Ferromagnetism and antiferromagnetism

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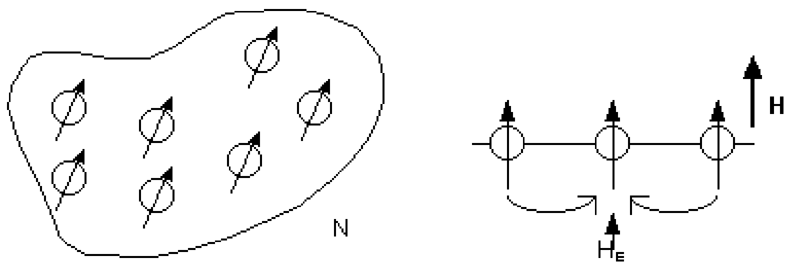
Ferromagentic order

A ferromagnet has a spontaneous magnetic moment --- a magnetic moment even in zero applied magnetic field.

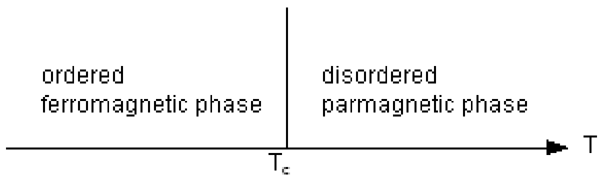
Curie point and the exchange integral



Consider a paramagnet with a concentration *N* ions of spin *S*.
We treat the exchange field as equivalent to a magnetic field H_E. ($H_E \sim 10^3$ T)

$$H_E = AM \qquad \text{(mean field theory)}$$

where *M* is the magnetization defined as the magnetic moment per unit volume (emu/cc). The Curie temperature T_c is the temperature above which the spontaneous magnetization vanishes.



For $T > T_c$

$$M = \chi_p (H + H_E)$$

where $\chi_p = \dfrac{C}{T}$ is the paramagnetic susceptibility and *C* is the Curie constant.

$$\chi = \frac{M}{H} = \frac{C}{T - CA} = \frac{C}{T - \Theta} \qquad \text{Curie-Weiss law,}$$

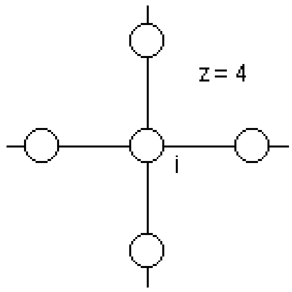
where $\Theta = CA$ is the Curie-Weiss temperature.

What is the background?

The exchange field gives an approximate representation of the quantum-mechanical exchange interaction.

$$E_{ex} = -2J\sum_{i<j}\mathbf{S}_i \cdot \mathbf{S}_j \ ,$$

where the sum is over nearest neighbor pairs. *J* is the exchange integral and is related to the overlap of the charge distribution of spins *i,j*. This equation is called the Heisenberg model.



$$E_{ex}\,|_i = -2Jz\langle\mathbf{S}\rangle\cdot\mathbf{S}_i = -(-g\mu_B\mathbf{S}_i)\cdot\mathbf{H}(i)$$

where ***H***(i) is the exchange field seen by i-th electron.

$$\mathbf{H}(i) = \frac{-2zJ}{g\mu_B}\langle\mathbf{S}\rangle$$

Magnetization

$$\mathbf{M} = -g\mu_B N\langle\mathbf{S}\rangle$$

The exchange field is

$$\mathbf{H}(i) = \frac{-2zJ}{g\mu_B}\frac{\mathbf{M}}{-g\mu_B N} = \frac{2zJ}{g^2\mu_B^2 N}\mathbf{M} = A\mathbf{M}\,,\ (A > 0),$$

which means that

$$A = \frac{2zJ}{g^2\mu_B^2 N}\,.$$

The Curie-Weiss temperature

$$\Theta = CA = \frac{Ng^2\mu_B^2 S(S+1)}{3k_B}\frac{2zJ}{g^2\mu_B^2 N} = \frac{2zJ}{3k_B}S(S+1)$$

The mean field theory result is

$$J = \frac{3k_B\Theta}{2zS(S+1)}.$$

Temperature dependence of the saturation magnetization

We use the complete Brillouin expression for the magnetization

$$M = Ng\mu_B SB_S(x) \qquad \Rightarrow \qquad y = \frac{M}{Ng\mu_B} = SB_S(x),$$

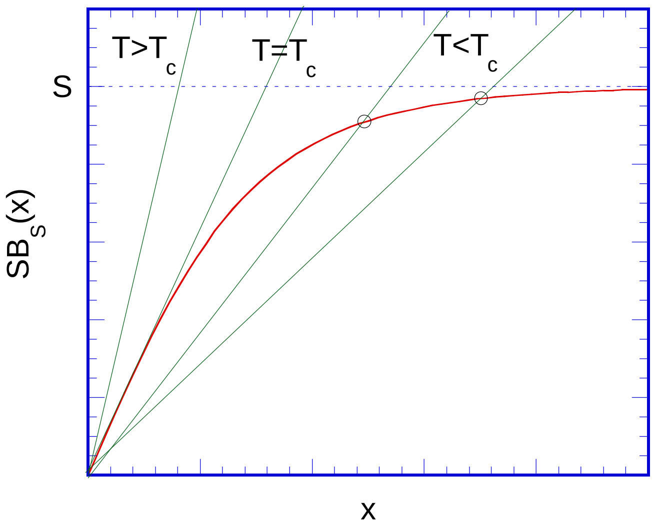
where $B_S(x)$ is the Brillouin function defined by

$$B_S(x) = \left(\frac{2S+1}{2S}\right)\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{x}{2S}\right)$$

$$x = \frac{g\mu_B S}{k_B T}(AM) = \frac{g\mu_B S}{k_B T}\frac{2zJ}{g\mu_B^2 N}M = \frac{2zJS}{k_B T g\mu_B N}M$$

$$y = \frac{M}{Ng\mu_B S} = \frac{k_B T g\mu_B N}{2zJS}x\frac{1}{Ng\mu_B} = \frac{k_B T}{2zJS}x$$

$$= \frac{k_B T}{2zJS}\frac{1}{T_c}\frac{2zJS(S+1)}{3k_B}x = \frac{T}{2T_c}(S+1)x$$



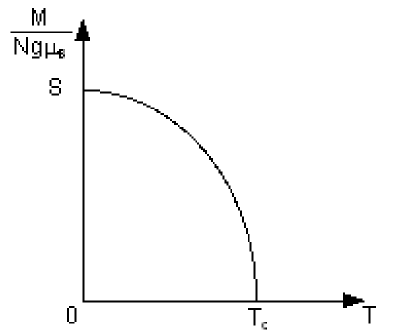
Property of Brillouin function

$$\lim_{x\to 0} B_S(x) = \frac{S+1}{3S}x \quad \Rightarrow \quad \lim_{x\to 0} SB_S(x) = \frac{1}{3}(S+1)x$$

$$\lim_{x\to\infty} SB_S(x) = S$$

In the molecular field theory we find that $T_c = \Theta$.

As T increases the magnetization decreases smoothly to zero at T_c. This behavior classifies the usual ferromagnetic/paramagnetic transition as a second order transition.



For sufficiently large x

$$B_S(x) = \left(\frac{2S+1}{2S}\right)\coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S}\coth\left(\frac{x}{2S}\right)$$

$$\coth z = \frac{e^z + e^{-z}}{e^z - e^{-z}} = \frac{1+e^{-2z}}{1-e^{-2z}} \approx 1 + 2e^{-2z} \qquad \text{for } e^{-2z} \ll 1.$$

Then $B_S(x)$ is approximated by

$$\begin{aligned} B_S(x) &= \left(\frac{2S+1}{2S}\right)\left[1 + 2e^{-2\left(\frac{2S+1}{2S}x\right)}\right] - \frac{1}{2S}\left(1 + 2e^{-2\frac{x}{2S}}\right) \\ &= 1 + \left(\frac{2S+1}{S}\right)e^{-2\left(\frac{2S+1}{2S}x\right)} - \frac{1}{S}e^{-\frac{x}{S}} = 1 + e^{-\frac{x}{S}}\left[\left(\frac{2S+1}{S}\right)e^{-x} - \frac{1}{S}\right], \\ &\approx 1 - \frac{1}{S}e^{-\frac{x}{S}} \end{aligned}$$

$$y = \frac{M}{Ng\mu_B} = SB_S(x) = S - e^{-\frac{x}{S}}.$$

We defined the magnetization deviation

$$\Delta M \equiv M(0) - M(T)$$
$$= Ng\mu_B S - Ng\mu_B \left[S - e^{-\frac{x}{S}} \right]$$
$$= Ng\mu_B e^{-\frac{x}{S}}$$

$$x = \frac{g\mu_B S}{k_B T}(AM) = \frac{g\mu_B S}{k_B T} \frac{2zJ}{g\mu_B^2 N} Ng\mu_B S = \frac{2zJ}{k_B T} S^2$$

Then

$$\Delta M \approx Ng\mu_B \exp\left[-\frac{2zJS}{k_B T} \right]$$

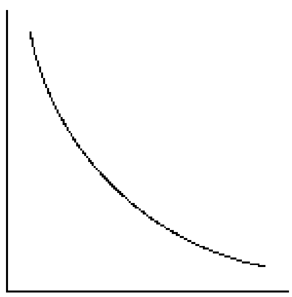
or

$$\frac{\Delta M}{Ng\mu_B} \approx \exp\left[-\frac{3}{S+1} \frac{T_c}{T} \right].$$

The experimental results show a much more rapid dependence of ΔM on T at low temperatures.

$$\frac{\Delta M}{M(0)} = AT^{3/2}$$ spin wave

((Note))



$$\chi_M = \frac{C_M}{T - \Theta}$$

$$\begin{cases} C_M = \dfrac{N_A g^2 \mu_B^2}{3k_B} S(S+1) \\ \Theta = \dfrac{2}{3} zJS(S+1) \end{cases}$$

$$C_M = \frac{1}{8} P_{eff}^2 \quad \Rightarrow \quad P_{eff}$$

$$\Theta \quad \Rightarrow \quad J$$

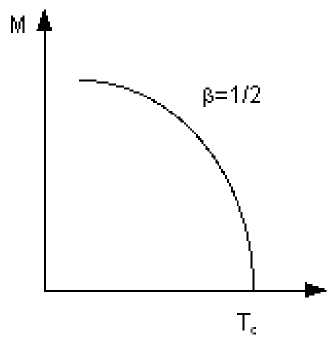
<u>typical example</u>

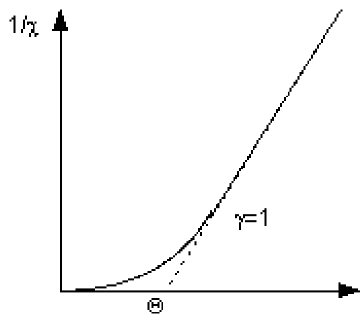
Θ = 23.5 K for $CoCl_2$ GIC

$z = 6$

$$23.5 = \frac{2}{3} 6J \frac{1}{2}\frac{3}{2} = 3J$$

$\Rightarrow$ $\underline{\underline{J = 23.5/3 = 7.8 \text{ K}}}$





Because of spin flustration

$\Downarrow$

deviation of χ_M from the molecular field theory

((S = ½ case))

$$M = N_A g \mu_B S B_S(x)$$

For S = ½

$$x = \frac{gS\mu_B H}{k_B T}, \quad y = \frac{M}{N_A g\mu_B S} = B_{1/2}(x) = \tanh x .$$

Note that

$$\begin{aligned} B_{1/2}(x) &= 2\coth\frac{2x}{2\cdot 1/2} - \coth x = 2\coth(2x) - \coth x \\ &= 2\frac{e^{2x}+e^{-2x}}{e^{2x}-e^{-2x}} - \frac{e^{x}+e^{-x}}{e^{x}-e^{-x}} = 2\frac{e^{2x}+e^{-2x}}{(e^{x}+e^{-x})(e^{x}-e^{-x})} - \frac{(e^{x}+e^{-x})^2}{(e^{x}+e^{-x})(e^{x}-e^{-x})} . \\ &= \frac{e^{2x}+e^{-2x}-2}{(e^{x}+e^{-x})(e^{x}-e^{-x})} = \frac{(e^{x}-e^{-x})^2}{(e^{x}+e^{-x})(e^{x}-e^{-x})} = \frac{e^{x}-e^{-x}}{e^{x}+e^{-x}} \\ &= \tanh x \end{aligned}$$

In general

$$x = \frac{\mu_B H_m}{k_B T} = \frac{\mu_B AM}{k_B T} = \frac{2zJS}{k_B T g\mu_B N} M = \frac{2zJS^2}{k_B T} y$$

or

$$y = \frac{k_B T}{2zJS^2} x = \frac{T}{T_c} x \frac{k_B}{2zJS^2} \frac{2}{3} \frac{zJS(S+1)}{k_B} = \frac{T}{3T_c} \frac{S+1}{S} x .$$

When S=1/2,

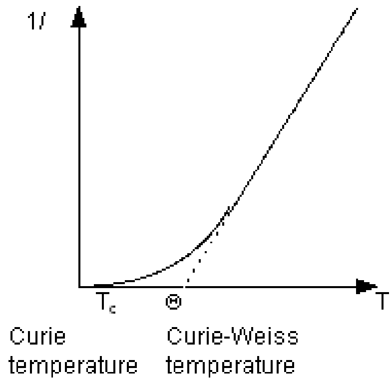
$$y = \frac{T}{3T_c} \frac{3/2}{1/2} x = \frac{T}{T_c} x .$$

$$\begin{cases} y = \tanh x \\ y = tx \end{cases}, \quad \frac{T}{T_c} \equiv t .$$

solution

$$\tanh x = tx = y \qquad \text{or} \qquad \tanh\left(\frac{y}{t}\right) = y$$

***T_c* and *Θ* (real system)**



T_c « Θ for real systems

((Example)) Ni: T_c = 627.2 K and $\Theta \cong$ 650 K

((Note))

T_c/Θ=1 in the molecular field theory
T_c/Θ<1 for 3D systems
T_c/Θ monotonically decreases with increasing dimensionality.
$T_c/\Theta \leq 0.1$ for 1D system

Critical exponent β and γ (critical behavior)
Molecular field theory approximation ($T_c = \Theta$);

$\beta = ½$
$\gamma = 1$

χ and M can be described by

$M \sim (T_c - T)^{\beta}$ for $T < T_c$, $H = 0$

$\chi \sim (T - T_c)^{-\gamma}$ for $T > T_c$

$C \sim (T - T_c)^{-\alpha}$, $M \sim H^{1/\delta} (T = T_c)$

where

$\alpha + 2\beta + \gamma = 2$.

2D Ising system (Onsager exact solution)

$\alpha \cong 0$, $\beta = 1/8 = 0.125$, $\gamma = 7/4 = 1.75$

Saturation Magnetization at absolute zero

$$M_s = M(0)(\text{emu/cc}) = Ng\mu_B S = n_B N\mu_B$$

N is the number of spins per unit volume.

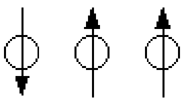
$$n_B = gS$$

Do not confuse n_B with the paramagnetic effective magneton $P_{eff} = g\sqrt{S(S+1)}$.
Observed values of n_B are often nonintegral.

	n_B
Fe	2.22
Co	1.72
Ni	0.606
Gd	7.63
Dy	10.2
EuO	6.8

There are many possible causes

(1) spin-orbit interaction which adds a subtracts some orbital magnetic moment.
(2) Another cause in ferromagnetic metals is the conduction electron magnetization induced locally about a paramagnetic ion core.
(3) spin arrangement in a ferrimagnet

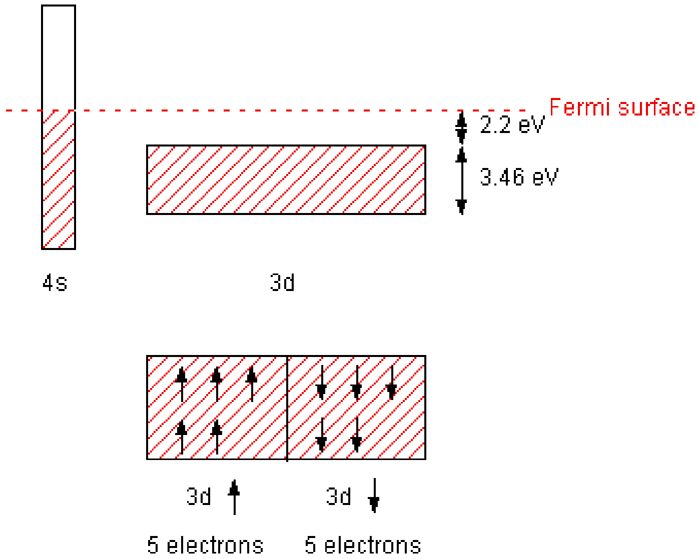


$\frac{1}{3}S$ = average spin

A band or itinerant electron model accounts for the ferromagnetism of Fe, Ni, and Co.

Cu: $(3d)^{10}(4s)^1$	Cu is not ferromagnetic
Ni: $(3d)^9(4s)^1$	Ni has the possibility of a hole in the 3d band

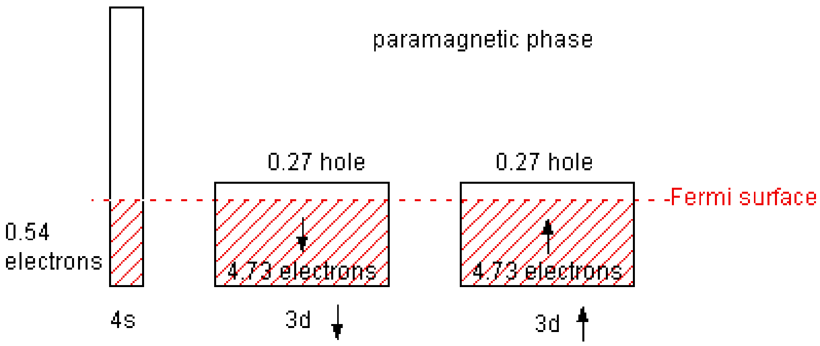
<u>Schematic relationship of 4s and 3d bands in metallic Cu</u>



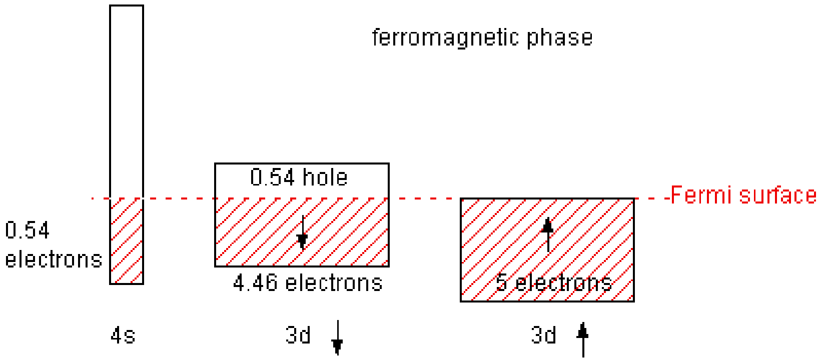
- Cu has one valence electron outside the filled 3d shell.
- The net spin of the d-band (net magnetization) is zero.

Band relationships in Ni above T_c

The net magnetization is zero



Schematic relationships in Ni at 0 K



$$2\mu_B\left(\frac{1}{2}\times 5-\frac{1}{2}\times 4.46\right)=\left(\frac{1}{2}\times 0.54\right)2\mu_B\ =0.54\mu_B$$

3d↑ and 3d↓ sub-bands are separated by an exchange interaction.