

Hard Magnetic Materials for the 21st Century

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UNIVEI
JOSEPH FOI
SCIENCES TECHNOLOGII



Outline

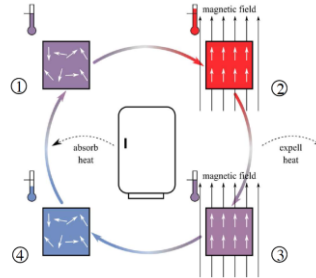
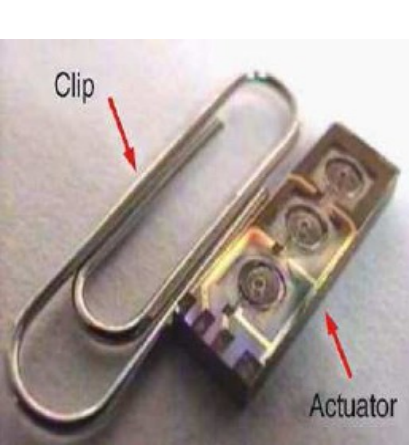
- **Introduction**
- **Mn-based magnetic phases**
- **Nanocomposites magnets=Spring magnets**
- **Conclusions**

Outline

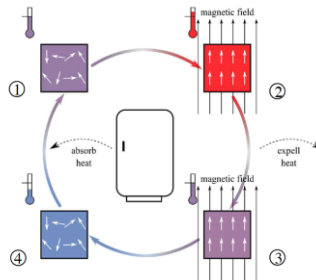
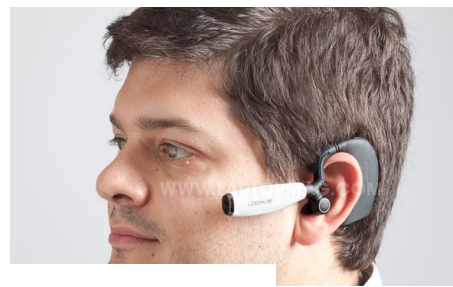
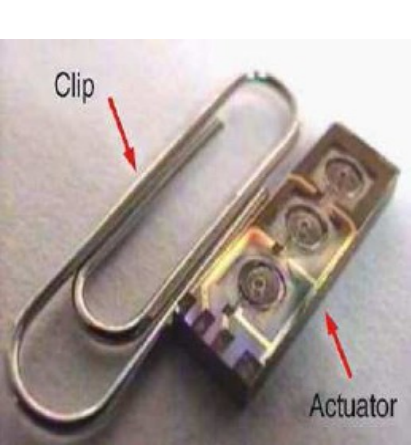
- **Introduction**
- Mn-based magnetic phases magnetic phases
- Nanocomposites magnets=Spring magnets
- **Conclusions**



➤ magnetic materials are *critical* components in many devices and for advanced technologies.

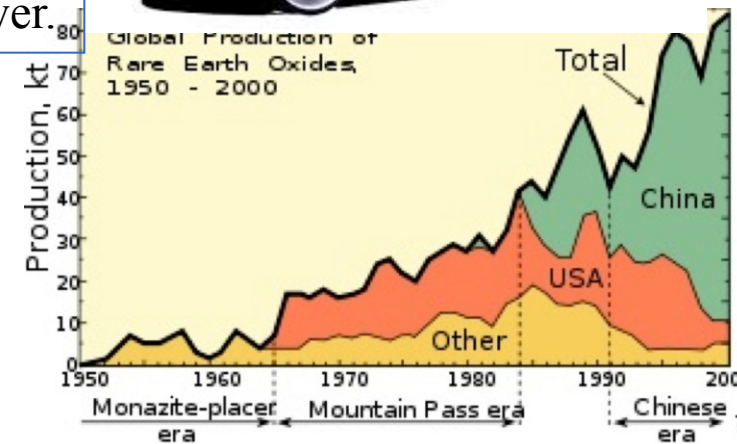


- magnetic materials are **critical** components in many devices and for advanced technologies.
- high performance magnet (HPM)/wind generator **1000-1600 kg/MW**.
- motors and generators: **2 kg** HPM/hybrid electric vehicle-**20 million** vehicles by 2018.
- Magnetocaloric applications **4 kg HPM/kW** cooling power.

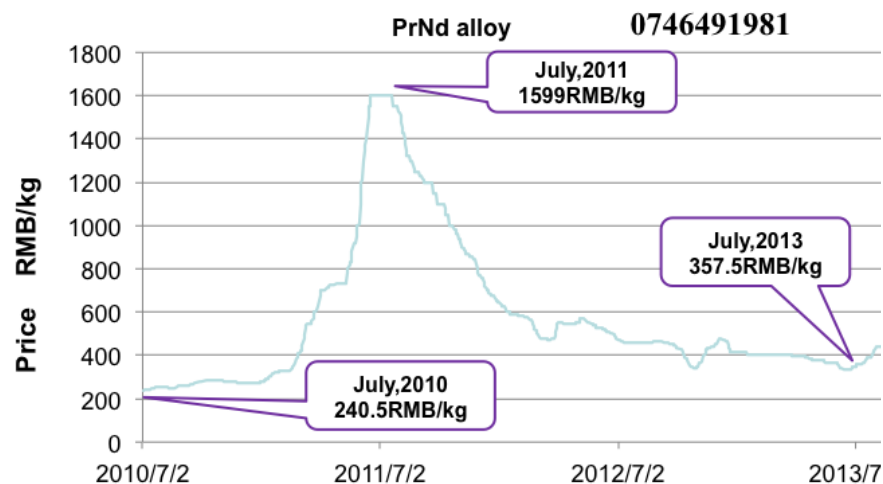


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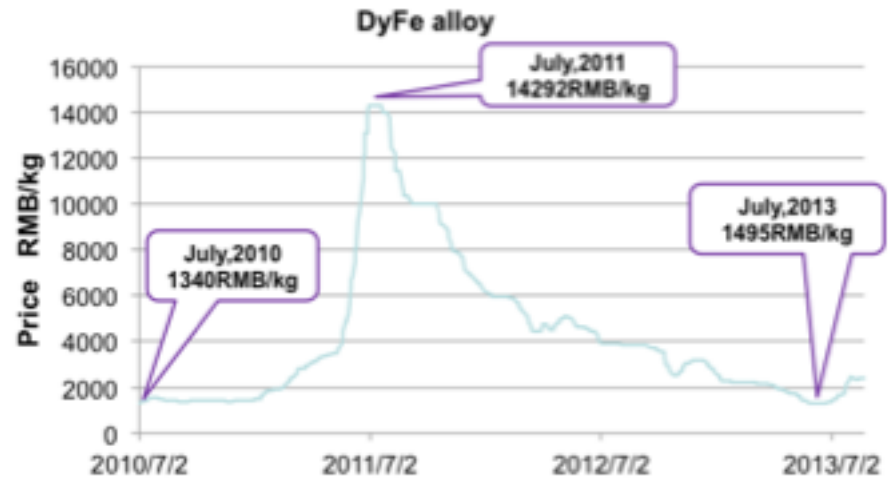
HPM= rare-earth based magnets
China manages about 96 % of
rare-earth resources in 2011



REE price fluctuations*



The price of **PrNd** alloy have **increased about 565%** form November 2010 to July 2011. In July 2013, it drop to 22.4% compare with top price.



The price of **DyFe** alloy have **increased about 967%** form July 2010 to July 2011. In July 2013, it drop to 10.46% compare with top price.

Instability of RE market, ex. Nd: 150 \$/kg/2013; 450 \$/kg/2011, 15 \$/kg/2009

*Kaihong Ding - *Yantai Shougang Magnetic Materials, China*, Energy and Materials Criticality Workshop, Santorini 2013

Why PM motors?

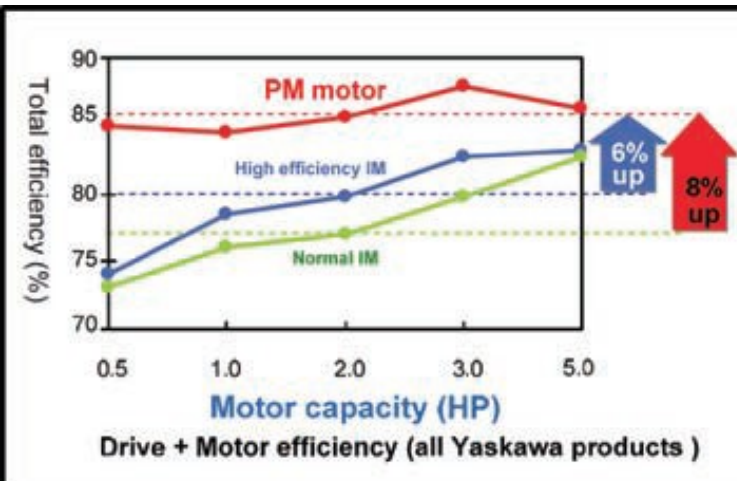
efficiency

volume

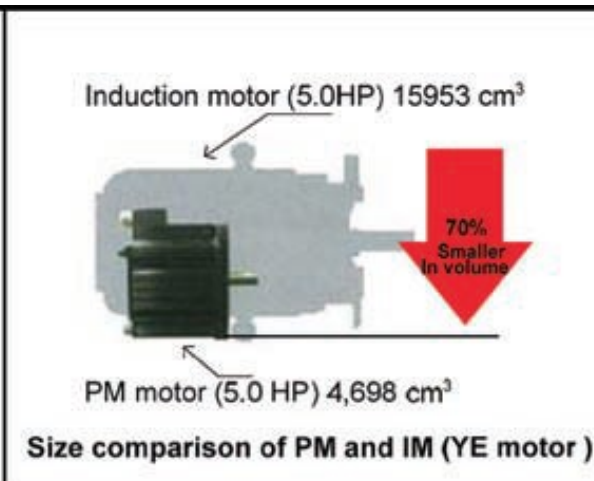
weight

Why PM motors?

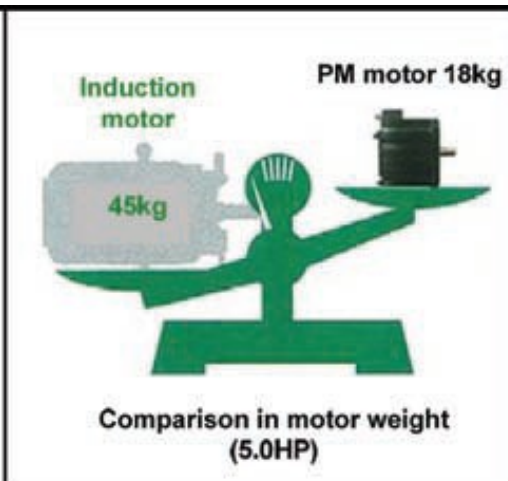
efficiency



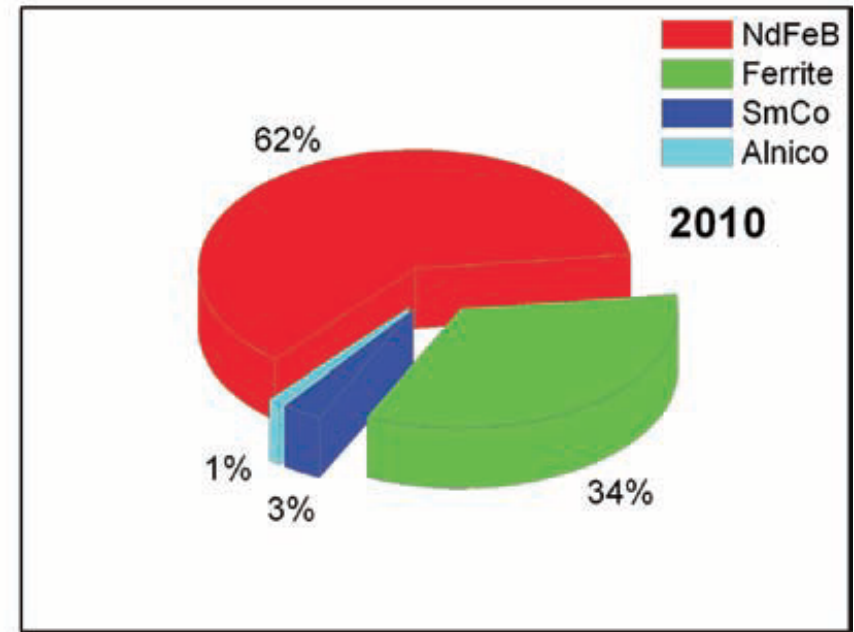
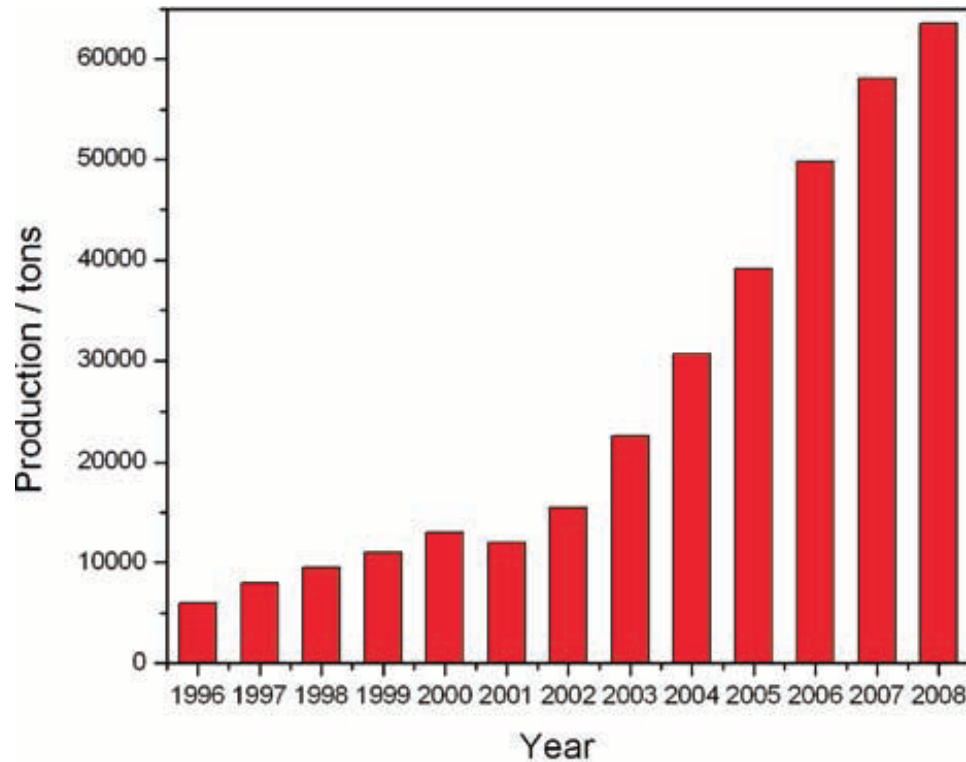
volume



weight



*Gutfleisch et al. Adv. Mater. 23 (2011) 821–842



Output of NdFeB permanent magnets during the past ten years (left) [1]

Percentage sales (\$) for 2010 of the major permanent magnets in the world (right) [2]*.

**Gutfleisch et al. Adv. Mater. 23 (2011) 821–842.*

[1] Yang Luo , Proc. 20 th Int. Workshop on Rare Earth Permanent Magnets and Their Applications , (Ed: D. Niarchos), 2008 , 27 .

[2] US Magnetic Materials Association, <http://www.usmagnetmaterials.com/documents/usmma-presentation-general-5-08.ppt>, (accessed September 2010).

Solutions ?

1. The increase of usage efficiency.
2. Recycling.
3. *New magnetic phases* without rare-earth with high magnetic properties for applications as permanent magnets and magnetic refrigeration: FePt, CoPt, Fe-Co and Fe-Ni tetragonal, Fe-Co ternary or quaternary, Fe₁₆N₂, MnBi, MnAl, Mn₃Ga, Heusler alloys
4. Soft/hard nanocomposite magnets ➔ *Spring magnets*

Typical magnetic characteristics of the main industrial magnets *

Shape anisotropy

1. AlNiCo magnets

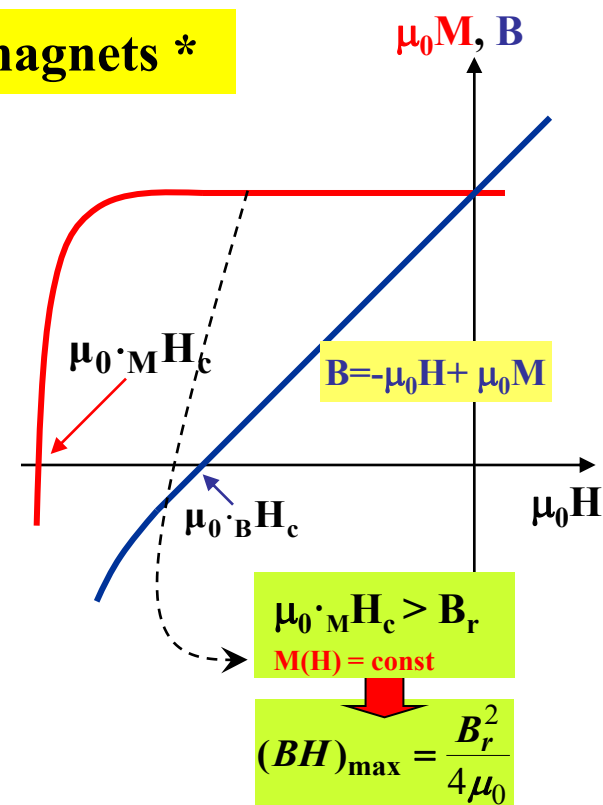
Magnetocrystalline anisotropy

2. Hard ferrites

- $\text{BaFe}_{12}\text{O}_{19}$
- $\text{SrFe}_{12}\text{O}_{19}$
- $\text{PbFe}_{12}\text{O}_{19}$

3. Rare-earth permanent magnets

- SmCo_5
- SmCo (2-17)
- $\text{Nd}_2\text{Fe}_{14}\text{B}$



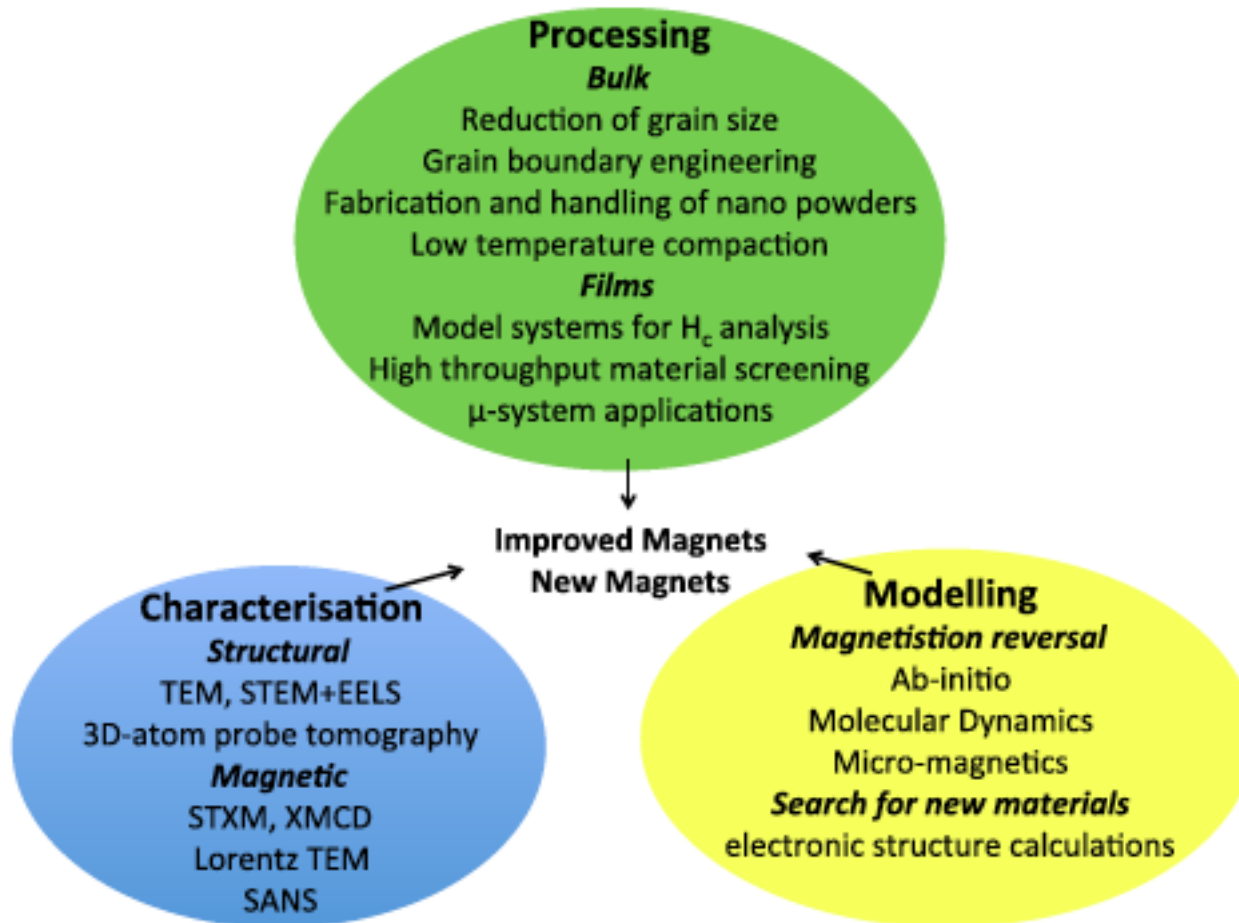
	B_r (T)	$\mu_0 \cdot M H_c$ (T)	$\mu_0 \cdot B H_c$ (T)	$(BH)_{\max}$ (kJ/m ³)	$B_r^2 / 4\mu_0$ (kJ/m ³)	T_c (°C)/(K)
AlNiCo	1,3	0,06	0.06	60-80	336	857/1130
Ferrite	0,4	0,4	0,37	30	31,8	447/720
SmCo_5	0,9	2,5	0,87	160-200	161	727/1000
SmCo (2-17)	1,1	1,3	0,97	220-256	241	827/1100
$\text{Nd}_2\text{Fe}_{14}\text{B}$	1,3	1,5	1,25	320-480	336	313/586

Rare Earth-Free Permanent Magnets ?

- ✧ **RE-free** hard magnetic compounds exist: FePt, CoPt, MnBi, MnAl, $\text{Zr}_2\text{Co}_{11}$, $\epsilon\text{-Fe}_2\text{O}_3$
- ✧ Even the Alnico-type magnets still have a room for improvement; their theoretical $(BH)_{\text{max}}$ is 36-49 MGOe and they have excellent temperature stability; **Artificial Alnicos!**

3. *New magnetic phases* without rare-earth with high magnetic properties for applications as permanent magnets and magnetic refrigeration: FePt, CoPt, Fe-Co and Fe-Ni tetragonal, Fe-Co ternary or quaternary, Fe₁₆N₂, MnBi, MnAl, Mn₃Ga, Heusler alloys
4. Soft/hard nanocomposite magnets → *Spring magnets*

The complementary expertise and advanced techniques
are required to develop magnets



Some recent research in these directions

1. *New magnetic phases* without rare-earth with high magnetic properties
2. **Soft/hard** nanocomposite magnets → *Spring magnets*

Some recent research in these directions

1. New magnetic phases without rare-earth with high magnetic properties

✓ *MnBi*

✓ *MnAl*

- $\text{Mn}_{50+\delta}\text{Al}_{50-\delta}$; $\delta=4$
- $\text{Mn}_{50}\text{Al}_{50-\delta}\text{X}_{\delta}$; $\delta=4$, X=Ni, Zn, Ti

2. **Soft/hard** nanocomposite magnets → Spring magnets

✓ hard magnetic phases of **SmCo_5 , SmCo_3Cu_2 , $\text{R}_2\text{Fe}_{14}\text{B}$**

✓ soft magnetic phases of **$\alpha\text{-Fe}$, Fe-Co (~20 or 10 wt%)**

Some recent research in these directions

1. New magnetic phases without rare-earth with high magnetic properties

✓ *MnBi*

✓ *MnAl*

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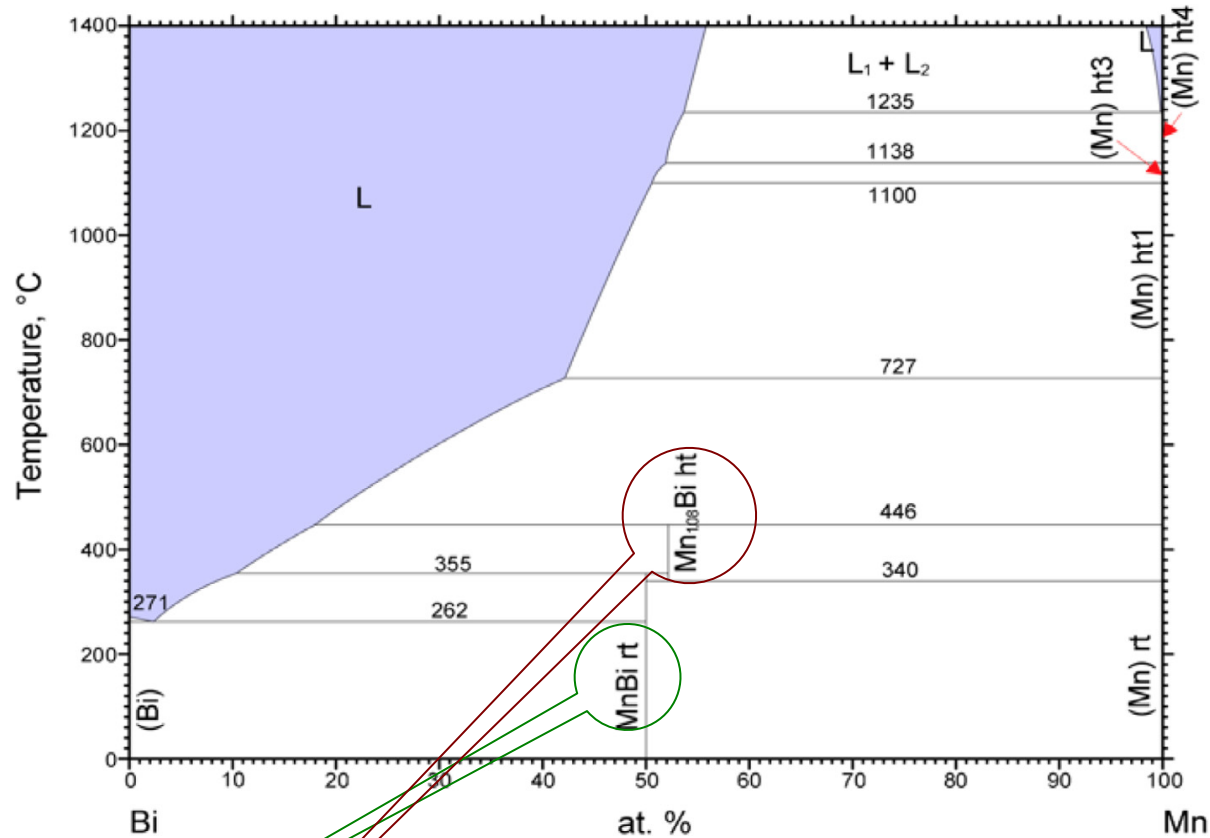
2. **Soft/hard** nanocomposite magnets → Spring magnets

- ✓ hard magnetic phases of **SmCo_5 , SmCo_3Cu_2 , $\text{R}_2\text{Fe}_{14}\text{B}$**
 - **SmCo_5** large anisotropy
 - **SmCo_3Cu_2** large coercivity
 - **$\text{R}_2\text{Fe}_{14}\text{B}$** best magnets
- ✓ soft magnetic phases of **α -Fe, Fe-Co (~20 or 10 wt%)**

Outline

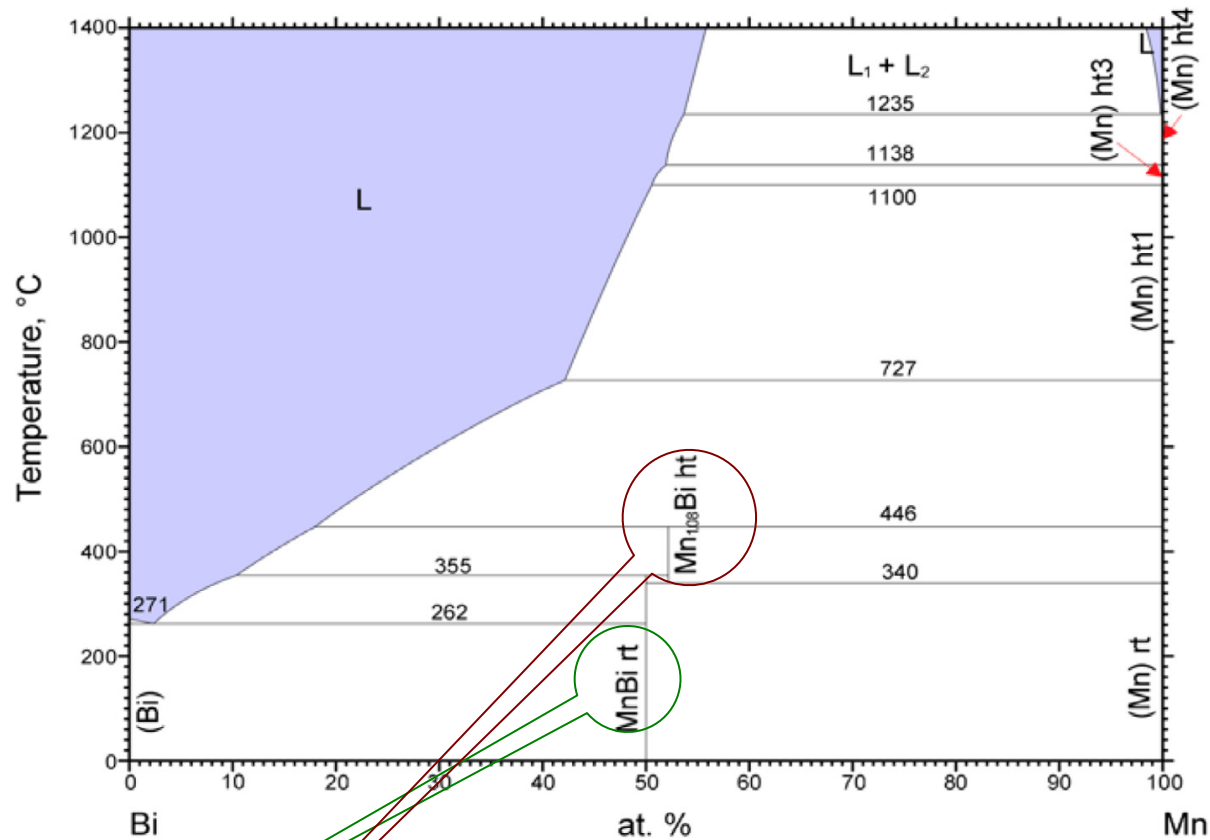
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- Conclusions

MnBi magnetic phase



- Low temperature phase (LTP)-NiAs type Hexagonal (Ferromagnetic)
- High temperature phase (HTP) -Distorted Ni₂In type hexagonal (paramagnetic)

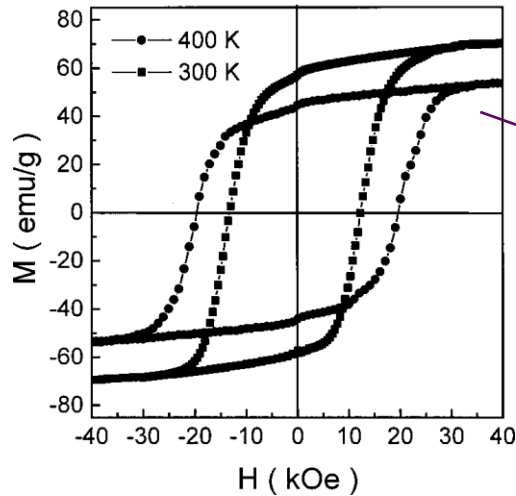
MnBi magnetic phase



- Low temperature phase (LTP)-NiAs type Hexagonal (Ferromagnetic)
- High temperature phase (HTP) -*Distorted Ni₂In type hexagonal (paramagnetic)*
- Quenched high temperature phase (QHTP)-*Orthorhombic (Ferromagnetic-low M_s)*

Some previous works in MnBi magnetic compound*

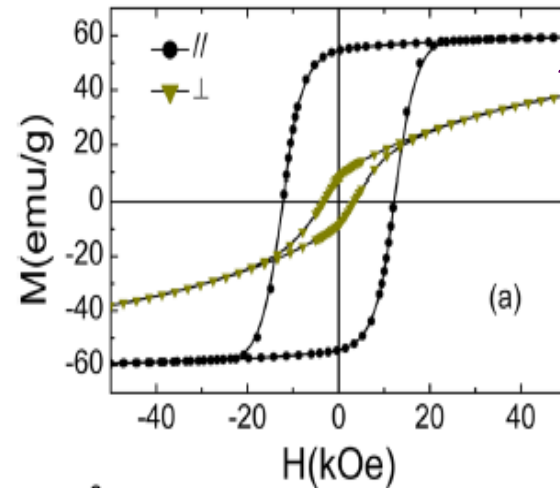
Powders: Sintered method & magnetic separation



$(BH)_{\max} = 7.7$ MGOe
(powders)

J B Yang et al. *J. Phys.: Condens. Matter* 14 (2002) 6509

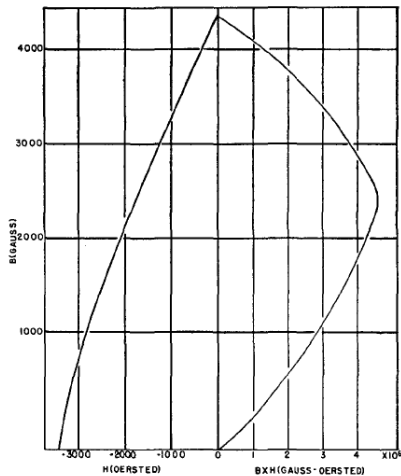
Nanocrystalline MnBi by melt-spinning technique



$(BH)_{\max} = 7.1$ MGOe
(powders of melt-spun ribbons)

Yang et al. *Appl. Phys. Lett.* 99, 082505 (2011)

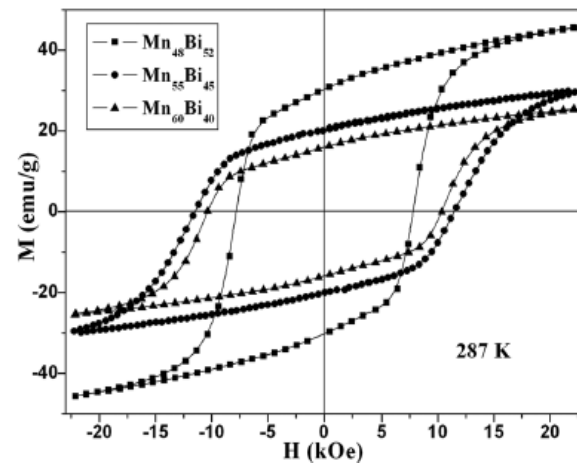
Hot pressed bulk magnet



$(BH)_{\max} = 4.3$ MGOe
Density: 90%

Adams et al. *J. Appl. Phys.* 23 1207 (1952)

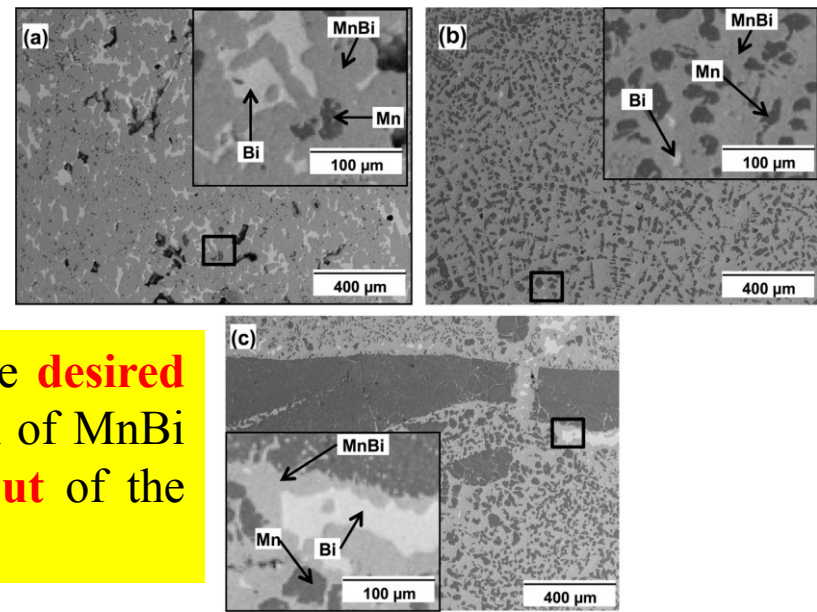
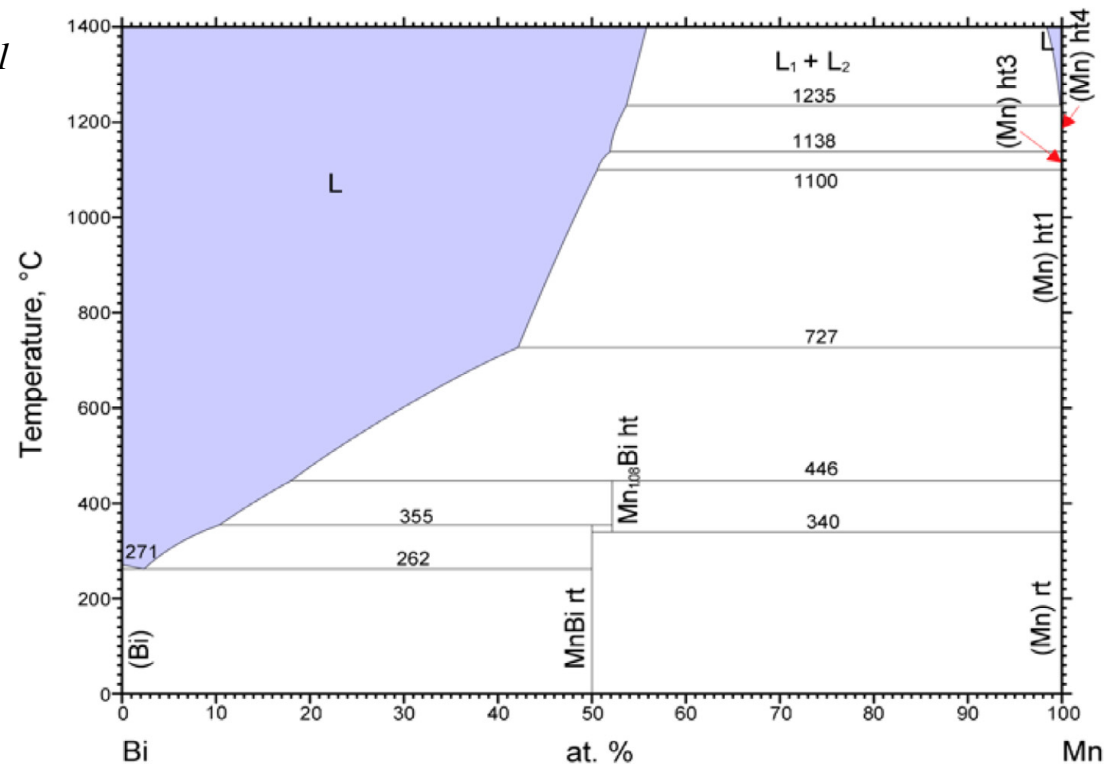
Spark plasma sintered bulk magnet



$(BH)_{\max} < 2$ MGOe
Density: 93%

Zhang et al. *J. Appl. Phys.* 109, 07A722 (2011)

*G. Hadjipanayis, Delaware University, Energy and Materials Criticality Workshop, Santorini 2013



Difficulty of obtaining a high volume fraction of the **desired LTP MnBi**, originated from the **peritectic** formation of MnBi LTP and hence **Mn and Bi tends to precipitate out** of the MnBi liquid during the solidification process

Our main results

MnBi

Synthesis:

- ✓ melting: Mn and Bi of 99,99% purity (1 wt % Mn in excess)
- ✓ annealing: 258-420°C/ from 2 hours to 4 days
- ✓ mechanical milling: of bulk MnBi phase for 2 hours

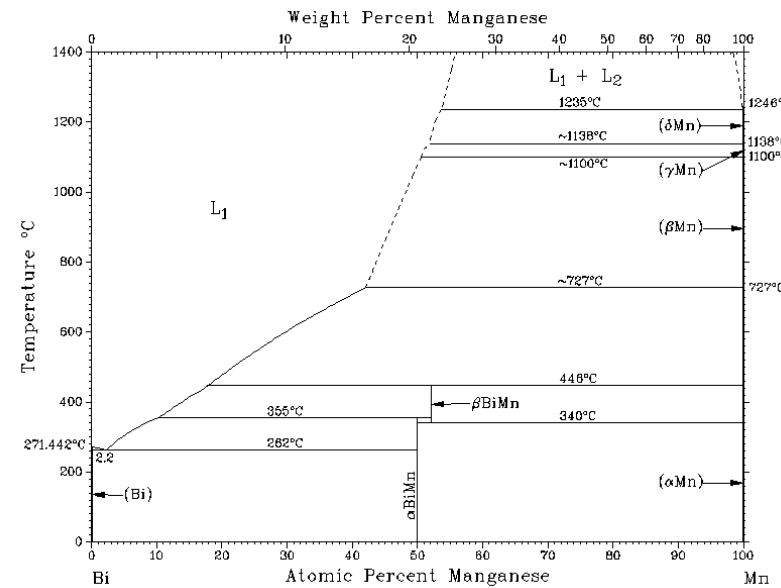
X-rays powder diffraction:

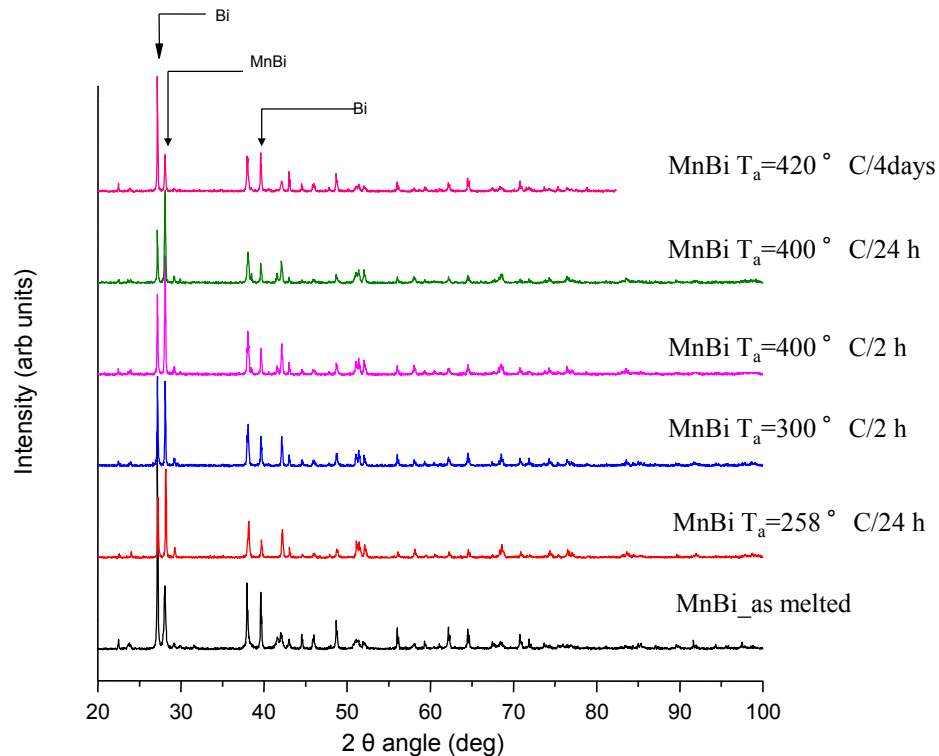
- ✓ K_{α} radiation of copper in the angular range $2\theta = 20 - 100^{\circ}$ and
- ✓ $K_{\alpha 1}$ radiation of cobalt in angular range $2\theta = 20 - 80^{\circ}$

Magnetic measurements:

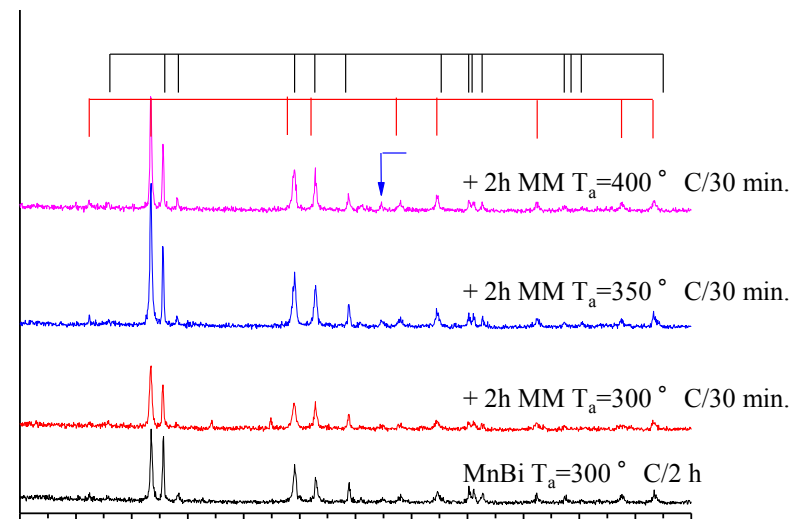
- ✓ extraction method in a continuous magnetic field of up to ± 10 T

MnBi: influence of *annealing*

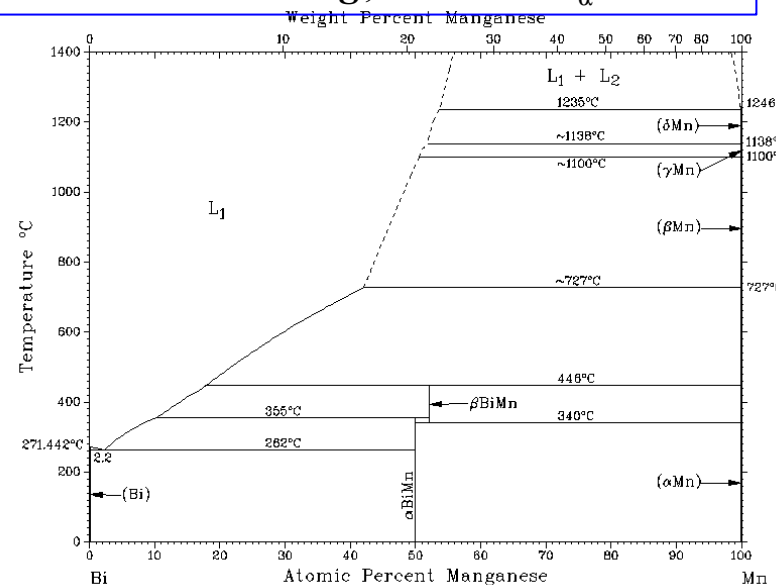


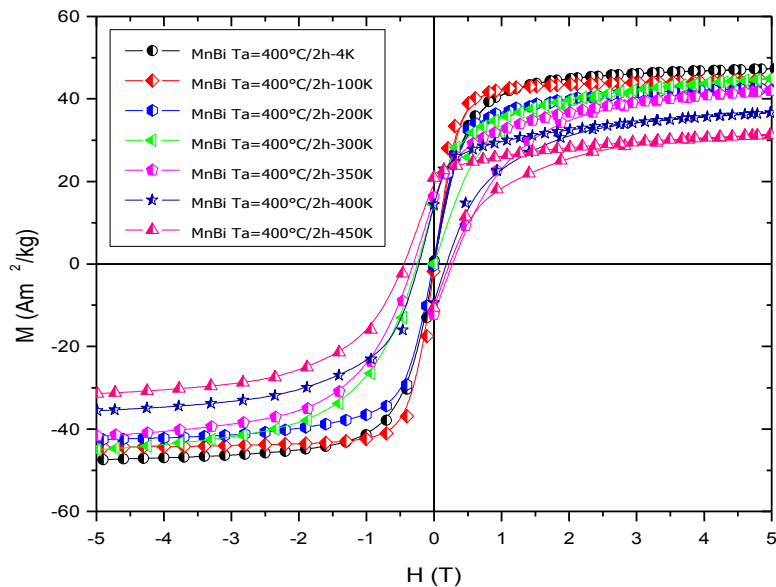


MnBi: influence of *annealing*; XRD Cu K_α radiation

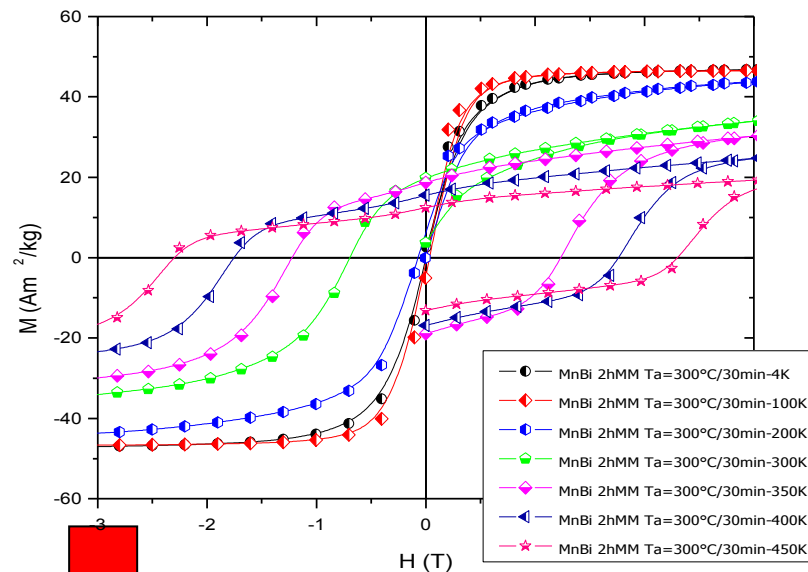


MnBi: influence of *milling*; XRD Co K_α radiation





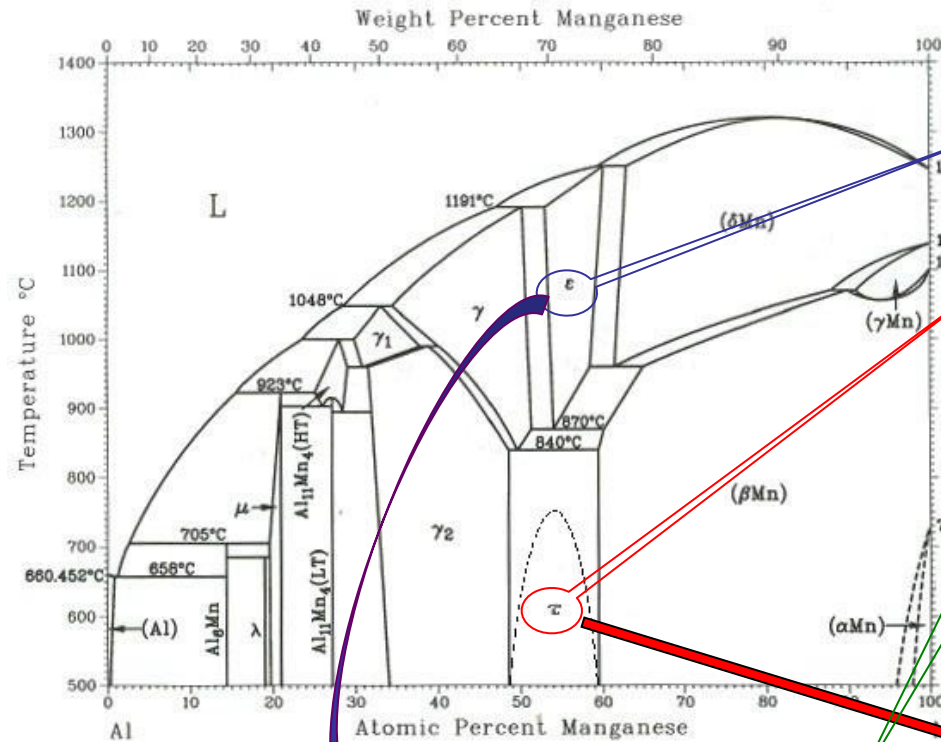
$M(H)$ for different T ,
MnBi melted samples, annealed at 400°C for 2 h



Hysteresis loops for different T ,
MnBi 2h MM+TT 300 °C/30 min

**Important coercivity at high temperature,
competition with REPM**

Mn-Al magnetic phase

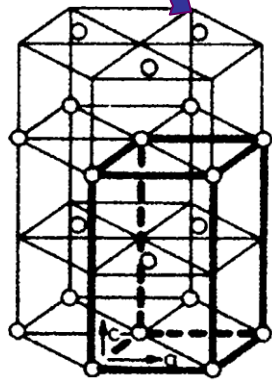


ε phase –
antiferromagnetic hexagonal structure

τ phase –
L1₀- ferromagnetic tetragonal structure

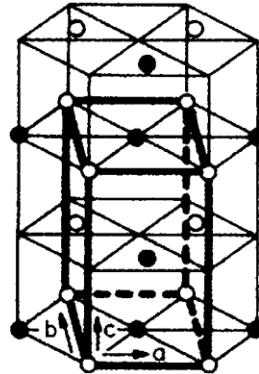
ε' phase –
Intermediate ferromagnetic *ordered*
orthorhombic phase

Mn₅₄Al₄₆- the best results



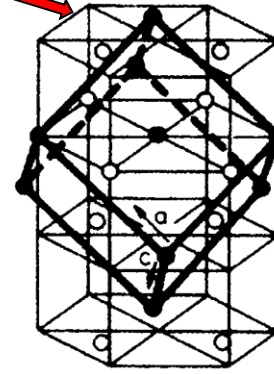
A3 (ε)

ordering
reaction



B19 (ε')

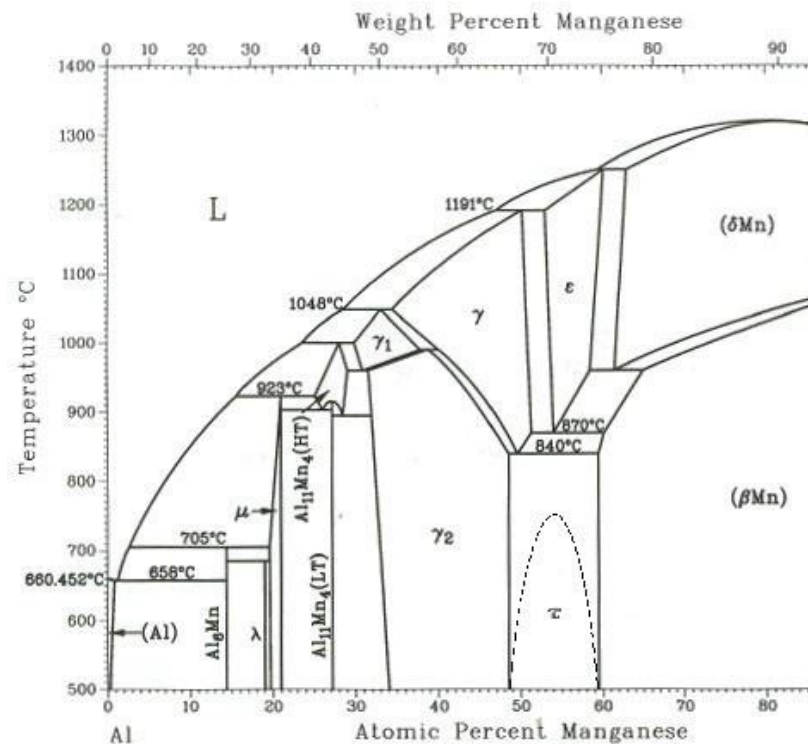
martensitic
shear



L1₀ (τ)

- Phase transformation proposed by Broek et. al. with intermediate ordered orthorhombic phase (B19) denoted by ε'.
- Acta Metall.,27(1979) 1497

Phase formation, microstructure, magnetic properties of the Mn–Al–C; bulk or MM*



- DSC: the transformation $\epsilon(\epsilon') \rightarrow \tau$ phase,
- τ -phase stabilized by C doping,
- C doping *cannot prevent* the formation of the equilibrium phases from the metastable ϵ -phase during annealing.

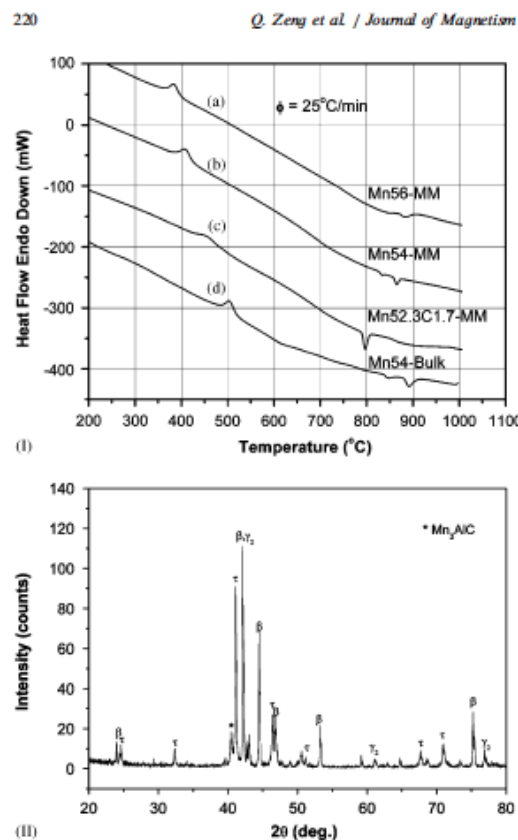


Fig. 7. (I) DTA curves for (a) MM $\text{Mn}_{56}\text{Al}_{46}$, (b) MM $\text{Mn}_{54}\text{Al}_{46}$, (c) $\text{Mn}_{52.3}\text{Al}_{46}\text{C}_{1.7}$, and (d) bulk $\text{Mn}_{54}\text{Al}_{46}$. The heating rate was 25°C/min. (II) XRD pattern for MM $\text{Mn}_{52.3}\text{Al}_{46}\text{C}_{1.7}$ heated to 760°C at the heating rate of 25°C/min and quenched.

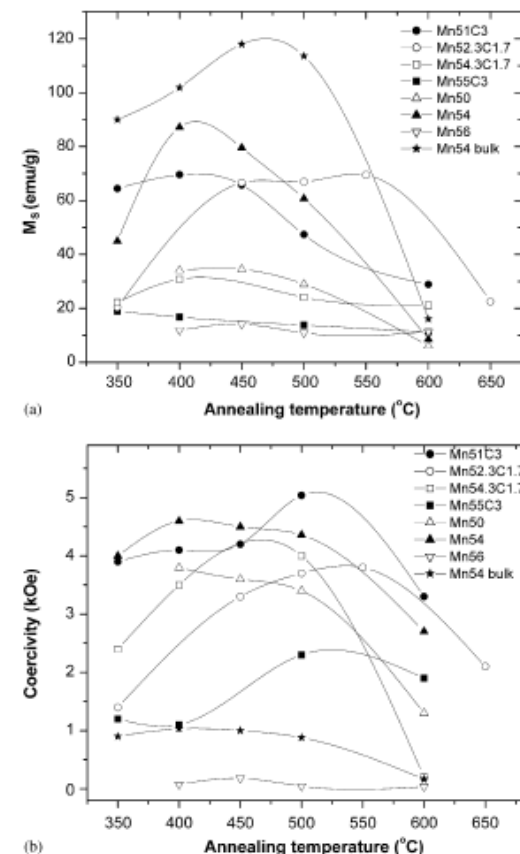
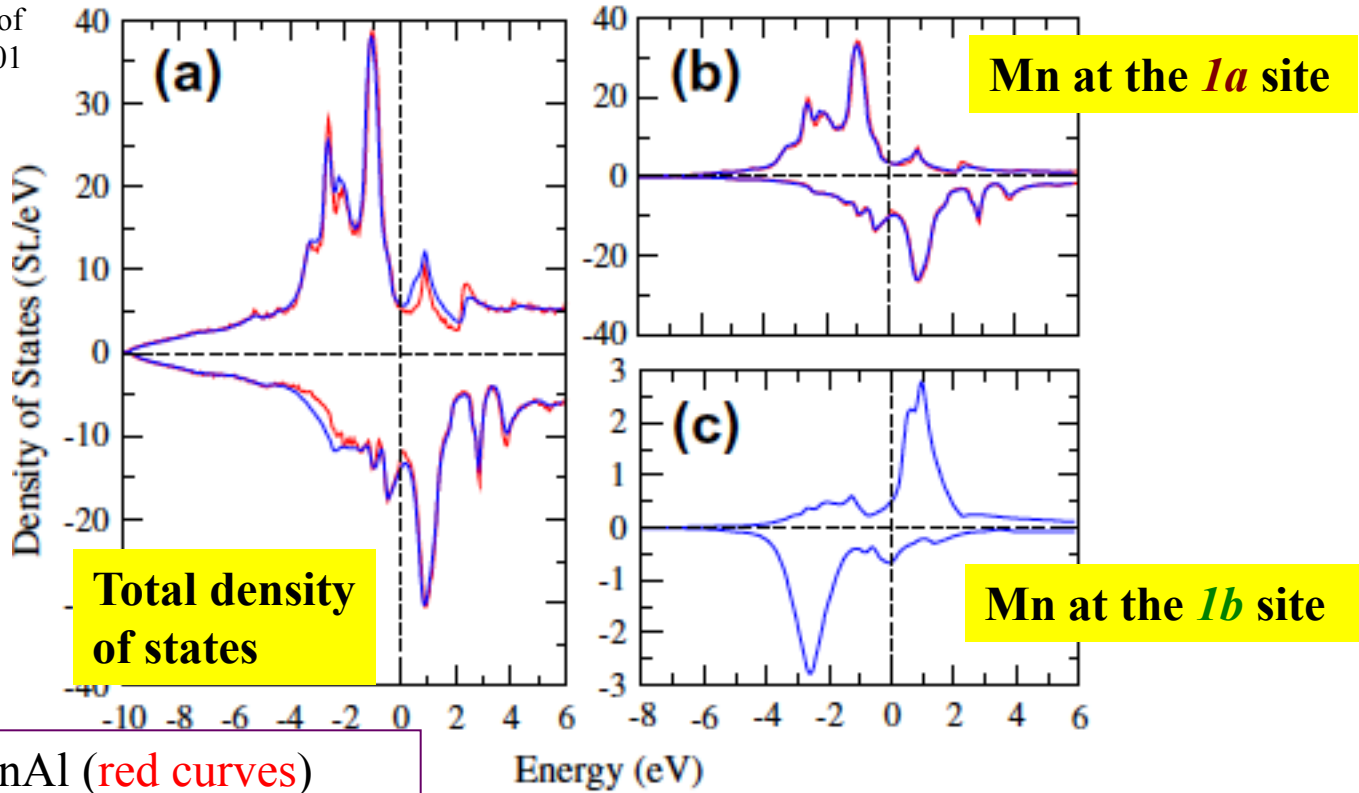
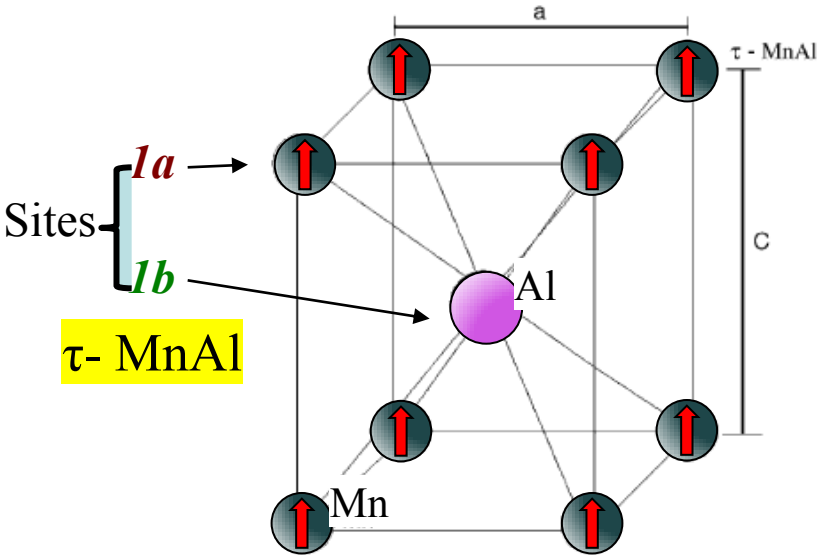
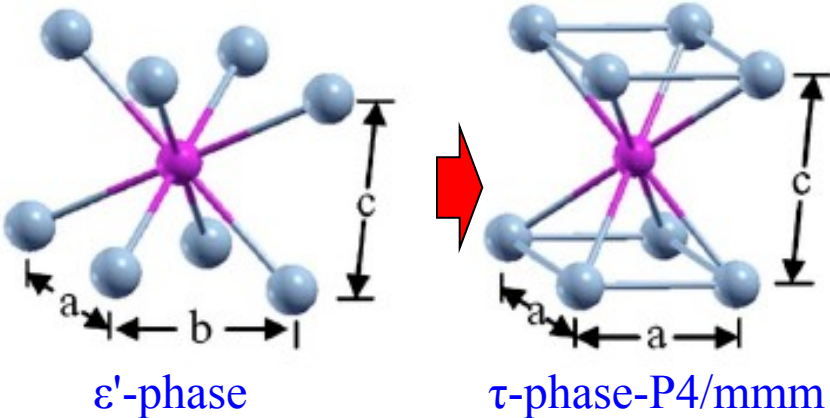


Fig. 8. Dependence of M_s and H_c on the annealing temperatures for MM and bulk samples with various compositions as indicated. The annealing time was 30 min.

The optimal magnetic properties for the MM samples, $H_c=4.8$ kOe, $M_r=45$ emu/g and $M_s=89$ emu/g, were obtained for $\text{Mn}_{54}\text{Al}_{46}$ annealed at 400 ° C for 10 min



stoichiometric MnAl (red curves)
 $\text{Mn}_{50+\delta}\text{Al}_{50-\delta}$; $\delta=4$ (blue curves) .



Our results

Mn₅₀Al₄₆Ni₄ and Mn₅₄Al₄₆

- Ingots were prepared by arc or induction melting
- Different heat treatment to stabilize the desired magnetic phase

Measurements

- Differential thermal analysis (DTA)
- XRD on Brüker D8 Advance diffractometer
- Thermomagnetic measurements up to 800 K

Electronic structure calculations

were performed in the framework of the Local Density Approximation (LDA) of the Density Functional Theory [31] using the SPRKKR method. The calculation method is based on the KKR-Green's function formalism that makes use of multiple scattering theories

DTA_Mn₅₀Al₄₆Ni₄ and Mn₅₄Al₄₆

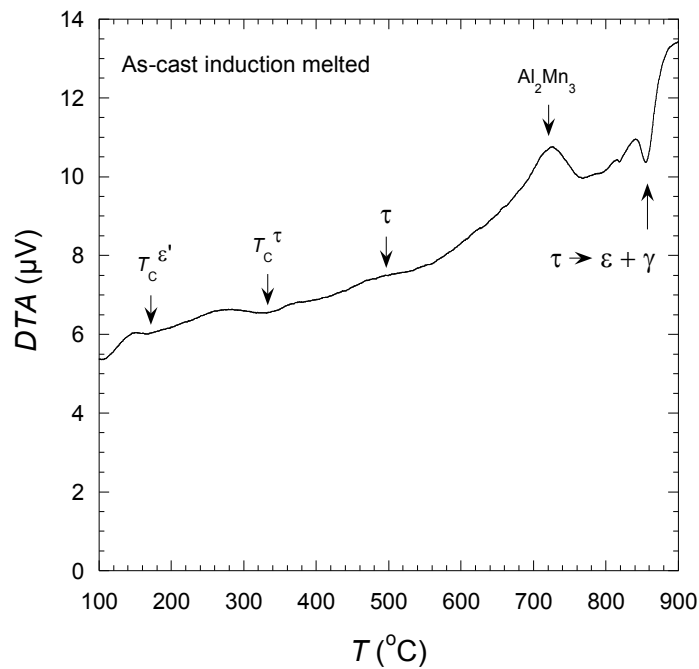
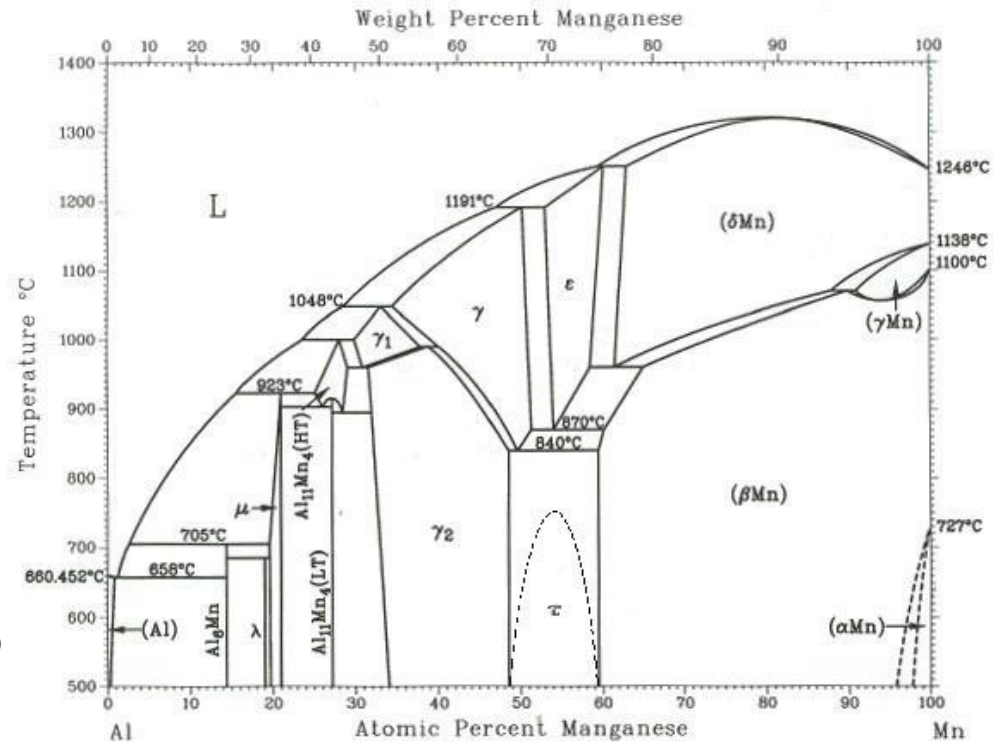
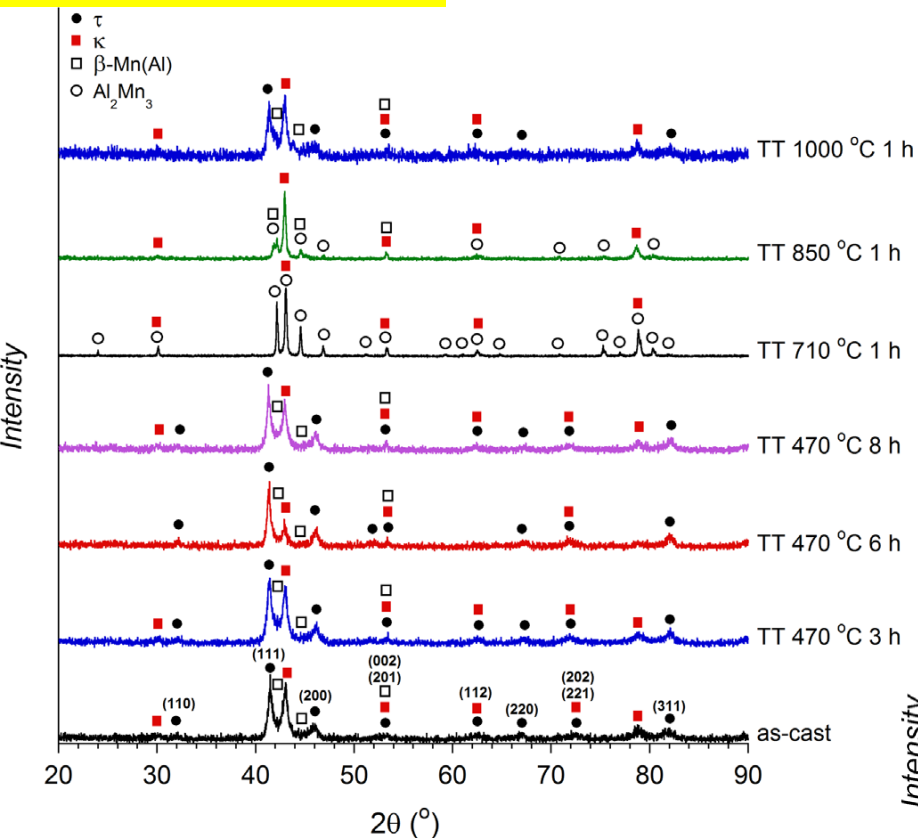


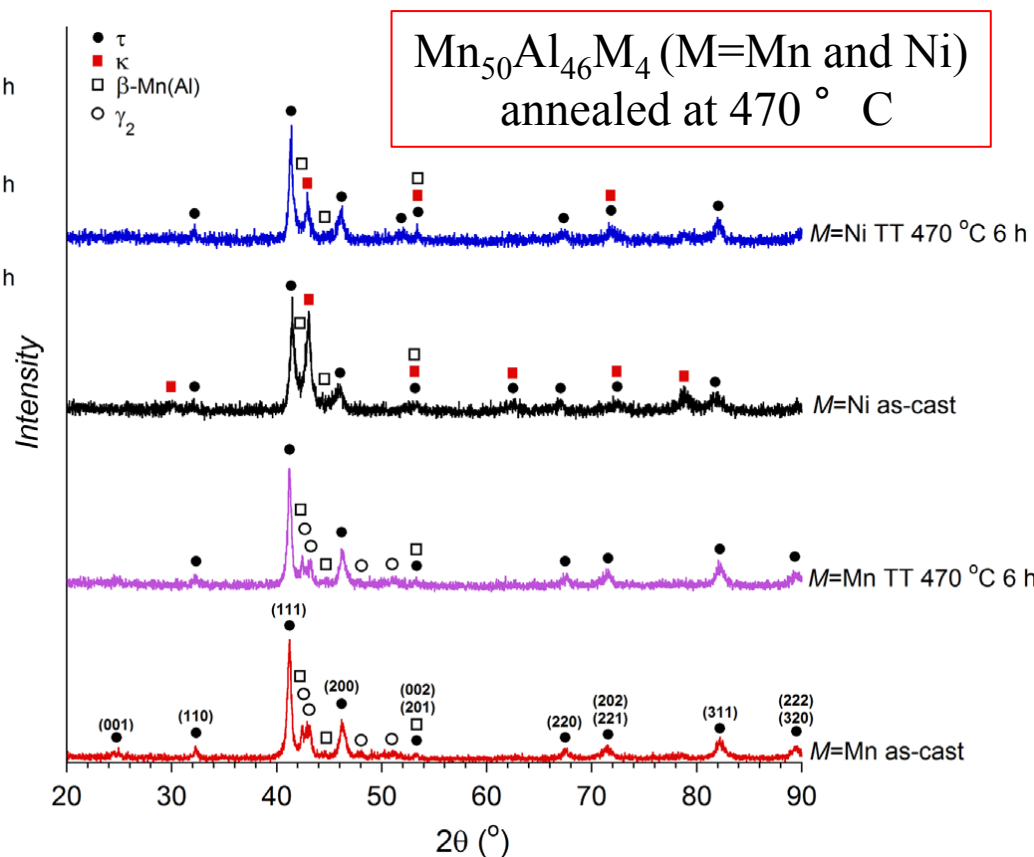
Fig. 1. DTA curve for the as-cast Mn₅₀Al₄₆Ni₄ alloy.



XRD



$\text{Mn}_{50}\text{Al}_{46}\text{M}_4$ – different heat treatments



Some XRD results

Sample	a (Å)	c (Å)	c_{τ} (wt%) $\pm 2\%$	$c_{\gamma 2}$ (wt%) $\pm 2\%$	c_{β} (wt%) $\pm 2\%$	c_{κ} (wt%) $\pm 2\%$
Mn ₅₄ Al ₄₆ as-cast	3.93	3.57	68	25	7	–
Mn ₅₄ Al ₄₆ + 470 °C 6 h	3.93	3.57	76	20	4	–
Mn ₅₀ Al ₄₆ Ni ₄ as-cast	3.96	3.47	50	–	5	45
Mn ₅₀ Al ₄₆ Ni ₄ + 470 °C 6 h	3.94	3.52	74	–	6	20

τ phase

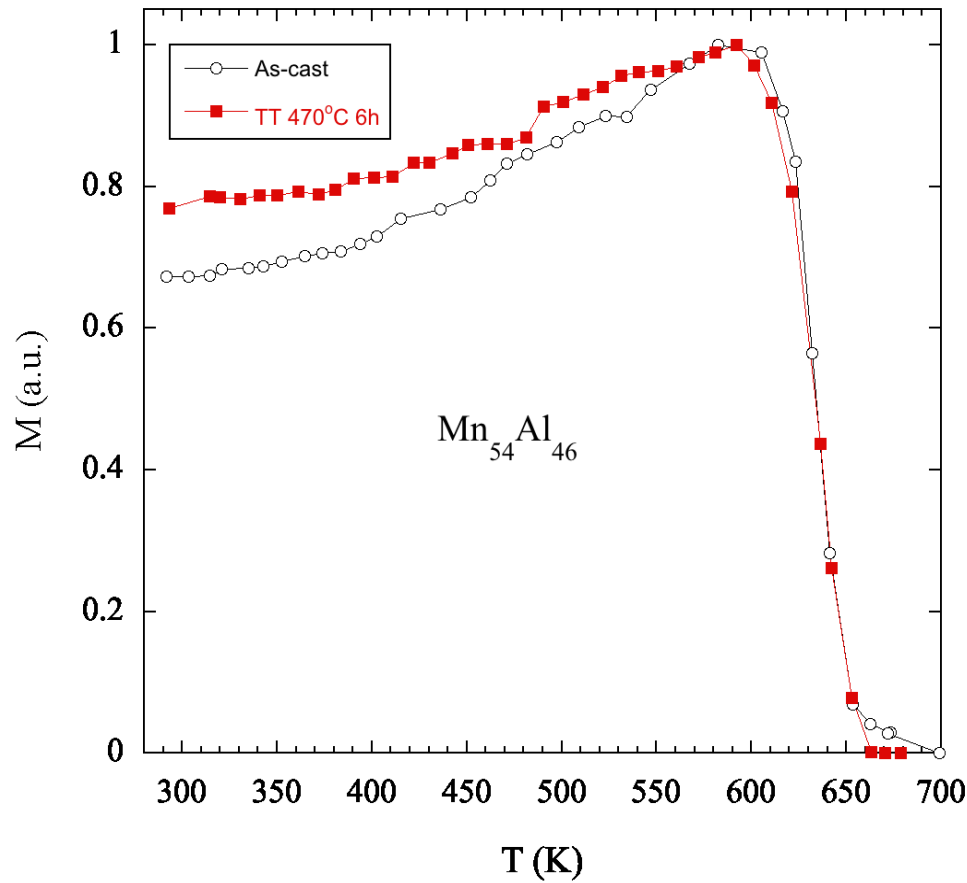
Band structure (SPRKKR) calculations: Mn₅₄Al₄₆ and Mn₅₀Al₄₆Ni₄ in the AFM configuration.

Sample	Atom	m_{spin} (μ_B)	m_{orbit} (μ_B)
Mn ₅₄ Al ₄₆	Al ^{2e}	–0.08	0
	Mn ^{2e}	–3.22	–0.01
	Mn ^{1a,1c}	2.33	0.04
	Total (μ_B/f.u.)	1.00	0.02
(Mn ₄₆ Ni ₄) ^{1a,1c} (Al ₄₆ Mn ₄) ^{2e}	Mn ^{1a,1c}	2.27	0.04
	Ni ^{1a,1c}	–0.09	–0.01
	Al ^{2e}	–0.08	0
	Mn ^{2e}	–3.21	–0.02
	Total (μ_B/f.u.)	0.88	0.02

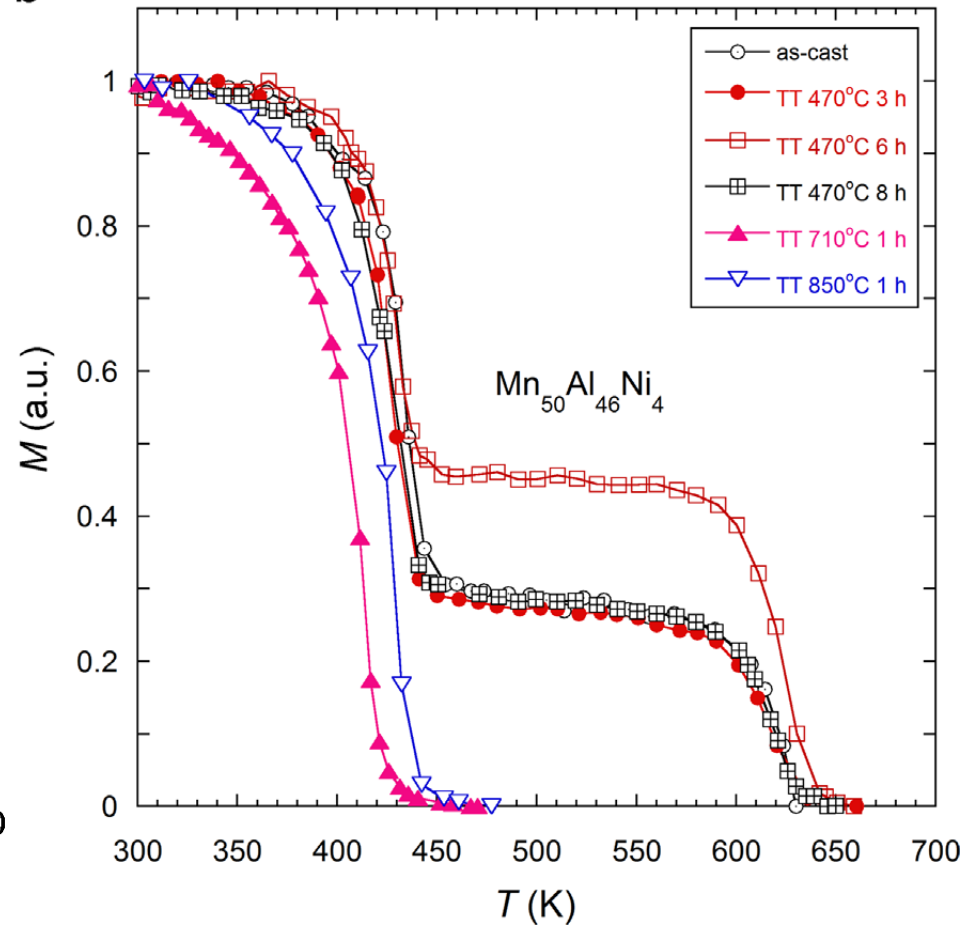
Thermomagnetic studies

$\text{Mn}_{50}\text{Al}_{46}\text{Ni}_4$ and $\text{Mn}_{54}\text{Al}_{46}$

a



b



Magnetic behavior

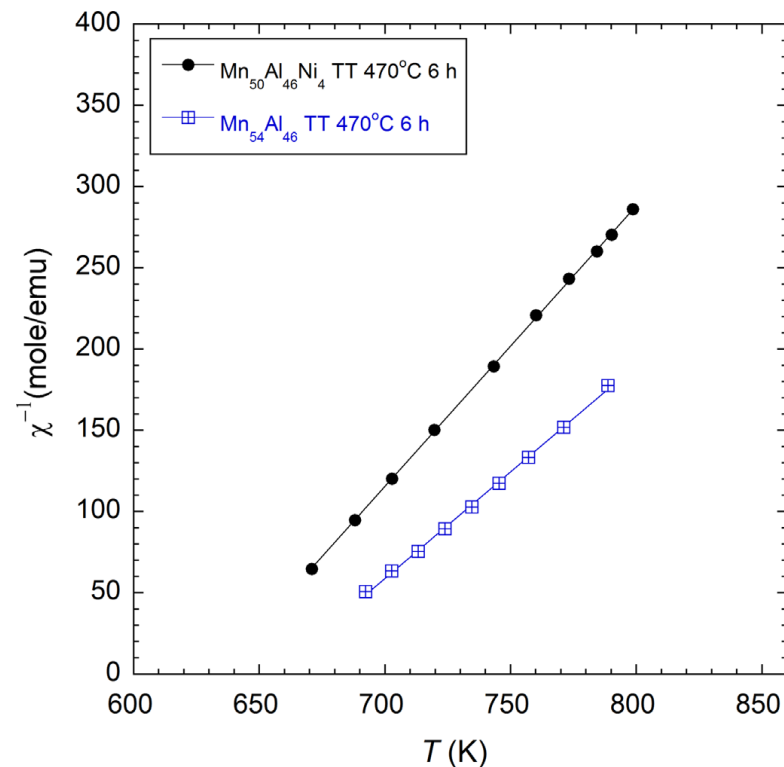
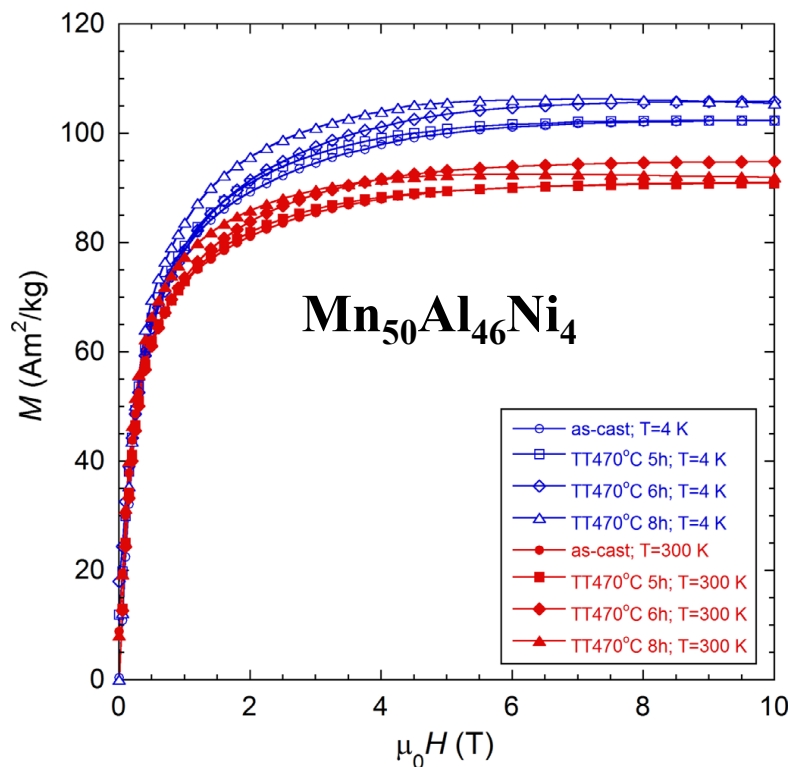


Table 3. The magnetic moments in the ordered (m) and paramagnetic state (μ_{eff}), the ferromagnetic (T_c) and paramagnetic (θ) Curie temperatures for the $\text{Mn}_{54}\text{Al}_{46}$ and $\text{Mn}_{50}\text{Al}_{46}\text{Ni}_4$ alloys annealed at 470°C for 6h.

Sample	m_{tot} ($\mu_{\text{B}}/\text{f.u.}$)	m_{Mn} (μ_{B}/Mn atom)	T_c (K)	μ_{eff} ($\mu_{\text{B}}/\text{f.u.}$)	θ (K)	$\mu_{\text{eff}}^{\gamma^2}$ (μ_{B}/Mn atom)	$\mu_{\text{eff}}^{\gamma^2}$ (μ_{B}/Mn atom)	μ_{eff}^{β} (μ_{B}/Mn atom) [43]	$\mu_{\text{eff}}^{\kappa}$ (μ_{B}/Mn atom)
$\text{Mn}_{54}\text{Al}_{46}$	1.11	2.41	645	2.47	655	3.26	3.94	1.70	-
$\text{Mn}_{50}\text{Al}_{46}\text{Ni}_4$	0.92	2.19	634	2.15	633	3.03	-	1.70	3.37

Outline

- Introduction
- Mn-based magnetic phases
- **Nanocomposites magnets=Spring magnets**
- Conclusions

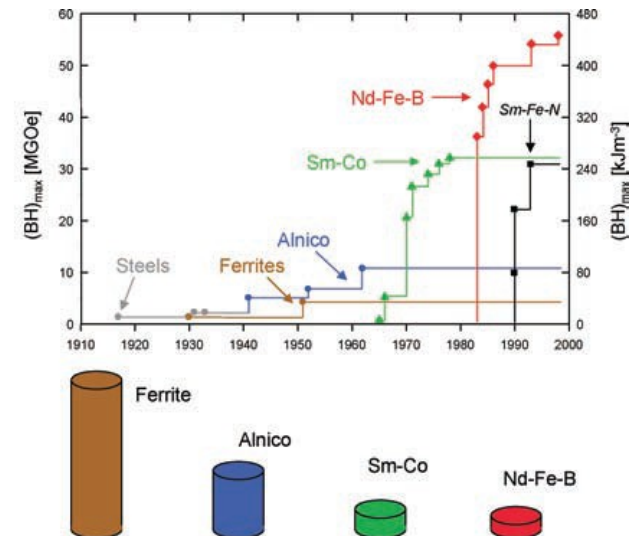
magnetit magnet (1750)

ferrite magnet (1940)

rare earth based magnet (1980)

exchange-spring magnets (20??)

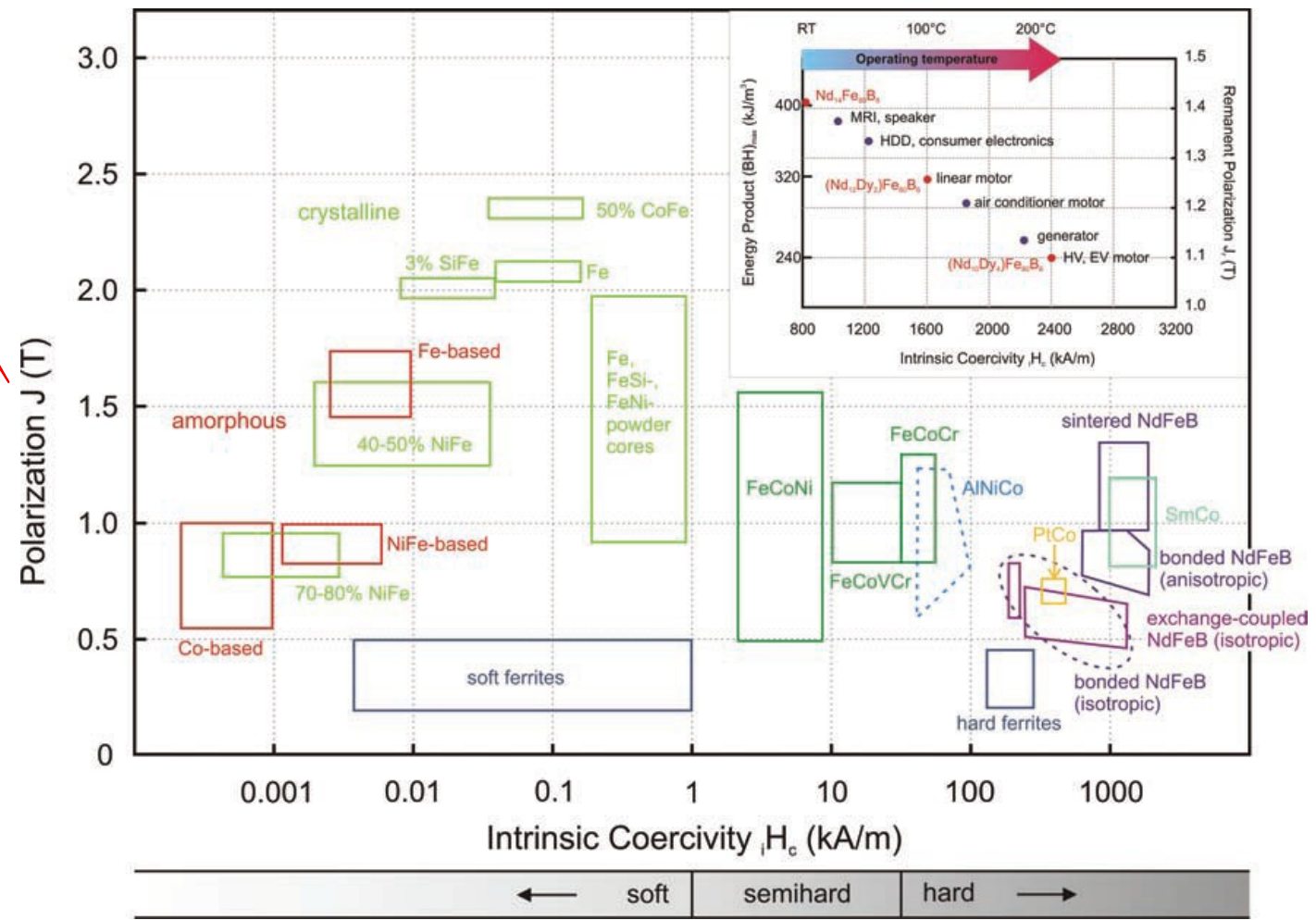
All this magnets have the same energy !



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

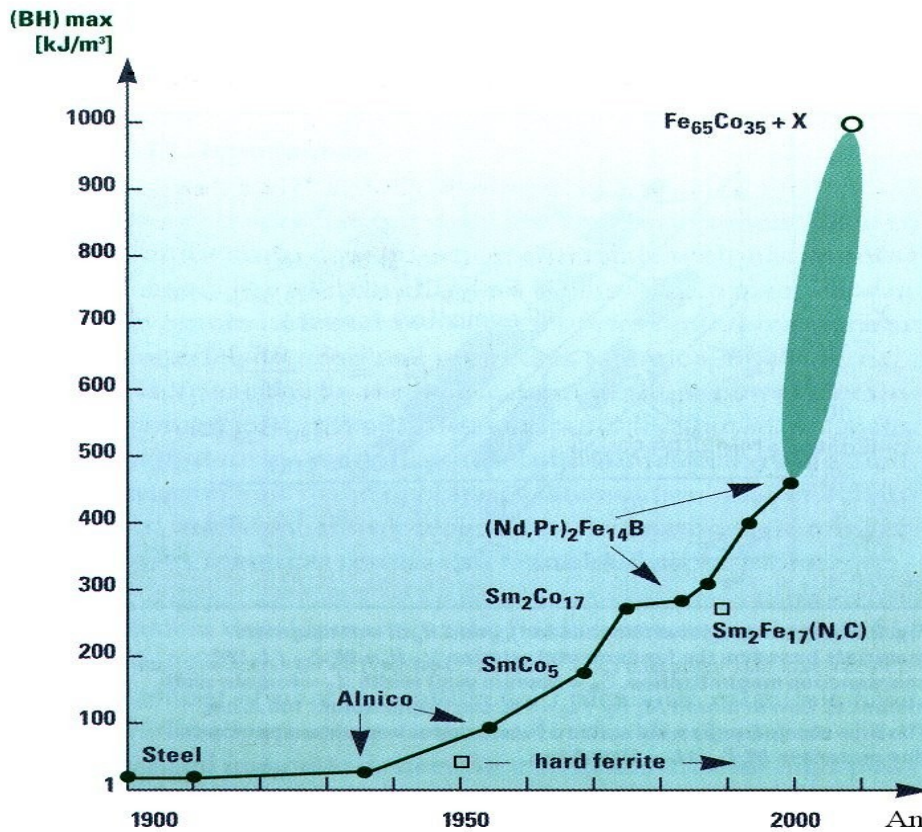
$$\mu_0 \vec{H} + \vec{J}$$

$$(BH)_{\max} = \frac{J_r^2}{4\mu_0}$$



*O. Gutfleisch, M. A. Willard, E. Brück, C. a H. Chen, S. G. Sankar, and J. P. Liu, *Adv. Mater.* 2011, 23, 821–842)

Theoretical predictions:



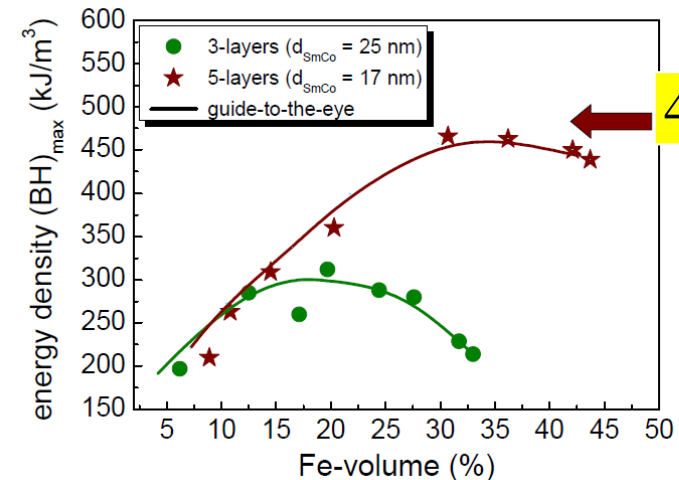
Best magnets on the market:
 $(BH)_{\max} \approx 500 \text{ kJ/m}^3$

$(BH)_{\max} = 1090 \text{ kJ/m}^3$ for nanostructured
 multilayers $\text{Sm}_2\text{Fe}_{17}\text{N}_3/\text{Fe}_{65}\text{Co}_{35}$

R. Skomski, J. Appl. Phys. 76 (1994) 7059

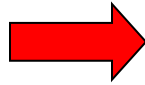
Kronmüller & Coey *Magnetic Materials*, in *European White book on Fundamental Research in Materials Science* Max Planck Inst. Metallforschung, Stuttgart, 2001, 92-96

Experimental realisations: ??????????

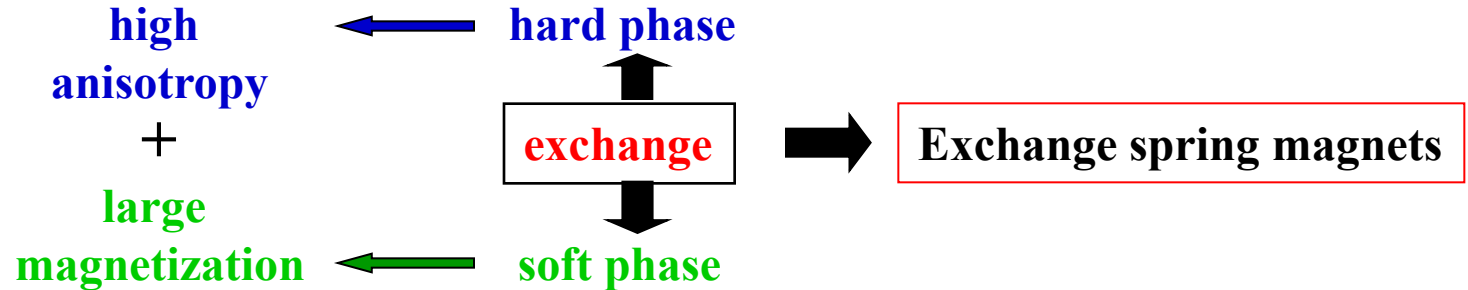


460 kJ/m³

**Structure
Microstructure**



Soft-hard exchange hardness



$$D_{cr} \approx 2\delta_h$$

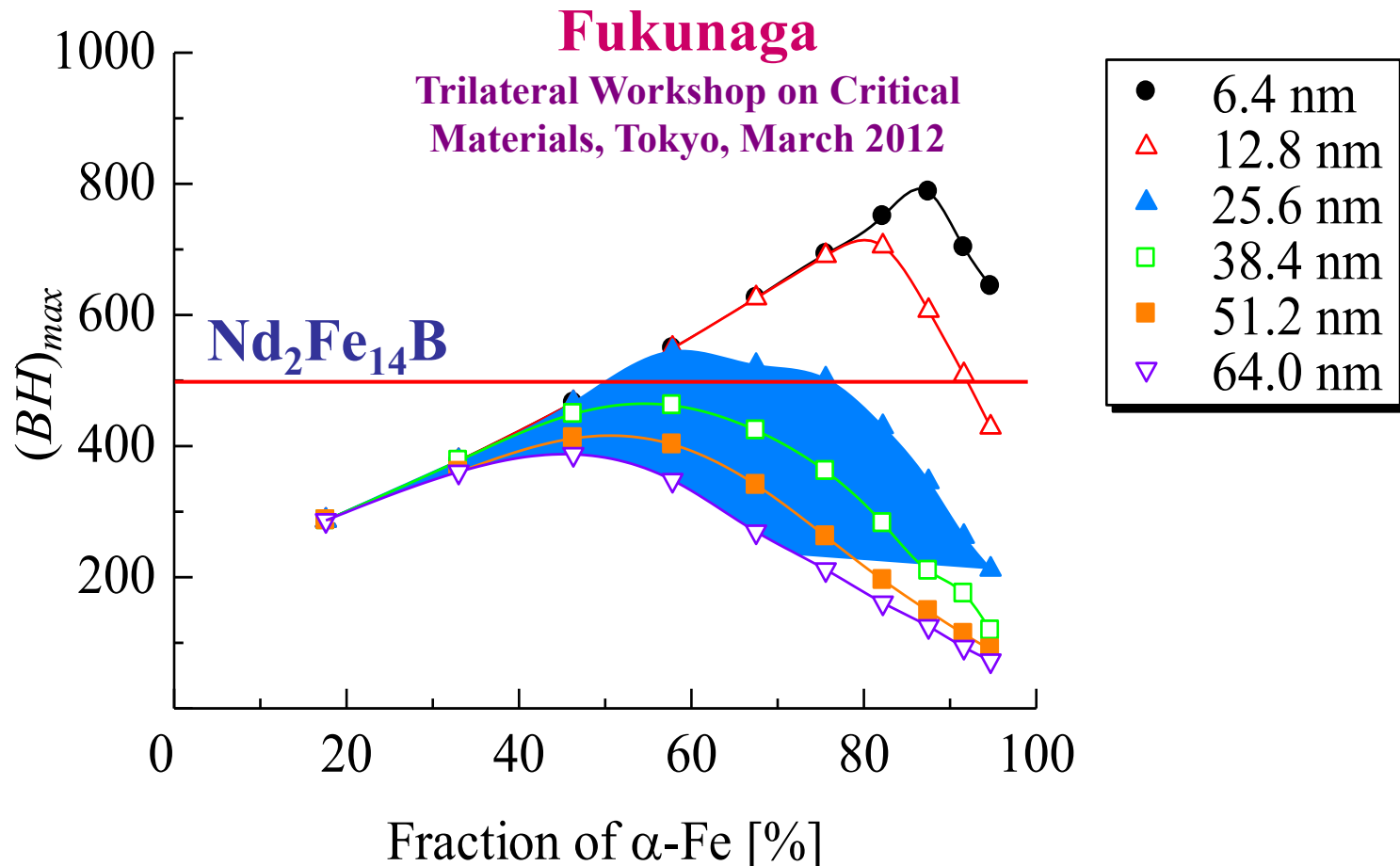
$$\delta_h = \pi \sqrt{A_h / K_h}$$

D_{cr} = soft phase critical dimension

δ_h = width of domain wall in the hard phase

A_h and K_h are the exchange and anisotropy constants

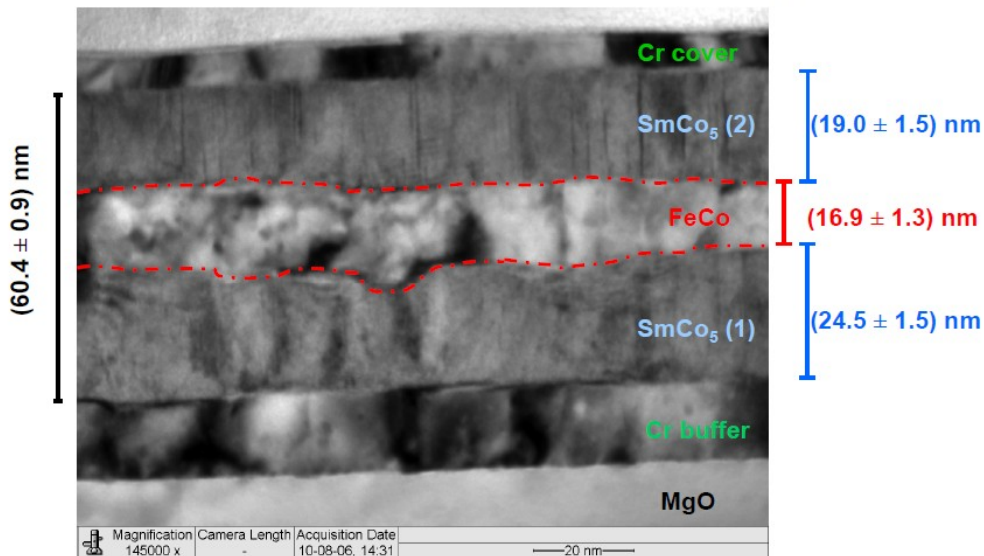
SmCo₅/α-Fe Core-Shell Nanocomposite Magnet



✧ Fukunaga predicted a drastic increase in $(BH)_{max}$ of SmCo₅/α-Fe as a function of α-Fe fraction. The Dresden Group (Neu et al) obtained similar results in SmCo₅/Fe multilayers (Intermag 2012). Very recently Hono's Group fabricated Fe/Nd-Fe-B multilayers with $(BH)_m=61$ MGOe (Advanced Materials, 2012).

cross-sectional TEM:

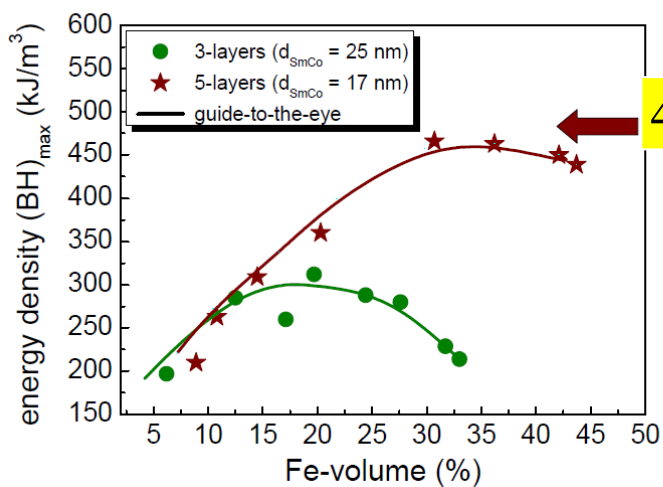
$$d_{\text{nom}}(\text{Fe}) = 12 \text{ nm}$$



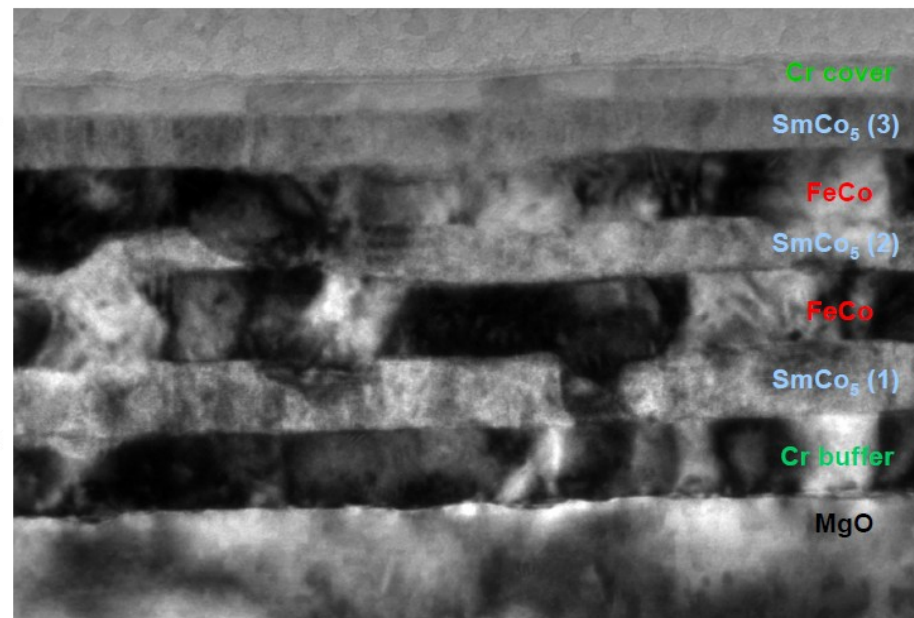
Ch. Damr

cross-sectional TEM:

5 layers



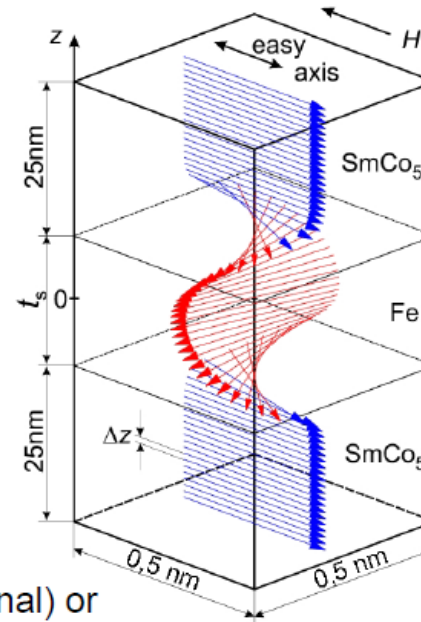
(64.4 ± 0.9) nm



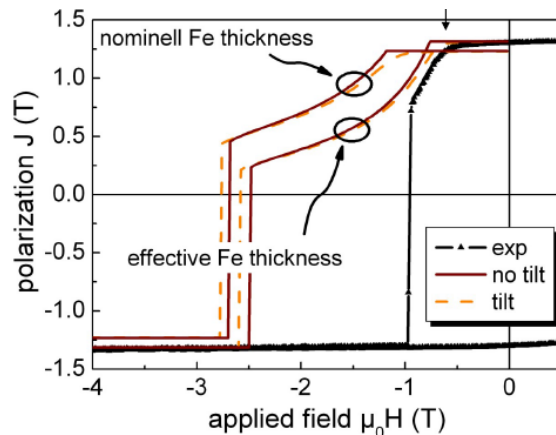
- ❖ code: OOMMF, version 1.2
- ❖ 1-dim approach; no x-y discretization
- ❖ discretization in z-direction: $\Delta z = 0.5 \text{ nm}$
- ❖ intrinsic parameters:

	A (pJ/m)	J_s (T)	K_1 (MJ/m ³)
SmCo ₅	12	1.0	10
Fe	28	2.15	-1.84

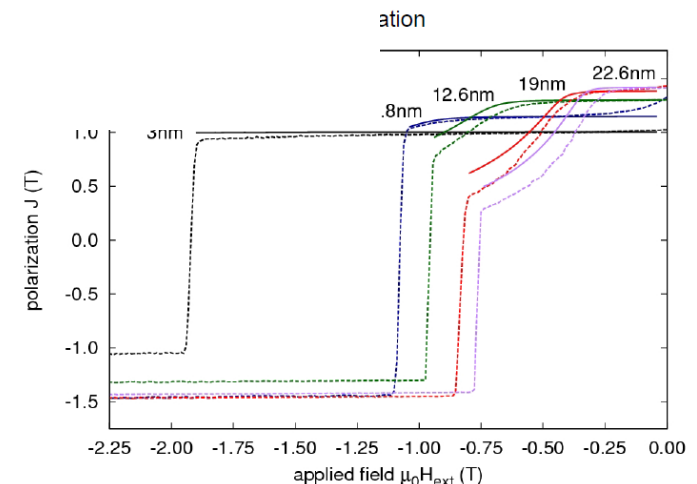
- ❖ strong coupling at interface: $A_i = 20 \text{ pJ/m}$
- ❖ geometry: $2 \times 25 \text{ nm SmCo}_5 + t_s \text{ nm Fe}$ (nominal) or reduced SmCo₅ + increased t_s (diffusion)
- ❖ field axis: parallel e.a. or tilted (texture)



11



13



Our researches

- hard magnetic phases of SmCo_5 , SmCo_3Cu_2 , $\text{R}_2\text{Fe}_{14}\text{B}$
- soft magnetic phases of $\alpha\text{-Fe}$, Fe-Co (~20 or 10 wt%)

Magnetic Hard/Soft nanocomposites – Spring magnets

$(\text{SmCo}_5, \text{SmCo}_3\text{Cu}_2, \text{R}_2\text{Fe}_{14}\text{B}) + x\% (\alpha\text{-Fe or Fe}_{65}\text{Co}_{35})$

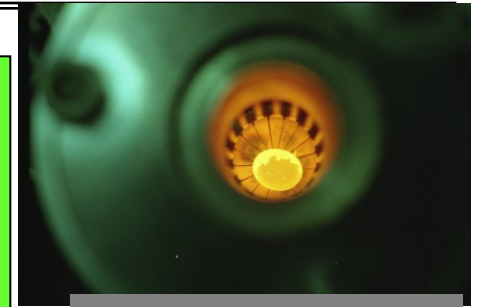
- composition, $x = 10$ or 22 wt % Fe
- milling time
- conventional annealing/short time annealing

Material preparation

- milling of the powders in a high energy planetary mill
- heat treatments (temperatures and duration)

Starting materials :

- **hard magnetic phases**
ingots – prepared by melting
- Fe NC 100.24 powder (Höganäs), ($< 40 \mu\text{m}$) and
- $\text{Fe}_{65}\text{Co}_{35}$ obtained by melting



Fritsch Pulverisette 4



Mechanical milling experiments:

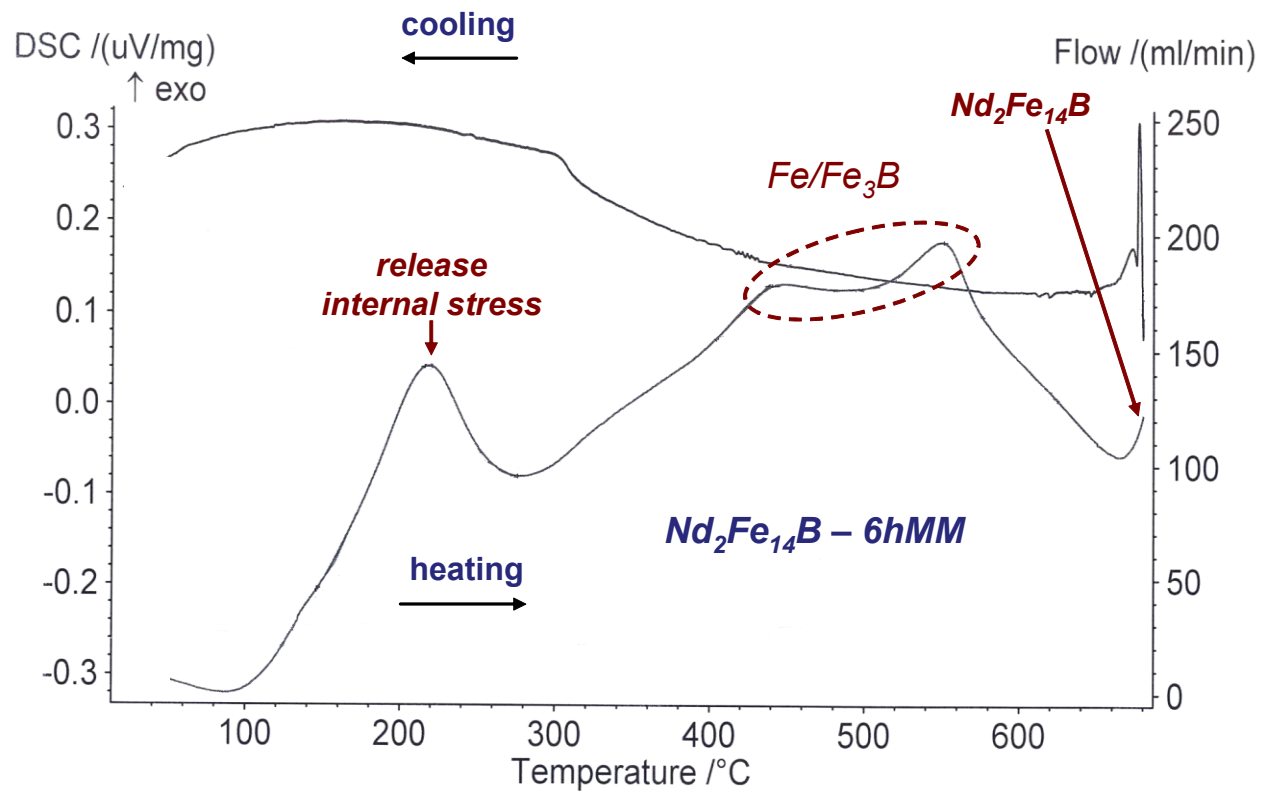
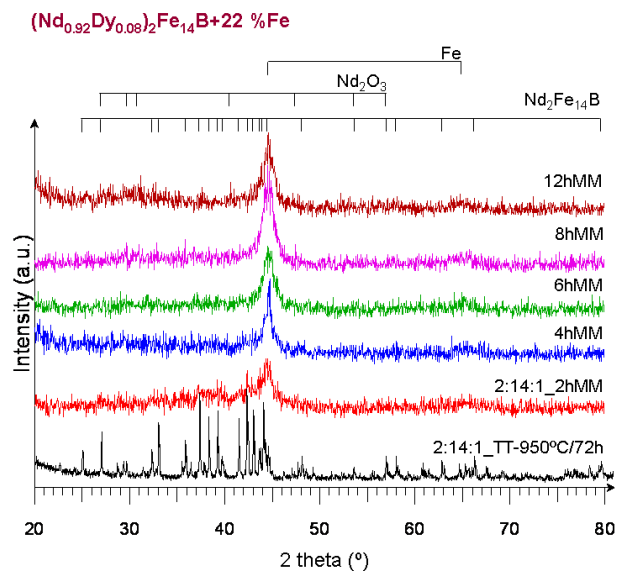
- premilling of hard and soft magnetic ingots
- **hard magnetic** + $\alpha\text{-Fe}$ (or $\text{Fe}_{65}\text{Co}_{35}$) mixed powders – milled in Ar for 1.5 – 12 h

Annealing:

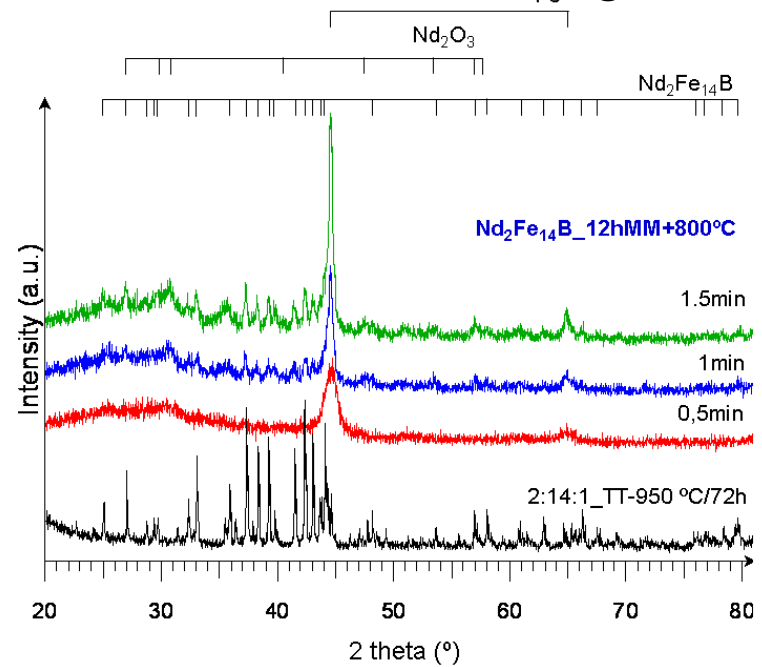
- conventional annealing: in vacuum/ $450\text{--}650^\circ \text{C}$ for 0.5 up to 10 h.
- short time annealing: in argon/ $700, 750$ or 800°C for 0.5 to 3 min.

Material characterisation

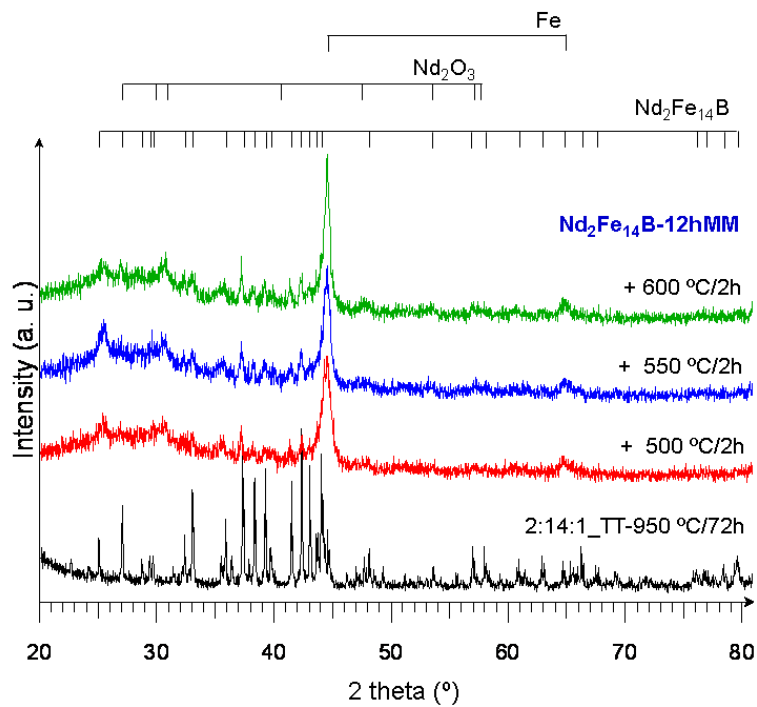
- **X-rays diffraction (XRD)**
- **DSC measurements**
- **Electron microscopy (SEM and TEM)**
 - morphology**
 - chemical composition checked by EDX**
- **Magnetic measurements**
- **Mössbauer spectroscopy**
- **Atom probe tomography (APT)**



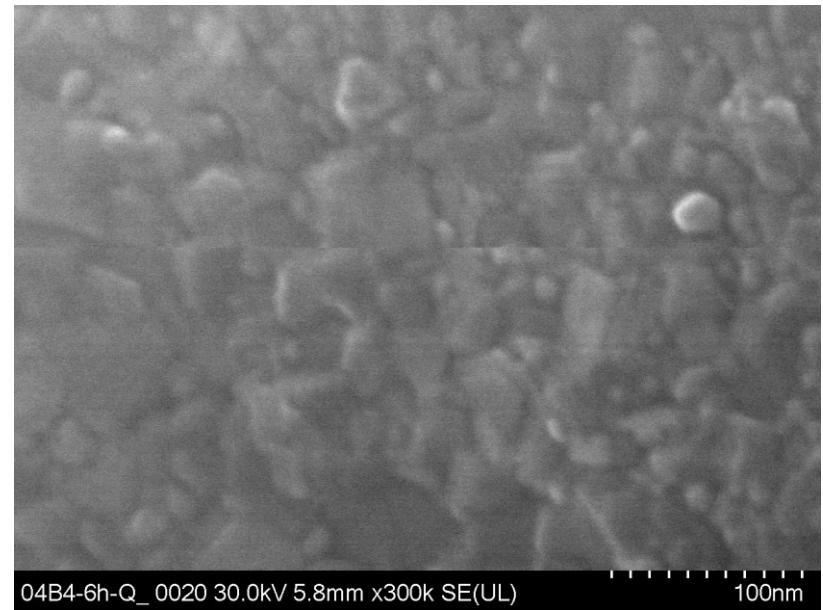
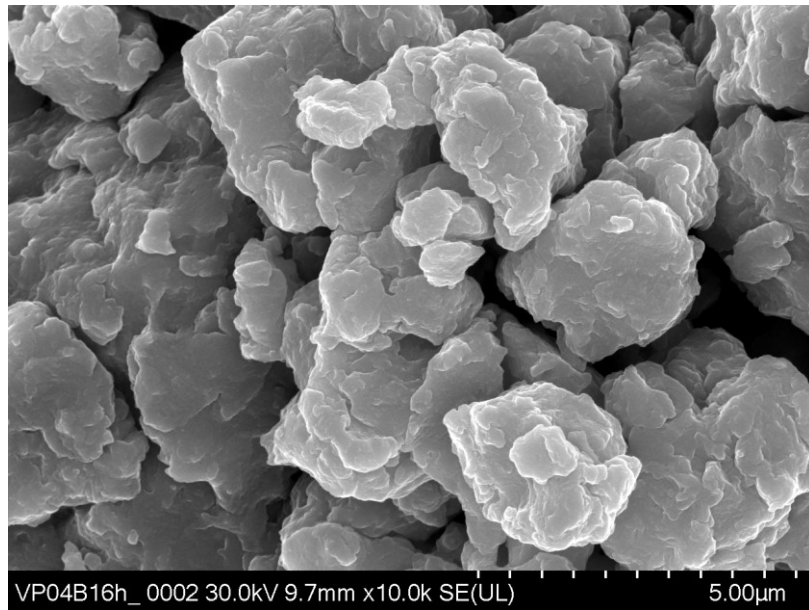
Short time annealing



Classical annealing



Microstructure; Nd₂Fe₁₄B+10 wt% Fe



TEM

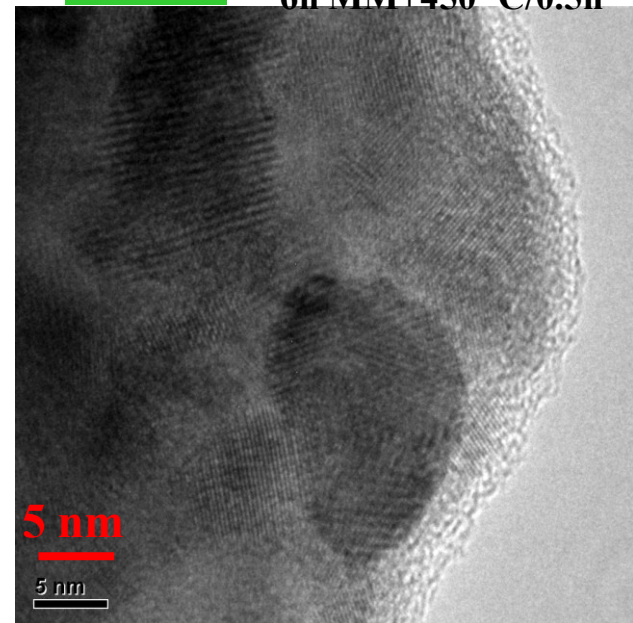
SmCo₅ + 20% α-Fe
6h MM+450 °C/0.5h

From XRD measurements

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta}; \quad \beta \equiv \beta_{1/2} \Rightarrow K = 0.9$$

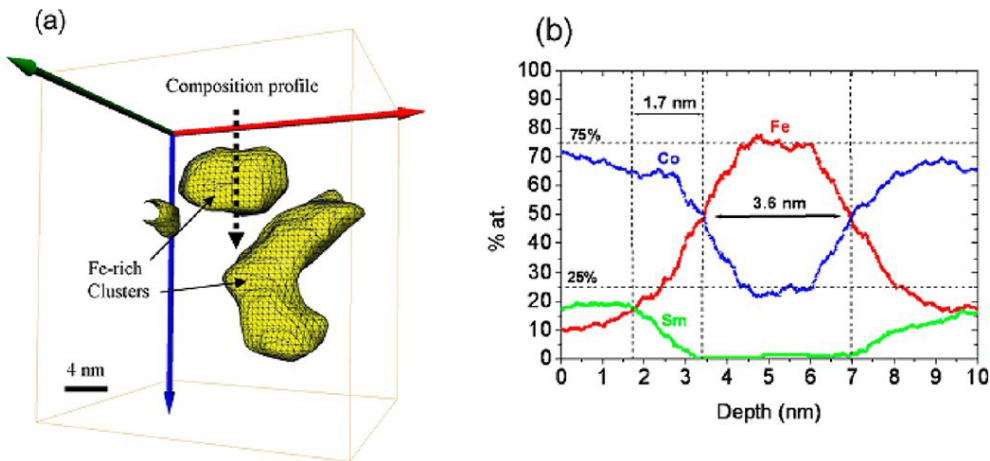


For 6 h or more MM sample D < 30 nm



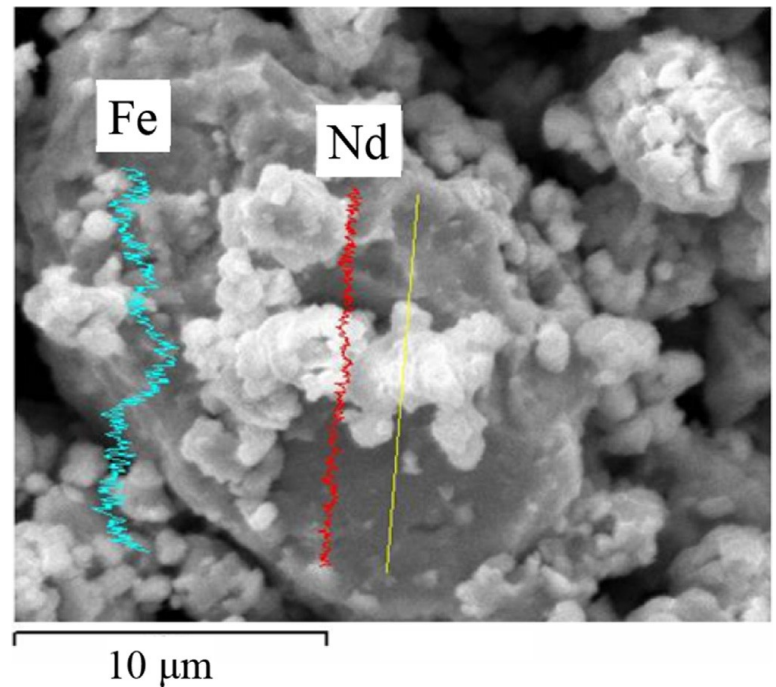
Microstructure/ composition

SmCo₅+20 wt% Fe; Atomic-Scale Investigation



R. Lardé, J-M. Le Breton, A. Maître, D. Ledue, O. Isnard, V. Pop and I. Chicinaş, J. Phys. Chem., 117 (2013) 7801

Nd₂Fe₁₄B+10 wt% Fe



S. Gutoiu, O. Isnard, I. Chicinas, F. Popa, A. Takacs, V. Pop / JALCOM 646 (2015) 859

Mossbauer studies/interphase diffusion

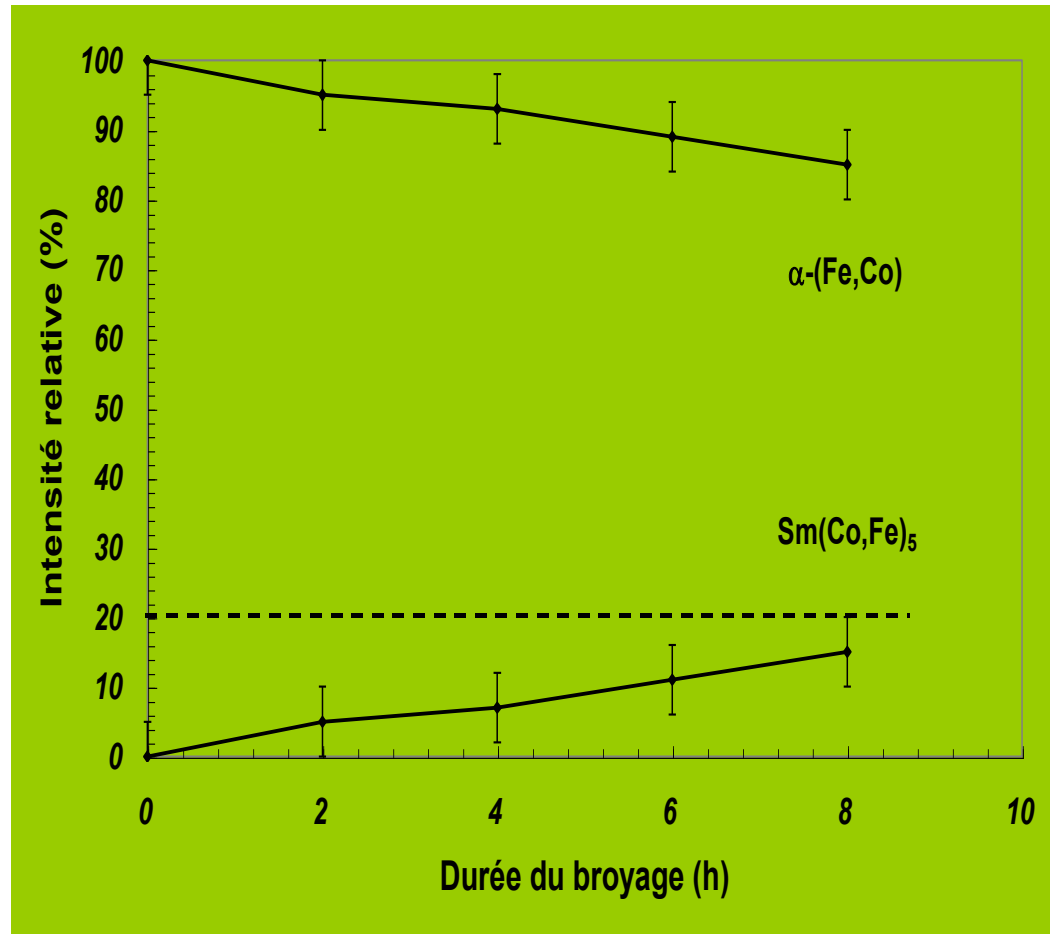
6h-as milled

450° C/0.5 h

450° C/1.5 h

450° C/10 h

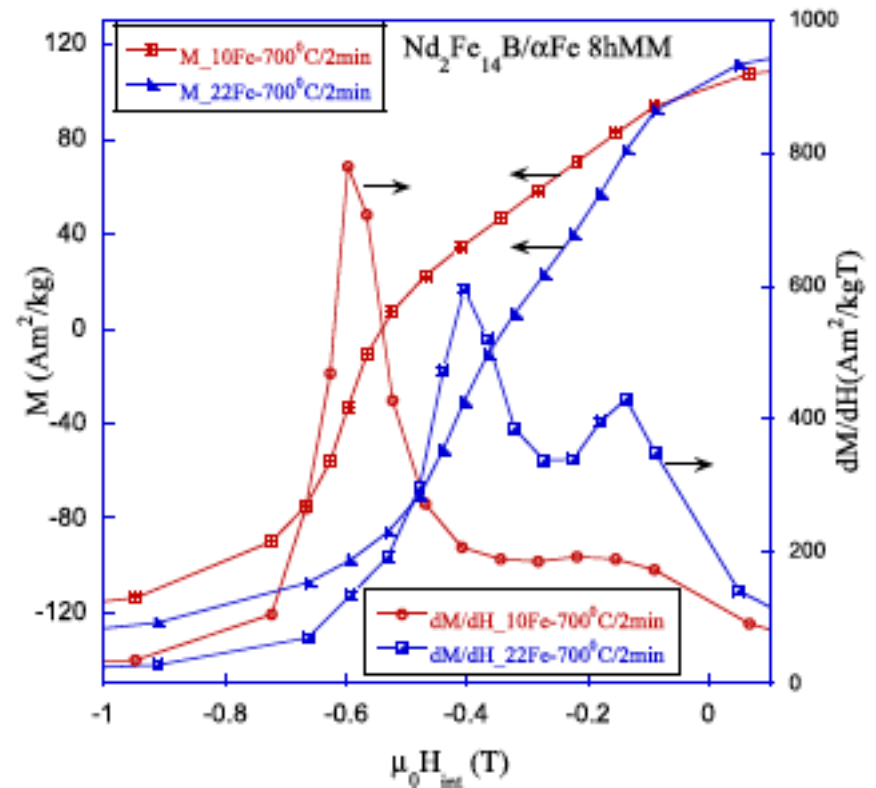
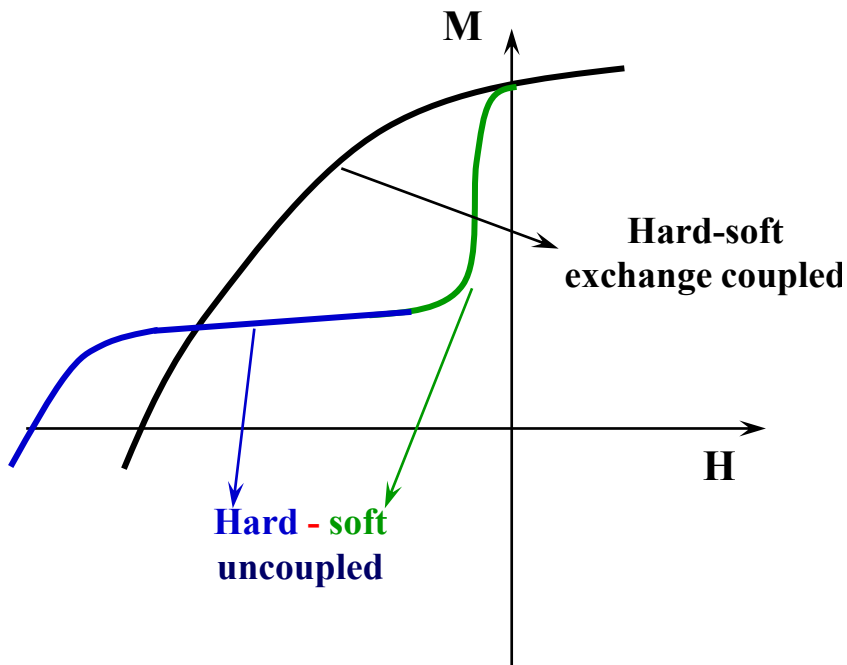
$\text{SmCo}_5 + 20 \text{ wt\% Fe}$

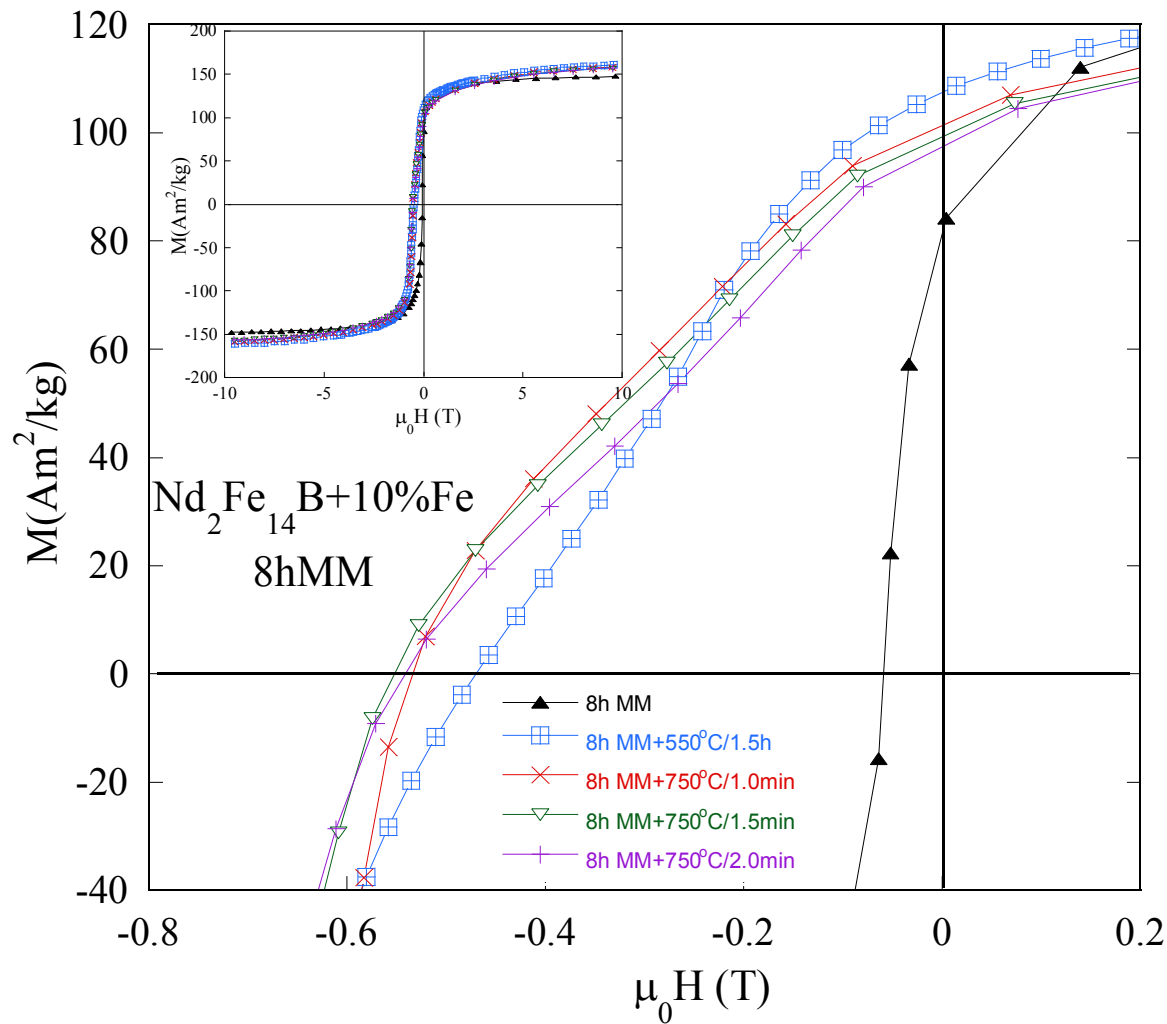


high anisotropy
 +
 large magnetization

← hard phase
 exchange
 → soft phase

Exchange spring magnets





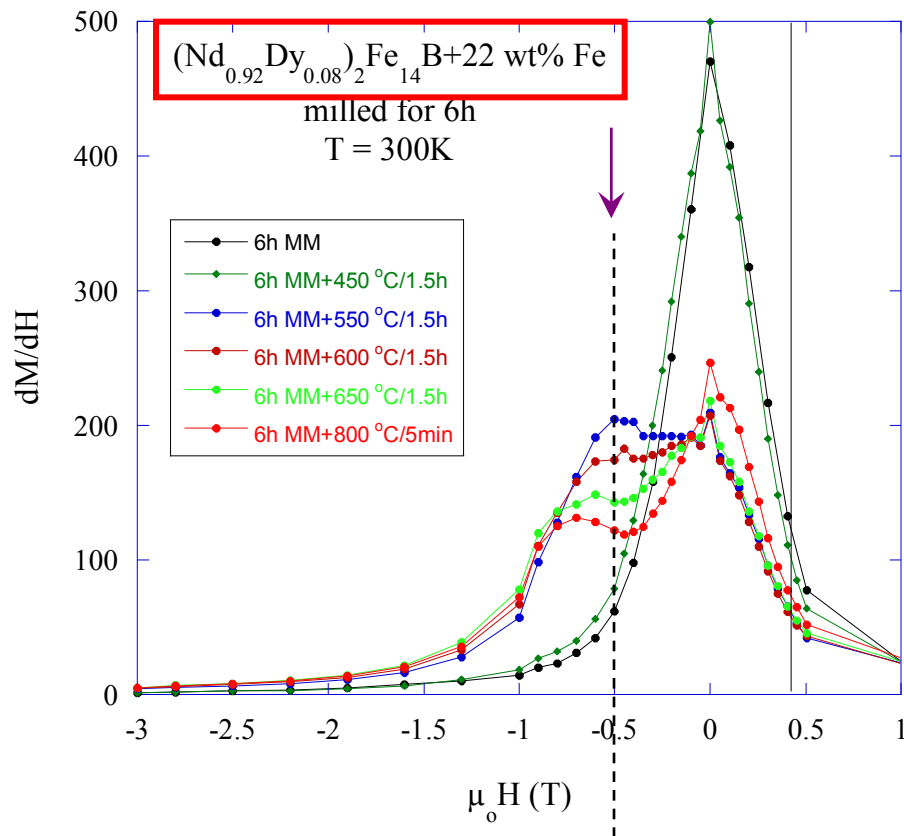
$\text{Nd}_2\text{Fe}_{14}\text{B}$ + 10 % $\alpha\text{-Fe}$; 8h MM

Classical annealing $\longleftrightarrow$ **Short time annealing**

H_c - evident increasing

M_r - small decreasing

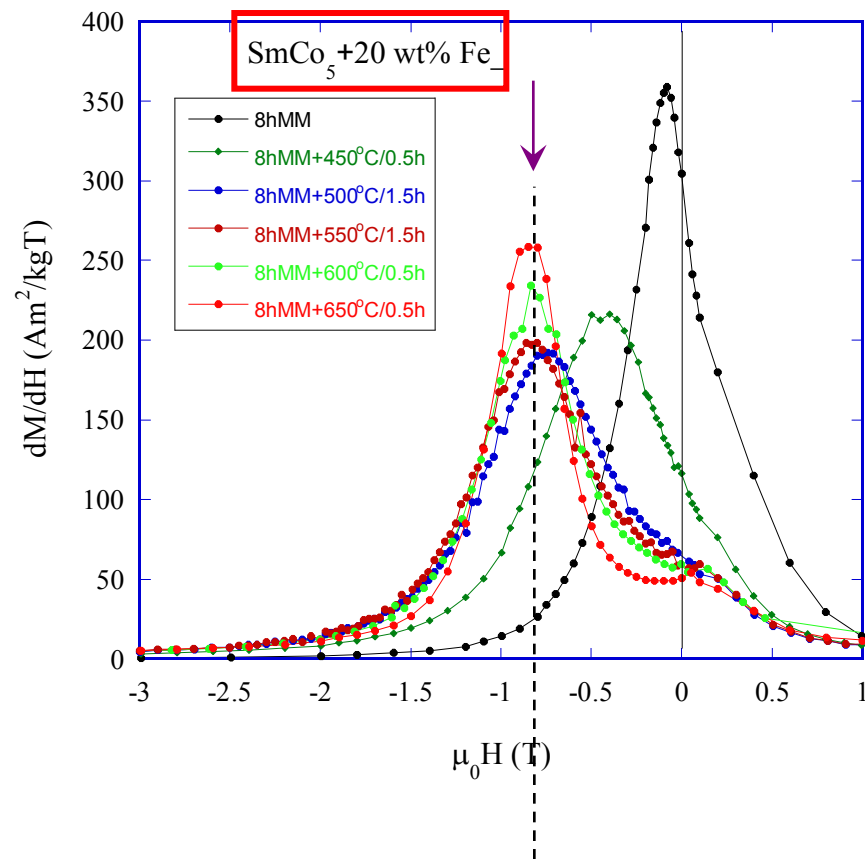
The influence of the type of hard magnetic phase



$\text{R}_2\text{Fe}_{14}\text{B}/\text{Fe}$

Lower coercivity

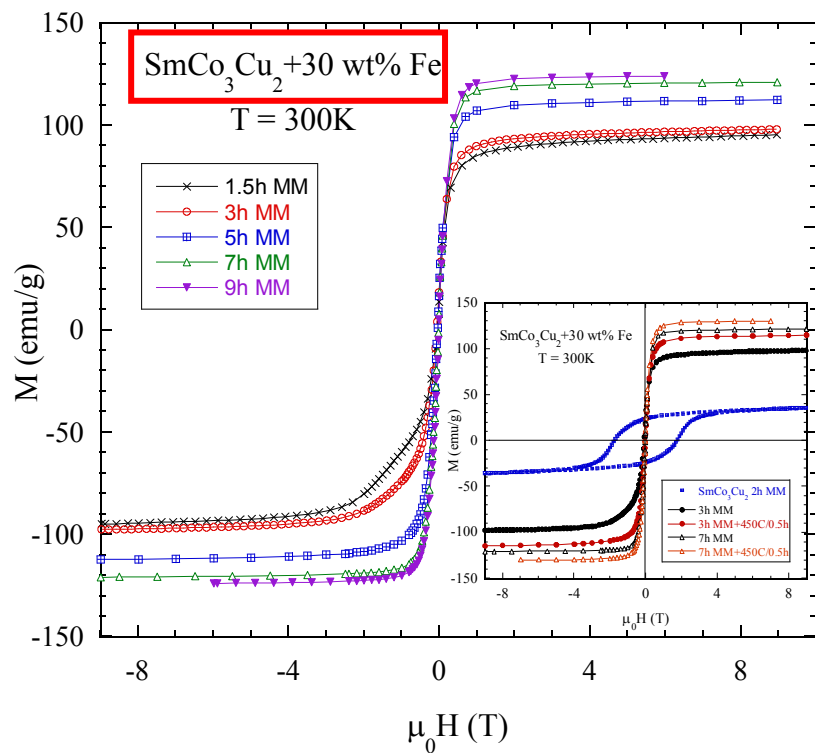
Two peaks,
pour hard/soft magnetic coupling



SmCo_5/Fe

Higher coercivity

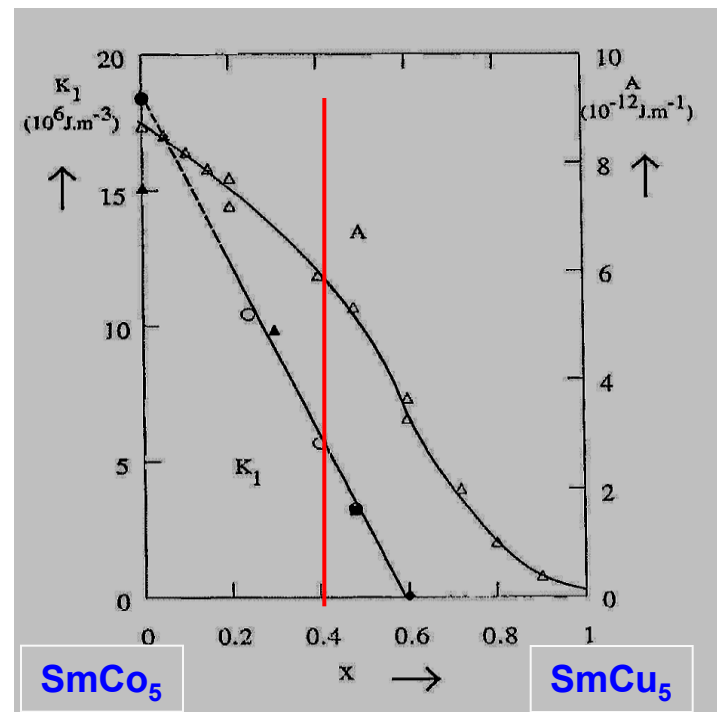
One peak,
good hard/soft magnetic coupling



**the importance of the
intrinsic anisotropy***

*D. Givord, O. Isnard,, V. Pop, I. Chichinas, JMMM 316 (2007)

This behavior was connected with coercivity mechanism of the SmCo₃Cu₂ phase given by the microstructure [1-2] and diminishing of the intrinsic coercivity by Co substitution with Cu [3].

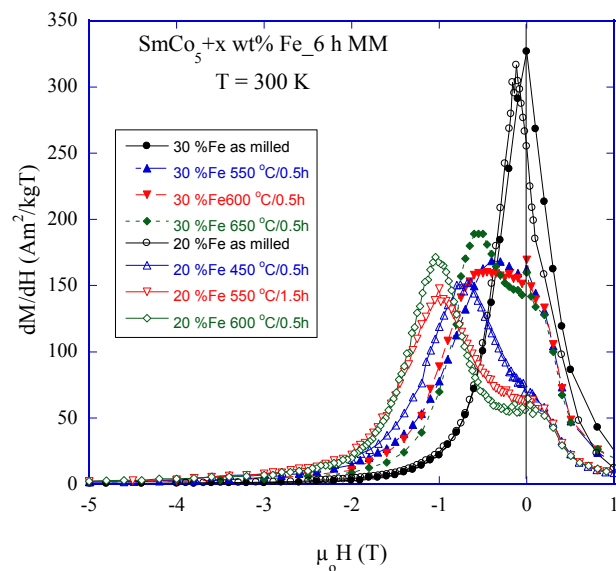
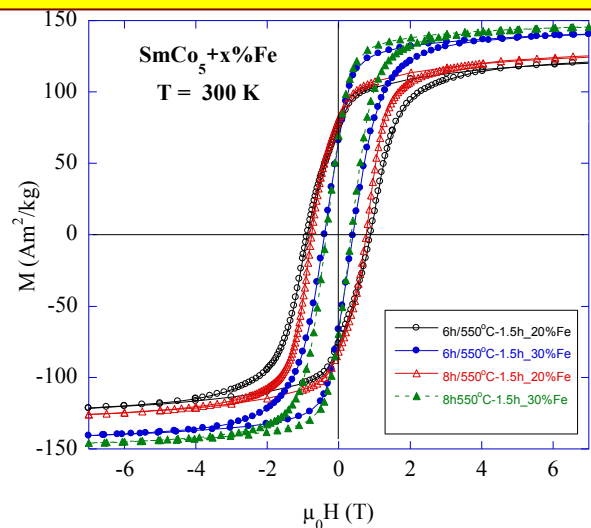


- [1] E. Estevez-Rams, J. Fidler, A. Penton, J.C. Tellez-Blanco, R.S. Turtelli, R. Grossinger, J. Alloys Compounds, 283 (1999) 327.
- [2] P. Kersch, A. Handstein, K. Khlopkov, O. Gutfleisch, D. Eckert, K. Nenkov, J.-C. Tellez-Blanco, R. Grossinger, K.-H. Müller, L. Schultz, J. Magn. Magn. Matter. 290–291 (2005) 420.
- [3] E. Lectard, C.H. Allibert, R. Ballou, J. Appl. Phys. 75 (1994) 6277.

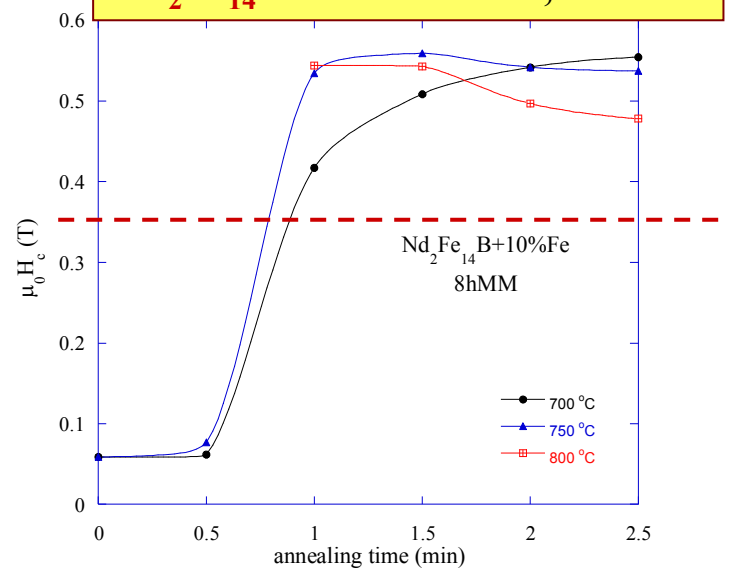
The influence of the hard/soft ratio

SmCo₅+x% Fe (x=20 or 30),

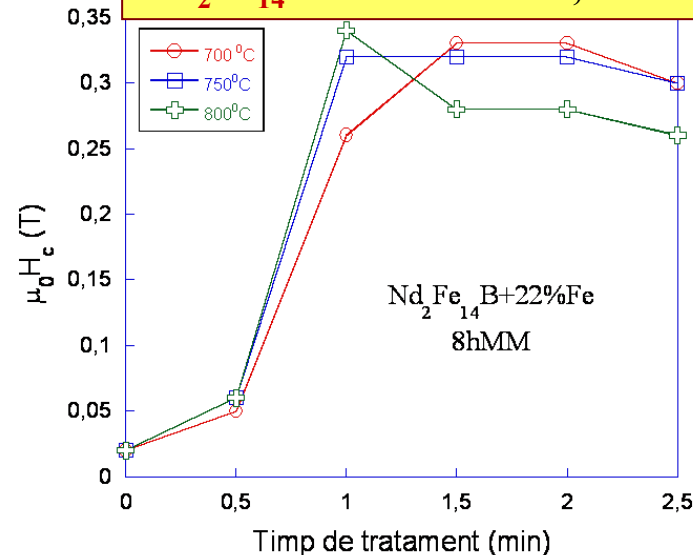
milled 6 and 8 h and annealed at 550° C for 1.5 h*



Nd₂Fe₁₄B + 10 % α-Fe; 8h MM



Nd₂Fe₁₄B + 22 % α-Fe; 8h MM

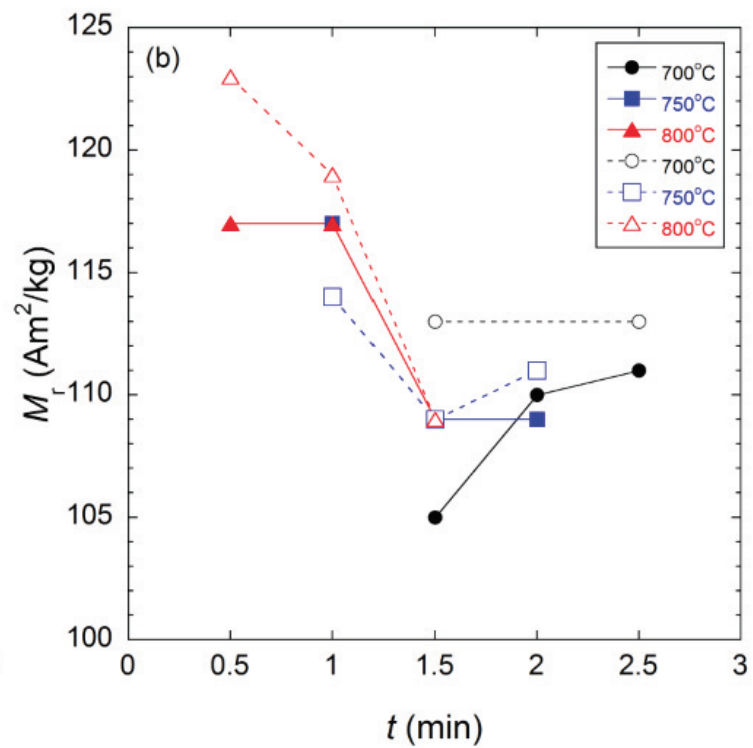
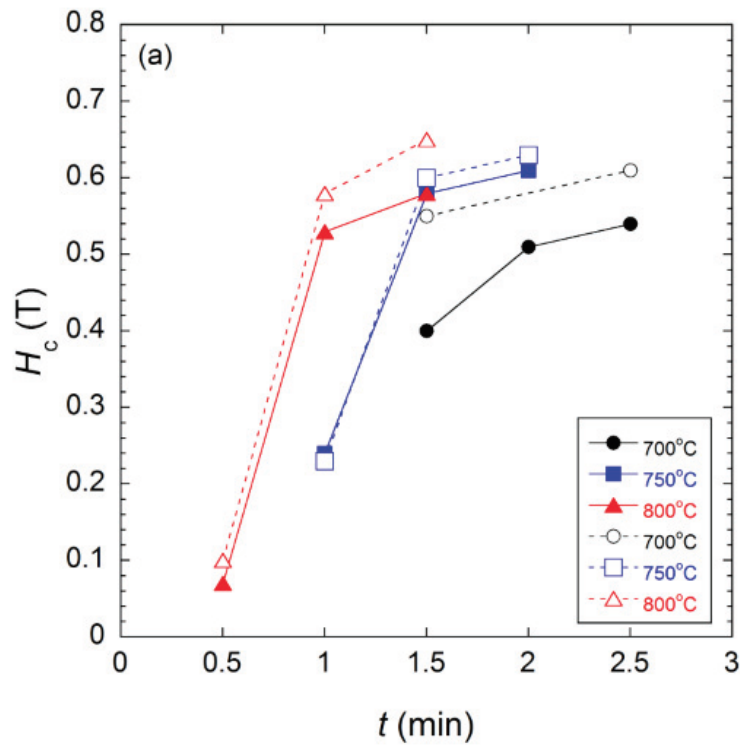


*V. Pop, O. Isnard, D. Givord, I. Chicinas, JMMM 310 (2007) 2489

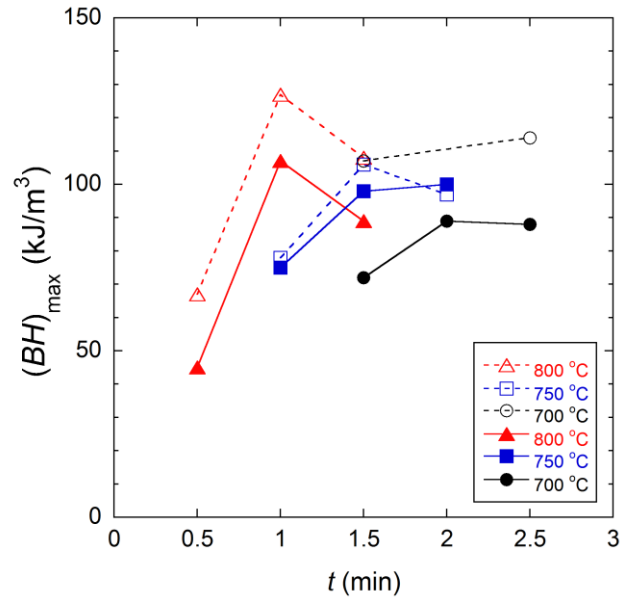
V. Pop, O. Isnard, D. Givord, I. Chicinas, J. M. Le Breton, JOAM 8 (2006) 494

V. Pop et al., J. Alloys Compd. (2011)

V. Pop et al. , J. Alloys Compd. 581 (2013) 821–827



$\text{Nd}_2\text{Fe}_{14}\text{B}+10 \text{ wt\% Fe}$: milled with $\varnothing = 10 \text{ mm}$ (filled symbols) and $\varnothing = 15 \text{ mm}$ (empty symbols) balls.



S.Mican, R. Hirian, O. Isnard, I. Chicinaș,
V. Pop, Physics Procedia 75 (2015) 1314

Conclusions

- **MnBi LTP**: large coercivity at high temperature $\Rightarrow$ a good candidate for performance spring magnets
- **MnAl**: stabilisation of τ with conservation of Mn moments
- The *structure and microstructure* $\Rightarrow$ strong impact on hard/soft exchange hardness.
- **Intrinsic anisotropy** $\Rightarrow$ the **strength** of the interphase exchange coupling
- *Annealing* linked to the *recrystallisation temperature* of soft phases and hard magnetic phases; *recover* the crystallinity of the hard phase and *hinder the increase* of Fe crystallites.
- For *higher α -Fe concentration* the magnetic properties are poorer because non correlation with Fe size crystallites.
- The *short time annealing* is more appropriate for higher coercivity of the nanocomposites.
- The **geometry and energy of milling** influence the microstructure and the interphase exchange coupling

Prof.dr. Viorel POP

Prof.dr. Marin Coldea **intermetallic compounds**

Dr. Diana Benea **band structure calculation**

Lector dr. Sever Mican **magnetic materials/thin layers**

Dr. Albert Takacs **magnetic thin layers**

Drd. Razvan Hirian **spring magnets**

Drd. Radu Gavrea **Mn-Al and Heusler compounds**

Stud. Roxana One **Fe₁₆N₂, chemical methods**

Stud. Georgiana Taran **Mn-Al compounds**

Stud. Akos Ferenczi **SPS spring magnets**

Thank you for your attention

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