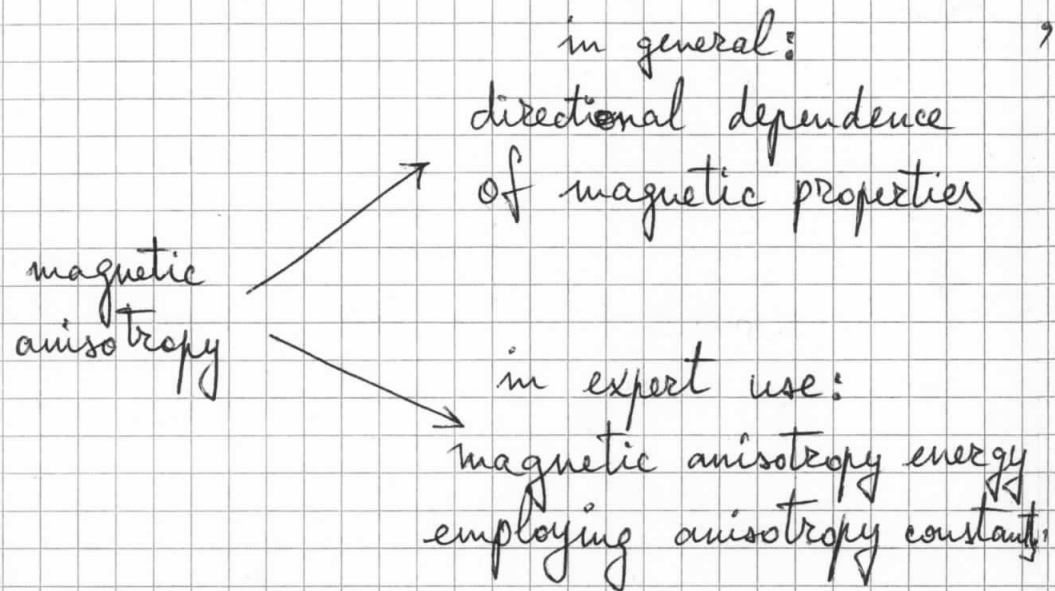


# Magnetic anisotropy and crystal el. field

## 1. Phenomenological description



Let all pre-conditions of equilibrium thermodynamics be fulfilled:

- \* the system is large,  $\log_{10} N \sim 23$
- \* the system is at thermal equilibrium
- \* all changes are quasi-stationary

The system is described by the free energy  $F(T, \vec{B}, \dots)$  —  
 a characteristic function of its arguments  
 — external parameters: temperature, magnetic field, (pressure etc.)

Internal parameters are expressed by equations of state:

$$S(T, \vec{B}, \dots) = - \left( \frac{\partial F}{\partial T} \right)_{\vec{B}} \quad \text{caloric EOS}$$

$$\vec{M}(T, \vec{B}, \dots) = - \left( \frac{\partial F}{\partial \vec{B}} \right)_T \quad \text{magnetic EOS}$$

Pairs of conjugate parameters:  
 $\vec{B} - \vec{M}$ ,  $T - S$ ,  $P - V$  etc.

This was the usual equilibrium thermodynamics.

An alternative formulation in terms of a non-equilibrium (with respect to  $\vec{M}$ ) thermodynamic potential  $\Phi(T, \vec{B}, \vec{M}, \dots)$ , such that

$$\min_{\vec{M}} \Phi(T, \vec{B}, \vec{M}, \dots) = F(T, \vec{B}, \dots)$$

$$\left( \frac{\partial \Phi}{\partial \vec{M}} \right)_{T, \vec{B}} = 0 \quad \text{magnetic EOS}$$

$$\left( \frac{\partial^2 \Phi}{\partial \vec{M}^2} \right)_{T, \vec{B}} > 0$$

An example (Landau's expansion):

$$\Phi = \Phi_0 + \frac{1}{2} a M^2 + \frac{1}{4} b M^4 + \dots - \vec{B} \cdot \vec{M}$$

the coefficients  $\Phi_0, a, b, \dots$  depend on temperature (pressure etc.) but not on  $\vec{B}$  or  $\vec{M}$ .

In fact,  $\vec{B}$  and  $\vec{M}$  are vectors -

3 pairs of conjugate variables:

$$B_x - M_x, \quad B_y - M_y, \quad B_z - M_z$$

So far the system was assumed isotropic

Let it now possess a ~~uniaxial~~ anisotropy

$$(x = y \neq z)$$

$$\Phi = \Phi_0 + \frac{1}{2} a_{\perp} (M_x^2 + M_y^2) + \frac{1}{2} a_{\parallel} M_z^2 + O(M^4) - \vec{B} \cdot \vec{M}$$

There are many phenomena where  $|\vec{M}| = M = \text{const.}$  From now on we restrict ourselves to just such phenomena.

\* the system is a ferromagnet at  $T \ll T_c$

\*  $B$  is not too strong:  $\mu_B B \ll kT_c$

Replace  $M_x$  in  $\Phi$  by  $M \sin\theta \cos\varphi$  etc.

$$\Phi = \Phi_0 + \frac{1}{2} a_{\parallel} M^2 + \underbrace{K_1 \sin^2\theta + \dots}_{\text{anisotropy energy}} - \vec{B} \cdot \vec{M}$$

$$\text{where } K_1 = \frac{a_{\perp} - a_{\parallel}}{2} M^2$$

is the anisotropy constant (called so because  $M = \text{const.}$ )

Since  $a_{\perp}$  and  $a_{\parallel}$  depend on  $T, P, \dots$  but not on  $\vec{B}$ , so does  $K_1$ .

Anisotropy energy is an expansion in even powers of  $\vec{n} \equiv \vec{M}/|\vec{M}|$ . The form of this expansion is determined by the symmetry (point group) of the system. Namely, only terms invariant under all symmetry transformations of the point group are permitted.

## Examples.

tetragonal point groups  $D_4, C_{4v}, D_{2d}, D_{4h}$ :

$$E_a = K_1 \sin^2 \theta \\ + K_2 \sin^4 \theta + K_2' \sin^4 \theta \cos 4\varphi \\ + K_3 \sin^6 \theta + K_3' \sin^6 \theta \cos 4\varphi + \dots$$

tetragonal point groups  $C_4, S_4, C_{4h}$ :

$$E_a = K_1 \sin^2 \theta \\ + K_2 \sin^4 \theta + K_2' \sin^4 \theta \cos 4\varphi + K_2'' \sin^4 \theta \sin 4\varphi \\ + K_3 \sin^6 \theta + K_3' \sin^6 \theta \cos 4\varphi + K_3'' \sin^6 \theta \sin 4\varphi + \dots$$

cubic point groups  $T_d, O, O_h$ :

$$E_a = K_1 (n_x^2 n_y^2 + n_y^2 n_z^2 + n_z^2 n_x^2) \\ + K_2 n_x^2 n_y^2 n_z^2 + \dots$$

The expansion for the cubic groups  $T$  and  $T_h$  contains an extra 6<sup>th</sup>-order term.

## Observations:

- \* Saying just "tetragonal" or "cubic" about the symmetry is not good enough.
- \* The tetragonal  $K_1$  is of 2<sup>nd</sup> order and has nothing to do with the cubic  $K_1$ , which is of 4<sup>th</sup> order.

Q. How many terms in the expansion one has to take?

Under the assumptions made ( $|\vec{M}| = \text{const.}, T \ll T_c$ ) the expansion for  $E_a$  does not generally converge.

(unlike in Landau's theory of second-order phase transitions, where  $T \rightarrow T_c, |\vec{M}| \rightarrow 0$ )

Possible reasons for convergence:

- \* weak spin-orbit coupling
- \* weak crystal field
- \* 'high' temperature <sup>still</sup> ( $T \ll T_c$ )

Truncation of the expansion must be justified in each individual case.

## 2. Crystal (electric) field

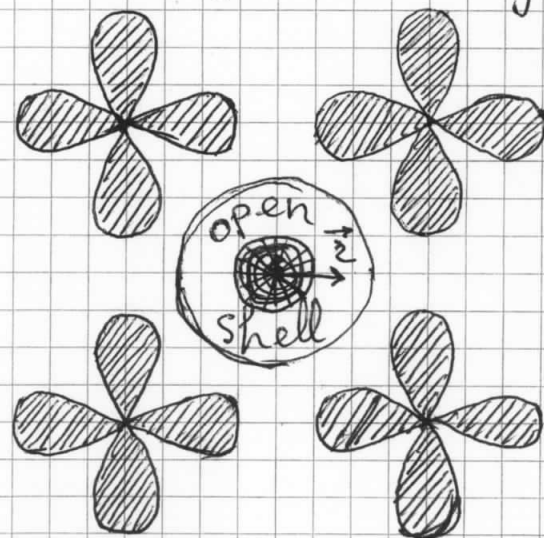
Consider a crystal containing atoms with an unclosed electron shell (d or f). For one of such atoms one writes

$$H_{\text{CF}} = -e \sum_i V(\vec{r}_i)$$

summation over all electrons of the open shell

$V(\vec{r})$  satisfies Poisson's equation:

$$\Delta V(\vec{r}) = -4\pi \rho_{\text{ligand}}(\vec{r})$$



There is no overlap:  $\text{ligand}(\vec{r}) = 0$   
 for  $\vec{r}$  inside the open shell,  $\Rightarrow$   
 $V(\vec{r})$  satisfies Laplace's equation,  $\Delta V = 0$ .  
 Therefore  $V(\vec{r})$  can be expanded in a series

$$-eV = \sum_{n=0}^{\infty} \sum_{m=-n}^n A_{nm} r^n C_{nm}(\theta, \varphi)$$

↑  
CF parameters

$$C_{nm}(\theta, \varphi) = \sqrt{\frac{4\pi}{2n+1}} Y_{nm}(\theta, \varphi)$$

↑  
irreducible  
tensor operators

↑  
spherical  
harmonics

$C_{nm}(\theta, \varphi)$  are more convenient than  $Y_{nm}(\theta, \varphi)$

Examples:

$$C_{20}(\theta, \varphi) = \frac{3}{2} \cos^2 \theta - \frac{1}{2}$$

$$C_{2\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{3}{2}} \sin \theta \cos \theta e^{\pm i\varphi}$$

$$C_{2\pm 2}(\theta, \varphi) = \frac{1}{2} \sqrt{\frac{3}{2}} \sin^2 \theta e^{\pm i2\varphi}$$

in general,

$$C_{nm}(\theta, \varphi) = f_{nm}(\theta) e^{im\varphi}$$

where  $f_{nm}(\theta)$  is real

Normalisation:

$$C_{n0}(0, \varphi) = 1$$

Harmonicity ( $\Delta V = 0$ ):

$$z^2 C_{20}(\theta, \varphi) = z^2 - \frac{1}{2} x^2 - \frac{1}{2} y^2$$

$$z^2 C_{2\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{3}{2}} z(x \pm iy)$$

etc.

Let us restrict the space of states under consideration to just the open shell,  $|lm\rangle$  with  $l=3$  (f) or  $l=2$  (d).

The relevant matrix elements are

$$\langle r^n \rangle \langle lm' | C_{nm}(\theta, \varphi) | lm'' \rangle$$

Many of them equal zero.

Parity:

$$\langle lm' | C_{nm}(\theta, \varphi) | lm'' \rangle = 0 \quad \text{for } n \text{ odd}$$

Triangle rule for  $(lnl)$ :

$$\langle lm' | C_{nm}(\theta, \varphi) | lm'' \rangle = 0 \quad \text{if } n > 2l$$

Observation:

the summation over  $n$  can be limited to  $n=2, 4, 6$  (f elements) or  $n=2, 4$  (d elements).

Selection rule for the projections:

$$\langle lm' | C_{nm}(\theta, \varphi) | lm'' \rangle = 0 \quad \text{if } m+m'' \neq m'$$

$$\begin{array}{ccc} \downarrow & \downarrow & \downarrow \\ e^{-im'\varphi} & e^{im\varphi} & e^{-im''\varphi} \end{array}$$

Observation:  $C_{n0}(\theta, \varphi)$  are diagonal in the  $lm$  representation,  $C_{nm}(\theta, \varphi)$  with  $m \neq 0$  have only off-diagonal matrix elements

\* \* \*

Let us restrict the space of accessible states to just the ground multiplet,  $|JM\rangle$ ,  $M = -J, \dots, J$  ( $2J+1$  states in all)

We now seek

$$\langle JM' | C_{nm}(\theta, \varphi) | JM \rangle$$

Define equivalent operators  $C_{nm}(\hat{J})$  as follows

1. Convert  $z^n C_{nm}(\theta, \varphi)$  to Cartesian coordin.

$$\text{e.g. } z^2 C_{2\pm 1}(\theta, \varphi) = \mp \sqrt{\frac{3}{2}} z (x \pm iy)$$

2. Replace  $x, y, z$  by  $\hat{J}_x, \hat{J}_y, \hat{J}_z$  respectively  
replace  $z^2$  by  $J(J+1)$ .

$$\longrightarrow \mp \sqrt{\frac{3}{2}} \hat{J}_z (\hat{J}_x \mp i \hat{J}_y)$$

3. Symmetrise non-commuting operators

$$C_{2\pm 1}(\hat{J}) = \mp \frac{1}{2} \sqrt{\frac{3}{2}} \left[ (\hat{J}_x \pm i \hat{J}_y) \hat{J}_z + \hat{J}_z (\hat{J}_x \pm i \hat{J}_y) \right]$$

Theorem:

$$\langle JM' | C_{nm}(\theta, \varphi) | JM \rangle = \theta_n \langle JM' | C_{nm}(\hat{J}) | JM \rangle$$

↑  
Stevens' factors (tabulated)

The selection rule for the projections holds:  
 $M' = m + M$ . Therefore,  $C_{n0}(\hat{J})$  are diagonal in the JM representation.

$$C_{20}(\hat{J}) = \frac{3}{2} \hat{J}_z^2 - \frac{1}{2} J(J+1)$$

$$C_{40}(\hat{J}) = \frac{35}{8} \hat{J}_z^4 - \left[ \frac{15}{4} J(J+1) - \frac{25}{8} \right] \hat{J}_z^2 - \frac{3}{4} J(J+1) + \frac{3}{8} J^2(J+1)^2 \text{ etc.}$$

The matrix elements are obtained through the substitution of  $M$  for  $\hat{J}_z$ :

$$\langle JM | C_{20}(\hat{J}) | JM \rangle = \frac{3}{2} M^2 - \frac{1}{2} J(J+1)$$

$$\langle JM | C_{40}(\hat{J}) | JM \rangle = \frac{35}{8} M^4 - \left[ \frac{15}{4} J(J+1) - \frac{25}{8} \right] M^2 - \frac{3}{4} J(J+1) + \frac{3}{8} J^2(J+1)^2 \text{ etc.}$$



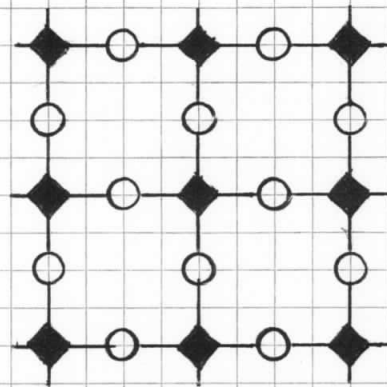
We have seen that the outer sum in the CF Hamiltonian was taken over  $n=2,4,6$  (for the rare earths). As regards  $m$ , it was supposed to run from  $-n$  to  $n$ , i.e. there are  $2n+1$  values of  $m$  for each  $n$ . That makes a total of 27 CF parameters ( $5+9+13$ ).

In actual fact, this number is reduced by the symmetry. Namely,  $A_{nm}$  is nonzero only if the corresponding term is invariant under all symmetry transformations of the local point group of the lattice site occupied by the rare earth.

The local point group should be distinguished from the global one (= ~~symmetry~~ <sup>crystallographic</sup> class). The local symmetry cannot be higher than the global one (but can be lower).

Examples:

\* the lattice as a whole has a 4-fold symmetry axis and so do the dark diamonds but not the open circles.



\* tetragonal point groups  $D_4, C_{4v}, D_{2d}, D_{4h}$

$$\begin{aligned}
 H_{CF} = & A_{20} \langle 2^2 \rangle C_{20}(\theta, \varphi) + A_{40} \langle 2^4 \rangle C_{40}(\theta, \varphi) \\
 & + A_{44} \langle 2^4 \rangle [C_{44}(\theta, \varphi) + C_{4-4}(\theta, \varphi)] \\
 & + A_{60} \langle 2^6 \rangle C_{60}(\theta, \varphi) \\
 & + A_{64} \langle 2^6 \rangle [C_{64}(\theta, \varphi) + C_{6-4}(\theta, \varphi)]
 \end{aligned}$$

## Observations:

- \* invariant are the sums  $C_{nm} + C_{n-m}$  rather than individual terms
- \* if all the terms are expressed in trigonometric functions, one obtains an expression similar to  $E_a(\theta, \varphi)$  for the same symmetry group.

## 3. The single-ion model

Consider a lattice containing rare earth atoms exposed to an exchange field  $\vec{B}_{ex}$ . The latter may originate from the same atoms or from a different magnetically ordered species, such as 3d atoms (Fe or Co). The following Hamiltonian describes a single rare earth atom (ion):

$$\hat{H} = 2\mu_B \vec{B}_{ex} \cdot \hat{S} + \hat{H}_{CF}$$

Project  $\hat{H}_{CF}$  onto the ground  $J$  multiplet. Note that  $\hat{S} = (2\hat{S} + \hat{L}) - (\hat{S} + \hat{L}) \doteq g_J \hat{J} - \hat{J}$ .

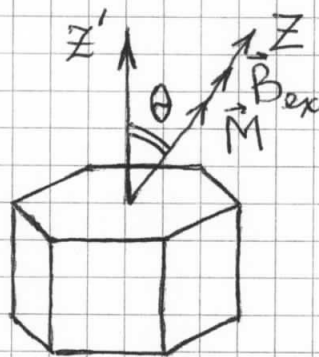
$$\hat{H} = 2(g_J - 1)\mu_B \vec{B}_{ex} \cdot \hat{J} + \sum_n \sum_m B_{nm} C_{nm}(\hat{J})$$

$$n = 2, 4, 6$$

$m$  adapted to the symmetry

$$B_{nm} = \theta_n \langle r^n \rangle A_{nm}$$

direct Z axis  
(non-primed)  
along  $\vec{B}_{ex} \parallel \vec{M}$



$$\hat{H} = 2(g_J - 1) \mu_B B_{ex} \hat{J}_Z + \underbrace{\sum_n \sum_m B_{nm} C_{nm}(\hat{J}')}_{\hat{H}_{cf}, \text{ perturbation}}$$

unperturbed eigenstates:  $|JM\rangle$ ,  $M = -J, \dots, J$   
 —||— eigenenergies:  $2(g_J - 1) \mu_B B_{ex} M$

Partition function:

$$Z = \sum_M \exp\left(-\frac{2(g_J - 1) \mu_B B_{ex} M}{kT}\right)$$

$$= \sum_M \exp\left(-\frac{x}{J} M\right) = \frac{\sinh\left(\frac{2J+1}{2J} x\right)}{\sinh\left(\frac{x}{2J}\right)}$$

where  $x = \frac{2J(g_J - 1) \mu_B B_{ex}}{kT}$

1<sup>st</sup>-order corrections to  $F = -kT \ln Z$ :

$$E_a = \langle \hat{H}_{cf} \rangle = \frac{1}{Z} \sum_M \langle JM | \hat{H}_{cf} | JM \rangle \exp\left(-\frac{x}{J} M\right)$$

$\hat{H}_{cf}$  was written in the crystallographic (primed) coordinate system, in order to take full advantage of the symmetry. Now, for averaging over  $|JM\rangle$ , it needs to be transformed into the exchange field-related (non-primed) coordinate system, which has the advantage that  $\langle C_{nm}(\hat{J}) \rangle = 0$  for  $m \neq 0$ .

$$C_{nm}(\hat{J}') = C_{nm}(\theta, \varphi) C_{n0}(\hat{J})$$

+ terms in  $C_{nm'}(\hat{J})$ ,  $m' \neq 0$

orientation angles of  $\vec{M}$   
with respect to  $x', y', z'$

Hence

$$E_a = \sum_n \sum_m B_{nm} C_{nm}(\theta, \varphi) \langle C_{no}(\hat{J}) \rangle$$

We use the identity

$$\langle (-\hat{J}_z)^n \rangle = \frac{1}{Z} \sum_M (-M)^n \exp\left(-\frac{x}{J} M\right) = \frac{1}{Z} \frac{\partial^n Z}{\partial (x/J)^n}$$

to find

$$\langle -\hat{J}_z \rangle = \frac{2J+1}{2} \coth\left(\frac{2J+1}{2J} x\right) - \frac{1}{2} \coth\left(\frac{x}{2J}\right)$$

$$= J B_J(x)$$

Brillouin function

$$\langle C_{20}(\hat{J}) \rangle = \frac{3}{2} \langle \hat{J}_z^2 \rangle - \frac{1}{2} J(J+1)$$

$$= J(J+1) - \frac{3}{2} J \coth\left(\frac{x}{2J}\right) B_J(x) = J^2 B_J^{(2)}(x)$$

2<sup>nd</sup>-order generalised Brillouin function  
(K. Yoshida, 1951)

In general,

$$\langle C_{no}(\hat{J}) \rangle = J^n B_J^{(n)}(x)$$

↑  
generalised Brillouin function  
(known explicitly)

Observation.

For  $B_J^{(4)}(x)$  one needs to find  $\langle \hat{J}_z^4 \rangle$   
in addition to the already known  $\langle \hat{J}_z^2 \rangle$ , etc.

Final result:

$$E_a = \sum_n \sum_m J^n B_{nm} B_J^{(n)}(x) C_{nm}(\theta, \varphi) \\ = \sum_n \sum_m x_{nm} C_{nm}(\theta, \varphi)$$

where

$$x_{nm} = J^n B_{nm} B_J^{(n)}(x)$$

anisotropy  
constants

$$n = 2, 4, 6$$

m according to the symmetry

$E_a$  can be recast in the more conventional form, in terms of trigonometric functions.

Thus,

$$C_{20}(\theta, \varphi) = 1 - \frac{3}{2} \sin^2 \theta$$

$$C_{40}(\theta, \varphi) = 1 - 5 \sin^2 \theta + \frac{35}{8} \sin^4 \theta$$

$$C_{44}(\theta, \varphi) + C_{4-4}(\theta, \varphi) = \sqrt{\frac{35}{32}} \sin^4 \theta \cos 4\varphi$$

etc.

The resulting expressions for the  $K$ 's are non-universal and convention-dependent. For example, one has for the tetragonal point groups  $D_4$ ,  $C_{4v}$ ,  $D_{2d}$ ,  $D_{4h}$ :

$$K_1 = -\frac{3}{2} J^2 B_{20} B_J^{(2)}(x) - 5 J^4 B_{40} B_J^{(4)}(x) - \frac{21}{2} J^6 B_{60} B_J^{(6)}(x)$$

$$K_2 = \frac{35}{8} J^4 B_{40} B_J^{(4)}(x) + \frac{189}{8} J^6 B_{60} B_J^{(6)}(x)$$

$$K_3 = -\frac{231}{16} J^6 B_{60} B_J^{(6)}(x)$$

$$K'_2 = \sqrt{\frac{35}{32}} J^4 B_{44} B_J^{(4)}(x) + 15 \sqrt{\frac{7}{32}} J^6 B_{64} B_J^{(6)}(x)$$

$$K'_3 = -33 \sqrt{\frac{7}{128}} J^6 B_{64} B_J^{(6)}(x)$$

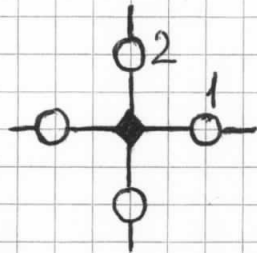
## Observations

- \* The anisotropy constants above are normalised per 1 rare earth atom.
- \* They have been obtained in an approximation linear in  $B_{nm}$ . It requires that the CF be small in comparison with the exchange,  $|B_{nm}| \ll \mu_B B_{ex}$  (an exchange-dominated system).
- \* The condition  $|\vec{M}| = \text{const.}$  is fulfilled in zeroth approximation.
- \* It has been tacitly assumed that the local ( $\hat{H}_{CF}$ ) and global ( $E_a$ ) symmetry is the same. Hence the one-to-one correspondence between  $B_{nm}$  and  $x_{nm}$ . If the local symmetry is lower, there are more  $B_{nm}$ 's than  $x_{nm}$ 's. There will also be multiple rare earth sites in the elementary cell.

Those  $B_{nm}$  which are allowed by the global symmetry have the same value for all the sites. Those  $B_{nm}$  that are allowed locally but forbidden globally have different values for different (equivalent!) sites, so that the sum over the cell is zero.

in this example

$$B_{22}(1) = -B_{22}(2)$$



\* Crystallographically non-equivalent sites have distinct  $B_{nm}$ 's. Appropriate average values enter into the expressions for the anisotropy constants.

### 3a. Properties of generalised Brillouin functions

\* parity:  $B_J^{(n)}(-x) = (-1)^n B_J^{(n)}(x)$

\* for  $x$  small,  $B_J^{(n)}(x) \approx \text{const. } x^n$

\* monotonicity in the 1<sup>st</sup> quadrant

\*  $\lim_{x \rightarrow +\infty} B_J^{(n)}(x) = \frac{(2J)!}{(2J)^n (2J-n)!}$

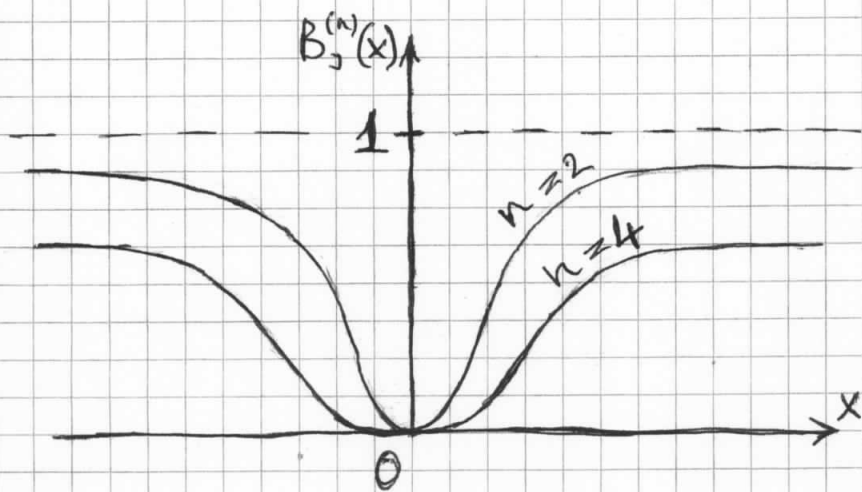
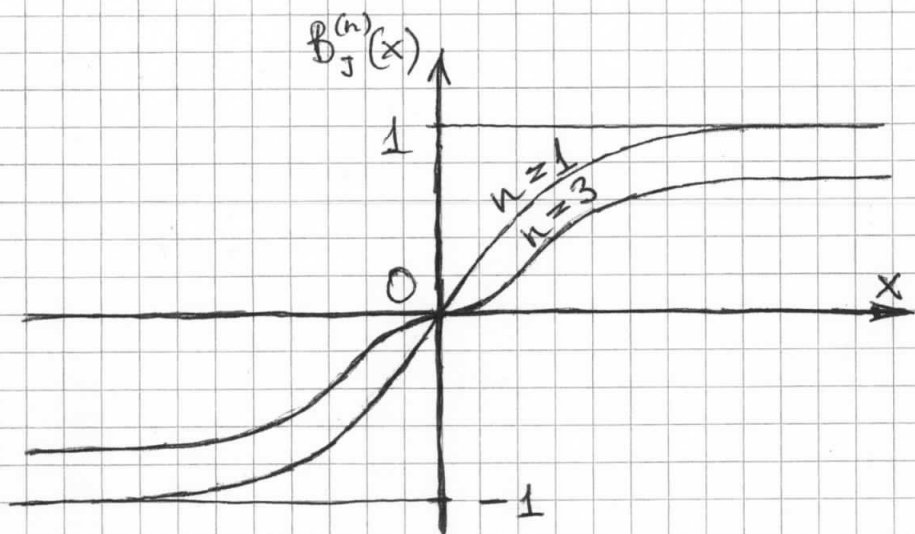
$$= \left(1 - \frac{1}{2J}\right) \left(1 - \frac{2}{2J}\right) \dots \left(1 - \frac{n-1}{2J}\right)$$

hence follows a triangle rule for  $(J, n, J)$ :

$$B_J^{(n)}(x) \equiv 0 \quad \text{if } n > 2J$$

Proof:

if  $n = 2J + 1$ , the last parenthesis is zero.  
 if  $n = 2J + 2$ , the last but one parenthesis is zero, etc.



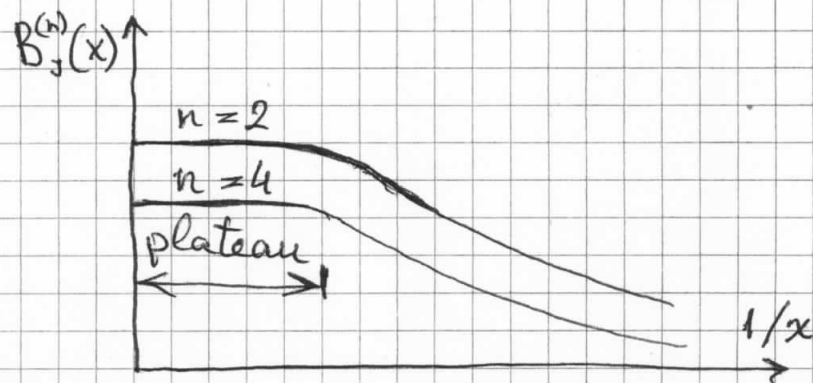
### 36. Low-temperature behaviour

$$\frac{1}{x} \approx T \rightarrow 0, \quad x \rightarrow +\infty$$

for  $x \gg J$

$$B_J^{(n)}(x) \approx \frac{(2J)!}{(2J)^n (2J-n)!} \left[ 1 - \frac{n(n+1)}{2J} \exp\left(-\frac{x}{J}\right) \right]$$

exponential approach to saturation



One can therefore speak about low-temperature values of anisotropy constants without specifying the exact  $T$ .

At low temperatures

$$|x_{2m}| \sim |x_{4m}| \sim |x_{6m}|$$

or (in uniaxial crystals)

$$|K_1| \sim |K_2| \sim |K_3|$$

There is no valid physical reason for neglecting 6<sup>th</sup> or 4<sup>th</sup>-order anisotropy constants ( $K_3$  and  $K_2$ , respectively).

Low-temperature anisotropy constants for a given  $J$  are linear functions of  $B_{nm}$ 's with constant coefficients.

### 3c. High-temperature behaviour

$$T \gtrsim 300 \text{ K} \quad (\text{relevant to applications})$$

Strictly speaking, it must be

$$T \gg \frac{2|g_J - 1| \mu_B B_{ex}}{k} \sim 300 \text{ K}$$

$$x \text{ small, } B_J^{(n)}(x) \approx \text{const. } x^n$$

$$B_J^{(2)}(x) \gg B_J^{(4)}(x) \gg B_J^{(6)}(x)$$

In uniaxial systems (permanent magnets)

$$E_a = K_1 \sin^2 \theta$$

$$\text{where } K_1 = -\frac{3}{2} J^2 B_{20} B_J^{(2)}(x)$$

all higher-order  $K$ 's can be neglected.  $B_{20}$  plays a very special role among the crystal field parameters. An insufficient  $B_{20}$  cannot be made up for by any other crystal field parameter.

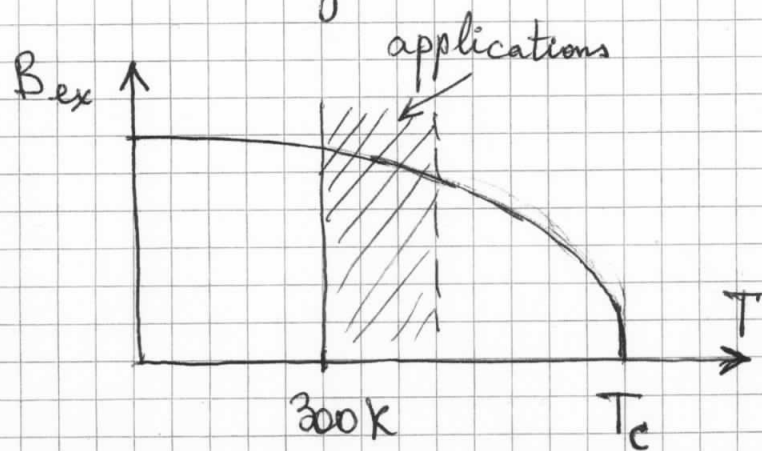


Q. What other factors affect the anisotropy at  $T \gtrsim 300$  K?

$$K_1 \propto B_{20} B_J^{(2)}(x) \propto B_{20} x^2 \propto B_{20} \left( \frac{\mu_B B_{ex}}{kT} \right)^2$$

$B_{ex}$  is even more important than  $B_{20}$

N.B.  $B_{ex}$  depends on  $T$ , but not much, as long as  $T \ll T_c$



Asymptotic correctness of the linear theory at high  $T$ . Our main result,

$$\chi_{nm} = J^n B_{nm} B_J^{(n)}(x)$$

is an approximate one.

If the condition  $|B_{nm}| \ll \mu_B B_{ex}$  is not quite satisfied, corrections of higher orders in  $B_{nm}$  will come into play (quadratic, cubic, etc.).

At high  $T$  (small  $x$ )

$$\chi_{nm} = \text{const.} B_{nm} \left( \frac{\mu_B B_{ex}}{kT} \right)^n + o\left( \frac{1}{(kT)^n} \right)$$

It can be proved rigorously that the non-linear in  $B_{nm}$  corrections do not affect the leading term in the high-temperature expansion. This term, including the prefactor, is given by the linear theory exactly.

Conclusion. The higher the temperature, the more accurate is the linear-in- $B_{nm}$  approximation. The non-linear corrections die out with temperature more rapidly than the leading term, linear in  $B_{nm}$ .



Equation for spontaneous magnetisation:

$$M = M_0 B_J \left( \frac{\mu \lambda M}{kT} \right) \quad (\text{implicit})$$

Parametric description

\* start from

$$M = M_0 B_J(x) \quad (1)$$

$$x = \frac{\mu \lambda M}{kT} \quad (2)$$

\* solve Eq. (2) for T:

$$T = \frac{\mu \lambda M}{kx}$$

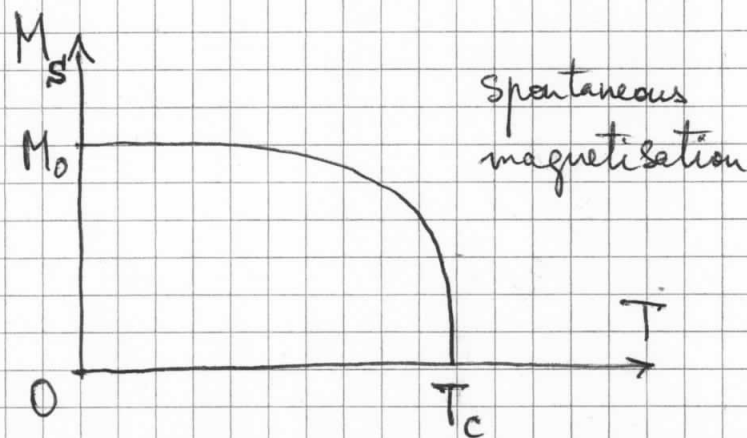
\* eliminate M using Eq. (1),  
take (1) as a second equation

$$T = \frac{\mu \lambda M_0 B_J(x)}{kx}$$

$$M_s = M_0 B_J(x)$$

x is a parameter running from 0 to  $\infty$

x	T	M <sub>s</sub>
0	T <sub>c</sub>	0
⋮	⋮	⋮
∞	0	M <sub>0</sub>



Condition for T<sub>c</sub>:

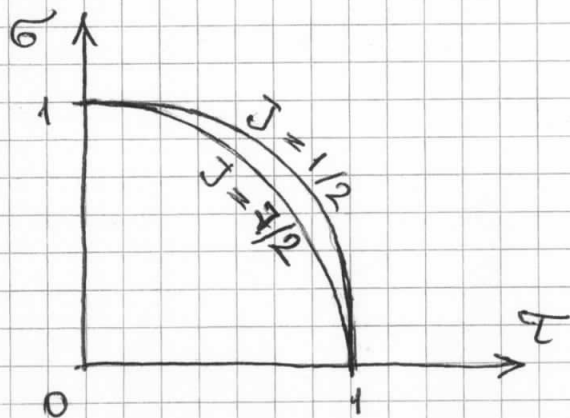
$$x \rightarrow 0, \quad B_J(x) \approx \frac{J+1}{3J} x$$

$$T_c = \frac{J+1}{3J} \frac{\mu \lambda M_0}{k}$$

Reduced form ( $\sigma = M/M_0$ ,  $\tau = T/T_0$ ):

$$\tau = \frac{3J}{J+1} \frac{B_J(x)}{x}$$

$$\sigma = B_J(x)$$



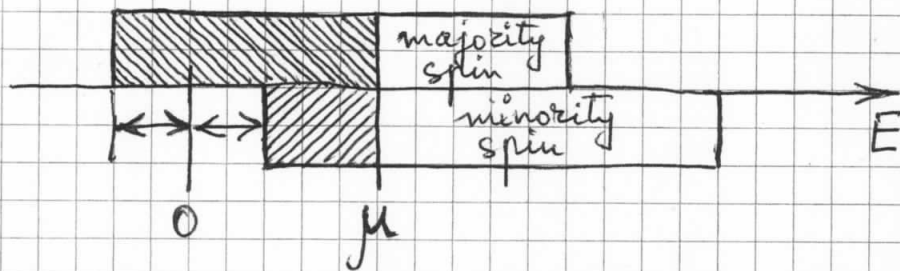
Special case of  $J=1/2$ :

$$\tau = \frac{\tanh x}{x}$$

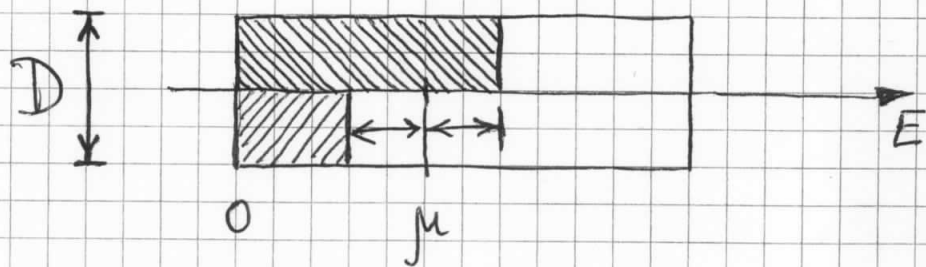
$$\sigma = \tanh x$$

## Itinerant (Stoner's) molecular field theory

For simplicity, rectangular bands,  $D(E) \equiv \text{const}$   
 Rigid bands, a common chemical potential  $\mu$   
 Band shift =  $\mp \mu_B \lambda M$  ← molecular field



Equivalent picture: no band shift,  
 but rather  $\mu \rightarrow \mu \pm \mu_B \lambda M$



Advantage: a common zero at the bottom  
 of the band (upper limit =  $\infty$ ).

Electron numbers in the two spin subbands  
(Fermi distribution):

$$N_{\pm} = \frac{D}{2} \int_0^{\infty} \frac{dE}{\exp\left(\frac{E - \mu \mp \mu_B \lambda M}{kT}\right) + 1}$$

$$= \frac{DkT}{2} \ln \left[ 1 + \exp\left(\frac{\mu \pm \mu_B \lambda M}{kT}\right) \right]$$

$$= \frac{DkT}{2} \ln (1 + e^{y \pm x})$$

where

$$x = \frac{\mu_B \lambda M}{kT} \quad (*)$$

$$y = \frac{\mu}{kT}$$

2 Conditions:

$$DE_F = N_+ + N_- \quad \text{total No. of electron}$$

$$M = \frac{\mu_B}{V} (N_+ - N_-) \quad \text{magnetisation}$$

$$DE_F = \frac{DkT}{2} \ln [(1 + e^{y+x})(1 + e^{y-x})] \quad (1)$$

$$M = \frac{\mu_B DkT}{2V} \ln \left( \frac{1 + e^{y+x}}{1 + e^{y-x}} \right) \quad (2)$$

Eliminate unknown  $y$  by solving (1) for  $e^y$ ,

$$e^y = \sqrt{\sinh^2 x + \exp\left(\frac{2E_F}{kT}\right)} - \cosh x$$

and setting this into (2). The result is

$$kT = \frac{E_F}{\ln\left(\frac{\sinh x}{\sinh \lambda x}\right)} \quad (3)$$

where

$$\Lambda = 1 - \frac{V}{\mu_B^2 \lambda D} = 1 - \frac{1}{ID}$$

$$I = \frac{\mu_B^2}{V} \lambda \quad \text{Stoner's exchange parameter}$$

For ferromagnets,  $ID > 1$  (Stoner's criterion)

$$\Rightarrow 0 < \Lambda < 1$$

$\Lambda$  can be interpreted as a measure of localisation. For example:

$$\text{Fe: } \Lambda \approx 0.3$$

$$\text{Ni: } \Lambda \approx 0.5$$

A second parametric equation is obtained by expressing  $M$  from Eq. (\*),

$$M = \frac{x kT}{\mu_B \lambda}$$

and eliminating  $kT$  by means of Eq. (3):

$$kT = \frac{E_F}{\ln\left(\frac{\sinh x}{\sinh \Lambda x}\right)} \quad (3)$$

$$M = \frac{E_F}{\mu_B \lambda} \frac{x}{\ln\left(\frac{\sinh x}{\sinh \Lambda x}\right)} \quad (4)$$

The parameter  $x$  runs from 0 to  $\infty$ .

Taking the limit  $x \rightarrow 0$  in Eq. (3) yields

$$kT_c = \frac{E_F}{-\ln \Lambda}$$

$$T_c \sim E_F/k \sim 10^4 \text{ K} \quad \text{too high!}$$

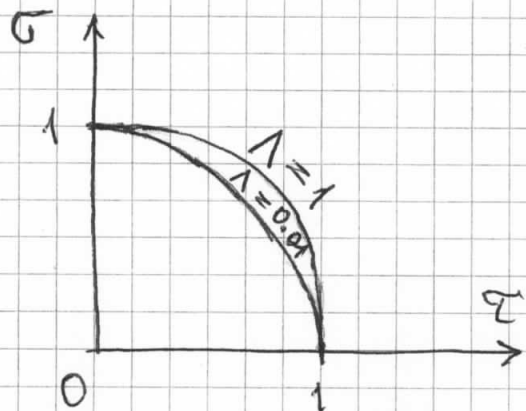
Taking the limit  $x \rightarrow \infty$  in Eq. (4) yields

$$M_0 = \frac{E_F}{\mu_B \lambda (1-\Lambda)} = \frac{\mu_B E_F D}{V}$$

Rewrite Eqs. (3,4) in reduced variables,  $\tau = T/T_c$  and  $\sigma = M/M_0$ :

$$\tau = \frac{-\ln \Lambda}{\ln\left(\frac{\sinh x}{\sinh \Lambda x}\right)}$$

$$\sigma = \frac{(1-\Lambda)x}{\ln\left(\frac{\sinh x}{\sinh \Lambda x}\right)}$$



Fe ( $\Lambda \approx 0.3$ ) and Ni ( $\Lambda \approx 0.5$ ) are indistinguishable from  $\Lambda = 1$ .

In the limit of full localisation ( $\Lambda \rightarrow 1$ ) one obtains

$$\tau = \frac{\tanh x}{x}$$

$$\sigma = \tanh x$$

This is the localised theory for  $J = 1/2$ .

## Critique of the molecular field theory

(a) At low temperatures ( $x \gg J$ )

$$T \approx \frac{\mu \lambda M_0}{kx}$$

$$M_s \approx M_0 \left[ 1 - \frac{1}{J} \exp\left(-\frac{x}{J}\right) \right]$$

$$= M_0 \left[ 1 - \frac{1}{J} \exp\left(-\frac{\mu \lambda M_0}{JkT}\right) \right]$$

exponential approach to saturation - incorrect  
In reality, Bloch's  $\frac{3}{2}$  power law is valid:

$$M_s \approx M_0 \left( 1 - \text{const. } T^{3/2} \right)$$

This is obtained in the spin-wave theory (leading to a low-temperature expansion) or from a self-consistent equation (Tyabliko)

The latter yields  $M_s$  at arbitrary  $T$  and the asymptotic behaviour at  $T \rightarrow 0$  is correct.

(b) near the Curie point:  $x \rightarrow 0$   
 $\tau = \frac{T}{T_c} \rightarrow 1$

$$\sigma \approx \left[ \frac{10}{3} \frac{(J+1)^2}{(J+1)^2 + J^2} \right]^{1/2} (1-\tau)^{1/2}$$

(localised)

$$\sigma \approx \left( \frac{\Lambda-1}{\Lambda+1} \frac{6}{\ln \Lambda} \right)^{1/2} (1-\tau)^{1/2}$$

(itinerant)

In either case,

$$\sigma \approx \text{const.} (1-\tau)^\beta$$

$$\beta = 1/2$$

In experiment,  $\beta \approx 1/3$  approx.,  
but no true power-law behaviour.

No microscopic theory can explain this

Landau's theory of 2<sup>nd</sup>-order phase transitions

thermodynamic potential:

$$\Phi = \Phi_0 + \frac{1}{2} a M^2 + \frac{1}{4} b M^4 + \frac{1}{6} c M^6 + \dots - \vec{H} \cdot \vec{M}$$

condition for equilibrium (at  $H=0$ ):

$$a M + b M^3 + c M^5 + \dots = 0$$

The theory is limited to  $T \approx T_c$ ,  
the series converges because  $M \rightarrow 0$ .

There is a trivial solution,  $M=0$ , whose  
stability is decided by the sign of  $a$   
So we set  $a = a_0 (T - T_c)$   $\left( = \frac{\partial^2 \Phi}{\partial M^2} \Big|_{M=0} \right)$

In addition, we assume that  $a_0 > 0$   
(FM at  $T < T_c$ , PM at  $T > T_c$ )



(i)  $b > 0$  "normal" case in Landau's theory  
 a 2<sup>nd</sup>-order phase transition at  $T = T_c$

$$M \equiv 0, \quad \text{at } T > T_c$$

$$M = \left(\frac{a_0}{b}\right)^{1/2} (T_c - T)^{1/2}, \quad \text{at } T \leq T_c$$

that is,

$$M = \text{const.} (1 - \tau)^\beta$$

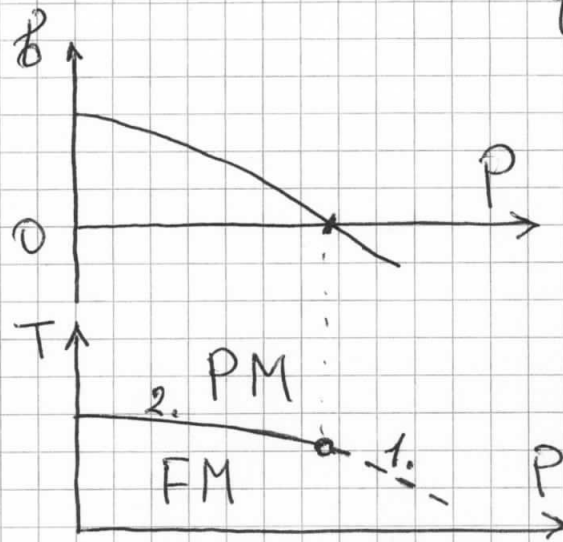
$$\beta = 1/2$$

(ii)  $b < 0, c > 0$

a 1<sup>st</sup>-order transition takes place  
 (not considered further)

(iii)  $b = 0, c > 0$

special case  
 tricritical point



$$M \equiv 0, \quad T > T_c$$

$$M = \left(\frac{a_0}{c}\right)^{1/4} (T_c - T)^{1/4}, \quad T \leq T_c$$

i.e.  $\beta = 1/4$

If  $b = 0$ , by the symmetry, the system belongs to a distinct universality class.

Even more exotic universality classes are possible within Landau's theory:  $\beta = 1/6, 1/8$  etc

Real ferromagnets:  $b > 0$  but small

$$a_0(T - T_c) + bM^2 + cM^4 = 0$$

The last term can be neglected only in the limit  $M \rightarrow 0$ ; then  $\beta = 1/2$

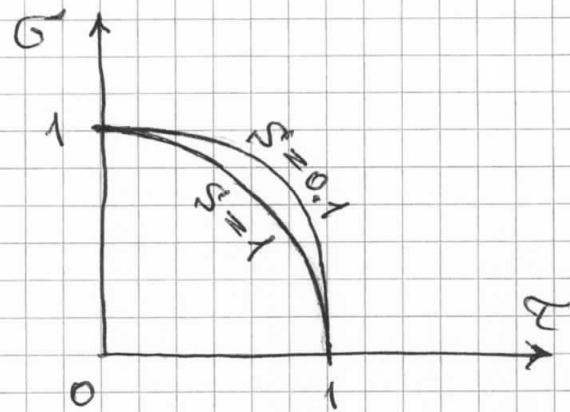
(asymptotic regime, not attained experimentally)

~~For~~  $M$  small but finite, neither  $bM^2$  nor  $cM^4$  can be neglected  $\Rightarrow$  no true power law  $\beta \approx 1/3$  approx.

A useful empirical formula:

$$\sigma = \left[ 1 - s\tau^{3/2} - (1-s)\tau^{5/2} \right]^{1/3}$$

$s$  is a shape parameter,  $0 < s < \frac{5}{2}$



$$\text{For } \tau \ll 1, \quad \sigma \approx 1 - \frac{1}{3}s\tau^{3/2}$$

Bloch's law

$$\text{For } \tau \rightarrow 1, \quad \sigma \approx \left(\frac{5}{2} - s\right)^{1/3} (1 - \tau)^{1/3}$$

critical behaviour  
(approx.)