

10. Magnetism [Kittel ch 14, 15]

3 sources: all quantum mechanical.

- i) electron spin
- ii) electron orbital angular momentum.
- iii) change induced by applied field.

Susceptibility, $\chi = \frac{\mu_0 M}{B} = \frac{\text{magnetisation}}{\text{applied field}}$

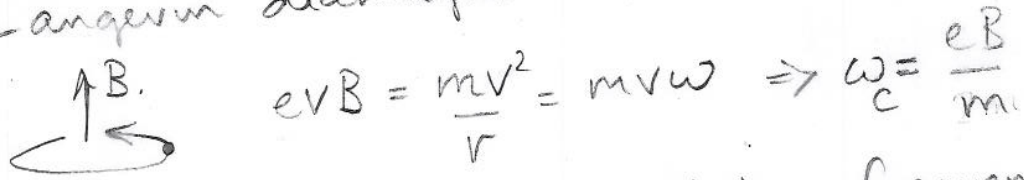
$[\chi = M/H]$
 $[B = \mu_0 H]$

[can be per mole, unit mass, volume etc]

- $\chi > 0$ Paramagnetism
- $\chi < 0$ Diamagnetism

Diamagnetic material is magnetised in the direction opposing the applied field.

10.1 Larmor diamagnetism



$$e v B = \frac{m v^2}{r} = m v \omega \Rightarrow \omega = \frac{e B}{m}$$

classical picture gives cyclotron frequency of free electron. Lenz law: induced current opposes.

In an atom, Larmor theorem says all electrons experience addition precession at $\omega_L = eB/2m$.
[notes have elem. argument / Kittel uses vector potential]
Current loop of radius ρ : Z electrons / atom

Magnetic moment, $\mu = I A = I \pi \rho^2 = \frac{-Ze}{2\pi} \omega_L \pi \rho^2$

Spherical orbital $\langle \rho^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle$
 $\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle$

$\mu = -\frac{Ze^2 B}{4m} \frac{2}{3} \langle r^2 \rangle$ $M = N \mu$ for N atoms.

$\chi = \frac{\mu_0 M}{B} = -\frac{\mu_0 N Z e^2}{6m} \langle r^2 \rangle$ Larmor formula.

10.2 Paramagnetism.

An unpaired electron has S & L contributions which strongly override the diamagnetism of all the other (paired) electrons in the atom.

Quantum origin, associated with the total angular momentum, $\hbar \vec{J}$, sum of $\hbar \vec{L}$ and $\hbar \vec{S}$.

$$\text{moment } \vec{\mu} = \gamma \hbar \vec{J} = -g \mu_B \vec{J}$$

γ = gyromagnetic ratio.

g = Landé g-factor

$$\mu_B = \text{Bohr magneton} = \frac{e\hbar}{2m} = \text{unit of moment}$$

$$g = 2.0023 \rightarrow 2.00 \text{ for a single electron.}$$

$$= 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \text{ for an atom.}$$

where J (total), L (orbital) and S (spin) angular momenta come from Hund's rules (below).

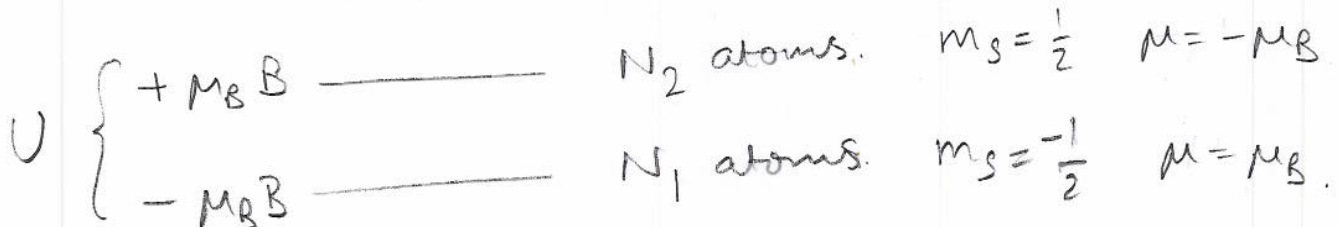
$$\text{Energy levels, } U = -\vec{\mu} \cdot \vec{B}$$

$$= m_J g \mu_B B$$

where $m_J = -J, -J+1, \dots, J$ is the quantum number for the component of J along B

In thermal equilibrium at temperature T , these states will follow a Boltzmann distribution. We consider only the case of a single spin: $J=S$

$$m_J = \pm \frac{1}{2}, g=2, U = \pm \mu_B B. \quad (2 \text{ states})$$



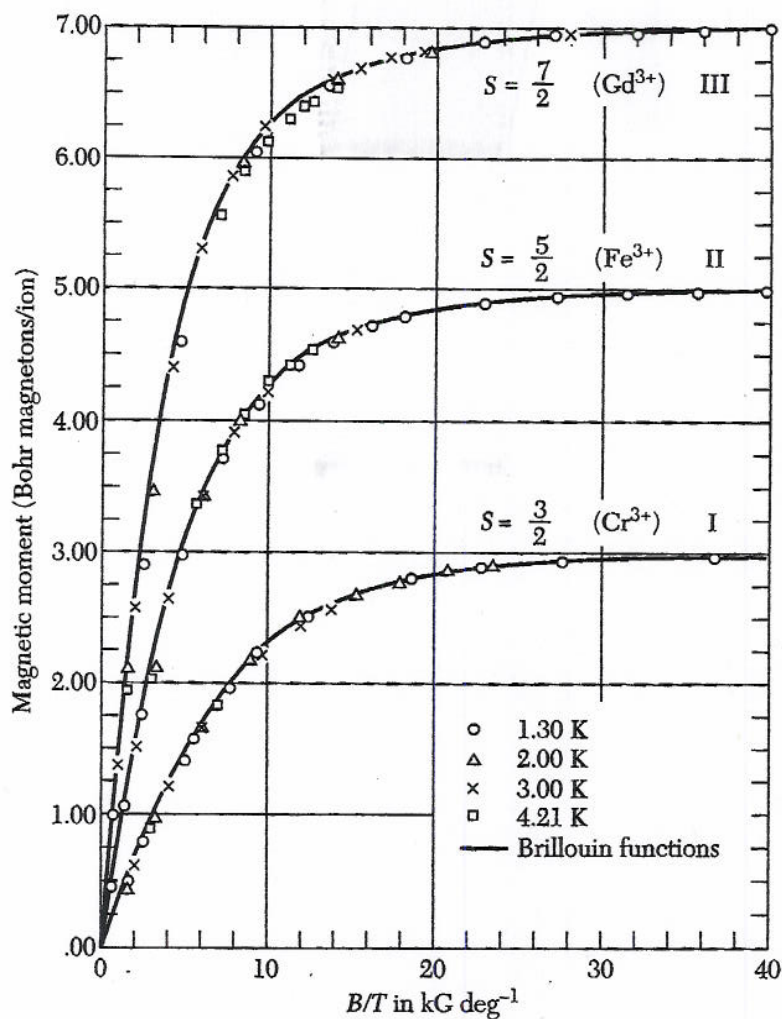


Figure 4 Plot of magnetic moment versus B/T for spherical samples of (I) potassium chromium alum, (II) ferric ammonium alum, and (III) gadolinium sulfate octahydrate. Over 99.5% magnetic saturation is achieved at 1.3 K and about 50,000 gauss (5T). After W. E. Henry.

where the **Brillouin function** B_J is defined by

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh} \left(\frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \operatorname{ctnh} \left(\frac{x}{2J} \right). \quad (20)$$

Boltzmann factors: $x = \mu_B B / k_B T$

$$\frac{N_1}{N} = \frac{e^{+\mu_B B / k_B T}}{(e^{+\mu_B B / k_B T} + e^{-\mu_B B / k_B T})} \quad \frac{N_2}{N} = \frac{e^{-x}}{(e^x + e^{-x})}$$

Projection of moment for N_2 is $-\mu_B$, N_1 is μ_B

$$\Rightarrow M = (N_1 - N_2) \mu_B$$

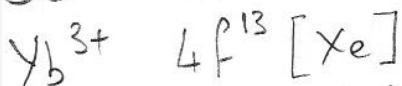
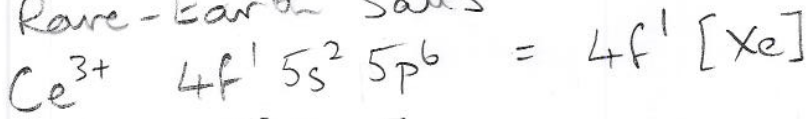
$$= N \mu_B \frac{e^x - e^{-x}}{e^x + e^{-x}} = N \mu_B \tanh \frac{\mu_B B}{k_B T}$$

Low field limit, $x \ll 1$ $\tanh x = x$

$$M = N \frac{\mu_B^2 B}{k_B T} \Rightarrow \chi = \frac{\mu_0 M}{B} = \mu_0 N \frac{\mu_B^2}{k_B T} = \frac{C}{T}$$

This is Curie's law with $C =$ Curie constant.
 [see notes] General case: $\mu_B \rightarrow \frac{1}{3} p^2 \mu_B^2$ where $p = g [J(J+1)]^{1/2}$
 and the tanh function becomes the Brillouin funct.
 [check $J = S = 1/2$]

10.3 Rare-Earth Salts



As the f-shell fills up, the electrons follow Hund's rules to separate electrons optimally:

H I: maximum S allowed by Pauli ex. princ.
so one parallel spin in every f state

H II: maximum L, consistent with H I

H III: $J = |L - S|$ less than half full
 $J = L + S$ more " " " "

Agreement for $p = g [J(J+1)]^{1/2}$

is excellent for rare-earth trivalent ions
[table]

Table 1 Effective magneton numbers p for trivalent lanthanide group ions

(Near room temperature)

Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{exp}),$ approximate
Ce ³⁺	4f ¹ 5s ² p ⁶	² F _{5/2}	2.54	2.4
Pr ³⁺	4f ² 5s ² p ⁶	³ H ₄	3.58	3.5
Nd ³⁺	4f ³ 5s ² p ⁶	⁴ I _{9/2}	3.62	3.5
Pm ³⁺	4f ⁴ 5s ² p ⁶	⁵ I ₄	2.68	—
Sm ³⁺	4f ⁵ 5s ² p ⁶	⁶ H _{5/2}	0.84	1.5
Eu ³⁺	4f ⁶ 5s ² p ⁶	⁷ F ₀	0	3.4
Gd ³⁺	4f ⁷ 5s ² p ⁶	⁸ S _{7/2}	7.94	8.0
Tb ³⁺	4f ⁸ 5s ² p ⁶	⁷ F ₆	9.72	9.5
Dy ³⁺	4f ⁹ 5s ² p ⁶	⁶ H _{15/2}	10.63	10.6
Ho ³⁺	4f ¹⁰ 5s ² p ⁶	⁵ I ₈	10.60	10.4
Er ³⁺	4f ¹¹ 5s ² p ⁶	⁴ I _{15/2}	9.59	9.5
Tm ³⁺	4f ¹² 5s ² p ⁶	³ H ₆	7.57	7.3
Yb ³⁺	4f ¹³ 5s ² p ⁶	² F _{7/2}	4.54	4.5

Table 2 Effective magneton numbers for iron group ions

Ion	Configuration	Basic level	$p(\text{calc}) = g[J(J+1)]^{1/2}$	$p(\text{calc}) = 2[S(S+1)]^{1/2}$	$p(\text{exp})^a$
Ti ³⁺ , V ⁴⁺	3d ¹	² D _{3/2}	1.55	1.73	1.8
V ³⁺	3d ²	³ F ₂	1.63	2.83	2.8
Cr ³⁺ , V ²⁺	3d ³	⁴ F _{3/2}	0.77	3.87	3.8
Mn ³⁺ , Cr ²⁺	3d ⁴	⁵ D ₀	0	4.90	4.9
Fe ³⁺ , Mn ²⁺	3d ⁵	⁶ S _{5/2}	5.92	5.92	5.9
Fe ²⁺	3d ⁶	⁵ D ₄	6.70	4.90	5.4
Co ²⁺	3d ⁷	⁴ F _{9/2}	6.63	3.87	4.8
Ni ²⁺	3d ⁸	³ F ₄	5.59	2.83	3.2
Cu ²⁺	3d ⁹	² D _{5/2}	3.55	1.73	1.9

^aRepresentative values.

10.4 Transition Metals

The rule does not work well for the "iron groups" ions in their salts [table]

Explained instead by $P = g[S(S+1)]^{1/2}$ rule.

Orbital momentum turned off or "Quenched"

Effect discovered by Kittel in 1950's:

Due to electrostatic "crystal field splitting" of d-orbitals, no longer degenerate in energy.

Prevents orbital momentum reacting to the applied field.

19.03.07 II

10.5 Ferromagnetism.

Now introduce the crystal

Spins can now interact with each other.

Weak dipole-dipole interaction, but

Much stronger Q.M. exchange interaction.

Similar to tight-binding: overlap of wavefuns.

Depending on symmetry of wavefuncts:

-ve U for ↑↑ neighbours → ferromagnet

-ve U for ↑↓ " → antiferromagnet

Weiss effective field, due to neighbours,

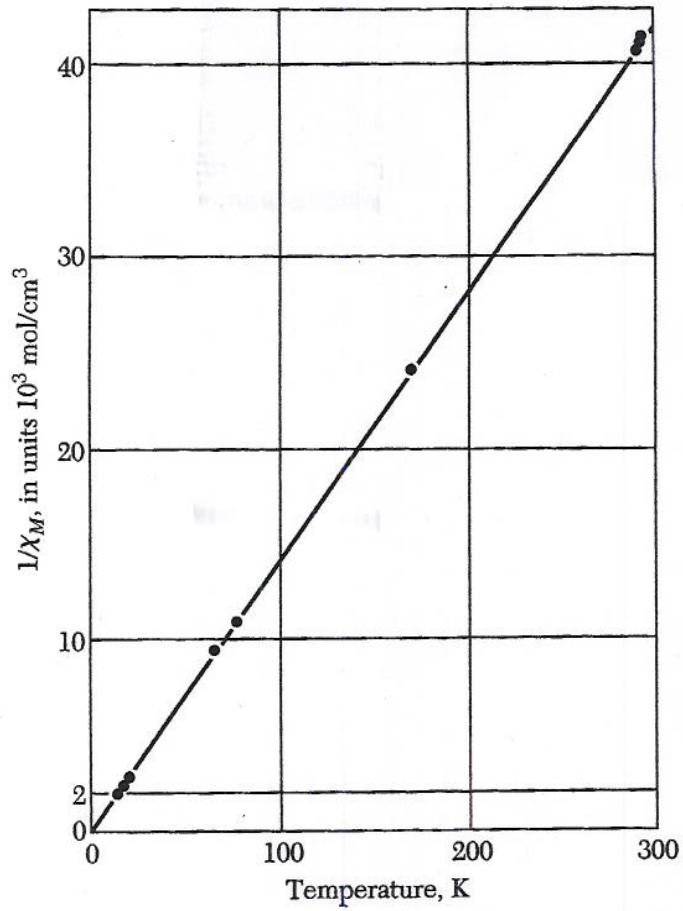
in mean field approximation of magnetisation

$$\vec{B}_E = \lambda \vec{M}$$

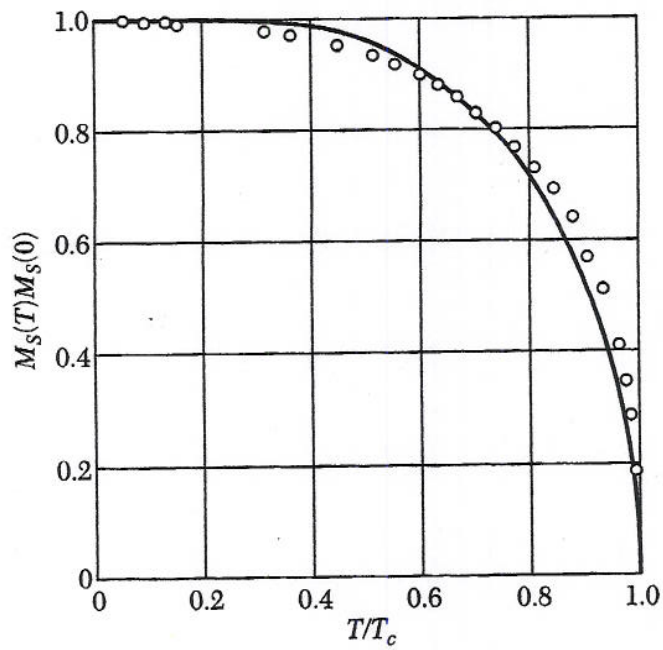
↑ property of crystal, indep of T.

Tendency to order is opposed by thermal excitation at $T > T_c$

$T_c =$ Curie temperature { ordered below
disordered above



Plot of $1/\chi$ vs T for a gadolinium salt, $\text{Gd}(\text{C}_2\text{H}_3\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$. The str
 . (After L. C. Jackson and H. Kamerlingh Onnes.)



ion magnetization of nickel as a function of temperature, to
 r $S = \frac{1}{2}$ on the mean field theory. Experimental values by P. We:

If $\chi_p > 0$ is the paramagnetic susceptibility of a free atom.

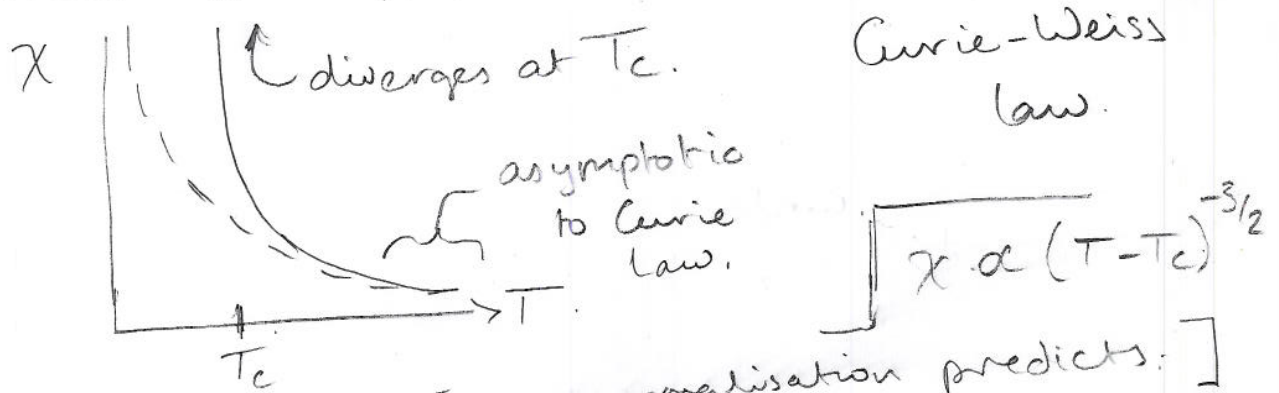
$\chi_p = \frac{C}{T}$ Curie law

$\mu_0 M = \chi_p (B + B_E) = \frac{C}{T} (B + \lambda M)$
↑ Applied field

$\Rightarrow (\mu_0 T - C\lambda) M = CB$

So $\chi_{\text{effective}} = \frac{\mu_0 M}{B} = \frac{\mu_0 C}{\mu_0 T - C\lambda} = \frac{C}{T - T_c}$

where $T_c = C\lambda/\mu_0$ is the Curie temperature.



[Very close to $T = T_c$, renormalisation predicts.]

10.6 Behaviour when $T < T_c$.

Still in mean-field approximation. The divergence is unphysical, but this is because we used the approximate form for χ_p .

Instead, for $S = 1/2$ we had:

$M = N\mu_B \tanh(\mu_B B/k_B T)$

For $T = T_c$, this can give a spontaneous M even when no field is applied:

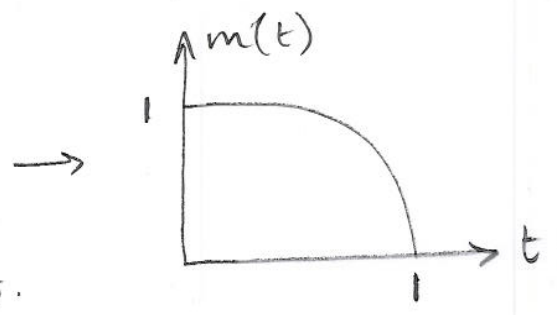
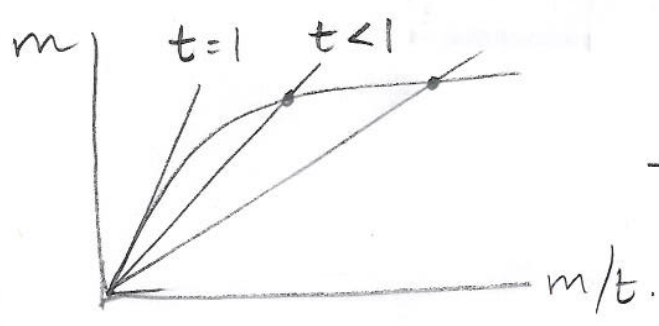
Keeping $B_E = \lambda M$:

$M = N\mu_B \tanh(\mu_B \lambda M/k_B T)$

implicit equation for $M(T)$.

Solve Graphically:
 where $m = M / N\mu_B$

$m = \tanh m/t$
 $t = k_B T / N\mu_B^2 \lambda$



Critical temperature, $t=1$

$$T_c = \frac{N\mu_B^2 \lambda}{k_B}$$

Evaluate shape of $m(t)$ near $t=1 - \Delta t$

$$m = \tanh \frac{m}{t} \approx \frac{m}{t} - \frac{1}{3} \left(\frac{m}{t} \right)^3$$

$$\Rightarrow \frac{3t^2(1-t)}{1 - \Delta t} \approx m^2 \Rightarrow m = (3\Delta t)^{1/2}$$

Square-root dependence is characteristic of mean-field theory.

10.7 "Critical exponents" are an important property of phase transitions, Nobel Prize in 1980's.

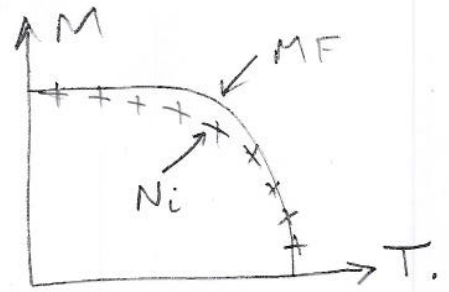
$$\left. \begin{aligned} \chi &\propto \frac{1}{(T-T_c)^\gamma} \quad T > T_c \\ M &\propto (T-T_c)^\beta \quad T < T_c \end{aligned} \right\} \begin{aligned} \gamma &= 1 \text{ for mean field} \\ \beta &= 1/2 \end{aligned}$$

	$T_c (K)$	γ	β
Fe	1043	1.33	0.34
Co	1388	1.21	-
Ni	627	1.35	0.42
MF		1	1/2
RG		4/3	1/3

depends on lattice

10.8 Spin Waves "Magnons"

Significant deviation from mean field theory at low temperature.



Explain as magnetic wave excitations, exactly analogous to phonons.

→ "magnons"

Measure by inelastic neutron scattering, with spin polarization if needed.

Neutrons see nuclear spin, coupled to electrons.

Different dispersion $\omega \propto k^2$ phonon
 $\omega \propto k$ acoustic phonon

Can show $\Delta M(T) \propto T^{3/2}$ Bloch $T^{3/2}$ law
exact analogy of Debye T^3 law for sp. heat.