

# Magnetism in Transition Metal Complexes

(continued)

**Spin-only magnetic moments ( $\mu_s$ )** are usually observed for first row TM ions as shown by the following table:

Ion	$d^n$	S	$\mu_s$ (BM)	$\mu_{\text{eff}}$ (obs. BM)
Sc <sup>3+</sup> , Ti <sup>4+</sup>	0	0	0	0
Ti <sup>3+</sup>	1	1/2	1.73	1.7-1.8
V <sup>3+</sup>	2	1	2.83	2.8-3.1
V <sup>2+</sup> , Cr <sup>3+</sup>	3	3/2	3.87	3.7-3.9
Cr <sup>2+</sup> , Mn <sup>3+</sup>	4	2	4.90	4.8-4.9
Mn <sup>2+</sup> , Fe <sup>3+</sup>	5	5/2	5.92	5.7-6.0
Fe <sup>2+</sup> , Co <sup>3+</sup>	6	2	4.90	<b>5.0-5.6</b>
Co <sup>2+</sup>	7	3/2	3.87	<b>4.3-5.2</b>
Ni <sup>2+</sup>	8	1	2.83	<b>2.9-3.9</b>
Cu <sup>2+</sup>	9	1/2	1.73	1.9-2.1
Zn <sup>2+</sup>	10	0	0	0

Values are different enough that they usually confirm the number of unpaired spins (S) and indicate whether the complex is high spin or low spin.

**Deviations are caused by two factors:**

**(a) orbital angular momentum (L) contributions to  $\mu$**

in cases where orbital angular momentum is not quenched a somewhat more elaborate expression for  $\mu$  applies:

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

which obviously simplifies to the  $\mu_s$  expression if  $L = 0$

If  $L \neq 0$  then  $\mu_{LS} > \mu_s$

NOTE one special case: for a  ${}^6S$  ground state,  $L = 0$  so  $\mu_{\text{eff}} = \mu_s$

Ion	$d^n$	S	L*	GS term	$\mu_s$	$\mu_{LS}$	$\mu_{\text{eff}}$
Fe <sup>2+</sup> , Co <sup>3+</sup>	6	2	2	${}^5T_{2g}$	4.90	<b>5.48</b>	<b>5.0-5.6</b>
Co <sup>2+</sup>	7	3/2	3	${}^4T_{1g}$	3.87	<b>5.20</b>	<b>4.3-5.2</b>
Ni <sup>2+</sup>	8	1	3	${}^3A_{2g}$	<b>2.83</b>	4.47	<b>2.9-3.9</b>

\* in an *Oh* complex

- orbital angular momentum is NOT quenched in degenerate ground states (especially T) so there is a significant contribution from L (egs. Co<sup>2+</sup> and Co<sup>3+</sup>, Fe<sup>2+</sup> above)
- non-degenerate ground states do not have a contribution from L so values close to the spin only moment are usually found (eg. Ni<sup>2+</sup>)

## **(b) contributions from spin-orbit coupling**

- Spin-orbit coupling means that S and L do not operate independently and J states need to be defined.
- Since spin-orbit coupling is usually small for lighter transition metals, we can treat S and L independently (as was done in the earlier equation for  $\mu_{LS}$ )
- This isn't true for heavy metals and their magnetism is MUCH more complicated to predict.

## **Temperature effects on $\mu_{\text{eff}}$**

**Curie Law predicts  $\mu$  should be T independent but that is often NOT the case:**

- orbital angular momentum and spin-orbit effects can come into play
- magnetic moment is determined by the L and S contributions (plus spin-orbit effects) of ALL populated levels weighted by their populations so if other thermally accessible states exists, their population will change with T and so will their contribution
- if there is any long range magnetic ordering (i.e. not behaving as isolated paramagnets) then  $\mu$  will vary because these effects are T dependent...

## Magnetic ordering: bulk properties

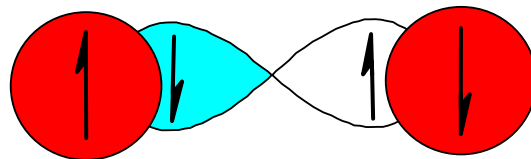
- direct effect of adjacent spins OR
- transmitted through bridging ligands

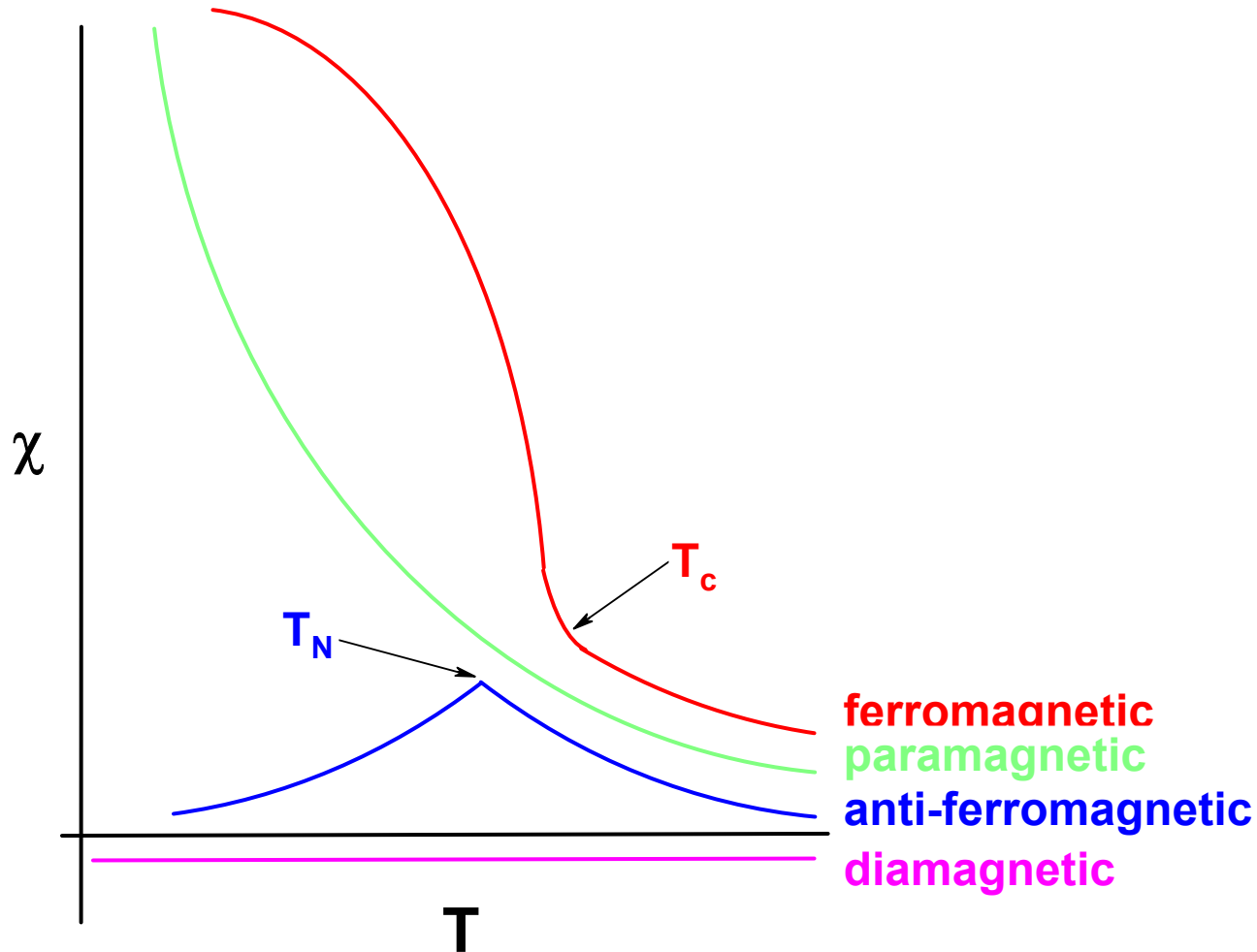
**Ferromagnetism:** neighbouring spins align parallel with one another below a certain critical temperature ( $T_c$  Curie temperature)

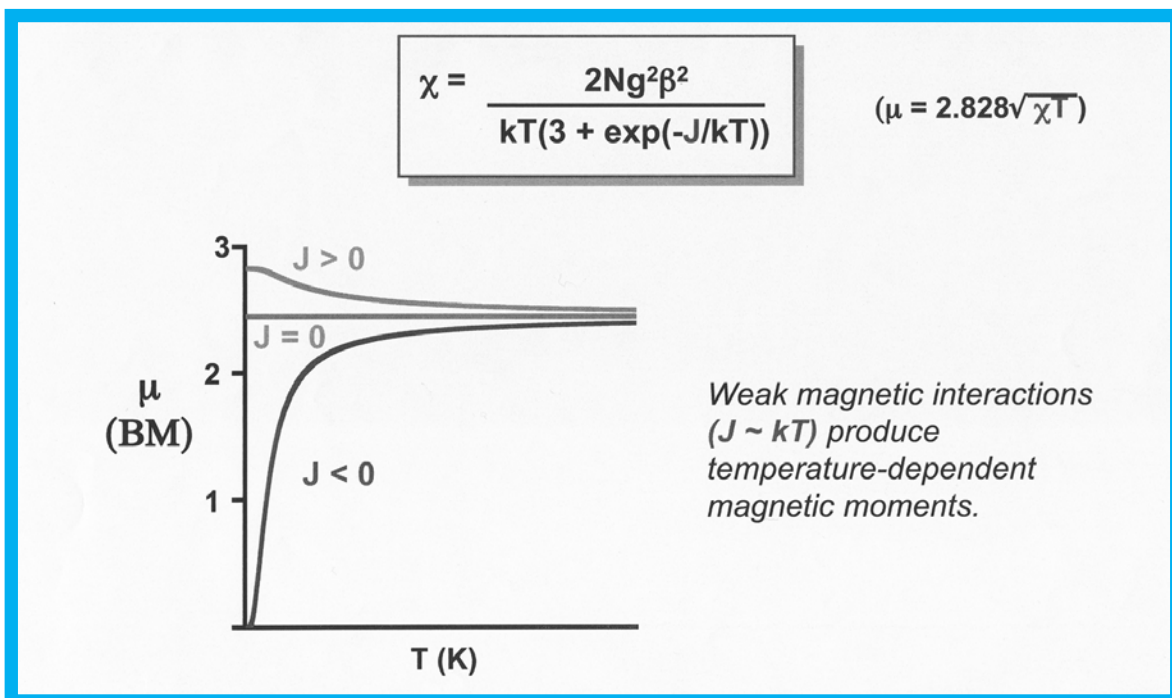
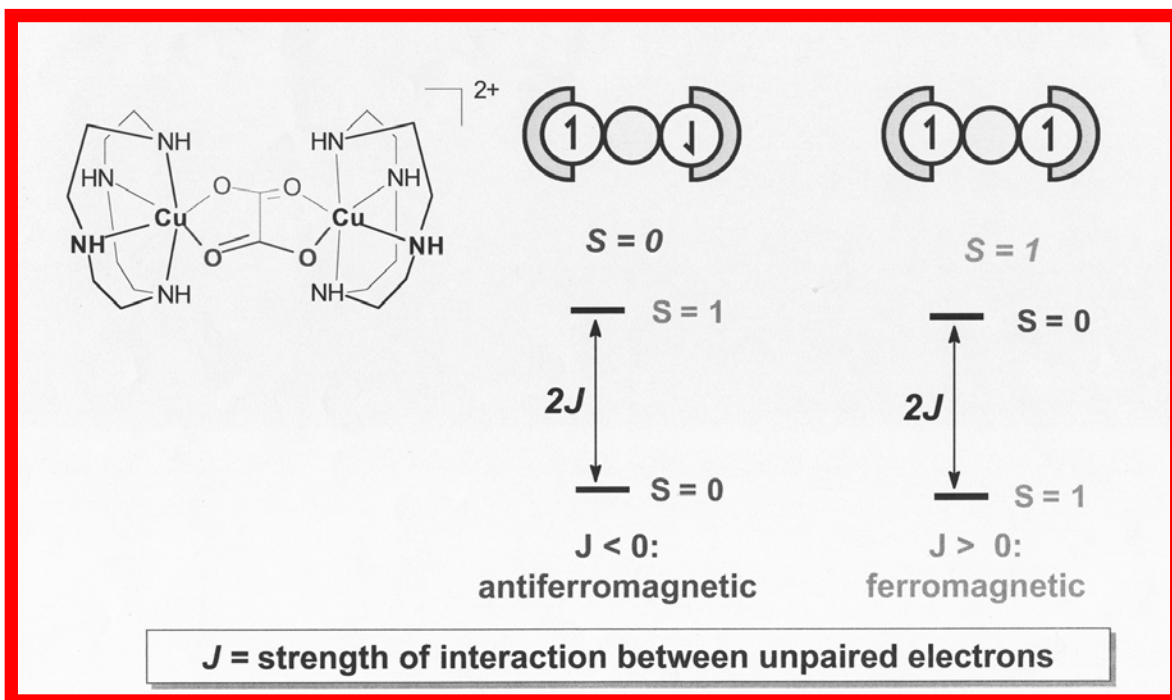
- below  $T_c$  the material remains permanently spin aligned even when the field is removed
- field dependent effect

**Antiferromagnetism:** neighbouring spins align anti-parallel with one another below a certain critical temperature ( $T_N$  Néel temperature)

- below  $T_N$  the material tends to remain spin aligned and has a lower moment than expected
- common effect through bridging ligand due to ‘**super-exchange**’







*(Figures courtesy of Robin Hicks)*