Introduction to Magnetism

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Introduction to Magnetism

1) Introduction and definitions

2) The Diamagnetism

3) The Paramagnetism

4) Magnetic phase transitions and magnetic orders

5) Molecular magnetism

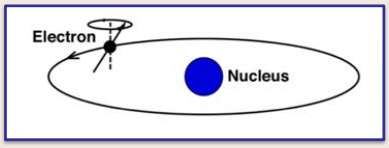
6) Superparamagnetism and Single-Molecule Magnets

7) Single-Chain Magnets

1) Introduction and definitions

The magnetic moment of a free atom has three principal sources:

a) the spin with which the electrons are endowed
b) their orbital angular momentum about the nucleus
c) the change in the orbital moment induced by an applied magnetic field.



a) and b) lead to **paramagnetism** (part 3) and c) to **diamagnetism** (part 2)

C. Kittel, *Introduction to Solid State Physics*, Wiley Ed.

1) Introduction and definitions

General relation between:

- ***B***: the magnetic induction
- ***H***: the magnetic field
- m_v: the magnetic moment defined per volume and μ_0 is the permeability of free space
- ***M***: the magnetization is defined as the magnetic moment defined per mol.

$$\vec{B} = \mu_0\left(\vec{H} + \vec{m}_V\right)$$

In simple magnetic systems (paramagnetic or diamagnetic), m_V is negligible in comparison to H then: $\vec{B} \approx \mu_0 \vec{H}$

Unit systems: SI versus cgs $X_{SI} \approx \alpha X_{cgs}$

	cgs (Gaussian)	Factor	SI (MKSA)
H	Oe (Oersted)	$1/(4\pi\ 10^{-3})$	Am^{-1}
B	G (Gauss)	10^{-4}	T (Tesla, $NA^{-1}m^{-1}$)
M	cm^3Oe/mol or emu Oe/mol	$4\pi\ 10^{-6}$	J/T/mol (Am^2/mol)
μ_0	1	$4\pi\ 10^{-7}$	N/A^2

J.D. Jackson, *Classical Electrodynamics*, Wiley Ed.

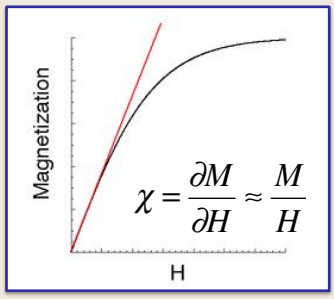
1) Introduction and definitions

k_B = 1.38062 10^{-23} J.K^{-1}
μ_B = 9.27410 10^{-21} J.Oe^{-1}

General definition of the magnetic susceptibility (in cm^3/mol):

$$\chi = \frac{\partial M}{\partial H}$$

When the field dependence of the magnetization is linear (simple paramagnetic or diamagnetic systems for $k_B T >> \mu_B H$, *small field limit*), the magnetic susceptibility can be simplified.



For a material, the magnetic susceptibility is the sum of all the magnetic contributions:

$$\chi = \sum \chi_i$$

In simple systems, it exists two types of contribution: from the **diamagnetism** and the **paramagnetism**

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2) The diamagnetism

All the descriptions will be done for localized spins (insulator systems)

Diamagnetism is a property of ALL atoms in molecules that is created by either paired or unpaired electrons.

Lenz law: "when the flux through an electrical circuit is changed, an induced current is set up in such a direction as to oppose the flux change"

Diamagnetism: "when a magnetic field, *H*, is applied on a free atom, an electrical current around the nucleus is induced generating an opposite local magnetic field to *H*. The associated/induced magnetization is thus opposite ($M < 0$) to the applied magnetic field."

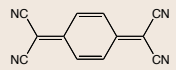
Therefore, the diamagnetic susceptibility is always negative:

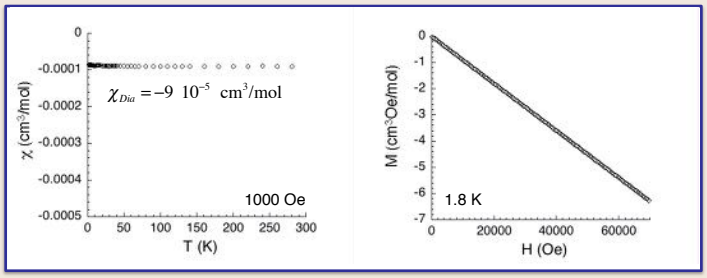
$$\chi_{Dia} = \frac{M}{H} < 0$$

2) The diamagnetism

A diamagnetic material is composed only of paired electron otherwise the magnetism is dominating by the unpaired electrons.

An example of an organic molecule:
TCNQ (7,7',8,8'-tetracyanoquinodimethane)





2) The diamagnetism

m = 9.10956 10^{-31} kg
c = 2.997925 10^{8} m.s^{-1}
e = 1.60219 10^{-19} C

How can we estimate the diamagnetism?

For free atoms, the calculation is possible based on the Larmor theorem that leads to the classical Langevin result:

$$\chi_{Dia} = -\frac{N_A Z e^2}{6mc^2}\langle r^2 \rangle$$

Z the number of electrons, N_A the avogadro number, e the electron charge, m the electron mass, c, the speed of light and $\langle r^2 \rangle$ the mean square distance of the electrons from the nucleaus.

C. Kittel, *Introduction to Solid State Physics*, Wiley Ed., p. 418.

but more generally the diamagnetism is estimated from the so-called **Pascal's constants**:

$$\chi_{Dia} = \sum_i \chi_{Di} + \sum_i \lambda_i$$

χ_{Di} and λ_i are diamagnetic susceptibility for every atom and bond, respectively

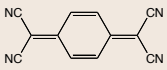
G.A. Bain, J. F. Berry, *J. Chem. Edu.* **2008**, *85*, p. 532-536

2) The diamagnetism

Pascal's constants:

G.A. Bain, J. F. Berry, *J. Chem. Edu.* **2008**, *85*, p. 532-536

An example: TCNQ



$$\chi_{Dia} = 6\chi_D(C_{ring}) + 6\chi_D(C) + 4\chi_D(H) + 4\chi_D(N) + 2\lambda(C=C) + \lambda(\text{benzene}) + 4\lambda(C\equiv N)$$

$$= \begin{bmatrix} 6(-6.24) + 6(-6) \\ +4(-2.93) + 4(-5.57) \\ +2(+5.5) + (-1.4) \\ 4(0) \end{bmatrix} \times 10^{-6}$$

$$= -97.8 \times 10^{-6} \text{ cm}^3/\text{mol}$$

$$\chi_{Dia} = -9\ 10^{-5} \text{ cm}^3/\text{mol}$$

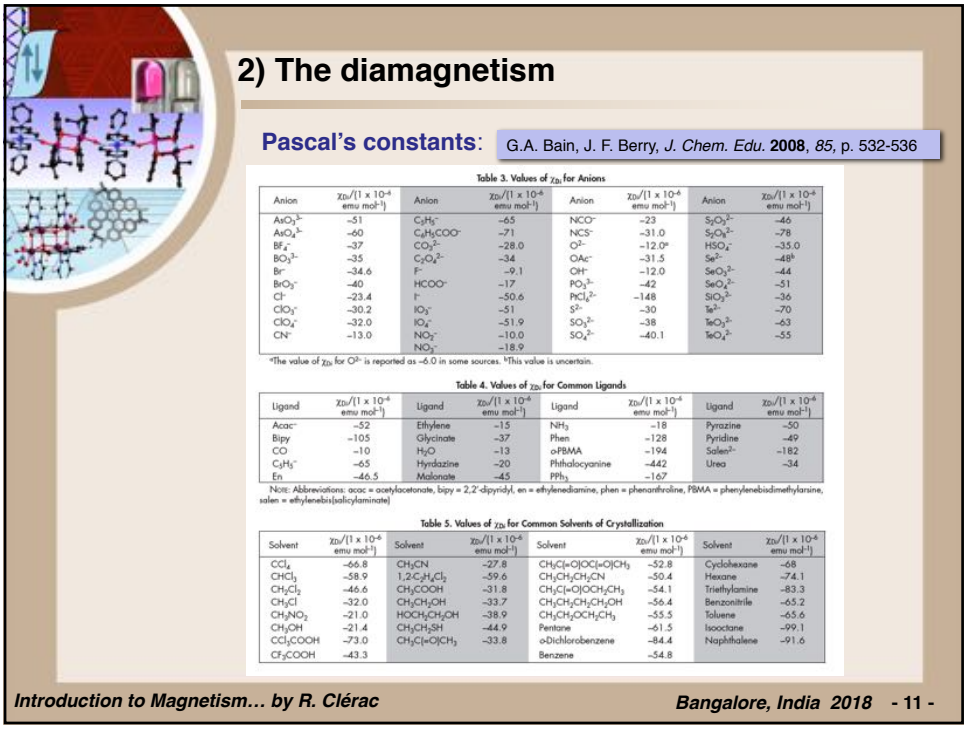
Table 1. Values of χ_D for Atoms in Covalent Species

Atom	χ_D/(1 × 10^{-6} emu mol^{-1})	Atom	χ_D/(1 × 10^{-6} emu mol^{-1})	Atom	χ_D/(1 × 10^{-6} emu mol^{-1})	Atom	χ_D/(1 × 10^{-6} emu mol^{-1})
Ag	−31.0	C (ring)	−6.24	Li	−4.2	S	−15.0
Al	−13.0	Ca	−15.9	Mg	−10.0	Sb(III)	−74.0
As(III)	−20.9	Cl	−20.1	N (ring)	−4.61	Se	−23.0
As(V)	−43.0	F	−6.3	N (open chain)	−5.57	Si	−13
B	−7.0	H	−2.93	Na	−9.2	Sn(IV)	−30
Bi	−192.0	Hg(II)	−33.0	O	−4.6	Te	−37.3
Br	−30.6	I	−44.6	P	−26.3	Tl(I)	−40.0
C	−6.00	K	−18.5	Pb(II)	−46.0	Zn	−13.5

Table 2. Values of λ for Specific Bond Types

Bond[a]	λ/(1 × 10^{-6} emu mol^{-1})	Bond	λ/(1 × 10^{-6} emu mol^{-1})	Bond	λ/(1 × 10^{-6} emu mol^{-1})	Bond	λ/(1 × 10^{-6} emu mol^{-1})
C=C	+5.5	Cl–CR_2–CR_2–Cl	+4.3	Ar–Br	−3.5	Imidazole	+8.0
C≡C	+0.8	R_2CCl_2	+1.44	Ar–Cl	−2.5	Isoxazole	+1.0
C=C–C=C	+10.6	$RCHCl_2$	+6.43	Ar–I	−3.5	Morpholine	+5.5
As–C≡C–As[b]	+3.85	C–Br	+4.1	Ar–COOH	−1.5	Piperazine	+7.0
CH_2=CH–CH_2–(allyl)	+4.5	Br–CR_2–CR_2–Br	+6.24	Ar–C(=O)NH_2	−1.5	Piperidine	+3.0
C=O	+6.3	C–I	+4.1	R_2C–N–N=CR_2	+10.2	Pyrazine	+9.0
COOH	−5.0	Ar–OH	−1	RC=N–C(=O)R	+0.8	Pyridine	+0.5
COOR	−5.0	Ar–NR_2	+1	Benzene	−1.4[c]	Pyrimidine	+6.5
C(=O)NH_2	−3.5	Ar–C(=O)R	−1.5	Cyclobutane	+7.2	α- or γ-Pyrone	−1.4
N=N	+1.85	Ar–COOR	−1.5	Cyclohexadiene	+10.56	Pyrrole	−3.5
C=N–	+8.15	Ar–C=C	−1.00	Cyclohexane	+3.0	Pyrrolidine	+0.0
–C=N	+0.8	Ar–C≡C	−1.5	Cyclohexene	+6.9	Tetrahydrofuran	+0.0
–N=C	+0.0	Ar–OR	−1	Cyclopentane	+0.0	Thiazole	−3.0
N=O	+1.7	Ar–CHO	−1.5	Cyclopropane	+7.2	Thiophene	−7.0
–NO_2	−2.0	Ar–Ar	−0.5	Dioxane	+5.5	Triazine	−1.4
C–Cl	+3.1	Ar–NO_2	−0.5	Furan	−2.5		

[a]Ordinary C–H and C–C single bonds are assumed to have a λ value of 0.0 emu mol^{-1}. [b]The symbol Ar represents an aryl ring. [c]Some sources list the λ value for a benzene ring as −18.00 to which three times λ(C=C) must then be added. To minimize the calculations involved, this convention was not followed such that λ values given for aromatic rings are assumed to automatically take into account the corresponding double bonds in the ring.



2) The diamagnetism

Pascal's constants: G.A. Bain, J. F. Berry, *J. Chem. Edu.* **2008**, *85*, p. 532-536

Table 3. Values of χ_D for Anions

Anion	χ_D/(1 x 10^{-6} emu mol^{-1})	Anion	χ_D/(1 x 10^{-6} emu mol^{-1})	Anion	χ_D/(1 x 10^{-6} emu mol^{-1})	Anion	χ_D/(1 x 10^{-6} emu mol^{-1})
AsO_3^{3-}	–51	$C_3H_5^-$	–65	NCO^-	–23	$S_2O_3^{2-}$	–46
AsO_4^{3-}	–60	$C_6H_5COO^-$	–71	NCS^-	–31.0	$S_2O_8^{2-}$	–78
BF_4^-	–37	CO_3^{2-}	–28.0	O^{2-}	–12.0[a]	HSO_4^-	–35.0
BO_3^{3-}	–35	$C_2O_4^{2-}$	–34	OAc^-	–31.5	Se^{2-}	–48[b]
Br^-	–34.6	F^-	–9.1	OH^-	–12.0	SeO_3^{2-}	–44
BrO_3^-	–40	$HCOO^-$	–17	PO_4^{3-}	–42	SeO_4^{2-}	–51
Cl^-	–23.4	I^-	–50.6	$PtCl_6^{2-}$	–148	SiO_3^{2-}	–36
ClO_3^-	–30.2	IO_3^-	–51	S^{2-}	–30	Te^{2-}	–70
ClO_4^-	–32.0	IO_4^-	–51.9	SO_3^{2-}	–38	TeO_3^{2-}	–63
CN^-	–13.0	NO_2^-	–10.0	SO_4^{2-}	–40.1	TeO_4^{2-}	–55
		NO_3^-	–18.9				

[a]The value of χ_D for O^{2-} is reported as –6.0 in some sources. [b]This value is uncertain.

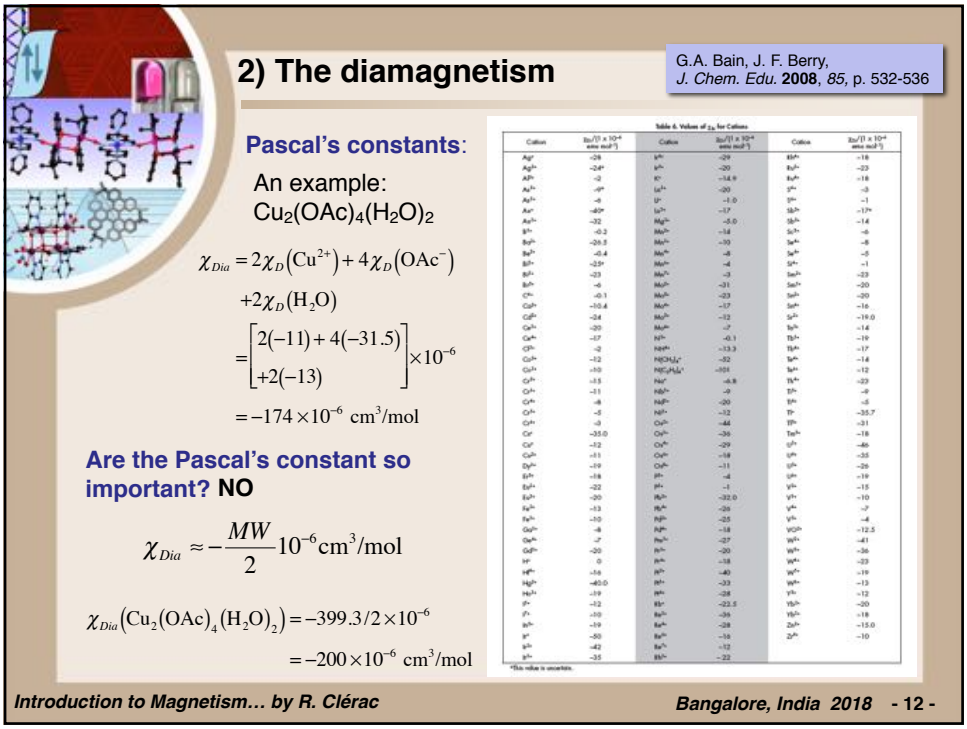
Table 4. Values of χ_D for Common Ligands

Ligand	χ_D/(1 x 10^{-6} emu mol^{-1})	Ligand	χ_D/(1 x 10^{-6} emu mol^{-1})	Ligand	χ_D/(1 x 10^{-6} emu mol^{-1})	Ligand	χ_D/(1 x 10^{-6} emu mol^{-1})
$Acac^-$	–52	Ethylene	–15	NH_3	–18	Pyrazine	–50
Bipy	–105	Glycinate	–37	Phen	–128	Pyridine	–49
CO	–10	H_2O	–13	o-PBMA	–194	$Salen^{2-}$	–182
$C_5H_5^-$	–65	Hyrdazine	–20	Phthalocyanine	–442	Urea	–34
En	–46.5	Malonate	–45	PPh_3	–167		

NOTE: Abbreviations: acac = acetylacetonate, bipy = 2,2'-dipyridyl, en = ethylenediamine, phen = phenanthroline, PBMA = phenylenebisdimethylarsine, salen = ethylenebis(salicylaminate)

Table 5. Values of χ_D for Common Solvents of Crystallization

Solvent	χ_D/(1 x 10^{-6} emu mol^{-1})	Solvent	χ_D/(1 x 10^{-6} emu mol^{-1})	Solvent	χ_D/(1 x 10^{-6} emu mol^{-1})	Solvent	χ_D/(1 x 10^{-6} emu mol^{-1})
CCl_4	–66.8	CH_3CN	–27.8	$CH_3C(=O)OC(=O)CH_3$	–52.8	Cyclohexane	–68
$CHCl_3$	–58.9	$1,2\text{-}C_2H_4Cl_2$	–59.6	$CH_3CH_2CH_2CN$	–50.4	Hexane	–74.1
CH_2Cl_2	–46.6	CH_3COOH	–31.8	$CH_3C(=O)OCH_2CH_3$	–54.1	Triethylamine	–83.3
CH_3Cl	–32.0	CH_3CH_2OH	–33.7	$CH_3CH_2CH_2CH_2OH$	–56.4	Benzonitrile	–65.2
CH_3NO_2	–21.0	$HOCH_2CH_2OH$	–38.9	$CH_3CH_2OCH_2CH_3$	–55.5	Toluene	–65.6
CH_3OH	–21.4	CH_3CH_2SH	–44.9	Pentane	–61.5	Isooctane	–99.1
CCl_3COOH	–73.0	$CH_3C(=O)CH_3$	–33.8	o-Dichlorobenzene	–84.4	Naphthalene	–91.6
CF_3COOH	–43.3			Benzene	–54.8		



2) The diamagnetism

G.A. Bain, J. F. Berry, *J. Chem. Edu.* **2008**, *85*, p. 532-536

Pascal's constants:

An example: $Cu_2(OAc)_4(H_2O)_2$

$$\chi_{Dia} = 2\chi_D(Cu^{2+}) + 4\chi_D(OAc^-) + 2\chi_D(H_2O)$$

$$= \begin{bmatrix} 2(-11) + 4(-31.5) \\ +2(-13) \end{bmatrix} \times 10^{-6}$$

$$= -174 \times 10^{-6} \text{ cm}^3/\text{mol}$$

Are the Pascal's constant so important? NO

$$\chi_{Dia} \approx -\frac{MW}{2} 10^{-6} \text{cm}^3/\text{mol}$$

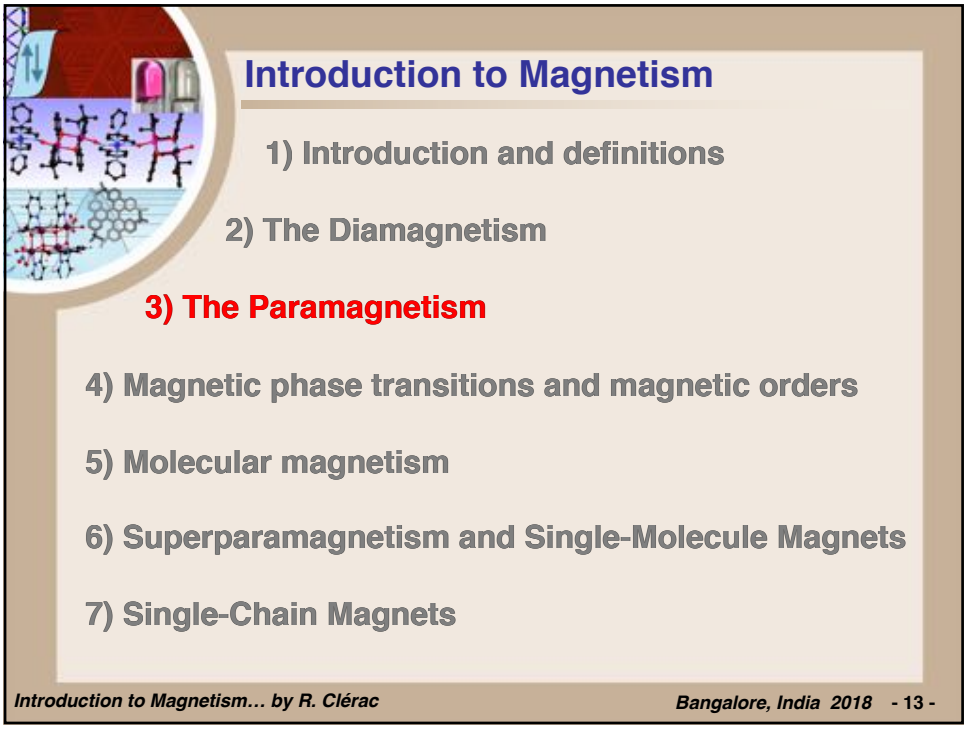
$$\chi_{Dia}(Cu_2(OAc)_4(H_2O)_2) = -399.3/2 \times 10^{-6}$$

$$= -200 \times 10^{-6} \text{ cm}^3/\text{mol}$$

Table 6. Values of χ_D for Cations

Cation	χ_D/(1 x 10^{-6} emu mol^{-1})	Cation	χ_D/(1 x 10^{-6} emu mol^{-1})	Cation	χ_D/(1 x 10^{-6} emu mol^{-1})
Ag^+	–28	Li^+	–0.9	Rb^+	–18
Ag^{2+}	–24[a]	Lr^{3+}	–20	Re^{7+}	–23
Al^{3+}	–5	Lu^{3+}	–14.9	Rh^{3+}	–18
Au^{3+}	–9[a]	Mg^{2+}	–12	Ru^{3+}	–30
As^{3+}	–6	Mn^{2+}	–1.0	S^{2-}	–1
Au^+	–40[a]	Mn^{3+}	–17	Sb^{3+}	–17[a]
Au^{3+}	–32	Mn^{4+}	–5.0	Sb^{5+}	–14
B^{3+}	–0.2	Mo^{3+}	–18	Sc^{3+}	–6
Ba^{2+}	–26.5	Mo^{4+}	–30	Se^{4+}	–8
Be^{2+}	–0.4	Mo^{6+}	–8	Se^{6+}	–5
Bi^{3+}	–23[a]	N^{3+}	–6	Si^{4+}	–1
Bi^{5+}	–23	Na^+	–3	Sm^{3+}	–23
B^{3+}	–6	Nb^{5+}	–31	Sn^{2+}	–20
Br^-	–0.1	Nd^{3+}	–23	Sn^{4+}	–20
Ca^{2+}	–10.4	Ni^{2+}	–12	Sr^{2+}	–16
Cd^{2+}	–24	Np^{3+}	–12	S_8^{2+}	–19.0
Ce^{3+}	–20	Np^{4+}	–7	Ta^{5+}	–14
Ce^{4+}	–17	N^{3+}	–0.1	Tb^{3+}	–19
Cl^-	–2	NpO^{2+}	–13.3	Tb^{4+}	–17
Co^{2+}	–12	$N(CH_3)_4^+$	–52	Te^{4+}	–14
Co^{3+}	–10	$NC_5H_5^+$	–104	Te^{6+}	–12
Cr^{2+}	–15	Na^+	–6.8	Th^{4+}	–23
Cr^{3+}	–11	Nb^{3+}	–9	Ti^{3+}	–9
Cr^{6+}	–8	Nd^{3+}	–20	Ti^{4+}	–5
Cs^+	–5	Ni^{2+}	–12	Tl^+	–35.7
Cu^+	–9	Os^{4+}	–44	Tl^{3+}	–31
Cu^{2+}	–13.0	Os^{6+}	–36	Tm^{3+}	–18
Cu^{3+}	–12	Os^{8+}	–29	U^{3+}	–46
Cu^{4+}	–11	Os^{8+}	–18	U^{4+}	–35
Dy^{3+}	–19	O^{2+}	–11	U^{6+}	–20
Er^{3+}	–18	P^{3+}	–4	U^{3+}	–19
Eu^{2+}	–22	P^{5+}	–1	V^{3+}	–15
Eu^{3+}	–20	Pb^{2+}	–32.0	V^{4+}	–10
Fe^{2+}	–13	Pb^{4+}	–26	V^{5+}	–7
Fe^{3+}	–10	Pd^{2+}	–25	V^{3+}	–4
Ga^{3+}	–8	Pd^{4+}	–18	VO^{2+}	–12.5
Ge^{4+}	–7	Pm^{3+}	–27	W^{4+}	–41
Gd^{3+}	–20	Pr^{3+}	–20	W^{5+}	–26
H^+	0	Pr^{4+}	–18	W^{6+}	–23
Hf^{4+}	–16	Pt^{2+}	–40	W^{4+}	–19
Hg^{2+}	–40.0	Pt^{4+}	–33	W^{6+}	–13
Ho^{3+}	–19	Pt^{6+}	–28	Y^{3+}	–12
I^-	–10	Rb^+	–22.5	Yb^{2+}	–20
I^{7+}	–10	Re^{3+}	–36	Yb^{3+}	–18
In^{3+}	–19	Re^{4+}	–28	Zn^{2+}	–15.0
Ir^{3+}	–50	Re^{5+}	–16	Zr^{4+}	–10
Ir^{4+}	–42	Re^{7+}	–12		
K^+	–15	Rh^{3+}	–22		

[a]This value is uncertain.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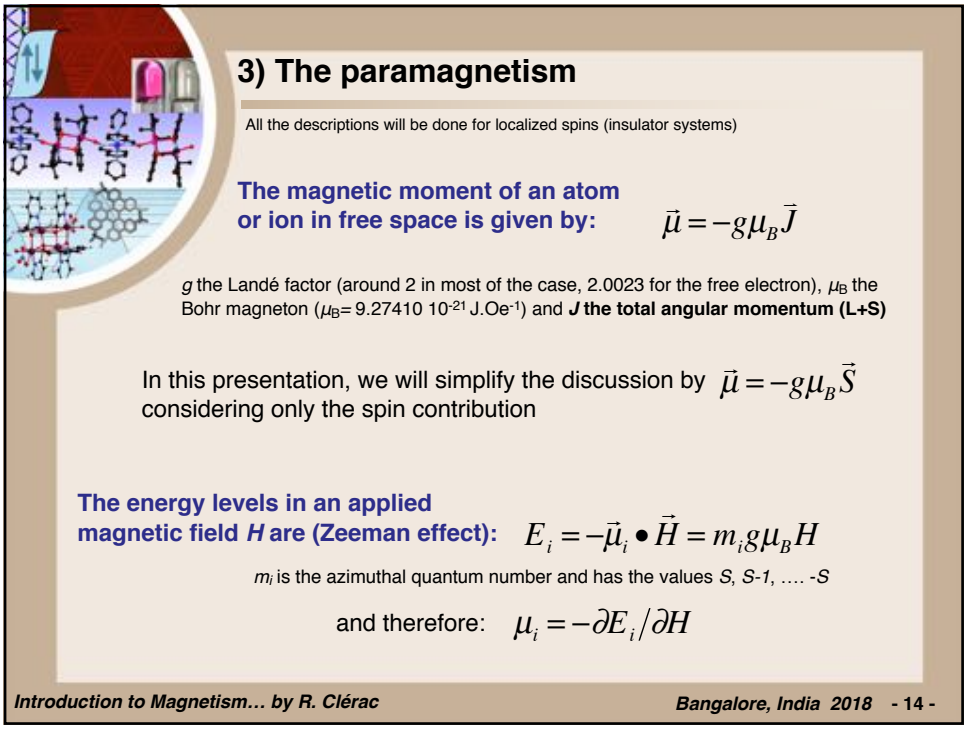
3) The paramagnetism
All the descriptions will be done for localized spins (insulator systems)
The magnetic moment of an atom or ion in free space is given by: $\vec{\mu} = -g\mu_B \vec{J}$
g the Landé factor (around 2 in most of the case, 2.0023 for the free electron), μ_B the Bohr magneton (μ_B= 9.27410 10-21 J.Oe-1) and J the total angular momentum (L+S)
In this presentation, we will simplify the discussion by $\vec{\mu} = -g\mu_B \vec{S}$ considering only the spin contribution
The energy levels in an applied magnetic field H are (Zeeman effect): $E_i = -\vec{\mu}_i \bullet \vec{H} = m_i g \mu_B H$
m_i is the azimuthal quantum number and has the values S, S-1, ... -S
and therefore: $\mu_i = -\partial E_i / \partial H$
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3) The paramagnetism

The magnetization is given by: $M = N\sum_i \mu_i P_i$

with $P_i = \frac{N_i}{N} = \frac{\exp(-E_i/k_BT)}{\sum_i \exp(-E_i/k_BT)}$

The probability to thermally populate an energy level, E_i, is given by the Bolzmann distribution.

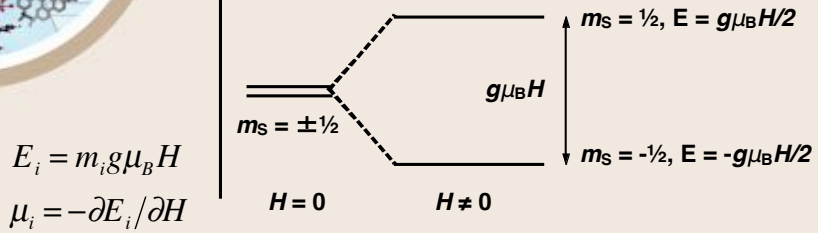
Therefore the magnetization is given by the **van-Vleck equation:**

$$M = N\sum_i \mu_i P_i = N\frac{\sum_i \mu_i \exp(-E_i/k_BT)}{\sum_i \exp(-E_i/k_BT)}$$

3) The paramagnetism

The simple case of *N* non-interacting *S* = ½ spins:

Energy $\mathbf{H} = g\mu_B \vec{H} \bullet \vec{S}$



$E_i = m_i g\mu_B H$

$\mu_i = -\partial E_i/\partial H$

The application of the van-Vleck equation gives:

$$M = N\frac{-\frac{1}{2}g\mu_B \exp(-\frac{1}{2}g\mu_B H/k_BT) + \frac{1}{2}g\mu_B \exp(\frac{1}{2}g\mu_B H/k_BT)}{\exp(-\frac{1}{2}g\mu_B H/k_BT) + \exp(\frac{1}{2}g\mu_B H/k_BT)}$$

3) The paramagnetism

The simple case of *N* spins with *S* = ½:

$$M = N\frac{-\frac{1}{2}g\mu_B \exp\left(-\frac{1}{2}g\mu_B H/k_B T\right)+\frac{1}{2}g\mu_B \exp\left(\frac{1}{2}g\mu_B H/k_B T\right)}{\exp\left(-\frac{1}{2}g\mu_B H/k_B T\right)+\exp\left(\frac{1}{2}g\mu_B H/k_B T\right)}$$

$$= \frac{1}{2}gN\mu_B \frac{-\exp\left(-\frac{1}{2}g\mu_B H/k_B T\right)+\exp\left(\frac{1}{2}g\mu_B H/k_B T\right)}{\exp\left(-\frac{1}{2}g\mu_B H/k_B T\right)+\exp\left(\frac{1}{2}g\mu_B H/k_B T\right)}$$

$$= \frac{1}{2}gN\mu_B \frac{-\exp(-x)+\exp(x)}{\exp(-x)+\exp(x)} \quad \text{with } x = \frac{1}{2}g\mu_B H/k_B T$$

$$= \frac{1}{2}gN\mu_B \tanh(x)$$

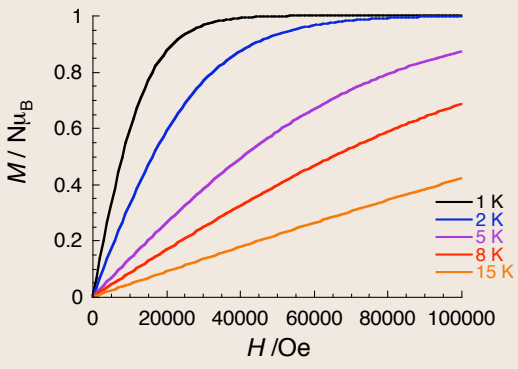
$$\boxed{M = \frac{1}{2}gN\mu_B \tanh\left(\frac{1}{2}g\mu_B H/k_B T\right)}$$

The Brillouin function for *S* = ½

3) The paramagnetism

The Brillouin function for *S* = ½ (with *g* = 2):

$$M = \frac{1}{2}gN\mu_B \tanh\left(\frac{1}{2}g\mu_B H/k_B T\right)$$



3) The paramagnetism

The simple case of *N* spins with *S* = ½: the two limit cases

• The high field approximation $g\mu_B H >> k_B T$ or $g\mu_B H / k_B T >> 1$:

$$M = \tfrac{1}{2} gN\mu_B \tanh\left(\tfrac{1}{2} g\mu_B H / k_B T\right)$$

$$M_{sat} \approx \tfrac{1}{2} gN\mu_B \text{ because } \tanh(x) \approx 1 \text{ if } x >> 1$$

• The weak field approximation $g\mu_B H << k_B T$ or $g\mu_B H / k_B T << 1$:

$$M = \tfrac{1}{2} gN\mu_B \tanh\left(\tfrac{1}{2} g\mu_B H / k_B T\right)$$
$$\approx \tfrac{1}{2} gN\mu_B \left(\tfrac{1}{2} g\mu_B H / k_B T\right) \quad \text{because } \tanh(x) \approx x \text{ if } x << 1$$
$$\approx \tfrac{1}{4} g^2 N\mu_B^2 H / k_B T$$
$$\approx CH/T$$

$$\chi = M/H \approx C/T \text{ with } C = g^2 N\mu_B^2 / 4k_B$$

note that $N\mu_B^2 / k_B \approx 3/8$

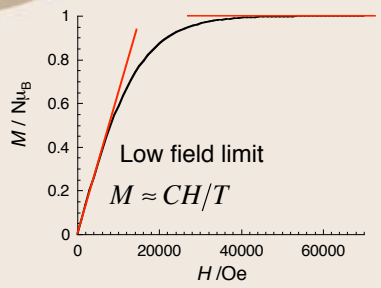
The Curie law for *S* = ½

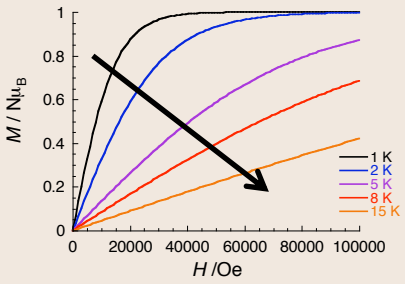
3) The paramagnetism

The simple case of *N* spins with *S* = ½: the two limit cases

High field limit

$$M \approx \tfrac{1}{2} gN\mu_B$$





Low field limit

3) The paramagnetism

Generalisation of the Brillouin function for a spin *S*:

$$M = gN\mu_B S\, \mathrm{B}_S(g\mu_B SH/k_BT)$$

$$\text{with } \mathrm{B}_S(x) = \frac{2S+1}{2S}\,\mathrm{cotanh}\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\,\mathrm{cotanh}\left(\frac{1}{2S}x\right)$$

The two limit cases:

- The high field approximation $g\mu_B H >> k_B T$ or $g\mu_B H / k_B T >> 1$:

$$M \approx gN\mu_B S \quad \text{because } \tanh(x) \approx 1 \text{ if } x >> 1 \text{ and thus } \mathrm{B}_S(x) \approx 1$$

- The weak field approximation $g\mu_B H << k_B T$ or $g\mu_B H / k_B T << 1$:

$$M \approx g^2 N\mu_B^2 S(S+1)H/3k_BT \quad \text{because } B_S(x) \approx \frac{S+1}{3S}x \text{ if } x << 1$$

$$\approx C_S H/T$$

$$\chi = M/H \approx C_S/T \text{ with } C_S = g^2 N\mu_B^2 S(S+1)/3k_B$$

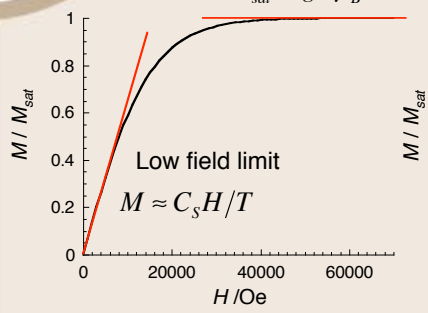
The Curie law for a spin *S*

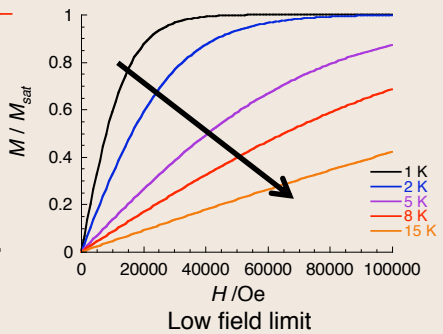
3) The paramagnetism

The simple case of *N* spins *S*: the two limit cases

High field limit

$$M_{sat} \approx gN\mu_B S$$



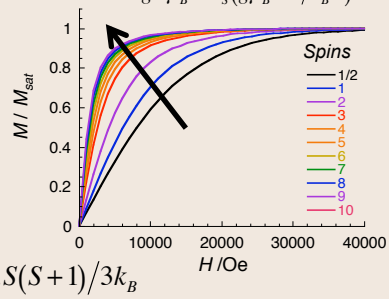


Low field limit

3) The paramagnetism

The simple case of *N* spins *S* (at 1 K):

$$M = gN\mu_B S\, B_S(g\mu_B SH/k_BT)$$

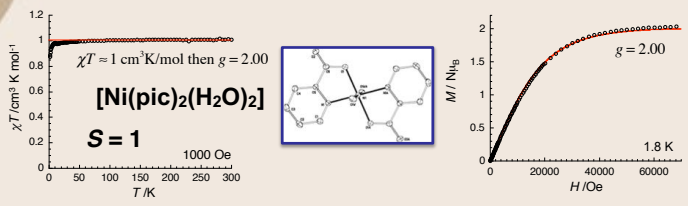


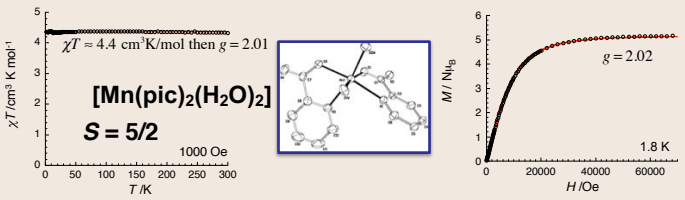
The Curie constants: $C_S = g^2N\mu_B^2S(S+1)/3k_B$

Spins	0	½	1	3/2	2	5/2	3	7/2	4
C (cm^3K/mol)	0	0.375	1	1.875	3	4.375	6	7.875	10
Names	singlet	doublet	triplet	quartet	quintet	sextet	…	…	…
Examples	Zn^{II}, Co^{III}…	Cu^{II},Co^{II}, Fe^{III}, …	Ni^{II}	Co^{II}, Cr^{III}, Mn^{IV}	Mn^{III}, Fe^{II}	Mn^{II}, Fe^{III}	-	Gd^{III}	-

3) The paramagnetism

Isolated spins:
Examples for *S* = 1 and 5/2 Curie behaviors





3) The paramagnetism

The case of *N* interacting spins:

$$\mathbf{H} = g\mu_B \sum_i \vec{H} \bullet \vec{S}_i - 2J \sum_{\langle i,j \rangle} \vec{S}_i \bullet \vec{S}_j$$

J is the magnetic interaction between spin pairs
when $J > 0$, ferromagnetic interactions are present
when $J < 0$, antiferromagnetic interactions are present

The mean field approximation:

$$\mathbf{H} = g\mu_B \left(\vec{H} - 4zJ \langle \vec{S} \rangle \right) \bullet \sum_i \vec{S}_i$$

$$E_i = f\left(m_i, H, S, zJ\right)$$

R. Boca, *Theoretical Foundations of Molecular Magnetism*, Elsevier Ed., p 536.

The application of the van-Vleck equation gives:

$$M = N \sum_i \mu_i P_i = N \frac{\sum_i \mu_i \exp(-E_i / k_B T)}{\sum_i \exp(-E_i / k_B T)} \approx gN\mu_B \frac{S(S+1) g\mu_B H}{3k_B T - 2zJS(S+1)}$$

3) The paramagnetism

The case of *N* interacting spins:

$$M \approx gN\mu_B \frac{S(S+1) g\mu_B H}{3k_B T - 2zJS(S+1)}$$

And therefore the Curie-Weiss law is given by:

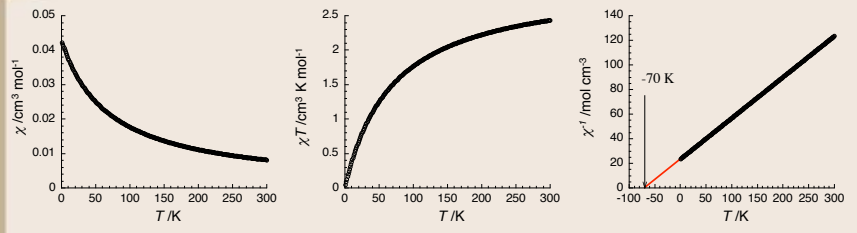
$$\chi = \frac{M}{H} = gN\mu_B \frac{S(S+1) g\mu_B}{3k_B T - 2zJS(S+1)} = \frac{C_S}{T - \theta}$$

with $C_S = g^2 N \mu_B^2 S(S+1) / 3k_B$ (the Curie constant)
and $\theta = 2zJS(S+1) / 3k_B$ (the Weiss constant)

3) The paramagnetism

Interacting $S = 2$ spins: Curie Weiss behaviors with $\theta = -70$ K

$$\chi = \frac{C_S}{T-\theta} \qquad \chi T = \frac{C_S T}{T-\theta} \qquad \frac{1}{\chi} = \frac{T-\theta}{C_S} = \frac{1}{C_S}T - \frac{\theta}{C_S}$$

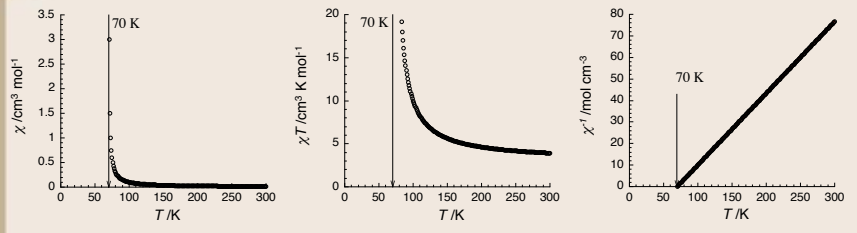


Room temperature: $\chi T = 2.43$ cm^{3}K/mol while $C = 3$ cm^{3}K/mol! 19% of Error! The room temperature χT is not the Curie constant in a system with strong interactions

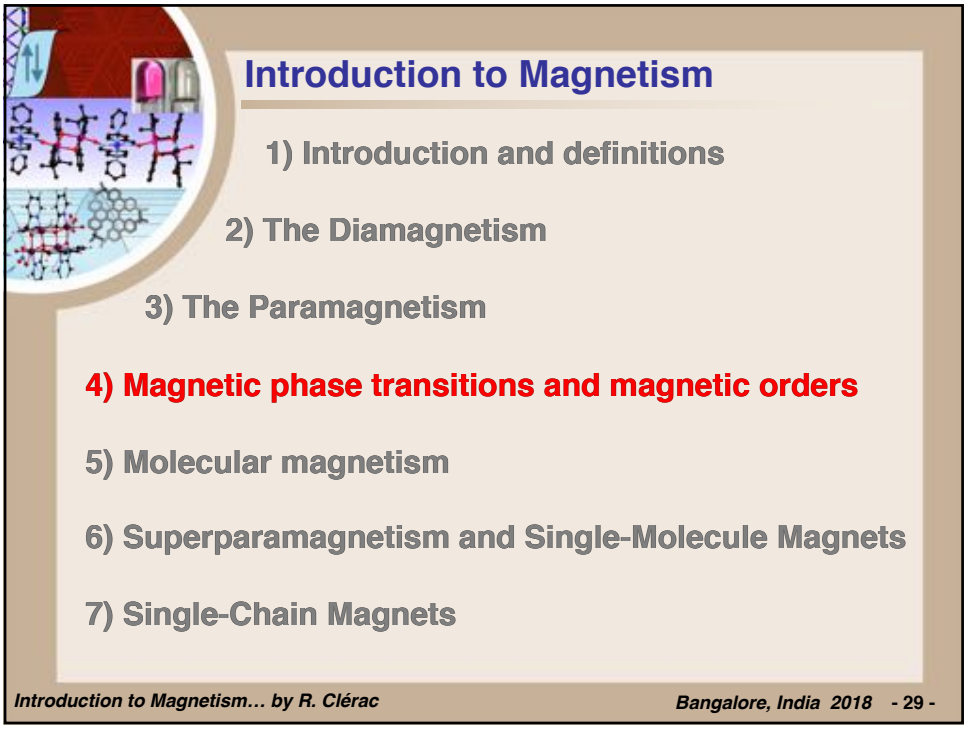
3) The paramagnetism

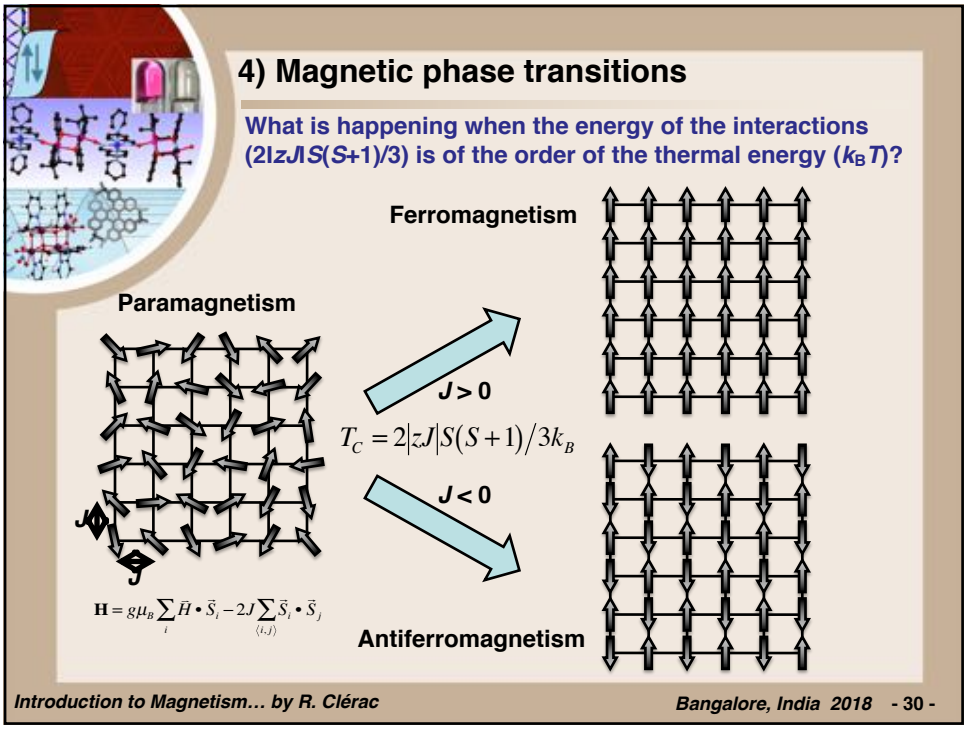
Interacting $S = 2$ spins: Curie Weiss behaviors with $\theta = +70$ K

$$\chi = \frac{C_S}{T-\theta} \qquad \chi T = \frac{C_S T}{T-\theta} \qquad \frac{1}{\chi} = \frac{T-\theta}{C_S} = \frac{1}{C_S}T - \frac{\theta}{C_S}$$



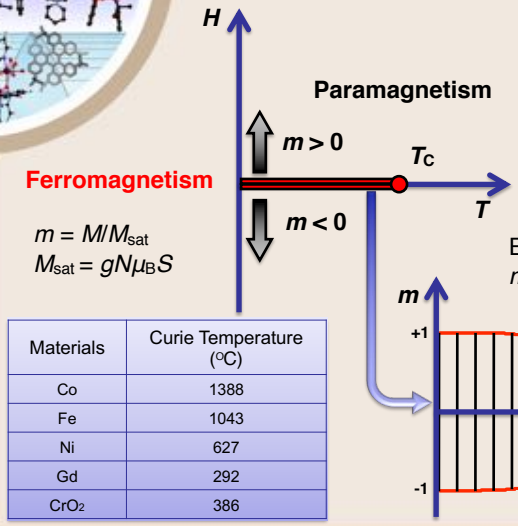
Room temperature: $\chi T = 3.97$ cm^{3}K/mol while $C = 3$ cm^{3}K/mol! 32% of Error! The room temperature χT is not the Curie constant in a system with strong interactions


Introduction to Magnetism
1) Introduction and definitions
2) The Diamagnetism
3) The Paramagnetism
4) Magnetic phase transitions and magnetic orders
5) Molecular magnetism
6) Superparamagnetism and Single-Molecule Magnets
7) Single-Chain Magnets
Introduction to Magnetism... by R. Clérac
Bangalore, India 2018 - 29 -


4) Magnetic phase transitions
What is happening when the energy of the interactions (2|z|JS(S+1)/3) is of the order of the thermal energy (kBT)?
Ferromagnetism
Paramagnetism
J > 0
$T_C = 2|zJ|S(S+1)/3k_B$
J < 0
$\mathbf{H} = g\mu_B \sum_i \vec{H} \cdot \vec{S}_i - 2J \sum_{\langle i,j \rangle} \vec{S}_i \cdot \vec{S}_j$
Antiferromagnetism
Introduction to Magnetism... by R. Clérac
Bangalore, India 2018 - 30 -

4) Magnetic phase transitions

Ferromagnetism: the general phase diagrams



$m = M/M_{sat}$

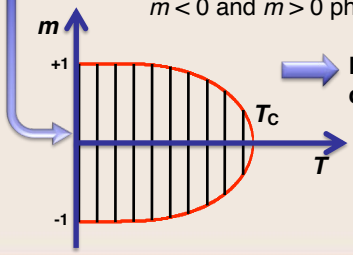
$M_{sat} = gN\mu_B S$

At the mean-field approximation:

$T_C = 2|zJ|S(S+1)/3k_B$

Curie temperature

Equilibrium between $m < 0$ and $m > 0$ phases:

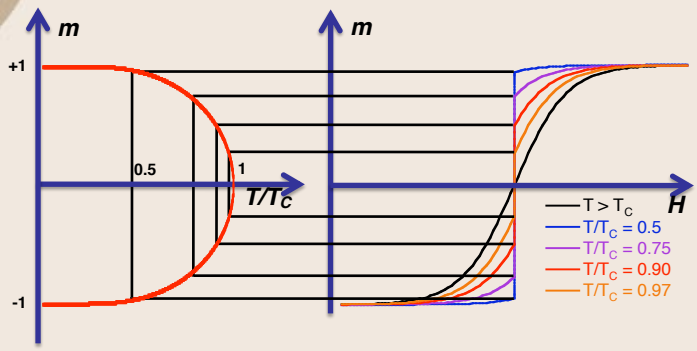


Magnetic domains

Materials	Curie Temperature (°C)
Co	1388
Fe	1043
Ni	627
Gd	292
CrO_2	386

4) Magnetic phase transitions

Ferromagnetism: Magnetization measurements

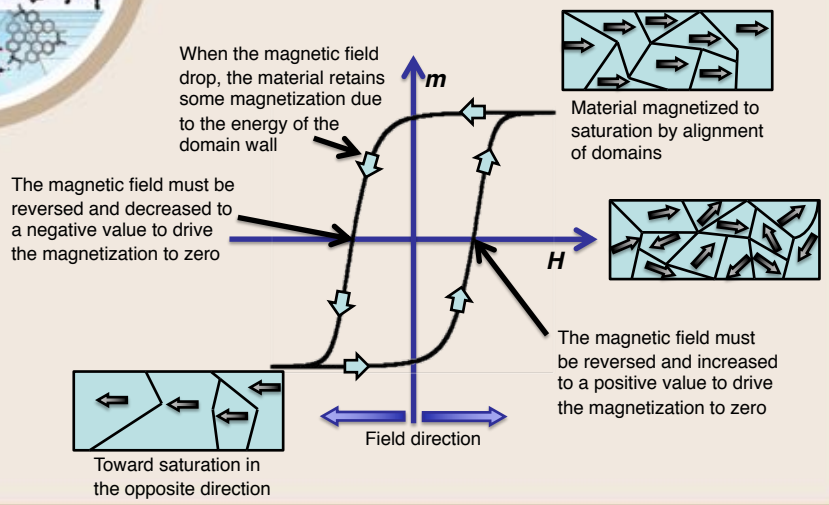


Experimentally the magnetization close to zero is never vertical due to demagnetization effects induced by the shape of the sample.

4) Magnetic phase transitions

Ferromagnetism: Influence of magnetic domains

Hysteresis effect (memory effect, bistability…)



4) Magnetic phase transitions

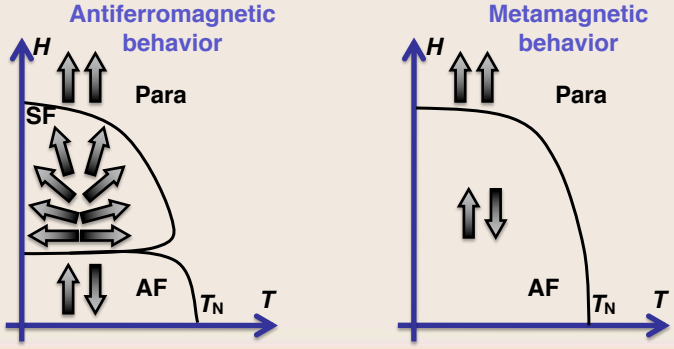
Antiferromagnetism: the general phase diagrams

At the mean-field approximation:

$$T_N = 2|zJ|S(S+1)/3k_B$$

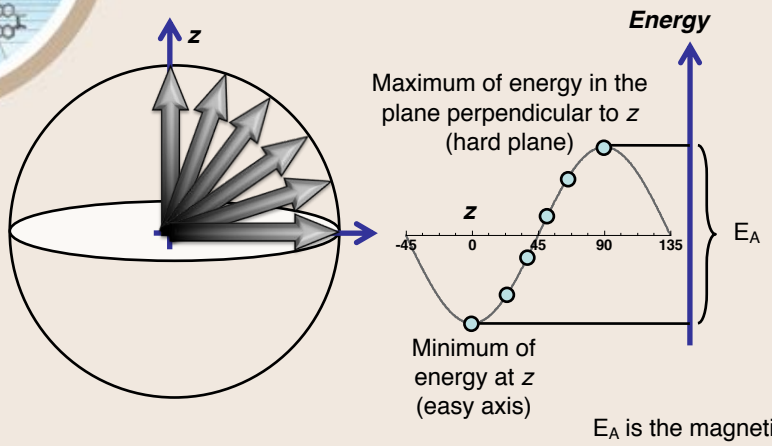
Néel Temperature

Materials	Néel Temperature (K)
MnO	116
FeO	198
Tb	229



4) Magnetic phase transitions

Antiferromagnetism:
Notion of magnetic anisotropy (uniaxial case)

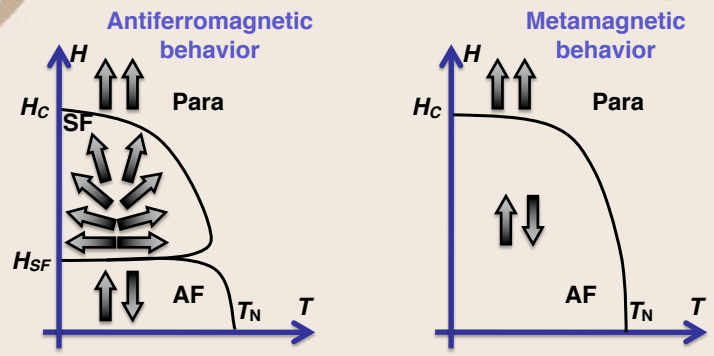


E_A is the magnetic anisotropy energy

4) Magnetic phase transitions

Antiferromagnetism: the general phase diagrams

Increasing magnetic anisotropy



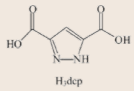
For a given magnetic model (in terms of spin, anisotropy and dimensionality), H_{SF}, H_C, T_N are used to evaluate J and E_A

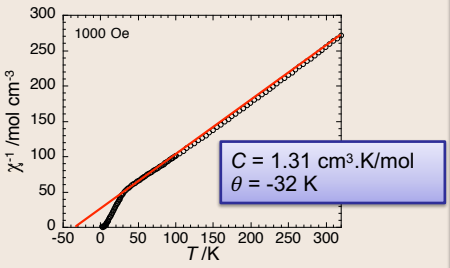
4) Magnetic phase transitions

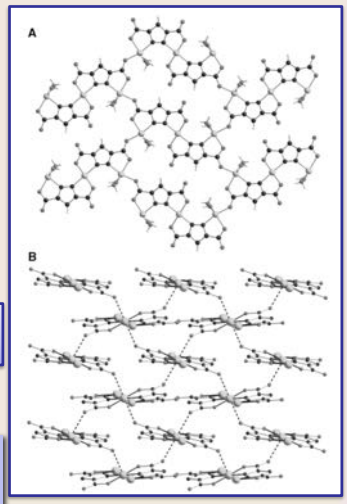
Antiferromagnetism: an example

$[Cu^{II}_3(dcp)_2(H_2O)_4]$

H_3dcp: 3,5-pyrazoledicarboxylic acid





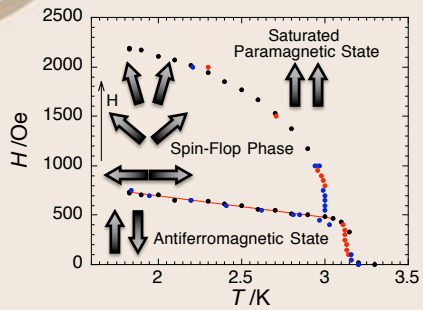


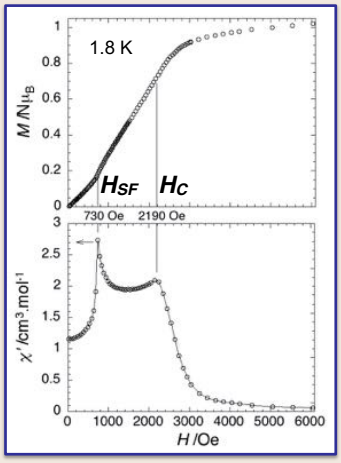
P. King, R. Clérac, C. E. Anson, C. Coulon and A. K. Powell, "Antiferromagnetic Three-Dimensional Order Induced by Carboxylate Bridges in a Two-Dimensional Network of $[Cu_3(dcp)_2(H_2O)_4]$ Trimers", ***Inorg. Chem.,*** (2003), ***42***, p. 3492-3500

4) Magnetic phase transitions

Antiferromagnetism: an example

$[Cu^{II}_3(dcp)_2(H_2O)_4]$

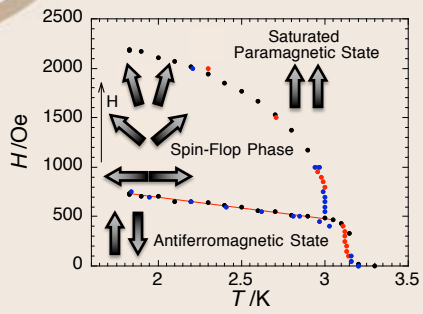


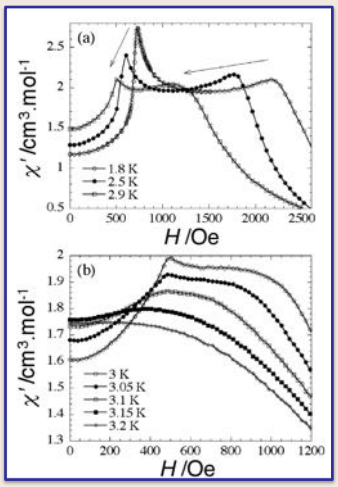


4) Magnetic phase transitions

Antiferromagnetism: an example

$[Cu^{II}_3(dcp)_2(H_2O)_4]$

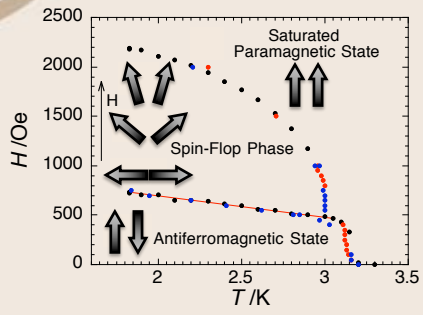


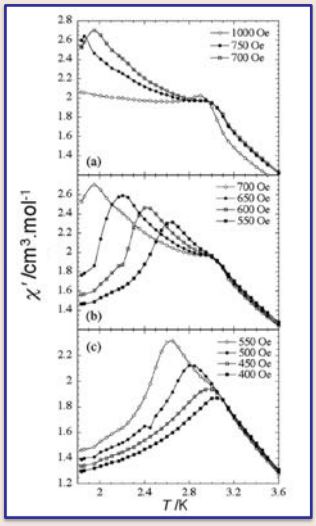


4) Magnetic phase transitions

Antiferromagnetism: an example

$[Cu^{II}_3(dcp)_2(H_2O)_4]$



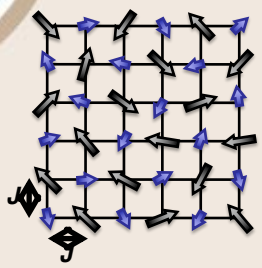


4) Magnetic phase transitions

Some other magnetic phases: Ferrimagnetism

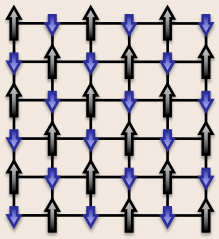
Paramagnetism

Ferrimagnetic phase



$J < 0$

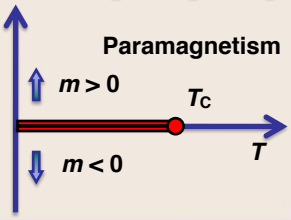
$$T_C = \frac{2|zJ|}{3k_B}\sqrt{S(S+1)s(s+1)}$$



Materials	Tc (°C)
Fe_3O_4 ($Fe^{II}Fe^{III}_2O_4$, magnetite)	575
γ–Fe_3O_4 ($Fe^{II}Fe^{III}_2O_4$, maghemite)	600
$NiFe_2O_4$ ($Ni^{II}Fe^{III}_2O_4$, Trevorite)	585

$m = M/M_{sat}$

$M_{sat} = gN\mu_B(S\text{-}s)$



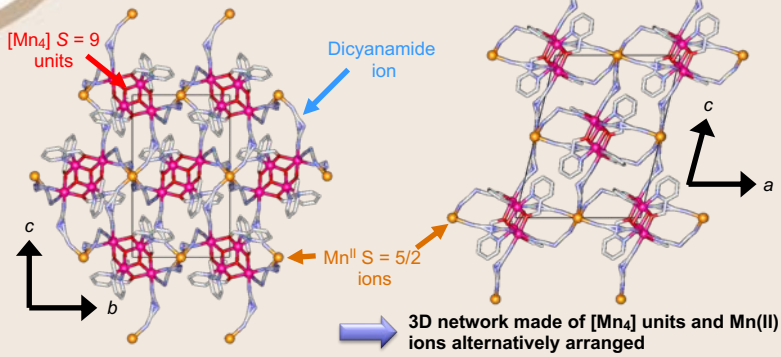
4) Magnetic phase transitions

Ferrimagnetism: an example

$[Mn_4(hmp)_4(OH)_2][Mn(dcn)_6]\cdot 2THF\cdot 2CH_3CN$

dcn⁻: dicyanamide anion 

Hhmp: 2-hydroxymethylpyridine 



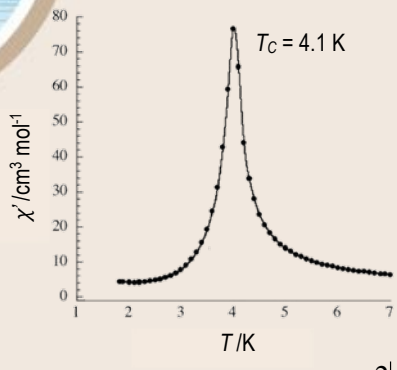
3D network made of [Mn_4] units and Mn(II) ions alternatively arranged

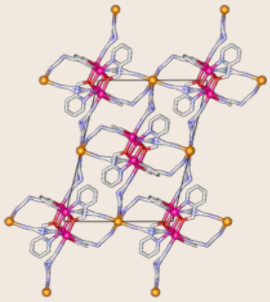
H. Miyasaka, K. Nakata, K.-i. Sugiura, M. Yamashita et R. Clérac, "A Three-Dimensional Ferrimagnet Composed of Mixed-Valence Mn_4 Clusters Linked by an $\{Mn[N(CN)_2]_6\}_4$ Unit", ***Angew. Chem. Int. Ed.***, (2004), ***43***, p. 707-711

4) Magnetic phase transitions

Ferrimagnetism: an example

$[Mn_4(hmp)_4(OH)_2][Mn(dcn)_6]$•2THF•2$CH_3CN$





➡ **Magnetic order at 4.1 K**

$$T_C = \frac{2|zJ|}{3k_B}\sqrt{S_{Mn_4}\left(S_{Mn_4}+1\right)S_{Mn}\left(S_{Mn}+1\right)}$$

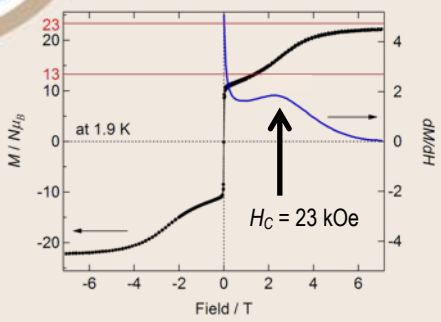
$J/k_B \approx -0.036$ K

4) Magnetic phase transitions

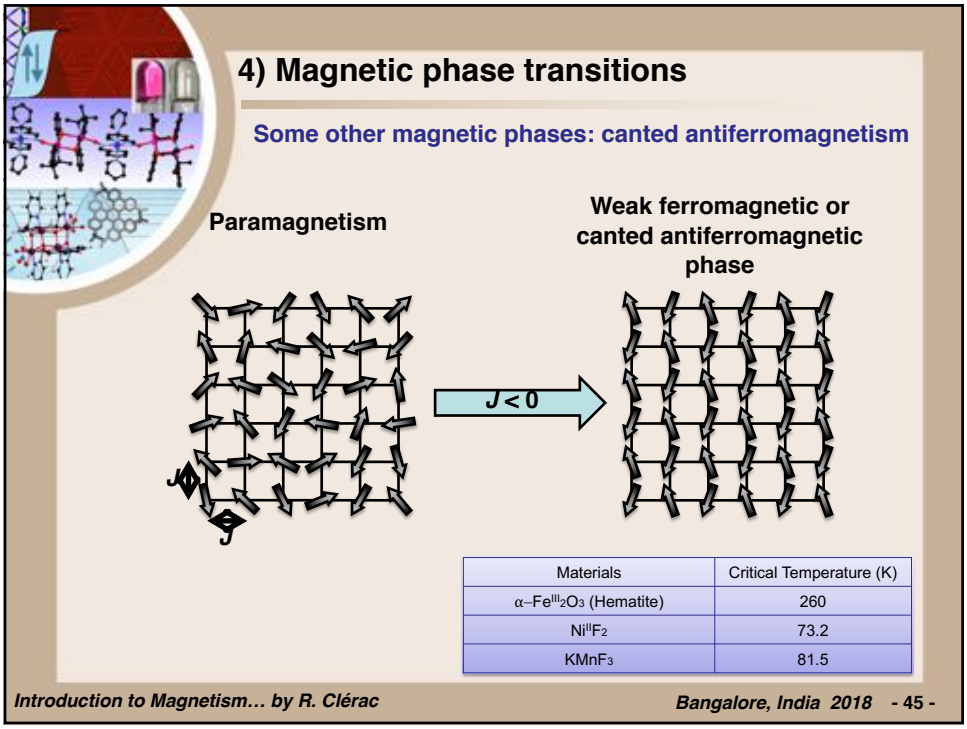
Ferrimagnetism: an example

$[Mn_4(hmp)_4(OH)_2][Mn(dcn)_6]$•2THF•2$CH_3CN$

$S = 9$ ⇧ $S = 5/2$ ⇩



$$g\mu_B H_C S_{Mn} = 2|zJ|S_{Mn_4}S_{Mn}$$ ➡ $J/k_B \approx -0.030$ K


4) Magnetic phase transitions
Some other magnetic phases: canted antiferromagnetism
Paramagnetism
Weak ferromagnetic or canted antiferromagnetic phase
J < 0
J
J
Materials
Critical Temperature (K)
α–Fe$^{III}_2$O$_3$ (Hematite)
260
Ni^{II}F$_2$
73.2
KMnF$_3$
81.5
Introduction to Magnetism... by R. Clérac
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