Some example magnetic moment data and their interpretation

Summary of applicable formulae

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

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

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

d^1

VCl4 V(IV) tetrahedral

80K	300K	µs.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 half-filled d shell the sign of λ is positive so the effect on μ should be that $\mu_{eff} < \mu_{s.o.}$

VCl6²⁻ V(IV) octahedral

80K	300K	µs.o. /B.M.
1.4	1.8	1.73

 $^{2}T_{2g}$ 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 found at 300K. So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$

showing that the magnetic moment is partially quenched.

d^2

V²⁺ in (NH4)V(SO4)₂.12H₂O (an alum) V(II) octahedral

80K 300K

2.7 2.83

 ${}^{3}T_{1g}$ 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 found at 300K.

So, $\mu_{0bs} < \mu_{s.o.} < \mu_{S+L}$

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

Cr³⁺ in KCr(SO₄)₂.12H₂O (an alum) Cr(III) octahedral

80K	300K	μ _{s.o.} /B.M.
3.8	3.8	3.87

 ${}^{4}A_{2g}$ 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 half-filled d shell the sign of λ is positive so the effect on μ should be that μ eff < μ s.o.

d^4

CrSO₄.6H₂O Cr(II) octahedral

80K	300K	µs.o. /B.M.
4.8	4.8	4.9

 ${}^{5}E_{g}$ 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 half-filled d shell the sign of λ is positive so the effect on μ should be that $\mu_{eff} < \mu_{s.o.}$

K₃Mn(CN)₆ Mn(III) low-spin octahedral

80K	300K	µ _{s.o.} /B.M.
3.1	3.2	2.83

 ${}^{3}T_{1g}$ 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 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

K₂Mn(SO₄)₂.6H₂O (an alum) Mn(II) high-spin octahedral

80K	300K	µs.o. /B.M.
5.9	5.9	5.92

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

Expect $\mu_{eff} = \mu_{s.o.}$

K₃Fe(CN)₆ Fe(III) low-spin octahedral

80K	300K	µs.o. /B.M.
2.2	2.4	1.73

 $^{2}T_{2g}$ 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 found at 300K.

So, $\mu_{S.O.} < \mu_{Obs} < \mu_{S+L}$

showing that the magnetic moment is partially quenched.

d^6

Fe²⁺ in (NH₄)₂Fe(SO₄)₂.6H₂O (an alum) Fe(II) high-spin octahedral

80K	300K	µs.o. /B.M.
5.4	5.5	4.9

 ${}^{5}T_{2g}$ 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 found at 300K.

So, $\mu_{S.O.} < \mu_{Obs} \sim \mu_{S+L}$

showing that the magnetic moment is not showing much quenching.

\mathbf{d}^7

Cs₂CoCl₄ Co(II) tetrahedral

80K	300K	μ _{s.o.} /B.M.
4.5	4.6	3.87

 ${}^{4}A_{2}$ 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 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!

Co²⁺ in (NH4)₂Co(SO4)₂.6H₂O (an alum) Co(II) high-spin octahedral

80K	300K	μ _{s.o.} /B.M.
4.6	5.1	3.88

 ${}^{4}T_{1g}$ 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 found at 300K. So, $\mu_{S.0.} < \mu_{Obs} \sim \mu_{S+L}$

showing that the magnetic moment is not showing much quenching.

d⁸

Ni²⁺ in (NH4)Ni(SO4)2.6H2O (an alum) Ni(II) octahedral

80K	300K	μ _{s.o.} /B.M.
3.3	3.3	2.83

 ${}^{3}A_{2}$ 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 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!

(Et4N)2NiCl4 Ni(II) tetrahedral

80K	300K	µ _{s.o.} /B.M.
3.2	3.8	2.83

 ${}^{3}T_{2}$ 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 found at

300K.

So, $\mu_{s.o.} < \mu_{obs} < \mu_{S+L}$ showing that the magnetic moment is partially quenched.

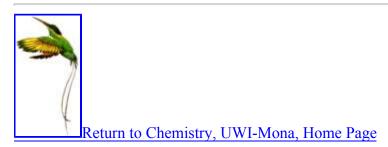
d⁹

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Cu<sup>2+</sup> in (NH4)Cu(SO4)2.6H2O (an alum)
Cu(II) octahedral
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80K	300K	μ _{s.o.} /B.M.
1.9	1.9	1.73

 $^{2}E_{g}$ 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 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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