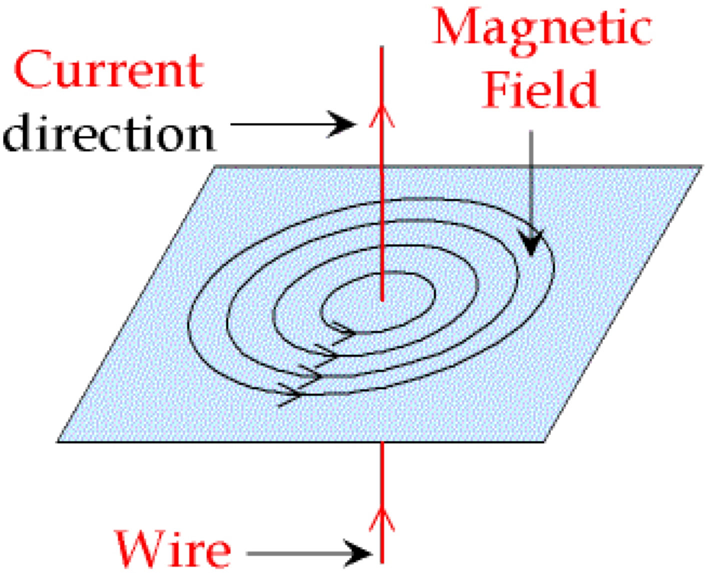
Magnetism

Introduction

Movement of an electrical charge (which is the basis of electric currents) generates a magnetic field in a material. Magnetism is therefore a characteristic property of all materials that contain electrically charged particles and for most purposes can be considered to be entirely of electronic origin.



The Right Hand Rule for an induced magnetic field

In an atom, the magnetic field is due to the coupled spin and orbital magnetic moments associated with the motion of electrons. The spin magnetic moment is due to the precession of the electrons about their own axes wherease the orbital magnetic moment is due to the motion of electrons around the nucleus. The resultant combination of the spin and orbital magnetic moments of the constituent atoms of a material gives rise to the observed magnetic properties.

Historically, magnetism has been recognised for thousands of years. An account, that is probably apochryphal, tells of a shepherd called Magnes in Crete who around 900 B.C discovered the naturally occurring magnet lodestone (a form of the the spinel magnetite, Fe_3O_4) in a region later named Magnesia. Supposedly while he was walking over a deposit, the lodestone pulled the nails out of his sandals and the metal tip from his staff.

The Classical Theory of Magnetism

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**, 4πI,
> which is proportional to the intensity of magnetization, **I**.
> That is; $\mathbf{B} = \mathbf{H} + 4\pi\mathbf{I}$
> where **B** is the magnetic field within the substance
> **H** is the applied magnetic field
> and **I** is the intensity of magnetisation

This can also be written as

$B/H = 1 + 4\pi\ I/H$, **or** $B/H = 1 + 4\pi\kappa$

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, so under those conditions the equation would reduce to B=H.

It is usually more convenient to measure mass than volume and the mass susceptibility, χ_g, is related to the volume susceptibility, κ, through the density.

$\chi_g = \kappa / \rho$
where ρ is the density.

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

$\chi_m = \chi_g * \mathrm{RMM}$

Since this value includes the underlying diamagnetism of paired electrons, it is necessary to correct for the diamagnetic portion of χ_m to get a corrected paramagnetic susceptibility.

$\chi'_m = \chi_m + \chi_{dia}$

Examples of these corrections are tabulated in the Laboratory Manual and are available on-line as well.

There are numerous methods for measuring magnetic susceptibilites, including, the **Gouy, Evans and Faraday methods**. These all depend on measuring the force exerted upon a sample when it is placed in a magnetic field. The more paramagnetic the sample, the more strongly it will be drawn toward the more intense part of the field.

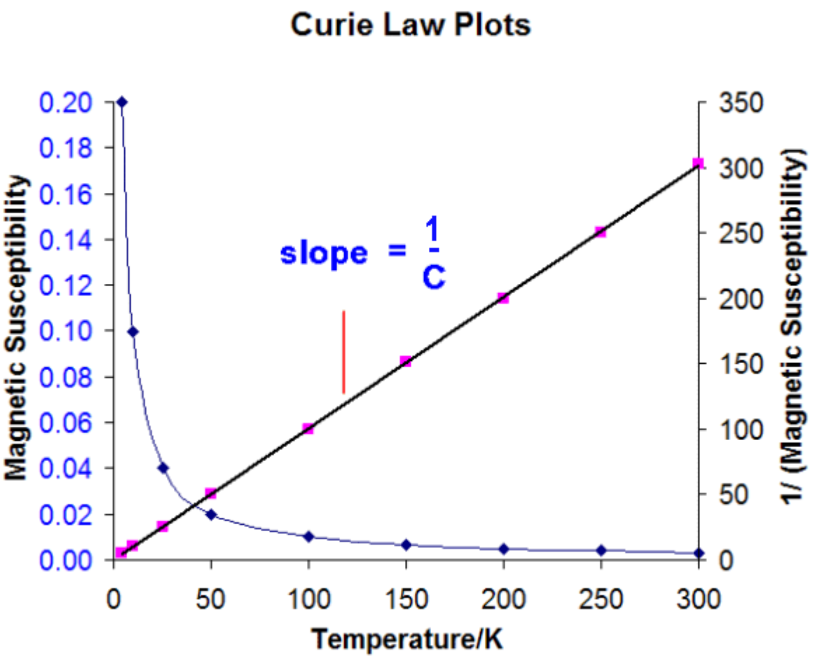
Curie Law

Normal paramagnetic substances obey the **Curie Law**

$\chi = C/T$

where C is the Curie constant. Thus a plot of $1/\chi$ versus T should give a straight line of slope 1/C passing through the origin (0K).
Whereas many substances do give a straight line it often intercepts just a little above 0K and these are said to obey the Curie-Weiss Law:

$\chi = C/(T+\Phi)$
where Φ is known as the Weiss constant.



Quantum Mechanics Approach

A similar expression (where χ is inversely proportional to Temperature) is obtained but now the constant C is given by the Langevin expression, which relates the susceptibility to the magnetic moment:

$\chi_m = N \mu^2 / 3kT$
where N is Avogadro's number
k is the Boltzmann constant
and T the absolute temperature

rewriting this gives the magnetic moment as
$\mu = 2.828 \sqrt{\chi_m T}$ B.M.

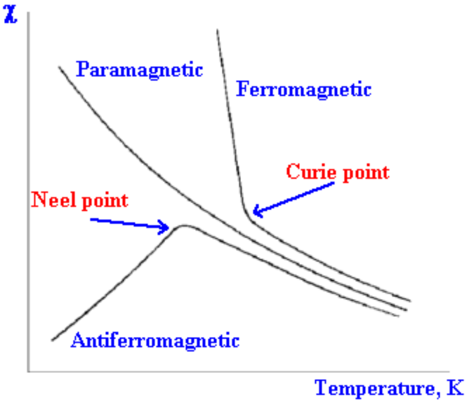
There are two main types of magnetic compounds, those that are diamagnetic (compounds that are repelled by a magnetic field) and those that are paramagnetic (compounds that are attracted by a magnetic field). All substances possess the property of diamagnetism due to the presence of closed shells of electrons within the substance. Note that diamagnetism is a weak effect while paramagnetism is a much stronger effect.

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.

If the diamagnetic atoms are removed from the system then the paramagnetic centres interact with each other. This interaction leads to ferromagnetism (in the case where the neighbouring magnetic dipoles are aligned in the same direction) and antiferromagnetism (where the neighbouring magnetic dipoles are aligned in alternate directions).

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 behaviour. 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 behaviour. 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.

Determination of magnetic susceptibility
The Gouy Method.
The underlying theory of the Gouy method is described here and a form for calculating the magnetic moment from the collected data is available as well.

The Evans method.
The Evans balance measures the change in current required to keep a pair of suspended magnets in place or balanced after the interaction of the magnetic field with the sample.
The Evans balance differs from that of the Gouy in that, in the former the permanent magnets are suspended and the position of the sample is kept constant while in the latter the position of the magnet is constant and the sample is suspended between the magnets.

Orbital contribution to magnetic moments

From a quantum mechanics viewpoint, the magnetic moment is dependent on both spin and orbital angular momentum contributions. The spin-only formula used last year was given as:

$\mu_{s.o.} = \sqrt{4S(S+1)}$

and this can be modified to include the orbital angular momentum

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

An orbital angular momentum contribution is expected when the ground term is triply degenerate i.e. a T state. These show temperature dependence as well.

In order for an electron to contribute to the orbital angular momentum the orbital in which it resides must be able to transform into an exactly identical and degenerate orbital by a simple rotation (it is the rotation of the electrons that induces the orbital contribution). For example, in an octahedral complex the degenerate t_{2g} set of orbitals (d_{xz},d_{yx},d_{yz}) can be interconverted by a 90° rotation. However the orbitals in the e_g subset (d_{z2},d_{x2-y2}) cannot be interconverted by rotation about any axis as the orbital shapes are different; therefore an electron in the e_g set does not contribute to the orbital angular momentum and is said to be quenched. In the free ion case the electrons can be transformed between any of the orbitals as they are all degenerate, but there will still be partial orbital quenching as the orbitals are not identical.
Electrons in the t_{2g} set do not always contribute to the orbital angular moment. For example in the d^3, $t_{2g}{}^3$ case, an electron in the d_{xz} orbital cannot by rotation be placed in the d_{yz} orbital as the orbital already has an electron of the same spin. This process is also called quenching.

Tetrahedral complexes can be treated in a similar way with the exception that we fill the e orbitals first, and the electrons in these do not contribute to the orbital angular momentum.

The tables in the links below give a list of all d^1 to d^9 configurations including high and low spin complexes and a statement of whether or not a direct orbital contribution is expected.

Octahedral complexes

Tetrahedral complexes

A and E ground terms

The configurations corresponding to the A_1 (free ion S term), E (free ion D term), or A_2 (from F term) do not have a direct contribute to the orbital angular momentum.

For the A_2 and E terms there is always a higher T term of the same multiplicity as the ground term which can affect the magnetic moment (usually by a only small amount).

$\mu_{eff} = \mu_{s.o.} (1-\alpha \lambda /\Delta)$

where α is a constant (2 for an E term, 4 for an A_2 term)
λ is the spin-orbit coupling constant which is generally only available for the free ion but this does give important information since the sign of the value varies depending on the orbital occupancy.

some spin-orbit coupling constants for 1st row TM ions

metal ion	Ti(III)	V(III)	Cr(III)	Mn(III)	Fe(II)	Co(II)	Ni(II)	Cu(II)
d configuration	1	2	3	4	6	7	8	9
λ / cm^{-1}	155	105	90	88	-102	-172	-315	-830

for d^1 to d^4 the value is positive hence μ_{eff} is less than $\mu_{s.o.}$
for d^6 to d^9 the value is negative hence μ_{eff} is greater than $\mu_{s.o.}$
Δ is the crystal field splitting factor which again is often not available for complexes.

For the tetrahedral Co(II) ion, $CoCl_4^{2-}$, the observed experimental magnetic moment, μ_{obs} = 4.59 Bohr Magneton (B.M.)
The spin-only magnetic moment, $\mu_{s.o.}$ = 3.88 B.M. which is not in good agreement. How can we improve the analysis?

Since the ground term in the tetrahedral field is split from a ^4F to a $^4A_2$ term then we can apply the formula above.

For an A term the constant $\alpha = 4$. The spin-orbit coupling constant, λ for the free ion is -172 cm^{-1} which we can use as an approximation and Δ= 3100 cm^{-1}.

Hence μ_{eff} = 3.88 x (1 - (4* -172) / 3100)
which comes out at μ_{eff} = 4.73 B.M.

This gives a much better fit than the spin-only formula.

In the case of the series;

CoI_4^{2-}, $CoBr_4^{2-}$, $CoCl_4^{2-}$, $Co(NCS)_4^{2-}$
the magnetic moments have been recorded as
4.77, 4.65, 4.59, 4.40 BM

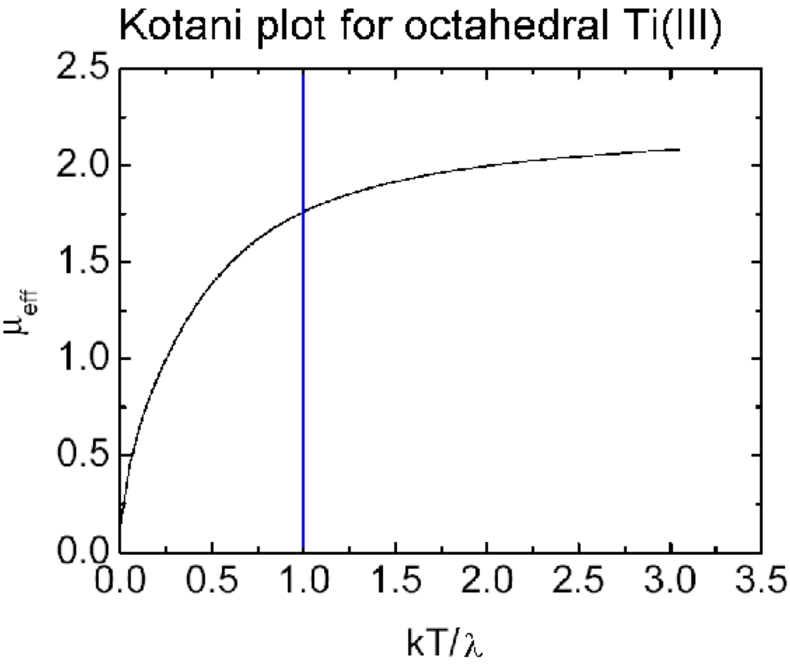
assuming that λ is roughly a constant, then this variation shows the inverse effect of the spectrochemical series on the magnetic moment, since Δ is expected to increase from I- to NCS-.

T ground terms

The configurations corresponding to the T_2 term (from D) or a T_1 term (from an F term) are those where there is a direct contribution to orbital angular momentum expected.

The magnetic moments of complexes with T terms are often found to show considerable temperature dependence. This is as a result of spin-orbit coupling that produces levels whose energy differences are frequently of the order *k*T, so as a result, temperature will have a direct effect on the population of the levels arising in the magnetic field.

In a Kotani plot μ_{eff} is plotted against kT/λ and when this corresponds to a value of 1 then μ equals the "spin-only" value. If this is extrapolated to infinity then the value corresponds to μ_{S+L}.



Measuring the magnetic moment at 80K and 300K often shows up this variation with temperature.

A worked example.

Account for the magnetic moments of the complex, $(Et_4N)_2[NiCl_4]$ recorded at 80, 99 and 300 K.

```
80K   99K   300K
3.25  3.43  3.89 B.M.
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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.

The observed values may be quite different then to the calculated spin only magnetic moment.

The value of μ_{S+L} can be calculated as:
$\mu_{S+L} = \sqrt{\{4S(S+1)+L(L+1)\}}$

or $\mu_{S+L} = \sqrt{\{8+12\}}$

or $\mu_{S+L} = \sqrt{20} = 4.472$B.M.

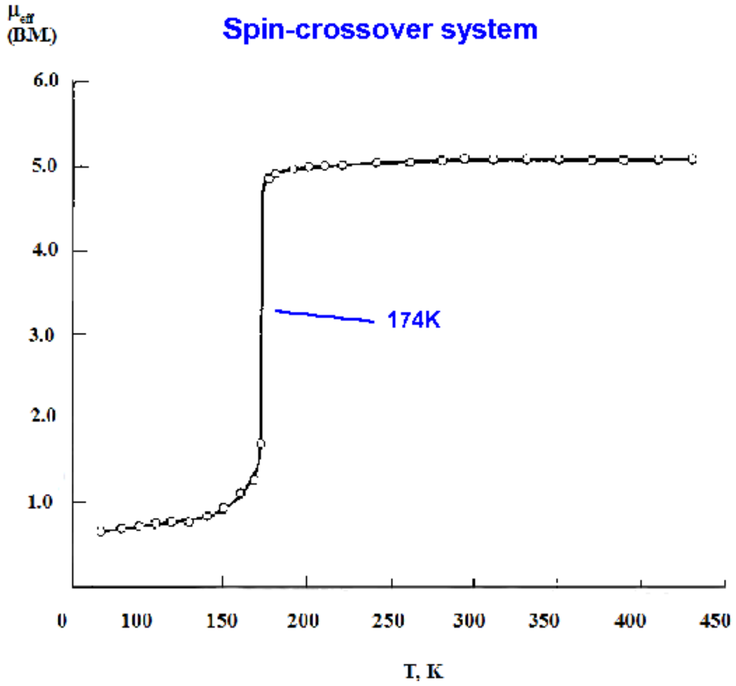
From the observed values it can be seen that the magnetic moment of the d^8 Ni^{2+} complex is intermediate between the μ_{so} and μ_{S+L} values (probably due to partial quenching of the orbital angular momentum contribution) and is dependent on temperature.

Further worked examples and some selected magnetic data are available.

High-spin / Low-spin crossovers

Octahedral complexes with between 4 and 7 d electrons can be either high-spin or low-spin depending on the size of Δ When the ligand field splitting has an intermediate value such that the two states have similar energies, then the two states can coexist in measurable amounts at equilibrium. Many "crossover" systems of this type have been studied, particularly for iron complexes.

In the d^6 case of $Fe(phen)_2(NCS)_2$, the crossover involves going from S=2 to S=0.



At the higher temperature the ground state is $^5T_{2g}$ while at low temperatures it changes to $^1A_{1g}$. The changeover is found at about 174K.

In solution studies, it is possible to calculate the heat of conversion from the one isomer to the other.

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Table of Diamagnetic Corrections
(Pascal's constants, 10^{-6} c.g.s. units)

Ion	DC	Ion	DC
Na^+	6.8	Co^{2+}	12.8
K^+	14.9	Co^{3+}	12.8
NH_4^+	13.3	Ni^{2+}	12.8
Hg^{2+}	40	VO^{2+}	12.5
Fe^{2+}	12.8	Mn^{3+}	12.5
Fe^{3+}	12.8	Cr^{3+}	12.5
Cu^{2+}	12.8	Cl^-	23.4
Br^-	34.6	SO_4^{2-}	40.1
I^-	50.6	OH^-	12
NO_3^-	18.9	$C_2O_4^{2-}$	34
ClO_4^-	32	OAc^-	31.5
IO_4^-	51.9	pyr	49.2
CN^-	13	Me-pyr	60
NCS^-	26.2	$Acac^-$	62.5
H_2O	13	en	46.3
$EDTA^{4-}$	~150	urea	33.4

these can be converted to S.I units of $m^3\ mol^{-1}$ by multiplying by $4\pi \times 10^{-7}$

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Comparison of calculated spin-only and spin+orbital magnetic moments with experimental data for some selected octahedral complexes

Ion	d configuration	OAM and T dependence	μ_{so} /B.M.	μ_{obs} /B.M.	μ_{S+L} /B.M.
Ti(III)	d^1	yes	1.73	1.6-1.7	3.00
V(IV)	d^1	yes	1.73	1.7-1.8	
V(III)	d^2	yes	2.83	2.7-2.9	4.47
Cr(IV)	d^2	yes	2.83	2.8	
V(II)	d^3	no	3.88	3.8-3.9	5.20
Cr(III)	d^3	no	3.88	3.7-3.9	
Mn(IV)	d^3	no	3.88	3.8-4.0	
Cr(II)	d^4 h.s	no	4.90	4.7-4.9	5.48
Cr(II)	d^4 l.s.	yes	2.83	3.2-3.3	
Mn(III)	d^4 h.s	no	4.90	4.9-5.0	
Mn(III)	d^4 l.s.	yes	2.83	3.2	
Mn(II)	d^5 h.s	no	5.92	5.6-6.1	5.92
Mn(II)	d^5 l.s	yes	1.73	1.8-2.1	
Fe(III)	d^5 h.s	no	5.92	5.7-6.0	
Fe(III)	d^5 l.s	yes	1.73	2.0-2.5	
Fe(II)	d^6 h.s	yes	4.90	5.1-5.7	5.48
Co(II)	d^7 h.s	yes	3.88	4.3-5.2	5.20
Co(II)	d^7 l.s	no	1.73	1.8	
Ni(III)	d^7 l.s	no	1.73	1.8-2.0	
Ni(II)	d^8	no	2.83	2.9-3.3	4.47
Cu(II)	d^9	no	1.73	1.7-2.2	3.00

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Comparison of calculated spin-only and spin+orbital magnetic moments with experimental data for some selected tetahedral complexes

Ion	d configuration	OAM and T dependence	μ_{so} /B.M.	μ_{obs} /B.M.	μ_{S+L} /B.M.
Cr(V)	d1	no	1.73	1.7-1.8	3.00
Mn(VI)	d1	no	1.73	1.7-1.8	
Cr(IV)	d2	no	2.83	2.8	4.47
Mn(V)	d2	no	2.83	2.6-2.8	
Fe(V)	d3	yes	3.88	3.6-3.7	5.20
-	d4	yes	4.90	-	5.48
Mn(II)	d5	no	5.92	5.9-6.2	5.92
Fe(II)	d6	no	4.90	5.3-5.5	5.48
Co(II)	d7	no	3.88	4.2-4.8	5.20
Ni(II)	d8	yes	2.83	3.7-4.0	4.47
Cu(II)	d9	yes	1.73	-	3.0

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Some example magnetic moment data and their interpretation

Summary of applicable formulae

1) Spin-Only magnetic moment
$\mu_{s.o.} = \sqrt{4S(S+1)}$ B.M.

2) For A and E ground terms
$\mu_{eff} = \mu_{s.o.} (1-\alpha \lambda / \Delta)$ B.M.
Do not expect Temperature dependence.

3) For T ground terms with orbital angular momentum contribution
$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$ B.M.
T terms generally show marked Temperature dependence.

The examples that follow are arranged showing the experimentally observed values, the theoretical "spin-only" value and possible variations expected.

A number of the examples involve "alums" where the central Transition Metal ion can be considered to be octahedrally coordinated by water molecules.

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d^1

VCl_4
V(IV) tetrahedral

80K	300K	$\mu_{s.o.}$ /B.M.
1.6	1.6	1.73

^2E ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For less than a half-filled d shell, the sign of λ is positive so the effect on μ should be that $\mu_{eff} < \mu_{s.o.}$

VCl_6^{2-}
V(IV) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
1.4	1.8	1.73

$^2T_{2g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = 3$ B.M. which is clearly much higher than the 1.8 B.M. found at 300K. So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$ showing that the magnetic moment is partially quenched.

d^2

V^{3+} in $(NH_4)V(SO_4)_2.12H_2O$ (an alum)
V(III) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
2.7	2.7	2.83

$^3T_{1g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(20)} = 4.47$ B.M. which is clearly much higher than the 2.7 B.M. found at 300K.
So, $\mu_{obs} < \mu_{s.o.} < \mu_{S+L}$
showing that the magnetic moment is significantly quenched.
In this case, there is no observed Temperature variation between 80 and 300K and it may require much lower temperatures to see the effect?

d^3

Cr^{3+} in $KCr(SO_4)_2.12H_2O$ (an alum)
Cr(III) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
3.8	3.8	3.87

$^4A_{2g}$ ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For less than a half-filled d shell the sign of λ is positive so the effect on μ should be that $\mu_{eff} < \mu_{s.o.}$

d^4

$CrSO_4.6H_2O$
Cr(II) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
4.8	4.8	4.9

^5E_g ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For less than a half-filled d shell the sign of λ is positive so the effect on μ should be that $\mu_{eff} < \mu_{s.o.}$

$K_3Mn(CN)_6$
Mn(III) low-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
3.1	3.2	2.83

$^3T_{1g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(20)} = 4.47$ B.M. which is clearly much higher than the 3.2 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$
showing that the magnetic moment is partially quenched.
In this case, there is a small Temperature variation observed between 80 and 300K.

d^5

$K_2Mn(SO_4)_2.6H_2O$ (an alum)
Mn(II) high-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
5.9	5.9	5.92

$^6A_{1g}$ ground term - hence do not expect Temperature dependence and L=0 so no orbital contribution possible.
Expect $\mu_{eff} = \mu_{s.o.}$

$K_3Fe(CN)_6$
Fe(III) low-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
2.2	2.4	1.73

$^2T_{2g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(9)} = 3$ B.M. which is clearly much higher than the 2.4 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$
showing that the magnetic moment is partially quenched.

d^6

Fe^{2+} in $(NH_4)_2Fe(SO_4)_2.6H_2O$ (an alum)
Fe(II) high-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
5.4	5.5	4.9

$^5T_{2g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(30)} = 5.48$ B.M. which is close to the 5.5 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} \sim \mu_{S+L}$
showing that the magnetic moment is not showing much quenching.

d^7

Cs_2CoCl_4
Co(II) tetrahedral

80K	300K	$\mu_{s.o.}$ /B.M.
4.5	4.6	3.87

$^4A_2$ ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For more than a half-filled d shell the sign of λ is negative so the effect on μ should be that $\mu_{eff} > \mu_{s.o.}$
The observed values are somewhat bigger than expected for the small (0.2 B.M.) variation due to equation 2) so other factors must be affecting the magnetic moment. These effects will not be covered in this course!

Co^{2+} in $(NH_4)_2Co(SO_4)_2.6H_2O$ (an alum)
Co(II) high-spin octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
4.6	5.1	3.88

$^4T_{1g}$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(27)} = 5.2$ B.M. which is close to the 5.1 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} \sim \mu_{S+L}$
showing that the magnetic moment is not showing much quenching.

d^8

Ni^{2+} in $(NH_4)_2Ni(SO_4)_2.6H_2O$ (an alum)
Ni(II) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
3.3	3.3	2.83

$^3A_{2g}$ ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For more than a half-filled d shell the sign of λ is negative so the effect on μ should be that $\mu_{eff} > \mu_{s.o.}$
The observed values are somewhat bigger than expected for the small (0.2 B.M.) variation due to equation 2) so other factors must be affecting the magnetic moment. These effects will not be covered in this course!

$(Et_4N)_2NiCl_4$
Ni(II) tetrahedral

80K	300K	$\mu_{s.o.}$ /B.M.
3.2	3.8	2.83

$^3T_2$ ground term - hence do expect Temperature dependence and large variation from spin-only value may be observed at low temperatures.
Since there is a direct orbital angular momentum contribution we should calculate μ_{S+L} from equation 3) above.
For a full S+L contribution this would give $\mu_{S+L} = \sqrt{(20)} = 4.47$ B.M. which is higher than the 3.8 B.M. found at 300K.
So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$
showing that the magnetic moment is partially quenched.

d^9

Cu^{2+} in $(NH_4)_2Cu(SO_4)_2.6H_2O$ (an alum)
Cu(II) octahedral

80K	300K	$\mu_{s.o.}$ /B.M.
1.9	1.9	1.73

^2E_g ground term - hence don't expect Temperature dependence and small variation from spin-only value can be accounted for by equation 2) above. For more than a half-filled d shell the sign of λ is negative so the effect on μ should be that $\mu_{eff} > \mu_{s.o.}$

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Created October 2005. Links checked and/or last modified 10th October 2010.
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