

MAGNETISM — A Few Basics

A. HISTORY

Magnetite or lodestone ($\text{Fe}^{\text{II}}\text{OFe}^{\text{III}}_2\text{O}_3$)

mineral in its natural state often has a strong attraction for iron and steel...mined in magnesia but Pliny says it was named for the discoverer, a shepherd, magnes, "the nails of whose shoes and the tip of whose staff stuck fast in a magnetick field while he pastured his flocks."

Lodestone appears in Greek writings by 800 B.C.

First magnetic technological invention — compass: in China, sometime between 2637 B.C. and 1100 A.D. (!)

others say it was introduced to China in 1200s by Italians or Arabs

Early theories and experiments on magnetism were developed by the great minds of all times — Gilbert, Descartes, Coulomb, Poisson, Green, Oertsted, Ampere, Davy, Fresnel, Faraday, Maxwell...

But: Quantum Mechanics is necessary to develop a viable model, and the model continues to evolve: MAGNETISM IS NOT A SOLVED PROBLEM

B. BASICS

All materials respond to an external magnetic field (H). The magnetization (M) of a sample is proportional to H:

$M = \chi H$. The proportionality constant, χ , is the magnetic susceptibility

C. TYPES OF MAGNETISM - see chart

The Big five

1. Diamagnetism

electrons in closed shells cause a material to be repelled by H ($\chi < 0$).

Typically, $\chi_m = -1 \times 10^{-6}$ emu/mol

usually a very small contribution to χ_{exp}

$$\chi_{\text{exp}} = \chi_{\text{dia}} + \chi_{\text{para}} + \chi_{\text{Pauli}}$$

χ_{dia} — diamagnetic term due to closed-shell (core) electrons. ALL materials have this. For our systems, which will probably have a very small χ , the diamagnetic correction is non-trivial — can be obtained from atom/group additivities or the Curie plot (see below).

χ_{dia} is temperature and field independent.

χ_{para} is due to unpaired electrons ($= \chi_p$)

χ_{Pauli} is typically seen in metals and other conductors - due to mixing excited states that are not thermally populated into the ground (singlet) state - temperature independent. Presumably not important in our systems.

ALL OTHER TYPES OF MAGNETISM REQUIRE UNPAIRED SPINS (MOMENTS) — THE INTERACTIONS AMONG SPINS DETERMINES THE TYPE OF MAGNETISM

2. Paramagnetism

randomly oriented, rapidly reorienting moments; no permanent, spontaneous magnetic moment ($M = 0$ if $H = 0$)

spins are non-interacting (non-cooperative)

all other forms of magnetism have a critical temperature, T_C , below which there is some interaction of moments. Above T_C paramagnet

χ_p varies with T empirically according to the Curie Law:

$$\chi_p = \frac{C}{T} \quad C = \text{Curie constant}$$

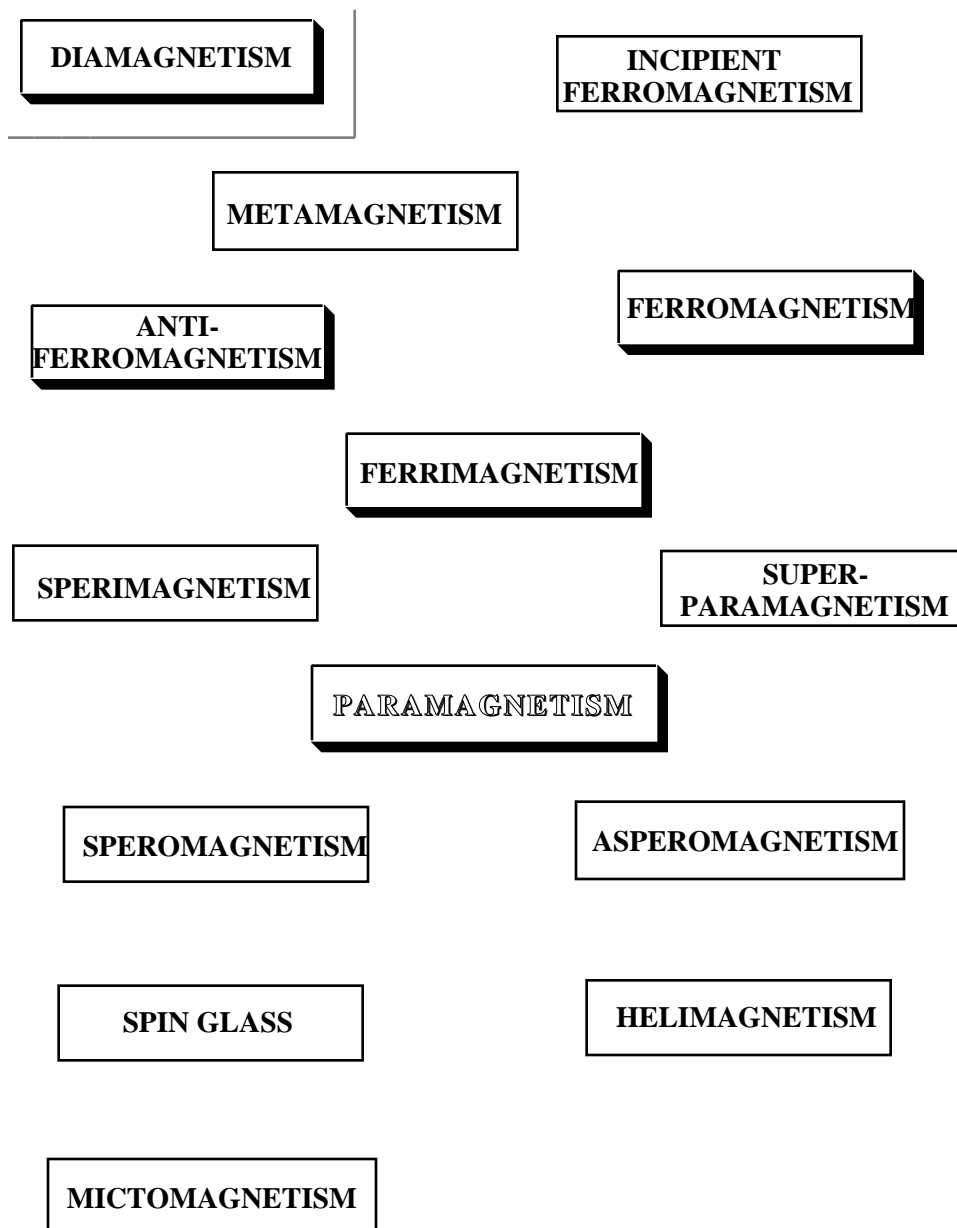
or the Curie-Weiss Law:

$$\chi_p = \frac{C}{T - T_c} \quad = \text{Weiss constant}$$

is indicative of *intermolecular* interactions among the moments

> 0 - ferromagnetic interactions (**NOT** ferromagnetism)

< 0 - antiferromagnetic interactions (**NOT** antiferromagnetism)

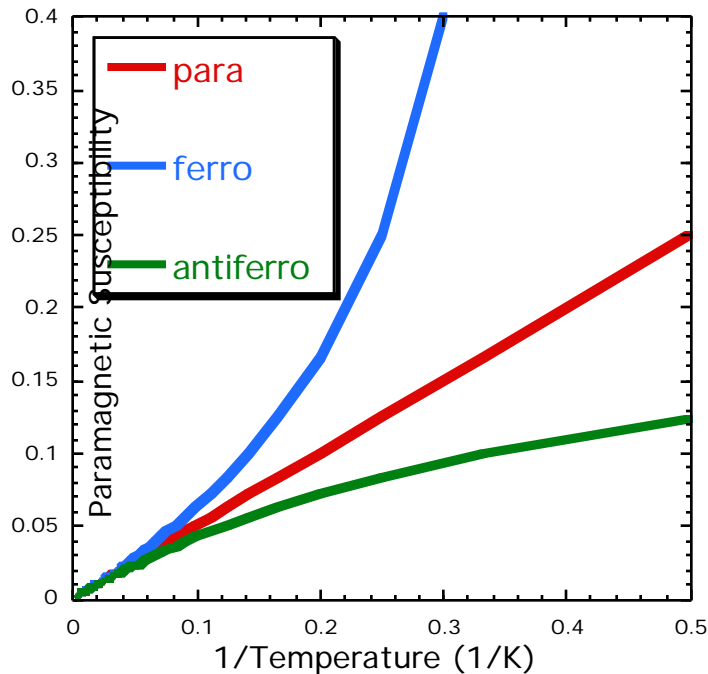


Using the Curie Plot:

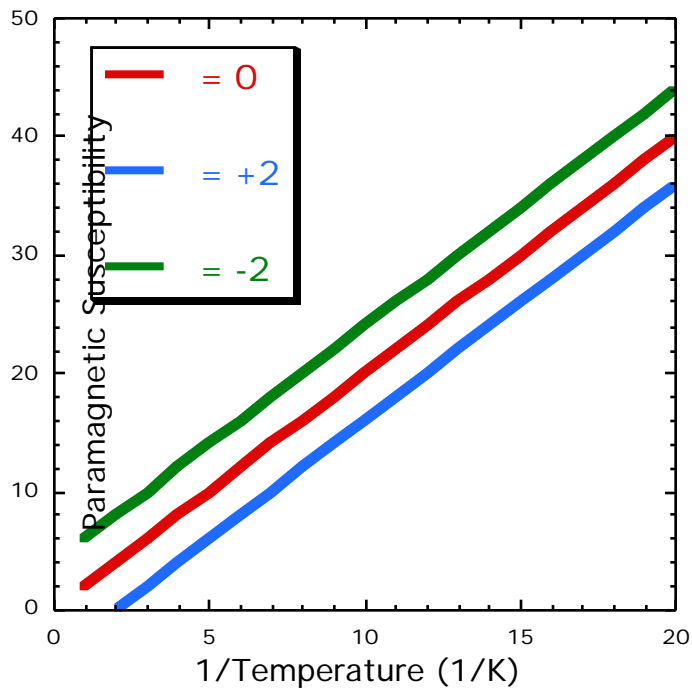
$$\chi_{\text{exp}} = \frac{C}{T - T_c} + T_c \quad (T_c = T_{\text{dia}} + T_{\text{Pauli}} = \text{temperature independent contribution})$$

$$\chi_{\text{exp}} = \frac{C}{T} + T_c \quad (\text{at high temperature if } T_c \text{ is small})$$

Plot χ_p vs $1/T$



slope = C; intercept = T; $\chi_p = C / (T - T_p)$
 ...then plot $1/\chi_p$ vs. T



slope = $1/C$; intercept = T_p/C

A magnetometer measures M which gives χ_p . Do the first plot to get T_p . Then at all T and H, $\chi_p = C / (T - T_p)$

The magnetization plot

For an atom with spin m_s , its energy in H is:

$$E(m_s) = m_s g \mu_B H \quad \mu = -m_s g \mu_B$$

μ_B is Bohr magneton ($= 9.27 \times 10^{-24} \text{J/T}$); g is the Lande constant ($= 2.0023192778$)
Consider N particles, with n_i in i th level

$$\sum_i n_i = N$$

$$P_i = \frac{n_i}{N} = \frac{\exp \left(-\frac{\epsilon_i}{kT} \right)}{\sum_i \exp \left(-\frac{\epsilon_i}{kT} \right)}$$

$$M = N \sum_i \mu_i P_i$$

now, consider two spin states ($m_s = \pm 1/2$),

$$\begin{aligned} M &= N \frac{\sum_{m_s=+1/2} \left(-m_s g \mu_B \right) \exp \left(-\frac{m_s g \mu_B H}{kT} \right)}{\sum_{m_s=-1/2} \exp \left(\frac{m_s g \mu_B H}{kT} \right)} \\ &= \frac{Ng \mu_B}{2} \frac{\exp \left(\frac{g \mu_B H}{2kT} \right) - \exp \left(-\frac{g \mu_B H}{2kT} \right)}{\exp \left(\frac{g \mu_B H}{2kT} \right) + \exp \left(-\frac{g \mu_B H}{2kT} \right)} \\ &= \frac{Ng \mu_B}{2} \tanh \left(\frac{g \mu_B H}{2kT} \right) \quad \text{since } \tanh(y) = \frac{e^y - e^{-y}}{e^y + e^{-y}} \end{aligned}$$

if $y \ll 1$, $\tanh y = y$

therefore if $(g \mu_B H)/2kT \ll 1$ (i.e. $H/T \ll 1.5 \text{ T/K}$)

$$\begin{aligned} M &= \frac{Ng^2 \mu_B^2 H}{4kT} \\ \text{(molar) } \chi_{\text{exp}} = M/H &= \frac{Ng^2 \mu_B^2}{4kT} = \frac{C}{T} = \text{Curie - Law} \end{aligned}$$

Therefore Curie Law only valid if $H/T \ll 1.5 \text{ T/K}$ - usually true

If $y \gg 1$, $\tanh y \Rightarrow 1$

$$M_{\text{sat}} = \frac{Ng \mu_B}{2} \quad \text{(or generally, } M_{\text{sat}} = Ng \mu_B S \dots \text{a constant - the saturation magnetization)}$$

A more general treatment with $\sum_{m_s=-S}^{m_s=+S}$ gives $M = Ng \mu_B S B_S(x)$, with

$$B_S(x) \text{ --- The Brillouin Function: } B_S(x) = \frac{1}{S} \left(S + \frac{1}{2} \right) \coth \left(\left(S + \frac{1}{2} \right) x \right) - \frac{1}{2} \coth \frac{x}{2}$$

$$\text{where } x = \frac{g \mu_B H}{kT}$$

As above, there are two limiting regions of the Brillouin function:

a) For $x \gg 1$, $B_S(x) = \frac{1}{S} \left(S + \frac{1}{2} \right) - \frac{1}{2} = 1$

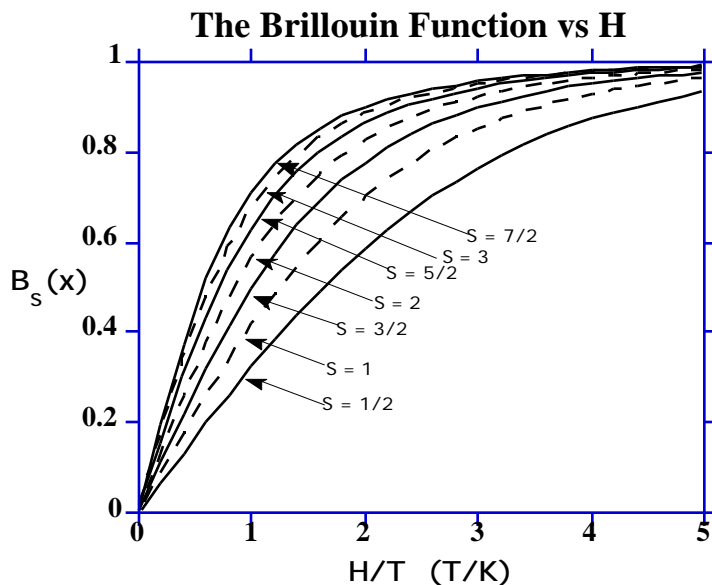
$$x = \frac{g\mu_B H}{kT} \gg 1 \text{ means } \frac{H}{T} \gg \frac{k}{g\mu_B} = \frac{1.38 \times 10^{-23} \text{ J/K}}{2 \times 9.27 \times 10^{-24} \text{ J/T}} = 0.7 \text{ T/K}$$

b) For $x \ll 1$,

$$B_S(x) = \frac{1}{S} \left(S + \frac{1}{2} \right) \frac{1}{\left(S + \frac{1}{2} \right)^x} + \frac{1}{3} \left(S + \frac{1}{2} \right) x - \frac{1}{2} \left(\frac{2}{x} + \frac{x}{6} \right) = \frac{1}{S} \frac{1}{3} \left(S + \frac{1}{2} \right)^2 x - \frac{1}{12x} =$$

$$\frac{x}{3S} \left(S^2 + S + \frac{1}{4} - \frac{1}{4} \right) = \frac{(S+1)x}{3}$$

and the initial slope of a plot of $B_S(x)$ vs x will be $(S+1)/3$.



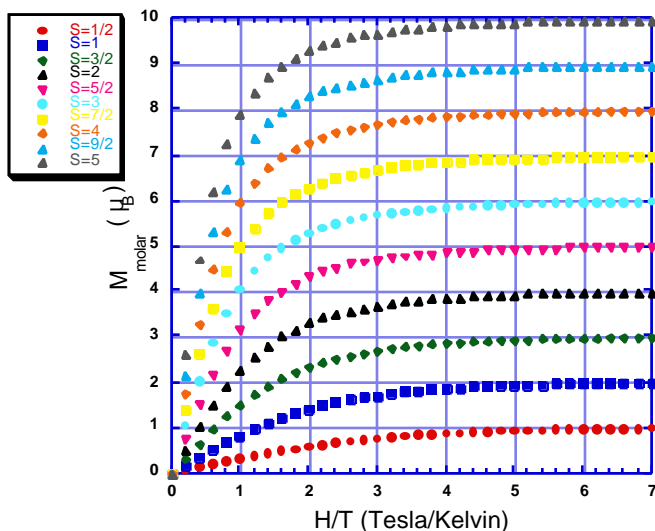
For non-interacting atoms, the mean magnetic moment, or magnetization, is

$$M = N \langle \mu_z \rangle = Ng\mu_B S B_S(x)$$

and so for small x , N is proportional to x , that is $M \propto \frac{H}{T}$.

In fact, for $\frac{g\mu_B H}{kT} \ll 1$, $M = H$, where $= \frac{Ng\mu_B^2 S(S+1)}{3kT}$, which is the Curie Law.

Below are plots of molar Magnetization (in units of μ_B with $g = 2$).



The effective magnetic moment
directly relates to number of spins:

$$\mu_{\text{eff}} = g[S(S+1)]^{1/2}\mu_B$$

S	μ_{eff}/μ_B
1/2	1.73
1	2.83
2	4.89

related to molar susceptibility ($\chi_m = \text{emu/mol}$)

$$\chi_m = \frac{N\mu_{\text{eff}}^2}{3kT} = \frac{C'}{T}$$

$$\mu_{\text{eff}} = \sqrt{\frac{3kC'}{N}} = 2.82\sqrt{C'}$$

Therefore,

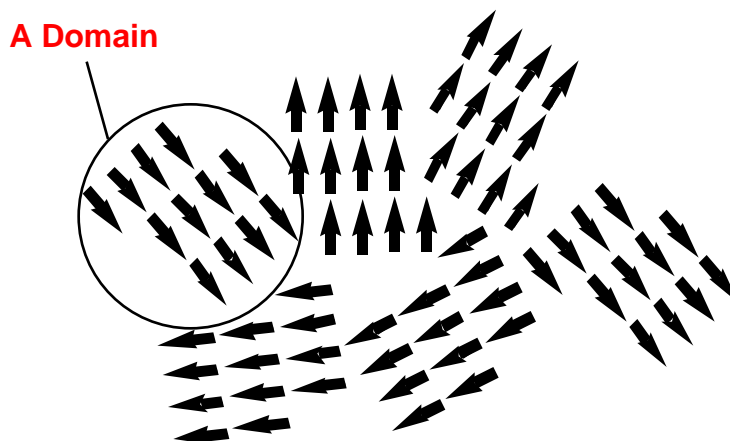
$$\mu_{\text{eff}} = 2.824\sqrt{\chi_m T}$$

3. Ferromagnetism

moments throughout a material in 3-D tend to align parallel

can lead to a spontaneous permanent M (in absence of H)

but, in a macroscopic system, it is energetically favorable for spins to segregate into regions called *DOMAINS* - domains need not be aligned with each other



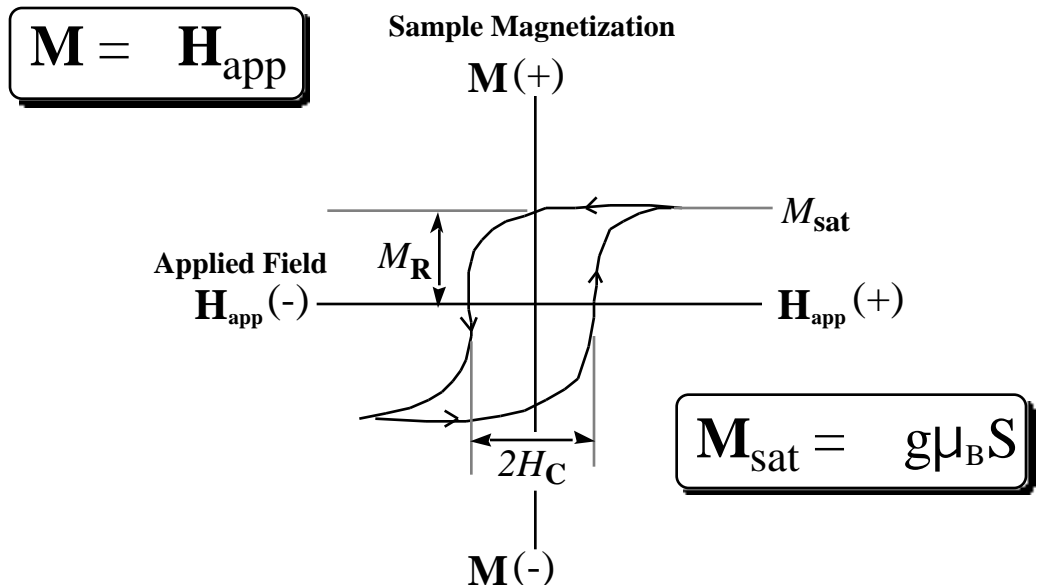
may or may not have spontaneous M

application of H causes aligned domains to grow at the expense of misaligned domains...alignment persists when H is removed

Ferromagnetism is a critical phenomenon, involving a phase transition that occurs at a critical temperature, $T_c = \text{Curie Temperature}$. Above T_c paramagnet

T_c is directly proportional to $S(S+1)$

It takes energy to move domain walls - hysteresis:



M_R = Remnant Magnetization (M at $H_{\text{app}} = 0$)

M_{sat} = Saturation Magnetization ($M_{\text{sat}} = Ng\mu_B S$)

H_C = Coercive Field (H_{app} required to flip M)

"Hard" magnetic material = high Coercivity

"Soft" magnetic material = low Coercivity

Electromagnets

- High M_R and Low H_C

Electromagnetic Relays

- High M_{sat} , Low M_R , and Low H_C

Magnetic Recording Materials

- High M_R and relatively High H_C

Permanent Magnets

- High M_R and High H_C

Remanence: Magnetization of sample after H is removed

Coercive field: Field required to flip M ($+M$ to $-M$)

4. Antiferromagnetism

spins tend to align antiparallel in 3-D

no spontaneous M

no permanent M

critical temperature: T_N (Neel Temperature)

above T_N paramagnet

5. Ferrimagnetism

requires two chemically distinct species with different moments

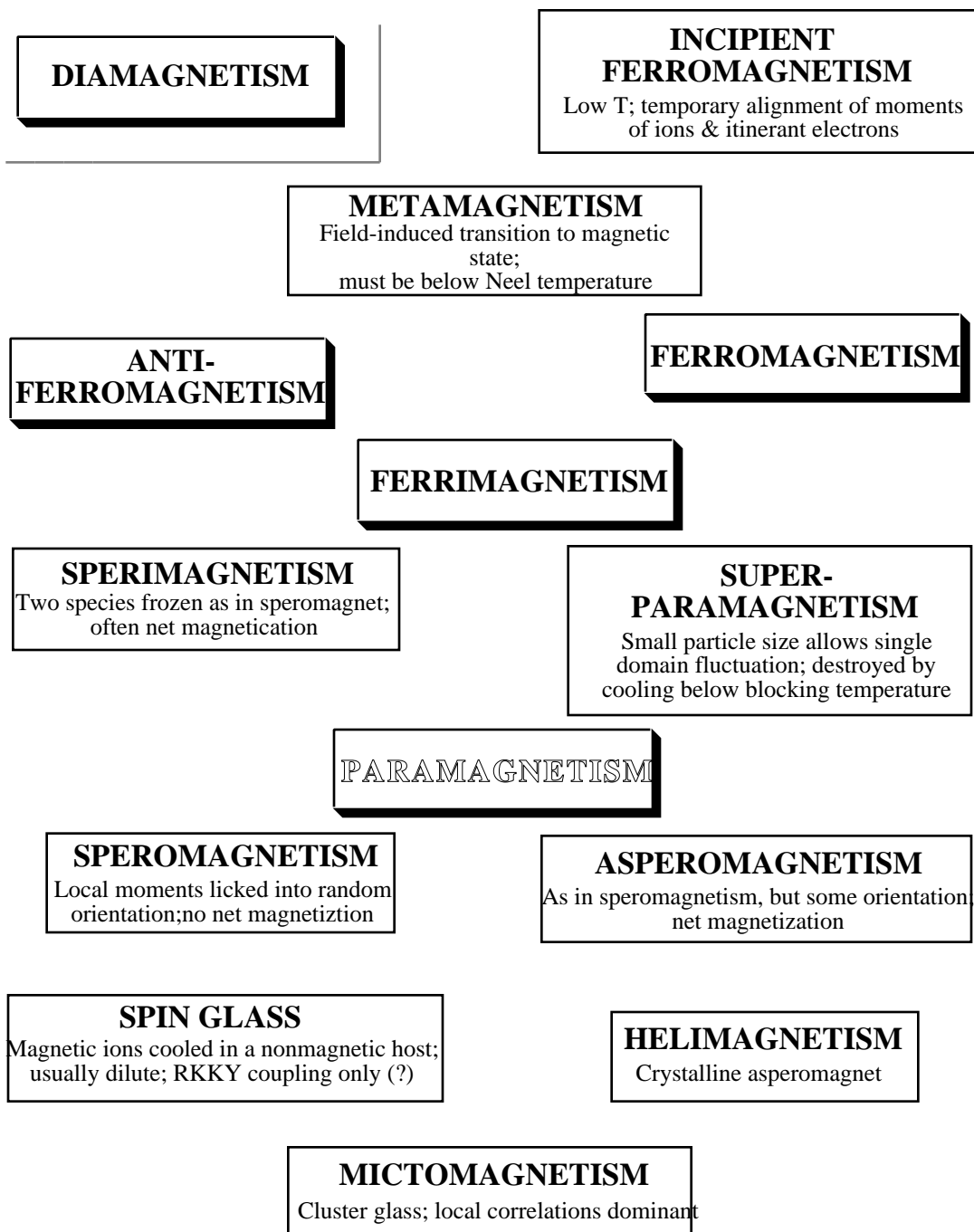
they couple antiferromagnetically:

no M ; critical $T = T_C$ (Curie Temperature)

bulk behavior very similar to ferromagnetism

Magnetite is a ferrimagnet

6. Other types



D. SPECIAL TOPICS

1. Magneto-optical Disks

a. Reading

Magnetic materials rotate plane polarized light

in transmission: Faraday effect

in reflection: Kerr effect (used in devices)

Direction of rotation depends on polarization of M

b. Writing

actually a thermo-magnetic process since a high-powered laser is used to heat the sample

1) Curie point writing-heat above T_C , then cool in applied field

2) Threshold (or compensation point) writing - if material has a temperature dependent coercive field heat to point where $H > H_c$, then on cooling $H < H_c$

c. Materials

Typically rare-earth transition metal alloys (RE-TM) RE: Gd, Tb; TM: Fe, Co

Many factors to tune: T_c , H_c , Magnetic anisotropy, reflectivity, Kerr rotation, stability, etc.

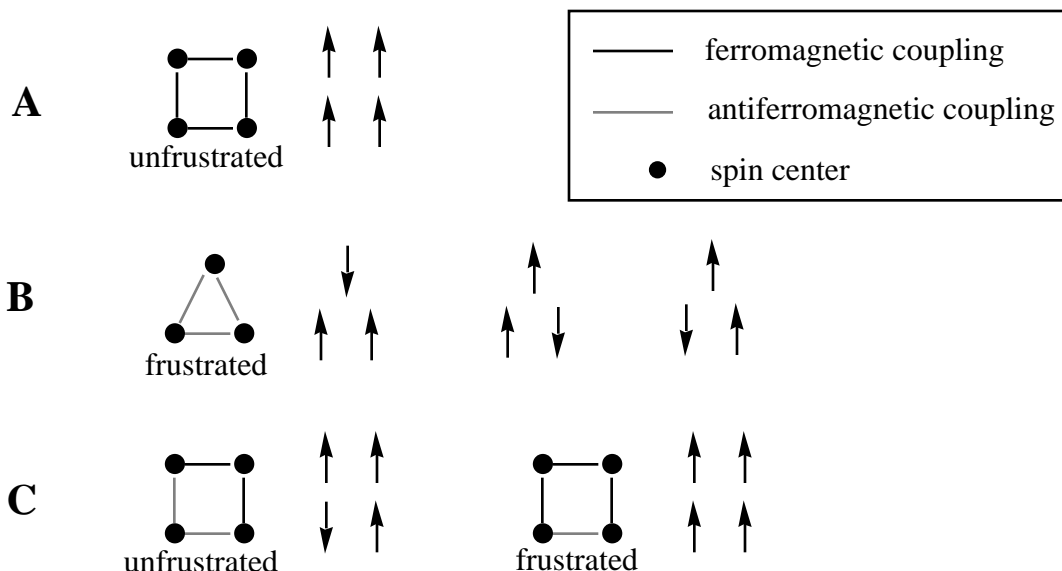
2. Spin Glasses — one of the more intriguing new forms of magnetism

may be a new state of matter, maybe not

prototypical SG is an alloy, with 1-10% of a paramagnetic impurity (e.g., Fe or Mn) in a diamagnetic metal (e.g. Cu or Au)

Spin coupling is mediated through the conduction electrons through the RKKY interaction (Ruderman, Kittel, Kasuya, Yosida) - oscillatory in nature

This leads to frustration:



A critical consequence of Frustration is a highly degenerate ground state - there are MANY equally probable, equally acceptable combinations of spins
Therefore, even at 0 Kelvin, many states are populated - novel thermodynamic and magnetic properties

Experimentally, the hallmark of a SG is a cusp in the AC susceptibility - defines a critical temperature - T_{SG}

Heat capacity measurements do not reveal the some critical temperature

SG do show remanence and hysteresis effects

SG theory has been adopted to other problems, including:

combinatorial optimization (traveling salesman) problems

neural networks

pre-biotic evolution

E. MISCELLANY

1. Units and fundamental constants

$$N = 6.022 \times 10^{23} \text{ mol}^{-1}$$

$$g = 2.0023$$

$$k = 1.3807 \times 10^{-23} \text{ J/K}$$

$$\mu_B = 9.274 \times 10^{-24} \text{ J/T}$$

$$N\mu_B^2/k = 0.375 \text{ emu K/mol}$$

$$g\mu_B/k = 1.3449 \text{ K/T}$$

$$G = g^{1/2} \text{ cm}^{-1/2} \text{ s}^{-1}$$

$$T = 10^4 \text{ G}$$

$$T^2 = 10 \text{ J/emu}$$

2. Saturation behavior of S-only paramagnets

$$M = M_{\text{sat}} B_S(g\mu_B H/kT)$$

$$B_S(x) = (1/S)((S + 1/2)x \coth(S + 1/2)x - (x/2) \coth(x/2))$$

$$M_{\text{sat}} = Ng\mu_B S = 11.18245 \text{ S J/mol}\cdot\text{T} = 1.118245 \times 10^4 \text{ S emu}\cdot\text{G/mol}$$

3. Curie Law for paramagnets

$$M = C H$$

$$T = C = \frac{Ng^2\mu_B^2 S(S+1)}{3k} = 0.125g^2S(S+1) \text{ emu}\cdot\text{K/mol}$$

$$\mu_{\text{eff}} = (g^2S(S+1))^{1/2} = (8 T)^{1/2}$$

4. Relation between saturation and Curie behaviors

$$\frac{C(\text{emu}\cdot\text{K})}{M_{\text{sat}}(\text{emu}\cdot\text{G})} = \frac{Ng^2\mu_B^2 S(S+1)}{3kNg\mu_B S} = \frac{g\mu_B(S+1)}{3k} =$$

$$\frac{2.0023\cdot 9.274 \times 10^{-28} \text{ J/G}}{3\cdot 1.3807 \times 10^{-23} \text{ J/K}} (S+1) = 4.4831 \times 10^{-5} \frac{\text{K}}{\text{G}} (S+1)$$

F. MAGNETIC DIMERS – THE HEISENBERG-DIRAC-VAN VLECK HAMILTONIAN

1. Introduction

In section C.2 we examined primary magnetochemistry relationships for paramagnets – species with **non-interacting** spins. The magnetic properties of such materials can be described by the Curie-Weiss law (for small values of H/T), or more generally by:

$$M = Ng\mu_B SB_S$$

However, in the next simplest case – a molecule with two **exchange-coupled** unpaired electrons – the magnetic properties cannot usually be described by this relation except at very low temperatures. This will be the case when the exchange coupling creates thermally accessible states of different spin multiplicity. Such is the case for most organic biradicals.

The Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian, eq 1, is an empirical operator that models interaction (coupling) of unpaired electrons. The form of the Hamiltonian suggests that coupling arises through interaction of spin angular momentum operators. The magnitude of the interaction depends on the interaction parameter, J_{ij} (called the exchange parameter). The J_{ij} term embodies all of the interactions that determine the ground state spin preference. The product of spin operators is a reasonable component since interaction of species containing unpaired electrons results in either a decrease (antiferromagnetic coupling) or increase (ferromagnetic coupling) in spin angular momentum. For example, two doublets can couple to yield a singlet and a triplet, the relative energies of which depend on J_{ij} . By definition, for ferromagnetic (high-spin) coupling $J_{ij} > 0$, while for antiferromagnetic coupling, $J_{ij} < 0$.

$$\hat{H}_{ij} = -2J_{ij}\hat{S}_i\hat{S}_j \quad (1)$$

The product of spin angular momentum operators may be expressed in terms of component and product (total) spin angular momentum operators,

$$\hat{S}_{\text{Tot}}^2 = \hat{S}_i + \hat{S}_j \quad ^2 = \hat{S}_i^2 + \hat{S}_j^2 + 2\hat{S}_i\hat{S}_j \quad (2)$$

$$\text{therefore, } \hat{S}_i\hat{S}_j = \frac{1}{2} \hat{S}_{\text{Tot}}^2 - \hat{S}_i^2 - \hat{S}_j^2 \quad (3)$$

Since the eigenvalue of \hat{S}^2 is $S(S+1)$, the energy of the state with spin S_{Tot} resulting from interaction of species with spins S_i and S_j is given by,

$$E_{\text{Tot}} = -J_{ij} \left[S_{\text{Tot}} (S_{\text{Tot}} + 1) - S_i (S_i + 1) - S_j (S_j + 1) \right] \quad (4)$$

Thus for two doublets ($2 \times$ multiplicity $2 = 4$ states), coupling results in a triplet and a singlet (multiplicity 3 and multiplicity 1 = 4 states). In the case of ferromagnetic coupling ($J > 0$), the energy of the triplet state ($S = 1$) is,

$$E_{\text{T}} = -J \left[1(1 + 1) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right] = -J \left[2 - \frac{3}{4} - \frac{3}{4} \right] = -\frac{J}{2} \quad (6)$$

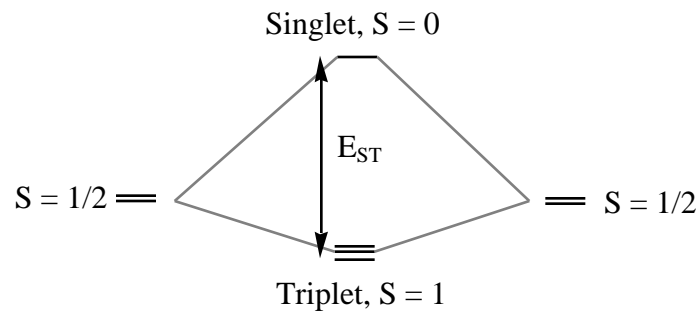
The energy of the singlet state ($S = 0$) is,

$$E_{\text{S}} = -J \left[0(0 + 1) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) - \frac{1}{2} \left(\frac{1}{2} + 1 \right) \right] = -J \left[0 - \frac{3}{4} - \frac{3}{4} \right] = \frac{3J}{2} \quad (7)$$

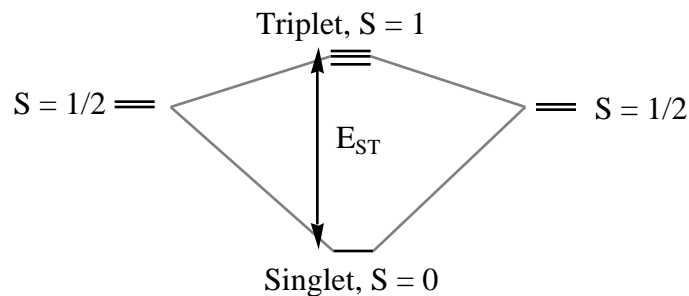
The singlet triplet gap, E_{ST} , is given by,

$$E_{\text{ST}} = E_{\text{S}} - E_{\text{T}} = \frac{3J}{2} - \left(-\frac{J}{2} \right) = 2J \quad (8)$$

The energy level diagram for ferromagnetic coupling is shown below.



The energy level diagram for antiferromagnetic coupling is shown below.



Note that by definition of the Hamiltonian, $J < 0$ describes antiferromagnetic coupling and $J > 0$. Had we defined the Hamiltonian as $\hat{H}_{ij} = 2J_{ij} \hat{S}_i \hat{S}_j$, then $J < 0$ would be for ferromagnetically coupled spins. Therefore, when reading the literature, always note the form of the Hamiltonian to be sure of the nature of the type of exchange coupling.

2. Measuring J by Electron Paramagnetic Resonance Spectroscopy

The intensity of the EPR signal is directly proportional to the paramagnetism which can be given by the Curie Law,

$$I_{\text{EPR}} = \frac{C}{T} \quad (9)$$

Although the paramagnetism of the triplet follows the Curie Law, the concentration of triplet is temperature dependent and is given by the Boltzmann distribution,

$$\frac{n_T}{n_T + n_S} = [\text{TRIPLET}]_{\text{rel}} = \frac{3 \exp \frac{-T}{RT}}{3 \exp \frac{-T}{RT} + \exp \frac{-S}{RT}} \quad (10)$$

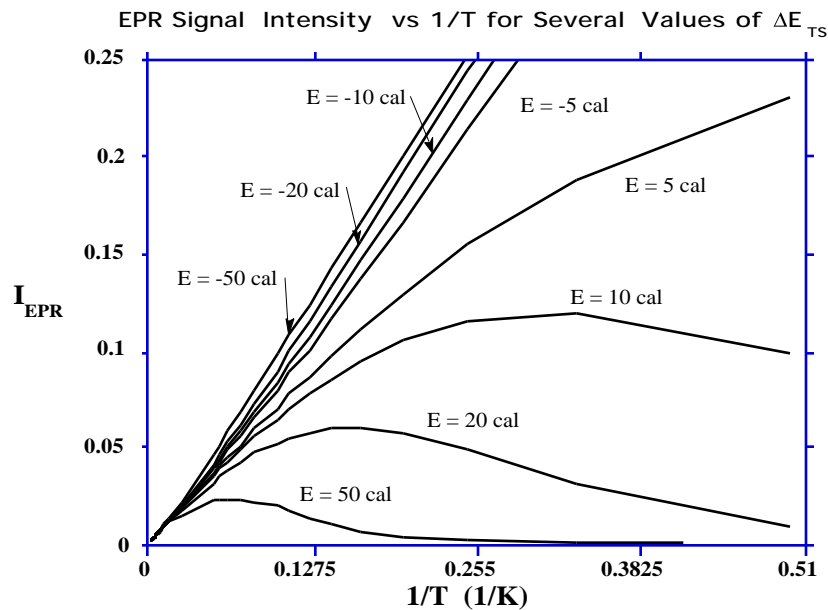
Multiplication of the numerator and denominator by $\exp \frac{S}{RT}$, and letting $T - S = E_{ST}$ gives,

$$[\text{TRIPLET}]_{\text{rel}} = \frac{3 \exp \frac{-E_{ST}}{RT}}{1 + 3 \exp \frac{-E_{ST}}{RT}} \quad (11)$$

Thus, the EPR signal intensity is given by,

$$I_{\text{EPR}} = \frac{C}{T} [\text{TRIPLET}]_{\text{rel}} = \frac{C}{T} \frac{3 \exp \frac{-E_{ST}}{RT}}{1 + 3 \exp \frac{-E_{ST}}{RT}} \quad (12)$$

A plot of EPR signal intensity versus $1/T$ for different singlet-triplet gaps is shown below. Note that very little change in the slope of the plot occurs as the triplet becomes more stable.



3. Measuring J by Magnetometry¹

Van Vleck derived a general equation for calculating paramagnetic susceptibility as a function of temperature.² Use of the equation requires knowledge of the energy levels, which we calculate with the HDVV Hamiltonian (see previous section). Van Vleck began the

derivation by letting the energy levels of the system be developed as a power series expansion in the applied field.

$$E_n = E_n^0 + HE_n^{(1)} + H^2 E_n^{(2)} + H^3 E_n^{(3)} + \dots \quad (13)$$

The term which is independent of H is the zero-order term (and has units of J, the exchange parameter), while the term linear in H is the first-order Zeeman term, and the term that scales as H^2 is the second-order Zeeman term, and so on. Neglecting Zero-field splitting, and assuming isotropic g, the total magnetic moment, M, for the system is:

$$M = N \frac{\sum_n \mu_n \exp\left(-E_n/k_B T\right)}{\sum_n \exp\left(-E_n/k_B T\right)} \quad (14)$$

Where μ_n is the magnetic moment of state n ($\mu_n = -E_n/H$). Now,

$$\exp\left(-E_n/k_B T\right) = \exp\left(\frac{-\left(E_n^0 + HE_n^{(1)} + H^2 E_n^{(2)} + \dots\right)}{k_B T}\right) = \exp\left(-E_n^0/k_B T\right) \exp\left(-HE_n^{(1)}/k_B T\right) \dots \quad (15)$$

Ignoring H^2 and higher-order exponentials, and recalling that for small x,

$$\exp(-x) \approx 1 - x$$

Then,

$$\exp\left(-E_n/k_B T\right) = \exp\left(-E_n^0/k_B T\right) \exp\left(-HE_n^{(1)}/k_B T\right) \dots \approx \left(1 - \frac{HE_n^{(1)}}{k_B T}\right) \exp\left(-E_n^0/k_B T\right) \quad (16)$$

(This assumes that first-order Zeeman splitting is much smaller than exchange coupling.) and,

$$\mu_n = -\frac{E_n}{H} = -E_n^{(1)} - 2HE_n^{(2)} + \dots \quad (17)$$

From the approximation and substitution we obtain,

$$M = N \frac{\sum_n \left(-E_n^{(1)} - 2HE_n^{(2)}\right) \left(1 - \frac{HE_n^{(1)}}{k_B T}\right) \exp\left(-E_n^0/k_B T\right)}{\sum_n \left(1 - \frac{HE_n^{(1)}}{k_B T}\right) \exp\left(-E_n^0/k_B T\right)} \quad (18)$$

If we limit the derivation to paramagnetic substances, such that $M=0$ at $H=0$, then

$$\sum_n -E_n^{(1)} \exp\left(-E_n^0/k_B T\right) = 0 \quad (19)$$

Retaining only terms linear in H, and ignoring second-order energy terms, we obtain,

$$M = NH_n \frac{\left(E_n^{(1)}\right)^2}{k_B T} \exp \left(-E_n^0 / k_B T\right)}{\exp \left(-E_n^0 / k_B T\right)} \quad (20)$$

Since $\chi = M/H$, then

$$\chi = N_n \frac{\left(E_n^{(1)}\right)^2}{k_B T} \exp \left(-E_n^0 / k_B T\right)}{\exp \left(-E_n^0 / k_B T\right)} \quad (21)$$

Recall that,

$$E_n^{(1)} = m_s g \mu_B \quad \text{and} \quad m_s^2 = \frac{1}{3} S(S+1)(2S+1) \quad (22)$$

and adding degeneracy terms gives,

$$\chi = \frac{N g^2 \mu_B^2}{3 k_B T} \frac{S(S+1)(2S+1) \exp \left(-E_S / k_B T\right)}{(2S+1) \exp \left(-E_S / k_B T\right)} \quad (23)$$

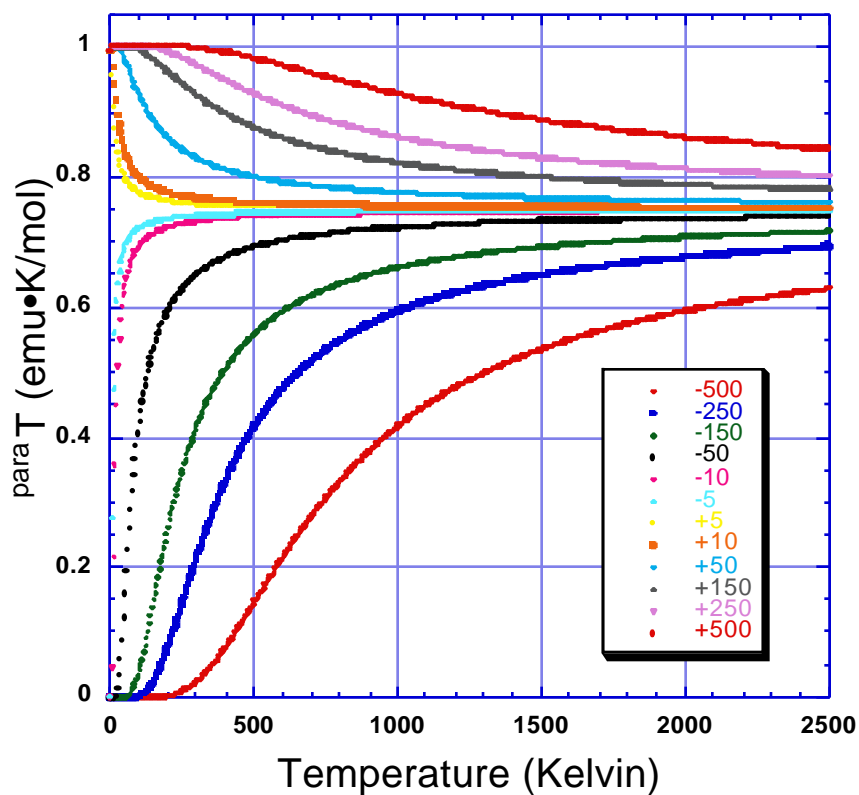
Plugging in the constants gives,

$$\chi = \frac{0.125 g^2 \text{emuK} / \text{mol}}{T} \frac{S(S+1)(2S+1) \exp \left(-E_S / k_B T\right)}{(2S+1) \exp \left(-E_S / k_B T\right)} \quad (24)$$

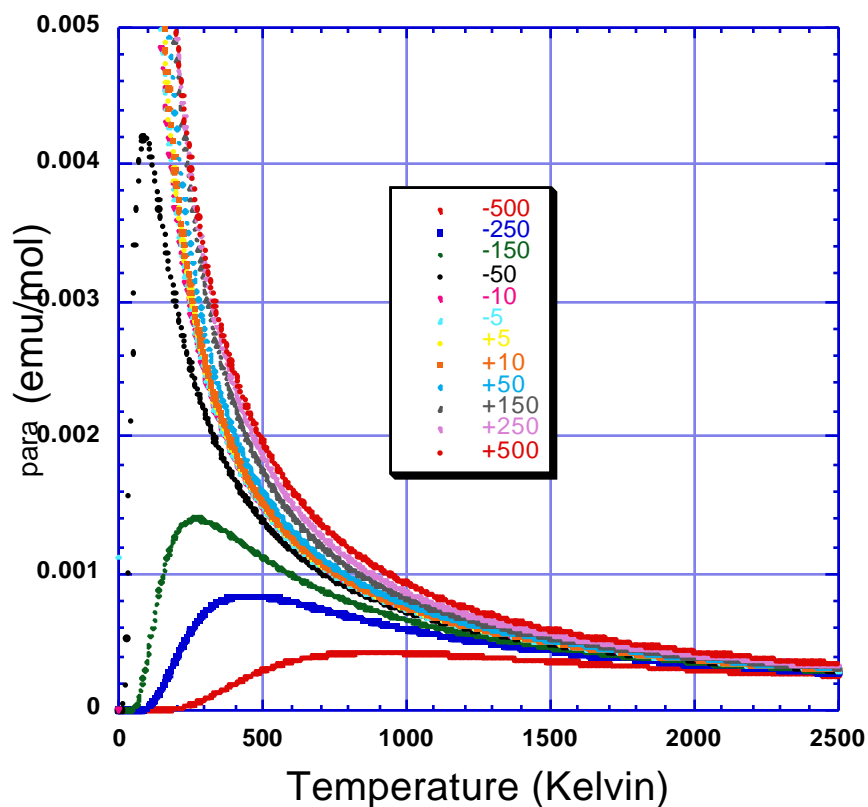
Where E_S is the energy of the exchange-coupled spin states determined using the HDVV Hamiltonian. The energies of the states (in units of J) are relative to the lowest state, which is taken as zero. The denominator can be modified according to the Curie-Weiss law to give:

$$\chi = \frac{0.125 g^2 \text{emuK} / \text{mol}}{(T - \theta)} \frac{S(S+1)(2S+1) \exp \left(-E_S / k_B T\right)}{(2S+1) \exp \left(-E_S / k_B T\right)} \quad (25)$$

Below are plots of χT vs T for $\theta = -0.01 \text{ K}$ and $-500 \text{ cm}^{-1} < J < +500 \text{ cm}^{-1}$.



Below are plots of χ vs T for $\theta = -0.01$ K and $-500 \text{ cm}^{-1} \leq J \leq +500 \text{ cm}^{-1}$. Note that for ferromagnetic coupling, χ increases asymptotically as the temperature is lowered, while for antiferromagnetic coupling, χ exhibits a maximum at T_{max} .



The exchange coupling parameter is related to T_{\max} by:

$$|J| = 0.8 kT_{\max} \quad (26)$$

Thus, a maximum in the plot of χ vs. T is the signature of antiferromagnetic coupling.

References

- 1)Kahn, O. *Molecular Magnetism*; VCH: New York, 1993.
- 2)Van Vleck, J. H. *The Theory of Electric and Magnetic Susceptibilities*; Oxford University Press: Oxford, 1932.