Condensed Matter Physics I

Prof. Dr. Ir. Paul H.M. van Loosdrecht

II Physikalisches Institut, Room 312

E-mail: pvl@ph2.uni-koeln.de

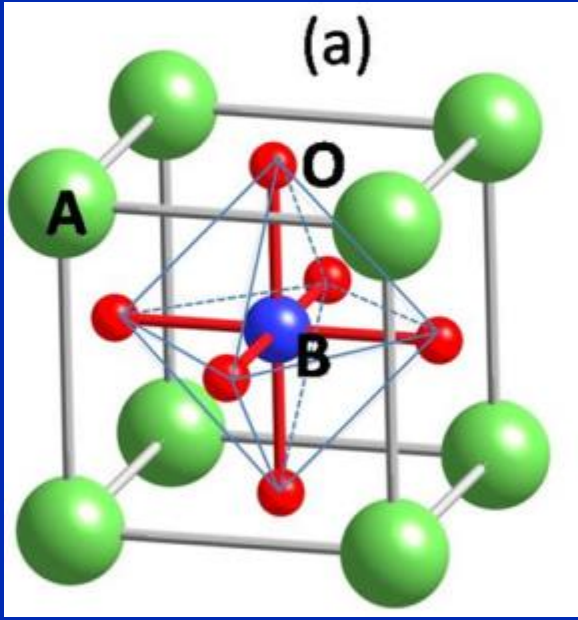
Website: http:/www.loosdrecht.net/

Last time

Langevin diamagnetism

Moments

- Free ions
- LS couping
- Hund's rules
- Spectroscopic splitting factor
- Crystal field effects



Today

Paramagnetism

- Curie paramagnetism
- van Vleck magnetism
- Pauli paramagnetism (metals)

PARAMAGNETISM

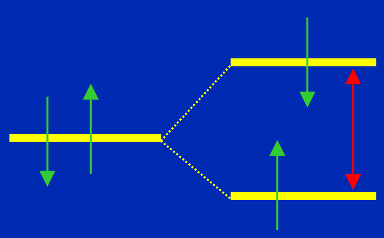
Curie law: G.S.

$$E_B \approx g_j \mu_B \vec{H} \cdot \langle n | \vec{J} | n \rangle + \sum_{n \neq n'} \frac{\left[g_j \mu_B \vec{H} \cdot \langle n | \vec{J} | n' \rangle \right]^2}{E_n - E_{n'}} + \frac{e^2}{8mc^2} H^2 \left\langle n \left| \sum_i \left(x_i^2 + y_i^2 \right) \right| n \right\rangle$$

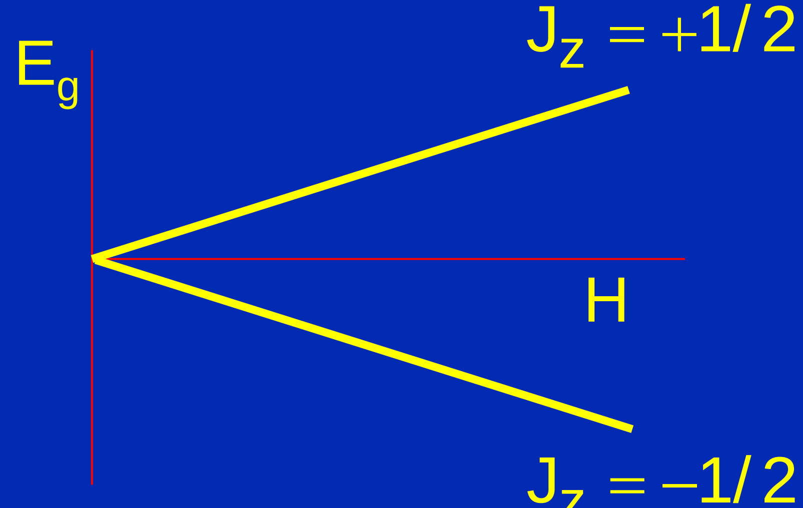
Magnetic ground state

Ground state splitting: $E_B = g_j \mu_B H_z J_z$

L=0; S=1/2



$2\Delta = \mu_B H_z$



Curie Law: J

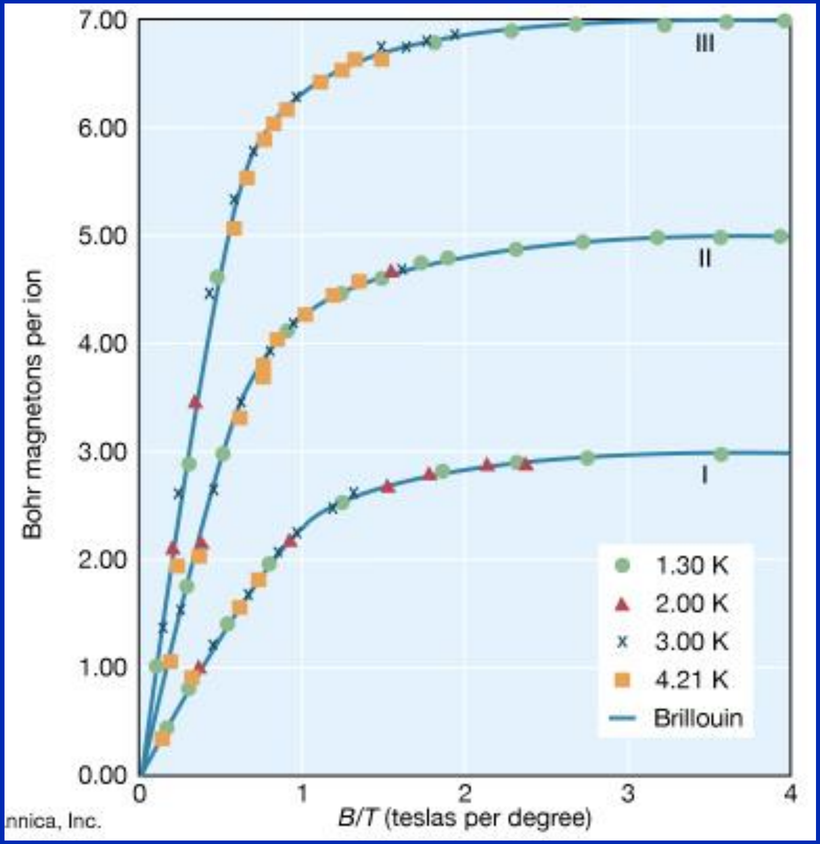
More general: for G.S. with J: 2J+1 equi-spaced levels

$$M = n\langle M\rangle = n\frac{\sum_{J_z=-J}^{J} g_j\mu_B J e^{-g_j\mu_B J_z H/kT}}{\sum_{J_z=-J}^{J} e^{-g_j\mu_B J_z H/kT}} = n g_j \mu_B J B_J(x)$$

With Brillouin function B_J:

$$B_J(x) = \frac{2J+1}{2J}\coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J}\coth\left(\frac{x}{2J}\right) \qquad x = \frac{g_j\mu_B JH}{kT}$$

Some paramagnetic salts



After W.E. Henry, Phys. Rev. 88, 559 (1952)

$Gd_2(SO4)_3 \cdot 8H_2O$
Gd^{3+}, [Xe]4*f* ^{7}, J=7/2
(L=0)

$NH_4Fe(SO_4)_2$
Fe^{3+}, [Ar]3*d*^{5}, J=5/2
L=0

$KCr(SO_4)_2$
Cr^{3+}, [Ar]3d^3, J=3/2
(L quenched)

van Vleck paramagnetism

$$E_B \approx g_j \mu_B \vec{H} \cdot \langle n | \vec{J} | n \rangle + \sum_{n \neq n'} \frac{\left[g_j \mu_B \vec{H} \cdot \langle n | \vec{J} | n' \rangle \right]^2}{E_n - E_{n'}} + \frac{e^2}{8mc^2} H^2 \left\langle n \left| \sum_i \left(x_i^2 + y_i^2 \right) \right| n \right\rangle$$

Non-magnetic groundstate $|0\rangle$

$$\chi = -\frac{N}{V} \frac{\partial^2 E_{B,0}}{\partial H^2} = 2 \frac{N}{V} \sum_{n \neq 0} \frac{\left(g_j \mu_B \langle n | J_z | 0 \rangle \right)^2}{E_n - E_0} - \frac{e^2}{4mc^2} \frac{N}{V} \left\langle 0 \left| \sum_i \left(x_i^2 + y_i^2 \right) \right| 0 \right\rangle$$

Only one excited state Δ above GS,

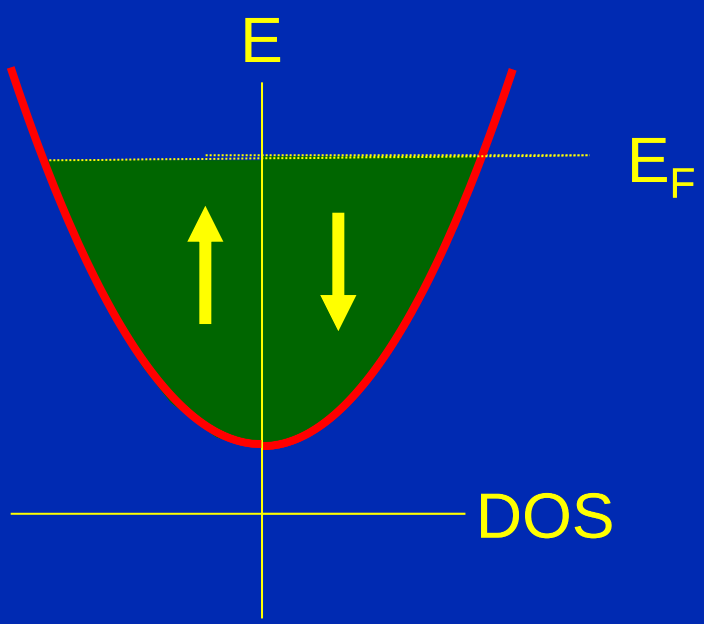
kT<< Δ $\qquad \chi = 2n \frac{\left(g_j \mu_B \langle n | J_z | 0 \rangle \right)^2}{\Delta} + \chi_{dia}$

kT>> Δ: $\qquad \chi = n \frac{\left(g_j \mu_B \langle n | J_z | 0 \rangle \right)^2}{kT} + \chi_{dia}$

Competition between van Vleck and Langevin

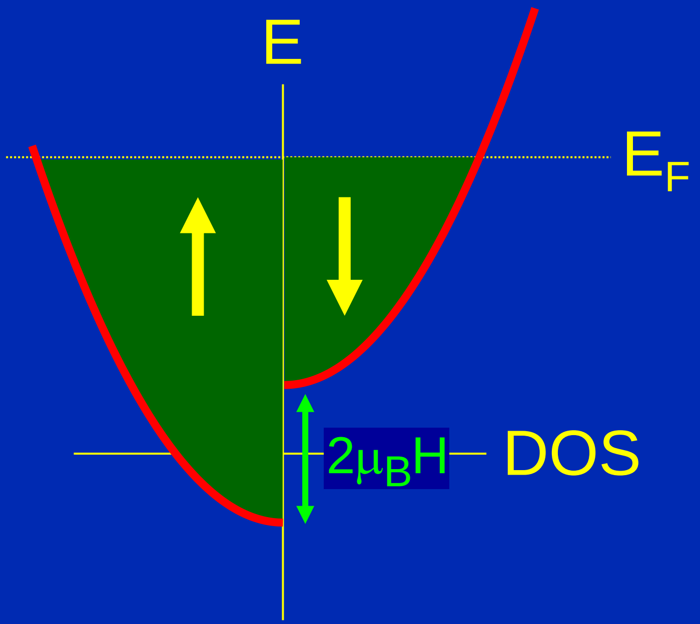
Conduction electrons: Pauli paramagnetism

No field: $E = \frac{\hbar^2 k^2}{2m^*}$ $E_F = \frac{\hbar^2}{2m^*}\left(3\pi^2 n\right)^{2/3}$ $D(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E}$



Pauli paramagnetism

$$E = \frac{\hbar^2 k^2}{2m^*} \pm \frac{1}{2} g_o \mu_B H$$



$$M = (N_\uparrow - N_\downarrow)\, g\mu_B S$$

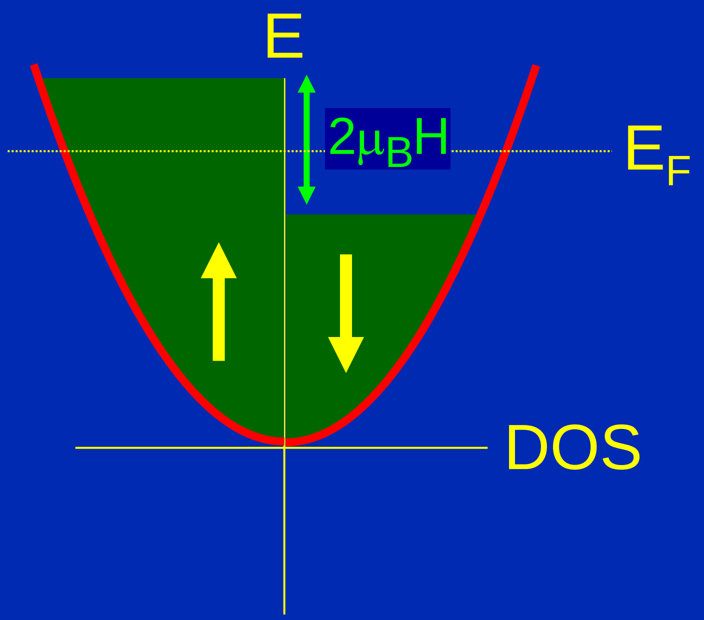
$$N_\uparrow = \frac{1}{2}\int_{-\mu_B H}^{E_F} D(E + \mu_B H) dE$$

$$N_\downarrow = \frac{1}{2}\int_{\mu_B H}^{E_F} D(E - \mu_B H) dE$$

$H \neq 0$

Pauli paramagnetism

H ≠ 0 : $E = \frac{\hbar^2 k^2}{2m^*} \pm \frac{1}{2} g_o \mu_B H$



$$N_\uparrow = \frac{1}{2} \int_{-\mu_B H}^{E_F} D(E + \mu_B H)\, dE$$

$$\approx \frac{1}{2} \left(\int_0^{E_F} D(E)\, dE + \mu_B H \cdot D(E_F) \right)$$

$$N_\downarrow \approx \frac{1}{2} \left(\int_0^{E_F} D(E)\, dE - \mu_B H \cdot D(E_F) \right)$$

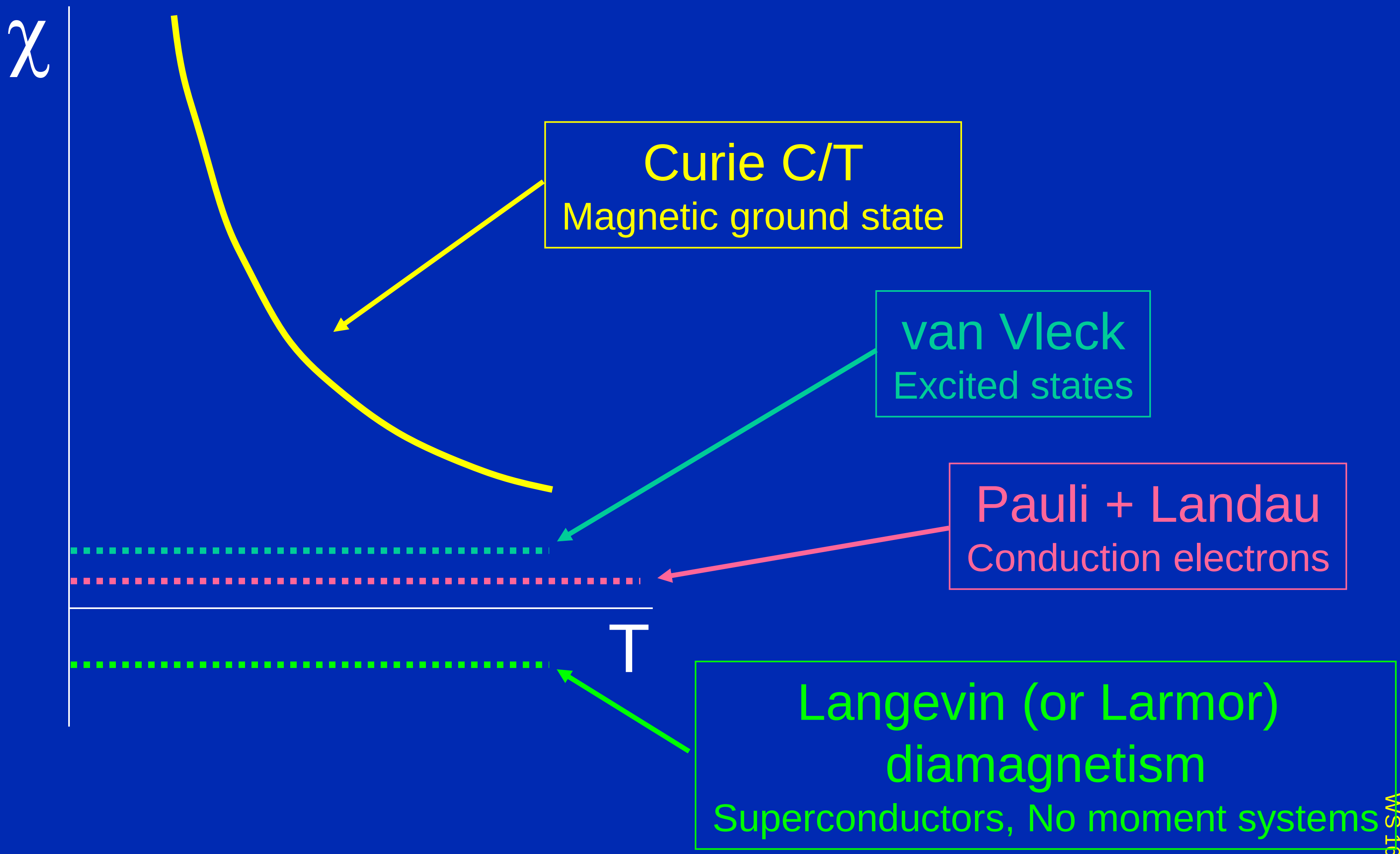
Pauli: $M = \mu_B (N_\uparrow - N_\downarrow)$

$$= \mu_B^2 D(E_F)\, H = \frac{3n\mu_B^2}{2kT_F} H$$

Landau (dia): $M = -\frac{n\mu_B^2}{2kT_F} H$

$$\Rightarrow \quad \chi_e = \frac{n\mu_B^2}{kT_F}$$

Overview para/diamagnetism



Magnetism

Diamagnetism:
- No magnetic moments
- No magnetic interaction
- Response due to induced currents — Ideal gases
- Magnetization <u>opposite</u> to field — Superconductors

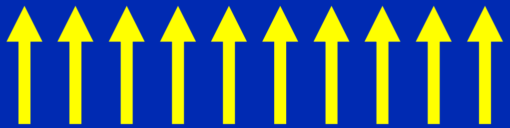
Paramagnetism:
- Magnetic moments (spin, orbit)
- Weak magnetic interactions — Metals
- Response due to orientation — 'odd electron' systems
- Magnetization in field direction — O_2, biradicals

Ordered magnetism:
- Magnetic moments
- <u>Strong magnetic interactions</u>
- Response due to polarization — Fe, Ni, Co, Gd, Dy
- Ferro-, antiferro-, ferrimagnetic — CoO, FeO, high-T_c (CuO systems)

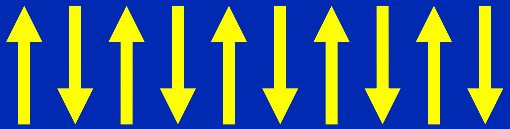
Ordered Magnetism

What if there is a strong interaction between moments ?

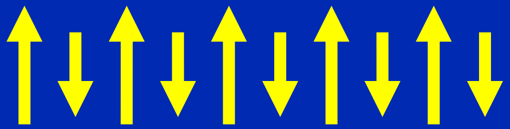
$$H_{i,j} = -2J_{i,j}\vec{S}_i \cdot \vec{S}_j$$



Ferromagnetism



Antiferromagnetism



Ferrimagnetism

Ferromagnetism in $Sm_{(3-x)}Ho_xFe_5O_{12}$ (x=2.4)

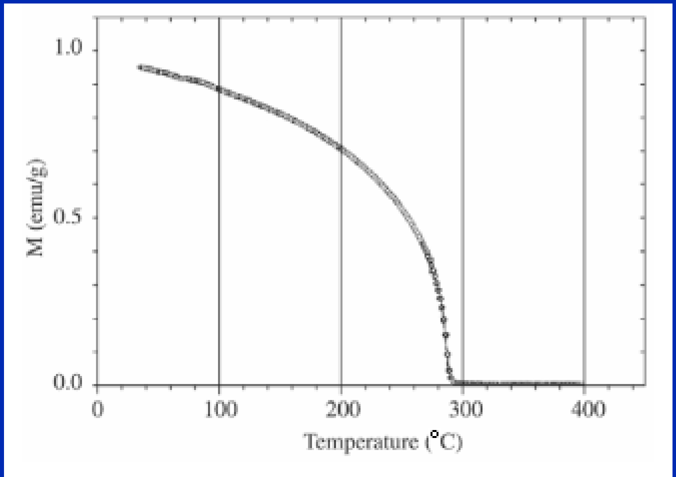


Figure 8. Magnetization-temperature curve of the powder calcined at 1450 °C when subsequently subjected to a 240 Oe magnetic field.

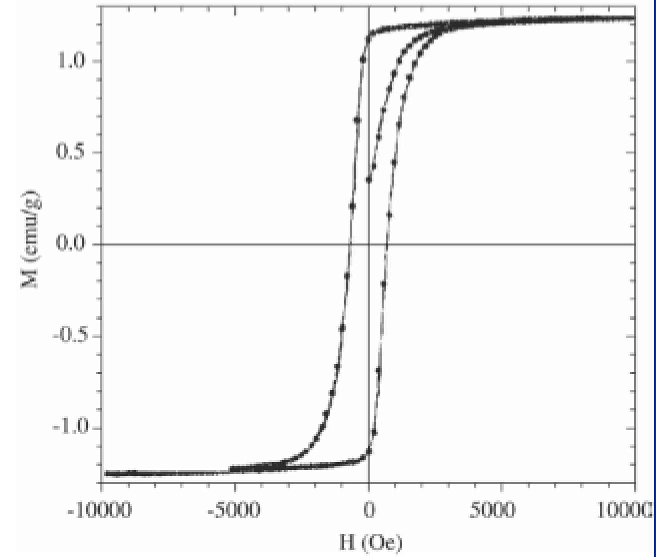
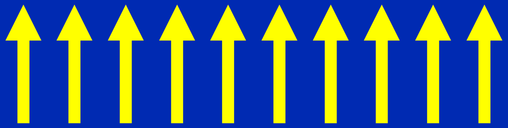
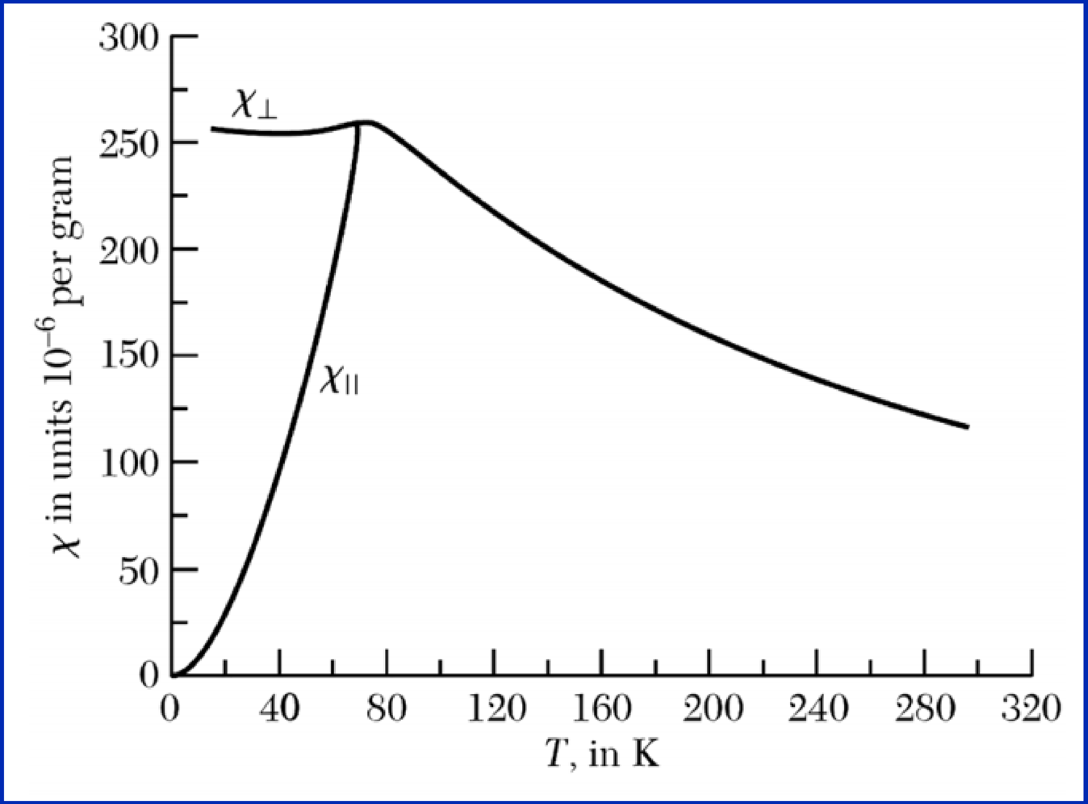


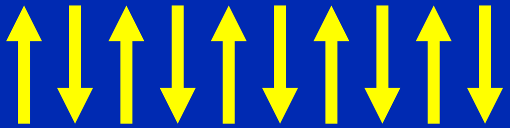
Figure 7. Hysteresis loop of the powder calcined at 1450 °C.

V. da Rocha Caffarena, T. Ogasawara, Mat. Res. 2003



Antiferromagnetism in MnF_2

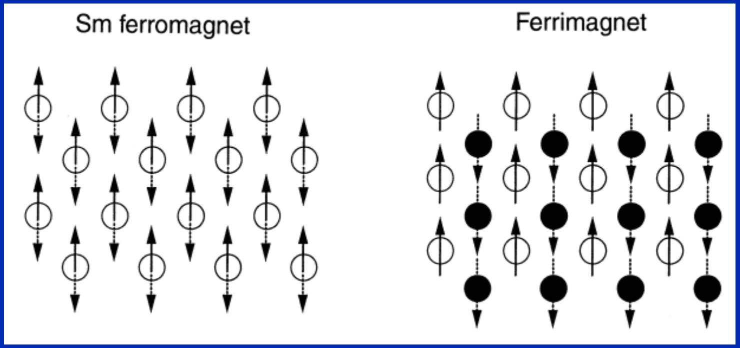


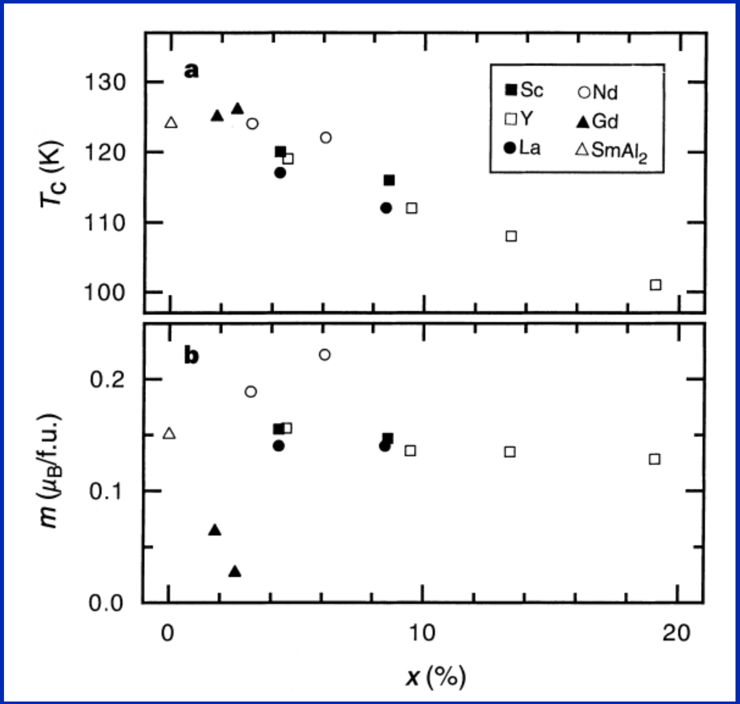


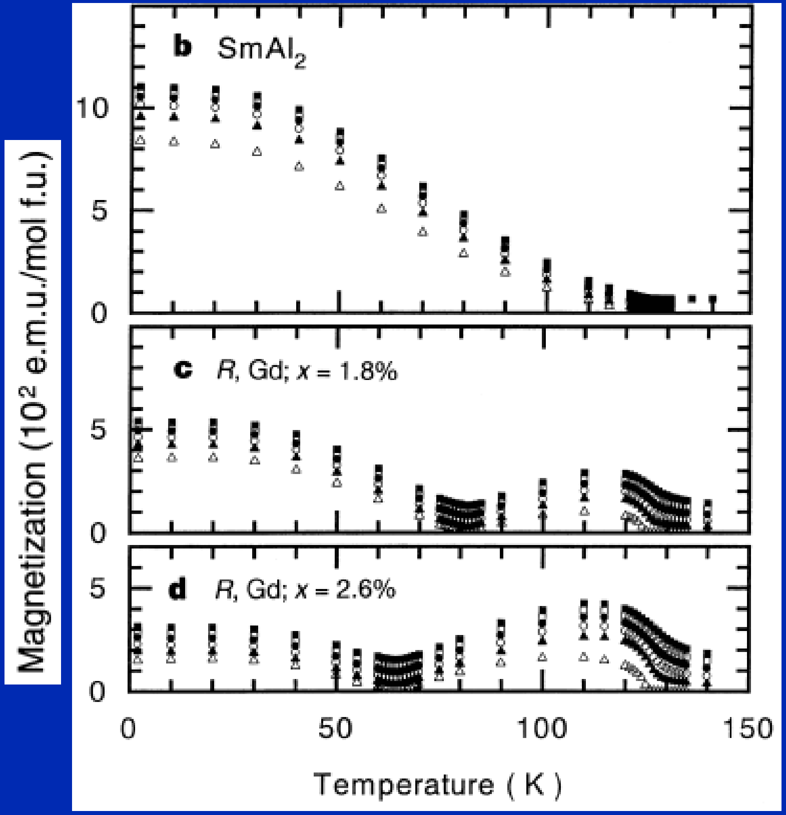
From:
C. Kittel, Introduction to solid state physics

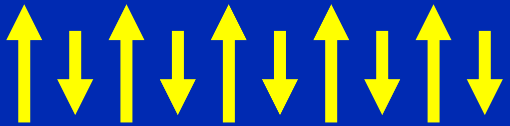
Ferrimagnetism in $SmAl_2$

Sm^{3+}: [Xe]$4f^5$
Spin moment ~ $4\mu_B$
Orbital moment ~ $4\mu_B$



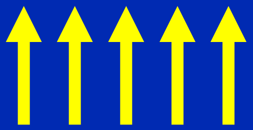


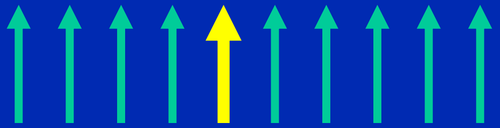


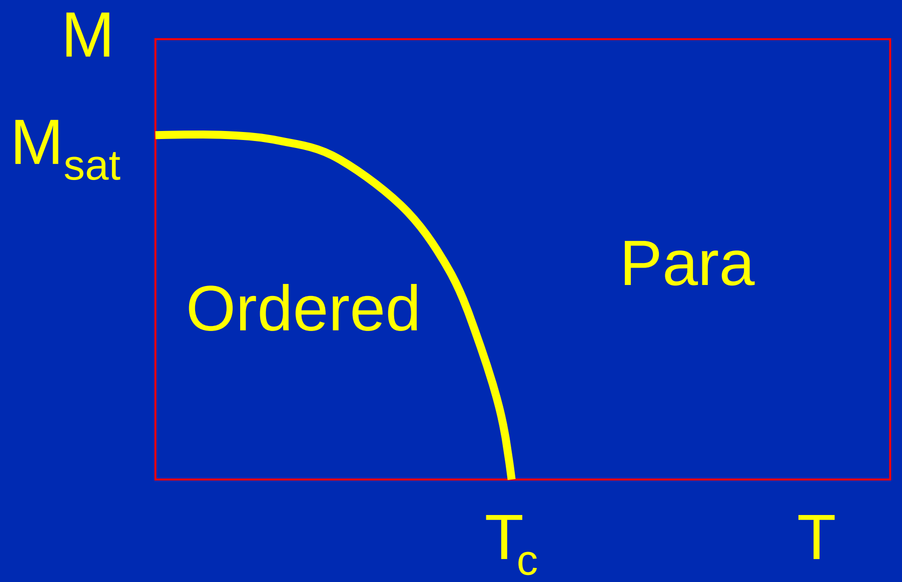


Adachi and Ino, Nature 1999

Ferromagnetic order





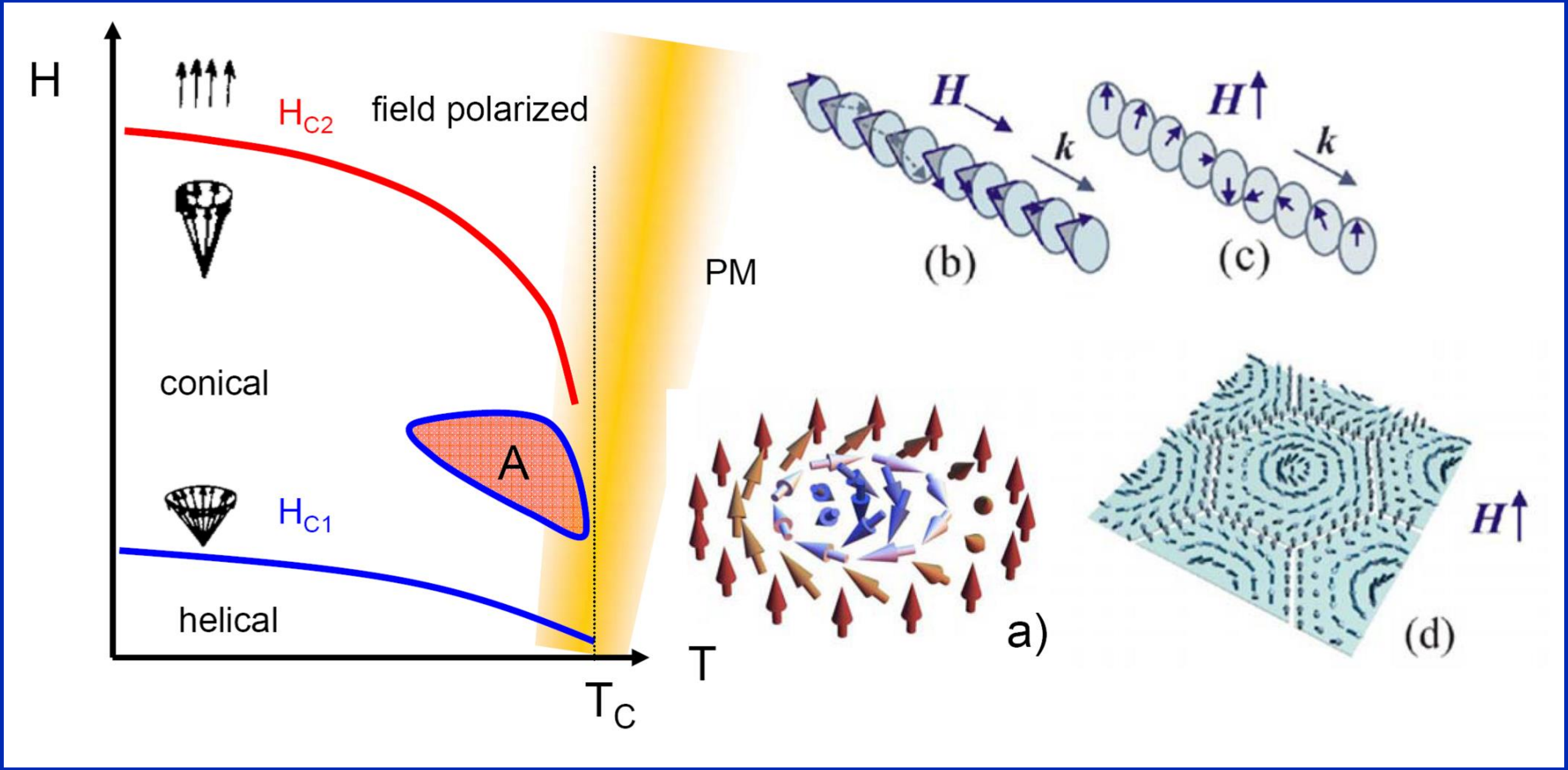


Mean field approximation:

Each moment experiences an additional "field" proportional to the magnetization due to the presence of all other moments.

$$H_{mf} = \lambda M$$

Helical order, skyrmions



$$H = J \sum S_i \cdot S_j + D \sum S_i \times S_j$$

e.g. MnSi, Cu_2OSeO_3

Image: https://www.cpfs.mpg.de/pqm/NMR-chiral-Baenitz

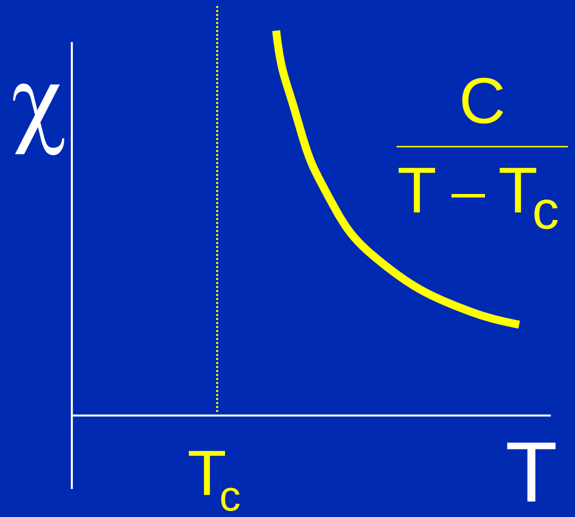
Mean field approach

Curie-Weiss Law

$T > T_c$: No ordering, paramagnetic

$$M = \chi_{para}(H_{ext} + H_{mf})$$

$$\chi = \frac{M}{H_{ext}} = \frac{C}{T}\frac{(H_{ext} + \lambda M)}{H_{ext}} = \frac{C}{T - C\lambda} = \frac{C}{T - T_c}$$



Curie-Weiss valid far above T_c
Close to T_c more precise calc:

$$\chi \propto (T - T_c)^{-\gamma} \qquad \gamma \approx 1.33$$

Mean field approach

$T < T_c$: Ordering, spontaneous ferromagnetic moment

For S=1/2 (Brouillin function, neglect external field):

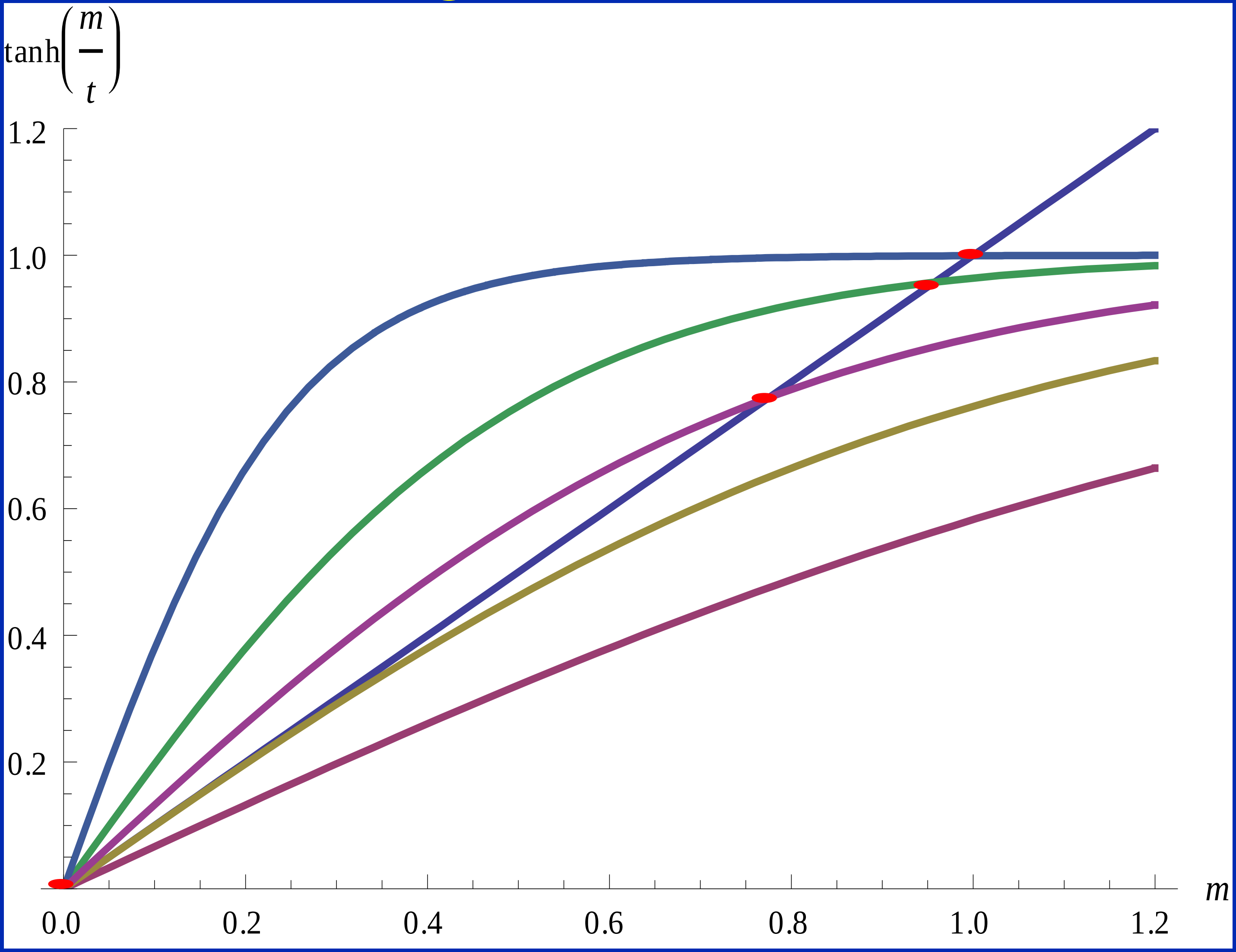
$$M = n\mu_B \tanh\left(\frac{\mu_B H}{kT}\right) = n\mu_B \tanh\left(\frac{\mu_B \lambda M}{kT}\right)$$

$$\left.\begin{aligned} t &= kT/\lambda n\mu_B{}^2 \\ m &= M/n\mu_B \end{aligned}\right\} \quad m = \tanh(m/t)$$

$$m/t \gg 1: \quad m = 1 - 2e^{-2m/t}$$

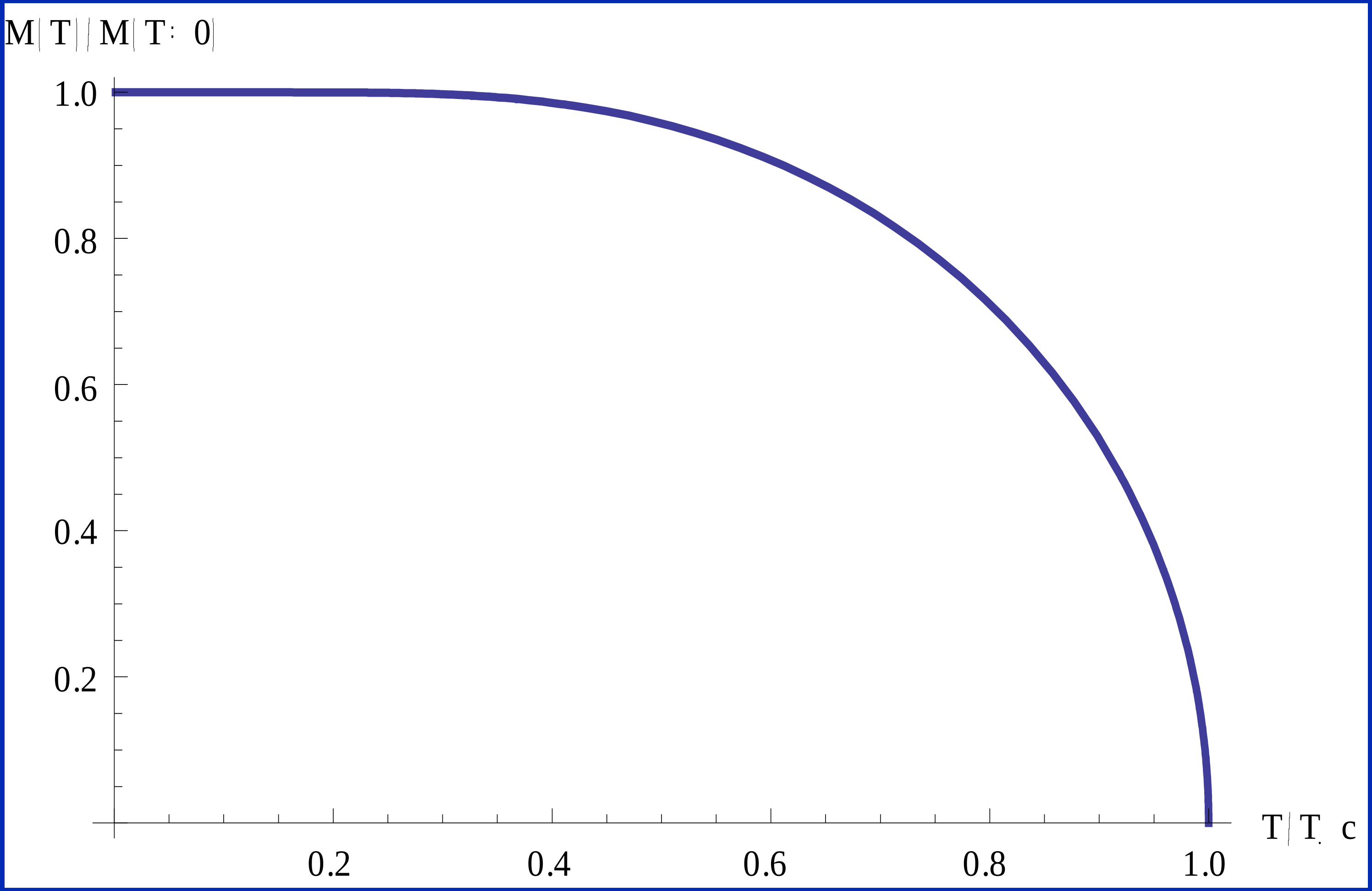
$$\rightarrow M = M(0) - 2n\mu_B e^{-2\lambda n\mu_B{}^2/kT}$$

Below T_C: Sponteneous order



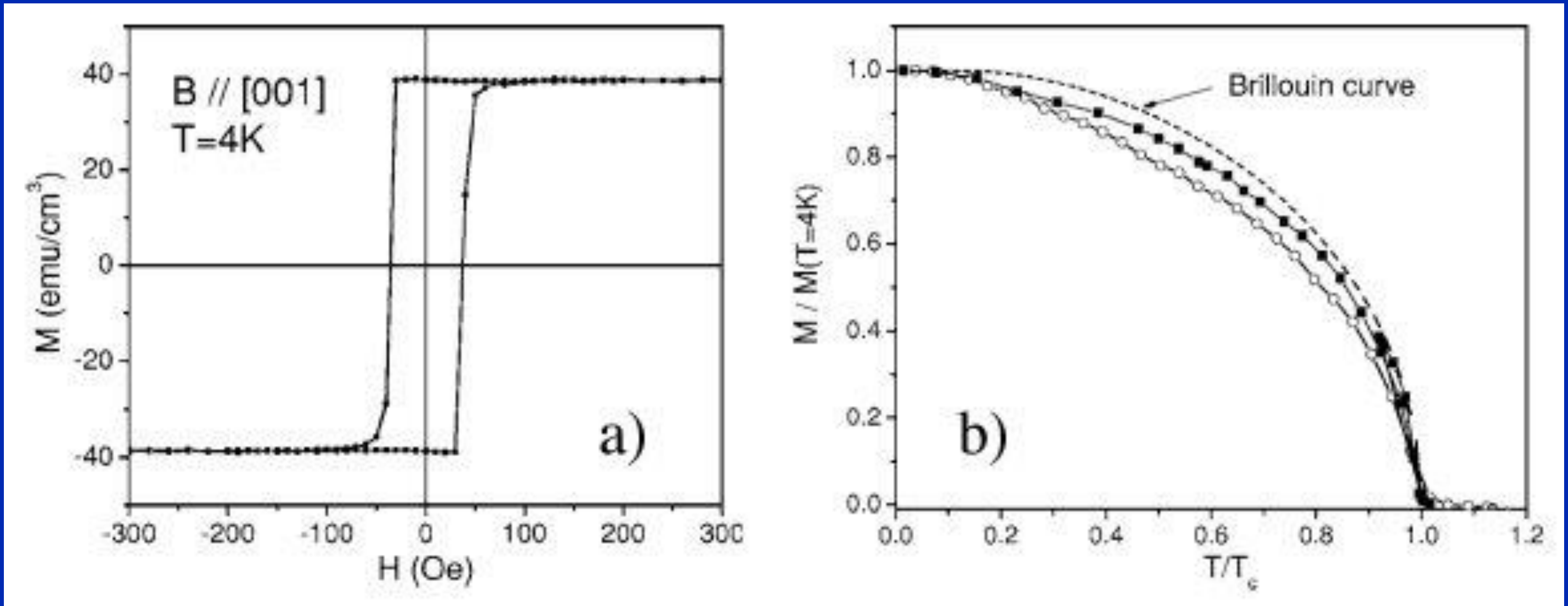
t
0.25
0.5
0.75
1
1.5

Below T_C: Sponteneous order



Numerically solved m=tanh(m/t)

Magnetization GaMnAs



Lemaitre et al., 2010