

12. Magnetism

Nov. 12, 2018

Magnetism

diamagnetism

paramagnetism

ferromagnetism (Fe, Ni, Co)

ferrimagnetism (Magnet Eisenstein)

antiferromagnetism

$$H = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_A \frac{\hbar^2}{2m_A} \nabla_A^2 - \sum_{i,A} \frac{Z_A e^2}{4\pi\epsilon_0 r_{iA}} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} + \sum_{A<B} \frac{Z_A Z_B e^2}{4\pi\epsilon_0 r_{AB}}$$

Coulomb interactions cause ferromagnetism not magnetic interactions.

Magnetism

$$\vec{B} = \mu_0 (\vec{H} + \vec{M})$$

magnetic induction field \vec{B} magnetic intensity \vec{H} magnetization \vec{M}

$$\vec{M} = \chi \vec{H}$$

χ is the magnetic susceptibility

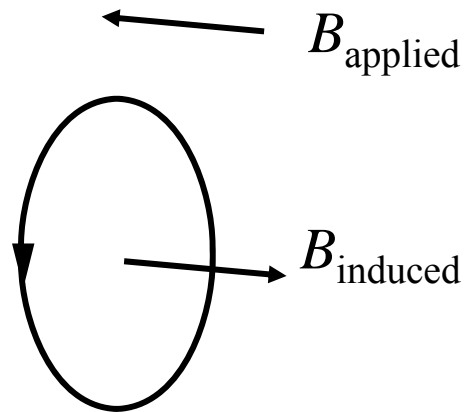
$\chi < 0$ diamagnetic

$\chi > 0$ paramagnetic

χ is typically small (10^{-5}) so $B \approx \mu_0 H$

Diamagnetism

A free electron in a magnetic field will travel in a circle



The magnetic created by the current loop is opposite the applied field.

Diamagnetism

Dissipationless currents are induced in a diamagnet that generate a field that opposes an applied magnetic field.

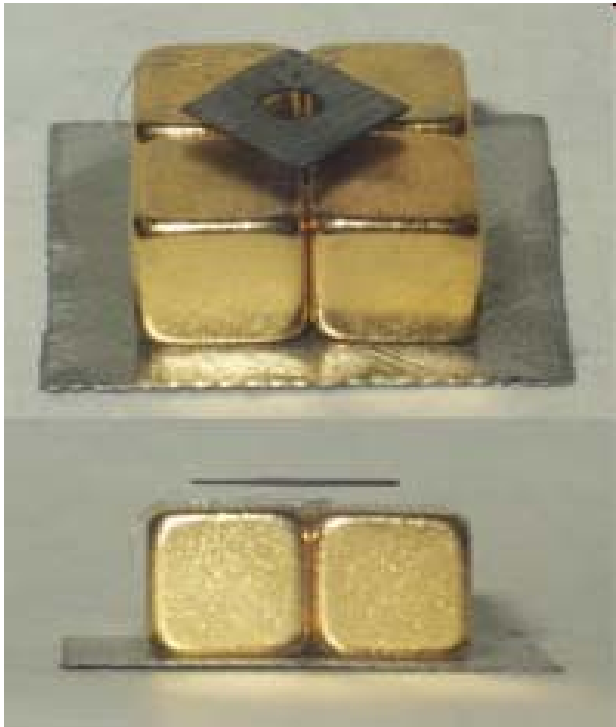
Current flow without dissipation is a quantum effect. There are no lower lying states to scatter into. This creates a current that generates a field that opposes the applied field.

$\chi = -1$ superconductor (perfect diamagnet)

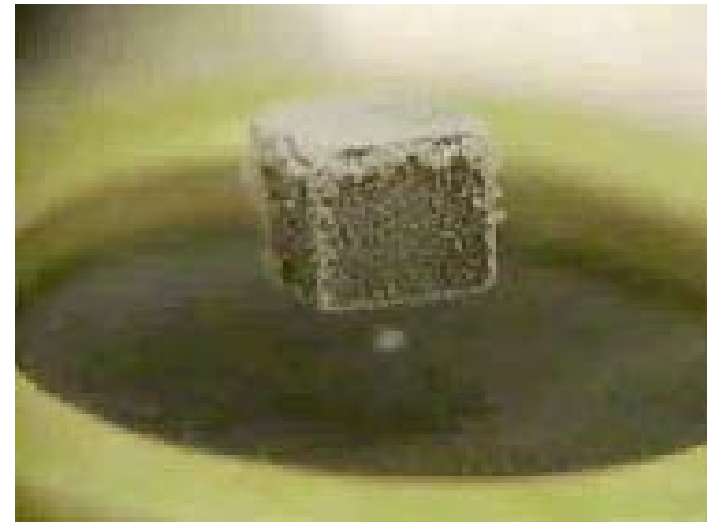
$\chi \sim -10^{-6} - 10^{-5}$ normal materials

Diamagnetism is always present but is often overshadowed by some other magnetic effect.

Levitating diamagnets



Levitating pyrolytic carbon



NOT: Lenz's law

$$V = -\frac{d\Phi}{dt}$$

Levitating frogs

χ for water is -9.05×10^{-6}



16 Tesla magnet at the Nijmegen High Field Magnet Laboratory

<http://www.hfml.ru.nl/froglev.html>

Andre Geim



2000 Ig Nobel Prize for levitating a frog with a magnet



The Nobel Prize in Physics 2010
Andre Geim, Konstantin Novoselov

The Nobel Prize in Physics 2010

Nobel Prize Award Ceremony

Andre Geim



Biographical

Nobel Lecture

Banquet Speech

Interview

Nobel Diploma

Photo Gallery

Other Resources

Konstantin Novoselov

Andre Geim

Born: 1958, Sochi, Russia

Affiliation at the time of the award:
University of Manchester,
Manchester, United Kingdom

Prize motivation: "for groundbreaking experiments regarding the two-dimensional material graphene"



Diamagnetism

A dissipationless current is induced by a magnetic field that opposes the applied field.

$$\vec{M} = \chi \vec{H}$$

Diamagnetic susceptibility

Copper	-9.8×10^{-6}
Diamond	-2.2×10^{-5}
Gold	-3.6×10^{-5}
Lead	-1.7×10^{-5}
Nitrogen	-5.0×10^{-9}
Silicon	-4.2×10^{-6}
water	-9.0×10^{-6}
bismuth	-1.6×10^{-4}

Most stable molecules have a closed shell configuration and are diamagnetic.

Paramagnetism

Materials that have a magnetic moment are paramagnetic.

An applied field aligns the magnetic moments in the material making the field in the material larger than the applied field.

The internal field is zero at zero applied field (random magnetic moments).

$$\vec{M} = \chi \vec{H}$$

Paramagnetic susceptibility

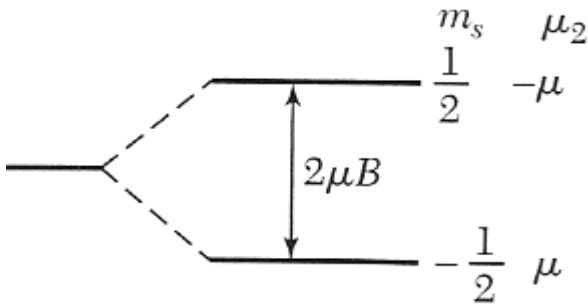
Aluminum	2.3×10^{-5}
Calcium	1.9×10^{-5}
Magnesium	1.2×10^{-5}
Oxygen	2.1×10^{-6}
Platinum	2.9×10^{-4}
Tungsten	6.8×10^{-5}

Boltzmann factors

To take the average value of quantity A

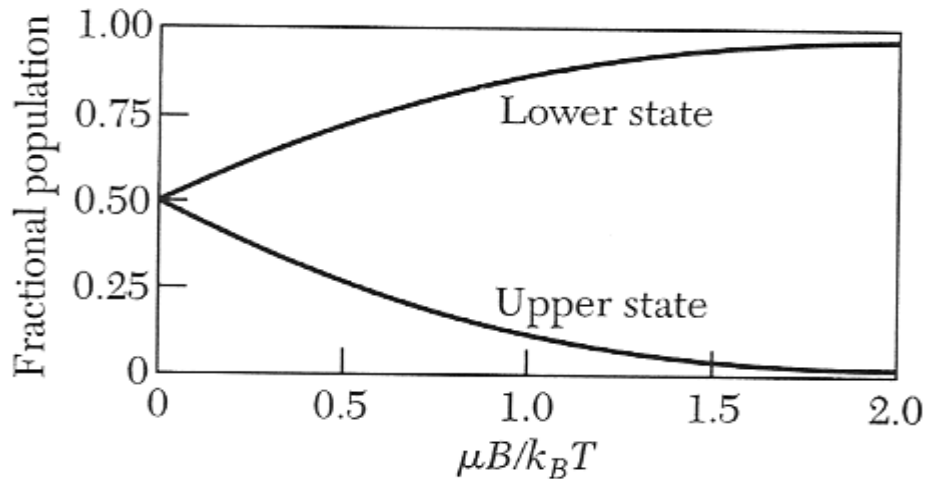
$$\langle A \rangle = \frac{\sum_i A_i e^{-E_i/k_B T}}{\sum_i e^{-E_i/k_B T}}$$

Spin populations



$$\frac{N_1}{N} = \frac{\exp(\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$

$$\frac{N_2}{N} = \frac{\exp(-\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$

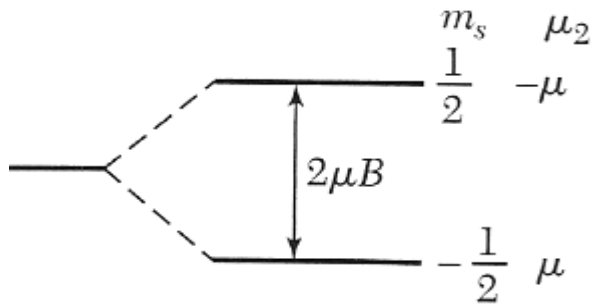


$$M = (N_1 - N_2)\mu$$

$$= N\mu \frac{\exp(\mu B / k_B T) - \exp(-\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$

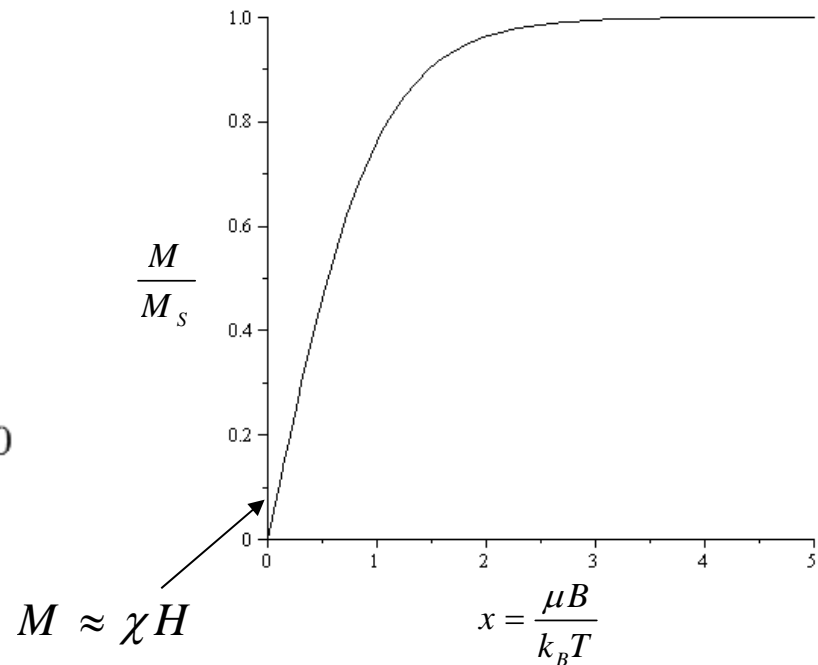
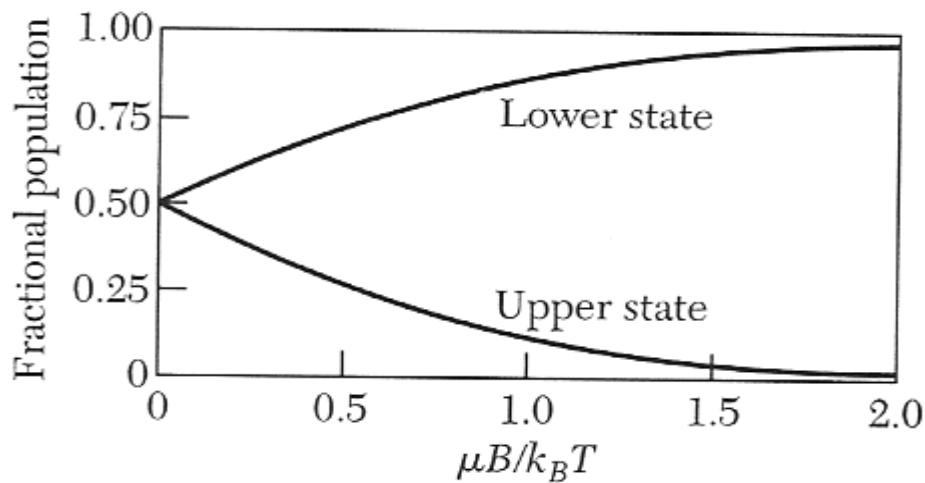
$$= N\mu \tanh\left(\frac{\mu B}{k_B T}\right)$$

Paramagnetism, spin 1/2

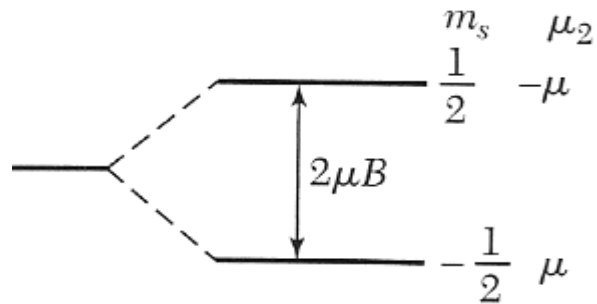


$$M = N\mu \tanh\left(\frac{\mu B}{k_B T}\right) \approx \frac{N\mu^2 B}{k_B T} = \frac{CB}{T}$$

for $\mu B \ll k_B T$ Curie law

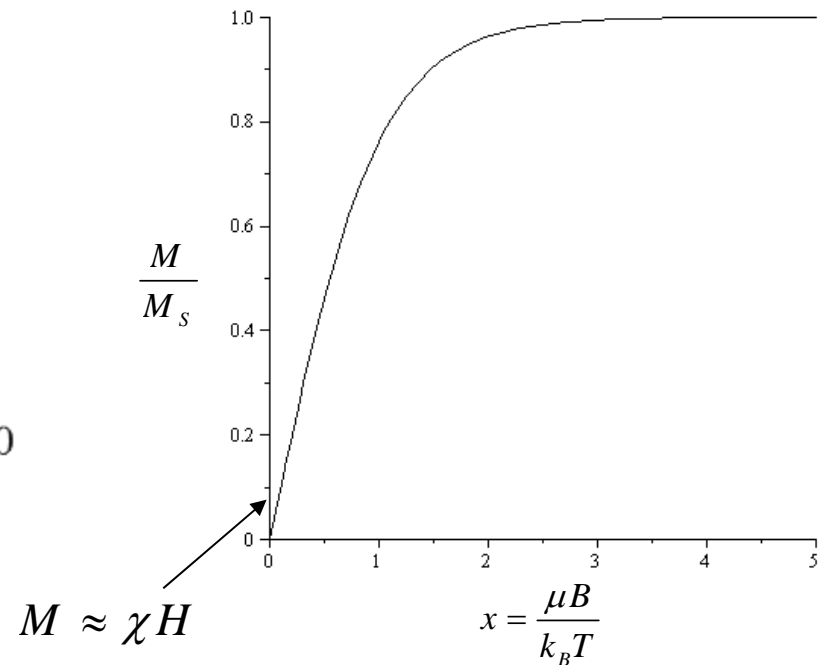
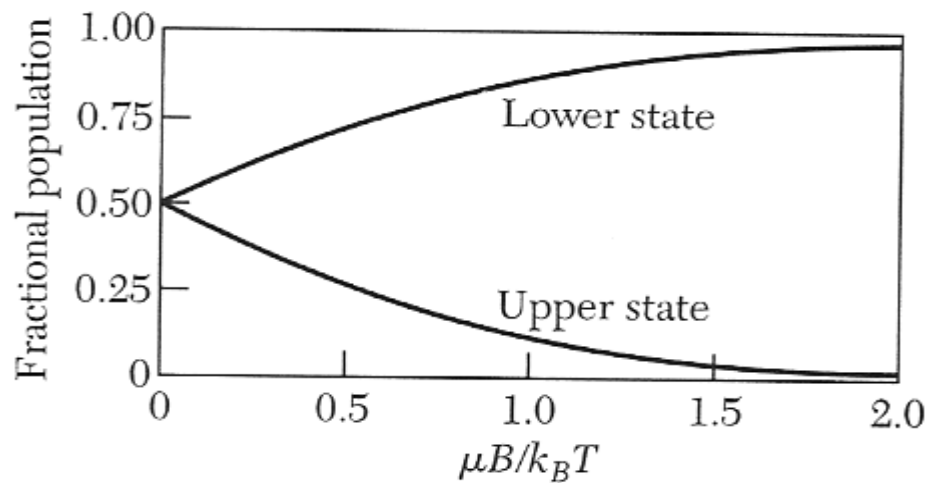


Paramagnetism, spin 1/2



$$M = N\mu \tanh\left(\frac{\mu B}{k_B T}\right) \approx \frac{N\mu^2 B}{k_B T} = \frac{CB}{T}$$

for $\mu B \ll k_B T$ Curie law

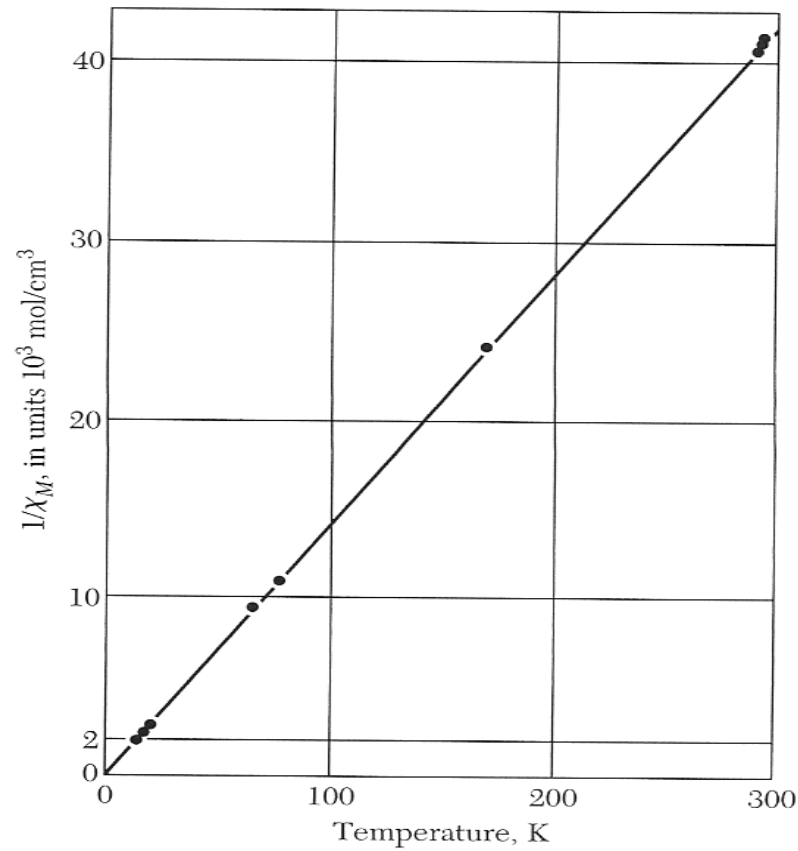


Curie law

for $\mu B \ll k_B T$ $M = CB / T$

$$\chi \propto \left. \frac{dM}{dB} \right|_{B=0} = \frac{C}{T}$$

C is the Curie constant



Hund's rules from atomic physics

Hund calculated the energies of atomic states:

$$\frac{\langle \psi_{Ne3s} | H | \psi_{Ne3s} \rangle}{\langle \psi_{Ne3s} | \psi_{Ne3s} \rangle} < \frac{\langle \psi_{Ne3p} | H | \psi_{Ne3p} \rangle}{\langle \psi_{Ne3p} | \psi_{Ne3p} \rangle} < \frac{\langle \psi_{Ar4s} | H | \psi_{Ar4s} \rangle}{\langle \psi_{Ar4s} | \psi_{Ar4s} \rangle} < \frac{\langle \psi_{Ne3d} | H | \psi_{Ne3d} \rangle}{\langle \psi_{Ne3d} | \psi_{Ne3d} \rangle}$$

H includes $e-e$ interactions

He formulated the following rules:

Electrons fill atomic orbitals following these rules:

1. Maximize the total spin S allowed by the exclusion principle
2. Maximize the orbital angular momentum L
3. $J=|L-S|$ when the shell is less than half full, $J=|L+S|$ when the shell is more than half full.

Atomic physics

In atomic physics, the possible values of the magnetic moment of an atom in the direction of the applied field can only take on certain values.

Total angular momentum

$$J = L + S \quad \text{Orbital } L + \text{ spin } S \text{ angular momentum}$$

Magnetic quantum number

$$m_J = -J, -J + 1, \dots, J - 1, J$$

Allowed values of the magnetic moment in the z direction

$$\mu_z = m_j g_J \mu_B$$

Lande g factor \swarrow \nwarrow Bohr magneton

$$g_J \approx \frac{3}{2} + \frac{S(S + 1) - L(L + 1)}{2J(J + 1)}$$

Brillouin functions

Average value of the magnetic quantum number

$$\langle m_J \rangle = \frac{\sum_{-J}^J m_J e^{-E(m_J)/k_B T}}{\sum_{-J}^J e^{-E(m_J)/k_B T}} = \frac{\sum_{-J}^J m_J e^{-m_J g_J \mu_B B / k_B T}}{\sum_{-J}^J e^{-m_J g_J \mu_B B / k_B T}} = -\frac{1}{Z} \frac{dZ}{dx}$$

Lande g factor $\xrightarrow{\hspace{10em}}$ $x = g_J \mu_B B / k_B T$

Bohr magneton $\xrightarrow{\hspace{10em}}$

$$Z = \sum_{-J}^J e^{-m_J x} = e^{Jx} (1 + e^{-x} + e^{-2x} + \dots) - e^{-(J+1)x} (1 + e^{-x} + e^{-2x} + \dots)$$

$$= \frac{e^{Jx} - e^{-(J+1)x}}{1 - e^{-x}} = \frac{e^{-\frac{x}{2}} e^{(J+\frac{1}{2})x} - e^{-(J+\frac{1}{2})x}}{e^{-\frac{x}{2}} (e^{\frac{x}{2}} - e^{-\frac{x}{2}})} = \frac{\sinh\left((2J+1)\frac{x}{2}\right)}{\sinh\left(\frac{x}{2}\right)}$$

Brillouin functions

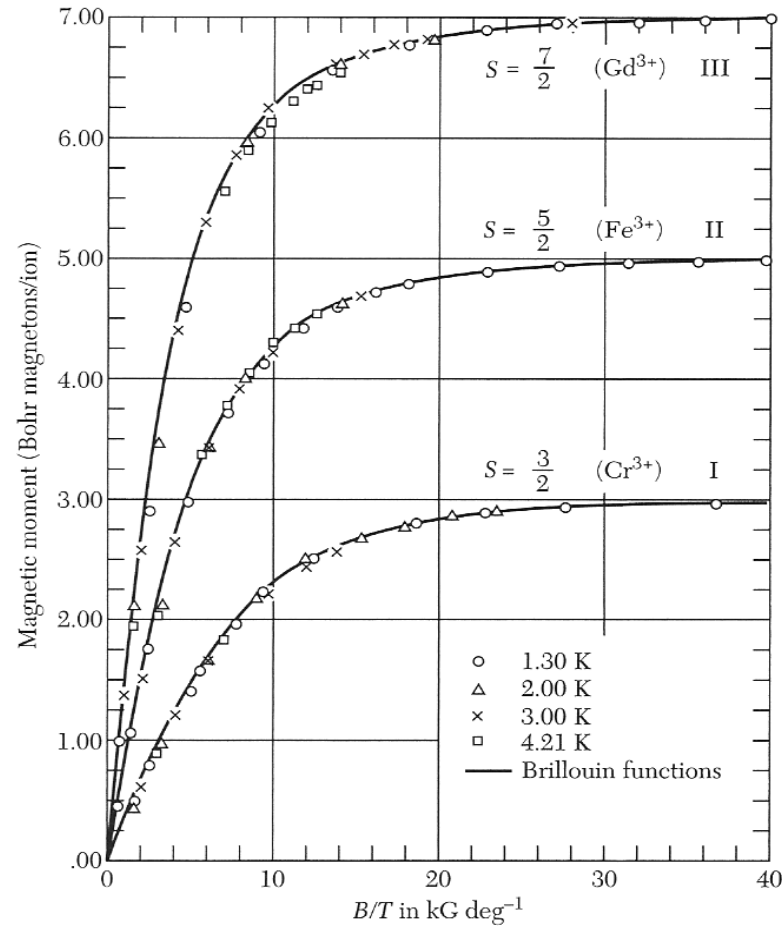
$$Z = \sum_{-J}^J e^{-m_J x} = \frac{\sinh\left(\left(2J+1\right)\frac{x}{2}\right)}{\sinh\left(\frac{x}{2}\right)}$$

$$M = Ng_J \mu_B \langle m_J \rangle = -Ng_J \mu_B \frac{1}{Z} \frac{dZ}{dx}$$

Brillouin function

$$M = Ng \mu_B J \left(\frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} \frac{g \mu_B JB}{k_B T}\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} \frac{g \mu_B JB}{k_B T}\right) \right)$$

Paramagnetism



$$M = Ng\mu_B J \left(\frac{2J+1}{2J} \coth \left(\frac{2J+1}{2J} \frac{g\mu_B JB}{k_B T} \right) - \frac{1}{2J} \coth \left(\frac{1}{2J} \frac{g\mu_B JB}{k_B T} \right) \right)$$

Hund's rules (f - shell)

n	$l_z = 3, 2, 1, 0, -1, -2, -3$	S	$L = \sum l_z $	J
1	↓	1/2	3	5/2
2	↓ ↓	1	5	4
3	↓ ↓ ↓	3/2	6	9/2
4	↓ ↓ ↓ ↓	2	6	4
5	↓ ↓ ↓ ↓ ↓	5/2	5	5/2
6	↓ ↓ ↓ ↓ ↓ ↓	3	3	0
7	↓ ↓ ↓ ↓ ↓ ↓ ↓	7/2	0	7/2
8	↑↑ ↑ ↑ ↑ ↑ ↑	3	3	6
9	↑↑ ↑↑ ↑ ↑ ↑ ↑ ↑	5/2	5	15/2
10	↑↑ ↑↑ ↑↑ ↑ ↑ ↑ ↑ ↑	2	6	8
11	↑↑ ↑↑ ↑↑ ↓ ↓ ↑ ↑ ↑	3/2	6	15/2
12	↑↑ ↑↑ ↑↑ ↓ ↓ ↓ ↑ ↑	1	5	6
13	↑↑ ↑↑ ↓ ↓ ↓ ↓ ↓ ↑	1/2	3	7/2
14	↑↑ ↑↑ ↓ ↓ ↓ ↓ ↓ ↓	0	0	0

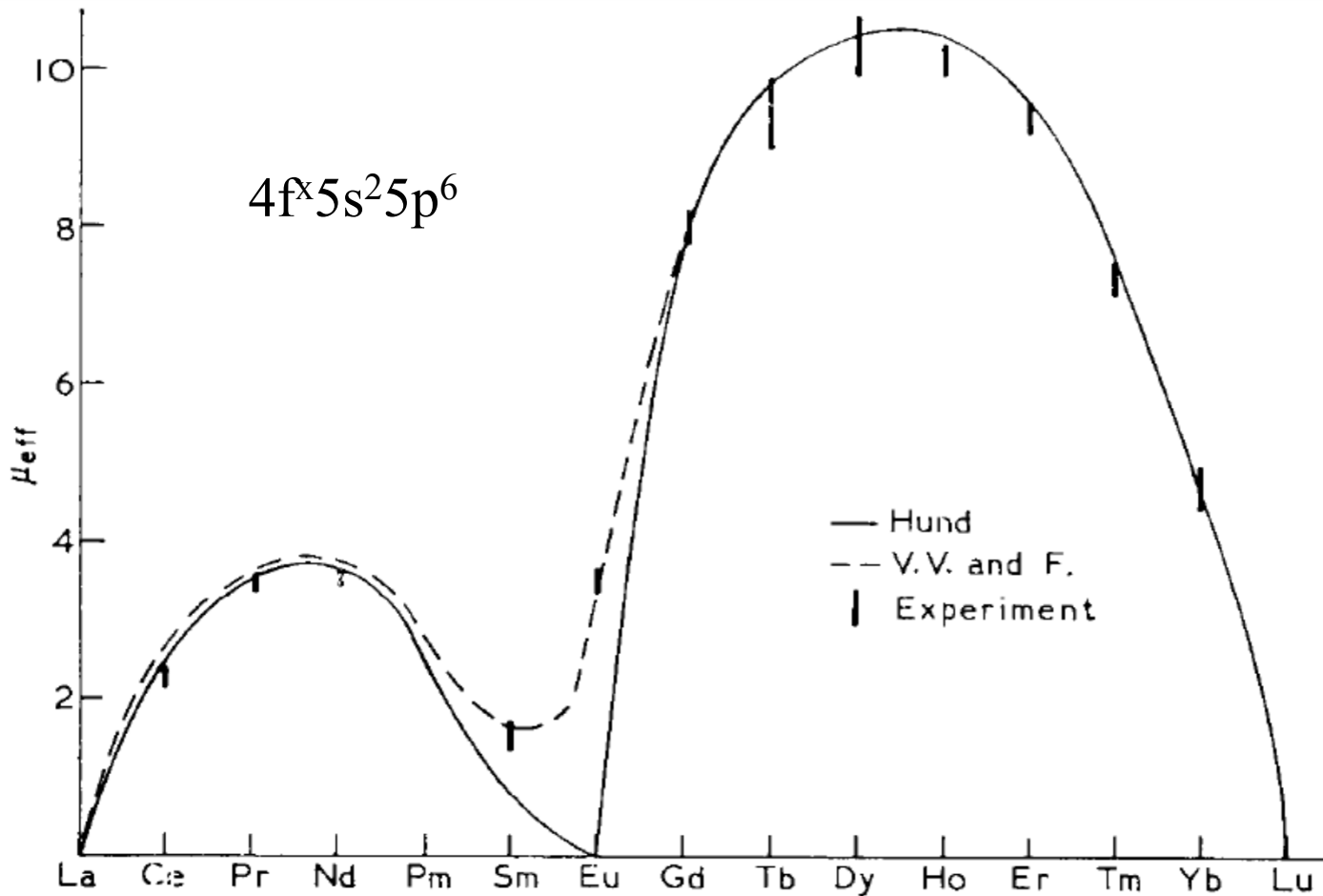
$J = |L - S|$

$J = L + S$

The half filled shell and completely filled shell have zero total angular mo.

Quantum Mechanics: The Key to Understanding Magnetism

John H. van Vleck



Pauli paramagnetism

Paramagnetic contribution due to free electrons.

Electrons have an intrinsic magnetic moment μ_B .

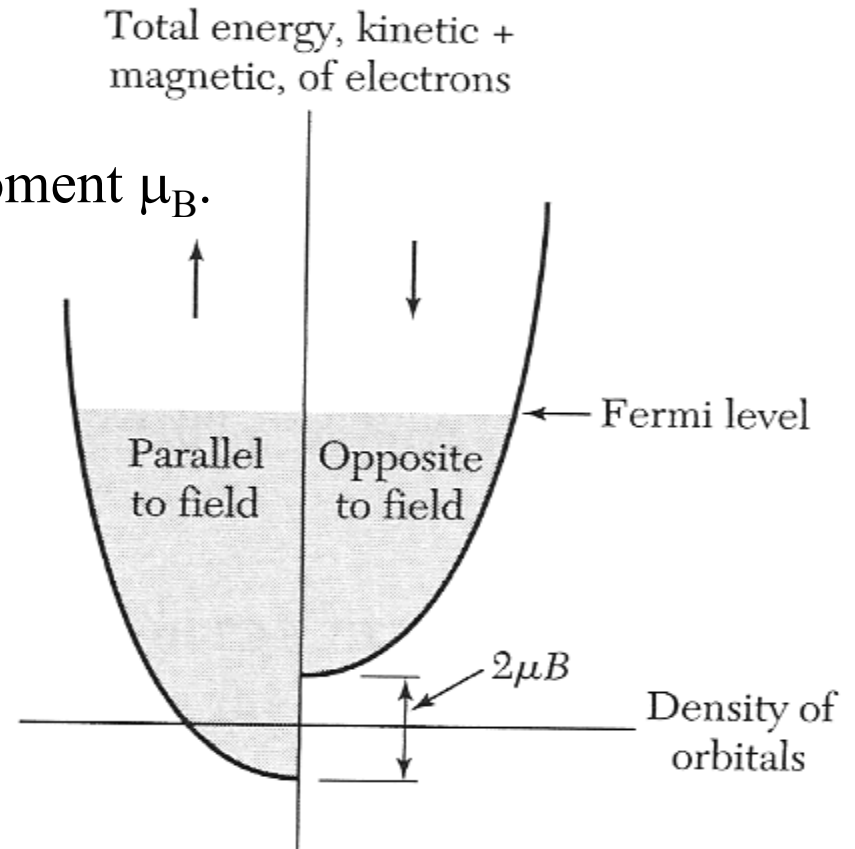
$$n_+ \approx \frac{1}{2}n + \frac{1}{2}\mu_B BD(E_F)$$

$$n_- \approx \frac{1}{2}n - \frac{1}{2}\mu_B BD(E_F)$$

$$M = \mu_B(n_+ - n_-)$$

$$M = \mu_B^2 D(E_F) B = \mu_0 \mu_B^2 D(E_F) H$$

$$\chi = \frac{dM}{dH} = \mu_0 \mu_B^2 D(E_F)$$



If E_F is 1 eV, a field of $B = 17000$ T is needed to align all of the spins.

Pauli paramagnetism is much smaller than the paramagnetism due to atomic moments and almost temperature independent because $D(E_F)$ doesn't change very much with temperature.

Ferromagnetism

Below a critical temperature (called the Curie temperature) a magnetization spontaneously appears in a ferromagnet even in the absence of a magnetic field.

Iron, nickel, and cobalt are ferromagnetic.

Ferromagnetism overcomes the magnetic dipole-dipole interactions. It arises from the Coulomb interactions of the electrons. The energy that is gained when the spins align is called the exchange energy.

Schrödinger equation for two particles

$$-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2)\psi + V_1(\vec{r}_1)\psi + V_2(\vec{r}_2)\psi + V_{1,2}(\vec{r}_1, \vec{r}_2)\psi = E\psi$$

$\psi(\vec{r}_1, \vec{r}_2) = \psi_1(\vec{r}_1)\psi_2(\vec{r}_2)$ is a solution to the noninteracting Hamiltonian, $V_{1,2} = 0$

$$\psi_A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) - \psi_1(\vec{r}_2)\psi_2(\vec{r}_1)) \begin{pmatrix} \uparrow\uparrow \\ \frac{1}{\sqrt{2}}(\uparrow\downarrow + \downarrow\uparrow) \\ \downarrow\downarrow \end{pmatrix}$$

$$\psi_S(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) + \psi_1(\vec{r}_2)\psi_2(\vec{r}_1)) \frac{1}{\sqrt{2}}(\uparrow(\vec{r}_1)\downarrow(\vec{r}_2) - \downarrow(\vec{r}_1)\uparrow(\vec{r}_2))$$

Exchange (Austauschwechselwirkung)

$$\psi_A(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) - \psi_1(\vec{r}_2)\psi_2(\vec{r}_1))$$

$$\begin{aligned} \langle \psi_A | H | \psi_A \rangle &= \frac{1}{2} [\langle \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) | H | \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \rangle - \langle \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) | H | \psi_1(\vec{r}_2)\psi_2(\vec{r}_1) \rangle \\ &\quad - \langle \psi_1(\vec{r}_2)\psi_2(\vec{r}_1) | H | \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \rangle + \langle \psi_1(\vec{r}_2)\psi_2(\vec{r}_1) | H | \psi_1(\vec{r}_2)\psi_2(\vec{r}_1) \rangle] \end{aligned}$$

$$\psi_S(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\psi_1(\vec{r}_1)\psi_2(\vec{r}_2) + \psi_1(\vec{r}_2)\psi_2(\vec{r}_1))$$

$$\begin{aligned} \langle \psi_S | H | \psi_S \rangle &= \frac{1}{2} [\langle \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) | H | \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \rangle + \langle \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) | H | \psi_1(\vec{r}_2)\psi_2(\vec{r}_1) \rangle \\ &\quad + \langle \psi_1(\vec{r}_2)\psi_2(\vec{r}_1) | H | \psi_1(\vec{r}_1)\psi_2(\vec{r}_2) \rangle + \langle \psi_1(\vec{r}_2)\psi_2(\vec{r}_1) | H | \psi_1(\vec{r}_2)\psi_2(\vec{r}_1) \rangle] \end{aligned}$$

The difference in energy between the ψ_A and ψ_S is twice the **exchange energy**.

Exchange

The exchange energy can only be defined when you speak of multi-electron wavefunctions. It is the difference in energy between the symmetric solution and the antisymmetric solution. There is only a difference when the electron-electron term is included. Coulomb repulsion determines the exchange energy.

In ferromagnets, the antisymmetric state has a lower energy. Thus the state with parallel spins has lower energy.

In antiferromagnets, the symmetric state has a lower energy. Neighboring spins are antiparallel.

Ordered states have a lower entropy than free electrons.

Mean field theory (Molekularfeldtheorie)

Heisenberg Hamiltonian $H = -\sum_{i,j} J_{i,j} \vec{S}_i \cdot \vec{S}_j - g \mu_B \vec{B} \cdot \sum_i \vec{S}_i$

Exchange energy

Mean field approximation

$$H_{MF} = \sum_i \vec{S}_i \cdot \left(\sum_{\delta} J_{i,\delta} \langle \vec{S} \rangle + g \mu_B \vec{B} \right)$$

δ sums over the neighbors of spin i

Looks like a magnetic field B_{MF}

$$\vec{B}_{MF} = \frac{1}{g \mu_B} \sum_{\delta} J_{i,\delta} \langle \vec{S} \rangle$$

magnetization $\longrightarrow \vec{M} = g \mu_B \frac{N}{V} \langle \vec{S} \rangle$

eliminate $\langle S \rangle$

Mean field theory

$$\vec{B}_{MF} = \frac{V}{Ng^2\mu_B^2} zJ\vec{M}$$

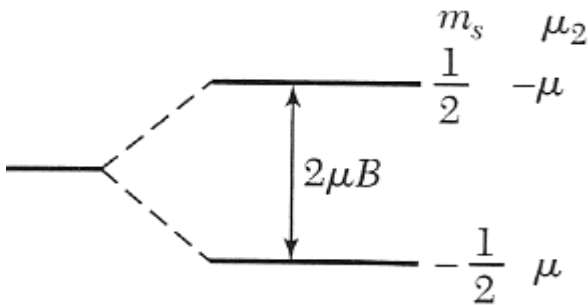
z is the number of nearest neighbors

In mean field, the energy of the spins is

$$E = \pm \frac{1}{2} g \mu_B (B_{MF} + B_a)$$

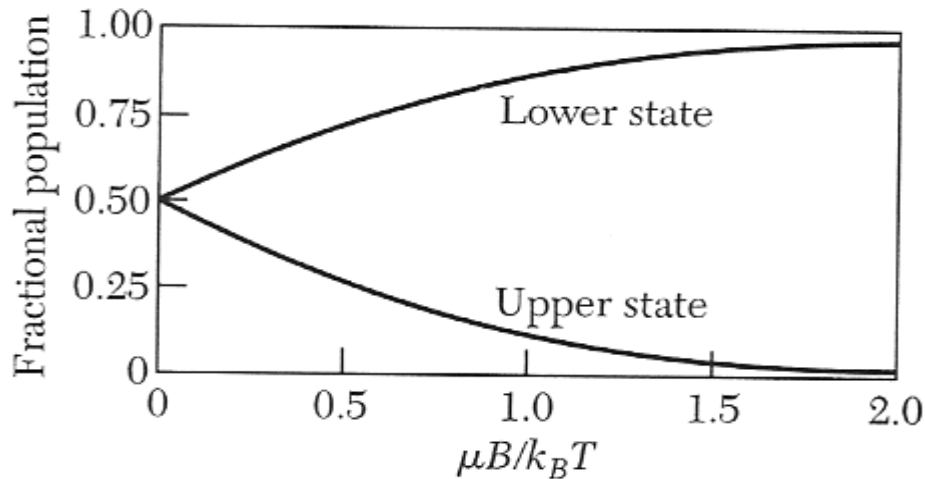
We calculated the populations of the spins in the paramagnetism section

Spin populations



$$\frac{N_1}{N} = \frac{\exp(\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$

$$\frac{N_2}{N} = \frac{\exp(-\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$



$$M = (N_1 - N_2)\mu$$

$$= N \mu \frac{\exp(\mu B / k_B T) - \exp(-\mu B / k_B T)}{\exp(\mu B / k_B T) + \exp(-\mu B / k_B T)}$$

$$= N \mu \tanh\left(\frac{\mu B}{k_B T}\right)$$

Mean field theory

$$M = \frac{1}{2} g \mu_B \frac{N}{V} \tanh \left(\frac{g \mu_B (B_{MF} + B_a)}{2k_B T} \right)$$

For zero applied field

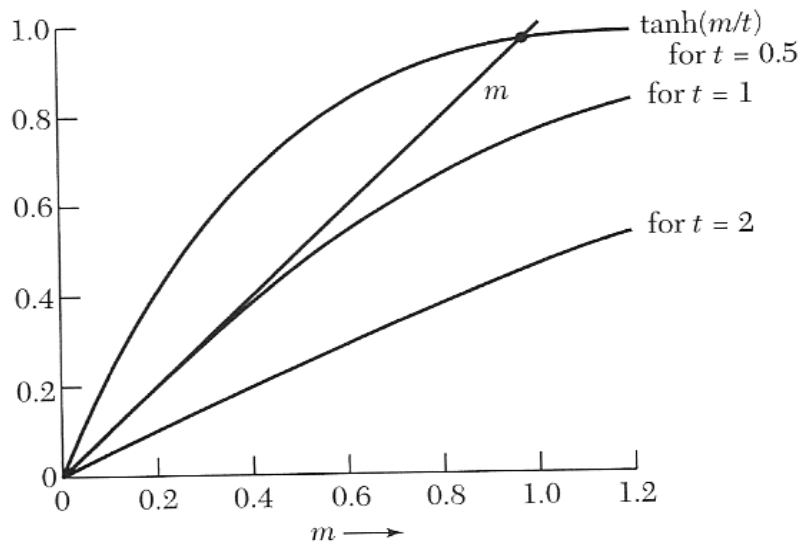
$$M = M_s \tanh \left(\frac{T_c}{T} \frac{M}{M_s} \right)$$

$$M_s = \frac{N}{2V} g \mu_B \quad \text{and} \quad T_c = \frac{z}{4k_B} J$$

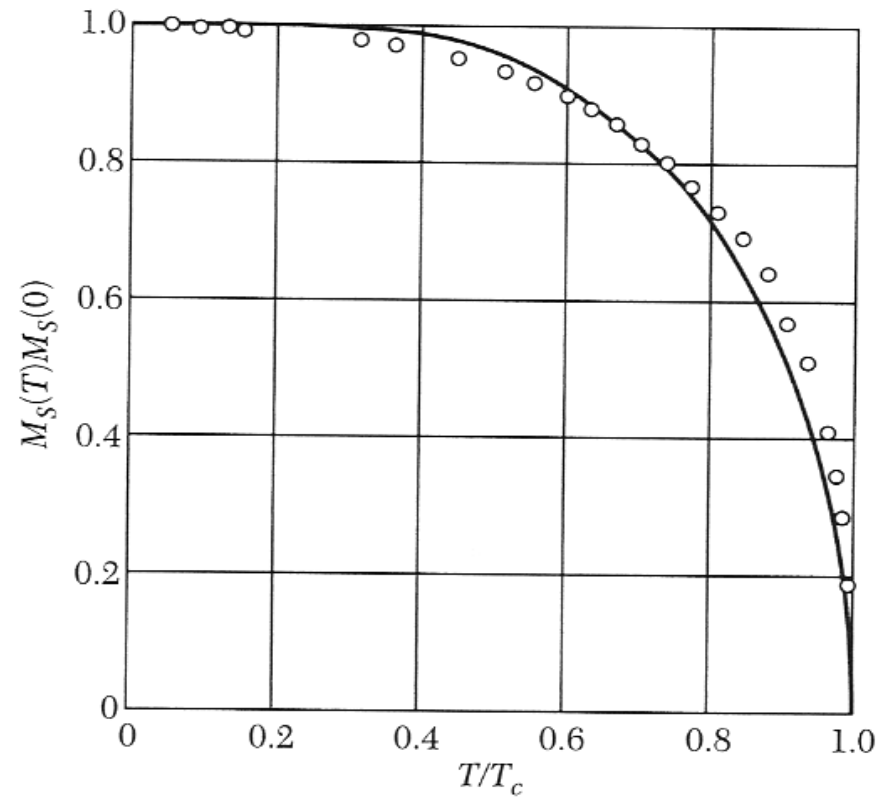
M_s = saturation magnetization T_c = Curie temperature

Mean field theory

$$M = M_S \tanh\left(\frac{T_c}{T} \frac{M}{M_S}\right)$$



$$m = \tanh\left(\frac{m}{t}\right)$$



Experimental points for Ni.

$$M_S = \frac{N}{2V} g \mu_B \quad \text{and} \quad T_c = \frac{z}{4k_B} J$$

Source: Kittel

Ferromagnetism

Material Curie temp. (K)

Co	1388	
Fe	1043	
FeOFe ₂ O ₃	858	
NiOFe ₂ O ₃	858	
CuOFe ₂ O ₃	728	
MgOFe ₂ O ₃	713	
MnBi	630	
Ni	627	
MnSb	587	
MnOFe ₂ O ₃	573	
Y ₃ Fe ₅ O ₁₂	560	
CrO ₂	386	
MnAs	318	
Gd	292	
Dy	88	
EuO	69	Electrical insulator
Nd ₂ Fe ₁₄ B	353	$M_s = 10 M_s(\text{Fe})$
Sm ₂ Co ₁₇	700	rare earth magnets

$$M_s = \frac{N}{2V} g \mu_B$$

$$T_c = \frac{z}{4k_B} J$$

Curie - Weiss law

$$M = \frac{1}{2} g \mu_B \frac{N}{V} \tanh \left(\frac{g \mu_B (B_{MF} + B_a)}{2k_B T} \right) \quad \vec{B}_{MF} = \frac{V}{Ng^2 \mu_B^2} zJ\vec{M}$$

Above T_c we can expand the hyperbolic tangent $\tanh(x) \approx x$ for $x \ll 1$

$$M \approx \frac{1}{4} g^2 \mu_B^2 \frac{N}{Vk_B T} \left(\frac{V}{Ng^2 \mu_B^2} zJM + B_a \right)$$

Solve for M

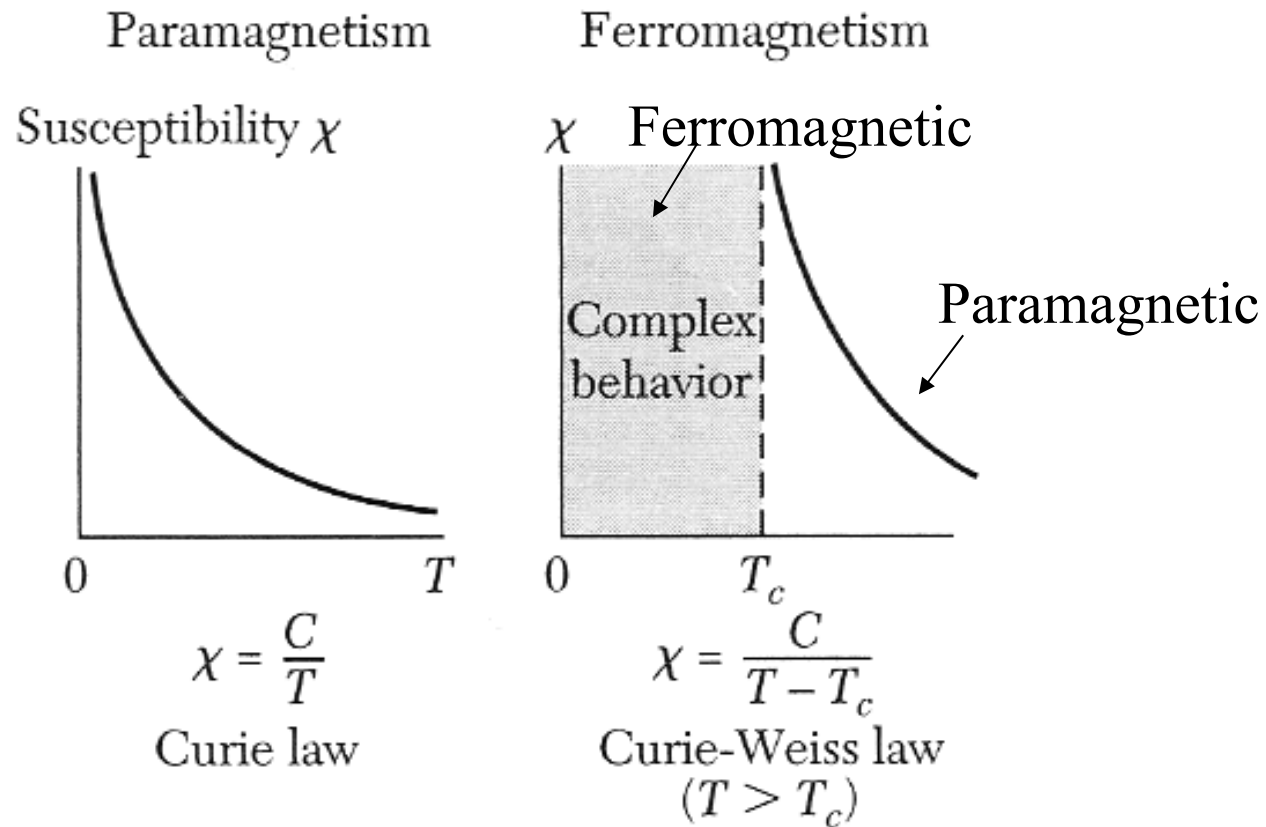
$$M \approx \frac{g^2 \mu_B^2 N}{4Vk_B} \frac{B_a}{T - T_c} \quad T_c = \frac{z}{4k_B} J$$

Curie Weiss Law $\chi = \frac{dM}{dH} \approx \frac{C}{T - T_c}$

Critical fluctuations near T_c

Ferromagnets are paramagnetic above T_c

Source: Kittel



Critical fluctuations near T_c .

Magnetization of a Magnetite Single Crystal Near the Curie Point*

D. O. SMITH†

Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts

(Received January 20, 1956)

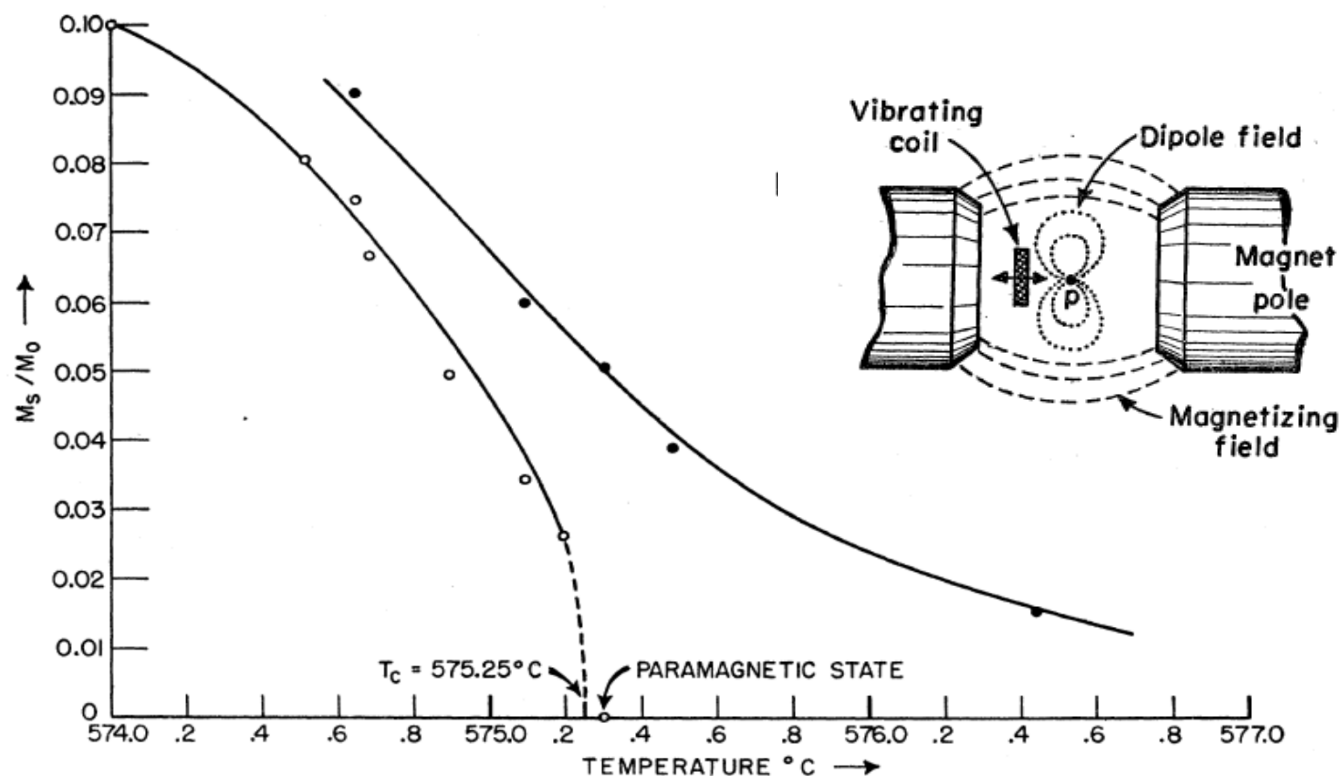


FIG. 2. Principle of the vibrating-coil magnetometer.

FIG. 9. M_s/M_0 vs T in the [111] direction near the Curie point for single-crystal magnetite.