

M.Sc Chemistry Inorganic Chemistry Semester-II



Course Title: Chemistry of d and f block elements

Course Code: 201-B

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Inorganic Group III and IV

REFERENCE BOOKS:

- 1. Electronic Spectra of Transition Metal Complexes by D. Sutton**
- 2. Introduction to Ligand Field Theory: Figgis**
- 3. Concise Inorganic Chemistry by J. D. Lee**

Magnetic Properties



INTRODUCTION

Magnetic properties depend upon:

Dipole properties of atoms/molecules

$B = H_0 + 4\pi I$ (where **B**=magnetic susceptibility, **I**=Induction)

$B/H_0 = 1 + 4\pi I/H_0$ (where **H₀** = magnetic permeability)

A magnetic field is generated by moving charge.

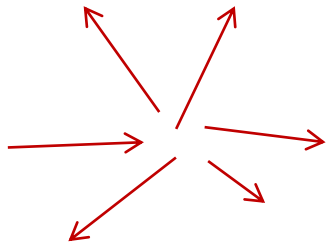
If magnetic properties are not interacting with each other, then it is called “MAGNETIC DILUTE.”

Diamagnetism and Paramagnetism

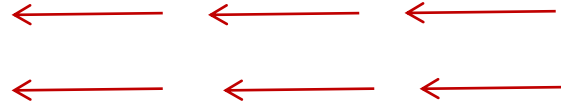
- **Diamagnetism** occurs in all substances and is a weak effect caused by circulation of electrons in atoms and molecules.
- A magnetic field induces electrons to circulate producing a magnetic moment in the opposite direction to the field.
- Diamagnetic substances are thus repelled weakly by magnetic field, but the effect is too small.

- Paramagnetic substances are attracted by a magnetic field.
- **Paramagnetism** is due to isolated unpaired spins of electrons on atoms or molecules.
- The set of unpaired electrons in one complex does not interact with the set in a neighbouring complex because the complexes are too far apart, the different set of unpaired electrons are thus oriented randomly with respect to one another and are said to be **MAGNETICALLY DILUTE**.

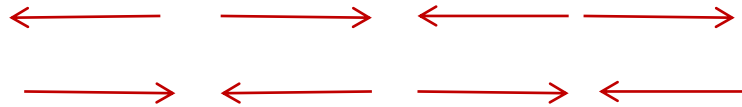
In Applied magnetic field:



Internal Thermal Energy = KT



FERROMAGNETIC



ANTI-FERROMAGNETIC

- If unpaired spins are coupled to each other so that they line up and re-inforce each other, then the material is said to be FERROMAGNETIC.
- **Ferromagnetism** occurs in iron and cobalt and it is this much stronger property that is generally referred to as “magnetism” in everyday life.
- In **antiferromagnetic** substances, the spins line up and interact with one another in such a way that they cancel each other out.

Paramagnetic magnetic moment

$$\mu_{\text{eff}} = 3KNB^2 (\chi T)^{1/2} = 2.828 (\chi T)^{1/2}$$

μ_{eff} = Magnetic moment

B = Bohr Magneton

χ = Susceptibility

Magnetic properties \propto Angular Momentum

Spin/Orbital/ Total angular momentum

For d^2 : 3F term (When an applied magnetic field perturbation of energy levels occurs. This is called Zeeman Effect.

Zeeman Effect

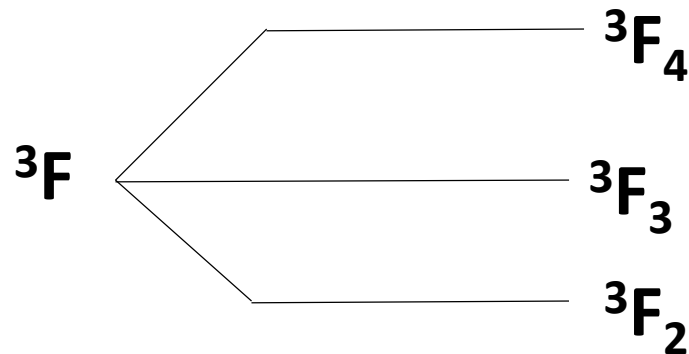
For d^2 : $3F$ term

When an applied magnetic field perturbation of energy levels occurs. This is called **Zeeman Effect**

$L=3$

$S=1$

**$J=L+S, L+S-1 \dots L-S$
 $= 4, 3, 2$**



(1) If $KT \ll \ll$ Multiplet width, $\mu_{\text{eff}} = \text{Ground State}$

$\mu_{\text{eff}} = g \sqrt{J(J+1)}$ where g is spectroscopic Lande Splitting Factor

$g = 1 + [S(S+1) - L(L+1) + J(J+1)] / 2J (J+1)$

Ce (f¹)

+3	+2	+1	0	-1	-2	-3
↑						

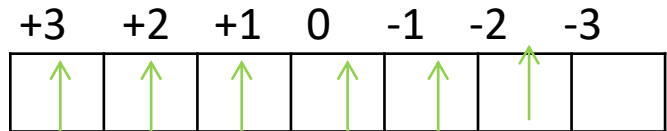
$$L=3$$
$$S=1/2$$

$$g = \frac{1 + [S(S+1) - L(L+1) + J(J+1)]/2J(J+1)}{2 \times 5/2 (5/2 + 1)}$$
$$1 + [1/2(1/2+1) - 3(3+1) + 5/2 (5/2+1)]$$

$$= 0.857$$

$$\mu_{\text{eff}} = g \sqrt{J(J+1)}$$
$$= 0.857 [5/2(5/2+1)]^{1/2}$$
$$= 2.535$$

Eu³⁺ (f⁶)



$$L=3$$

$$S=3$$

$$\mu_{\text{eff}} = g \sqrt{J(J+1)} \quad J = L - S = 0$$
$$= 0$$

But actual value is 3.4

Sm³⁺ (f⁵)

Calculated = 0.84

Observed = 1.6

Mostly in lanthanides,
Multiplet Width \gg KT (First Order Zeeman Effect)
But for Sm³⁺, Eu³⁺,
Multiplet Width \ll KT

Multiplet Width \ll KT

$$\mu_{\text{eff}} = [L(L+1) + 4S(S+1)]^{1/2} B$$

Second Order
Zeeman Effect
No first order
contribution

CASE: If there is no orbital contribution
 $L=0$

$$L=0, J=S$$

$$g = 1 + [S(S+1) - 0 + S(S+1)] / 2S(S+1) \\ = 2$$

$$\mu_{\text{eff}} = 2\sqrt{s(s+1)} \qquad s=n/2 \\ = \sqrt{4s(s+1)} \\ = \sqrt{4n/2(n/2+1)} = \sqrt{n(n+2)}$$

- For first row transition elements, there is a good agreement between experimental magnetic moment and calculated by spin only formula.
- However in some cases, experimental magnetic moment is higher than that of calculated by spin only formula. This is due to ORBITAL CONTRIBUTION.
- Orbital contribution is possible when an orbital will transform into an equivalent orbital by rotation. The t_{2g} orbitals (d_{xy} , d_{yz} , d_{zx}) can be transformed into each other by rotating about an axis by 90°