On permanent magnets

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I. Physical background

the term „magnetic“

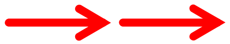
in physics

all materials are magnetic – at least **diamagnetic** – because the orbits of all of their electrons contribute to a small magnetic moment antiparallel to the applied field

In many materials there are additional persistent microscopic magnetic moments

- whose direction is thermally disordered, but can be partially aligned in a magnetic field → **paramagnetism**
- or they are periodically ordered but there is no net magnetization → **antiferromagnetism** 

There are materials where those microscopic moments are ordered resulting in a macroscopic net magnetization :

- canted antiferromagnets: e.g. α-Fe_2O_3 (Hematite) 
- ferrimagnets : e.g. **$BaFe_{12}O_{19}$** 
- ferromagnets: e.g. **$Nd_2Fe_{14}B$** 

common speech: this group is often called „magnetic“ or even „ferromagnetic“ whereas the former are called „non-magnetic“

Problems of the system of magnetic units

cgs system:

Maxwell´s equations *in vacuum* ⇒ ⇒ ⇒

$$\nabla \boldsymbol{E} = 0 \qquad \nabla \times \boldsymbol{E} = -\,\partial \boldsymbol{B}/c\partial t$$

$$\nabla \boldsymbol{B} = 0 \qquad \nabla \times \boldsymbol{B} = \partial \boldsymbol{E}/c\partial t$$

$$u = \frac{1}{2}(\boldsymbol{B}^2 + \boldsymbol{E}^2)$$

advantages: high symmetry; no new units; same units for $\boldsymbol{E}$ and $\boldsymbol{B}$

disadvantage: dim$[\boldsymbol{B}] = \frac{\sqrt{g/cm}}{s}$ → Oe, G, “emu”, “ esu” .....

In materials: additional equations such as

$\boldsymbol{B} = (\boldsymbol{H} + 4\pi\boldsymbol{M})$ (for the stationary case and no currents)

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SI system:

$\boldsymbol{B} = \mu_0(\boldsymbol{H} + \boldsymbol{M})$ *and* $u = \frac{1}{2}\left(\boldsymbol{BH} + \cdots\right)$

with the new physical constant μ_0 and the new unit Ampere (A)

$\mu_0 = 4\pi\, 10^{-7} kg\, ms^{-2} A^{-2}$

⇒ dim[$\boldsymbol{B}$] = $\frac{kg}{s^2 A} = \frac{Vs}{m^2} \equiv T$ ⇒ dim[$\boldsymbol{H}$] = $\frac{A}{m}$ ⇒ dim[$\mu_0\boldsymbol{H}$] = dim[$\boldsymbol{B}$] = T

⇒ advantage: these units are easier manageable

⇒ disadvantage: unnatural difference of B and H in vacuum **danger:** $4\pi\boldsymbol{M} \leftrightarrow \boldsymbol{M}$

sources of the magnetic field of magnets

Maxwell equations tell us (for the static case):

$$\nabla \times \boldsymbol{H} = \boldsymbol{j} \quad \text{and} \quad \nabla \boldsymbol{H} = -\nabla \boldsymbol{M}$$

to get a field H we need (somewhere) a current $\boldsymbol{j}$ or a magnetization M.

Note that the magnetization of our magnets nearly completely results from the spin of (a minority) of the electrons in the material!

$BaFe_{12}O_{19}$: M is <u>exclusively</u> a superposition of the spin magnetic moments of Fe^{+++} ions (from 5 of their 23 electrons)

$Nd_2Fe_{14}B$: M (at 300 K): ≈ 87% Fe (itinerant electron) spin moments and 13% Nd moment (a mixture of spin and orbital momentum contributions)

levels of description

microscopic level

subatomic level → the electron and its magnetism
atomic level → magnetism of atoms, ions and molecules
→ magnetism in solid state physics
→ thermostatistics

mesoscopic level

continuum theories → micromagnetism
effects of microstructure → nanometer-scale phenomena
magnetic (domain) structures

macroscopic level

thermodynamics
Landau theory of magnetic phase transitions
macroscopic properties of phases

Note that the magneticians all the time jump between those description levels thereby using rather different languages!

Elementary interactions:

1.) exchange interaction

Pauli, Heisenberg, Dirac, Heitler, London 1926…28

- in a two-electron system the quantum energy levels depend strongly on the electrostatic interaction between the two electrons

- Paulis principle requires that only antisymmetric wave functions are allowed:

$$\varphi(\boldsymbol{r}_{1,}\boldsymbol{s}_1,\boldsymbol{r}_{2,}\boldsymbol{s}_2) = -\varphi(\boldsymbol{r}_{2,}\boldsymbol{s}_2,\boldsymbol{r}_{1,}\boldsymbol{s}_1)$$

→ both is possible , ↑↑ i.e. parallel spins with antisymmetric $\varphi(\boldsymbol{r}_{1,}\boldsymbol{r}_2)$
or (↑↓ – ↓↑) , with symmetric $\varphi(\boldsymbol{r}_{1,}\boldsymbol{r}_2)$

→ thus a two-level system of the two electrons can be described by the

spin Hamiltonian $\boxed{\mathrm{H} = -J\, \boldsymbol{s}_1 \boldsymbol{s}_2}$

$\boldsymbol{J} > \mathbf{0}$: „ferromagnetic interaction“ ↑↑ $\boldsymbol{J} < \mathbf{0}$ „antiferromagnetic interaction“ ↑↓

a seemingly magnetic interaction though purely electrostatic in its nature (governed by quantum mechanics – including Paulis principle)

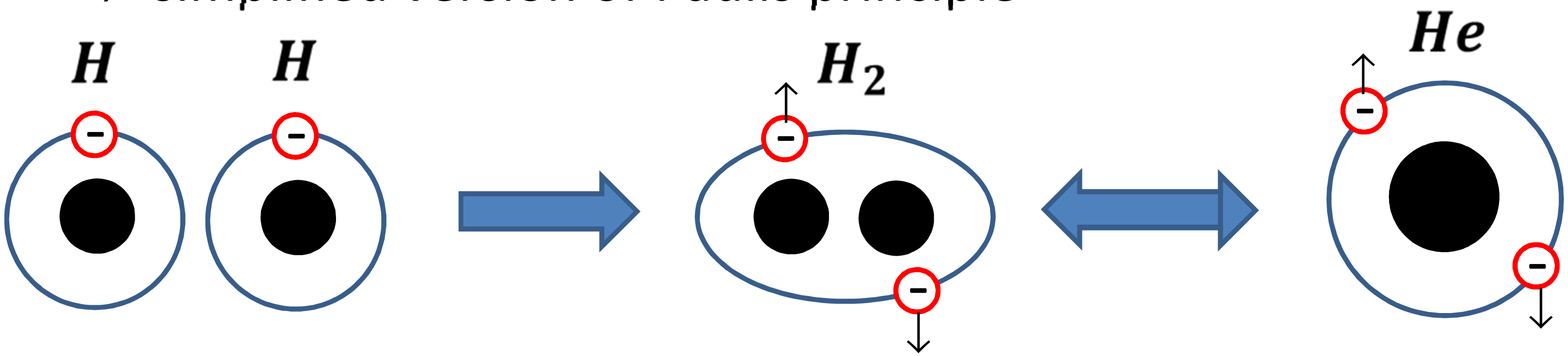
exchange interaction (continued)

Molecular orbital approach (*Hund, Mulliken 1927)*

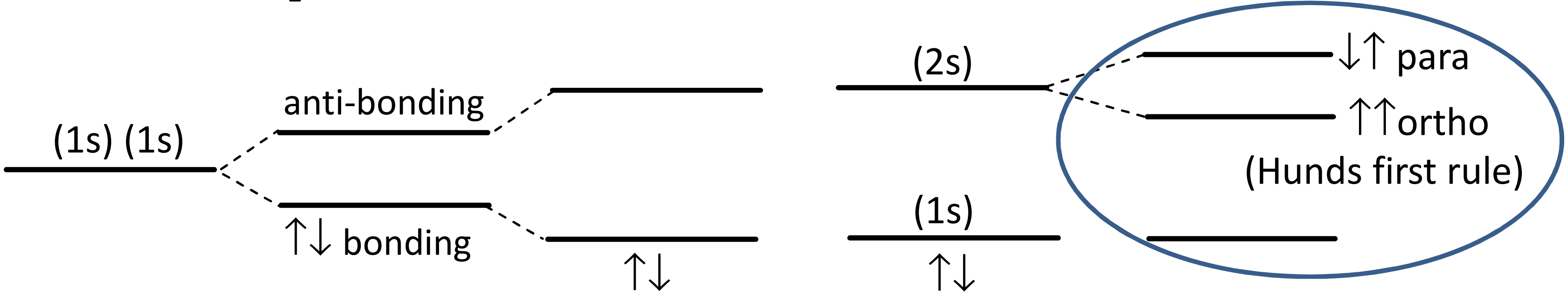
⇒ single-electron approximation

⇒ quantum numbers of single electrons

⇒ simplified version of Paulis principle



2 H-atoms → H_2 molecule → He-atom = H-like He atom → one electron excited :



Elementary interactions

2.) spin-orbit interaction

- The spin of the electron is an intrinsic angular momentum that can be well described only by relativistic quantum theory.

- The spin-orbit interaction (or L-S interaction) is the electromagnetic interaction of the spins of the electrons with their movement in space and can be expressed by the Hamiltonian

$$H = \sum_i \lambda_i \mathbf{s}_i \mathbf{l}_i$$

where λ_i contains information on the environment of the electron i ; and $\mathbf{s}_i$ and $\mathbf{l}_i$ are its spin and orbital momentum, respectively.

- **Important effects of the L-S interaction are:**

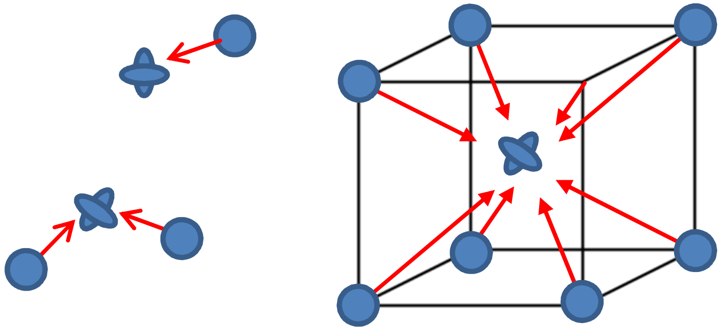
1.) it governs the third Hunds rule (→ L-S coupling in atoms and ions)

2.) it mediates anisotropic interactions in the solid to the spin
(which originally is a fundamentally isotropic phenomenon)
→ magnetic anisotropy

Elementary interactions

3.) crystalline electric fields (CEF) or ligand fields (LF)

- for atoms and ions the orbital angular momentum L corresponds to the spherical symmetry of these objects and therefore it yields „good quantum numbers “



- In molecules and solids the considered atoms or ions experience electrostatic or „chemical“ interactions from a nonspherical environment
- Now the components of the orbital angular momentum, L_x, L_y, L_z are no more good quantum numbers.
- $\Rightarrow$ their contribution to the measured magnetic moment is reduced or even disappears (this is called quenching of the orbital momentum or simply **L quenching**)
- **Note: 1.) the square L^2 often „survives“ i.e. it remains a constant of motion**
  2.) the CEF are the major source of magnetic anisotropy (and consequently of coercivity) in modern permanent magnets
- There is a well developed sophisticated description the CEF and their effects on physical properties, using terms as CEF wave functions, CEF coefficients, Stevens operators etc.

Elementary interactions

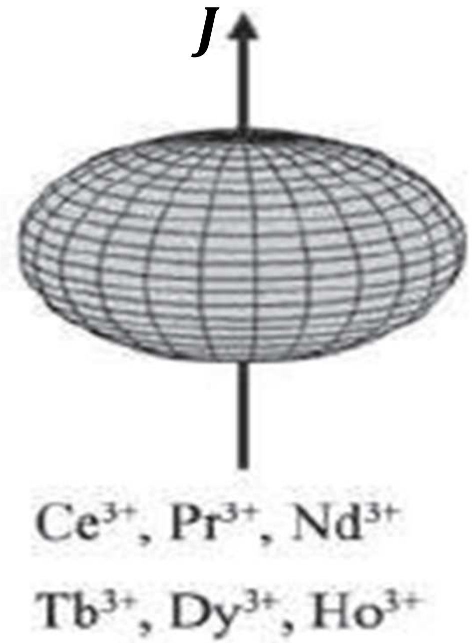
crystalline electric fields (CEF) or ligand fields (LF) – (continued)

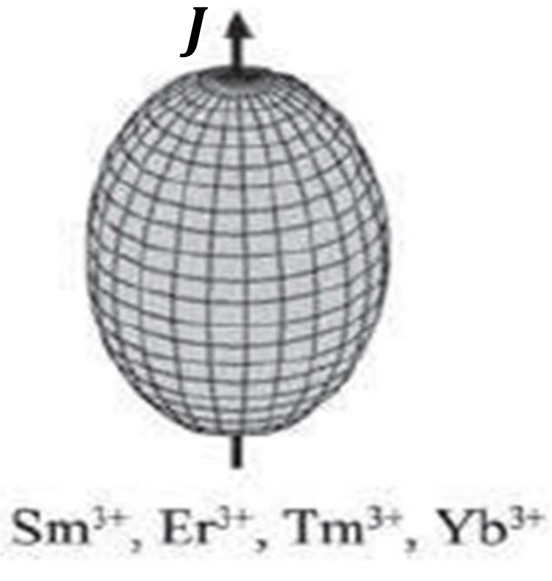
The rare-earth 4f electron clouds have well-defined values of total spin (S), total orbital momentum (L) and total angular momentum $(J = L \pm S)$.

J is rigidly coupled to the charge cloud (see below) that is fixed by the CEF

$\Rightarrow$ the CEF want to fix the direction of J

$\Rightarrow$ This is the magnetic anisotropy caused by CEF





crystalline electric fields (CEF) or ligand fields (LF) –(continued)

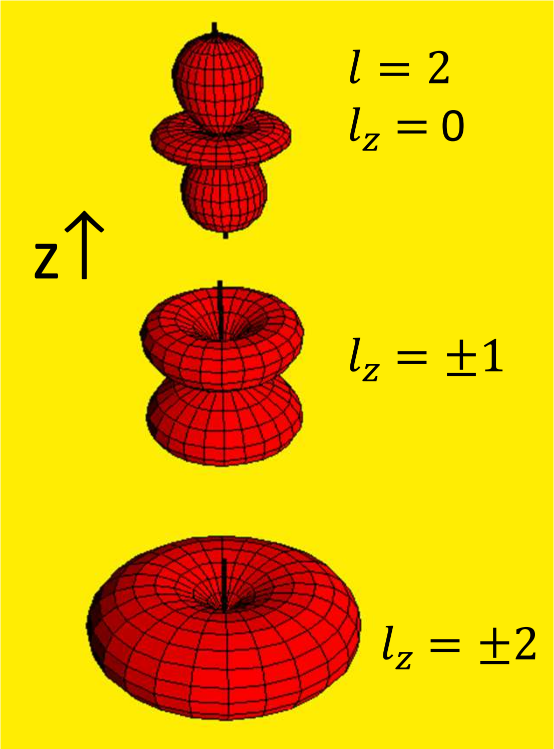
In localized-3d-electron systems strong crystalline electric fields „quench“ the 3d orbital momentum i.e. the five rotational-symmetric atomic orbitals transform into five crystal-field functions that do not carry a magnetic moment.

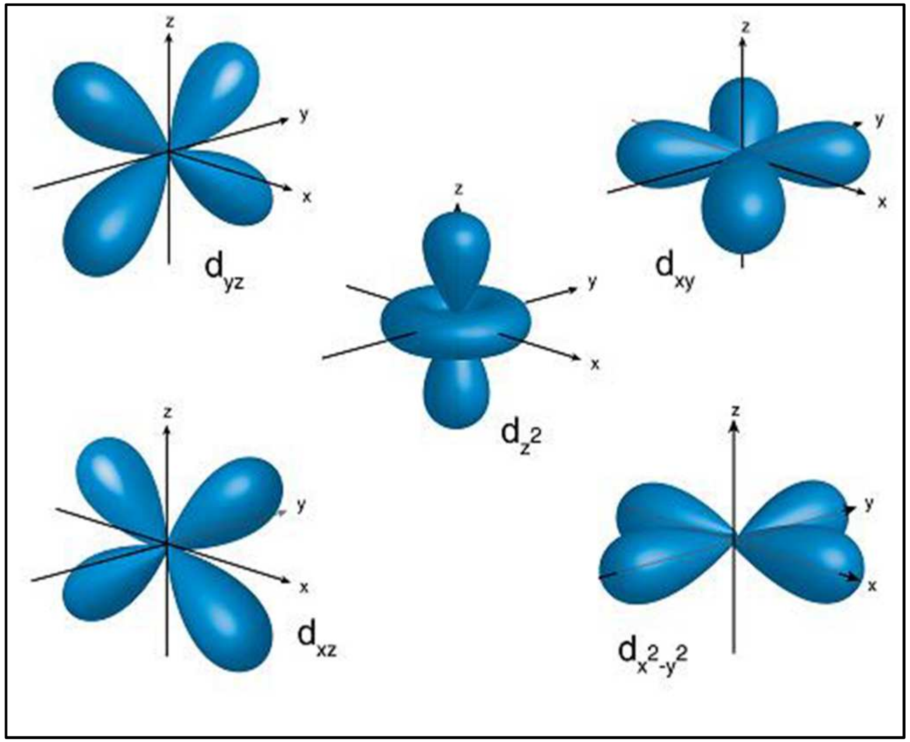
Nevertheless the spin orbit interaction mediates the magnetic anisotropy caused by the CEF to the spin based magnetization of the system.

example: charge clouds of a 3d electron:

in an axial environment:

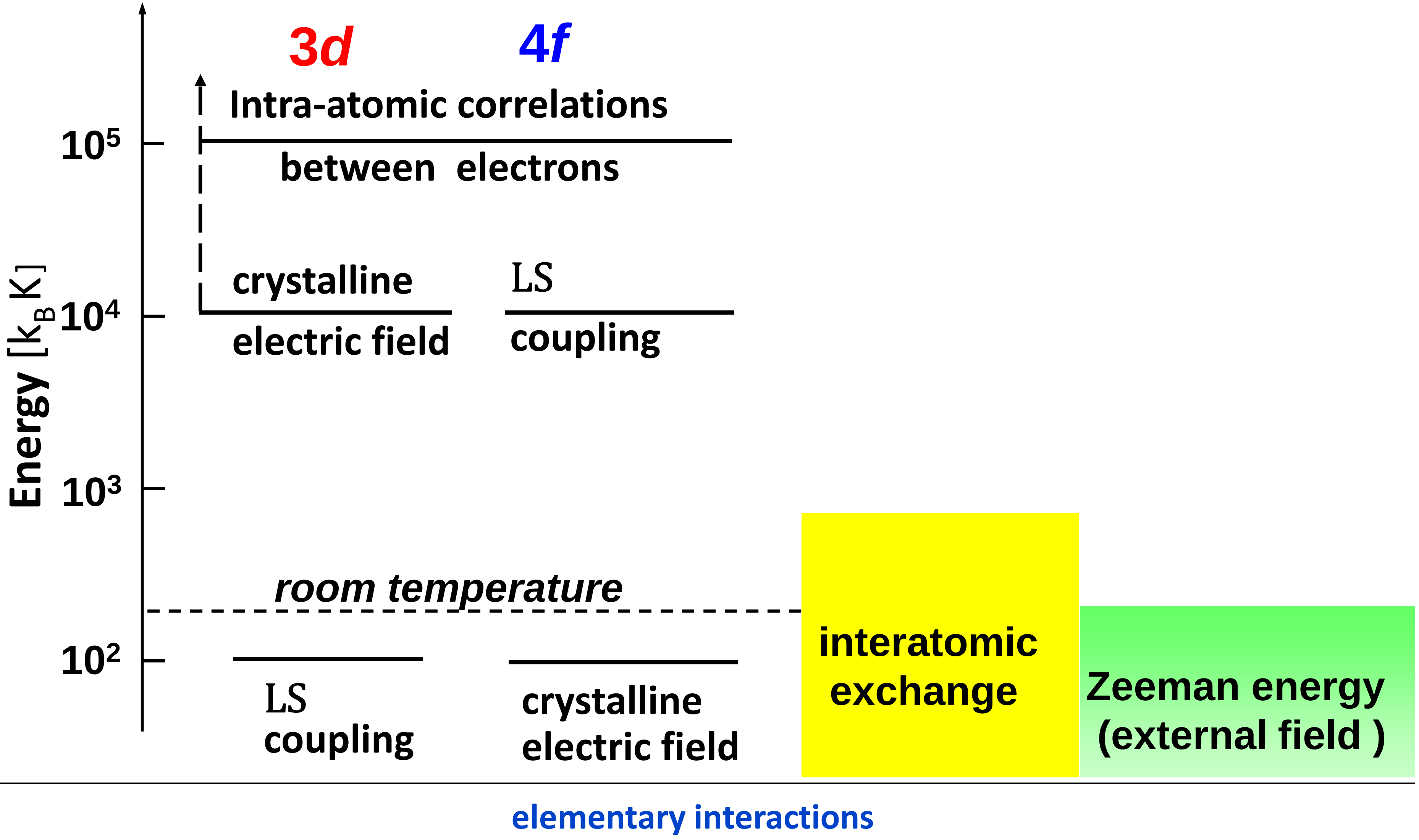
in a non-rotational-symmetric environment:
(no finite component of $\boldsymbol{l}$ → "$\boldsymbol{l}$ quenching"





Energy scales in magnetic materials

dominated by localized *3d* or *4f* electrons



3d ***4f***

Intra-atomic correlations between electrons

crystalline electric field (3d) **LS coupling** (4f)

room temperature

LS coupling (3d) **crystalline electric field** (4f)

interatomic exchange

Zeeman energy (external field)

elementary interactions

Elementary interactions

4.) magnetostatic interaction ; stray fields

- On the **macroscopic scale** the magnetostatic fields coming from the magnetization, according to $\nabla H = -\nabla M$, are the most outstanding property of permanent magnets.
  → this is what we use in permanent magnet applications
  → the term „stray fields“ is mostly used for unwanted fields of that type
- The field strength of a magnetic dipole $\boldsymbol{m}$ (the elementary field source because magnetic monopols do not exist) is given by

$$H(\mathrm{r}) \sim \left(\frac{3\boldsymbol{r}(\boldsymbol{mr})}{r^5} - \frac{\boldsymbol{m}}{r^3}\right)$$

→ the interaction between dipoles is anisotropic
→ it is a long-range interaction

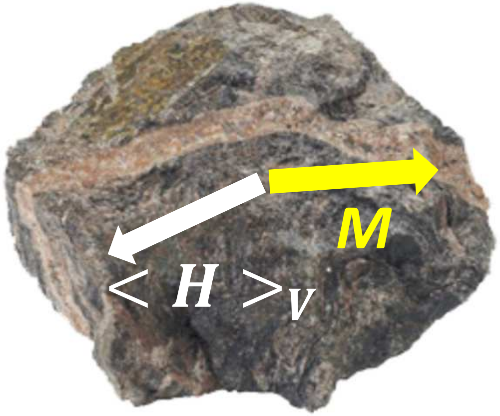
- one consequence of this is the formation of magnetic domains
- ⇒ conventional thermodynamics cannot be applied because the magnetostatic energy depends on sample size and sample shape (see for example domain branching and demagnetization factor, respectively)
- This interaction is very difficult to handle
- → **on the mesoscopic scale** : modern computational micromagnetism
- **on the miccroscopic scale** , in permanent magnets the magnetostaic interaction is relatively small and can often be neglected

The demagnetization factor $\mathbb{D}$

W.F. Brown and A.H. Morrish 1957

If a body of arbitrary shape is magnetized
by a uniform magnetization ***M***

1.) the average field in the body is $< \boldsymbol{H} >_V = -\,\mathbf{D}\boldsymbol{M}$
2.) **D** is a symmetric tensor
3.) its eigenvalues $D_i = D_1, D_2, D_3$
obey $0 \leq D_i \leq 1$ and $D_1 + D_2 + D_3 = 1$
4.) in ellipsoids the field H is uniform



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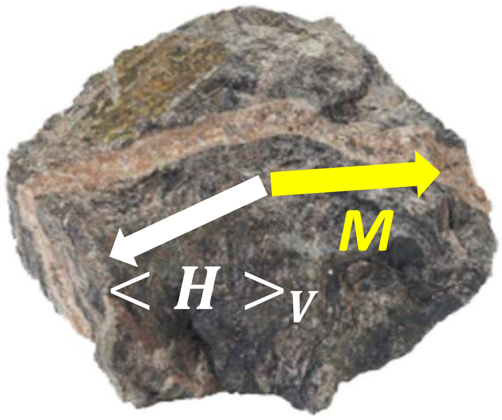


⇒ the magnetostatic self-energy of the magnet

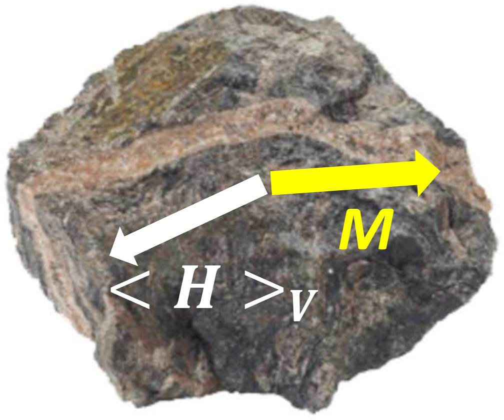
$$E = -\frac{\mu_0}{2}\int_{body} dV\,\boldsymbol{MH} = \frac{\mu_0}{2}\int_{space} H^2\,dV \quad \textit{is given by} \quad \frac{\mu_0}{2} V\boldsymbol{M}\mathbf{D}\boldsymbol{M} \rightarrow \frac{\mu_0}{2} V\mathrm{D}\boldsymbol{M}^2$$

this is correct also for irregular shapes!

The demagnetization factor $\mathbb{D}$

- continued -

If a body of arbitrary shape is magnetized
by a uniform magnetization $\boldsymbol{M}$



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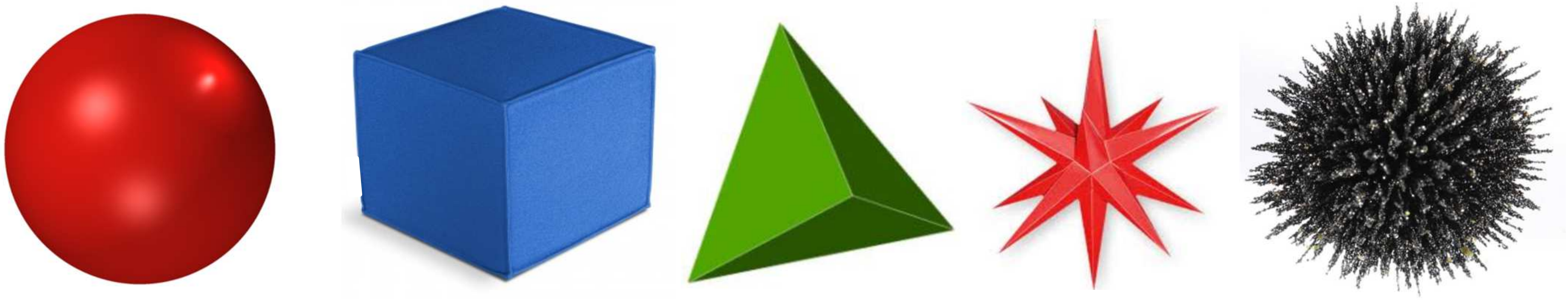
4.) in ellipsoids the field H is homogeneous

Consequently all of these bodies have D = 1/3:



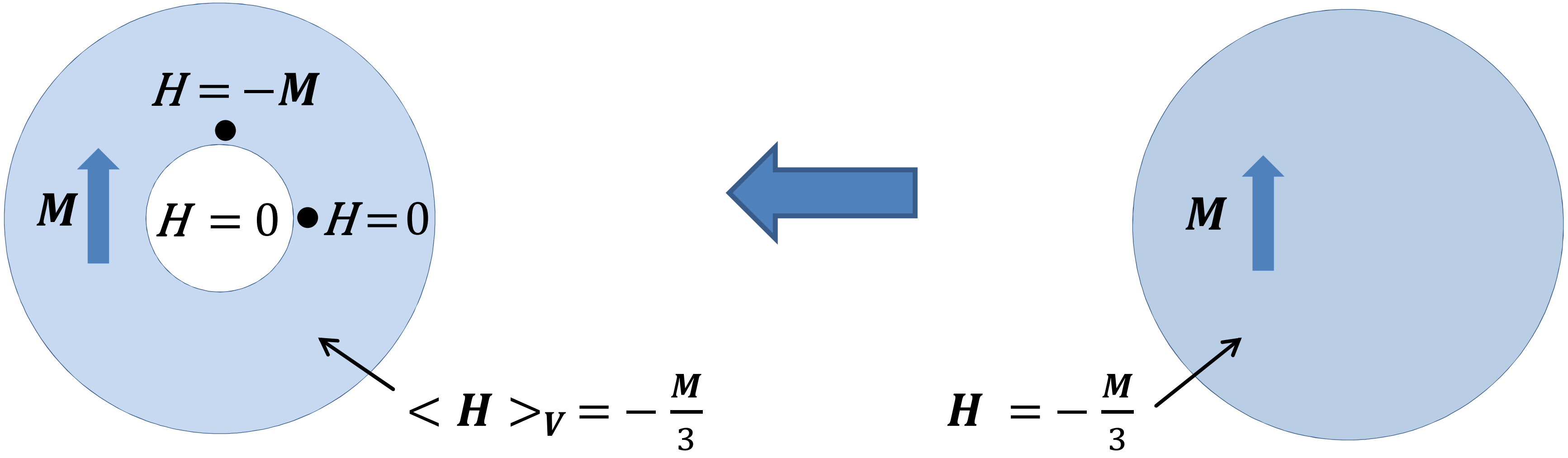
$$\boldsymbol{H} = -\frac{\boldsymbol{M}}{3}$$

H is non-uniform but $< \boldsymbol{H} >_V = -\frac{\boldsymbol{M}}{3}$

The demagnetization factor $\mathbb{D}$

- further examples -

- **hollow sphere:**
- **full sphere:**

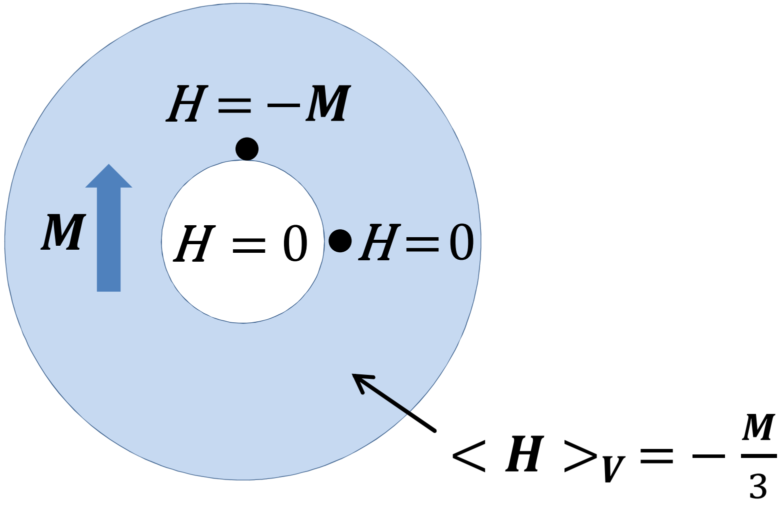


governed by $\nabla(H + M) = 0$ *and* $\nabla \times H = 0$

The demagnetization factor $\mathbb{D}$

- further examples -

- **hollow sphere:**



$H = -M$

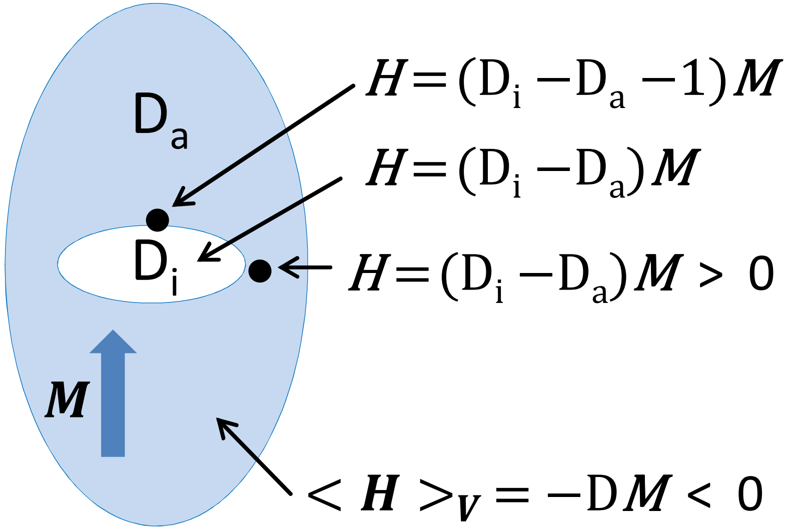
M

$H = 0$

$H = 0$

$< H >_V = -\frac{M}{3}$

- **hollow spheroid:**



$\mathrm{D_a}$

$\mathrm{D_i}$

M

$H = (\mathrm{D_i} - \mathrm{D_a} - 1) M$

$H = (\mathrm{D_i} - \mathrm{D_a}) M$

$H = (\mathrm{D_i} - \mathrm{D_a}) M > 0$

$< H >_V = -\mathrm{D} M < 0$

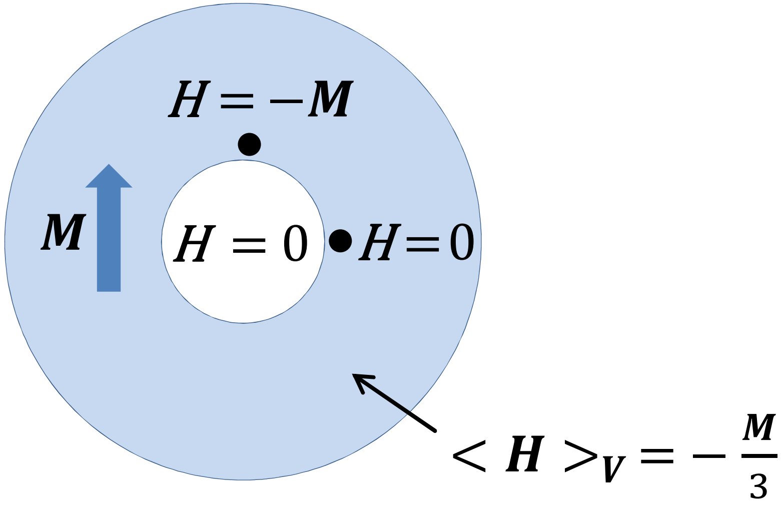
⇒ Although the average field in a homogeneously magnetized body $< H >_V = -\mathrm{D} M$ is always negative H is mostly inhomogeneous and can locally become even positive!

governed by $\nabla(H + M) = 0 \; and \; \nabla \times H = 0$

The demagnetization factor $\mathbb{D}$

- further examples -

- **hollow sphere:**



$H = -\boldsymbol{M}$

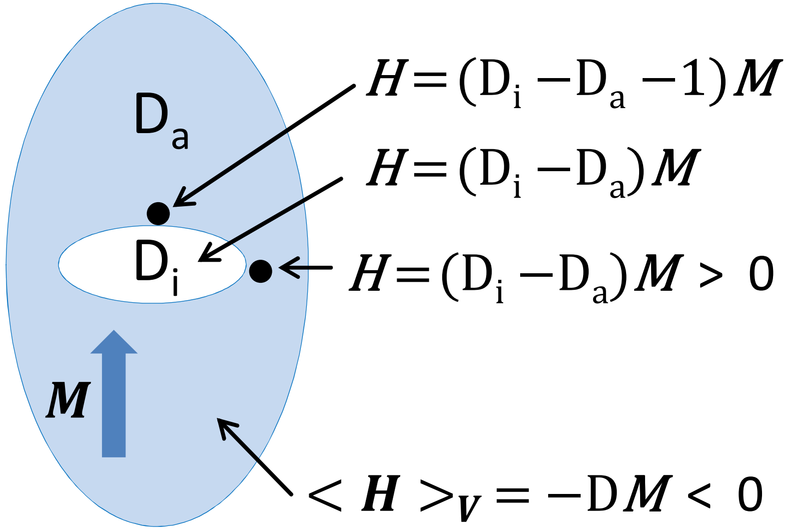
$\boldsymbol{M}$

$H = 0$

$H = 0$

$< \boldsymbol{H} >_V = -\frac{\boldsymbol{M}}{3}$

- **hollow spheroid:**



$\mathrm{D_a}$

$\mathrm{D_i}$

$\boldsymbol{M}$

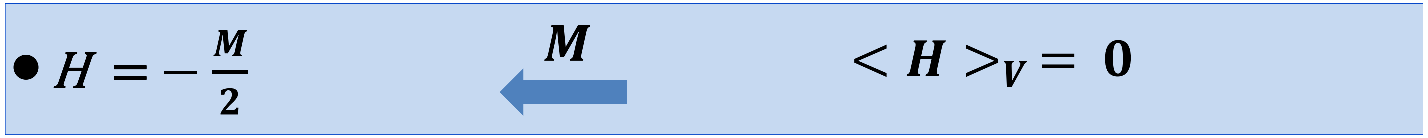
$H = (\mathrm{D_i} - \mathrm{D_a} - 1)\boldsymbol{M}$

$H = (\mathrm{D_i} - \mathrm{D_a})\boldsymbol{M}$

$H = (\mathrm{D_i} - \mathrm{D_a})\boldsymbol{M} > 0$

$< \boldsymbol{H} >_V = -\mathrm{D}\boldsymbol{M} < 0$

- **long cylinder:**



$H = -\frac{\boldsymbol{M}}{2}$

$\boldsymbol{M}$

$< \boldsymbol{H} >_V = \mathbf{0}$

⇒ Although the average field in a homogeneously magnetized body $< \boldsymbol{H} >_V = -\mathrm{D}\boldsymbol{M}$ is always negative H is mostly inhomogeneous and can locally become even positive!

governed by $\boldsymbol{\nabla}(\boldsymbol{H} + \boldsymbol{M}) = 0$ *and* $\boldsymbol{\nabla} \times \boldsymbol{H} = 0$

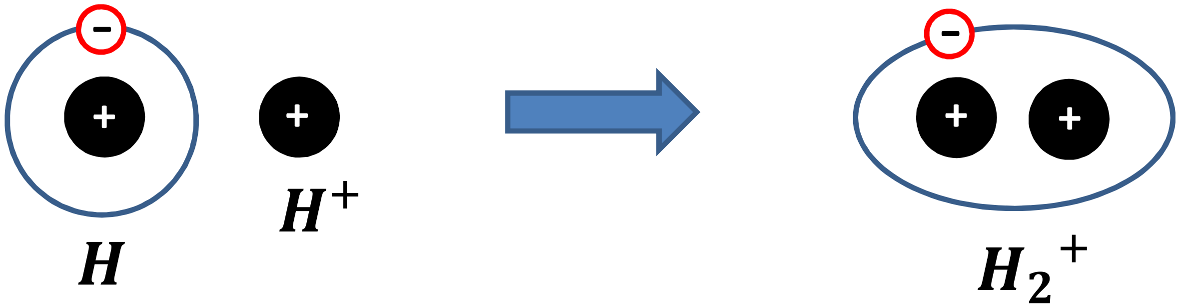
Elementary interactions

5.) delocalization and tunneling of electrons

as in the case of exchange interaction: electrostatic interaction combined with quantum mechanics

⇒ an electronic system can lower its energy by delocalization of electrons (without any effects of electron exchange)

- **a classical example is the H_2^+ ion (the simplest molecule):**



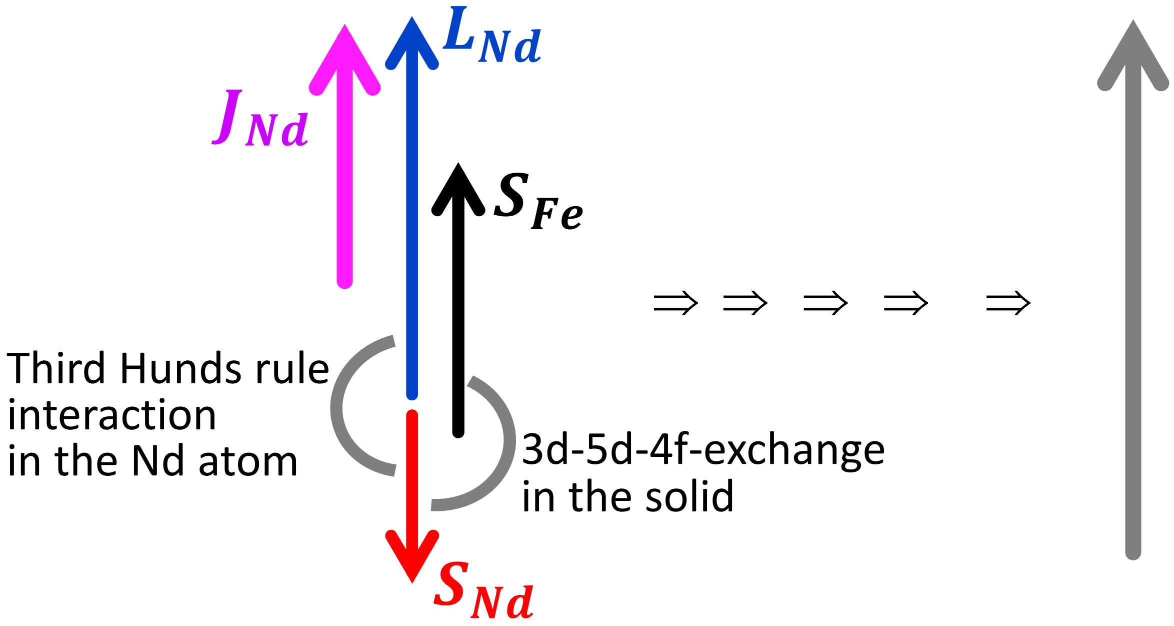
- the electron can become „itinerant"
- many solids are itinerant-electron systems: the metals including alloys and various intermetallic compounds
- e.g. s and d electrons in Fe and **in $Nd_2Fe_{14}B$**
  - but not the Nd 4f electrons and not the Fe core electrons there
  - and not the electrons in **$BaFe_{12}O_{19}$**

The most important atomic-scale interactions and their effects

interaction	origin	resulting phenomena
delocalization + exchange	**electrostatic interaction** + **quantum effects**: -Paulis principle, -delocalization, -tunneling	- atomic magnetic moments (by Hund rules) - magnetic ordering - (covalent) chemical bond - metallic bond
magnetic anisotropy (main type)	**electrostatic interaction** + **spin-orbit interaction**	- macroscopic magnetic anisotropy - coercivity
magnetostatic interaction	- primary interaction - but small on the atomic scale	- macroscopic fields of magnets - magnetic domains - long-range

The magnetic moment of $Nd_2Fe_{14}B$

- on the atomic scale -



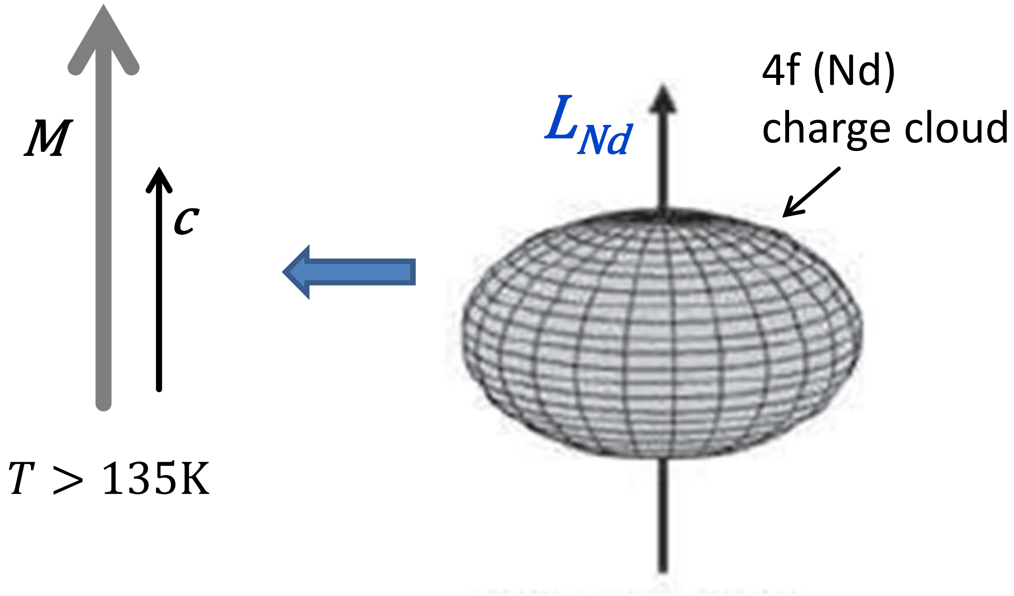
Third Hunds rule
interaction
in the Nd atom

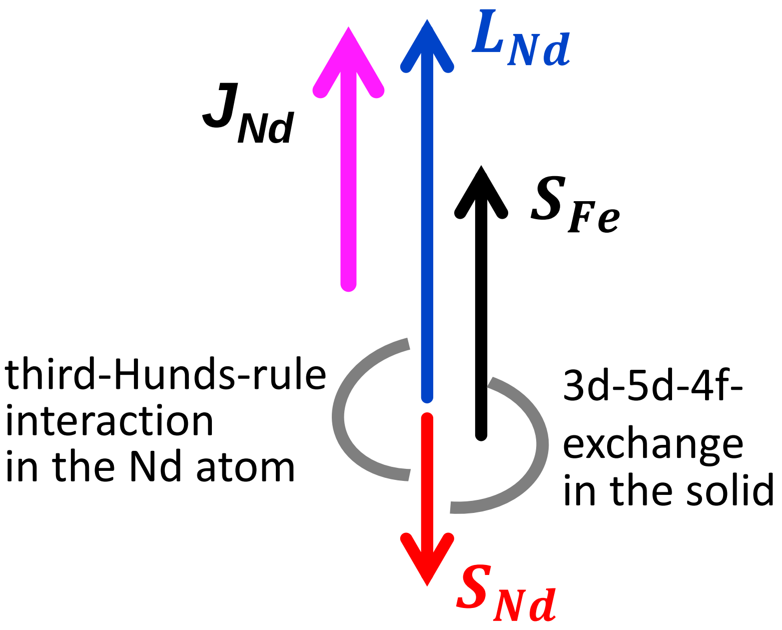
3d-5d-4f-exchange
in the solid

μ[at 4K] = 38 μ_B/f.u.

Magnetic anisotropy of $Nd_2Fe_{14}B$

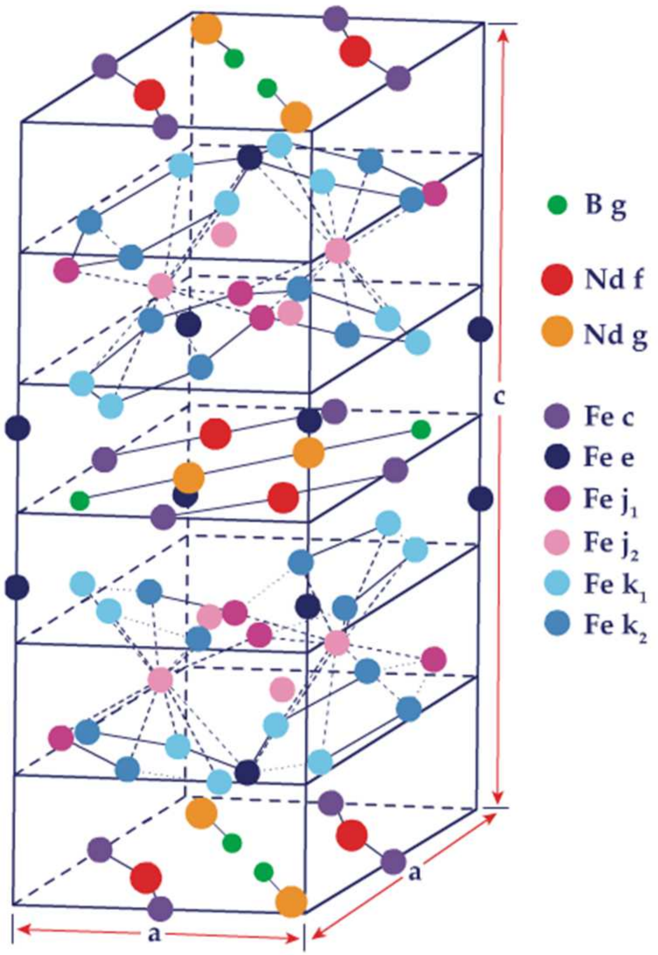
- on the atomic scale -





- the charge cloud of Nd is not spherical but oblate
- it is rigidly coupled to $\boldsymbol{L_{Nd}}$
- due to the coupling (on the right above) the total magnetic moment of **$Nd_2Fe_{14}B$** is parallel to the axis of the charge cloud
- **(mainly electrostatic) interactions of the Nd-4f-charge cloud with neighboring atomic sites in the solid („crystalline electric fields“ - CEF)** force the cloud – and hence the total magnetic moment of $Nd_2Fe_{14}B$ - in a certain direction
- In the case of $Nd_2Fe_{14}B$ this „easy axis“ it is the tetragonal c axis

$Nd_2Fe_{14}B$



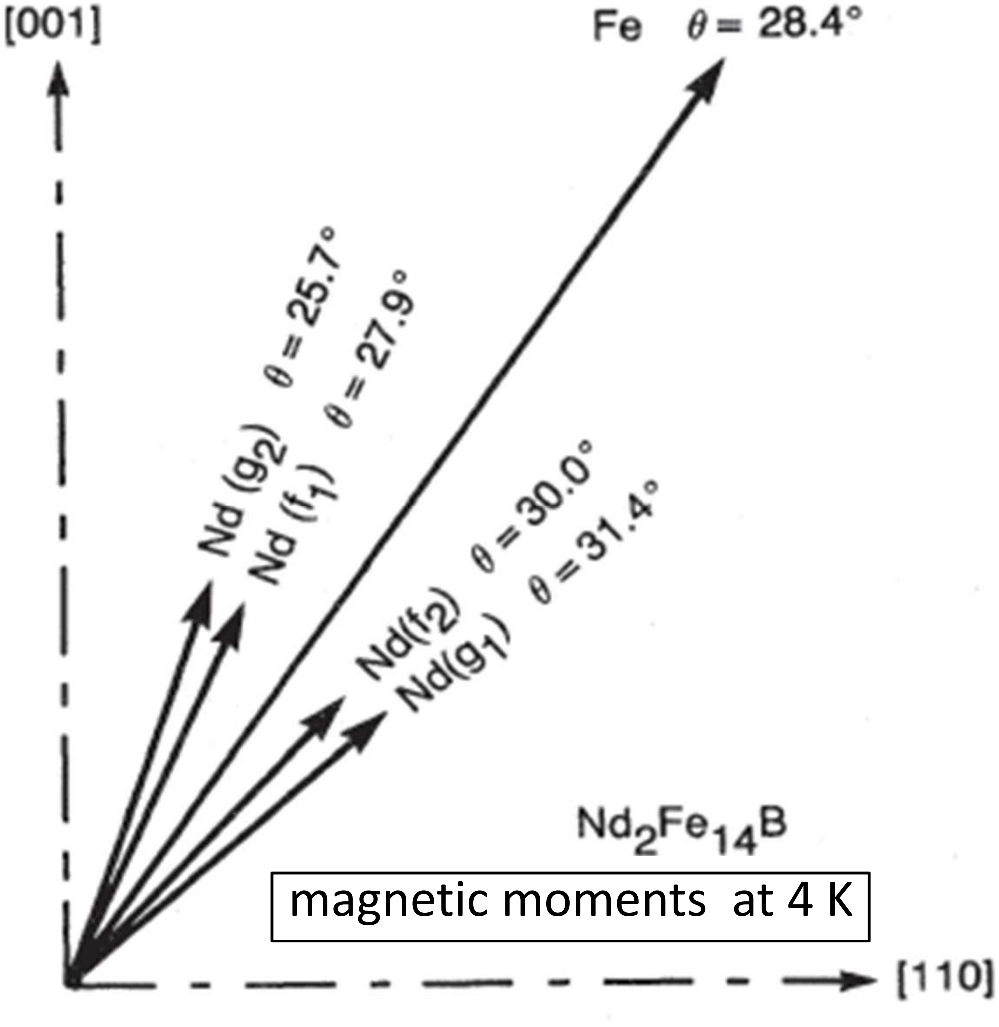
space group $P4_2/mmm$

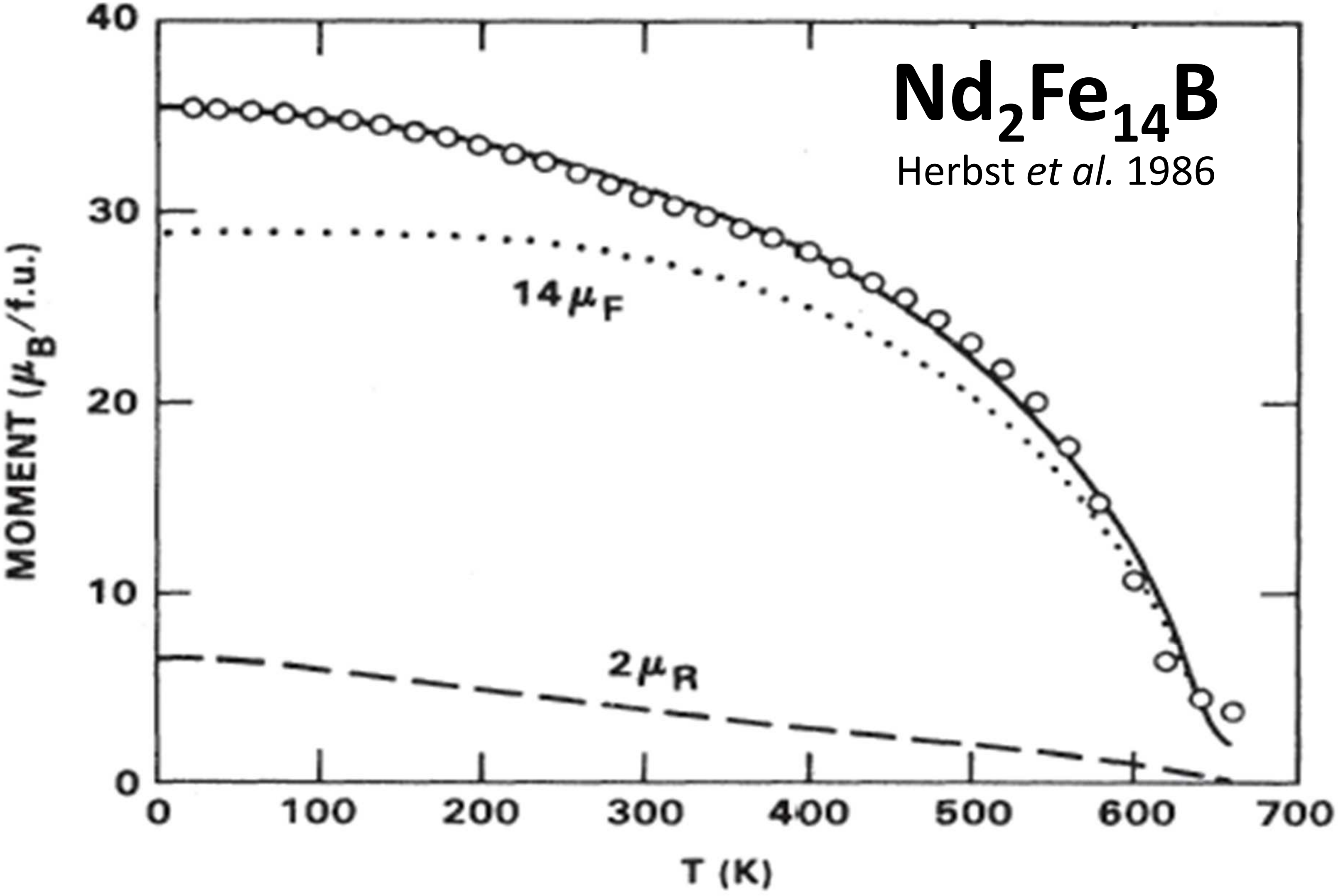
unit cell: 4 formula units = 68 atoms

2 R positions → 4 (magnetically)

6 Fe positions

1 B position





$Nd_2Fe_{14}B$

Herbst *et al.* 1986

The ferromagnetic to paramagnetic transition
on the macroscopic description level
→ Landau theory of second-order phase transitions

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provided that

- there is a homogeneous phase
- the system is magnetically isotropic (absence of magnetic anisotropy)
- The values of p, T, H (measured in an arbitrary direction) are fixed
- there is a transition temperature T_c (Curie temperature)
  i. e. $M = 0$ for $T > T_c$, $H = 0$ and $M \neq 0$ for $T < T_c$

the ingenious ansatz of Landau:
(for small values of M)

$$\boxed{\Phi(p,T,H,M) = \Phi_0(p,T) + \mathrm{a}(p,T)\,M^2 + \mathrm{b}(p,T)\,M^4 + \;\ldots\; - \mu_0 M H \;\rightarrow \mathit{Minimum}}$$

- a hypothetical thermodynamic potential describing fictive arbitrary (non-equilibrium) M states, that has to be minimized with respect to M
- being analytic

→ $\Phi(p,T,H,M)_{min} = G(p,T,H)$ the equilibrium magnetic Gibbs free energy

→ $\mathrm{a} = \alpha(T - T_c)$ → $\alpha > 0$ $\mathrm{b} \rightarrow \mathrm{b}(p) > 0$

→ **equilibrium magnetization $\boldsymbol{M(p,T,H)}$ or simply $\boldsymbol{M(T,H)}$**

Landau theory of second-order phase transitions

1.) $H = 0$ and $T > T_c \rightarrow M = 0$

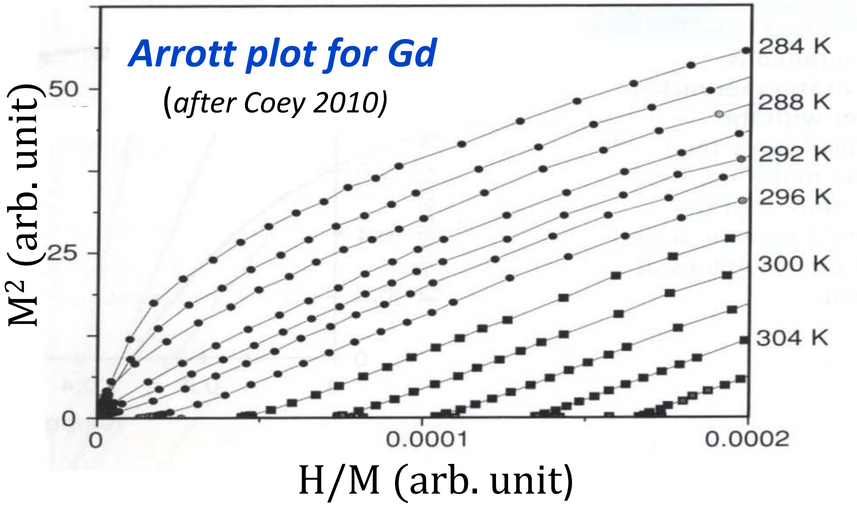
$T < T_c \rightarrow \quad M \equiv M_s = \pm\sqrt{\frac{\alpha}{b}(T - T_c)}$

spontaneous magnetization

2.) $H \neq 0$: $\quad \frac{\partial}{\partial M}\Phi(p, T, H, M) = 0$

$\rightarrow \alpha(T - T_c)\, M \quad + bM^3 = H \qquad \Rightarrow \qquad M^2 = \frac{1}{b} H/M + \frac{\alpha}{b}(T_C - T)$ ***equation of state***

to find the value of $T_c \Rightarrow \Rightarrow$



Arrott plot for Gd

(*after Coey 2010)*

$\boldsymbol{T} = \boldsymbol{T_c}$: $\qquad M = \frac{1}{b} H^{1/3}$

$\boldsymbol{T} > \boldsymbol{T_c}$: $\qquad M_{H=0} = \frac{H}{\alpha(T - T_C)}$

Curie-Weiss Law

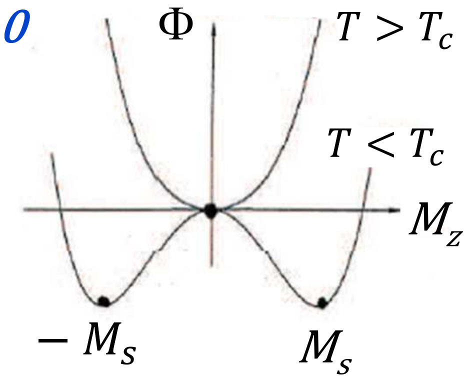
3.) H: arbitrary direction and values ; $T < T_c$; isotropic material:

$$\frac{\partial}{\partial M}\Phi(p, T, H, M) = 0$$

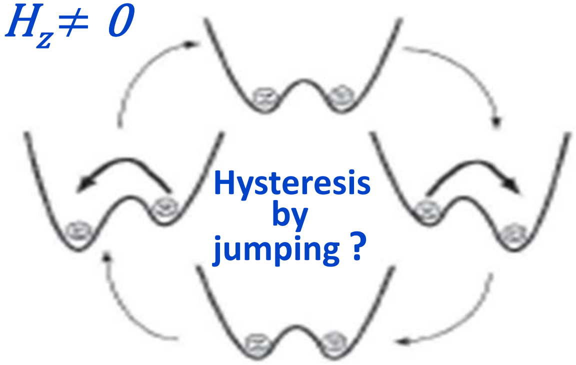
$$\downarrow$$

equation of states $M = M(H)$
(magnetization curve)

$H_z = 0$



$H_z \neq 0$



Hysteresis by jumping ?

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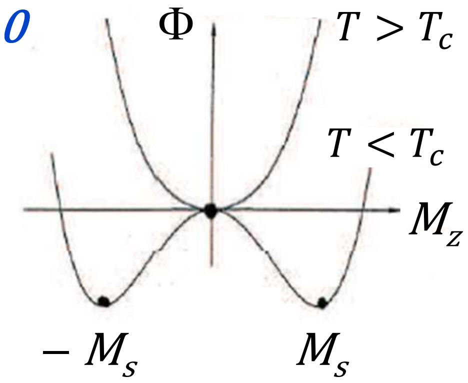

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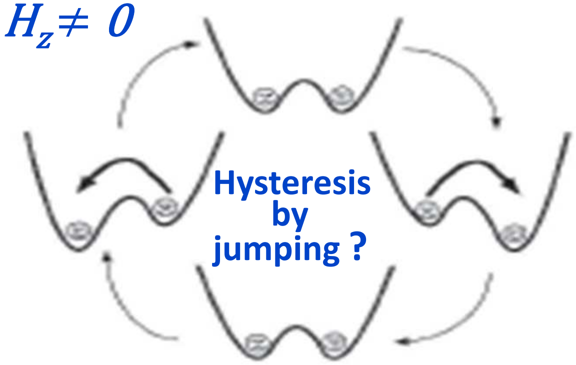
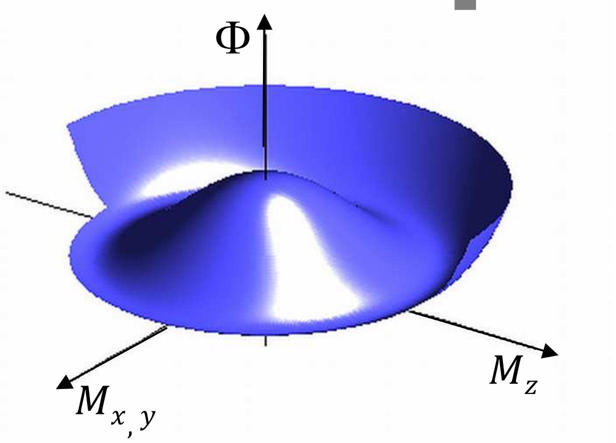
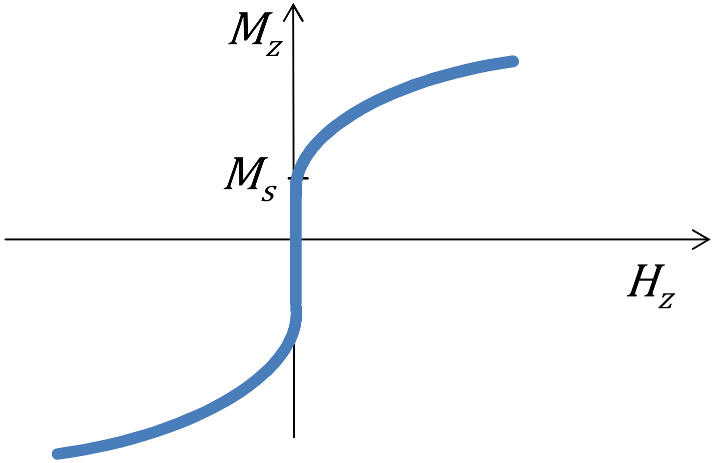


Hysteresis by jumping ?

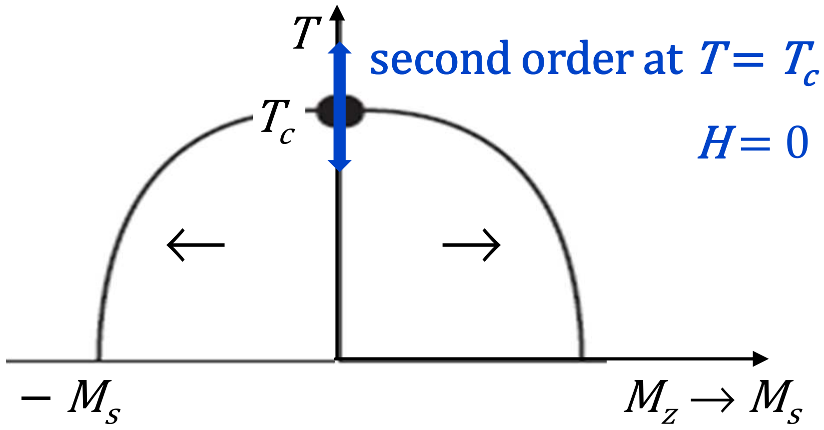
no jumping !



no hysteresis !

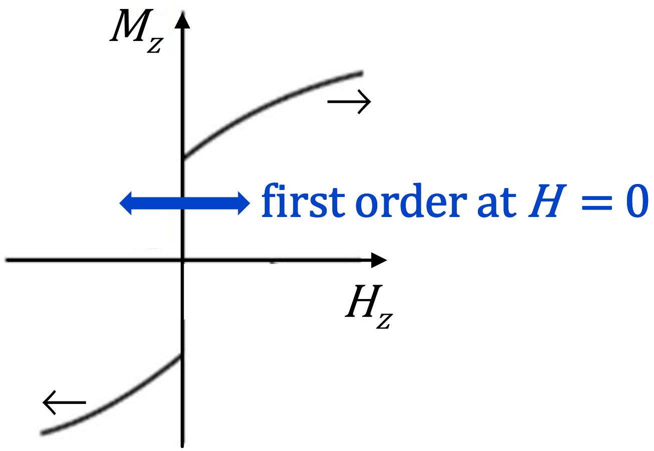


Thermodynamic order of these transitions



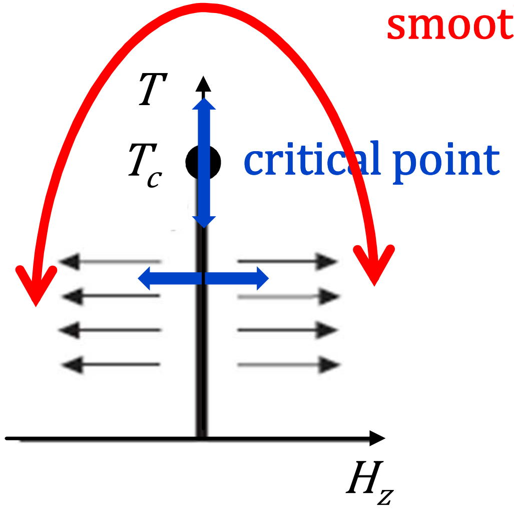
second order at $T = T_c$

$H = 0$

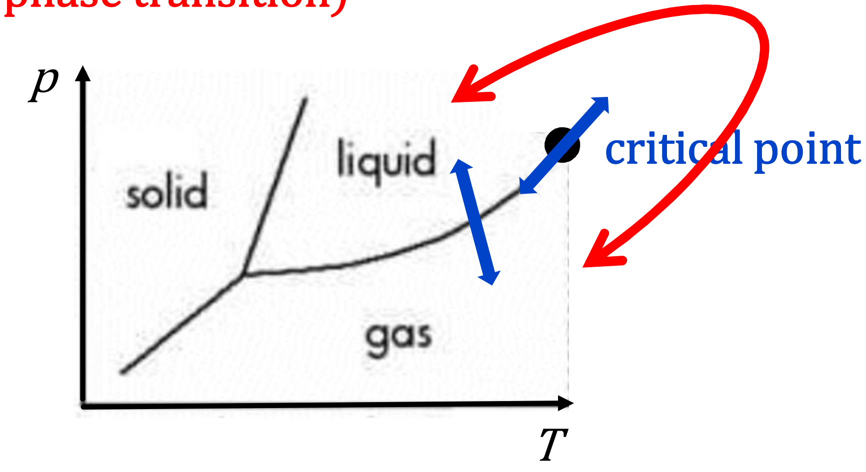


first order at $H = 0$

smooth transition (no phase transition)



critical point



critical point

The ferromagnetic to paramagnetic transition → Landau theory

Landau theory of second-order phase transitions
- magnetic easy-axis systems -

The simplest case of a non-isotropic material

- one prefered direction $\rightarrow\ z$
- x is a representative direction perpendicular to z
- ($\rightarrow$ two-dimensional pictures / representations: $z-x$)
- at least (lowest order in magnitude) anisotropy in the second-order term:

$$\Phi(p,T,H,\boldsymbol{M}) =$$

$$= \Phi_0(p,T) + \mathrm{a}(p,T)_z\, M_z{}^2 + \mathrm{a}(p,T)_x\, M_x{}^2 + \mathrm{b}(p,T) + M^4 + \ \dots - \mu_0 M H_z - \mu_0 M H_x$$

to be minimized wih respect to M_z and M_x

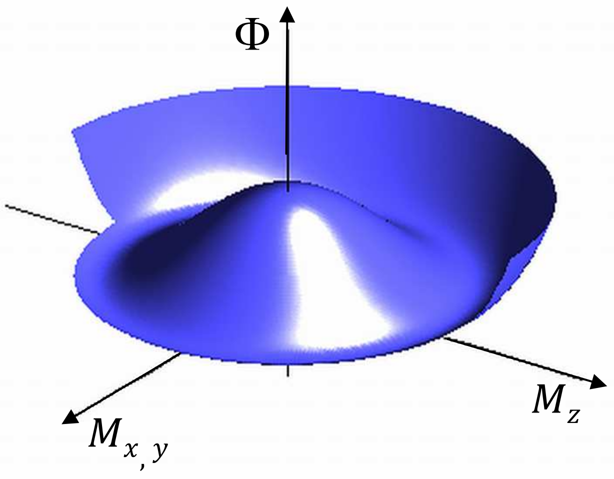
1.) the case $\boldsymbol{H_z} = 0$ and $\boldsymbol{H_x} = 0$

$\rightarrow$ $\boldsymbol{M}$ points in z direction ($M_x = 0$) if $a(p,T)_z < a(p,T)_x$

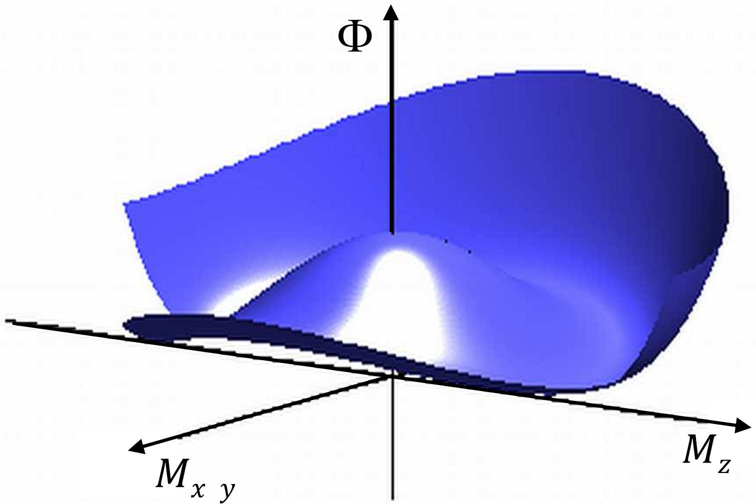
$\rightarrow$ „z axis is the easy axis of magnetization“

2.) the case $\boldsymbol{H_z} \neq 0$ and $\boldsymbol{H_x} = 0$ $\Rightarrow$ magnetic hysteresis

Landau theory of second-order phase transitions
- magnetic-easy-axis systems -



isotropic case
$\boldsymbol{a_z = a_x}$



anisotropic case
$|\boldsymbol{a_z}| > |\boldsymbol{a_x}|$

Moving from $M_z > 0$ to $M_z < 0$, the magnetization has to cross a saddle point on the $M_{x,y}$ axis .

→ magnetic anisotropy (*z* is the „easy“ axis)

→ *x, y* are magnetically „hard“ axes

→ magnetic hysteresis

In treating magnetic anisotropy on macroscopic or mesoscopic scales, $|\boldsymbol{M}(\boldsymbol{H},T)|$ can usually be replaced by $M_s(T)$ and $(\boldsymbol{a}_x - \boldsymbol{a}_z)\boldsymbol{M}_s{}^2 = K$ is the anisotropy „constant“.

In summary , ***the crucial point of*** ***Landau Theory***
is phase transitions of second order

→ many consequences/results can be concluded from few simple assumptions

→ one of these conclusions is the presence of a first-order transition accompanying the second-order one

→magnetic anisotropy (→ hysteresis) can also be included

micromagnetism or micromagnetics

- continuum theory of ferromagnetism -

provided that

the magnitude of magnetization $|\boldsymbol{M}(\boldsymbol{T},\boldsymbol{H})| = M(T) \equiv M$ does neither depend on the diection of $\boldsymbol{M}$ nor on $\boldsymbol{H}$ which is a very good approxomation for T not too close to T_c and not too large magnetic anisotropy

then the magnetization $\boldsymbol{M}(\boldsymbol{r};\boldsymbol{T},\boldsymbol{H}) \equiv M\boldsymbol{\alpha}(\mathrm{r},H)$ *,*
for a uniaxial material , can be calculated by minimizing

$$\boxed{\Phi = \int \boldsymbol{dV} \left\{A\sum_{i,j=1}^{3}\left(\frac{\partial\alpha_i}{\partial x_j}\right)^2 - K\alpha_1{}^2 + \frac{\mu_0}{2}\boldsymbol{H_e}{}^2 - \mu_0 M\boldsymbol{\alpha} H\right\} \rightarrow \boldsymbol{Min}}$$

- where the components $\alpha_i(\boldsymbol{r})$ of the unit vector $\boldsymbol{\alpha}(\boldsymbol{r})$ have to be varied for given H **.**
- A is the exchange „constant“ and K the anisotropy „constant“ both depending on T.
- additionally the field produced by the material, $\boldsymbol{H_e}$, has to obey Maxwell´s equations:

$$\boxed{\nabla\boldsymbol{H_e} = -M\boldsymbol{\nabla}\boldsymbol{\alpha} \quad \textbf{and} \quad \boldsymbol{\nabla}\times\boldsymbol{H_e} = \boldsymbol{0}}$$

Bloch 1935; Landau, Lifshitz 1935; Becker, Döhring 1939; **Brown 1940/41**

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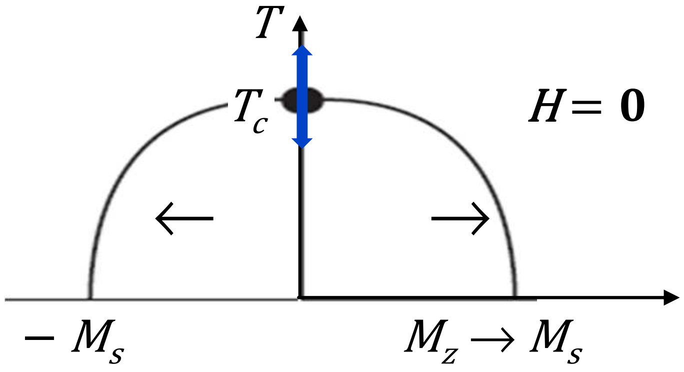
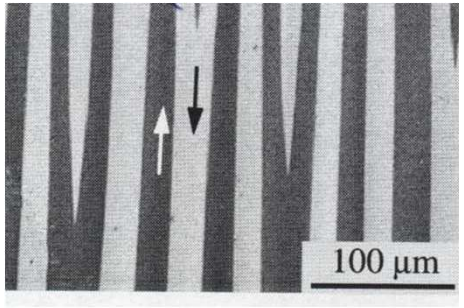
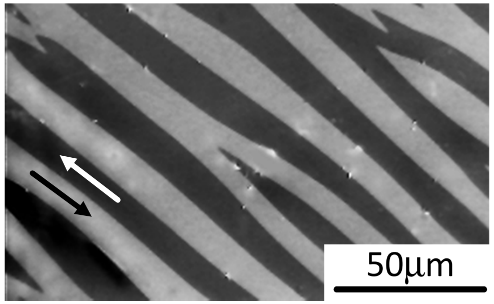
Domains and domain walls

- in easy-axis materials -





as cast $Nd_2Fe_{14}B$



as cast Sm_2Co_{17}

→ In thermal equilibrium the two phases (up and down „domains“) expected to occur in the second order phase transition in uniaxial materials are actually observed.

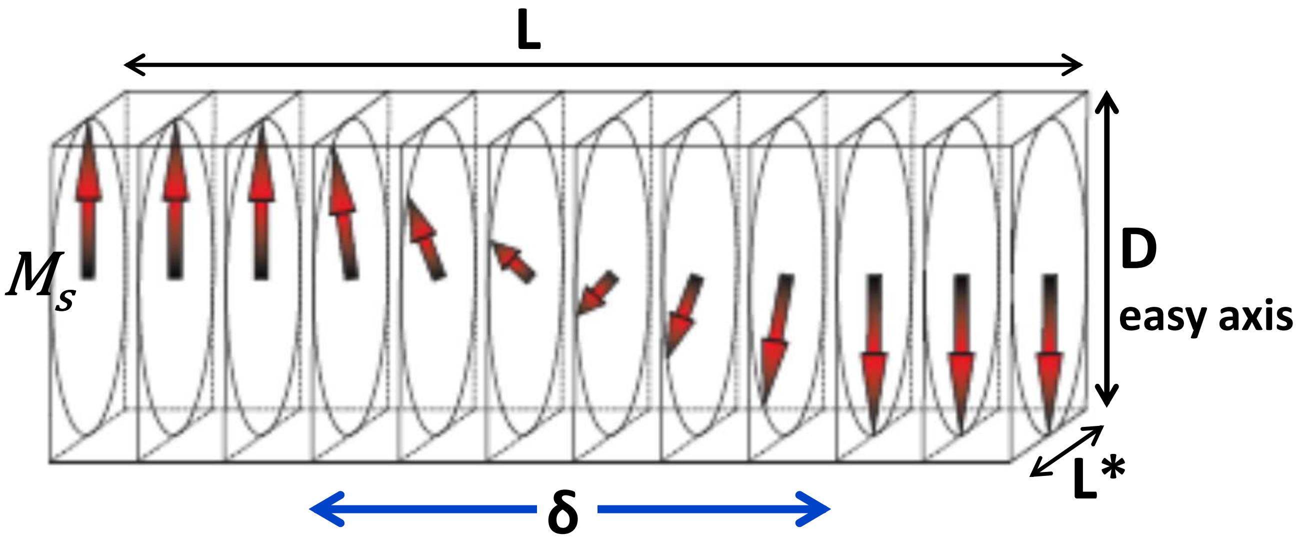
→ What is the nature of the phase boundary between them ?

→ Why is the fraction of each phase obviously about 50% ?

→ width of the domains ?

The Bloch wall

- L. Landau and E. Lifshitz 1935 -



$$\boxed{\delta = \pi\sqrt{A/K}}$$ ← width of the Bloch wall

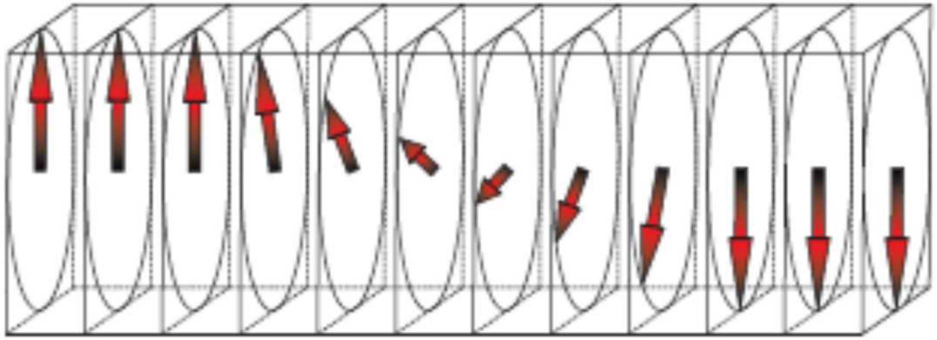
δ is an intrinsic „magnetic length“

→ it is independent of M_s, L, L*, D (povided that L, L*, D >> δ)

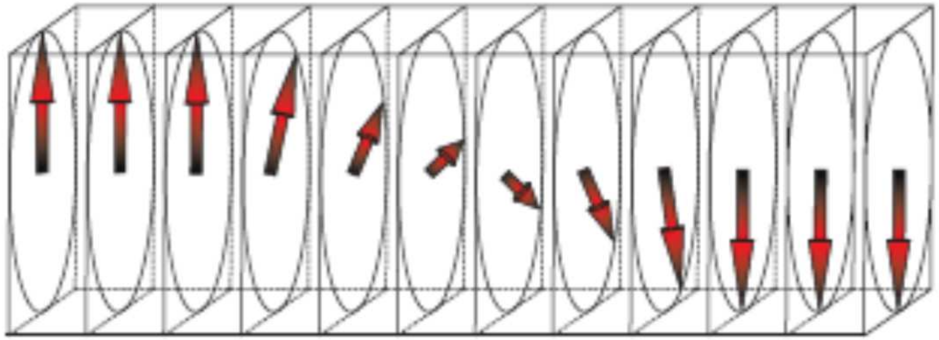
→ the Bloch wall is the „magnetic phase boundary“

→ it is easily movable (along the x axis: ⟷)

Bloch wall as a screw (helix)



right-handed chirality



left-handed chirality

The two types of chirality are energetically equivalent

Domain branching (Hubert 1967)

- the role of magnetostatic (stray) fields -

The domain width close to the surface is independent of the sample dimensions:

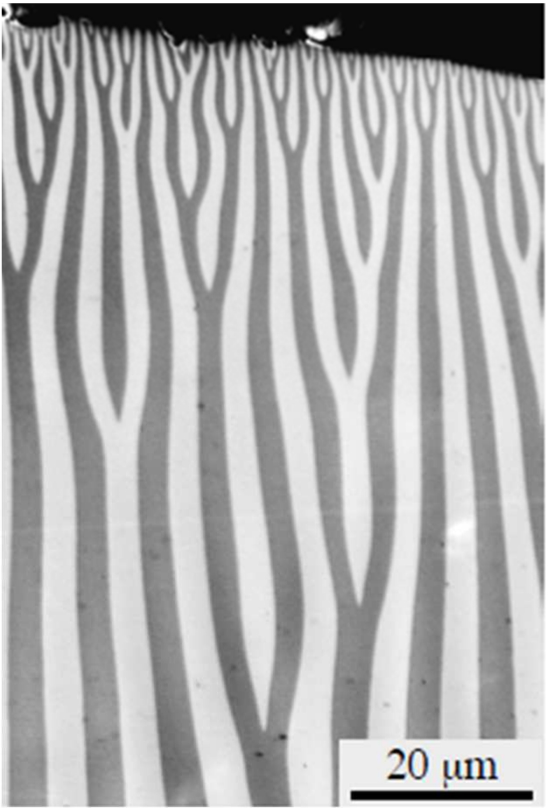
$$\boxed{W_s \approx 200 \frac{\sqrt{AK}}{\mu_0 M_s^2}}$$

→ **the second of two independent intrinsic magnetic lengths**

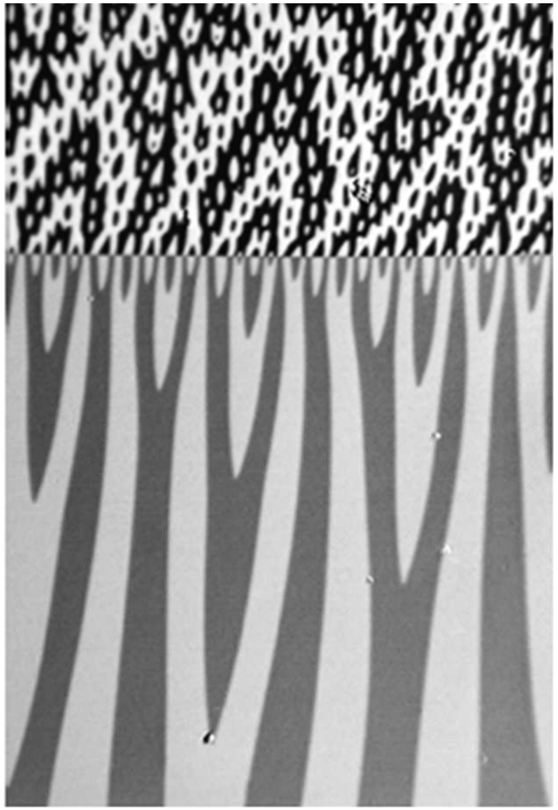
as cast $Nd_2Fe_{14}B$ ⇒ ⇒ ⇒

Hubert, Schäfer, Handstein, Müller

Free surface



neighbouring grain
(misoriented)



Domain branching

- the role of magnetostatic (stray) fields -

⇒ a hirarchy of branched domains

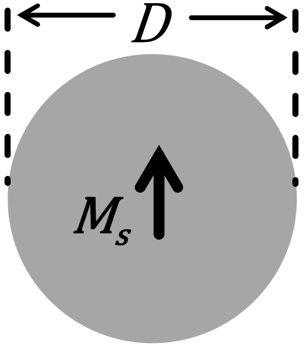
⇒ an example of fractal structures

⇒ a fundamental difference to normal thermodynamic systems with short-range interactions (as e.g. solids with their lattice structures)

The single domain particle size D_c

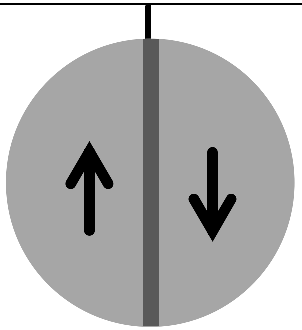
- the role of magnetostatic (stray) fields -

comparison of the thermodynamical potential of a spherical particle containing a single magnetic domain with that of a two-domain particle of same size **(Kittel 1946):**



$$\Phi = \Phi_0 = \frac{1}{3}\frac{4\pi}{3}\left({}^{D}\!/_{2}\right)^3 \frac{1}{2}\mu_0 M_s^2$$

Bloch wall
energy per unit area $\gamma = 4\sqrt{AK}$



$$\Phi \approx \frac{1}{2}\Phi_0 + \pi\left({}^{D}\!/_{2}\right)^2 \gamma$$

⇒ **single-domain particles have the lower potential for**

$$D < D_c = 72\frac{\sqrt{AK}}{\mu_0 M_s^2} \approx \frac{1}{3} W_s$$

Domains in summary,

- ***domains are magnetic thermodynamic phases***
- ***they are needed to reduce stray field energy***
  (⇒ ideally: M = 0 for H = 0)
- ***their size depends on sample dimensions***
- ***however (in larger easy-axis samples) the domain width close to the sample surface is an intrinsic length*** W_s ***(independent of sample size)***
- ***there is a critical single domain size*** $D_c \approx \frac{1}{3} W_s$
- ***the Bloch-wall width δ is also an intrinsic length***

deepening and specialisation
in micromagnetism

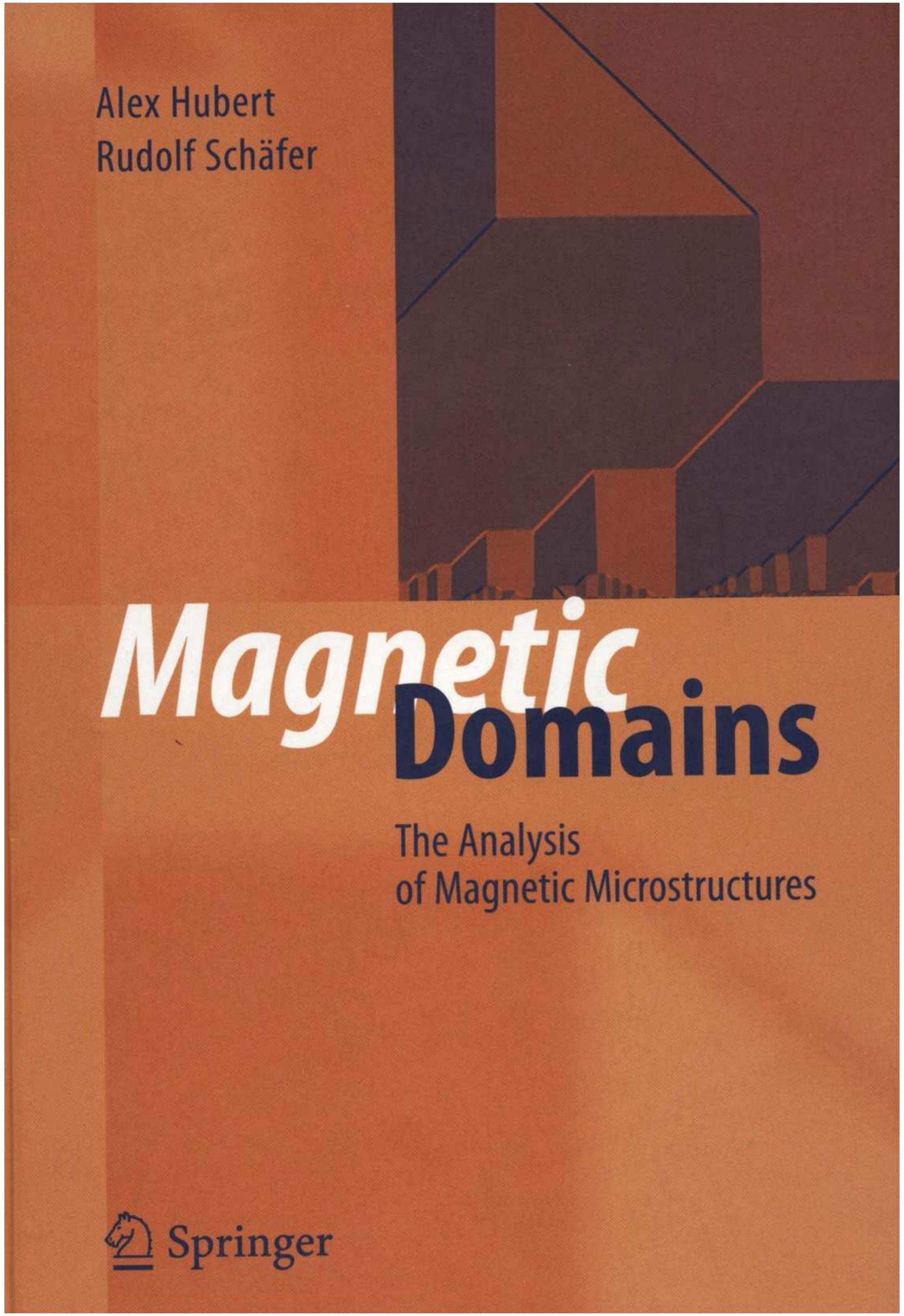
Micromagnetism has been further developed , in particular, taking into account:

- higher order anisotropy constants
- other types of lattice symmetries
- „anisotropic exchange“
- magneto-mechanical (particularly magnetoelastic) phenomena
- inhomogeneous materials (spatial variation of M_s , A , K, …)

The influence of

- **higher order anisotropy**
- **non-uniaxial anisotropy**
- **dimensions of the samples**
- **shape of the samples**
- **microstructure of the samples**

results in a very rich variety of domain phenomena.



Alex Hubert
Rudolf Schäfer

Magnetic Domains

The Analysis
of Magnetic Microstructures

Springer

intrinsic magnetic properties of some easy-axis materials

- room temperature values -

phase	$\mu_0 M_s$ (T)	T_C (K)	K (MJm^{-3})	$\mu_0 H_A$ (T)	A (pJm^{-1})	δ (nm)	D_c (μm)
Co	1.8	≈1400	0.45	0.75	25	20	0.6
$BaFe_{12}O_{19}$	0.48	≈730	0.3	1.8	6	14	0.6
Sm_2Co_{17}	1.27	≈1190	3.3	7	15	6	0.4
$Nd_2Fe_{14}B$	1.61	588	4.5	7.5	8	4	0.22
$SmCo_5$	1.06	≈1000	17	40	12	2.6	1.2

anisotropy field

$$H_A = \frac{2K}{\mu_0 M_s}$$

Bloch-wall width

$$\delta = \pi\sqrt{A/K}$$

critical
single-domain particle diameter

$$D_c = 72\,\frac{\sqrt{AK}}{\mu_0 M_s^2}$$

Magnets and thermodynamics

1.) long-range nature of magnetostatic interaction

⇒ properties strongly depend on shape and size of the samples, as eg.:

- shape dependence of the demagnetization factor
- the hierarchy of branched domains (fractal structures !)
- Critical single-domain-particle diameter D_c

⇒ a fundamental difference to normal thermodynamic systems with short-range interactions

2.) metastability

Magnetized bodies and hysteresis phenomena are away from thermal equilibrium.

⇒ Thermodyamics is only restrictedly applicable to magnets

Characteristic time scales in magnetism

- intrinsic and extrinsic -

1.) magnetic viscosity or „after effect“ or „lag in magnetization“

(Ewing 1885; Preisach 1935 ; Street-Woolley 1949)

⇒ the slow relaxation of the metastable magnetization of a magnetized body

$$\boldsymbol{M(t) = M(0) - S\, ln\left(1 + \frac{t}{t_o}\right)}$$

$\boldsymbol{S}$ is the „viscosity“ – an extrinsic property of the relaxation process

$\boldsymbol{t_o}$ is a parameter describing the initial condition of the measurement procedure

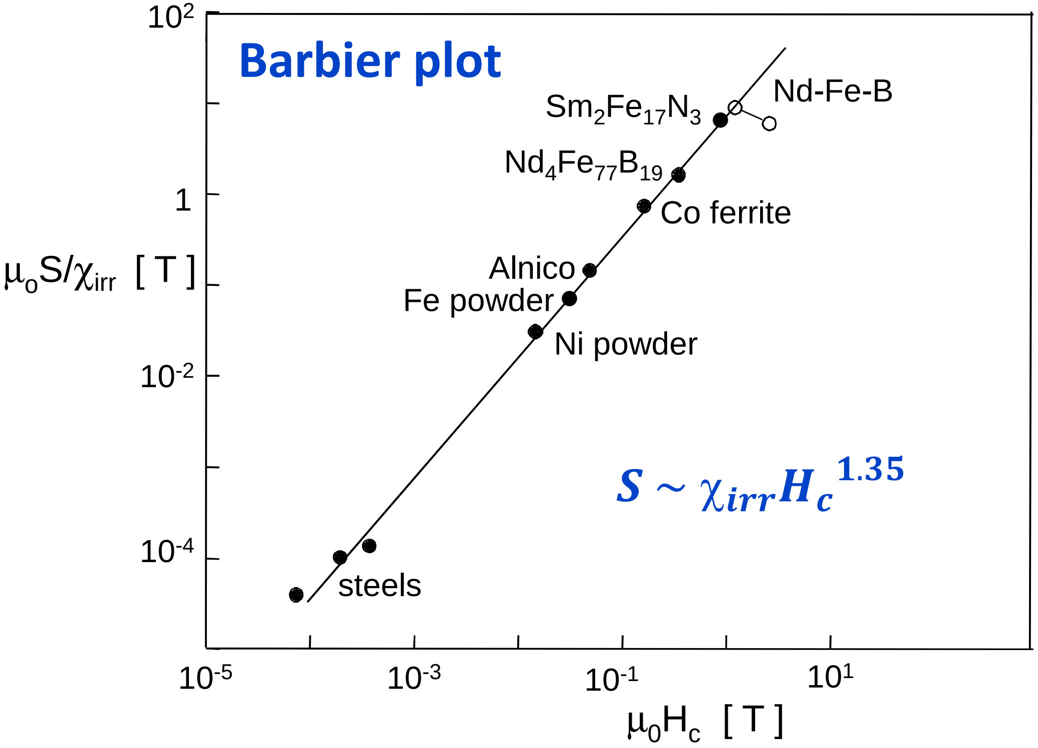
⇒ **There is no chacteristic time scale for magnetic viscosity:**
the process runs in microseconds in the same way as after years !

Characteristic time scales in magnetism

- intrinsic and extrinsic -

The extrinsic properties viscosity (S) and coercivity (H_c) are (roughly) related to each other.

(Barbier 1954)



$$S \sim \chi_{irr} H_c{}^{1.35}$$

Characteristic time scales in magnetism

- intrinsic and extrinsic -

2.) relaxation of small magnetized particles due to thermal excitation

(L. Neel, W.F. Brown, A. Aharoni)

- characteristic time between two flipping events in an easy-axis particle

flipping time $\tau_N = \tau_0 e^{\frac{KV}{k_B T}}$ **← an extrinsic time scale**

$with$: τ_0 - 10^{-9} … 10^{-11} s **← an intrinsic time constant**

k_B – Boltzmann constant

V – volume of the particle

$\Rightarrow$ τ_N is extremely sensitive to V/T !

- **e.g. a Co – cube** (at room temperature ; edge length *a*)*:*

***a* = 2 nm** $\rightarrow \tau_N \approx 2.5$ ns

***a* = 4 nm** $\rightarrow \tau_N \approx 10$ μs

***a* = 6 nm** $\rightarrow \tau_N \approx 1000$ s

***a* = 8 nm** $\rightarrow \tau_N \approx 10^{16}$ s

***a* = 10 nm** $\rightarrow \tau_N \approx 10^{31}$ years

this is called superparamagnetism

Characteristic time scales in magnetism

- intrinsic and extrinsic -

⇒Blocking temperature for superparamagnetism

$$\tau_N = \tau_0 e^{\frac{KV}{k_B T}} \quad \Rightarrow \; T = \frac{KV}{k_B \, ln\,({}^{\tau_N}/_{\tau_0})} \equiv T_\text{b}$$

- if the duration of the mesasurement t_m does not exceed the flipping time τ_N

$t_m \leq \tau_N$ the particle will be seen as a ferromagnet

- but for $t_m \geq \tau_N$ it seems to be paramagnetic
- ⇒ the transition ferromagnetism to superparamagnetism depends on t_m
- however $ln\,({}^{t_m}/_{\tau_0})$ is a weakly varying function with a typical value of 25
- ⇒ the transition occurs at the " Blocking temperature"

$$\boxed{T_\text{b} = \text{KV}/25\text{k}_\text{B}}$$

Explanation of some terms

- **uniaxial materials**

  (one special axis of second order magnetic anisotropy)

- **tetragonal: $Nd_2Fe_{14}B$**
- **hexagonal: Co ($T \leq 723$ K), $SmCo_5$, $BaFe_{12}O_{19}$**
- **rhombohedral: Sm_2Fe_{17}**

alternatives:

cubic: no axis of second order magnetic anisotropy; 3 or 4 axes of fourth order

orthorhombic, monoclinic, trigonal: 3 axes of second order magnetic anisotropy

- (magnetically) **easy-axis materials** (sloppy speech: „easy direction“)

- **$Nd_2Fe_{14}B$** ($T > 135$ K)
- **$SmCo_5$**
- **Co ($T < 535$K)**

alternatives:

- easy cone: $Nd_2Fe_{14}B$ ($T < 135$ K) , Co ($535 \text{ K} < T < 595$ K)
- easy plane: Sm_2Fe_{17} , Tb_2Fe_{17} , Co ($T > 595$ K)

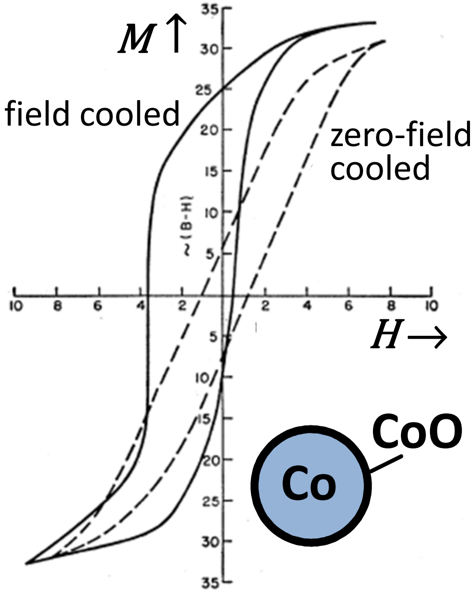
- (seemingly magnetically) **easy-direction materials**

  metastable states with a magnetically **preferred direction** due to magnetic history

  → exchange anisotropy: **Meiklejohn and Bean 1957**

  (⇒ now used as „exchange bias“)

  → also in spin glasses



Superconducting permanent magnets

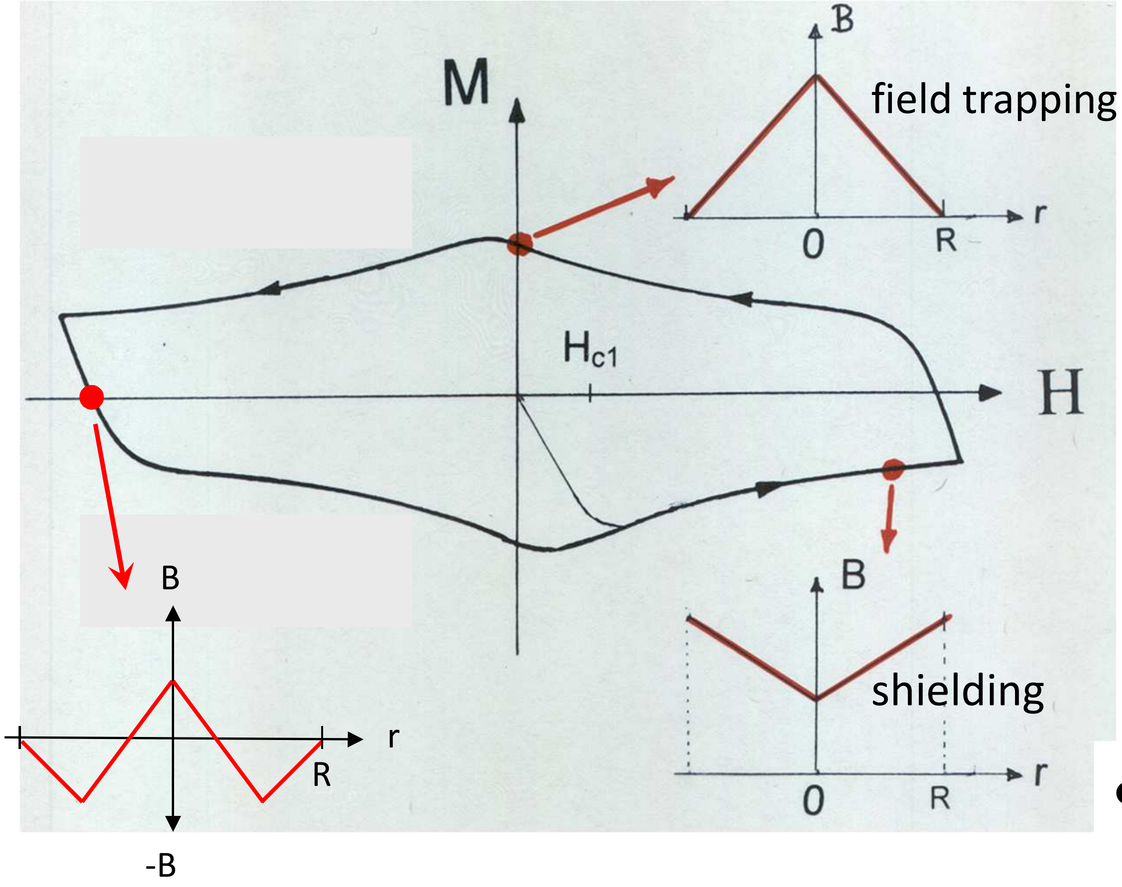
- Permanent magnets can also be made of hard type-II superconductors.

- Different from their ferromagnetic counterparts they are diamagnetic and carry macroscopic persistent currents.

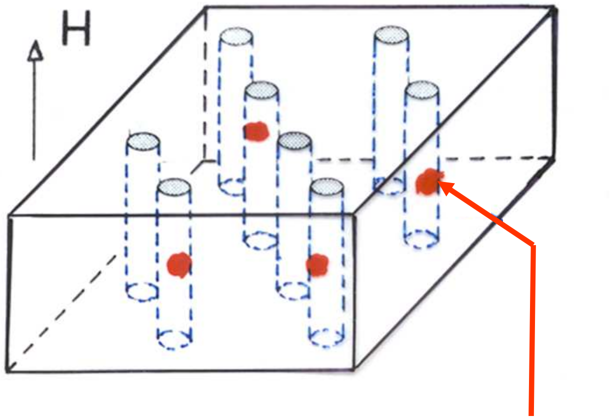
- This results in a fundamentally different hysteretic behaviour.

A type-II superconductor in a magnetic field

- $H > H_{c1}$: **penetration of flux lines** ⇒ **type-II superconductor**
- **Hysteresis loop and field profiles:**

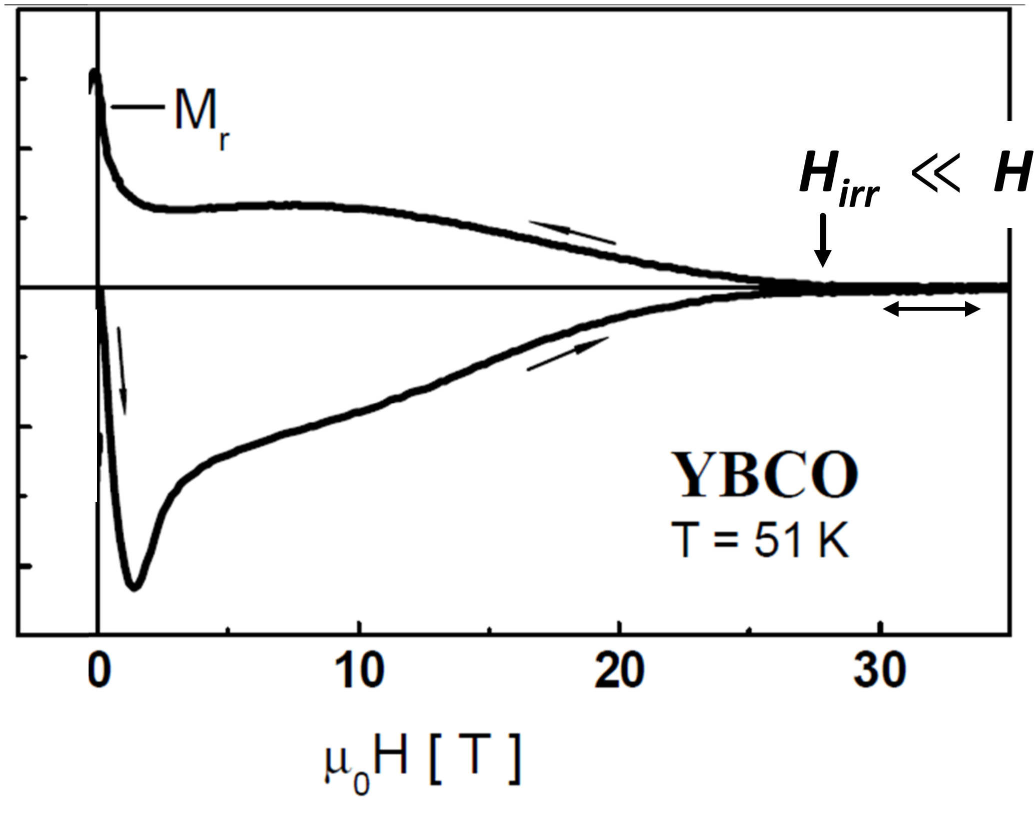


$\Phi_0 = 2 \cdot 10^{-15}\ \mathrm{Tm}^2$
$\xi = 1{,}8\ \mathrm{nm}$



- pinning of flux lines by defects
  ⇒ **hard type-II superconductor**

Hysteretic part of the magnetization in a hard type-II superconductor



$H_{irr} \ll H_{c2} \approx 150\ \mathrm{T}$

Levitation with permanent magnets

- ***Samuel Earnshaw* 1842:**
  „No static levitation with fixed magnets and charges“
- However, *Earnshaw* did not know **Diamagnetism!**
- **Levitation with diamagnetic samples is possible!**

Levitation with permanent magnets

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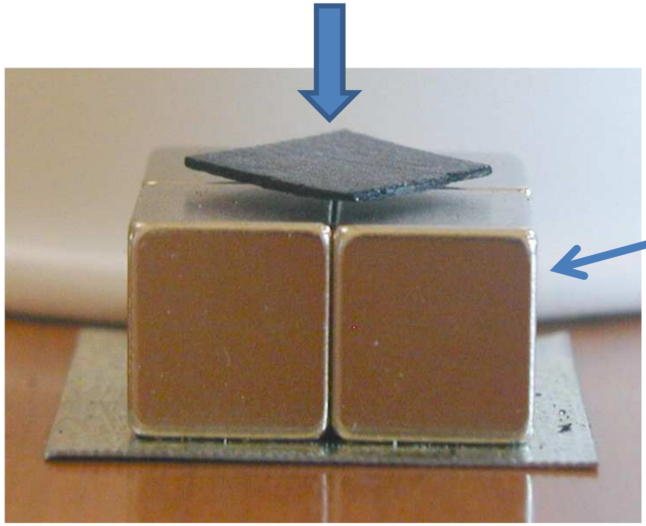
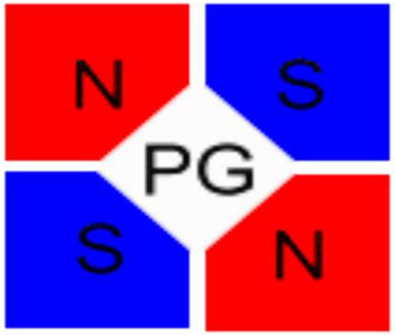
pyrolithic graphite
(thickness and distance to the magnets $\approx 1\,mm$)



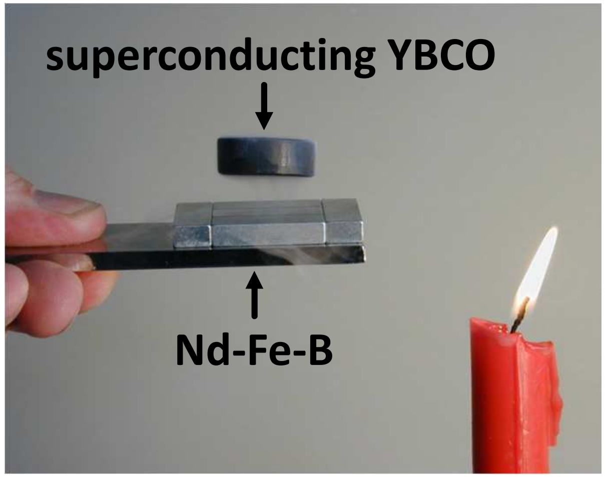
4 sintered Nd-Fe-B magnets



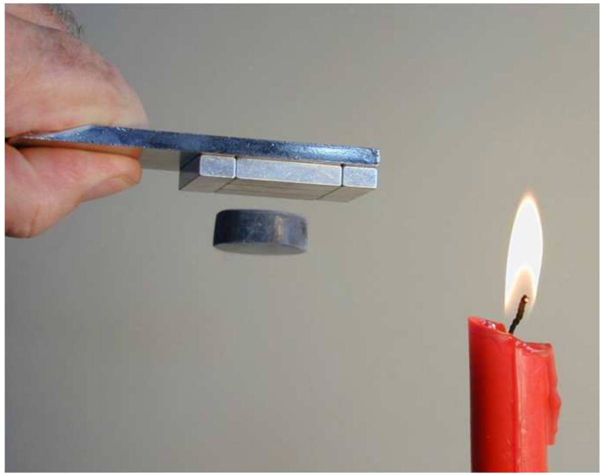
from *Simon Field* (Internet)

A ferromagnetic + a superconducting permanent magnet

Levitation



Suspension



Cross stiffness

- by varying the field distribution of the ferromagnetic permanent magnet the position of the superconducting magnet may have different degrees of freedom :

0 D – as in the examples above
1 D – as a train on a rail

Further reading: some textbooks and monographs

- on physics of magnetism and magnetic matrials -

- Becker-Döhring (1939) – difficult to get
- Brown, W.F. (1962) - difficult to get
- Döhring in Handbuch der Physik; Vol. XVIII/2 (1966)
- Landau–Lifshitz (Course of Theoretical Physics)
- Handbook of magn. Materials (Edit. Wohlfarth/Buschow)
  ⇒ various articles in various volumes
- Kuzmin (↑ Vol. 17)
- Aharoni (1996)
- Coey (1996)
- Chikazumi (1997)
- Bertotti (1998)
- Skomski-Coey (1999)
- Kronmüller-Fähnle (2003)
- Buschow-DeBoer (2003)
- Coey (2010)

Thank you

On permanent magnets

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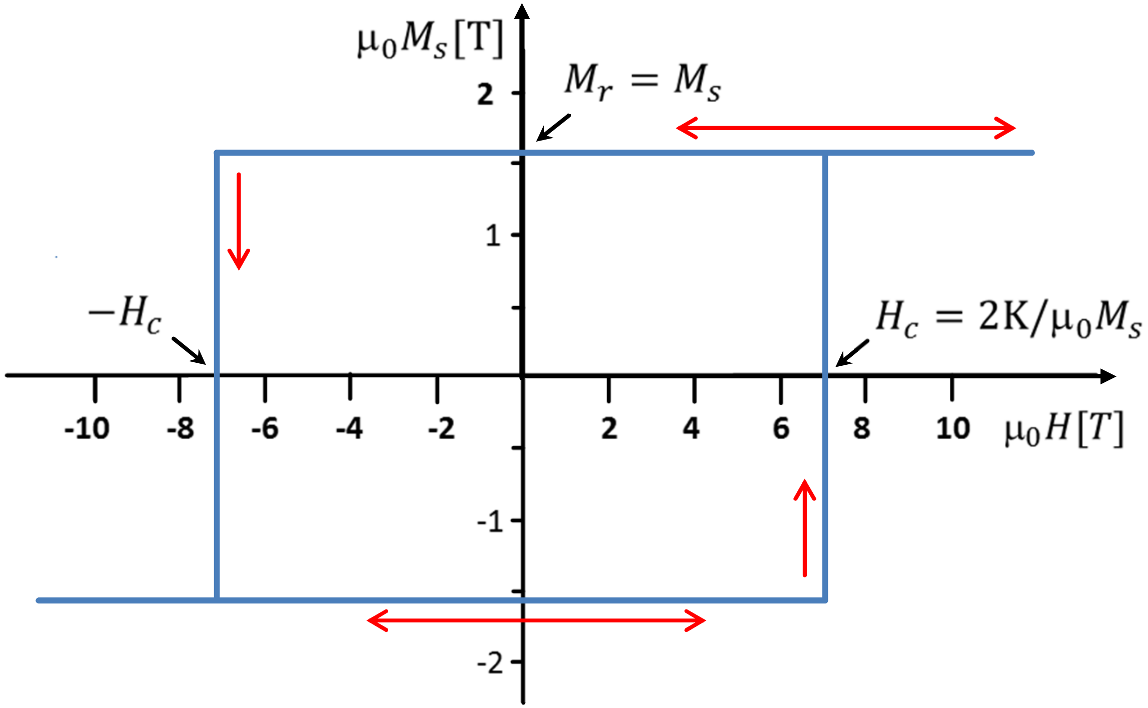
Institute of Metallic Materials at IFW Dresden

Leibniz-Gemeinschaft

II. Permanent magnet materials
or
Hard-magnetic materials

Browns paradox (W.F. Brown 1945)

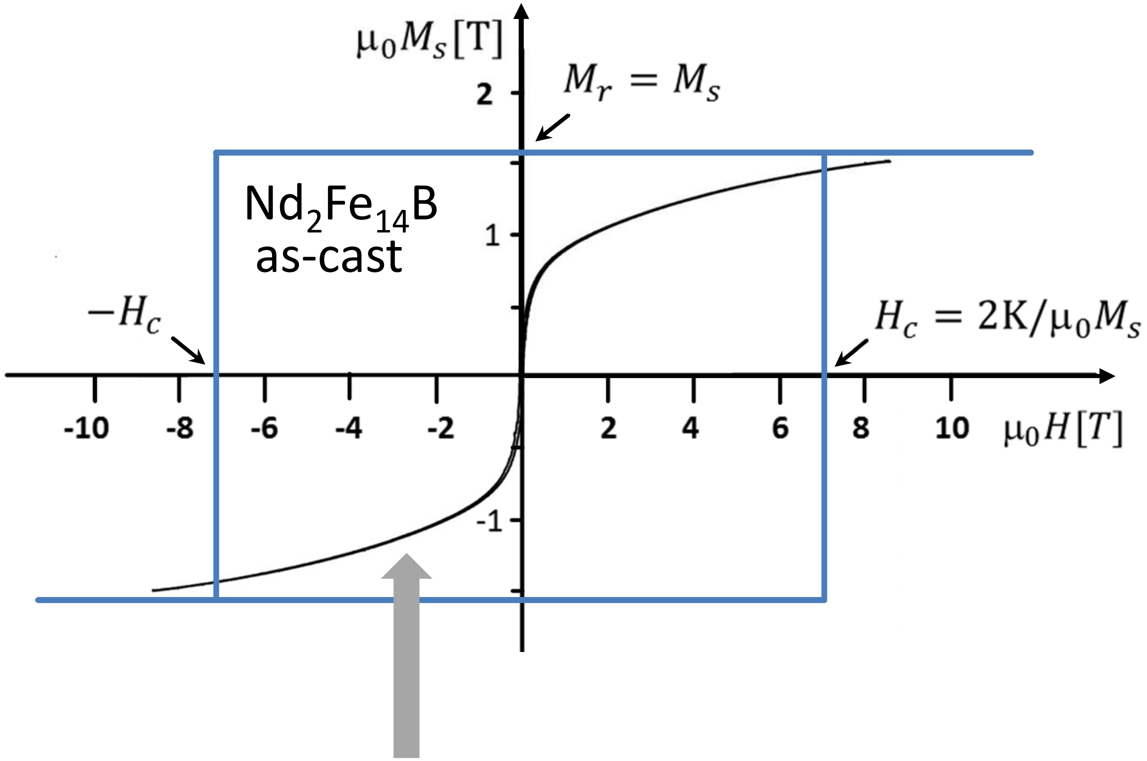
- an unsolved problem of our present physics -



- According to W.F. Brown a spherical sample made of a homogeneous material with a magnetically easy axis parallel to the applied field $\boldsymbol{H}$ has a square hysteresis loop with a coercivity $H_c = 2K/\mu_0 M_s$.
- H_c is independent of the sample size
- **This is a rigorous result of micromagnetism**

Browns paradox (W.F. Brown 1945)

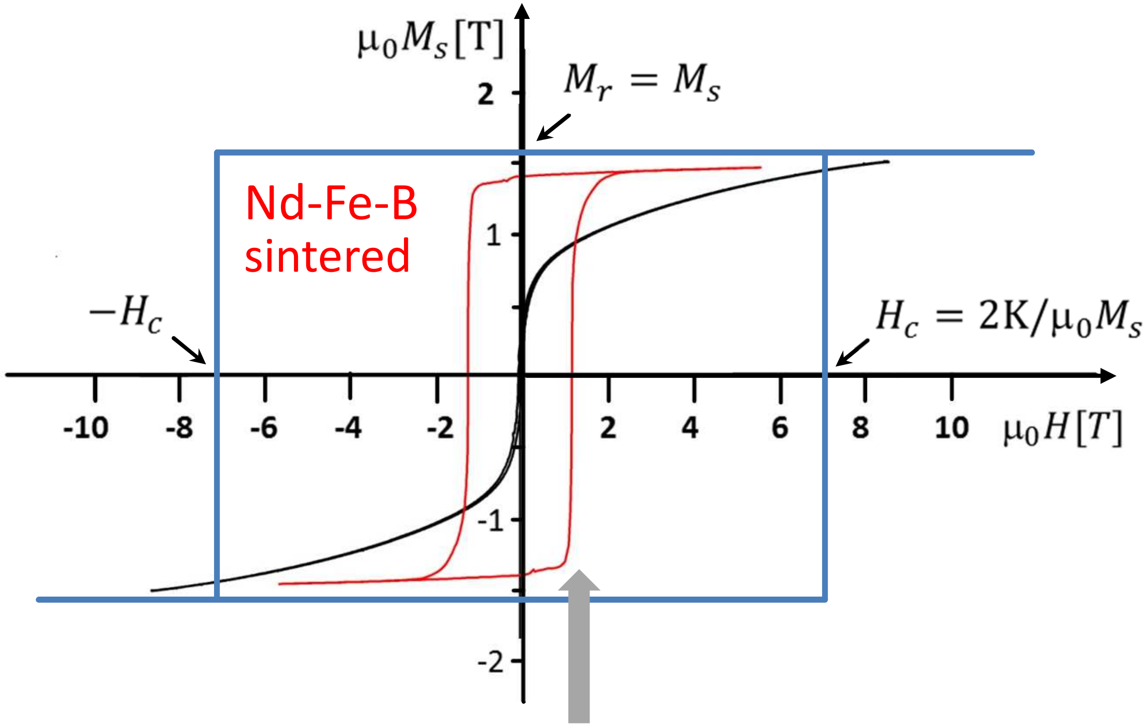
- an unsolved problem of our present physics -



as-cast $Nd_2Fe_{14}B$ has a negligibly small coercivity

Browns paradox (W.F. Brown 1945)

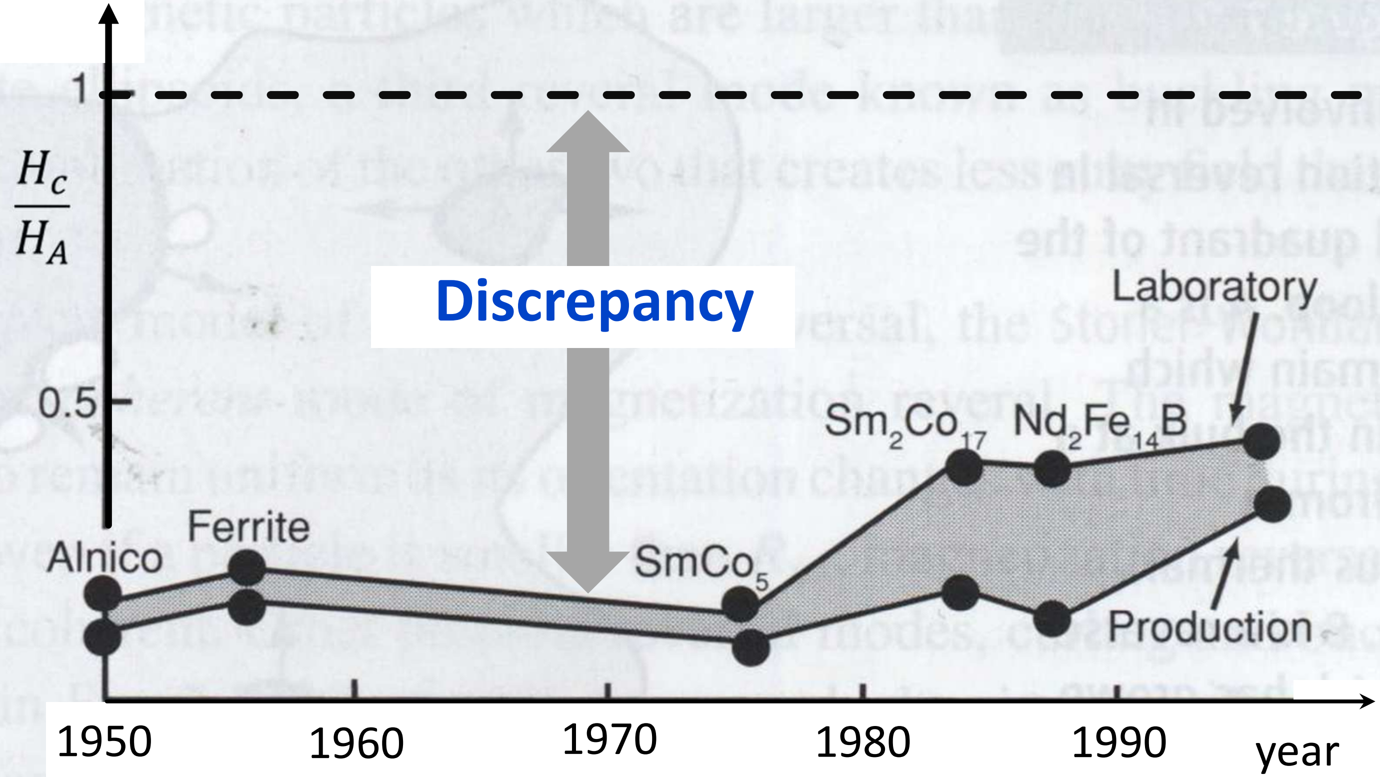
- an unsolved problem of our present physics -



Well textured well prepared samples also have a coercivity far below the predicted value

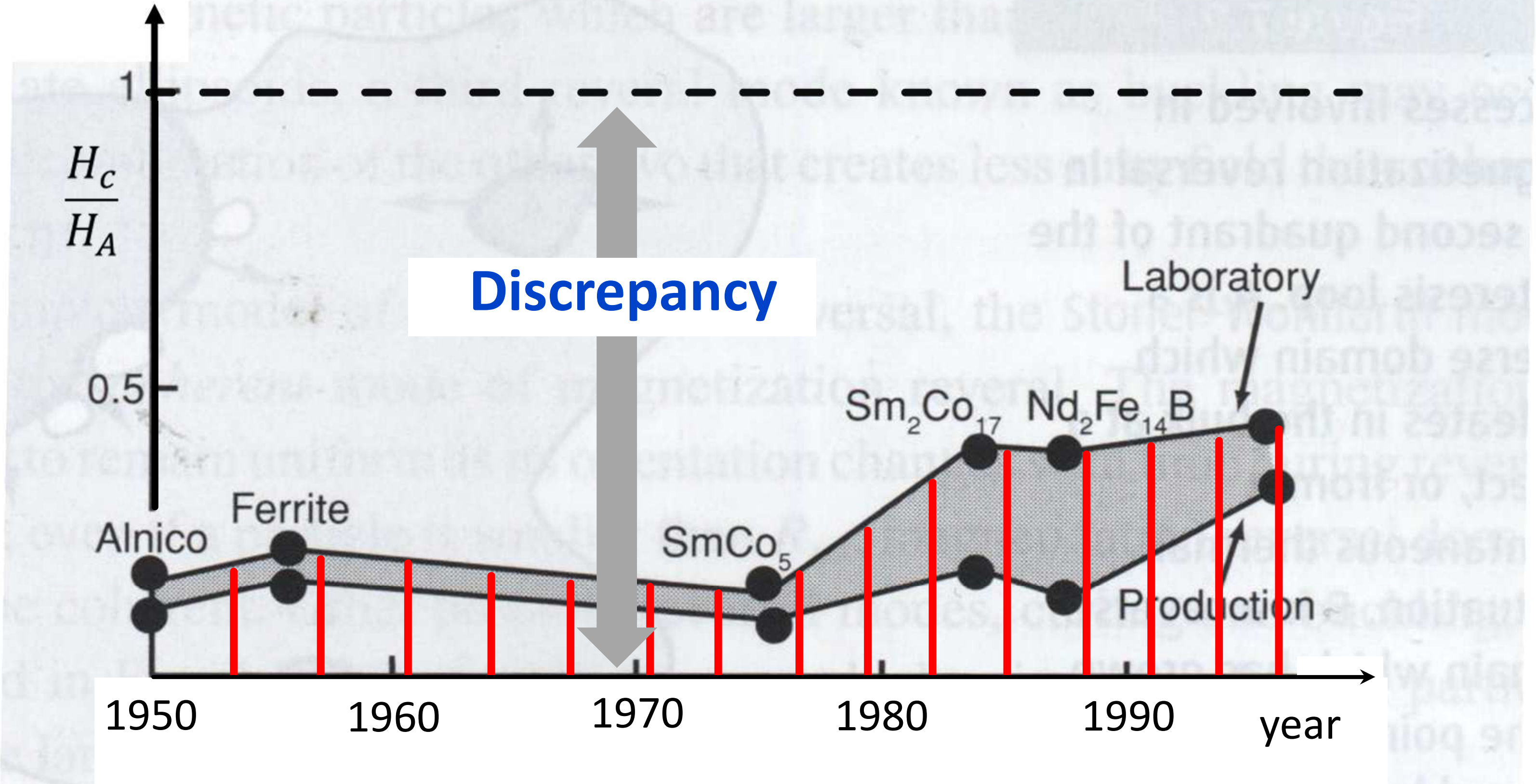
The gap beween the values of H_c achieved in permanent magnet materials and their anisotropy field $H_A = 2\mathrm{K}/\mu_0 M_s$.

These seemingly small values have been achieved only after a long time-consuming and money-consuming struggle of material science.



(after Kronmüller)

- **If the non-optimized materials are included the gap becomes even considerably larger.**
- With increasing perfectness of the material H_c even decreases.
- This phenomenon is definitely related to the metastability of the magnetic state at $|H| = H_c$. But it is not really understood.



Extrinsic properties of permanent magnet materials

1.) the energy density „$(BH)_{max}$“ („energy product“)

- An arbitrary body with an arbitrary magnetization $\boldsymbol{M}$ generates a magnetic field $\boldsymbol{H}$ in the whole space, according to $\boldsymbol{\nabla}(\boldsymbol{H}+\boldsymbol{M})=0$ and $\boldsymbol{\nabla}\times\boldsymbol{H}=0$ $(\boldsymbol{H}+\boldsymbol{M})\equiv\boldsymbol{B}$

$\Rightarrow$ (easy to show): $\int_{space} dV\boldsymbol{BH} = 0$

$$\Rightarrow \int_{body} dV\,\boldsymbol{BH} = -\int_{out} dV\,\boldsymbol{BH} = -\mu_0 \int_{out} dV\,H^2 = -2E_{out}$$

or $\boxed{<\boldsymbol{BH}>_{\boldsymbol{body}} = -2\frac{E_{out}}{V}}$

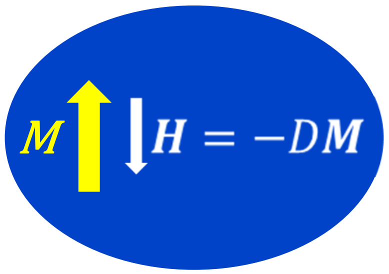
$<\boldsymbol{BH}>_{\boldsymbol{body}}$ is twice the negative of the stray-field energy that the body generates outside of it, divided by the body´s volume.

Extrinsic properties of permanent magnet materials

1.) the energy density „$(BH)_{max}$“ („energy product“) - continued

⇒ Realization of M-vs.-H and B-vs.-H curves using permanent magnets.

- take a homogeneously magnetized spheroid with a demagnetization factor D
- ⇒ the fields $\boldsymbol{H} = -\mathrm{D}\boldsymbol{M}$ and $\boldsymbol{B} = \mu_0(\boldsymbol{M} + \boldsymbol{H}) = \mu_0(1 - \mathrm{D})\boldsymbol{M}$ are uniform
- thus we can realize the complete B-vs.-H curve in its „third“ quadrant ($\boldsymbol{B} > 0$, $\boldsymbol{H} < 0$)
- For a certain value of D = $\mathrm{D}_{\mathrm{opt}}$ the magnet generates the maximum stray-field energy in the space outside of the magnet. Here „maximum“ is related to all positions on the B-vs.-H or M-vs.-H curves
- Note that actually „$(\boldsymbol{BH})_{max}$“ is $(-\boldsymbol{BH})_{max}$
- Note the well-known rectangle construction!



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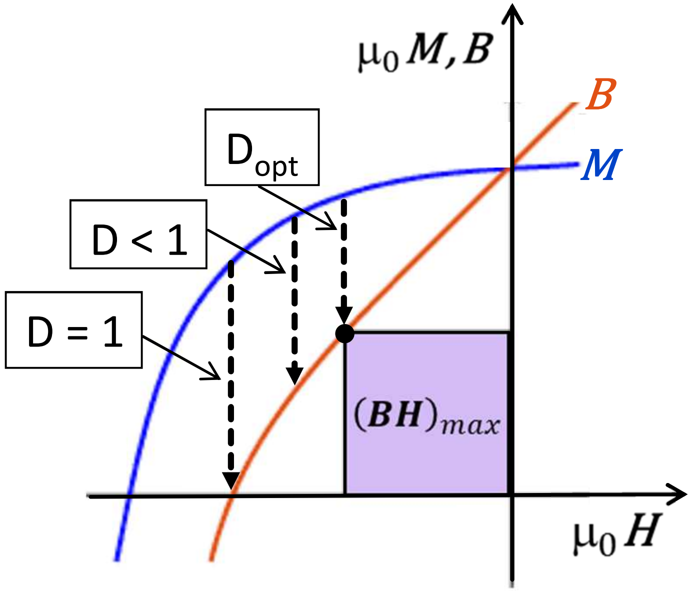
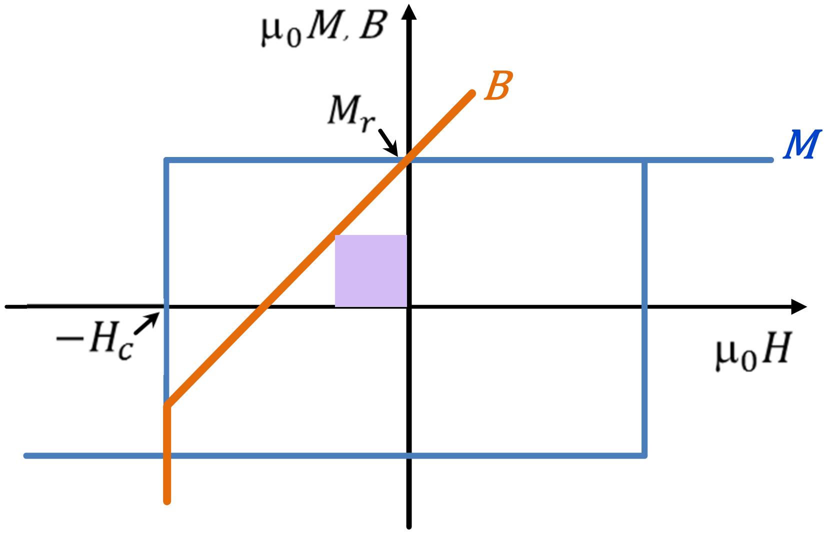


Extrinsic properties of permanent magnet materials

1.) the energy density „$(BH)_{max}$“ („energy product“) - continued

$\Rightarrow$ **ideal and non-ideal materials**



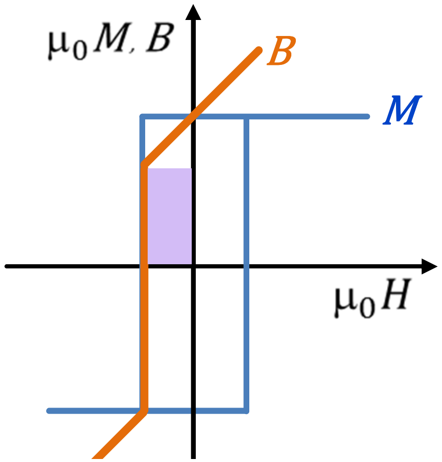
- **ideal mateial** (easy to show):

  If $H_c > \frac{M_r}{2}$ and $M = M_r \approx const$

  $\Rightarrow$ the $(BH)_{max}$ rectangle is a square

  $\Rightarrow$ $(BH)_{max} = \frac{\mu_0 {M_r}^2}{4}$ $\quad D_{opt} = \frac{1}{2}$

  $\Rightarrow$ **examples: Ferrites, rare-earth magnets (both well textured)**



- **low-coercivity material:**

  If $H_c < \frac{M_r}{2}$ and (still) $M = M_r \approx const$

  $\Rightarrow (BH)_{max} = (M_r - H_c)H_c < \frac{\mu_0 {M_r}^2}{4}$

  $D_{opt} = \frac{H_c}{M_r} < \frac{1}{2}$

  $\Rightarrow$ **examples: steels, ALNICO**

Extrinsic properties of permanent magnet materials

1.) the energy density „$(BH)_{max}$“ („energy product“) - continued

Although “$(BH)_{max}$“ has been introduced for potential permanent-magnet applications it can be investigated and determined also using external fields instead of stray fields produced by the considered material.

Extrinsic properties of permanent magnet materials

2.) coercivity or the coercive field (H_c) - continued

Terminology

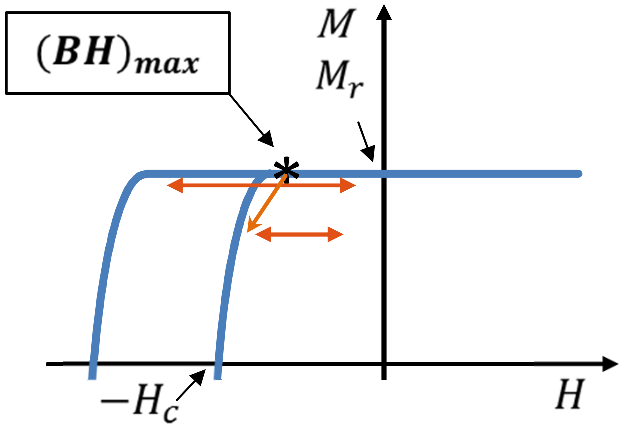
there are various types of coercivity, notations and symbols such as

$${}_jH_c\,,\ {}_iH_c\ ,\ {}_JH_c,\ {}_MH_c\ \Rightarrow \text{"}H_c\text{"}\ \text{ but also }\ {}_BH_c\ \text{ and }\ {}_{B_r}H_c$$

What is needed?

- to get the optimum value of the energy product , $(\boldsymbol{BH})_{max} = \frac{\mu_0 {M_r}^2}{4}$,

  a coercivity of $\boldsymbol{H_c = \frac{M_r}{2}}$ would be sufficient
- however, if the opposite field, $-H$, is little increased the magnetIzation will decrease irreversibly
- H_c decreases faster with increasing temperature than M_r



⇒ for many applications the coercivity should be $H_c \approx M_r$ or even larger

Extrinsic properties of permanent magnet materials

2.) coercivity or the coercive field (H_c) - continued

The main challenge in developing permanent magnet materials is „magnetic hardening“ i.e. to get appropriate values of coercivity H_c dealing with Browns paradox.

- generally this is tackled with the help of sophisticated microstructures taking into account the intrinsic magnetic lengths
- $\Rightarrow$ this is a typical topic of material science

- basically permanent magnets are polycrystalline materials with grains of size D that are more or less decoupled with respect to the exchange interaction

- there are three main concepts of magnetic hardening based on different types of magnetization processes (or „coercive mechanisms“)

$\Rightarrow$ nucleation type magnets, $D > D_c$
(e.g. sintered materials based on $Nd_2Fe_{14}B$ or $SmCo_5$)

$\Rightarrow$ pinning-type magnets, $D > D_c$ (e.g. sintered Sm_2Co_{17} based)

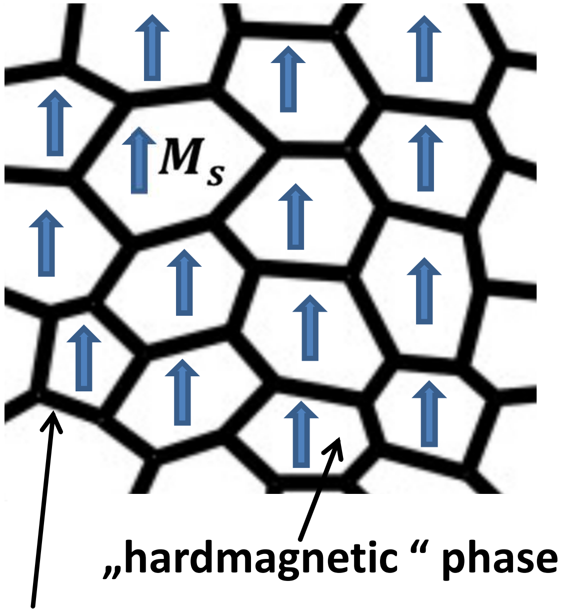
$\Rightarrow$ ***„fine-grained“ or „small particle“*** magnets , $D < D_c$,
(produced by rapid quenching, mechanical milling, HDDR,...)

Extrinsic properties of permanent magnet materials

3.) remanence or remanent magnetization (M_r)

To get a remanence , $M_r \leq M_s$ (⬆) ,
as large as possible we need:

- as little as possible non-magnetic phases
- grain alignment (texture)
  as perfect as possible



Extrinsic properties of permanent magnet materials
- a preliminary summary -

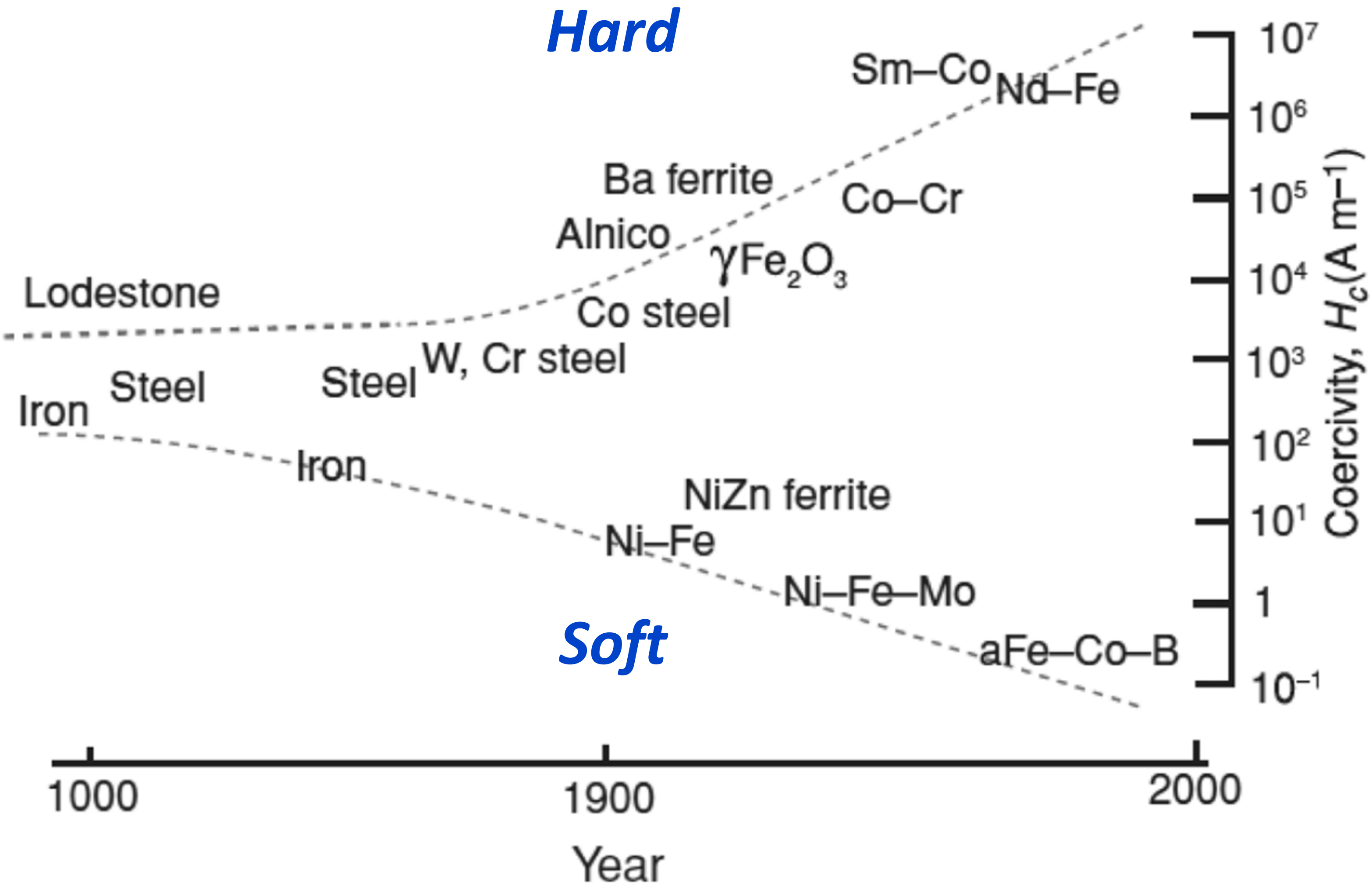
- Extrinsic magnetc properties of permanent magnets are governed by both, intrinsic magnetic properties and (details of the) microstructure:

$$\boxed{\textbf{extrinsic property} = \textbf{intrinsic properties} + \textbf{microstructure}}$$

- $(\boldsymbol{BH})_{\boldsymbol{max}}$, M_r and H_c are the main extrinsic properties of a permanent magnet material
- upper bounds for them result from the intrinsic properties M_s and H_A and their temperature dependencies (dominated by T_C)
- M_r and H_c often show opposite dependencies on microstructural parameters

Further important properties of permanent magnet materials:
mechanical properties, machinability, corrosion resistance, electrical conductivity, availability of needed raw materials, price, ...

Development of coercivity (after Coey 2011)



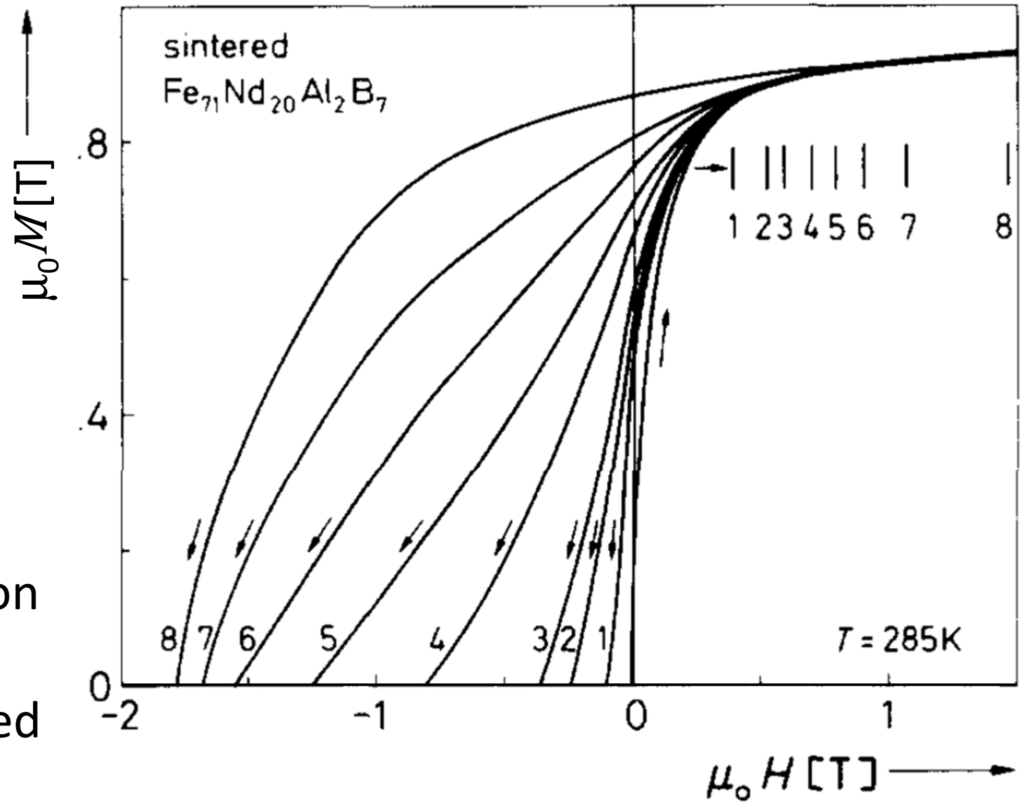
sintered Nd-Fe-B (Sagawa 1984)

- a typical nucleation-type magnet -

- the virgin curve is as steep as in the case of a soft-magnetic material (due to the presence of easily movable domain walls)

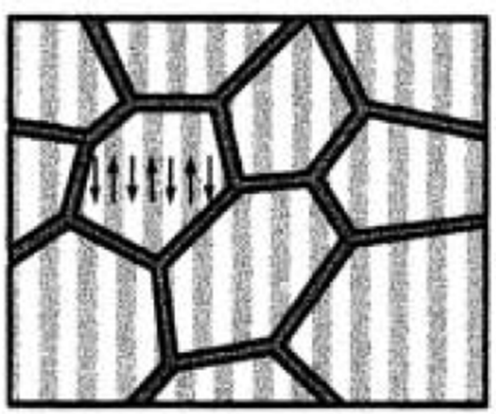
- demagnetization starts with the nucleation of reverse domains

- to attain the „major demagnetization curve“ (i.e. the full coercive field) larger magnetizing fields are needed because residual nuclei have to be removed

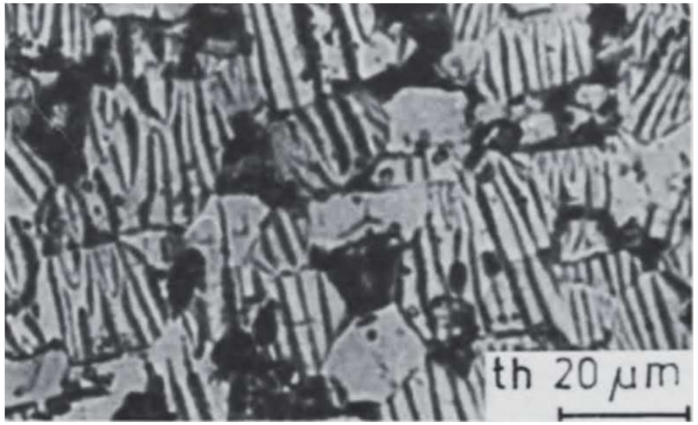


virgin curve and demagnetization curves measured after magnetizing in fields up to the values indicated by numbers

magnetic domains in a thermally demagnetized sintered Nd-Fe-B magnet



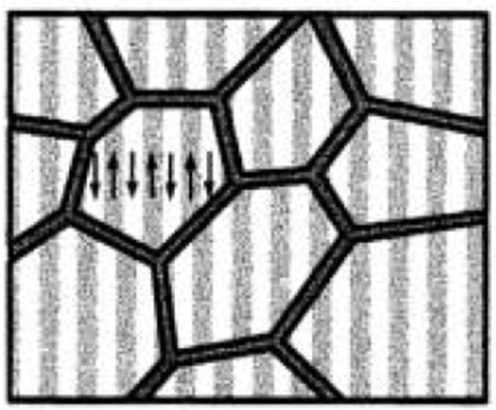
schematic



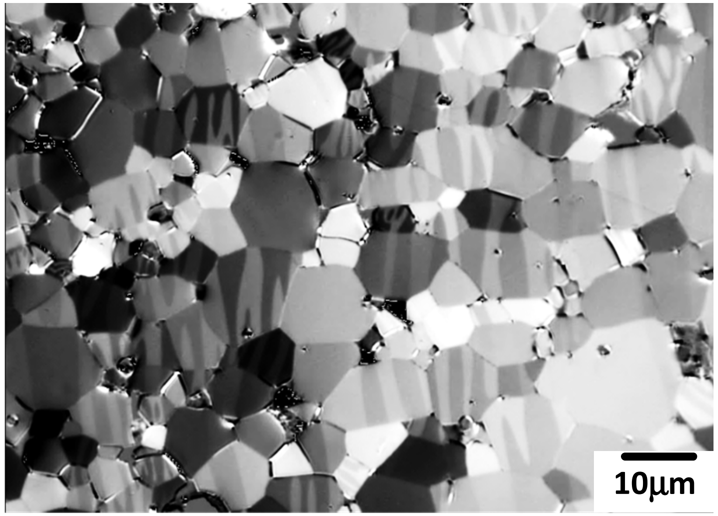
observed by Bitter technique

Each grain contains a domain structure because it is larger than the critical single-domain size, $D > D_c \approx 0.3\ \mu\mathrm{m}$.

magnetic domains in a thermally demagnetized sintered NdFeB magnet



schematic



observed by Kerr microscopy

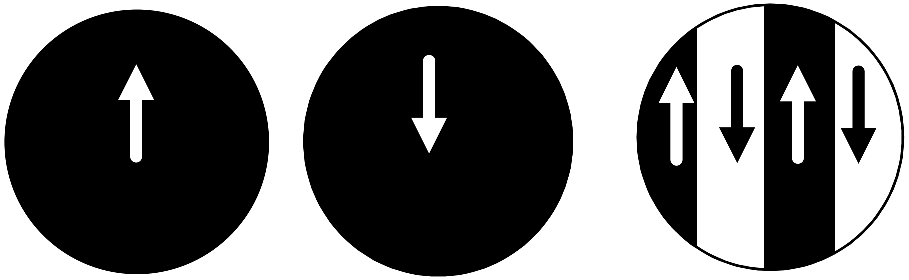
$$D > D_c \approx 0.3\ \mu\mathrm{m}$$

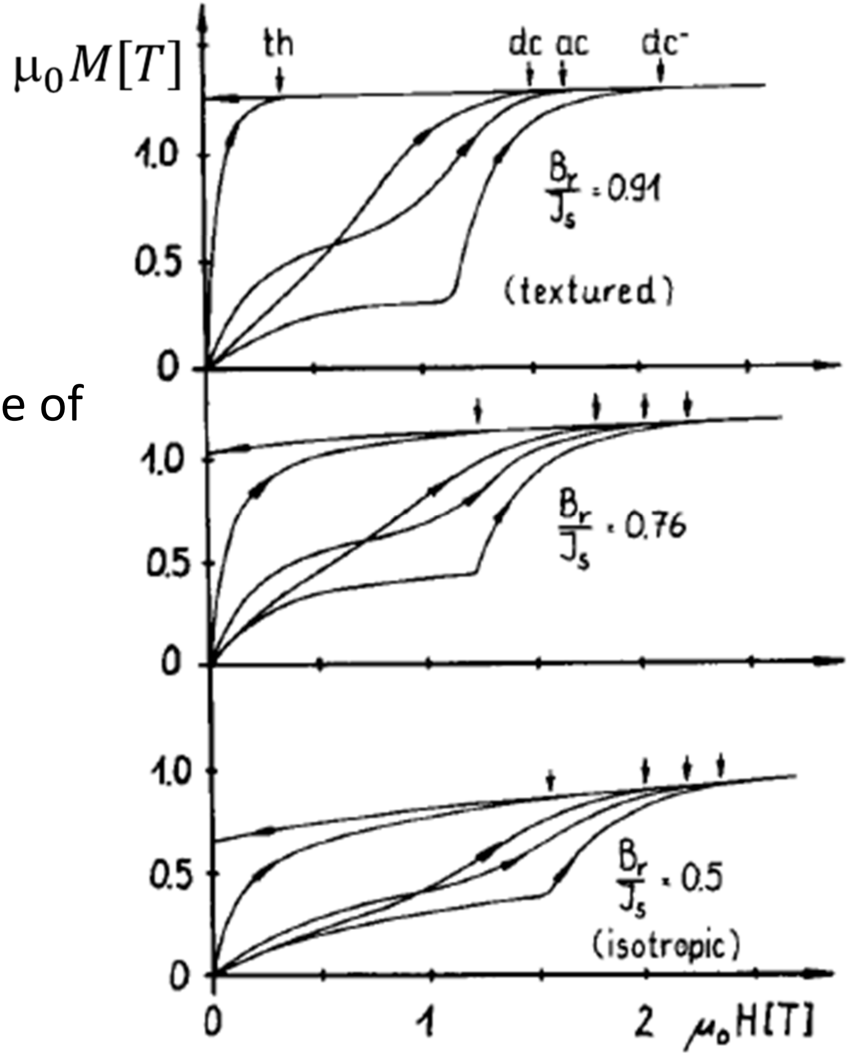
sintered Nd-Fe-B

- a typical nucleation-type magnet -

- In nucleation type magnets the initial magnetization curve is very sensitive to the magnetic history of the magnet.

- Generally the demagnetized state is a mixture of three types of grains.



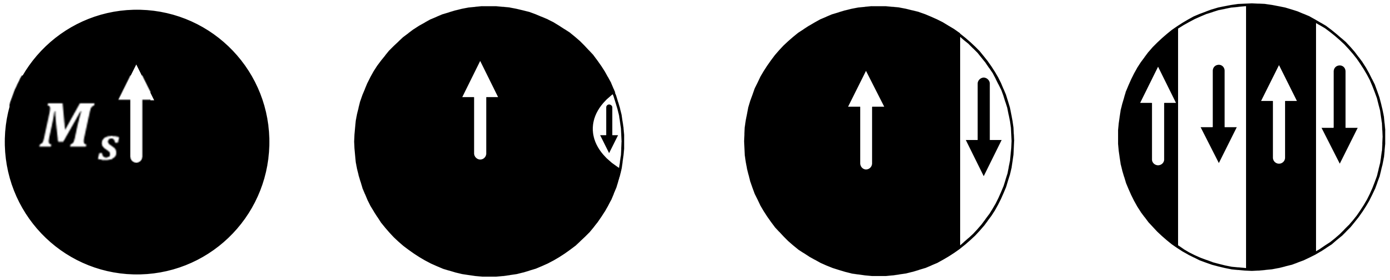


sintered Nd-Fe-B

- a typical nucleation-type magnet –

the concept „nucleation of reverse domains“

a $Nd_2Fe_{14}B$ grain in a sintered magnet in an increasing field opposite to M_s (schematically)



magnetized grain **nucleation event** **demagnetized grain**

Since the grains are „exchange-decoupled“ by „non-magnetic“ grain boundaries during demagnetizing of a magnet of 1cm size with a grain size of $D = 5\mu m$, such „nucleation“ has to take place at least 10^9 times!

The details of this nucleation process and what peculiarities of the microstructure do govern it is still largely unknown.

sintered Nd-Fe-B

- a typical nucleation-type magnet -

influence of post-sintering annealing near a eutectic temperature:

- **the effect is large**
- **annealing times of only 10 min are sufficient**
- **it is nearly reversible**
- **no microsturctural effects could be detected convincingly so far**

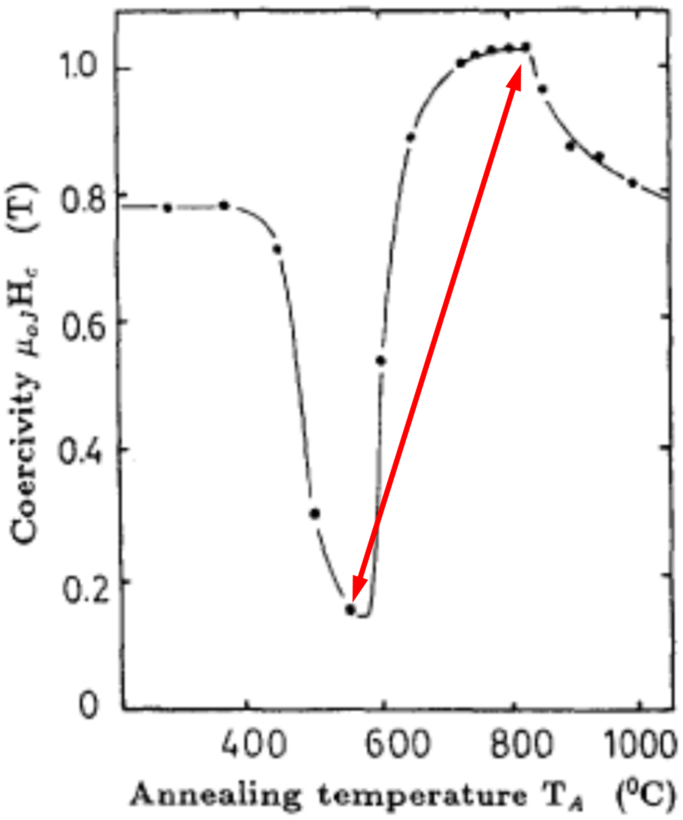


Fig.1. Coercivity of a $(Nd,Dy)_{15}(Fe,Co,Mo,Al)_{77}B_8$ magnet, measured at 150^{0}C, versus post-sintering heat treatment temperature. Annealing time: 1 hour.

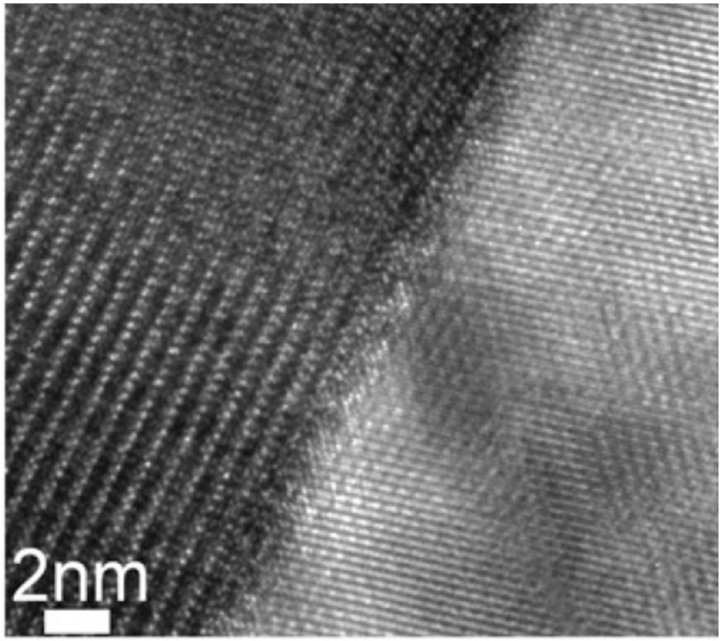
sintered Nd-Fe-B

- a typical nucleation-type magnet -

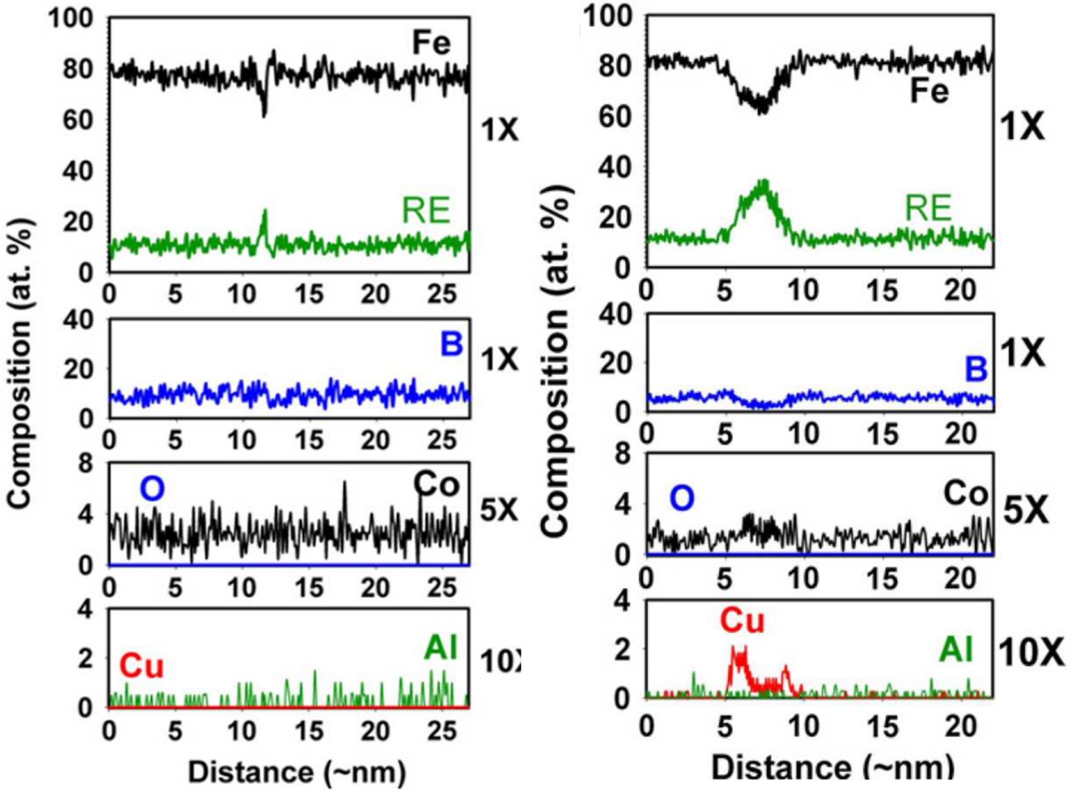
influence of post-sintering annealing (Sepehri-Amin/Hono-2012):

$Nd_2Fe_{14}B$ ↓

Nd-rich phase
in a triple point ↓



high-resolution TEM picture of the annealed state

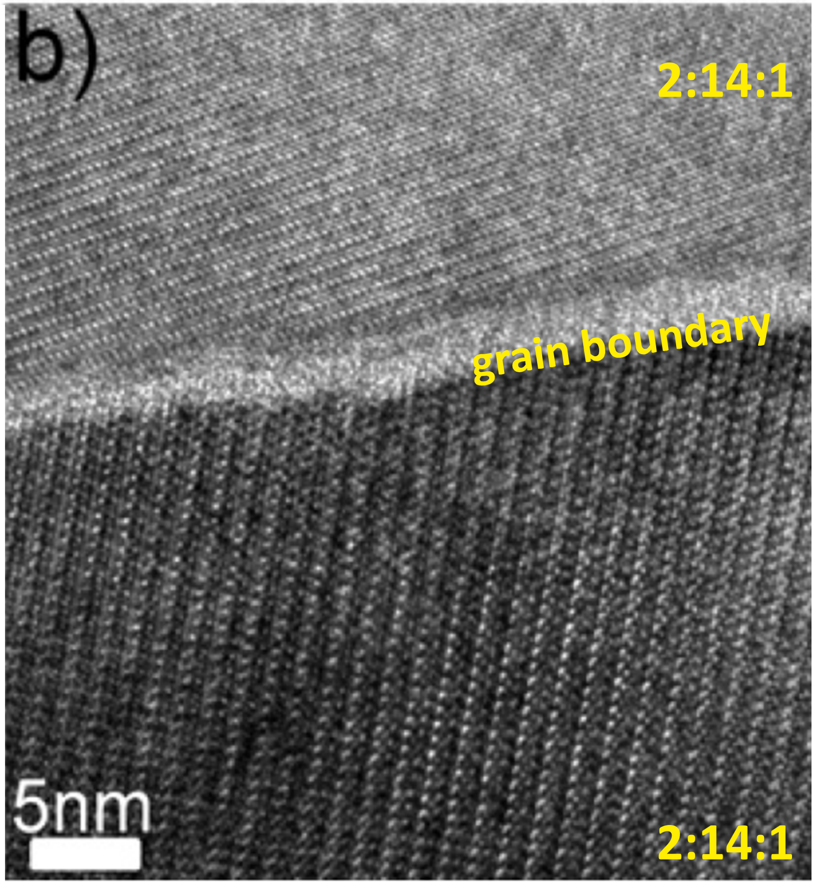


as sintered annealed
3D atom probe analysis across a grain boundary

sintered Nd-Fe-B

- a typical nucleation-type magnet -

post-sinter annealing and Dy grain-boundary diffusion



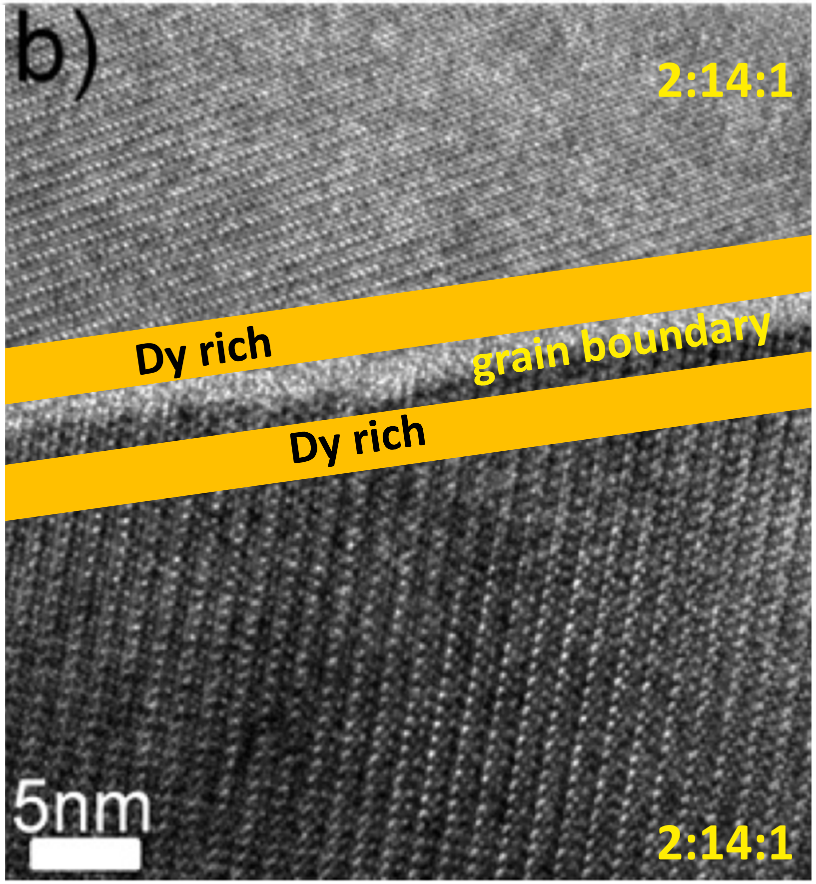
Sepehri-Amin et al. 2013

- To tell the truth, the detailed infuence of the Nd-rich metallic grain boundary phase on coercivity i.e. on the nucleation processes and how this is modified by post-sinter annealing is not really known.
- Additions of Dy are known to enhance the magnetic anisotropy and consequently the coercivity of the sintered magnets.
- However Dy also reduces the remanence and it is expensive.
- **An encouraging and successfully implemented idea is to concentrate the Dy close to the grain boundary, by grain-boundary diffusion, because it is needed only there.**

sintered Nd-Fe-B

- a typical nucleation-type magnet -

post-sinter annealing and Dy grain-boundary diffusion



Sepehri-Amin et sal. 2013

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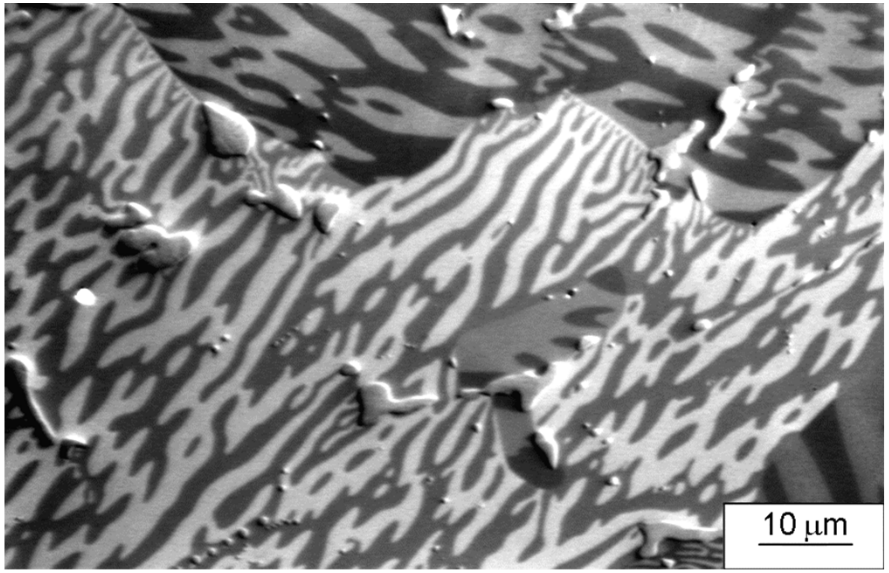
Permanent magnets based on Sm_2Co_{17}

- being considered as typical pinning-type magnets -



domain structure of as cast material indicating an easy-axis material

- „2:17 magnets“ are usually produced by a sintering procedure in order to get a large M_r where the 2:17 grains are aligned in a magnetic field before sintering
- However grain separation is unimportant for magnetic hardening based on pinning of domain walls
- $\Rightarrow$ large coercivity has also been achieved in bulk materials and melt-spun materials

Permanent magnets based on Sm_2Co_{17}

- being considered as typical pinning-type magnets -

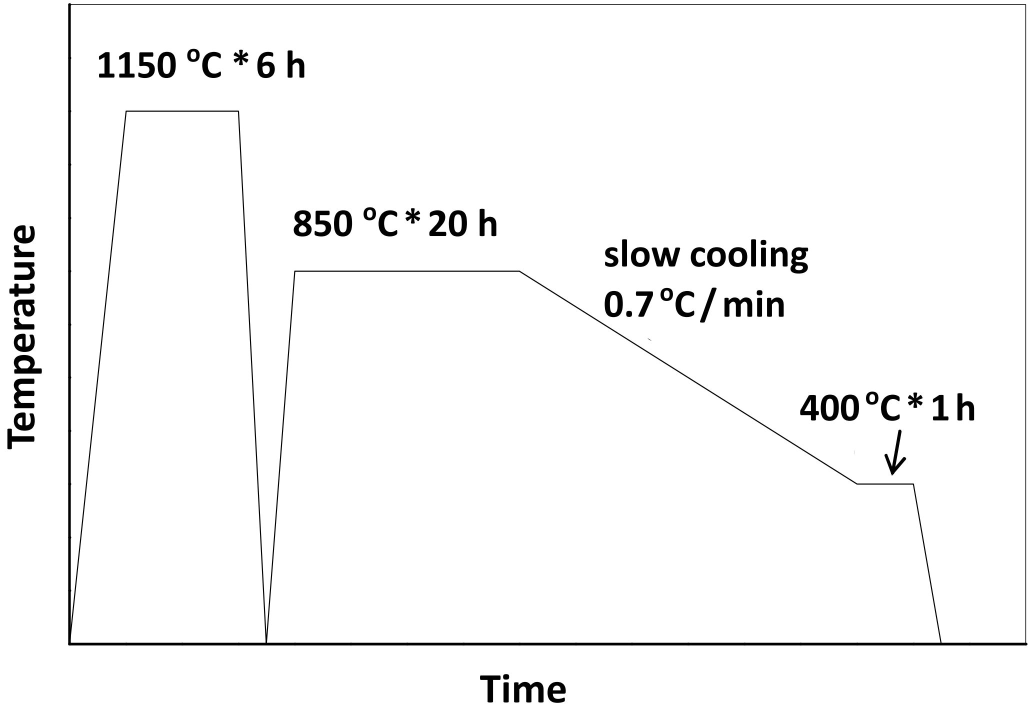
high-quality „2:17 magnets“ are obtained, by experience, by

1.) non-stoichiometric composition, as e.g. $Sm(Co_{0.784}Fe_{0.1}Cu_{0.088}Zr_{0.028})_{7.19}$
(the composition of our sintered magnet)

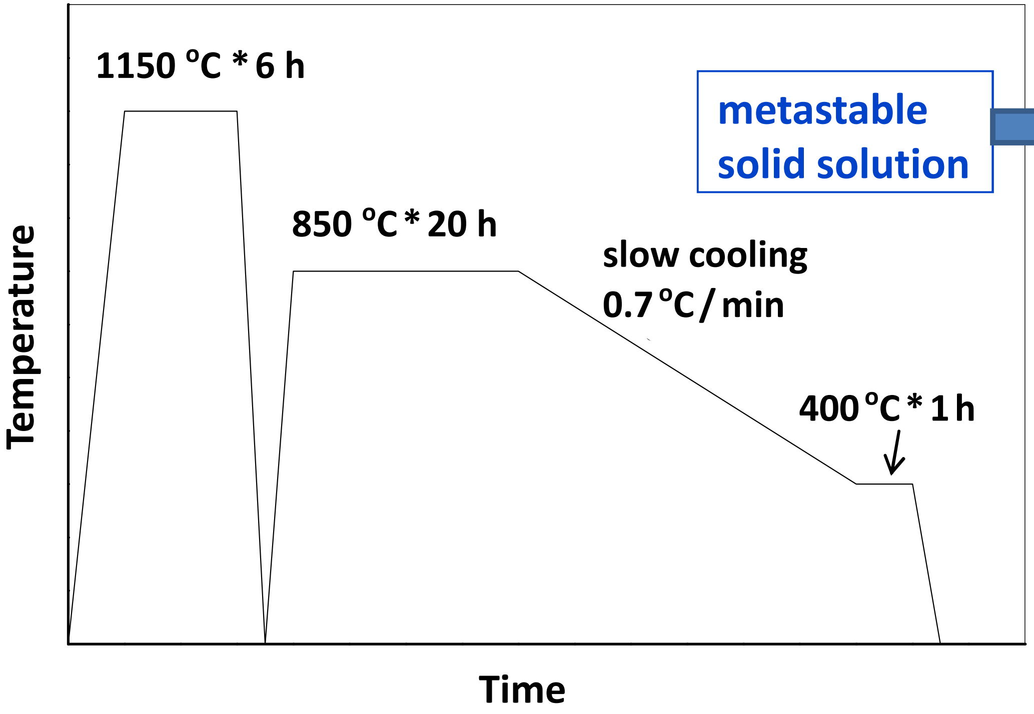
$\Rightarrow$ less cobalt than $\frac{17}{2+17}$
$\Rightarrow$ addition of Zr and Cu

2.) a very special heat treatment procedure

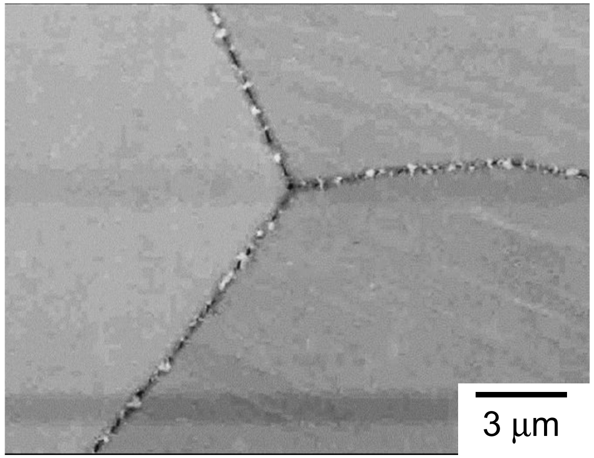
Heat treatments of 2:17 magnets



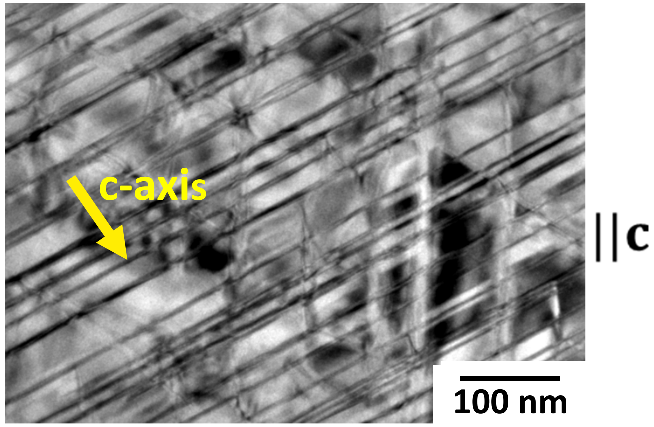
Heat treatments of 2:17 magnets



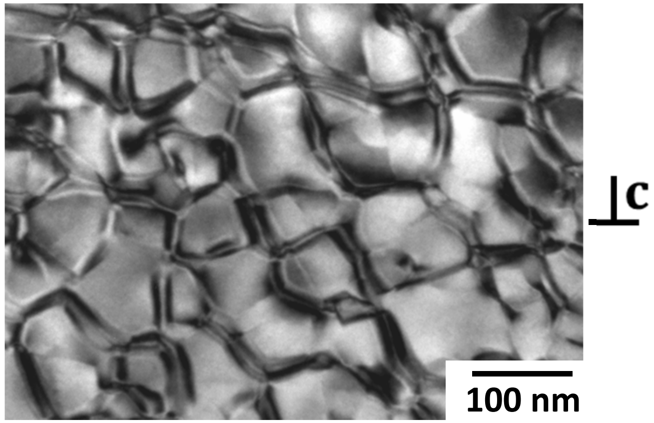
metastable solid solution



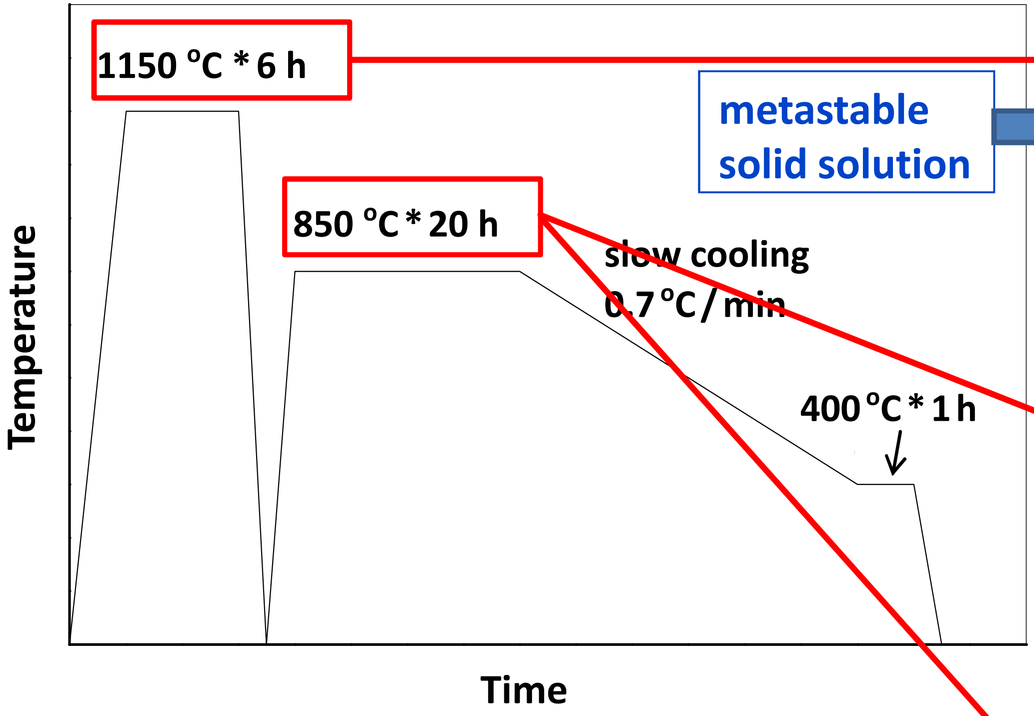
thin Zr rich lamellae perpendicular to the rhombohedral c-axis



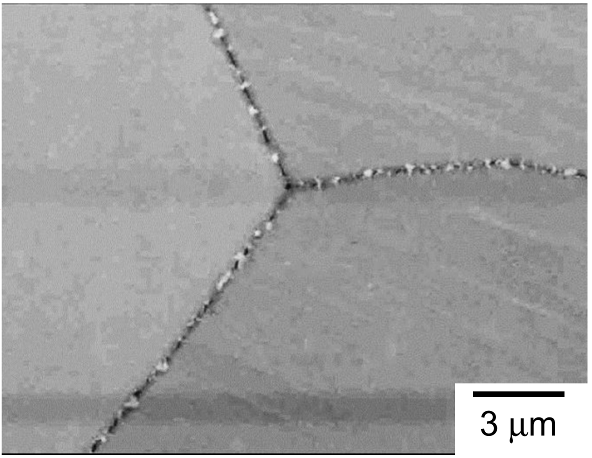
2:17 „cells“ separated by few nm thick cell boundaries consisting of 1:5 phase

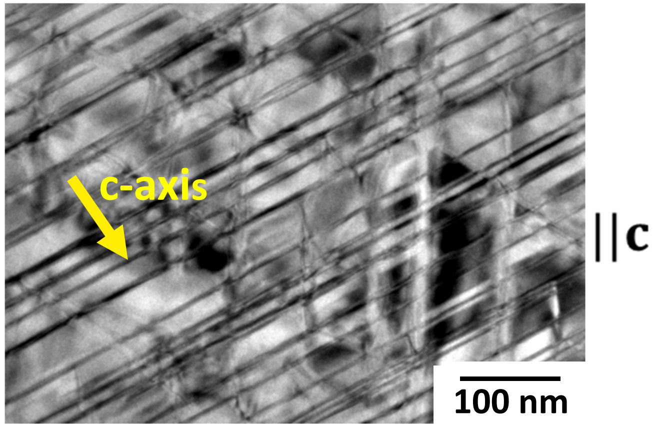


Heat treatments of 2:17 magnets



metastable
solid solution





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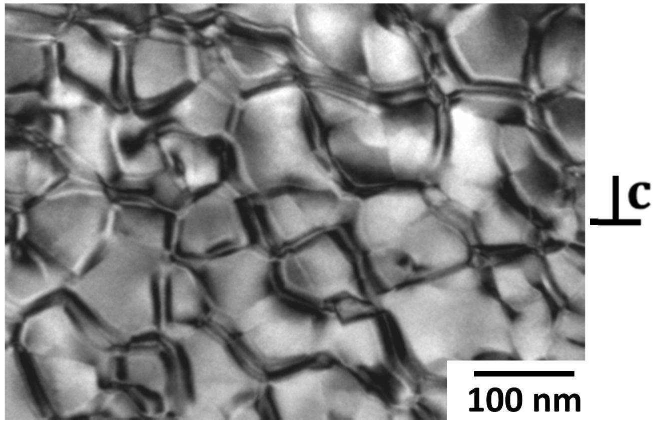
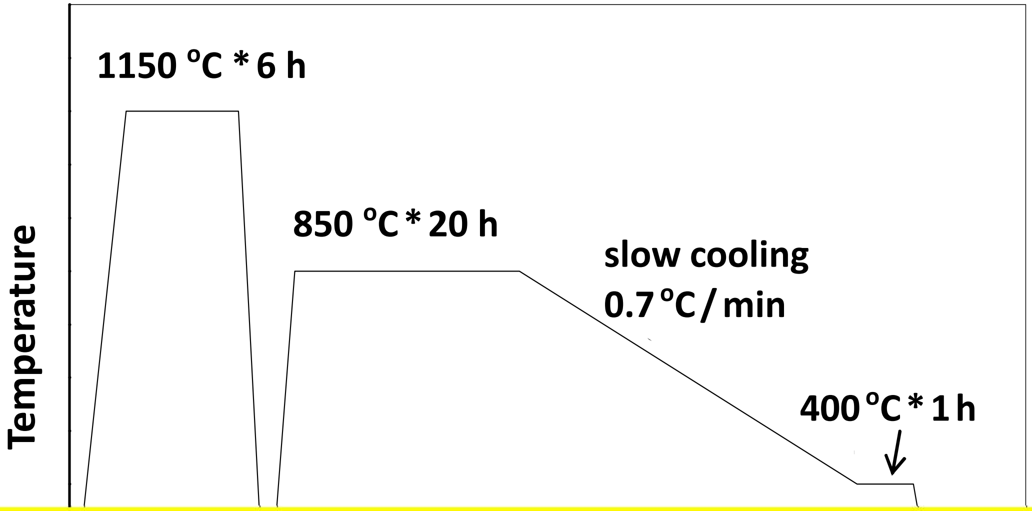
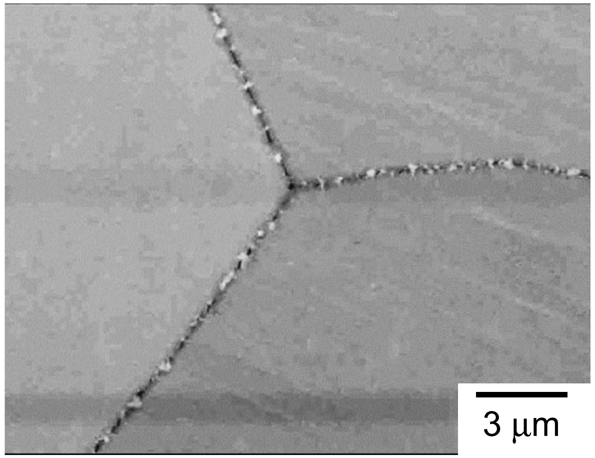


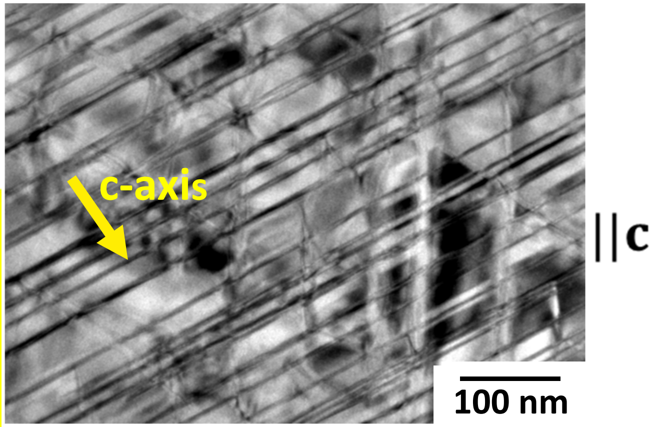
2:17 „cells“ separated
by few nm thick cell boundaries
consisting of 1:5 phase

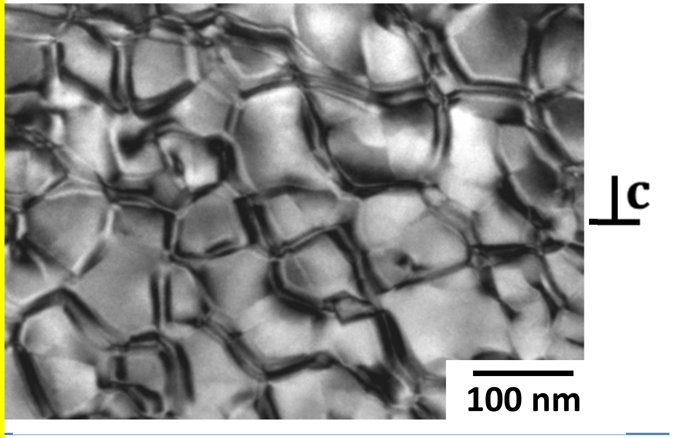
Heat treatments of 2:17 magnets



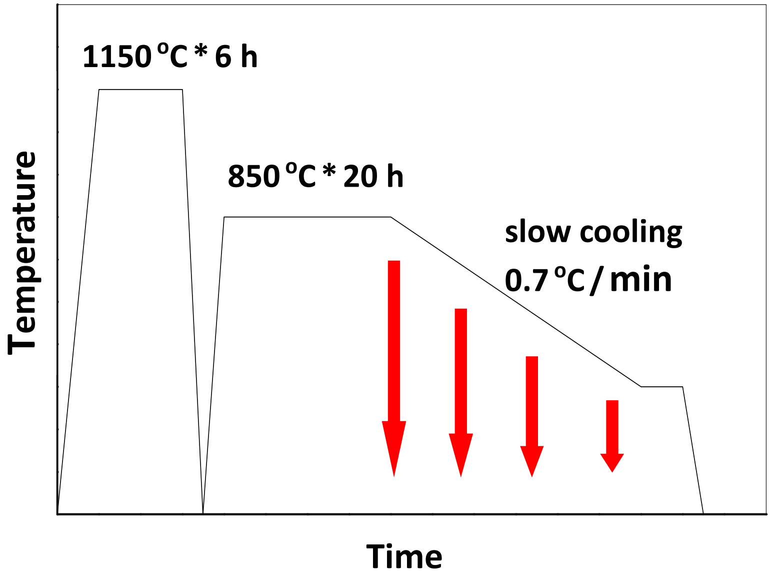
- the same microstructures are obtained for
  - sintered magnets,
  - ingots,
  - melt-spun samples
- microstructure is unchanged after slow cooling
- ⇒ what happens during slow cooling which strongly improves H_c ?

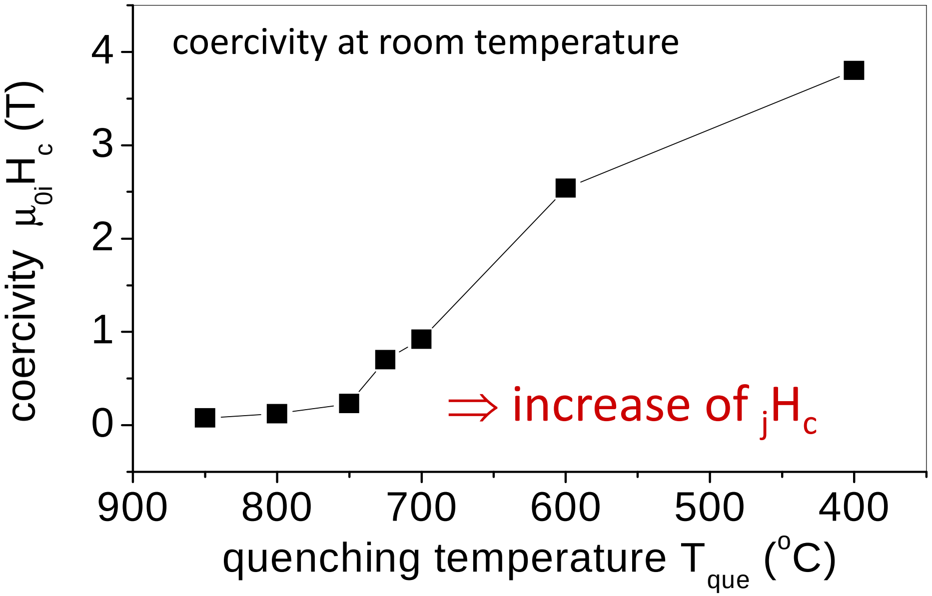






The influence of slow cooling in 2:17 magnets



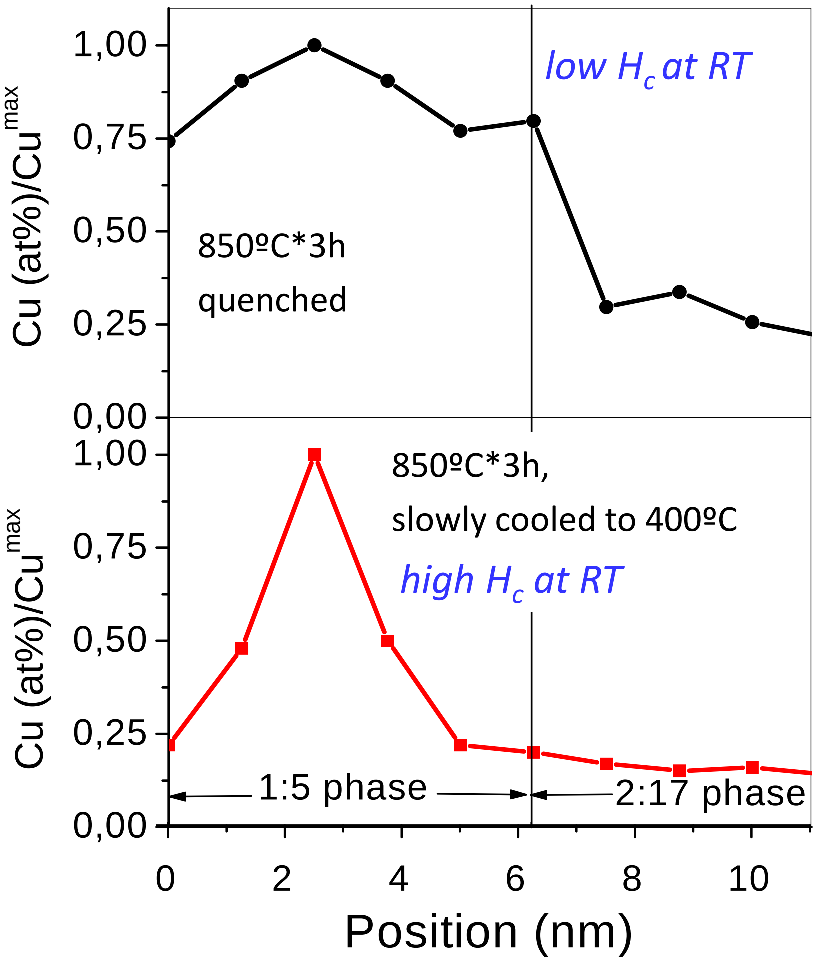


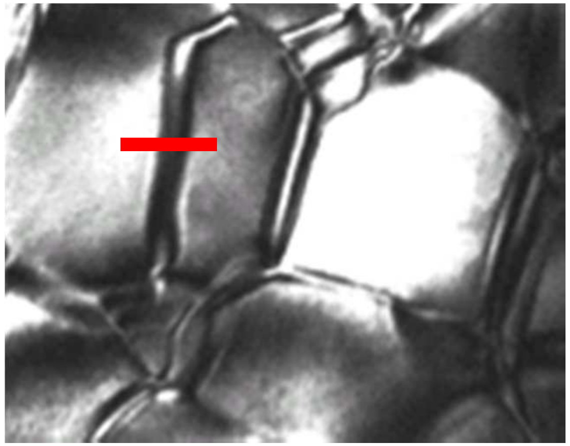
- there is a strong influence of the post-annealing slow cooling on the coercivity of 2:17 magnets

- the reason for this phenomenon was unclear until some years ago

- It has been successfully investigated and published in several papers by
  T. Gemming , O. Gutfleisch , A. Handstein, K. Khlopkov,
  A. Martinek, K.-H. Müller R. Schäfer, L. Schultz, M. Wolf, A. Yan

EDX profiles of Cu across a cell boundary

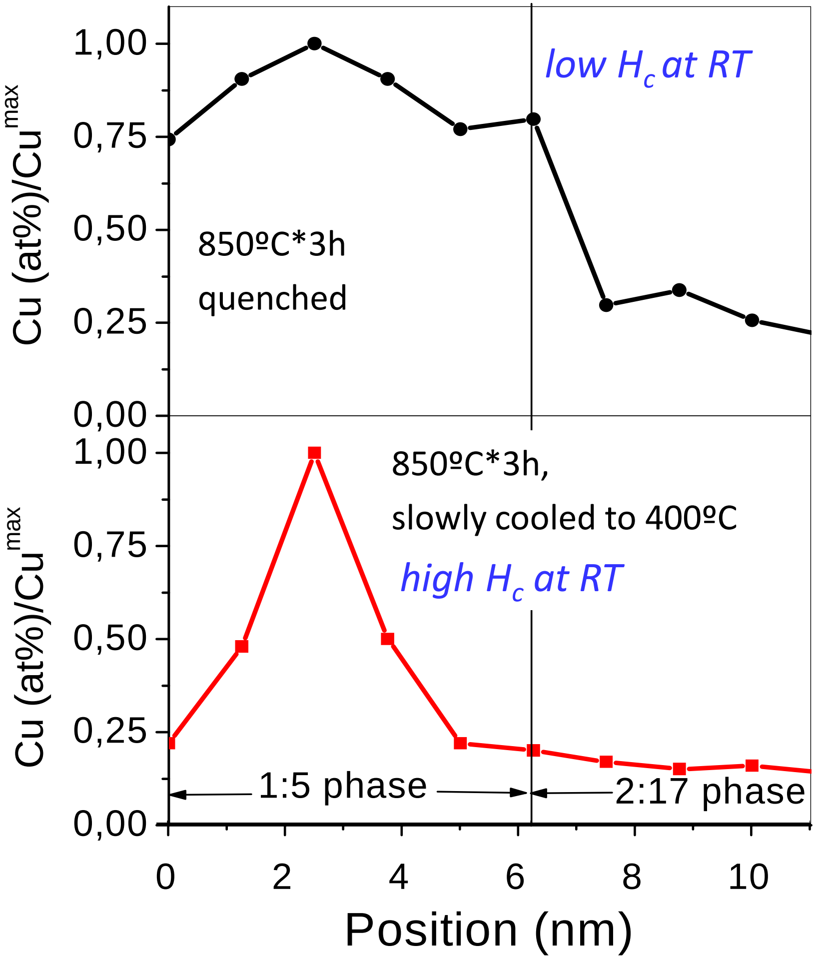


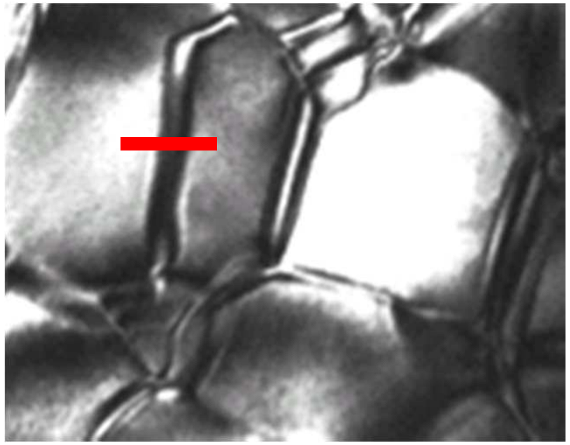


⇒ after the heat treatment at 850°C
Cu is enriched in the 1:5 cell boundary

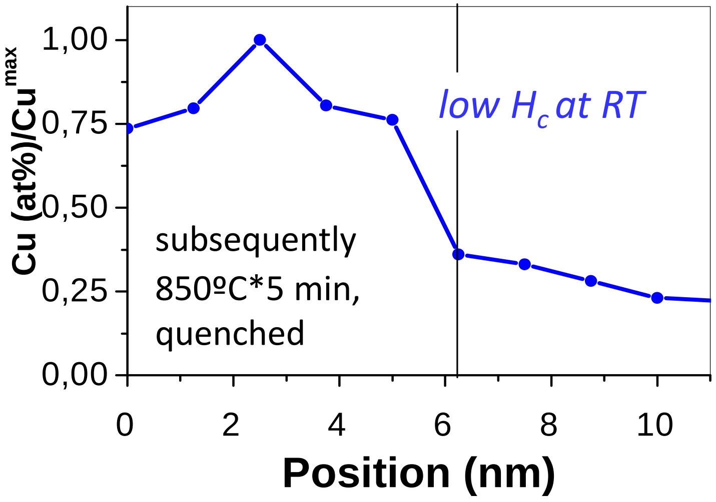
⇒ after slow cooling a narrow Cu concentration
profile has been formed in the cell boundary

EDX profiles of Cu across a cell boundary





⇒ ⇒

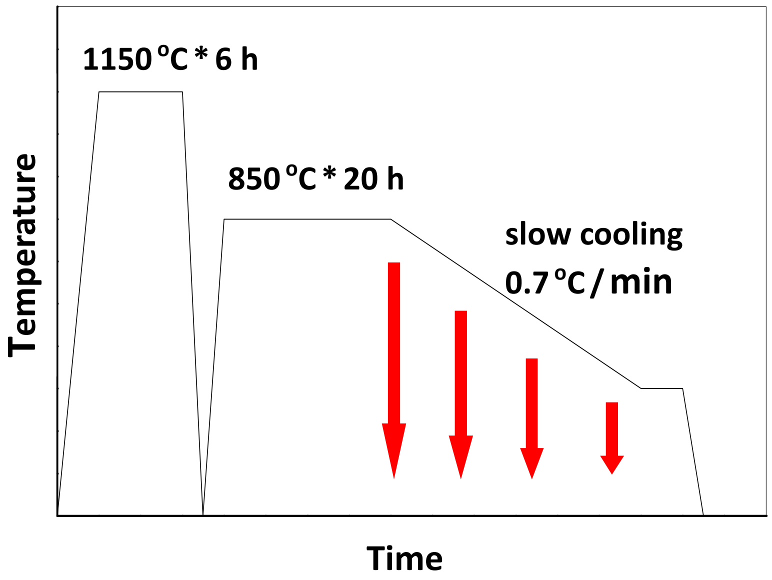


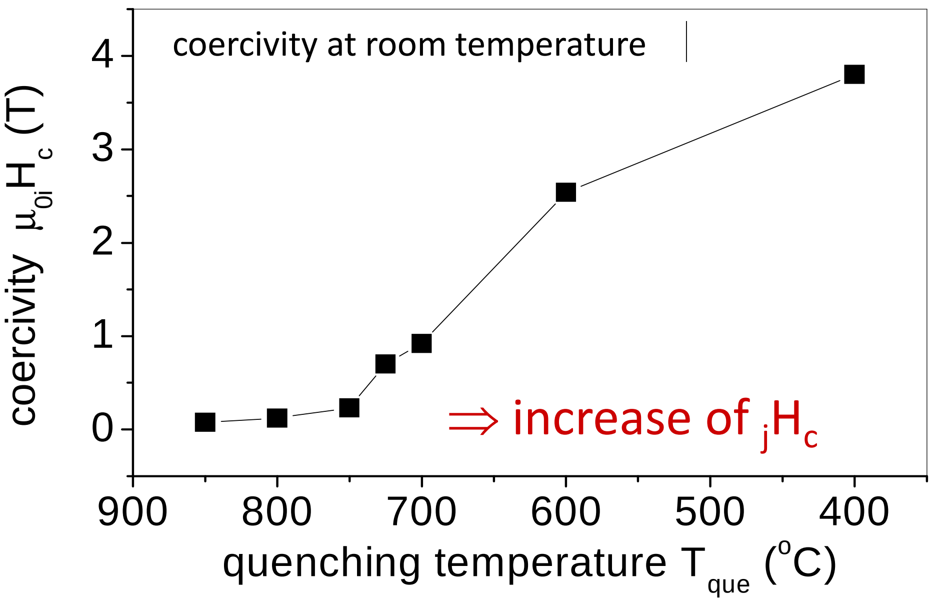
⇒ the formation of large gradient of Cu concentration *within* the 1:5 cell boundary is reversible ⇒ this gradient clearly causes the high coercivity

⇒ Different from the situaton in sintered NdFeB the effect of the critical heat treatment in Sm-Co 2:17 magnets could be clarified:

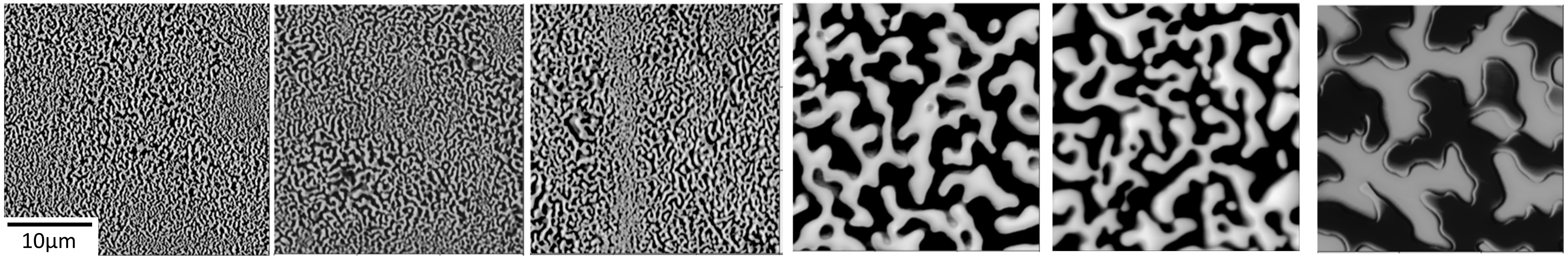
It is the formation of a certain
concentration profile (of Cu)
on a length scale of few nanometers.

The influence of slow cooling in 2:17 magnets





MFM: c-axis perpendicular to the imaging plane; thermally demagnetised:



400 °C $\mu_{0i}H_c$=3.8 T

600 °C $\mu_{0i}H_c$=2.54 T

700 °C $\mu_{0i}H_c$=0.92 T

750 °C $\mu_{0i}H_c$=0.23 T

800 °C $\mu_{0i}H_c$=0.12 T

850 °C $\mu_{0i}H_c$=0.08 T

⇒ The increase of coercivity goes along with a refinement of the domain structure

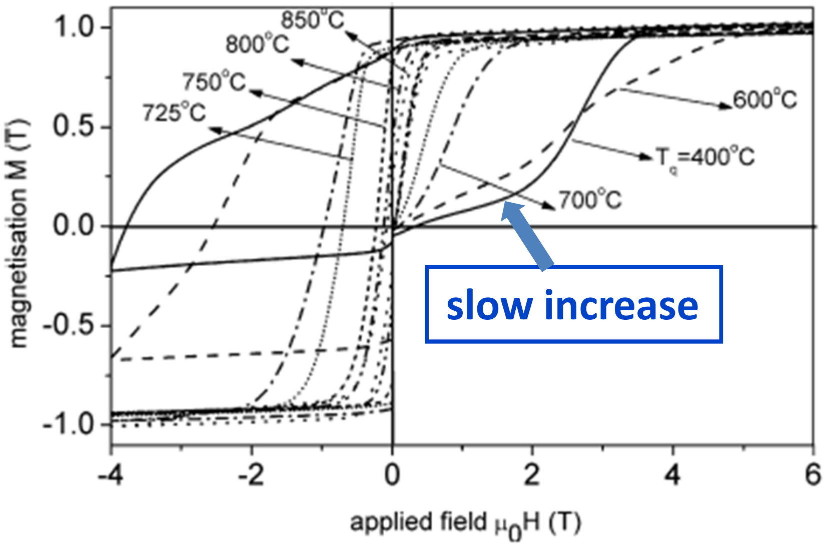
Domain-wall pinning versus „interaction domains“

- in Sm_2Co_{17} based magnets -

- In the 2:17 magnets the Sm_2Co_{17} cells are structurally coherent to each other as well as to the 1:5 cell-boundary phase

- The magnetic domains have been considered as extenting through this coherent material and the cell boundaries have been considered as „pinning centres“ that reduce the mobility of the domain walls during processes of magnetizing or demagnetizing the magnet in an external field

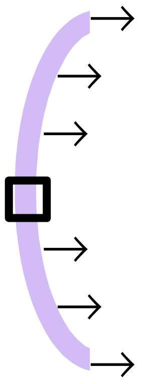
- This is supported by the typical pinning-type behaviour of these materials:



slow increase

- at low fields (thermally) demagnetized samples show a relatively slow increase of magnetization with increasing field

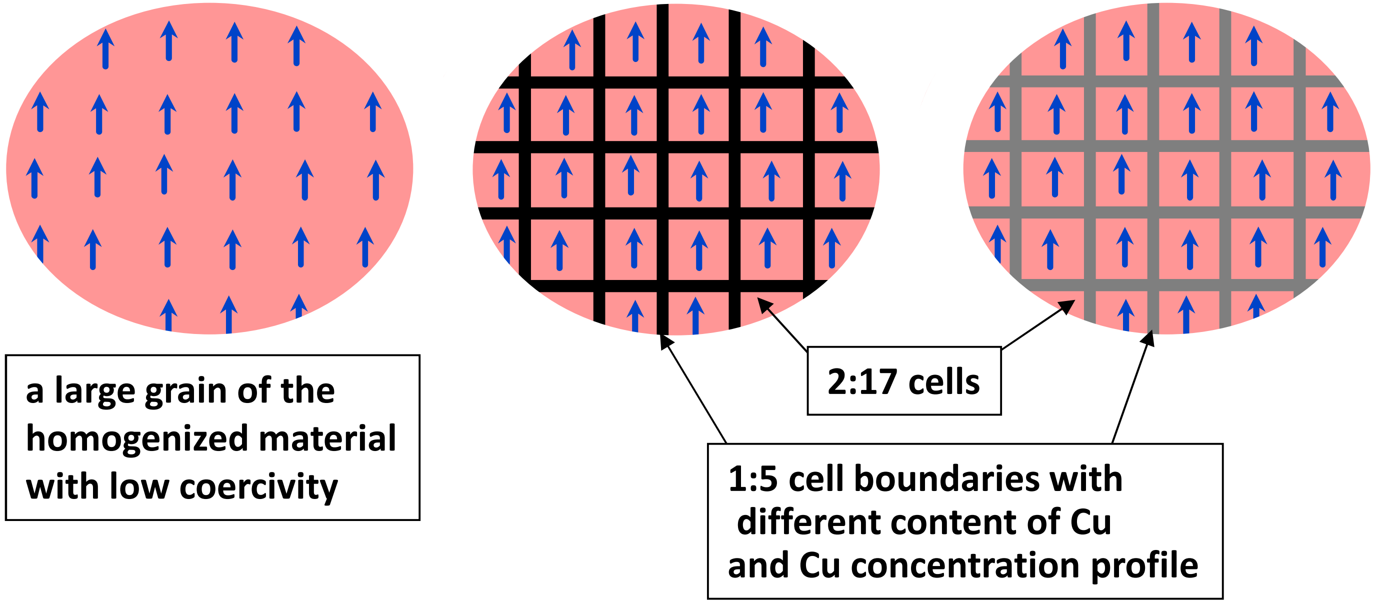
- the simplest version of a domain wall that is pinned at a “pinning centre“



Domain-wall pinning versus „interaction domains“

- in Sm_2Co_{17} based magnets -

- **In conventional understanding** of the coercivity in 2:17 magnets the celluar structure precipitated during the heat treatment is assumed to pin the domain walls
  $\Rightarrow$„precipitation hardening“
- enrichment of Cu in the cell boundaries results in further enhancement of H_c



a large grain of the homogenized material with low coercivity

2:17 cells

1:5 cell boundaries with different content of Cu and Cu concentration profile

Domain-wall pinning versus „interaction domains“

- in Sm_2Co_{17} based magnets -

- **In conventional understanding** of the coercivity in 2:17 magnets the celluar structure precipitated during the heat treatment is assumed to pin the domain walls
  ⇒„precipitation hardening“
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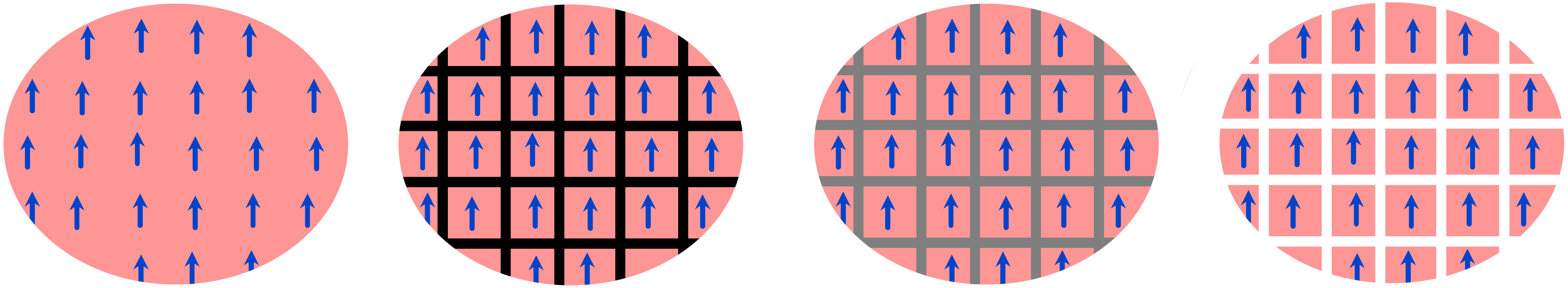
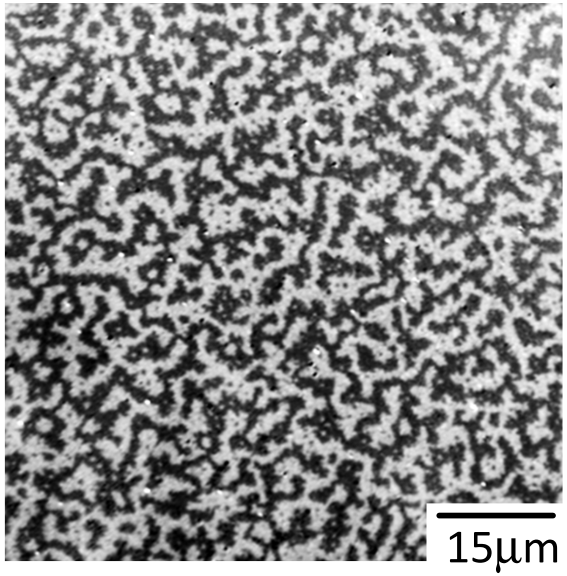


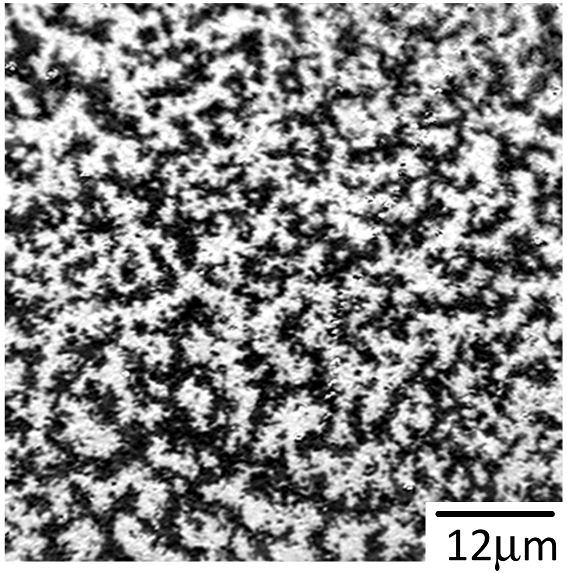
- **However our results show that the redistribution of the Cu not only modifies wall pinning but it changes the domain structure completely.**
- **If the Cu layers strongly reduce the exchange interaction between the cells the large grain consists of well aligned weakly coupled submicron-sized grains.**
- **In such a system „interaction domains“ are expected to appear instead of a conventional domain structure.**

Domain-wall pinning versus interaction domains

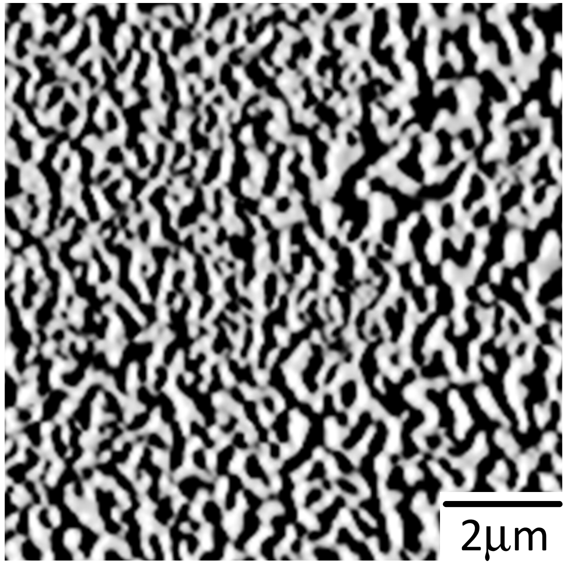
Interaction domains in different types of materials



Hot deformed melt-spun Nd-Fe-B
grain size: 0.4 µm (plane ⊥ c)



Anisotropic HDDR Nd-Fe-B
grain size: 0.2 µm



High-coercivity Sm-Co (2:17)
cell size: 0.08 µm (plane ⊥ c)

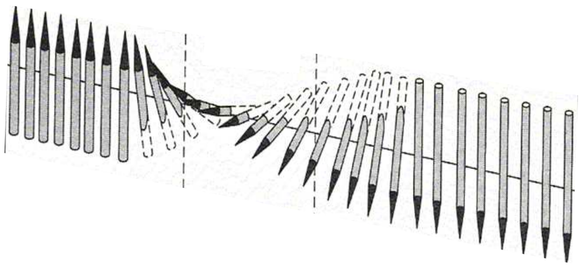
Common features of interaction domains:

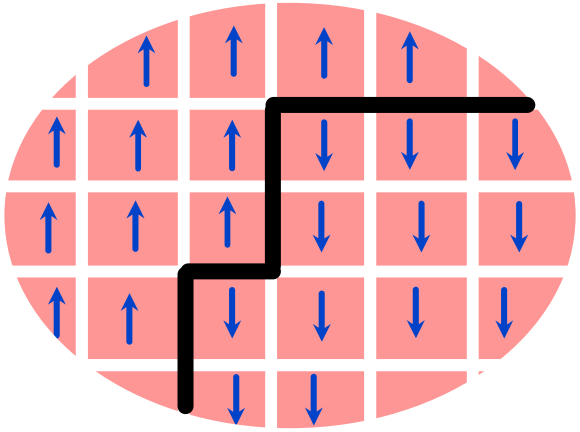
- **domain size > grain size**
- **grain size ≤ critical single-domain size**
- **no domain walls (comparable to Bloch walls)**
- **„walls“ separate single-domain units**

Domain-wall pinning versus interaction domains

the distinguishing feature „domain wall“

A „classical“ domain wall – in particular a Bloch wall - is the result of the competition between exchange energy and anisotropy energy *in a homogeneous (single-crystalline) material*.

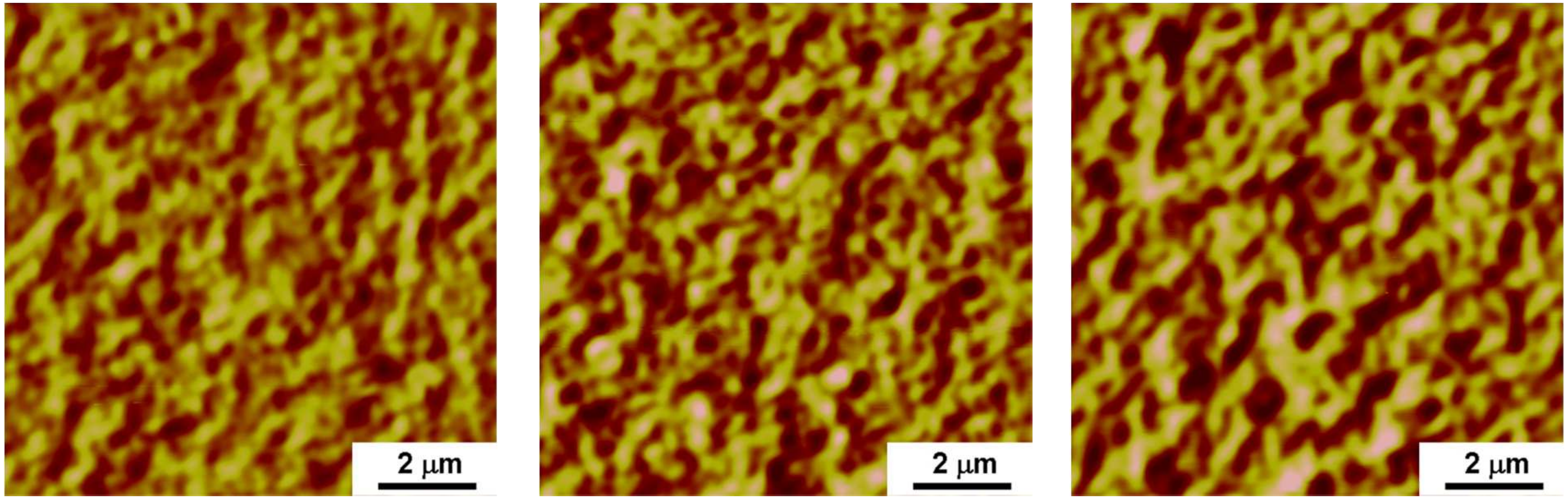




Interaction domains are found in fine grained materials (textured as well as non-textured). They are separated by grain boundaries that carry reduced or even zero exchange interaction.

Interaction domains in hot-deformed melt-spun Nd-Fe-B

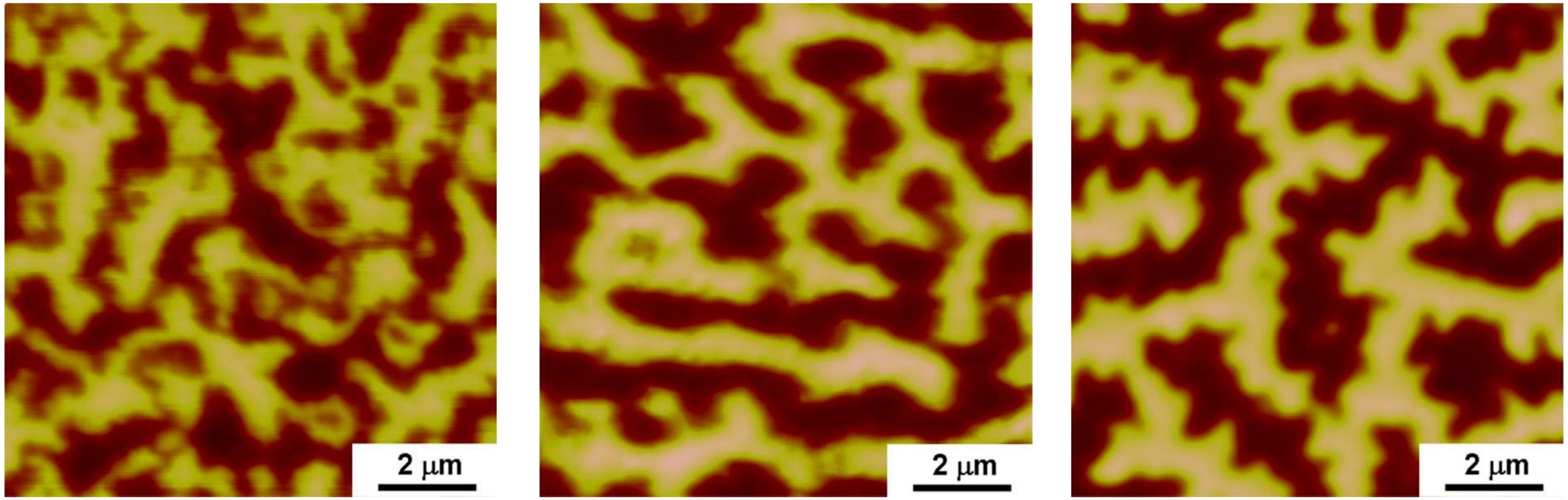
(thermally demagnetized; grain size: 0.1 … 0.4 μm; MFM)



$(B_r^{||}-B_r^{\perp})/B_r^{||}$

0.1	0.28	0.53
0.62	0.72	0.79

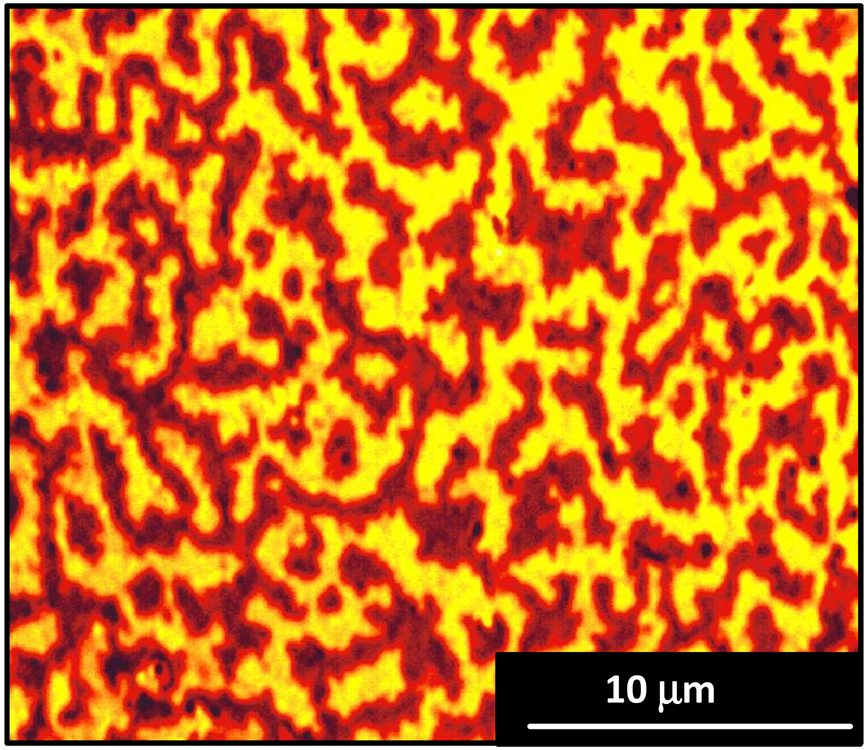
$\perp$



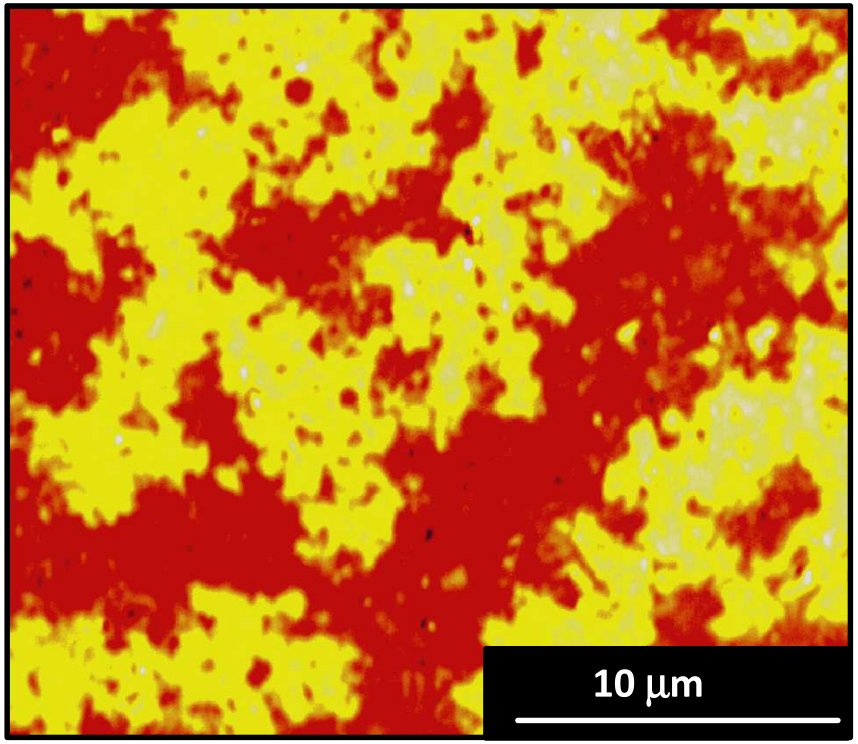
Interaction domains in hot-deformed melt-spun Nd-Fe-B

(observed by Kerr microscopy; grain syize $\approx 0.4\ \mu m$)

thermally demagnetized:



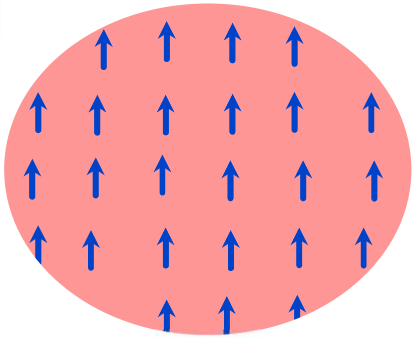
dc-field demagnetized:



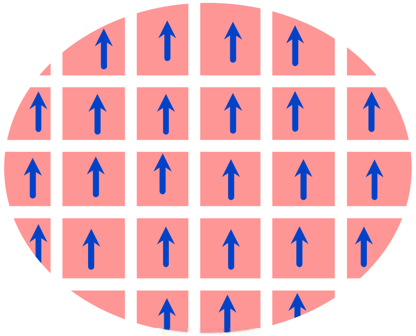
(D.Hinz and K.-H. Müller)

“Nanocrystalline materials“

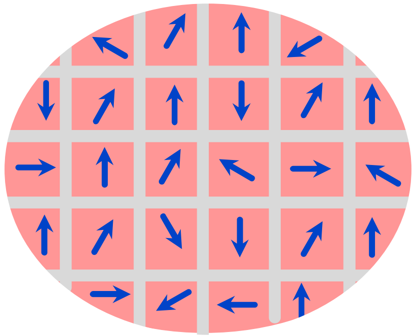
- the celluar structure in the large grains of Sm_2Co_{17} based permanent magnet materials can be considered as a model system for „nanocrysdtalline materials“
- a more realistic term would be submicron materials
- **the crucial point is that the „grain size“ is close to or below the single-domain size: $D \leq D_c$**



2:17 grain ; $D \gg 1\mu m$



2:17 cells; $D \ll 1\mu m$



$D \leq D_c$

most relevant properties (2:17):

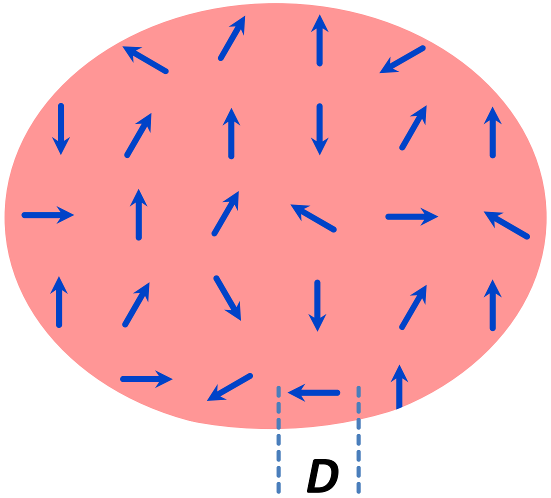
- alignment of the small units
- crystallographic coherence between them
- reduced exchange coupling between the units

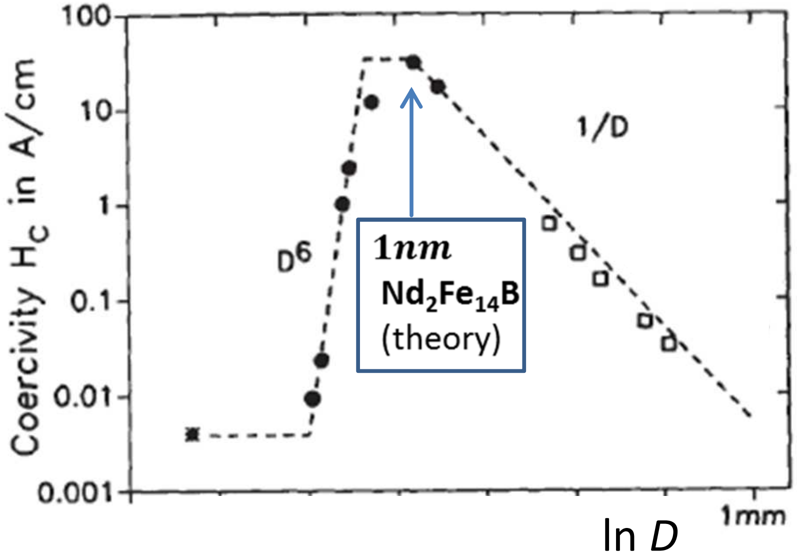
general case:

- often no alignment
- often no coherence
- single-phase **or** multiphase
- coupling varying
  → boundary phase

“Nanocrystalline materials“

1.) single-phase materials





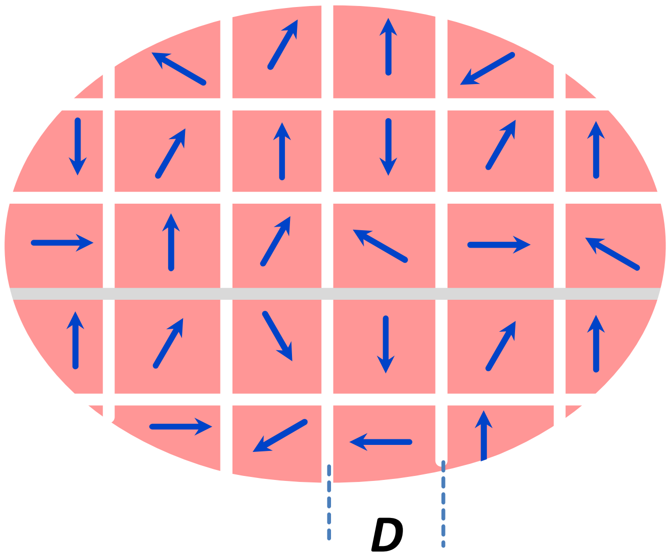
- According to a „random anisotropy“ approach of Herzer (1990) with decreasing grain size D the coerivity should increase until $D \approx \sqrt{\frac{A}{K}} = \frac{\delta}{\pi} \approx 1nm$ (for $Nd_2Fe_{14}B$)

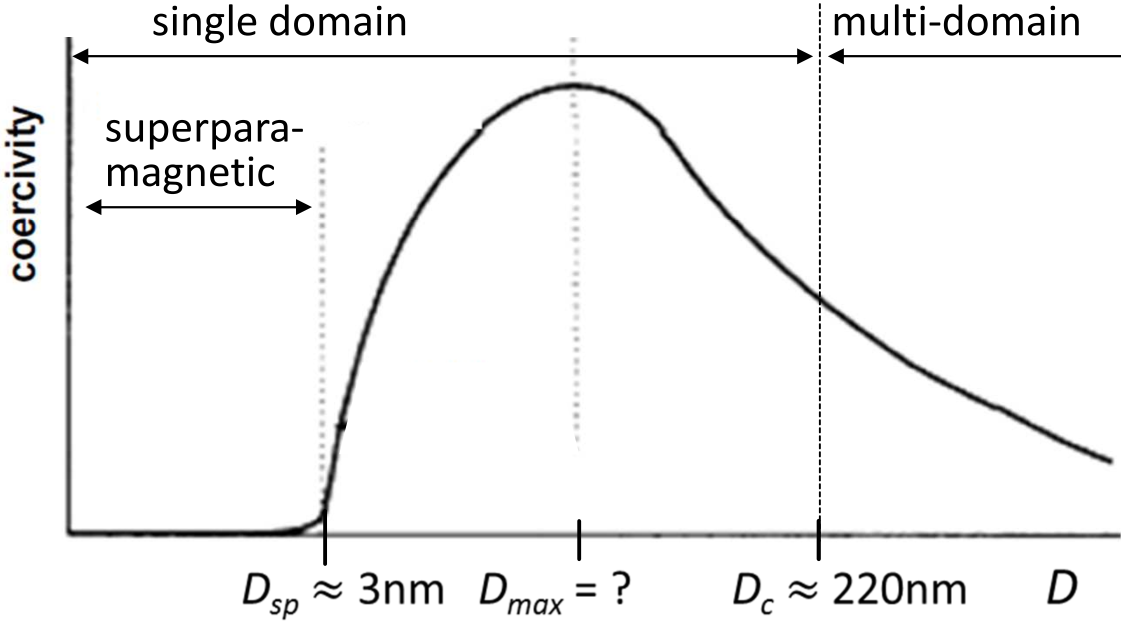
$\Rightarrow$ experimental verification ???

- Callen et al 1977: for given grain size: B_r / M_s should increase from ½ to 1 with increasing A/K (and H_c should decrease)
- Such **remanence enhancement** has been reported by Clemente et al. 1988 for rapidly quenched single- phase $Nd_2Fe_{14}B$ for typically D = 20 to 30nm
- **satisfying modelling and relevance for application are unclear!**

Nanocrystalline materials

2.) totally decoupled grains





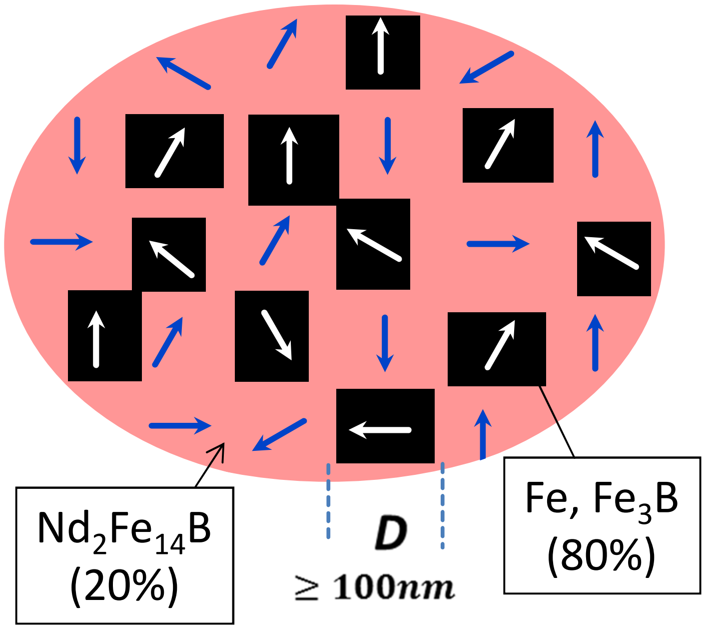
(values for $Nd_2Fe_{14}B$)

- The coercivity H_c of isolated grains is expected to increase with decreasing grain size.
- For $D = D_{sp}$ the grains become superparamagnetic and H_c vanishes.
- **The maximum value of H_c and its position D_{max} have not yet been determined (by experiments or modelling).**

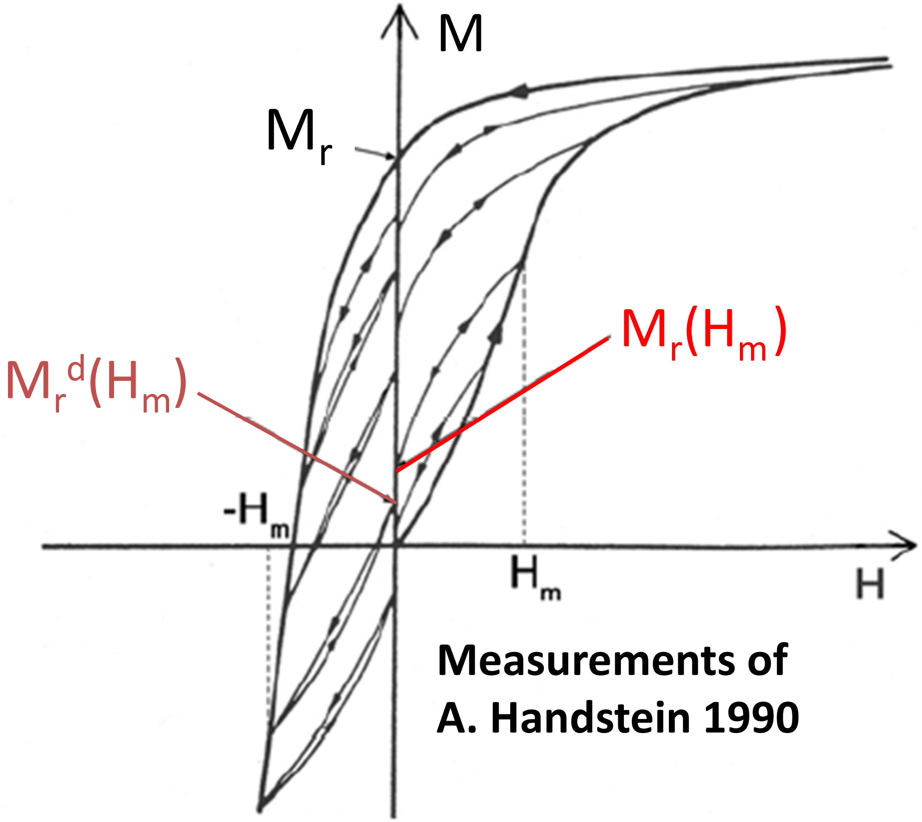
Nanocrystalline materials

3.) two-phase materials („spring magnets")

Microstructure (schemtic):



melt spun $Nd_4Fe_{77}B_{19}$
Coehorn et al. 1988



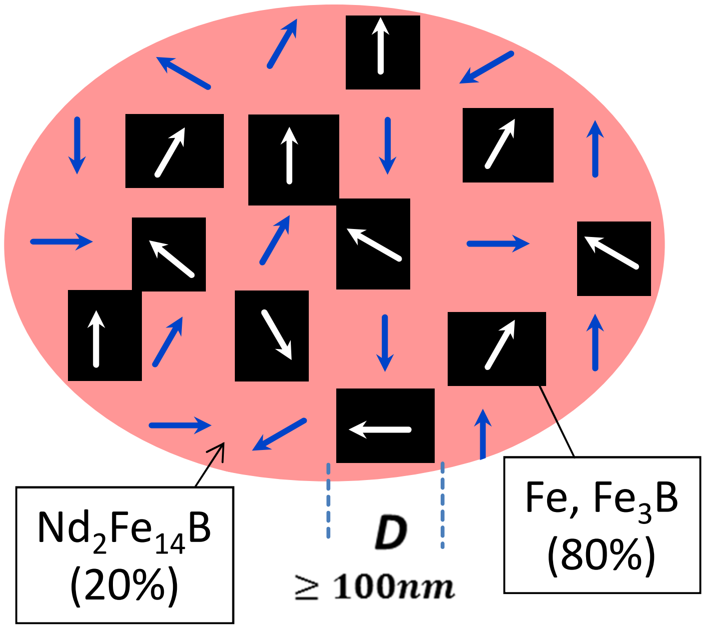
Measurements of A. Handstein 1990

Nanocrystalline materials

3.) two-phase materials („spring magnets“)

Kneller et al. 1991:

- exchange coupling between soft grains and hard ones results in a spring-like behaviour
- $M_r > M_s/2$
- needed grain sizes:
  $D_{soft} \approx D_{hard} \approx 2\delta \approx 10\text{nm}$

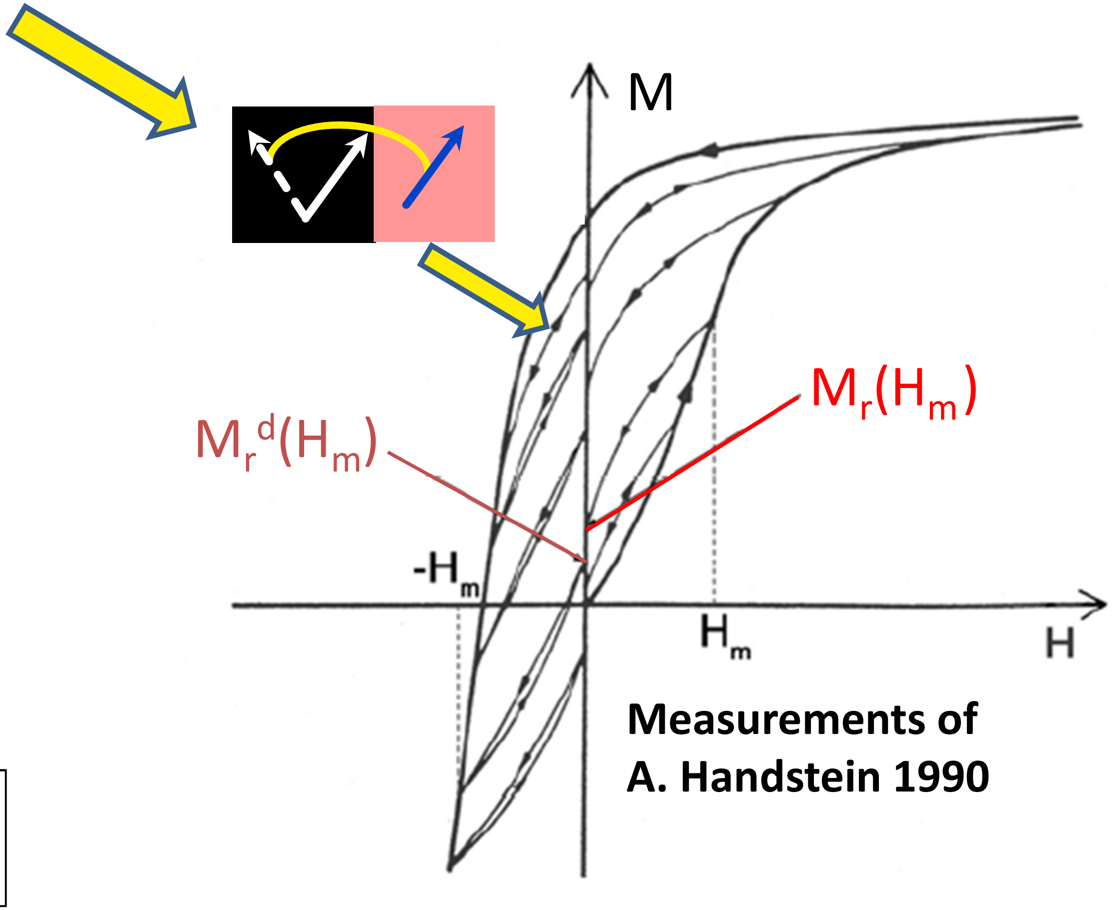


$Nd_2Fe_{14}B$
(20%)

D
$\geq 100nm$

Fe, Fe_3B
(80%)

melt spun $Nd_4Fe_{77}B_{19}$
Coehorn et al. 1988

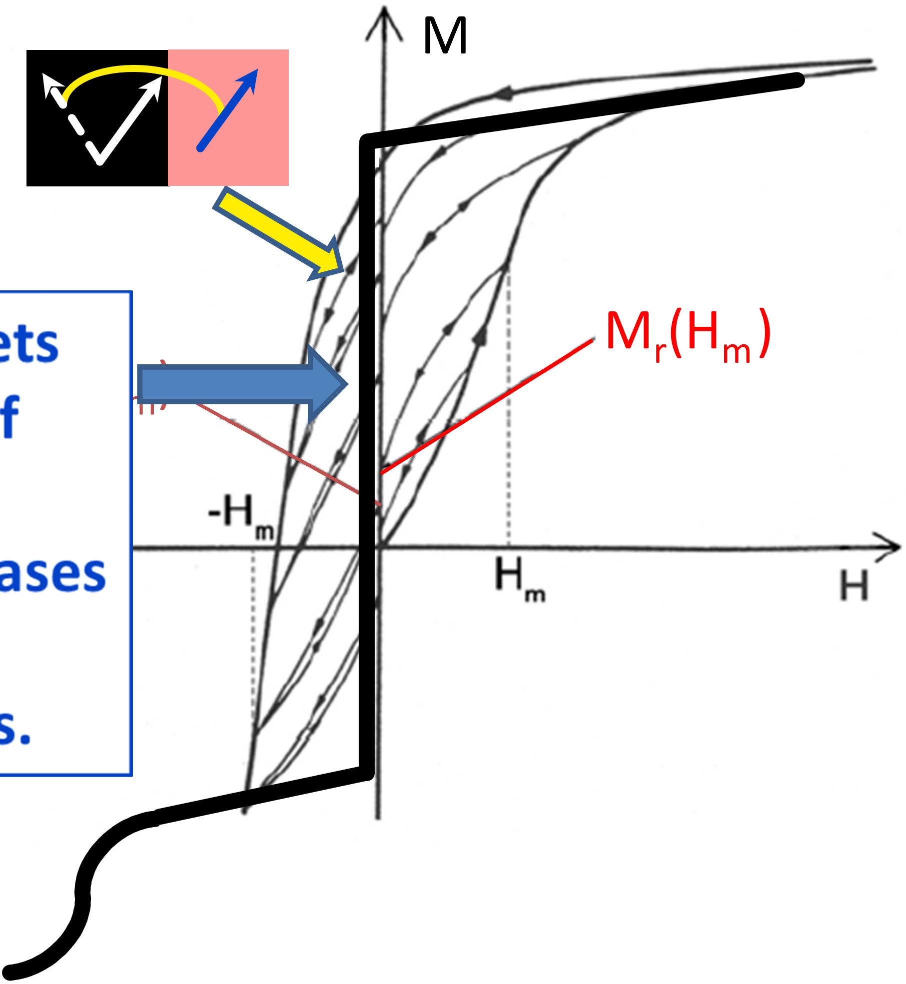


Measurements of A. Handstein 1990

Nanocrystalline materials

3.) two-phase materials („spring magnets“)

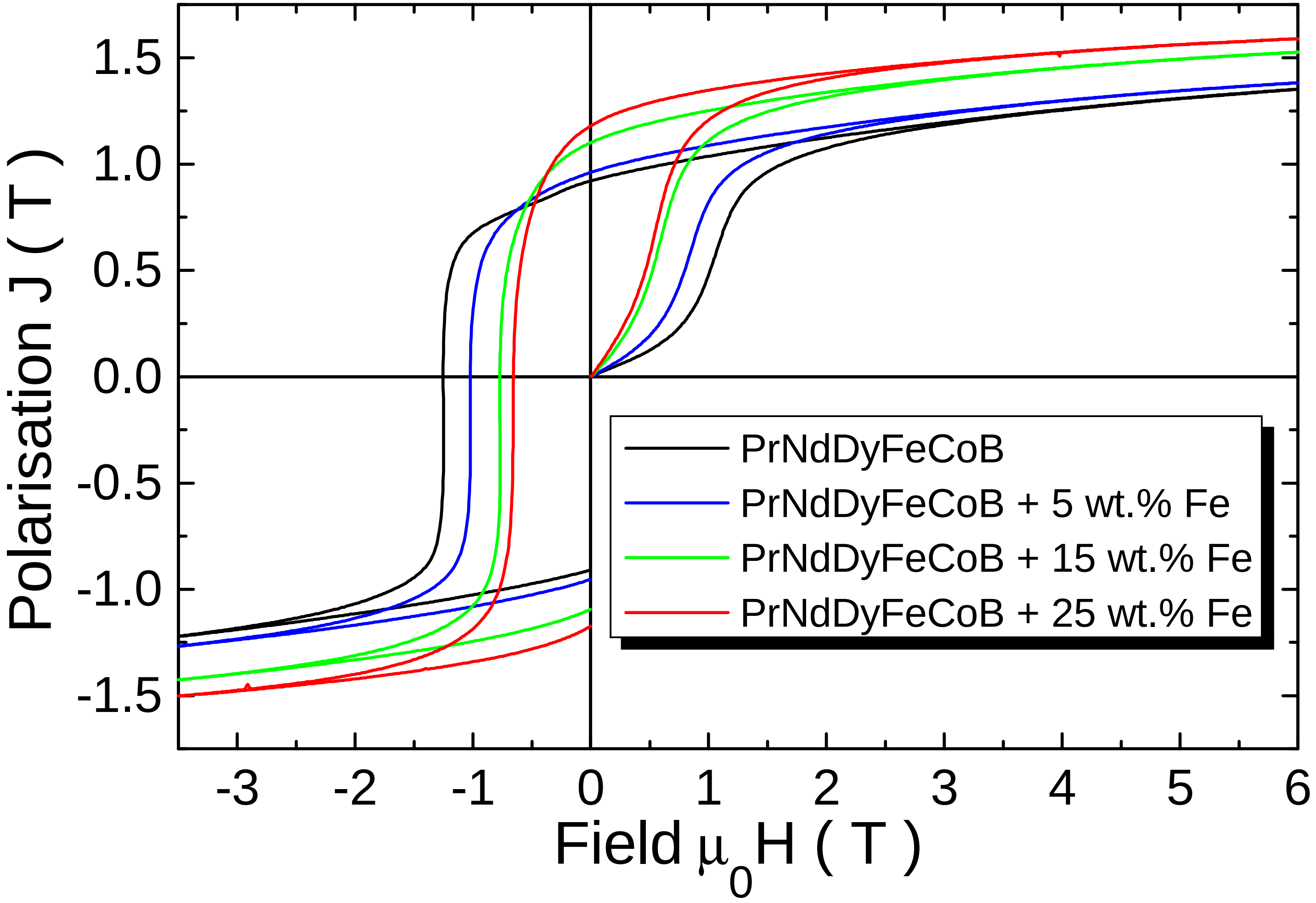
The crucial point in spring magnets is not a dubious enhancement of remanence but the fact that the interaction between the two phases removes the step at $H \approx 0$ that occurs for non-interacting phases.



Nanocrystalline materials

3.) two-phase materials („spring magnets“)

spring magnets obtained by intense milling



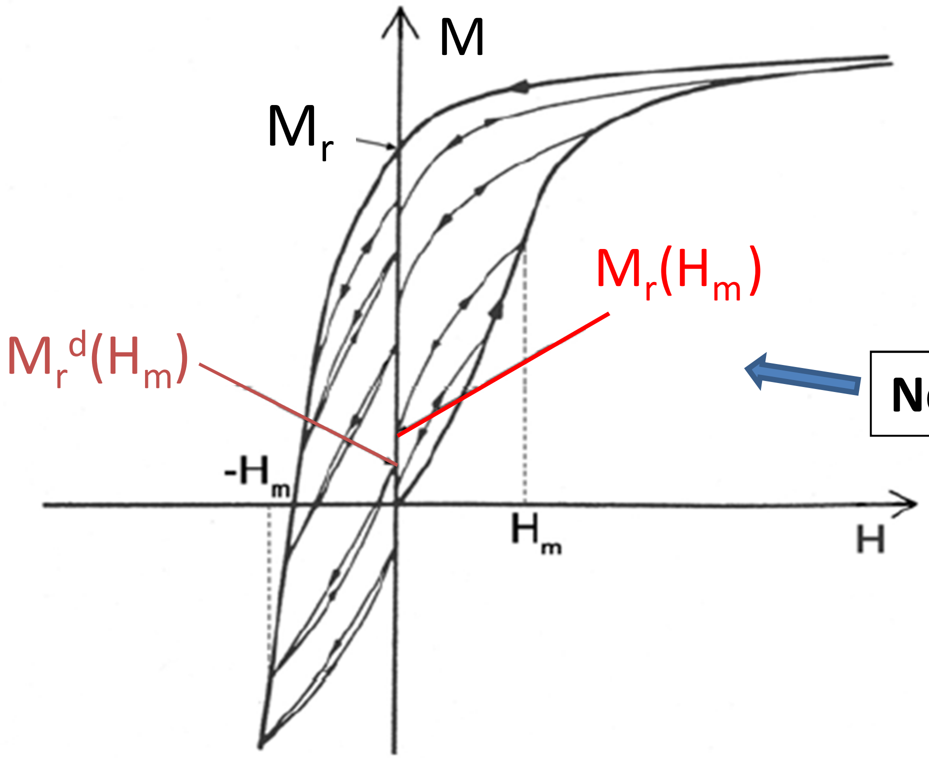
Nanocrystalline materials

3.) two-phase materials („spring magnets“)

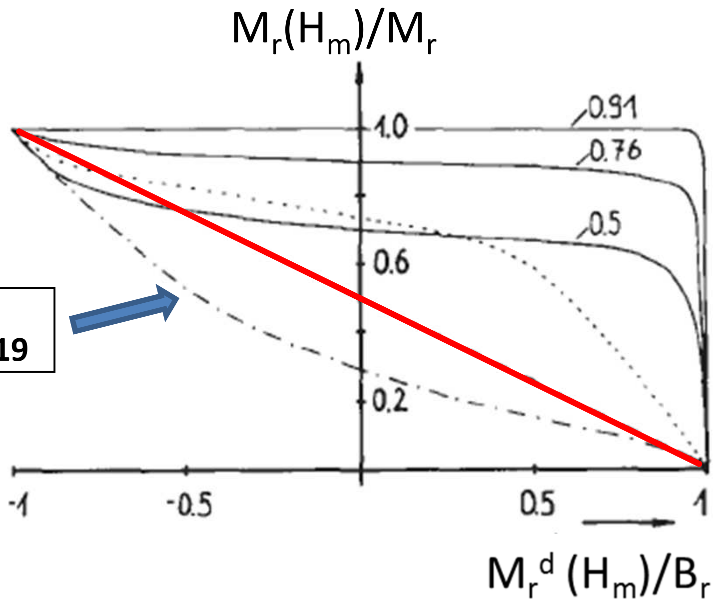
Wohlfarth´s remanence relation (EPW-1958)

for non-interacting easy-axis single-domain particles

$$M_r^d(H_m) = M_r - 2\,M_r(H_m)$$



$Nd_4Fe_{77}B_{19}$



Wohlfarth´s remanence relation

for non-interacting easy-axis single-domain particles

---

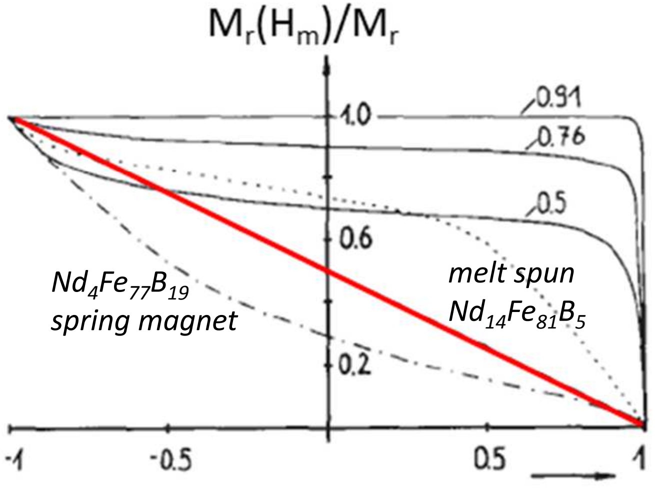
two representations of Wohlfarth´s remanence relation

„Henkel plot“:

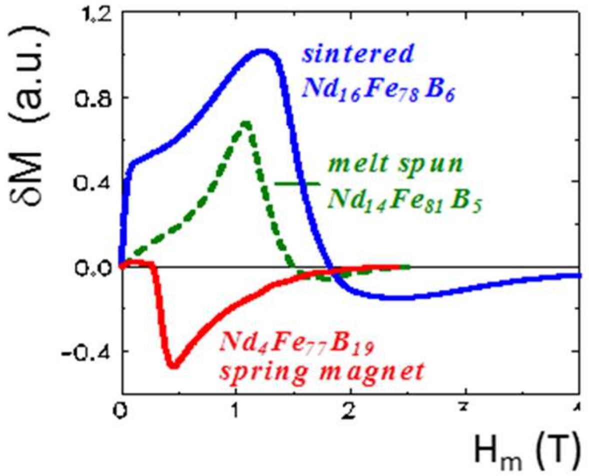
$$M_r^d(H_m) = M_r - 2\,M_r(H_m)$$

„δM plot“:

$$\delta M(H_m) \equiv M_r^d(H_m) + 2\,M_r(H_m) - M_r$$



upper curves: sintered $Nd_{16}Fe_{78}B_6$ with different degrees of texture



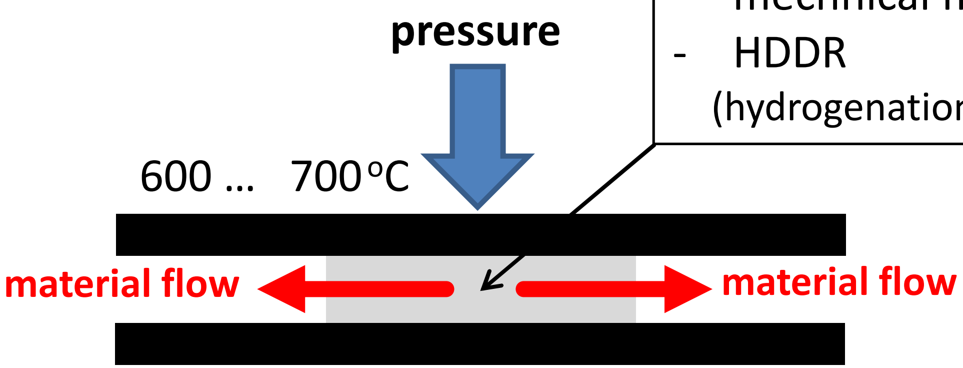
Nanocrystalline materials

4.) texture by hot deformation (die upsetting or hot extrusion)

Die upsetting:

fine-grained isotropic Nd-Fe-B powder obtained by
- rapid quenching or
- mechnical milling or alloying or
- HDDR

(hydrogenation- disproportionation-desorption-recombination)

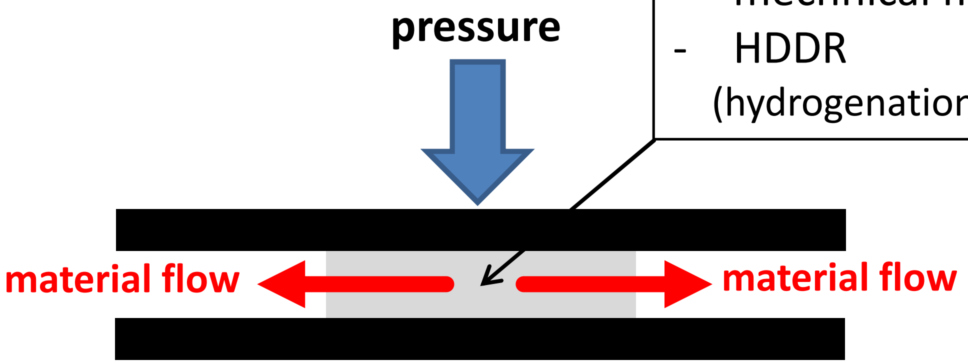


controlling mechanism: solution-precipitation creep

Nanocrystalline materials

4.) texture by hot deformation (die upsetting or hot extrusion)

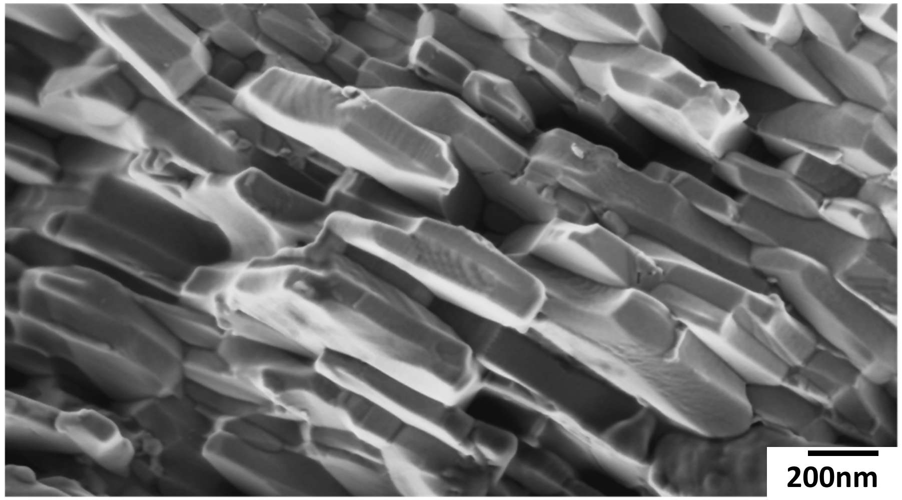
Die upsetting:

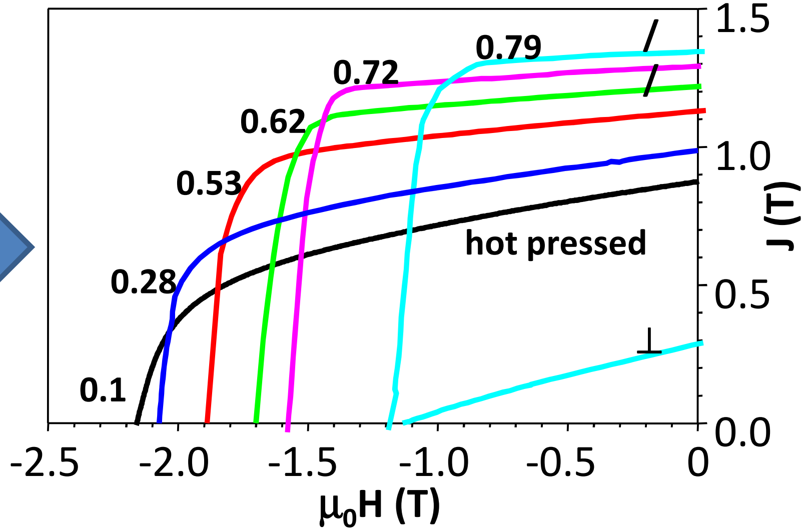


fine-grained isotropic Nd-Fe-B powder obtained by
- rapid quenching or
- mechnical milling or alloying or
- HDDR
  (hydrogenation- disproportionation-desorption-recombination)

controlling mechanism:
solution-precipitation creep

die-upset melt-spun $Nd_{13.6}Fe_{73.6}Ga_{0.6}Co_{6.6}B_{5.6}$





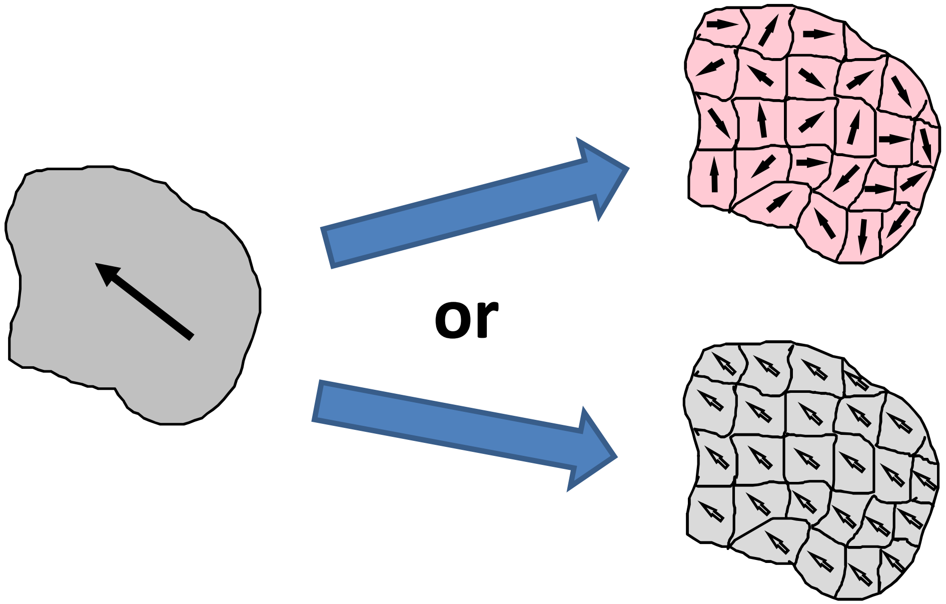
Nanocrystalline materials

5.) texture by a structural memory effect ⇒ „anisotropic HDDR“

Hydrogenation Disproportionation Desorption Recombination

$$Nd_2Fe_{14}B + (2 \pm x)\ H_2 \longleftrightarrow 2NdH_{2+x} + 12Fe + Fe_2B$$

Result: grain refinement :



O. Gutfleisch:

- Such anisotropic HDDR powder can be obtained by suitable thermodynamic and kinetic parameters → **„d-HDDR”** (dynamic-) process

- **Fe_2B is the anisotropy-mediating phase, i.e. it is the c-axis memory carrier**

“Nanocrystalline materials“

The **magnetization processes** are very different
in the different types of nanocrystalline materials.

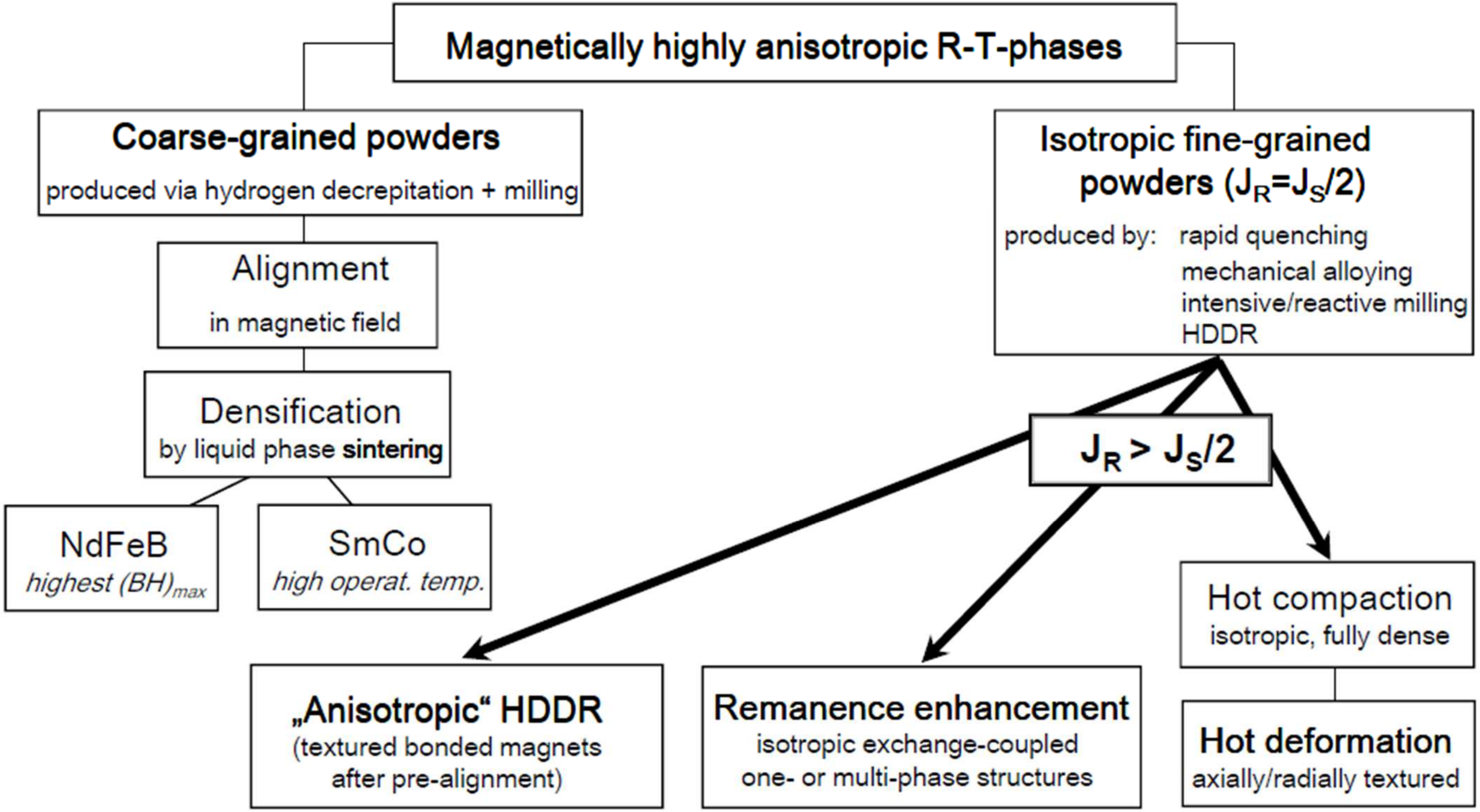
Definitely the classical effects dominating the magnetization processes
in coarse-grain materials, pinning of domain-walls and
nucleation of reverse domains, do not apply because these materials
do not contain classical domain structures.

Crude approaches are used to describe the magnetization porocesses in
such materials and how they can be modified during preparation.

A modern (and may be) promising means is to use sophisticated methods in numerical micromagnetism.

In such a situation systematic high-quality experiments are needed.

Processing routes for permanent magnet materials



Magnetically highly anisotropic R-T-phases

Coarse-grained powders
produced via hydrogen decrepitation + milling

Alignment
in magnetic field

Densification
by liquid phase **sintering**

NdFeB
highest $(BH)_{max}$

SmCo
high operat. temp.

Isotropic fine-grained powders ($J_R=J_S/2$)
produced by: rapid quenching
mechanical alloying
intensive/reactive milling
HDDR

$J_R > J_S/2$

„Anisotropic“ HDDR
(textured bonded magnets after pre-alignment)

Remanence enhancement
isotropic exchange-coupled one- or multi-phase structures

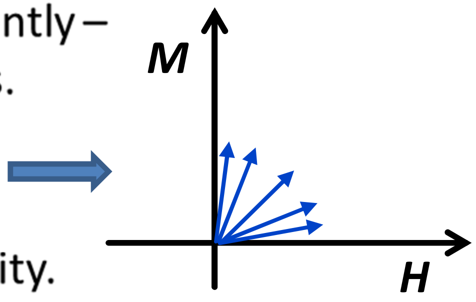
Hot compaction
isotropic, fully dense

Hot deformation
axially/radially textured

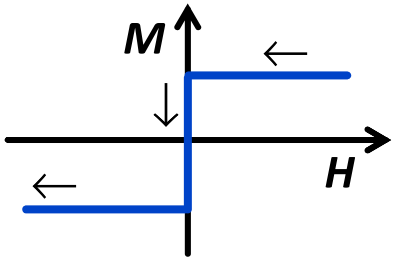
The different microstructures result in different magnetization processes !

The term magnetization processes

- The major problem of people working with permanent magnet materials is to understand ***M***-versus-***H*** curves that are dominated by hysteresis and – consequently – usually they are very sensitive to the magnetic history of the samples.



- As an example, in an ideal nucleation-type magnet, the initial susceptibility, i.e. the slope for curves starting at (0,0) depends on the magnetic prehistory of the samples and shows a large diversity.
- Segments of such hysteretic M–H curves and the mechanisms behind them are usually called magnetization processes:
- Typical examples: moving or pinning of domain walls, nucleations or annihilation of reverse domains; rotation of M in unison, curling, fanning, ….

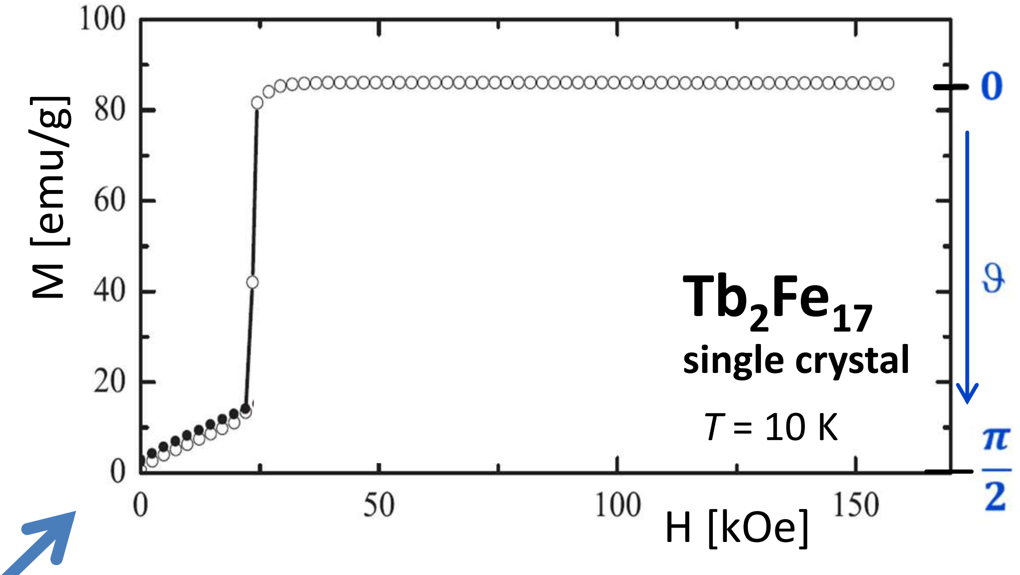


- **All of these hysteretic „processes“ are related to the first-order transition $M = M_S \to -M_S$ at $H = 0$**
- **Jumps in M-H dependencies, based on first-order transitions, i.e. on minima of generalized Landau potentials $\Phi(M, H; p, T, \dots)$ becoming metastable also occur in other physical situations, at non-zero values of H.**
- **Examples are metamagnetic transitions (of different type), transitions connected with first-order lattice transitions (as in magnetocalorics and magnetic shape memory alloys), and instability in the direction of *M*, governed by magnetic anisotropy → „FOMP“**

First-order magnetization process (FOMP)

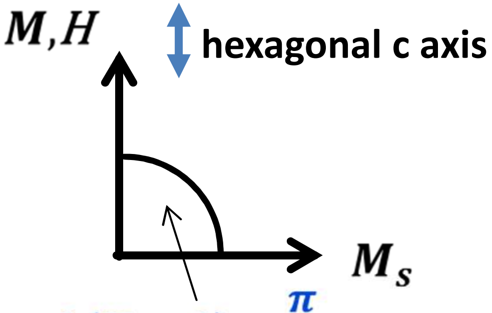
Kuzmin, Skourski, Skokov,
Müller, Gutfleisch (2008)

$$\Phi = -(K_1 + 2K_2)(cos\vartheta)^2 + K_2(cos\vartheta)^4$$
$$-M_s H(cos\vartheta) \rightarrow \text{Min.} \quad \Rightarrow \vartheta(H)$$



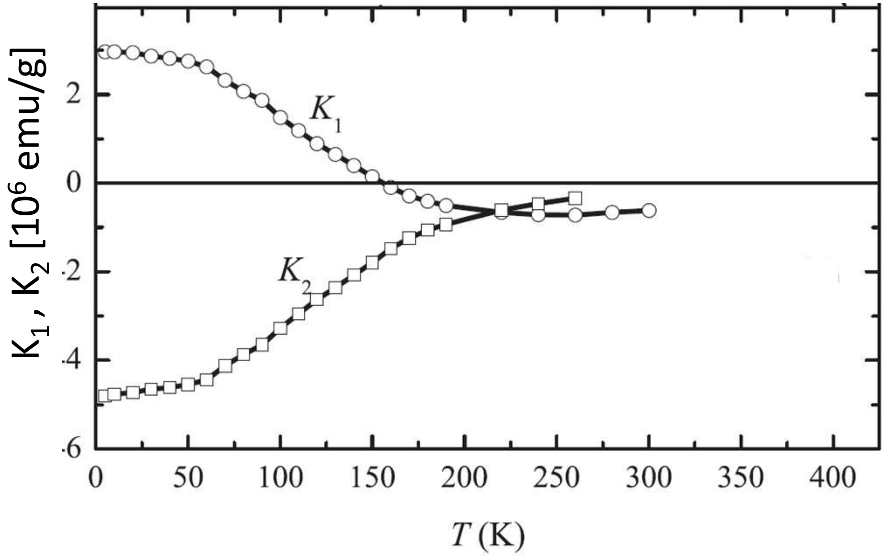
Tb_2Fe_{17}
single crystal

T = 10 K

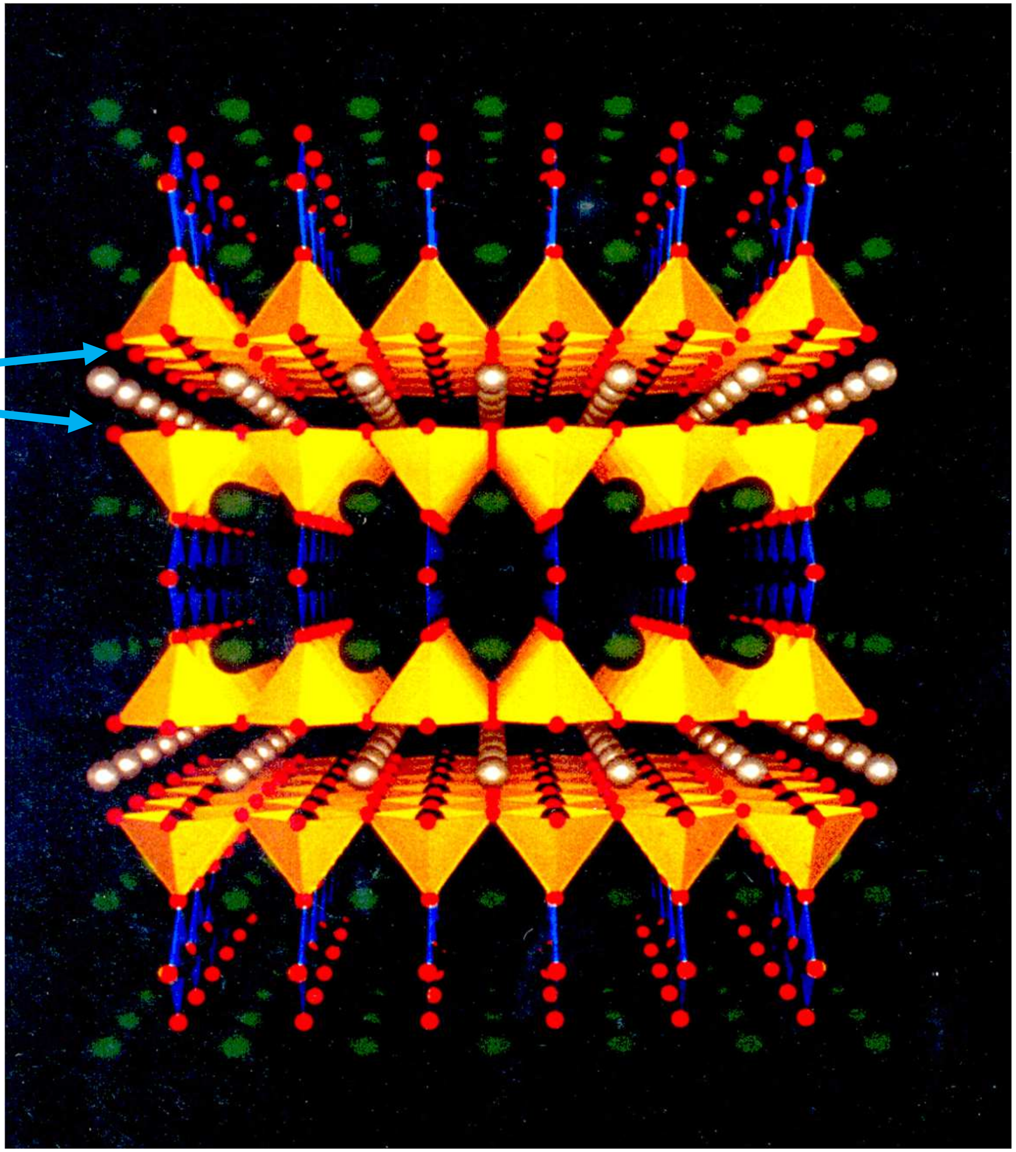


$$\vartheta(H = 0) = \frac{\pi}{2}$$

⇒ an easy-plane material



The high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO)



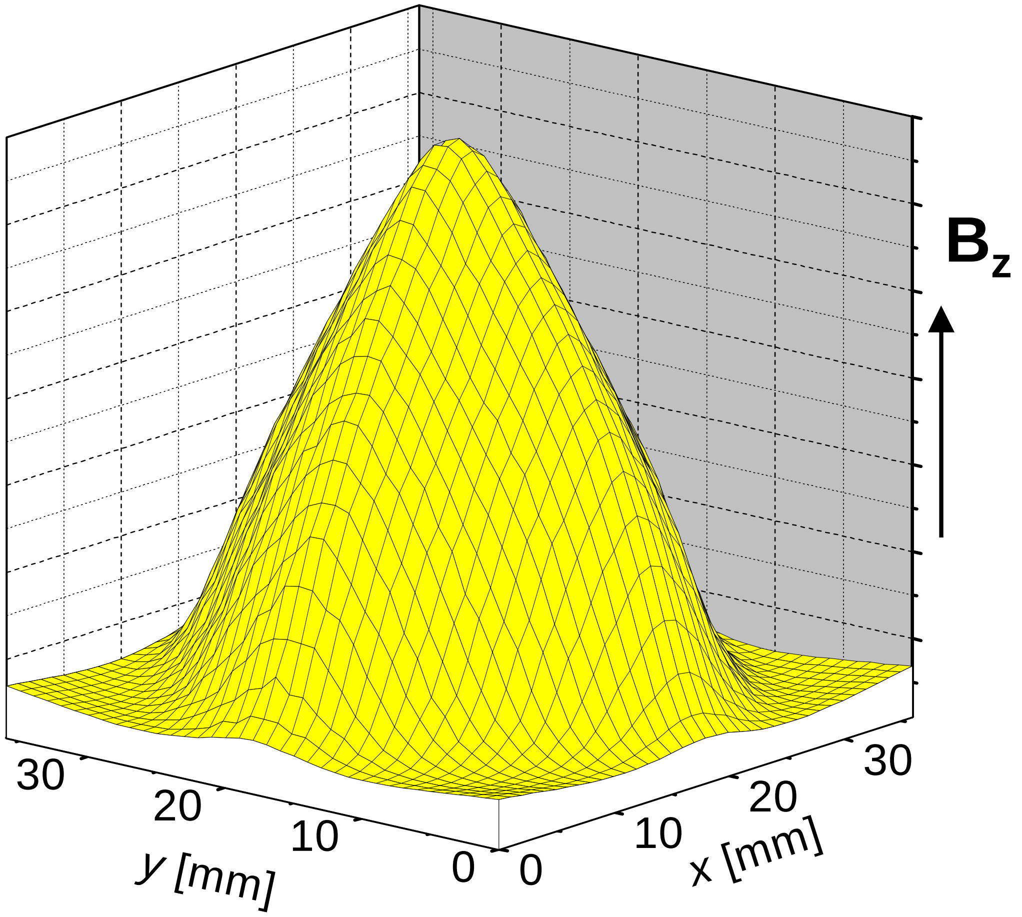
- superconducting CuO_2 planes

$\Rightarrow$ the superconductivity is highly anisotropic (quasi two dimensional)

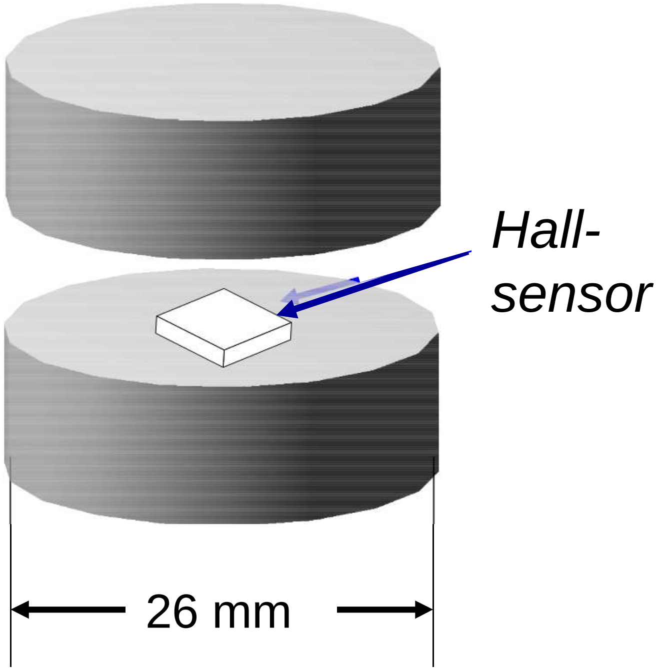
- $T_c \approx 90\ K$
  ($T_s[N_2]$ = 77 K)

Superconducting permanent magnets
- made of doped YBCO -

Trapped magnetic field:

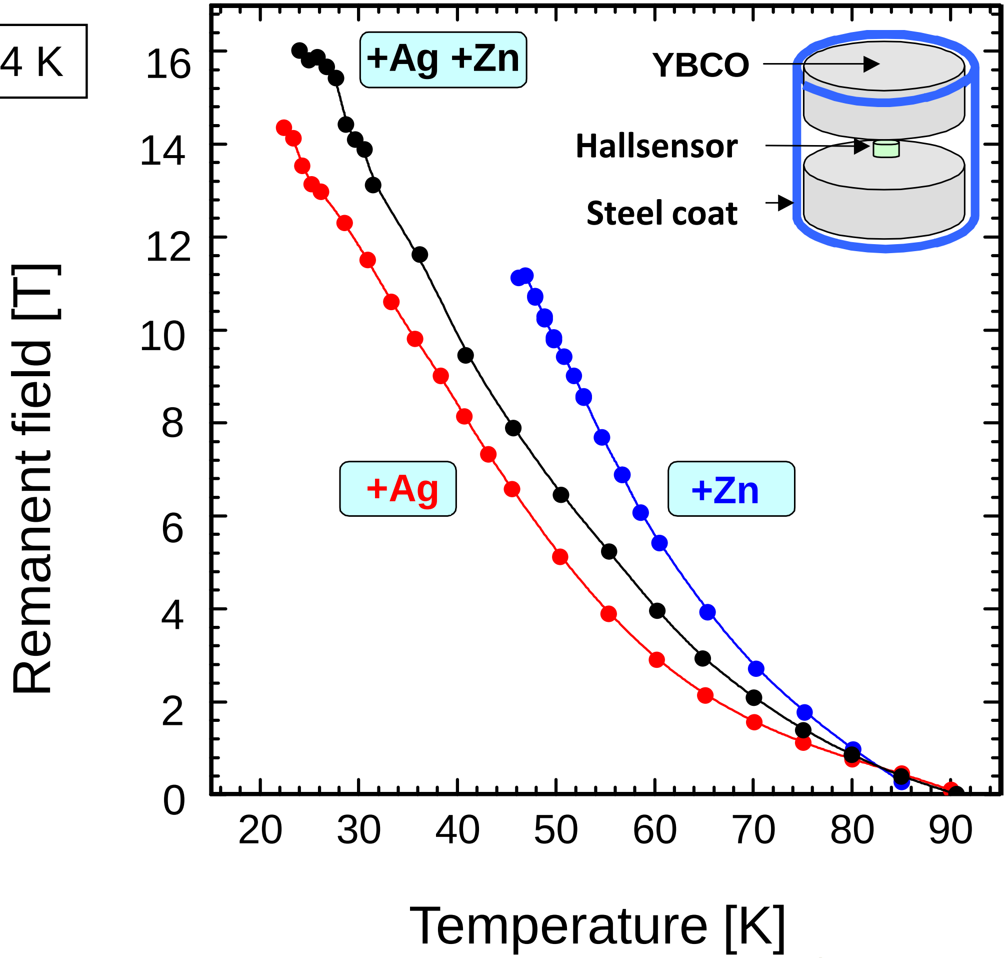


sample geometry



Remanent fields in Ag- and Zn-doped $YBa_2Cu_3O_{7-\delta}$

16,0 T – 24 K



(S. Gruss et al., APL 79 (2001) 3131)

The European Commissioner for Research ***Máire GEOGHEGAN-QUINN*** and *Ludwig Schultz* on a levitated superconducting model train

December 3, 2012

Further reading: some textbooks and monographs
- on physics of magnetism and magnetic matrials -

- Becker-Döhring (1939) – difficult to get
- W.F. Brown (1962) - difficult to get
- Döhring in Handbuch der Physik; Vol. XVIII/2 (1966)
- Landau–Lifshitz (Course of Theoretical Physics)
- Handbook of magn. Materials (Edit. Wohlfarth/Buschow)
  $\Rightarrow$ various articles in various volumes
- M. Kuzmin (↑ Vol. 17)
- A. Aharoni (1996)
- Coey (1996)
- Chikazumi (1997)
- Bertotti (1998)
- Skomski-Coey (1999)
- Kronmüller-Fähnle (2003)
- Buschow-DeBoer (2003)
- Coey (2010)

It is hard to find useful books on permanent magnet materials including details of preparation and microstructure!

Review papers and original papers of: Buschow, Coey, Givord,
Gutfleisch, Kuzmin, Schrefl

conclusions

- Knowledge on the physics of magnetism is very helpful for understanding of permanent magnet materials.
- However, recent methods of physics are not sufficient for getting success in this field because the magnetized state is metastable and, therefore, it is very sensitive to details of the microstructure.
- Materials science of permanent magnetism has two main aims:

  1.) to find novel phases with improved intrinsic properties T_c, M_s, K

  2.) to develop sophisticated microstructures resulting in
  extrinsic properties H_c, B_r, $(BH)_{max}$
  that utilize their intrinsic bounds as much as possible.
- High-T_c superconductors are a promising alternative to conventional permanent magnets.

Thank you