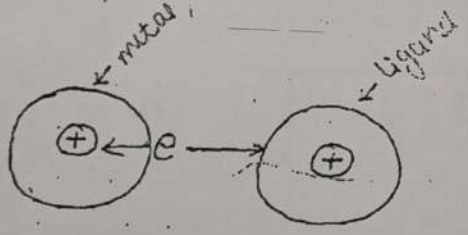
$$\mu_{L+S} = \mu_J = g\sqrt{J(J+1)} \quad B.M.$$

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

} used for heavier elements like lanthanides

$J = L+S$ (for more than half filled)

$J = L-S$ (for less than half filled)



due to +nce of ligand the orbital motion is cancelled in case of d block elements hence only spin motion is remained. It is called quenching of orbital motion.

In case of lanthanides there is no interaction with ligand hence no quenching of orbital motion occur hence both spin and orbital motion are counted.

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For | skin motion -

$L = 0$

$J = S$

$g = \frac{3}{2} + \frac{1}{2} = 2$

$\mu_S = 2\sqrt{S(S+1)} = \sqrt{4S(S+1)}$

For orbital motion -

$S = 0$

$J = L$

$g = \frac{3}{2} - \frac{1}{2} = 1$

$\mu_L = 1\sqrt{L(L+1)}$

$$\mu_{L+S} = \sqrt{4S(S+1)} + \sqrt{L(L+1)}$$

B.M. mathematically right

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}$$

B.M. ac to books

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In complexis of transition metal there is quenching of orbital motion i.e.

$$L = 0$$

$$\mu_{spin\ only} = \sqrt{4S(S+1)} \quad B.M.$$

For one unpaired e^- –

$$S = \frac{1}{2}$$

for n unpaired e^- –

$$S = \frac{n}{2}$$

$$\therefore \mu_S = \sqrt{4 \times \frac{n}{2}\left(\frac{n}{2}+1\right)}$$

$$\mu_{spin\ only} = \sqrt{n(n+2)} \quad B.M.$$

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Orbital contribution ⇒

For orbital contribution –

t_{2g} or t_2 → unsymmetrically filled → orbital contribution

In octahedral complexes –

$d^1 \rightarrow t_{2g}^1 e_g^0$ ← Orbital contribution

$d^2 \rightarrow t_{2g}^2 e_g^0$ ← "

$d^3 \rightarrow t_{2g}^3 e_g^0$

d^4 (HS) $\rightarrow t_{2g}^3 e_g^1$

d^4 (LS) $\rightarrow t_{2g}^4 e_g^0$ ← orbital contribution

d^5 (HS) $\rightarrow t_{2g}^3 e_g^2$

d^5 (LS) $\rightarrow t_{2g}^5 e_g^0$ ← orbital contribution

d^6 (HS) $\rightarrow t_{2g}^4 e_g^2$ ← "

d^6 (LS) $\rightarrow t_{2g}^6 e_g^0$

d^7 (HS) $\rightarrow t_{2g}^4 e_g^3$ ← orbital contribution

d^7 (LS) $\rightarrow t_{2g}^6 e_g^1$

d^8 (HS) $\rightarrow t_{2g}^6 e_g^2$

$d^9 \rightarrow t_{2g}^6 e_g^3$

$d^{10} \rightarrow t_{2g}^6 e_g^4$

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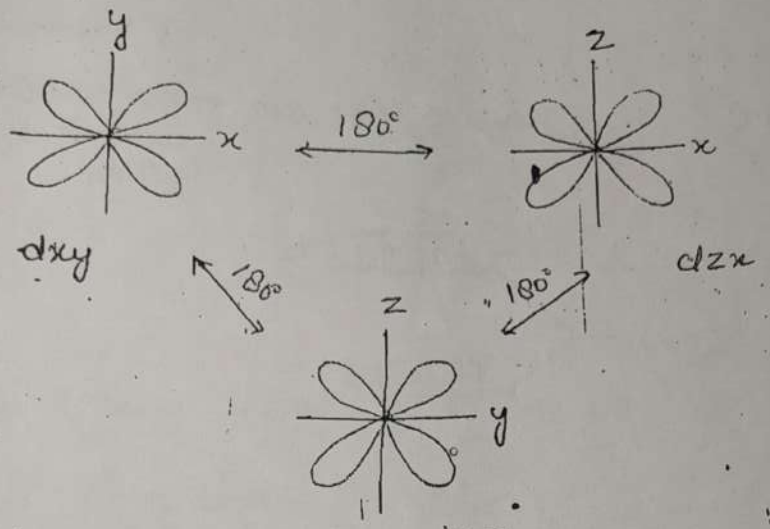
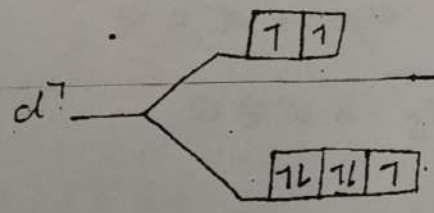


The dxy, dyz and dzx orbitals can be converted into one another due to same symmetry. Hence one may be present any one of these. In case of $d_{x^2-y^2}$ and d_{z^2} orbitals which are not of same symmetry, the conversion is not possible

d^7 (HS) octahedral complex ⇒

* Calculated and experimental magnetic moment.



$n = 3$

$\mu_S = 3.87$ B.M. ← calculated

$\mu_S = 5.2$ B.M. ← experimental → due to orbital contribution

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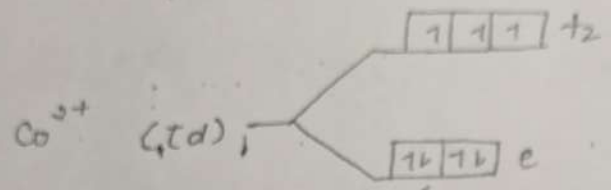
In case of tetrahedral complexes of d^7

$\mu_S = 3.87$ $\quad \mu_{exp} = 4.39$ BM. ← no orbital contribution as t_2 is symmetrically filled.



The experimental value is more in this case is due to spin orbital coupling.

$$\mu_{eff} = \mu_{s.o.}\left(1 - \frac{\alpha \cdot \lambda}{\Delta}\right)$$

α = constant

λ = spin orbital coupling constant

for $d^1, d^2, d^3, d^4 \rightarrow +ve$

$d^6, d^7, d^8, d^9 \rightarrow -ve$

for

^2D and $^5D \Rightarrow \alpha = 2$

^3F and $^4F \rightarrow \alpha = 4$

for $^6S \rightarrow \alpha = 0$

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Q⇒ which of the following complexes has highest value of magnetic moment ?

(a) $[CoF_4]^{2-}$ (c) $[CoBr_4]^{2-}$

(b) $[CoCl_4]^{2-}$ (d) $[CoI_4]^{2-}$

F is strong ligand, hence the value of Δ will be large. Hence μ_{eff} is greater for $[CoF_4]^{2-}$.

Here Co is +nt in +2 oxidation state means as d^7 in all complexes, hence it cant be determined by λ value.

The Atomic term symbol is ^4F for all, so it also cant be determined by α value.

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