

Magnetism

**Transition & Lanthanide ions
and their complexes**

Magnetism - Background

From paired & unpaired electron spins

Each spinning electron causes a magnetic field around it. In most cases, the magnetic field of one electron is cancelled by an opposite magnetic field produced by the other electron in the pair.

In metals, such as, iron, cobalt and nickel, there are several unpaired electrons, so they do not cancel all the electrons' magnetic fields.

As a result, each atom of these metals acts like a small magnet.

Magnetochemistry -- Introduction

Electron spin: An electron has two intrinsic spin states, which are referred as up and down or alpha and beta.

Electron orbital motion: A magnetic field is generated due to the electron moving around the nucleus.

Nuclear spin: Some nuclei, such as hydrogen, have a net spin, which generates a magnetic field.

Each of these magnetic fields interact with one another and with the external magnetic fields.

However, some of these interactions are strong, some are weak and some are negligible.

Dia and Paramagnetic compounds

N₂ diamagnetic

Pouring liquid dinitrogen



liquid dinitrogen
does NOT stick

Dia.M. ex. H₂O, KCl organic ligands,
etc.

Bismuth metal (most diamagnetic
of all metals)

diamagnetic

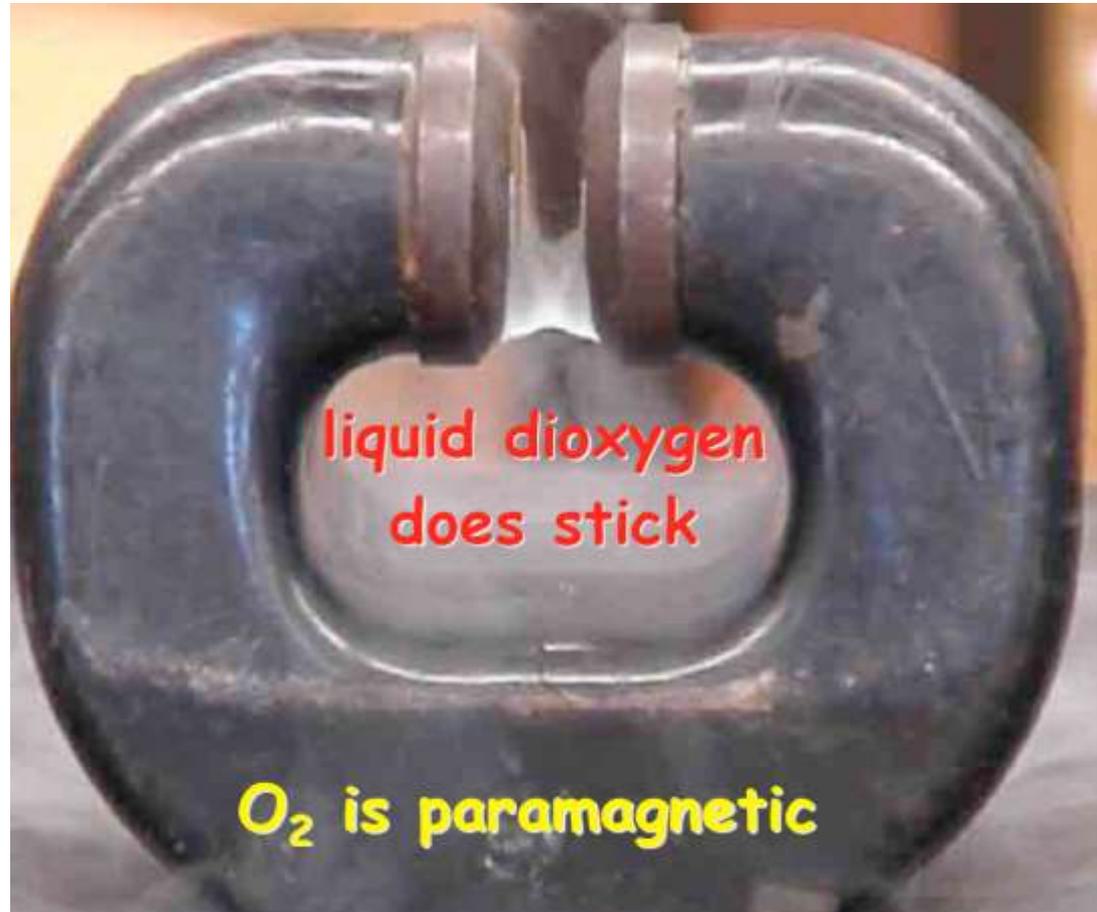


O₂ paramagnetic

when dioxygen is in its ground state it is a triplet (spin $S=1$) and its reactivity is weak.



Liquid O₂



Magnetic Levitation: Property of diamagnetic molecules



Magnetisation

The classical theory of magnetism was well developed before quantum mechanics. Lenz's Law (~1834), states that:

When a substance is placed within a magnetic field, H , the field within the substance, B , differs from H by the induced field, $4\pi I$, which is proportional to the intensity of magnetization, I .

$$\text{That is; } B = H + 4\pi I$$

B = the magnetic field within the substance

H = the applied magnetic field

I = the intensity of magnetisation

$$B/H = 1 + 4\pi I/H \quad \text{or} \quad B/H = 1 + 4\pi \kappa$$

where B/H is called the magnetic permeability of the material and κ is the magnetic susceptibility per unit volume, (I/H)

By definition, κ in a vacuum is zero,

$$\text{so, } B = H.$$

Molar Susceptibility

It is usually more convenient to measure mass (gram) susceptibility, χ_g , which is related to the volume susceptibility through the density.

$$\chi_g = \kappa/\rho \quad \text{where } \rho \text{ is density}$$

Finally to get our measured quantity on a basis that can be related to atomic properties, we convert it to molar susceptibility

$\chi_m = \chi_g \times \text{M.Wt.}$ Where, M. Wt. is molecular weight of the sample

Volume \rightarrow mass \rightarrow molar **SUSCEPTIBILITY**

Magnetic moment (μ) from susceptibility (χ)

Calculation of μ from χ

$$\chi_m = N\mu^2 / 3kT$$

where N is Avogadro's No.; k is the Boltzmann and T the absolute temp

Rewriting this gives the magnetic moment as

$$\mu_{so} = \sqrt{\frac{3k}{N\beta^2}} \sqrt{\chi T} = 2.828 \sqrt{\chi T}$$

Magnetism in Metal Complexes

Many transition metal salts and complexes are paramagnetic due to partially filled d-orbitals.

The experimentally measured magnetic moment (μ) (and from the equation in the previous page) can provide some important information about the compounds themselves:

- No of unpaired electrons present
- Distinction between HS and LS octahedral complexes
- Spectral behavior, and
- Structure of the complexes

Sources of Paramagnetism

Orbital motion of the electron generates ORBITAL MAG. MOMENT (μ_l)

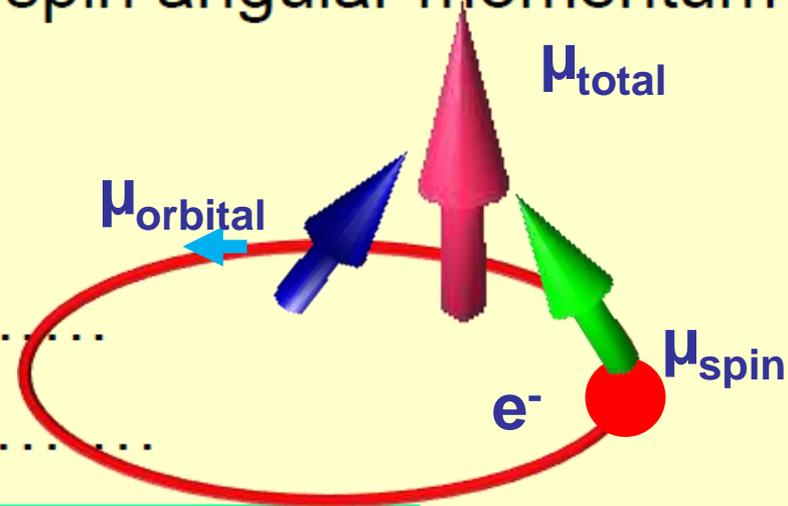
Spin motion of the electron generates SPIN MAG. MOMENT (μ_s)

l = orbital angular momentum; s = spin angular momentum

For multi-electron systems

$$L = l_1 + l_2 + l_3 + \dots$$

$$S = s_1 + s_2 + s_3 + \dots$$



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

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

For TM-complexes, the magnetic properties arise mainly from the exposed d -orbitals. The d -orbitals are perturbed by ligands.

\therefore The rotation of electrons about the nucleus is restricted which leads to $L = 0$

$$\mu_s = [4S(S+1)]^{1/2} \text{ B.M.}$$

$S = n(1/2) = n/2$; $n =$ no of unpaired electrons

Hence

$$\mu_s = [4(n/2)(n/2+1)]^{1/2} \text{ B.M.}$$

$$= [n(n+2)]^{1/2} \text{ B.M.}$$

This is called Spin-Only Formula

$\mu_s = 1.73, 2.83, 3.88, 4.90, 5.92$ BM for $n = 1$ to 5 , respectively

Conditions to exhibit orbital angular momentum (μ_L)

- The orbitals should be degenerate (t_{2g} or e_g)
- The orbitals should be similar in shape and size. Should be possible to transform an orbital into an equivalent one by rotation. This is indeed possible to transform the t_{2g} orbitals into each other by 90° rotation. Such transformation is not possible with the orbitals of e_g .
- The orbitals must not contain electrons of identical spin during this transformation and the movement of electron

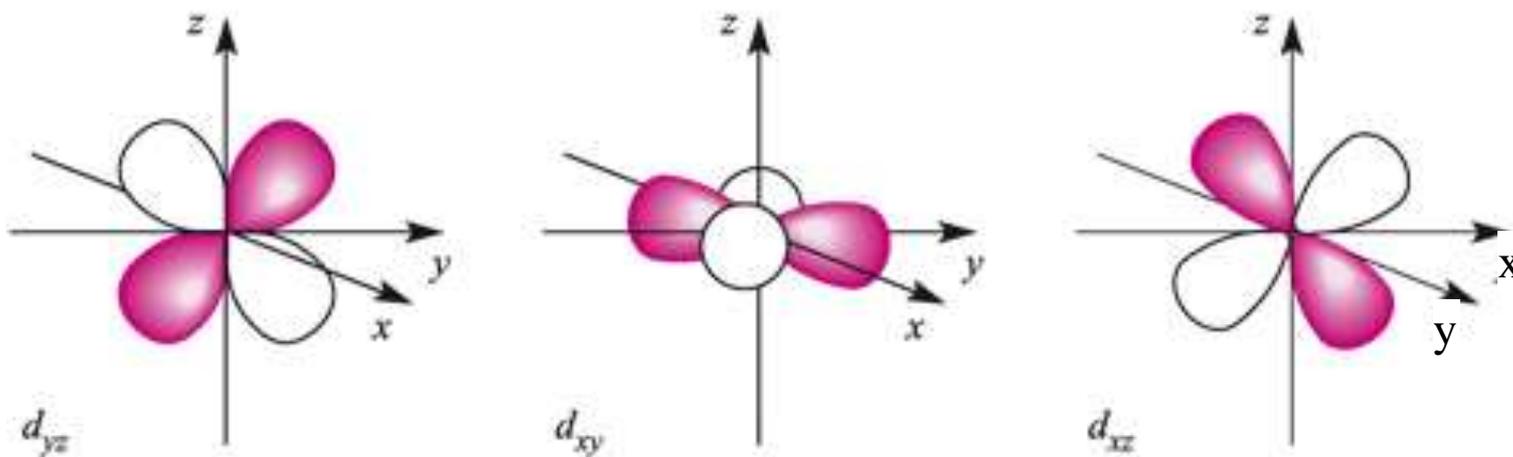
These conditions are fulfilled only when one or two orbitals contain partially filled electrons in t_{2g} and NOT in e_g

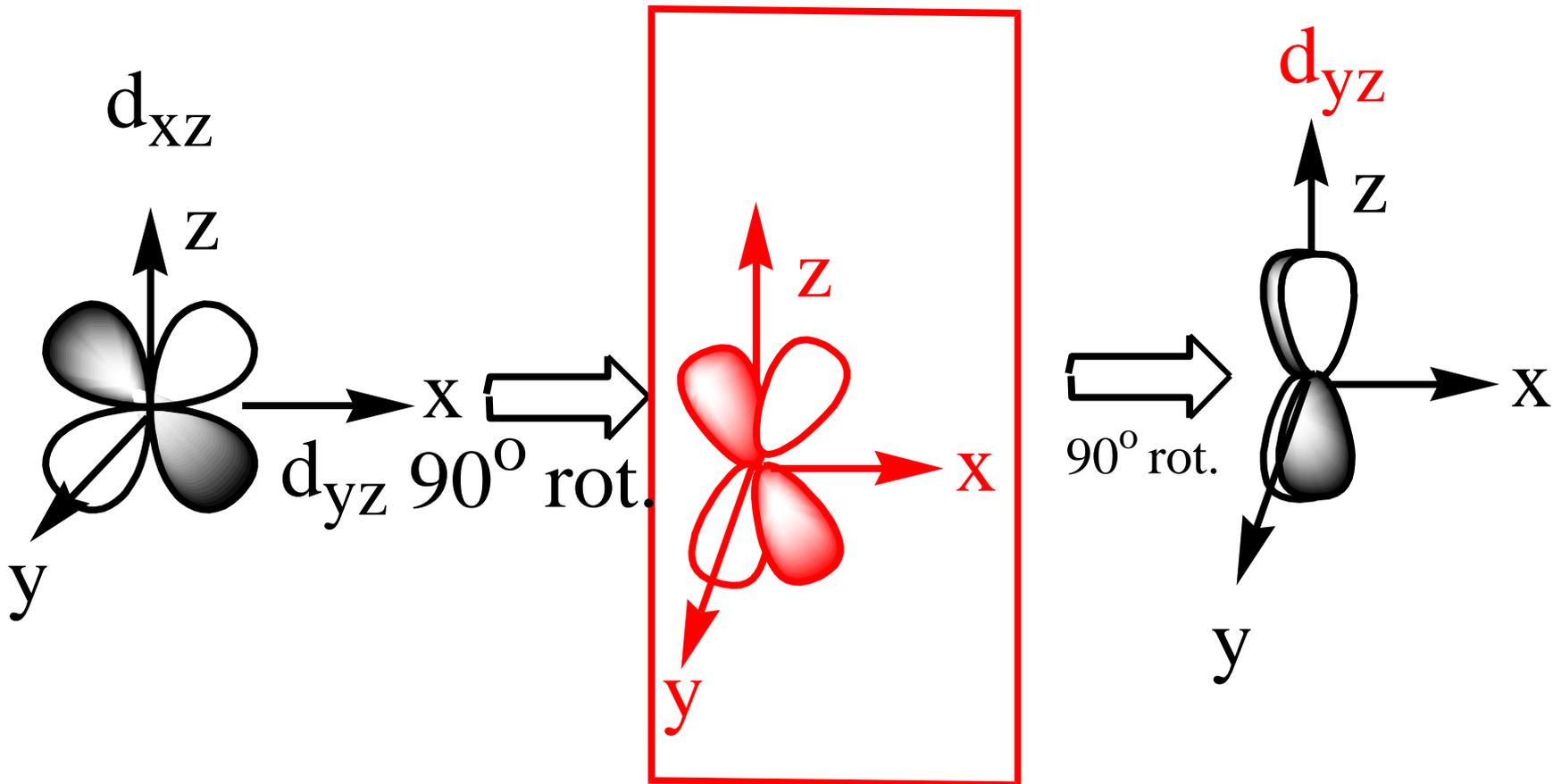
Octahedral complexes

The degenerate t_{2g} orbitals (d_{xy} , d_{xz} , d_{yz}) can be interconverted by 90° rotations

e.g. the d_{xz} orbital is transformed into the d_{yz} orbital by a rotation of 90° about the z-axis – during this rotation the electron is orbiting the nucleus

Thus, an electron in a t_{2g} orbital **can** contribute to orbital angular momentum

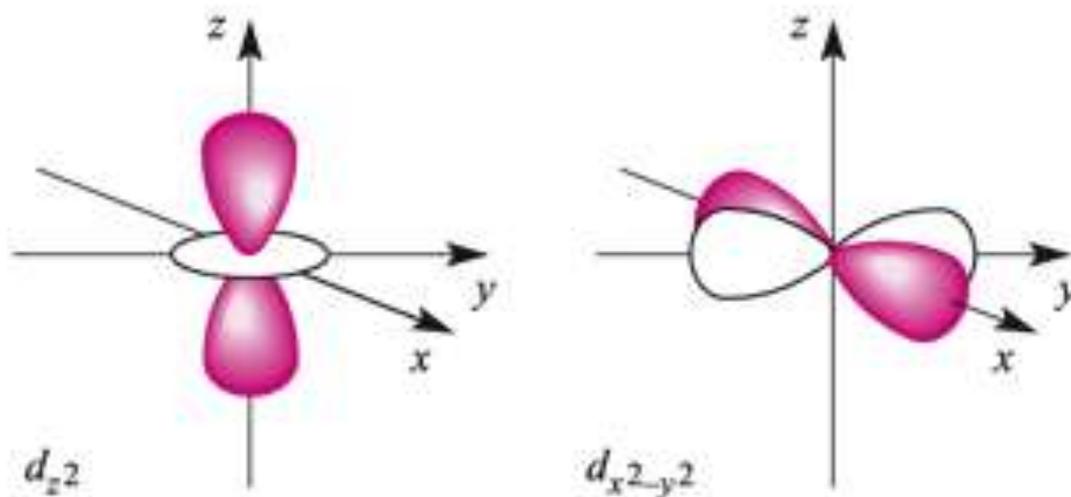




Octahedral complexes

However the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) cannot be interconverted by rotation as they are different shapes

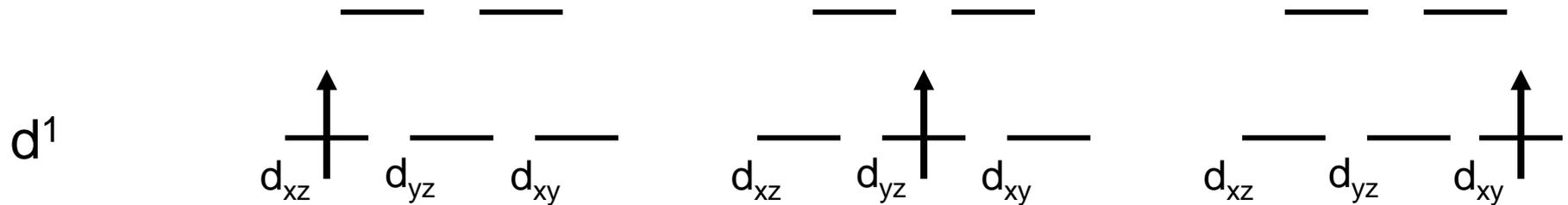
Thus an electron in an e_g orbital **can not** contribute to orbital angular momentum



Orbital contribution to the magnetic moment

high spin octahedral d^n ions

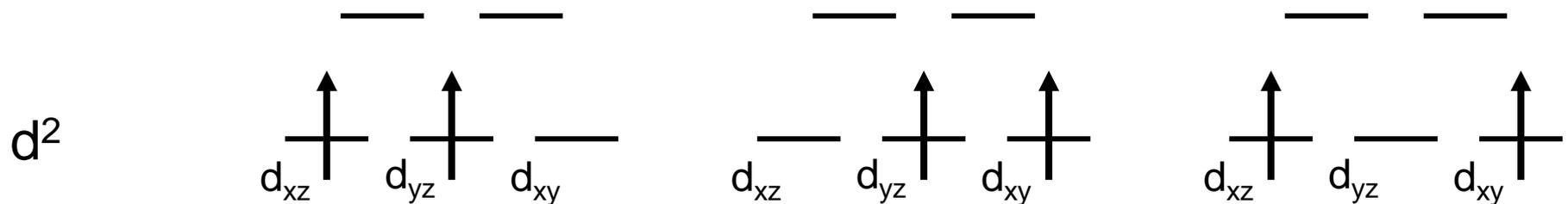
think of **possible** t_{2g} electron arrangements



Possible t_{2g} arrangements = 3

Orbital contribution = **YES**

d^1 e.g. Ti(III)



Possible t_{2g} arrangements = 3

Orbital contribution = **yes**

d^2 e.g. V(III)

Quenched orbital angular momentum

d^n	Octahedral	Tetrahedral
	high-spin	low-spin
d^1		e^1
d^2		e^2
d^3	t_{2g}^3	
d^4	$t_{2g}^3 e_g^1$	
d^5	$t_{2g}^3 e_g^2$	
d^6		t_{2g}^6
d^7		$t_{2g}^6 e_g^1$
d^8	$t_{2g}^6 e_g^2$	$e^3 t_2^3$
d^9	$t_{2g}^6 e_g^3$	$e^4 t_2^3$

High spin complexes

Ion	Number of unpaired electrons	Spin-only moment /μ_B	observed moment /μ_B
Ti³⁺	1	1.73	1.73
V⁴⁺	1		1.68–1.78
Cu²⁺	1		1.70–2.20
V³⁺	2	2.83	2.75–2.85
Ni²⁺	2		2.8–3.5
V²⁺	3	3.87	3.80–3.90
Cr³⁺	3		3.70–3.90
Co²⁺	3		4.3–5.0
Mn⁴⁺	3		3.80–4.0
Cr²⁺	4	4.90	4.75–4.90
Fe²⁺	4		5.1–5.7
Mn²⁺	5	5.92	5.65–6.10
Fe³⁺	5		5.7–6.0

Orbital Contributions in Octahedral Complexes

Ion	Config	OAM ?	μ_{so}	μ_{obs}
Ti(III)	d1	yes	1.73	1.6-1.7
V(IV)	d1	yes	1.73	1.7-1.8
V(III)	d2	yes	2.83	2.7-2.9
Cr(IV)	d2	yes	2.83	2.8
V(II)	d3	no	3.88	3.8-3.9
Cr(III)	d3	no	3.88	3.7-3.9
Mn(IV)	d3	no	3.88	3.8-4.0
Cr(II)	d4 h.s	no	4.90	4.7-4.9
Cr(II)	d4 l.s.	yes	2.83	3.2-3.3
Mn(III)	d4 h.s	no	4.90	4.9-5.0
Mn(III)	d4 l.s.	yes	2.83	3.2
Mn(II)	d5 h.s	no	5.92	5.6-6.1
Mn(II)	d5 l.s	yes	1.73	1.8-2.1
Fe(III)	d5 h.s	no	5.92	5.7-6.0
Fe(III)	d5 l.s	yes	1.73	2.0-2.5
Fe(II)	d6 h.s	yes	4.90	5.1-5.7
Co(II)	d7 h.s	yes	3.88	4.3-5.2
Co(II)	d7 l.s	no	1.73	1.8
Ni(III)	d7 l.s	no	1.73	1.8-2.0
Ni(II)	d8	no	2.83	2.9-3.3
Cu(II)	d9	no	1.73	1.7-2.2

High & Low – Spin Octahedral complexes & Spin Cross-Over

High and low -spin octahedral complexes

d-count	Number of unpaired electrons		examples
	high-spin	low-spin	
d ⁴	4	2	Cr ²⁺ , Mn ³⁺
d ⁵	5	1	Mn ²⁺ , Fe ³⁺
d ⁶	4	0	Fe ²⁺ , Co ³⁺
d ⁷	3	1	Co ²⁺

With one unpaired electron μ_{eff} values range from 1.8 to $2.5 \mu_{\text{B}}$ and with two unpaired electrons the range is 3.18 to $3.3 \mu_{\text{B}}$.

Spin cross-over

When the energy difference between the high-spin and low-spin states is comparable to kT (k is the Boltzmann constant and T the temperature) an equilibrium is established between the spin states, involving what have been called "electronic isomers".

Tris-dithiocarbamate iron(III), $\text{Fe}(\text{S}_2\text{CNR}_2)_3$, is a well-documented example. The effective moment varies from a typical d⁵ low-spin value of $2.25 \mu_{\text{B}}$ at 80 K to more than $4 \mu_{\text{B}}$ above 300 K.

Orbital Contributions in tetrahedral Complexes

Ion	Config	OAM ?	μ_{so}	μ_{obs}
Cr(V)	d1	no	1.73	1.7-1.8
Mn(VI)	d1	no	1.73	1.7-1.8
Cr(IV)	d2	no	2.83	2.8
Mn(V)	d2	no	2.83	2.6-2.8
Fe(V)	d3	yes	3.88	3.6-3.7
-	d4	yes	4.90	-
Mn(II)	d5	no	5.92	5.9-6.2
Fe(II)	d6	no	4.90	5.3-5.5
Co(II)	d7	no	3.88	4.2-4.8
Ni(II)	d8	yes	2.83	3.7-4.0
Cu(II)	d9	yes	1.73	

GS = Ground electronic State; ES = Excited electronic State

Other Reasons for Orbital Contribution:

Although μ normally develops from GS, sometimes ES also may contribute, especially the GS-ES energy difference is very small.

Example:

Take Ni^{2+} octahedral; d^8 ; GS: $t_{2g}^6 e_g^2$ no μ_l

ES: $t_{2g}^5 e_g^3$ μ_l contributes

Similarly,

Take Co^{2+} tetrahedral; d^7 GS: $e^4 t_2^3$ no μ_l

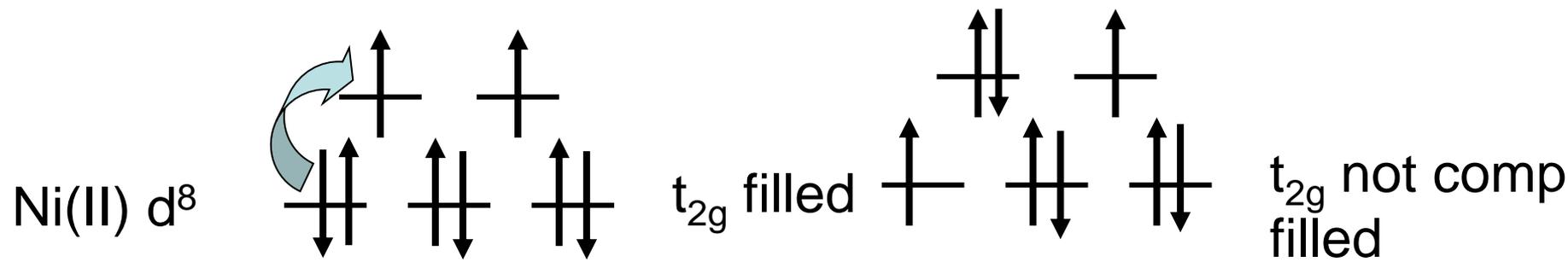
ES: $e^3 t_2^4$ μ_l contributes

Therefore; $\mu_{\text{obs}} > \mu_s$ for both $O_h \text{Ni}^{2+}$ and $T_d \text{Co}^{2+}$

Orbital contribution to the magnetic moment

Contribution due to the excited state(s)

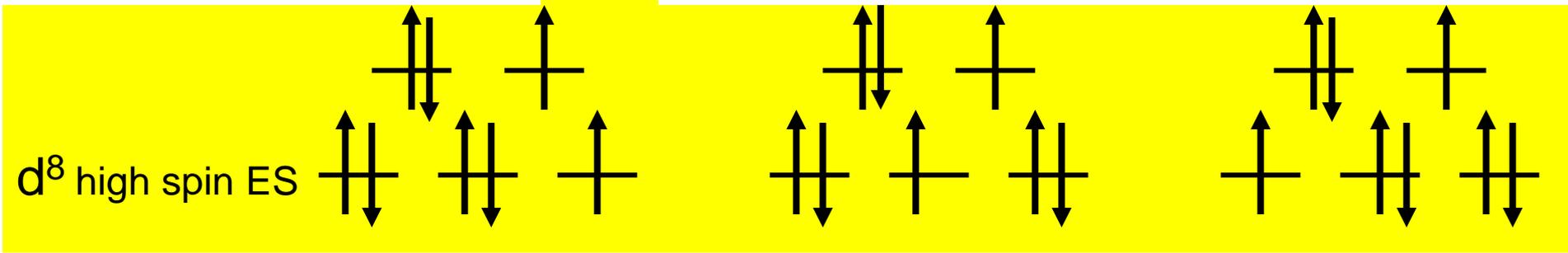
think of **possible** t_{2g} electron arrangements



Excited state

Possible t_{2g} arrangements = 1

Orbital contribution = **NO**



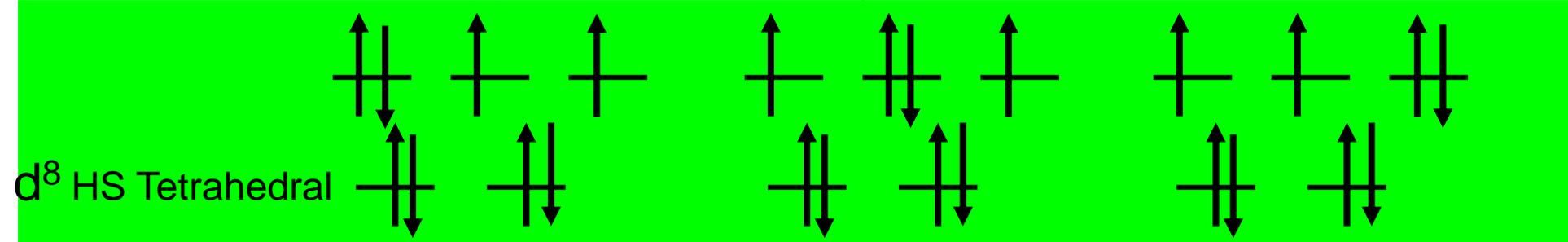
Possible t_{2g} arrangements = 3

Orbital contribution = **YES**

$\mu_{exp} > \mu_s$ for Oct. Ni^{2+}

Therefore for O_h Ni(II) the magnetic moments are larger if the GS-ES gap is small.

BUT FOR Tetrahedral Ni(II) situation is entirely different



Possible t_{2g} arrangements = 3

Orbital contribution = YES

$M_{\text{exp}} O_h \text{ Ni(II)}$ is smaller than $M_{\text{exp}} T_d \text{ Ni(II)}$

Exp. NiCl_4^{2-} , $\text{Ni}(\text{HMPA})_4^{2+}$ (HMPA=hexamethyl phosphoramidate) have mag. moment larger than 4 BM.

(Larger the distortion smaller the mag.moment)

USEFUL IN DISCRIMINATING O_h vs T_d structures.

Magnetic properties of lanthanides

- The f electrons in lanthanides are buried in the (n-2) shell

- \therefore Thus 4f normally unaffected by surrounding ligands
- Hence, the magnetic moments of Ln^{3+} ions are generally well-described from the coupling of spin and orbital angular momenta \sim Russell-Saunders Coupling to give J vector
- spin orbit coupling constants are large (ca. 1000 cm^{-1})
- ligand field effects are very small (ca. 100 cm^{-1})
 - only ground J-state is populated
 - spin-orbit coupling \gg ligand field splittings
- magnetism is essentially independent of environment

Spectroscopic Terms (& Term Symbols)

Different microstates exist for the same electronic configuration.

Russel-Saunders coupling is used to describe the terms.

The symbol will represent the total value of azimuthal quantum numbers ($L = \sum l_i$) and it takes the letters, 'S, P, D, F, G, H, I, K, L, M, N' respectively for L values of 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10.

The degeneracy $(2S+1)$ {S = sum of all the spins} is shown on the left superscript.

The term symbol is shown as $(2S+1)L$ {for eg., 3F corresponds to $S = 1$ and $L = 3$ }

No. of microstates for 3F is, $(2S+1) \times (2L+1) = 3 \times 7 = 21$

Magnetic moment of a J-state is expressed by:

$$\mu = g_J \sqrt{J(J+1)} \mu_B \quad g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$$J = L+S, L+S-1, \dots, L-S$$

For the calculation of g value, we use

minimum value of J for the configurations up to half-filled;

i.e. $J = L-S$ for f^0 - f^7 configurations

maximum value of J for config. more than half-filled;

i.e. $J = L+S$ for f^8 - f^{14} configurations

For f^0 , f^7 , and f^{14} , $L = 0$, hence μ_J becomes μ_S

	config	g.s.	No. e-	color	calcd	obsd
La	4f ⁰	¹ S ₀	0	Colorless	0	0
Ce	4f ¹	² F _{5/2}	1	Colorless	2.54	2.3 - 2.5
Pr	4f ²	³ H ₄	2	Green	3.58	3.4 - 3.6
Nd	4f ³	⁴ I _{9/2}	3	Lilac	3.62	3.5 - 3.6
Pm	4f ⁴	⁵ I ₄	4	Pink	2.68	-
Sm	4f ⁵	⁶ H _{5/2}	5	Yellow	0.85	1.4 - 1.7
Eu	4f ⁶	⁷ F ₀	6	Pale pink	0	3.3 - 3.5
Gd	4f ⁷	⁸ S _{7/2}	7	Colorless	7.94	7.9 - 8.0
Tb	4f ⁸	⁷ F ₆	6	Pale pink	9.72	9.5 - 9.8
Dy	4f ⁹	⁶ H _{15/2}	5	Yellow	10.65	10.4 - 10.6
Ho	4f ¹⁰	⁵ I ₈	4	Yellow	10.6	10.4 - 10.7
Er	4f ¹¹	⁴ I _{15/2}	3	Rose-pink	9.58	9.4 - 9.6
Tm	4f ¹²	³ H ₆	2	pale green	7.56	7.1 - 7.6
Yb	4f ¹³	² F _{7/2}	1	Colorless	4.54	4.3 - 4.9
Lu	4f ¹⁴	¹ S ₀	0	Colorless	0	0

Sample Landé Calculation for a Ln^{3+} ion

e.g $\text{Pr}^{3+} [\text{Xe}]4f^2$; find Ground State from Hund's Rules

- $S = 1/2 + 1/2 = 1$
- $L = 3 + 2 = 5$
- $J = 6, 5, 4$; $J = 4$ is chosen for f^2
- $g = (3/2) + [1(1+1) - 5(5+1)] / 2(4)(4+1) = 0.8$

□ $\mu_J = 3.577 \text{ B.M.}$ **Experiment = 3.4 - 3.6 B.M**

- Landé formula fits well with observed magnetic moments for all but Sm^{III} and Eu^{III} ions.
- Moments of these ions are altered from the Landé expression by temperature-dependent population of low-lying excited J-state(s)

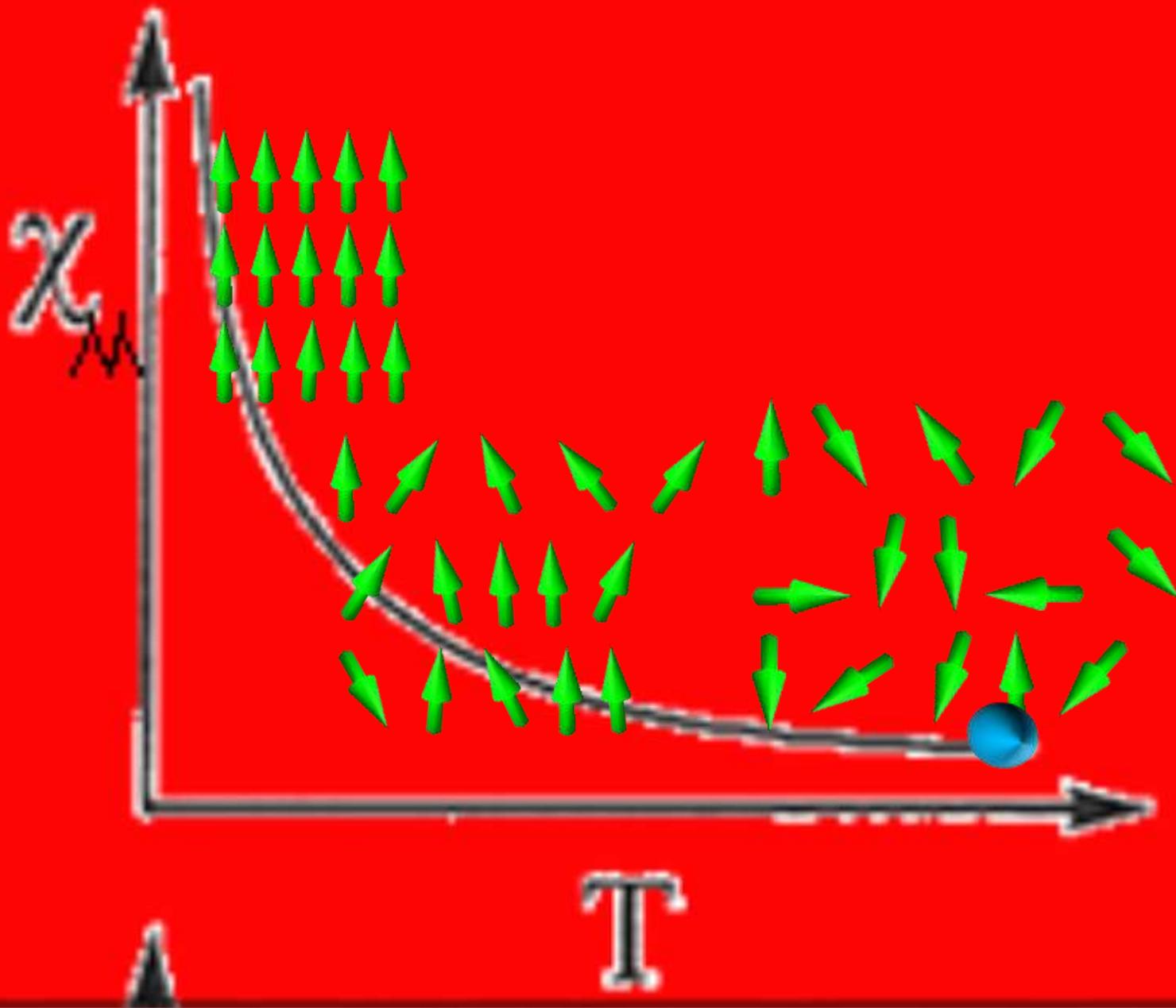
Magnetic States of Matter

Diamagnet - A diamagnetic compound has all of its electron spins paired giving a net spin of zero. Diamagnetic compounds are weakly repelled by a magnet.

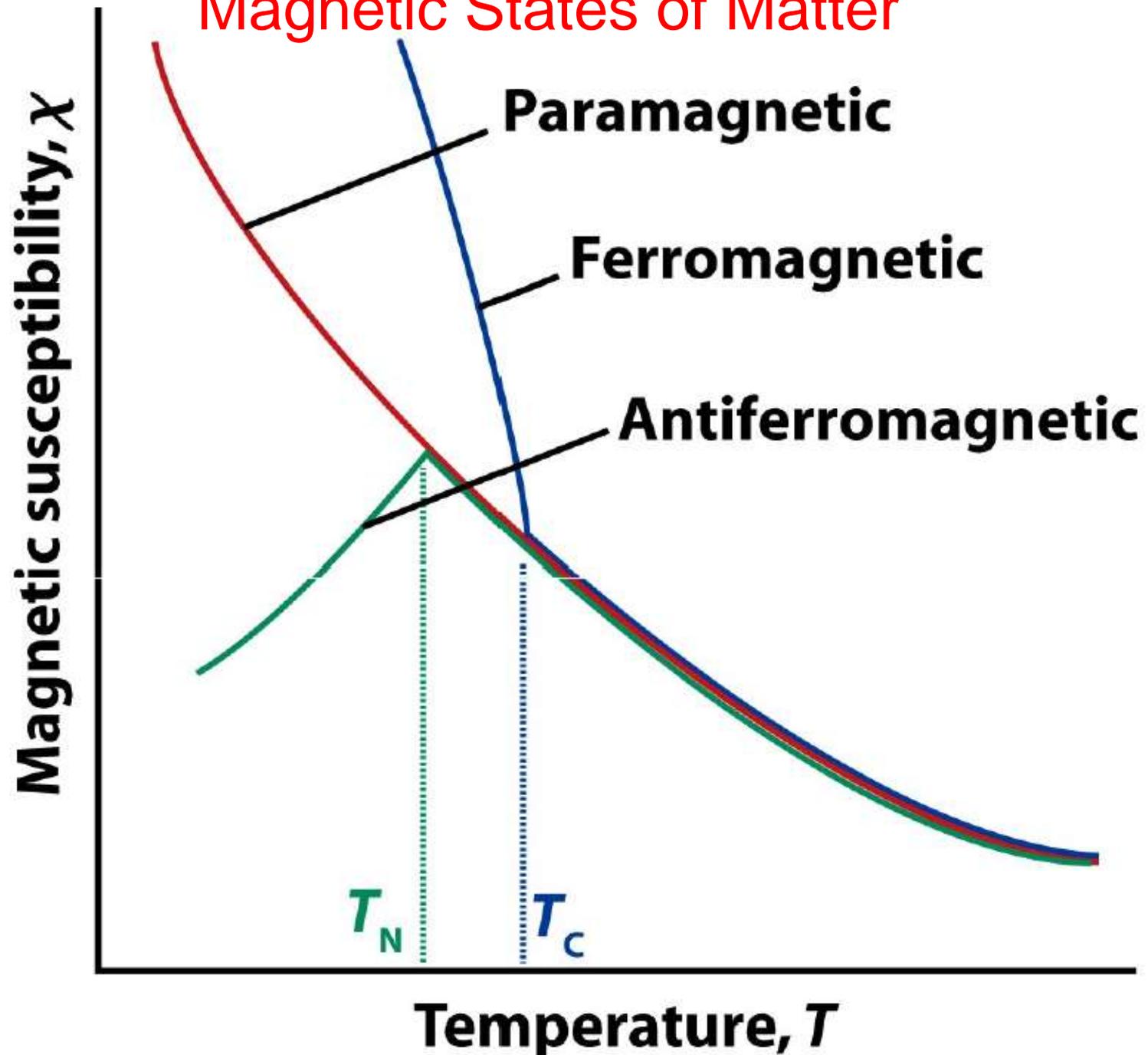
Paramagnet - A paramagnetic compound will have some electrons with unpaired spins. Paramagnetic compounds are attracted by a magnet.

Paramagnetism derives from the spin and orbital angular momenta of electrons. This type of magnetism occurs only in compounds containing unpaired electrons, as the spin and orbital angular momenta is cancelled out when the electrons exist in pairs.

Compounds in which the paramagnetic centres are separated by diamagnetic atoms within the sample are said to be magnetically dilute.

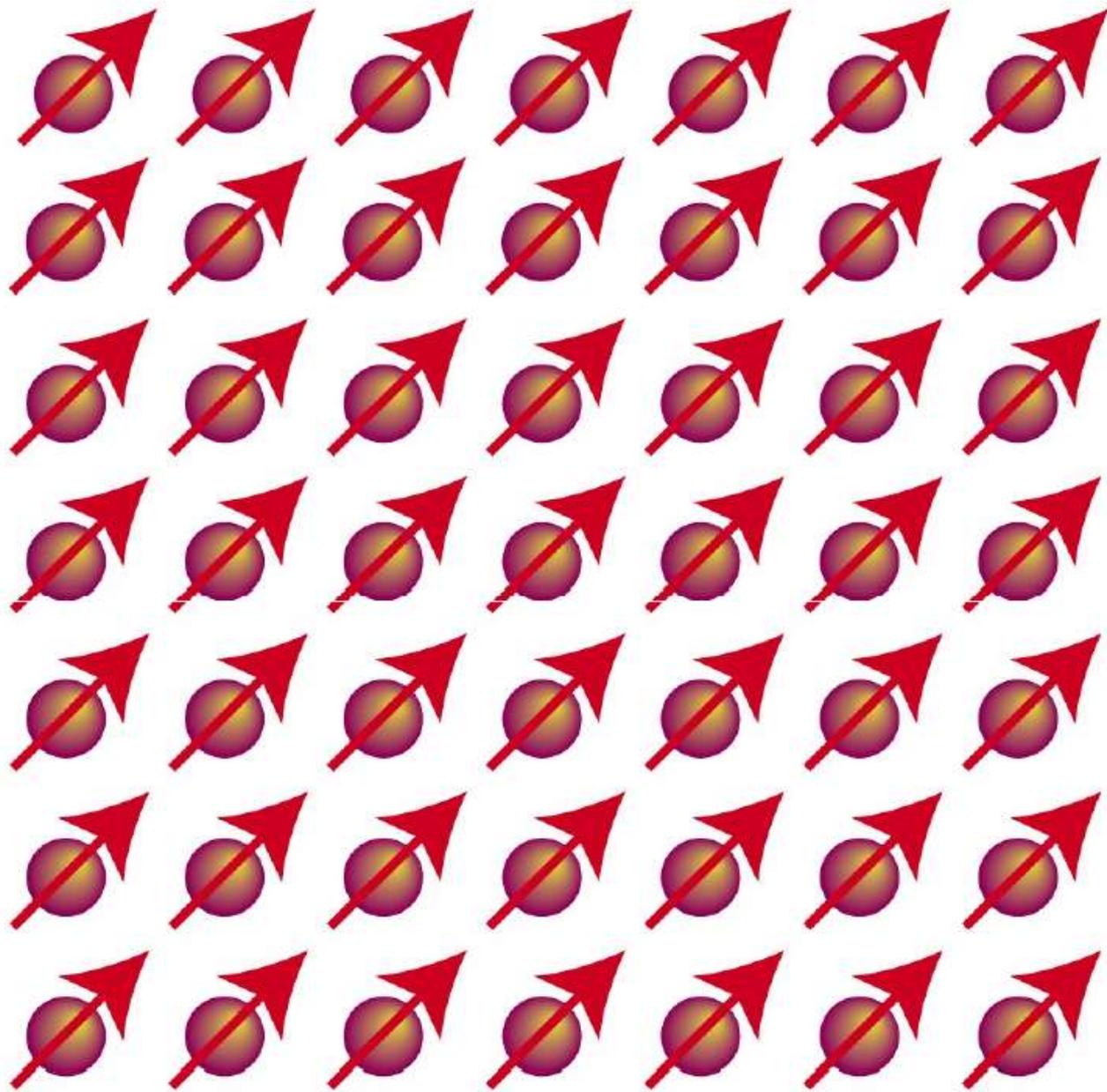


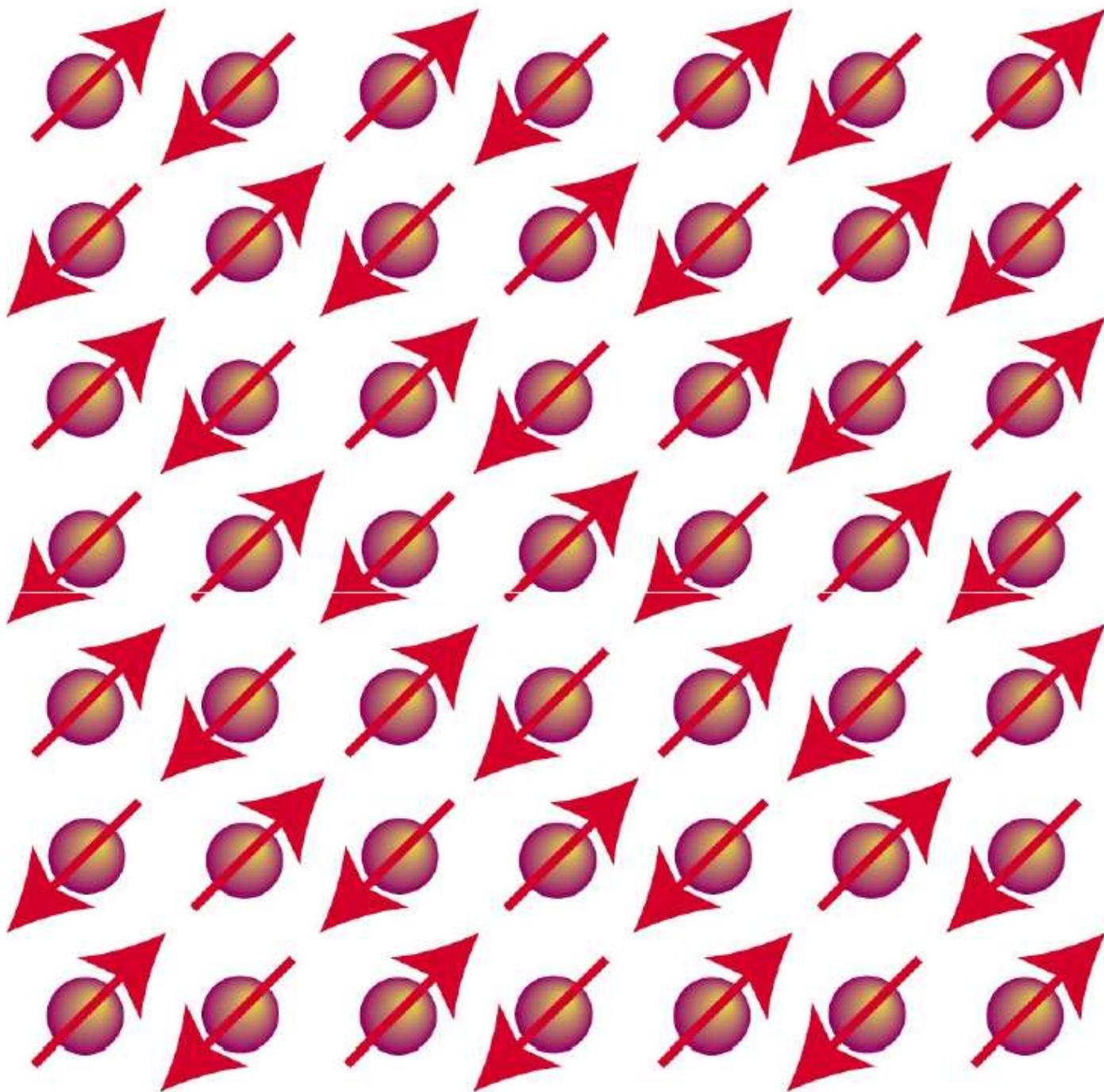
Magnetic States of Matter



Magnetic States of Matter

- These two forms of paramagnetism show characteristic variations of the magnetic susceptibility with temperature.
- In the case of ferromagnetism, above the Curie point the material displays "normal" paramagnetic behavior. Below the Curie point the material displays strong magnetic properties. Ferromagnetism is commonly found in compounds containing iron and in alloys.
- For antiferromagnetism, above the Neel point the material displays "normal" paramagnetic behavior. Below the Neel point the material displays weak magnetic properties which at lower and lower temperatures can become essentially diamagnetic. Antiferromagnetism is more common and is found to occur in transition metal halides and oxides, such as TiCl_3 and VCl_2 .



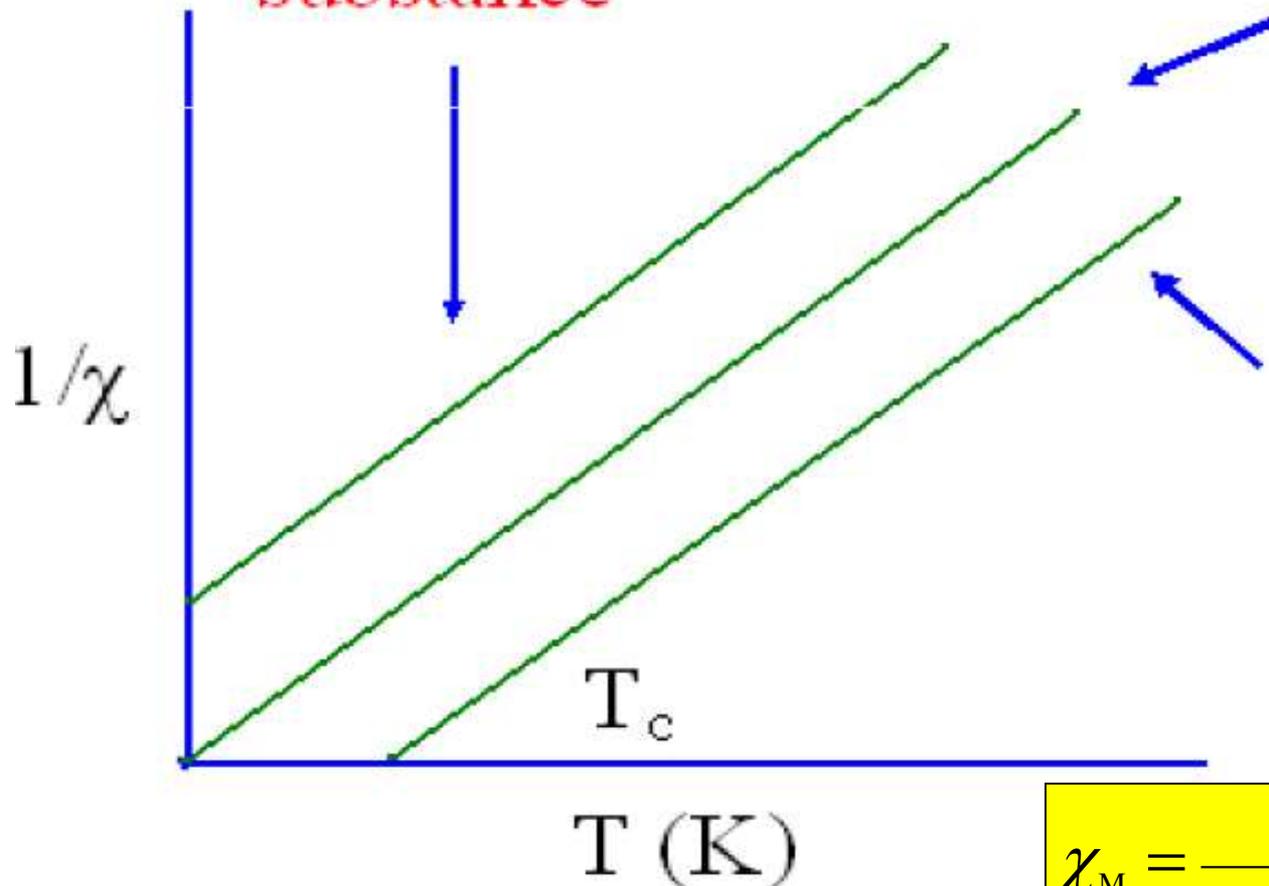


Magnetic States of Matter

Curie-Weiss Law
for anti-ferromagnetic
substance

Curie Law for
paramagnetic
substance

Curie-Weiss
Law for
ferromagnetic
substance

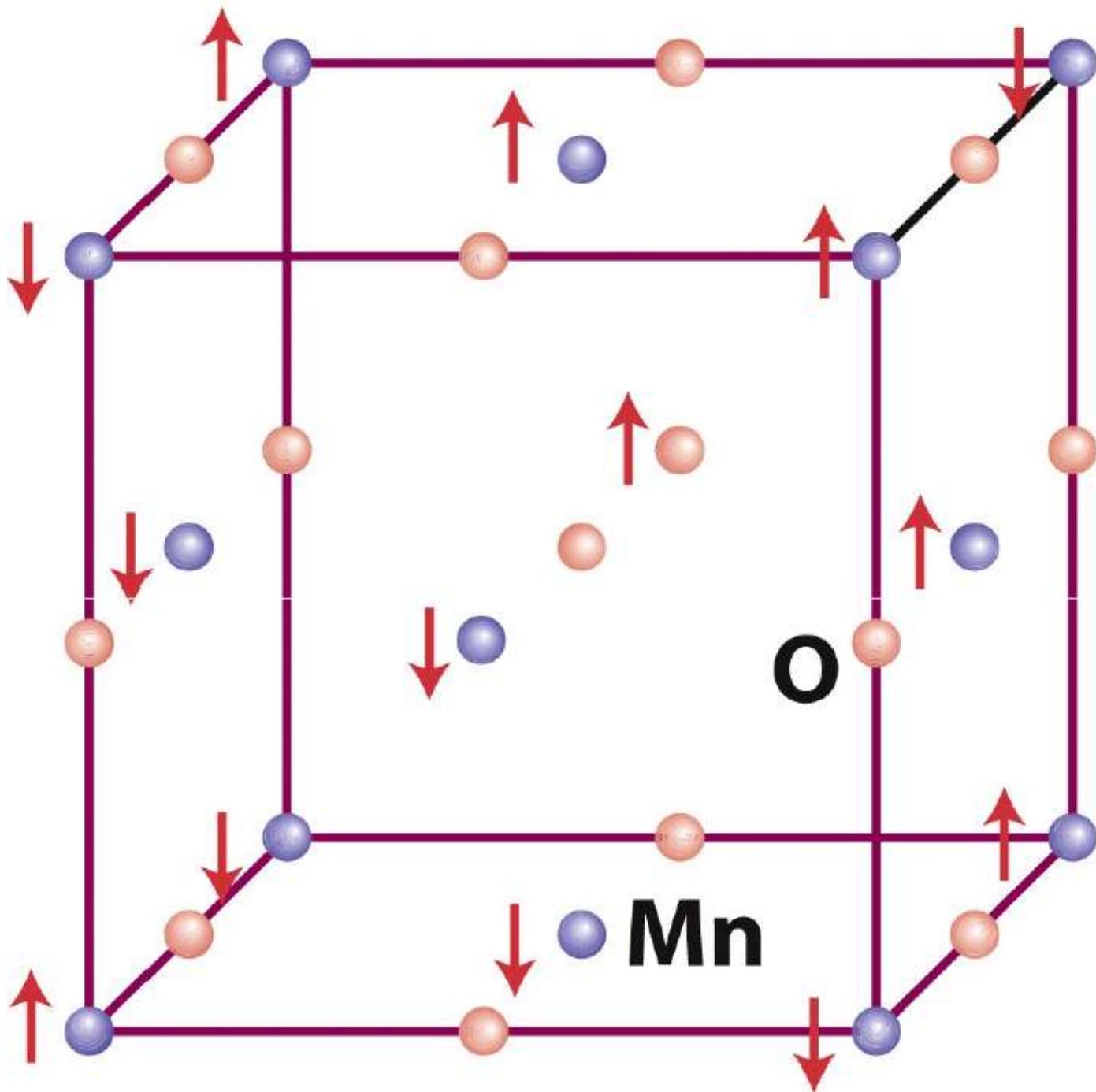


T_c

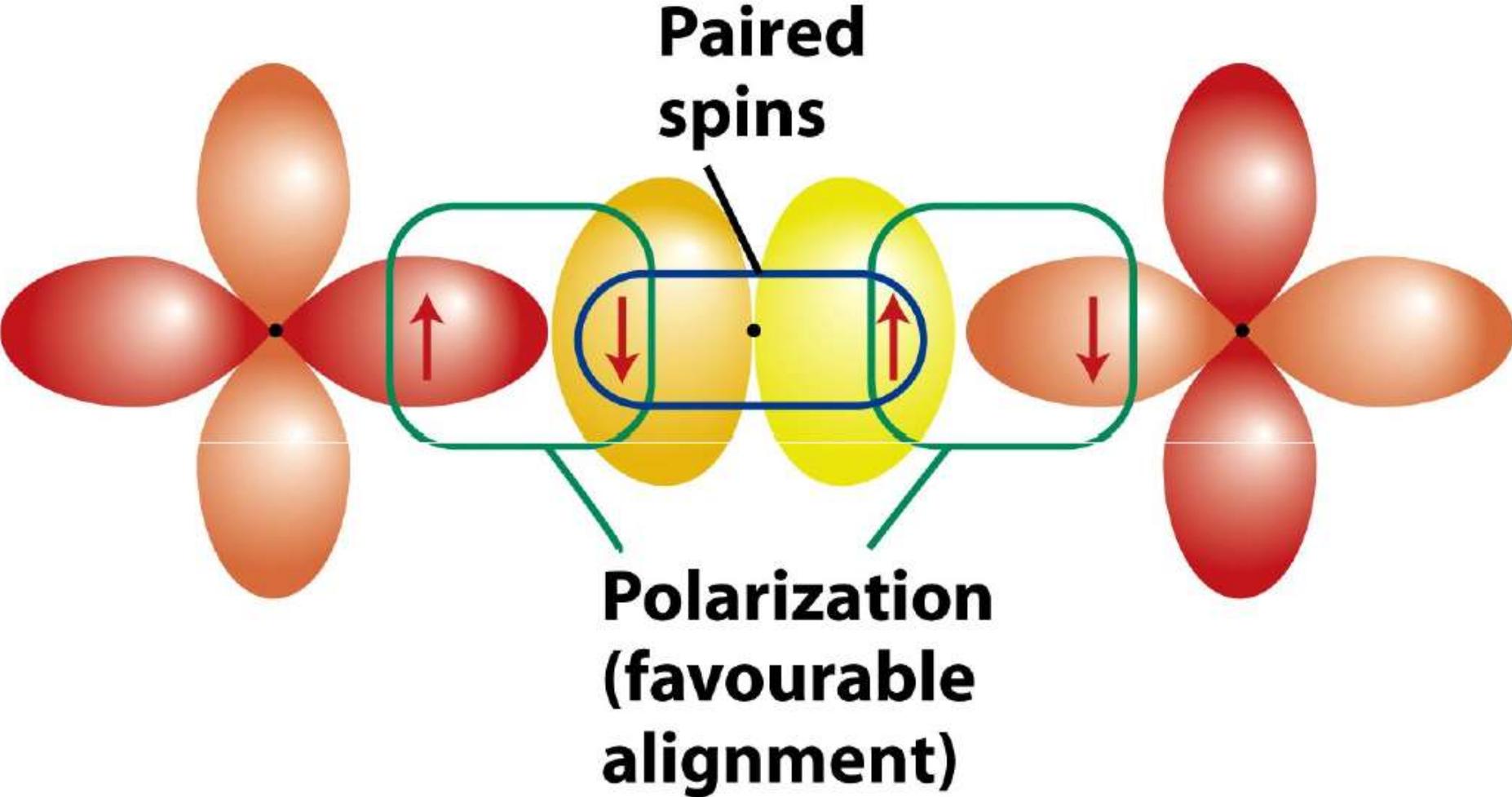
T (K)

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

$$\theta = \frac{zJS(S+1)}{3k}$$



Magnetic coupling: Origin of AF interaction



Hard & Soft Magnetic Materials

Hard Ferromagnet

As permanent magnet

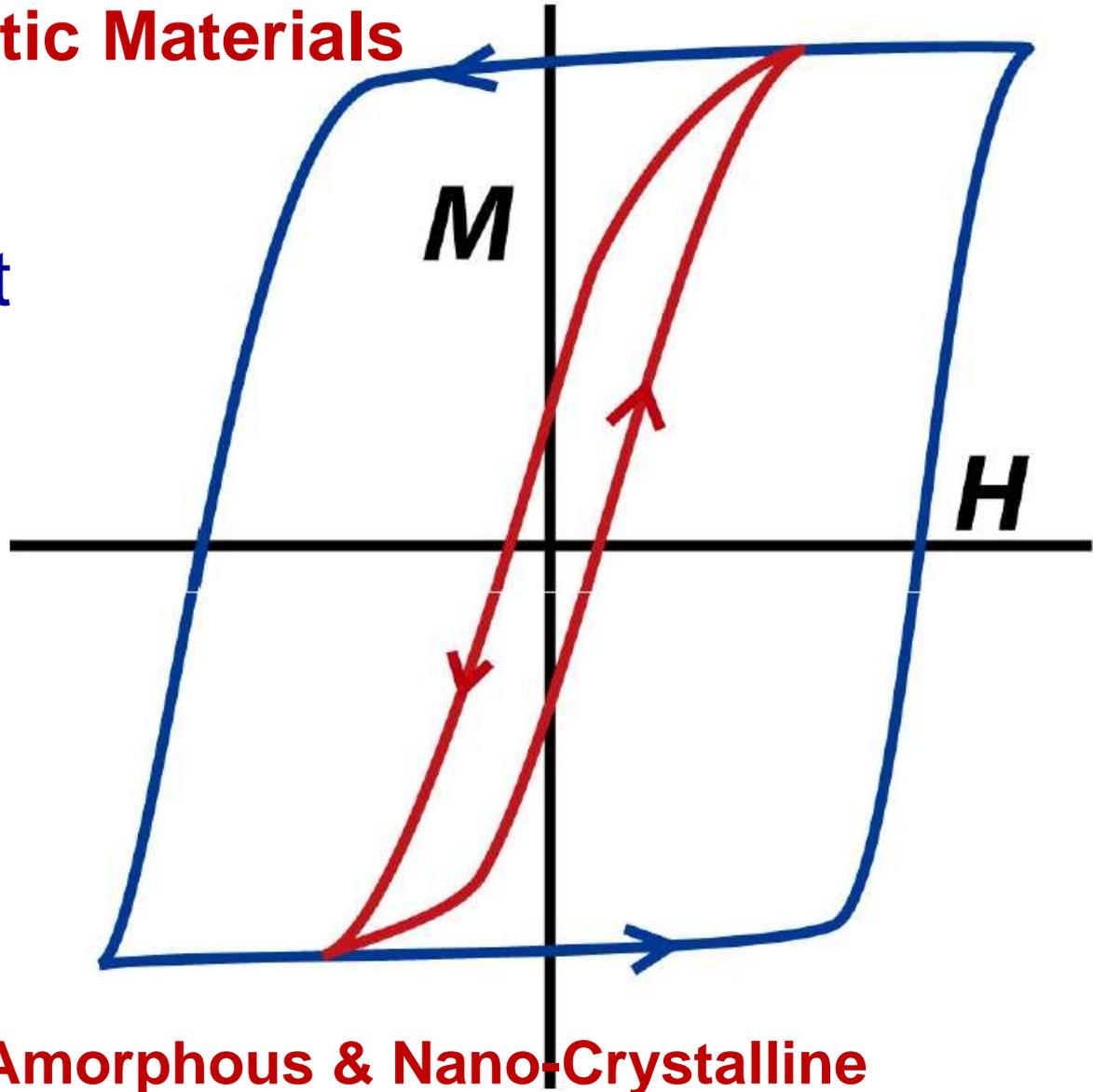
Alnicos

SmCo Type

NdFeB Type

Soft Ferromagnet

Used in transformers



Iron-Silicon Alloys; Amorphous & Nano-Crystalline Alloys; Nickel-Iron Alloys; AC & DC Applications

Applications of hard ferromagnetic materials

Automotive: Starter motors, Anti-lock braking systems (ABS), Motor drives for wipers, Injection pumps, Fans and controls for windows, seats etc, Loudspeakers, Eddy current brakes, Alternators.

Telecommunications: Loudspeakers, Microphones, Telephone ringers, Electro-acoustic pick-ups, Switches and relays.

Data Processing: Disc drives and actuators, Stepping motors, Printers.

Consumer Electronics: DC motors for showers, Washing machines, Drills, Low voltage DC drives for cordless appliances, Loudspeakers for TV and Audio, TV beam correction and focusing device, Compact-disc drives, Home computers, Video Recorders, Clocks.

Electronic and Instrumentation: Sensors, Contactless switches, NMR spectrometer, Energy meter disc, Electro-mechanical transducers, Crossed field tubes, Flux-transfer trip device, Dampers.

Industrial: DC motors for magnetic tools, Robotics, Magnetic separators for extracting metals and ores, Magnetic bearings, Servo-motor drives, Lifting apparatus, Brakes and clutches, Meters and measuring equipment.

Astro and Aerospace: Frictionless bearings, Stepping motors, Couplings, Instrumentation, Travelling wave tubes, Auto-compass.

Biosurgical: Dentures, Orthodontics, Orthopaedics, Wound closures, Stomach seals, Repulsion collars, Ferromagnetic probes, Cancer cell separators, Magnetomotive artificial hearts, NMR / MRI body scanner.

Problem:

- Account for the magnetic moments of $(\text{Et}_4\text{N})_2[\text{NiCl}_4]$ recorded at 80 and 300 K.
- 80K 300K
- 3.25 3.89 B.M.
- Ni^{2+} is a d^8 metal ion.
- The formula suggests a 4 coordinate complex and we can assume that the complex is tetrahedral with a d electron configuration of $e^4 t_2^4$ therefore the spin-only magnetic moment can be calculated as 2.83 BM
- Why did we ignore the possibility of it being square-planar?
- The free ion Russell-Saunders ground term is 3F ($L=3$ and $S=1$) which will give rise to a lowest energy T term in a tetrahedral field and hence the resultant magnetic moment is expected to be temperature dependent and have a direct orbital contribution.

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- The formula suggests a 4 coordinate complex and we can assume that the complex is tetrahedral with a d electron configuration of $e^4 t_2^4$ therefore the spin-only magnetic moment can be calculated as 2.83 BM
- Why did we ignore the possibility of it being square-planar?

This is understood from Spectroscopy. Without going into the spectroscopy related parameters, it can be said that the d^8 will be diamagnetic if it were square planar.

Problem: Continued

- The observed values may be quite different than to the calculated spin only magnetic moment.
- The value of μ_{S+L} can be calculated as: $\mu_{S+L} = \sqrt{4S(S+1)+L(L+1)}$
- $= \sqrt{8+12} = \sqrt{20} = 4.47$ B.M.
- If you use the spin-only formula $\mu_s = \sqrt{n(n+2)} = \sqrt{8} = 2.8$ BM
- Now go back and check above the observed magnetic moments at the given temperatures. What do you conclude?
- From the observed values it can be seen that the magnetic moment of the $d^8 \text{Ni}^{2+}$ complex is intermediate between the μ_s and μ_{S+L} values (probably due to partial quenching of the orbital angular momentum contribution) and is dependent on temperature.