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Magnets as enablers for renewable energy and resource efficiency

Oliver Gutfleisch

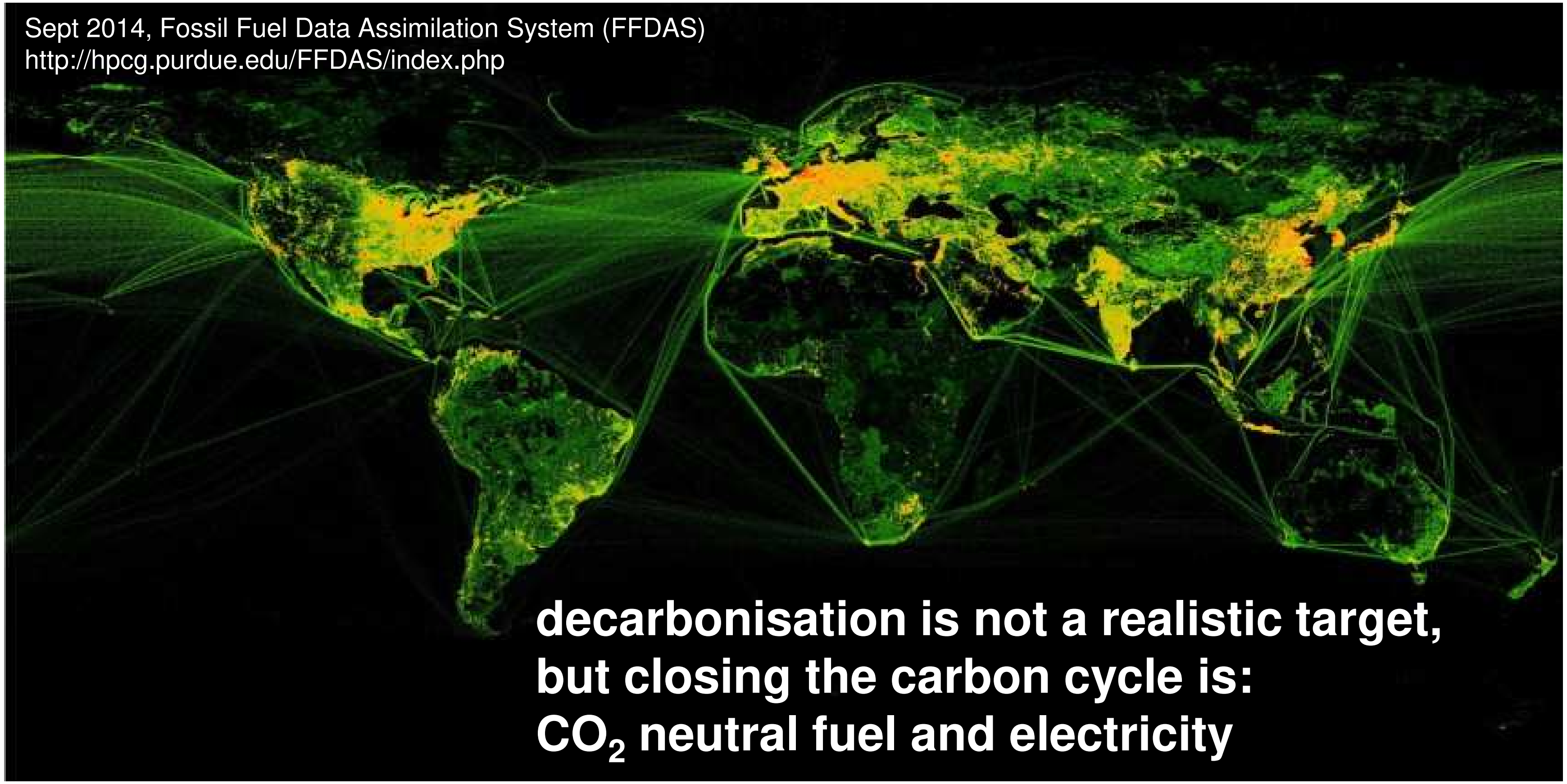
TU Darmstadt, Material Science, Functional Materials

Fraunhofer Project Group for Materials Recycling and Resource Strategy IWKS Hanau, Germany

Our research

- new permanent magnets for power applications
  (HREEs reduced/free → using free REEs → REE free)
- solid state energy efficient cooling (H-, p-, σ-caloric)
- ferromagnetic shape memory alloys,
  magnetic nanoparticles for biomedical applications
- tailoring structural and chemical properties on the nanoscale
- development of advanced processing routes
  (e.g. net-shaping or SPD combined with field-assisted processing)
- advanced characterisation
  (in-situ MFM in high H and wide T; HRTEM at high T, atomprobe)
- additive manufacturing of magnets → local functionalities
- modelling across all length scales
- substitution and resource efficiency on element, process and product levels
- recycling of rare earth containing materials
- general concepts of materials criticality

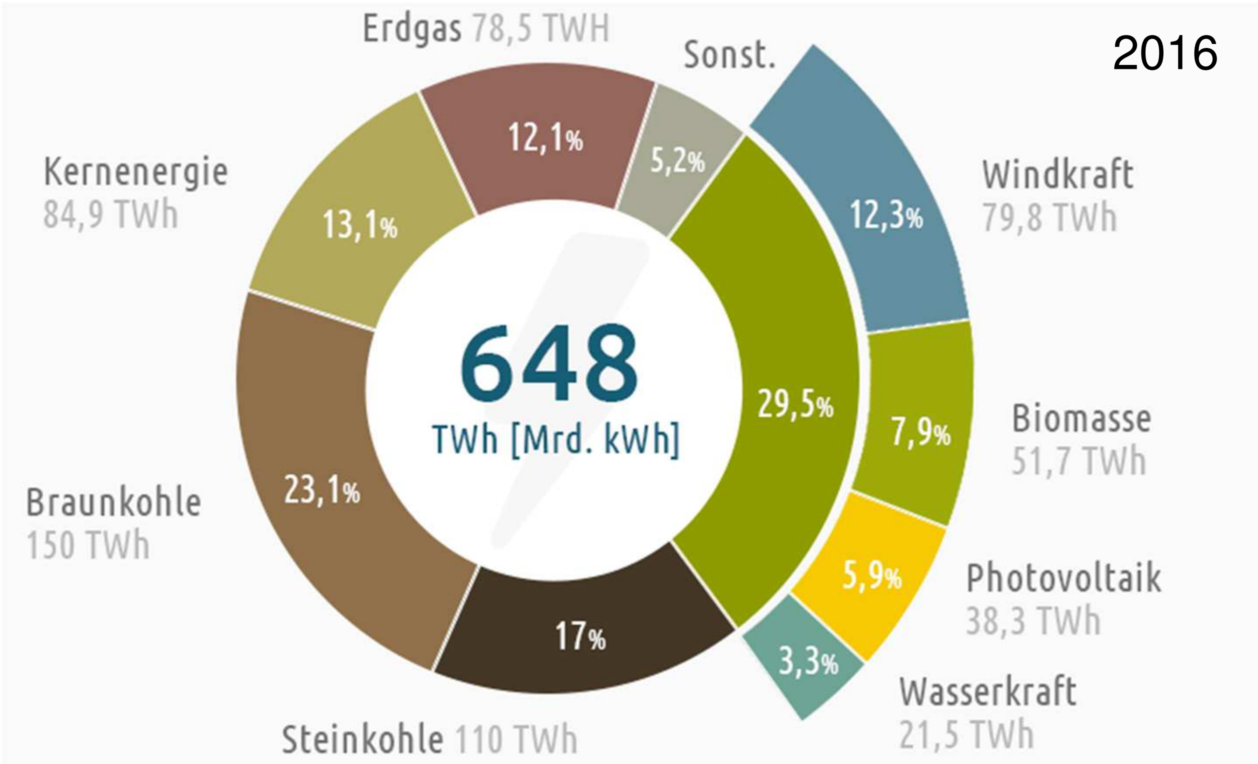
Distribution of CO_2 emission



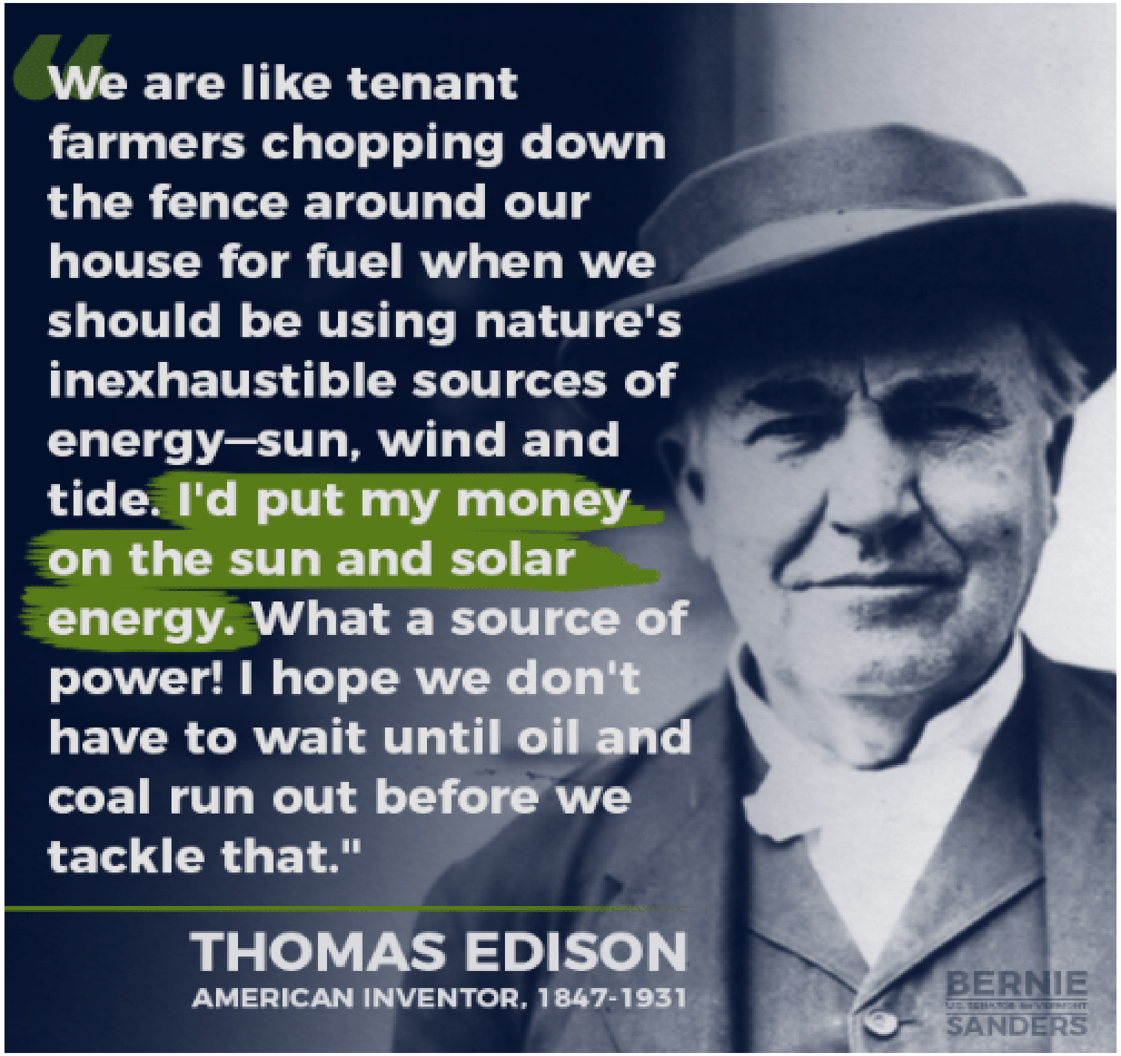
Global Carbon Project:

Total 2013 – 36 Billion tonnes	(28 % China, 14% USA, 10%EU, 7% India)
increase every year 2.5%	(2.0t/person, 4.5t/person, 1.9t/person, 0.5t/person)

Electricity distribution in Germany



Source: www.strom-report.de


"We are like tenant farmers chopping down the fence around our house for fuel when we should be using nature's inexhaustible sources of energy—sun, wind and tide. I'd put my money on the sun and solar energy. What a source of power! I hope we don't have to wait until oil and coal run out before we tackle that."
THOMAS EDISON
AMERICAN INVENTOR, 1847-1931
BERNIE
SANDERS

Rapid deployment of strategic metals in emerging technologies

- electronic and solar energy applications (gallium, germanium, selenium, indium, and tellurium)
- alloying elements in high-temperature applications (cobalt, hafnium, and rhenium)
- several rare earth elements (praseodymium, neodymium, terbium, dysprosium, and lutetium) important in offshore wind, e-mobility, lighting, and medical imaging
- Using the technosphere




https://en.wikipedia.org/wiki/cobalt/gallium/rhenium/Lutetium

Extraction of strategic metals

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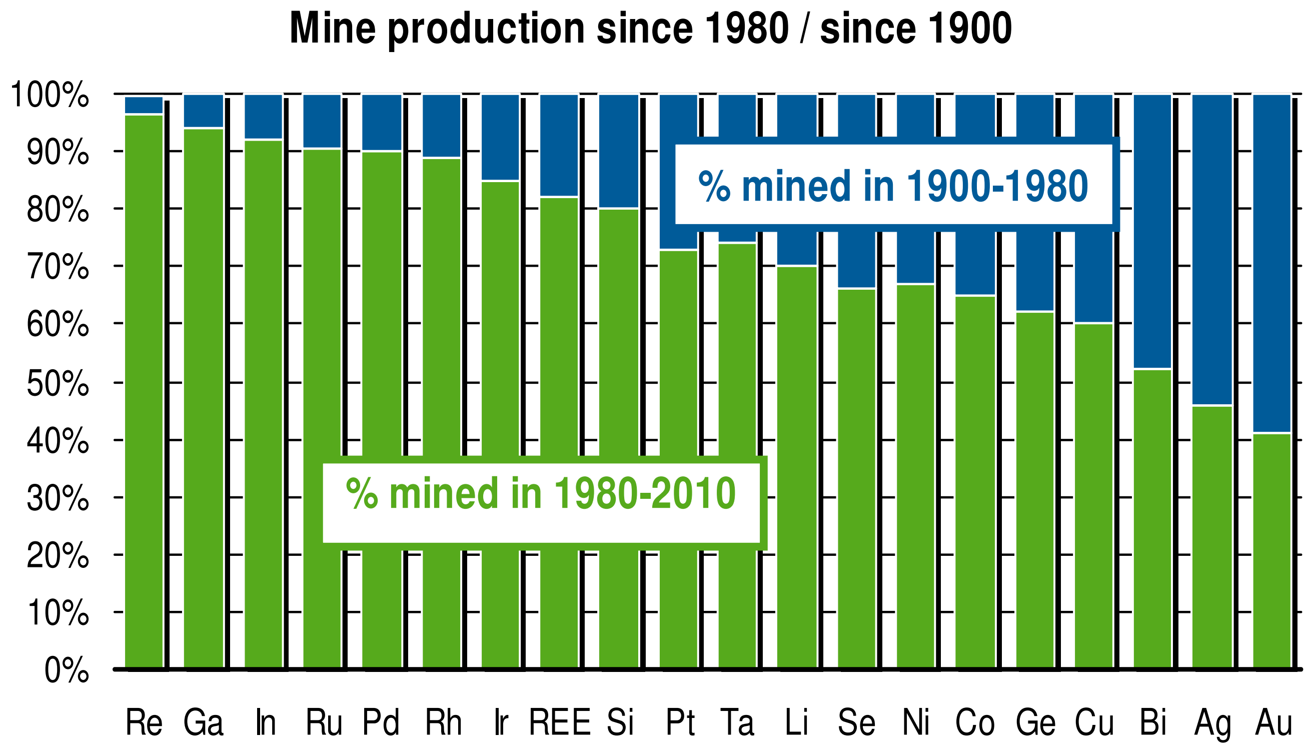
> 80% of the extraction of rare earths, PGM, Gallium, Indium, Rhenium … took place in the last 30 years



The great transformation to a sustainable, low carbon energy sector

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nature International weekly journal of science

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Archive > Volume 538 > Issue 7623 > Comment > Article

NATURE | COMMENT

Renewables need a grand-challenge strategy

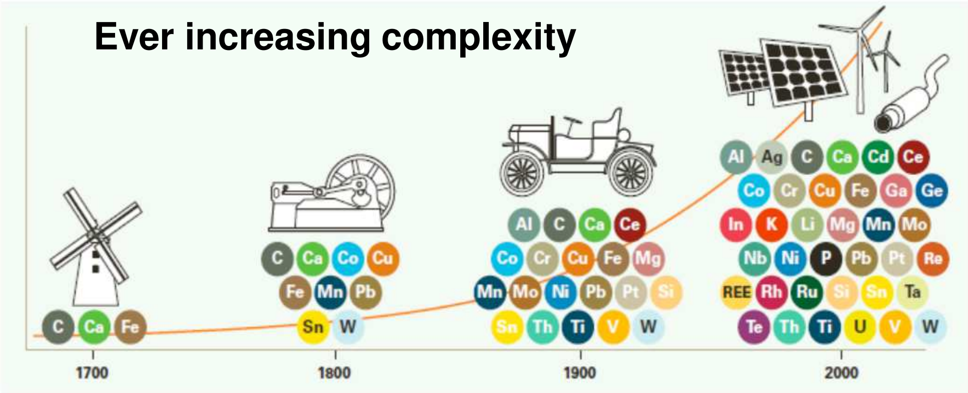
Alan Bernstein, Edward H. Sargent, Alán Aspuru-Guzik, Richard Cogdell, Graham R. Fleming, Rienk Van Grondelle & Mario Molina

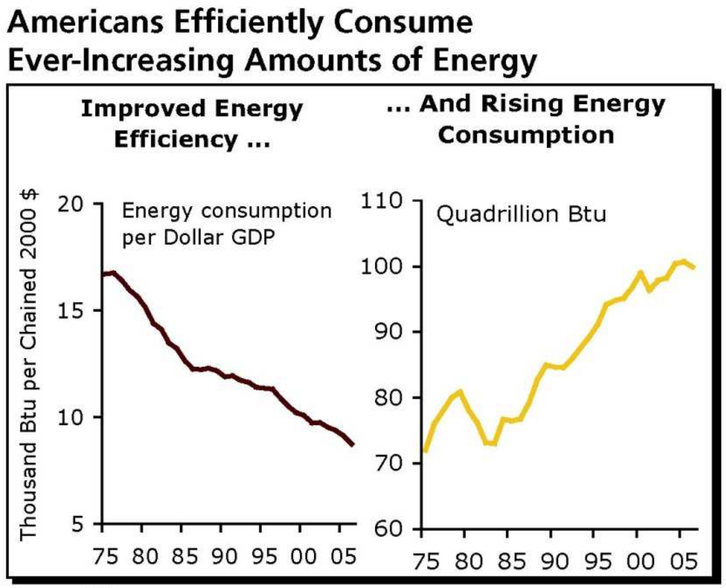
05 October 2016

- The challenge is to produce large- and small-scale energy storage and conversion systems that are scalable, inexpensive, flexible and easy to disseminate.
- Utilisation of earth-abundant materials for batteries, electrolytes, catalysts, fuel cells, sensors, actuators, motors and generators.
- Any system must be safe and sustainable, competitive and compatible with energy generation and distribution systems.
- Public policies to encourage the development of disruptive innovations to displace existing technologies.

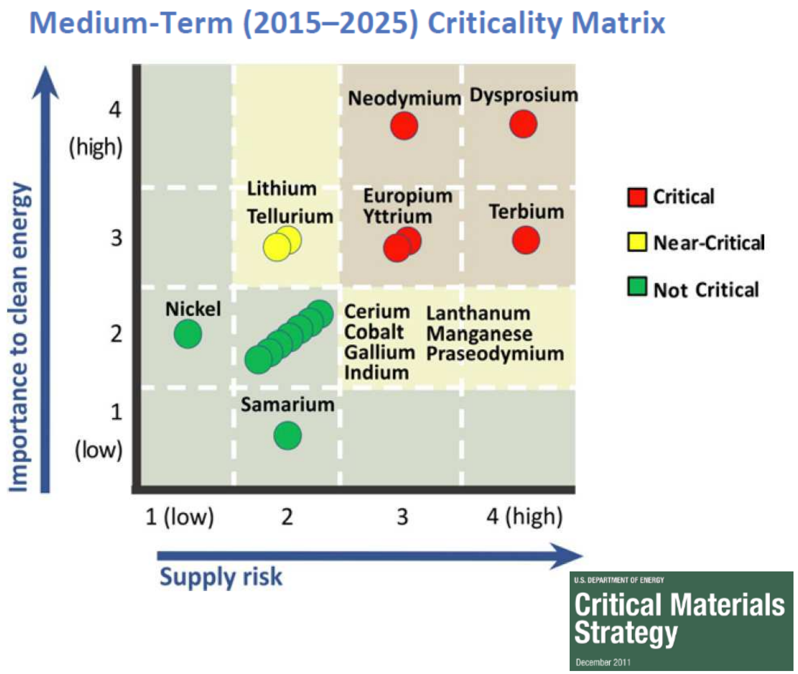
Critical materials and supply

© Fraunhofer IWKS

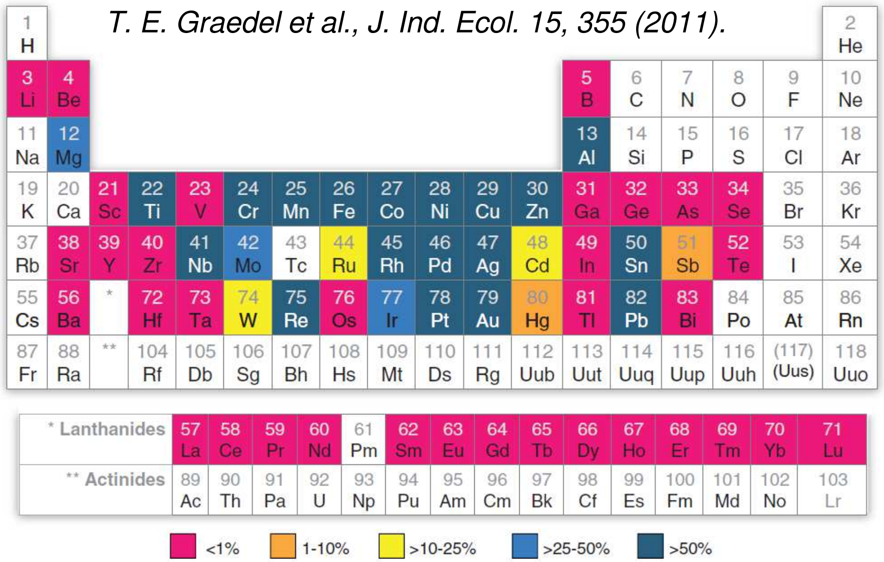




Source: EIA



T. E. Graedel et al., J. Ind. Ecol. 15, 355 (2011).



Contents

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- Material criticality in green technology
  - Finiteness of metals and resource strategy
- Rational design of novel magnetic materials
  - Reduction - Recycling - Substitution
  - Permanent magnets for E-mobility and wind turbines
  - Phase change materials for magnetic refrigeration and thermomagnetic power generation
- Efficient utilisation and substitution on different levels

Factors for criticality of metals

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Geological Availability

(Range, Reliance on by-product production)

Technical Development

(Need for Raw Materials, Primary Production, competing technologies)

Geopolitical Factors of Influence

Ecological Consequences

(Extraction, Application Disposal)

Economical Development

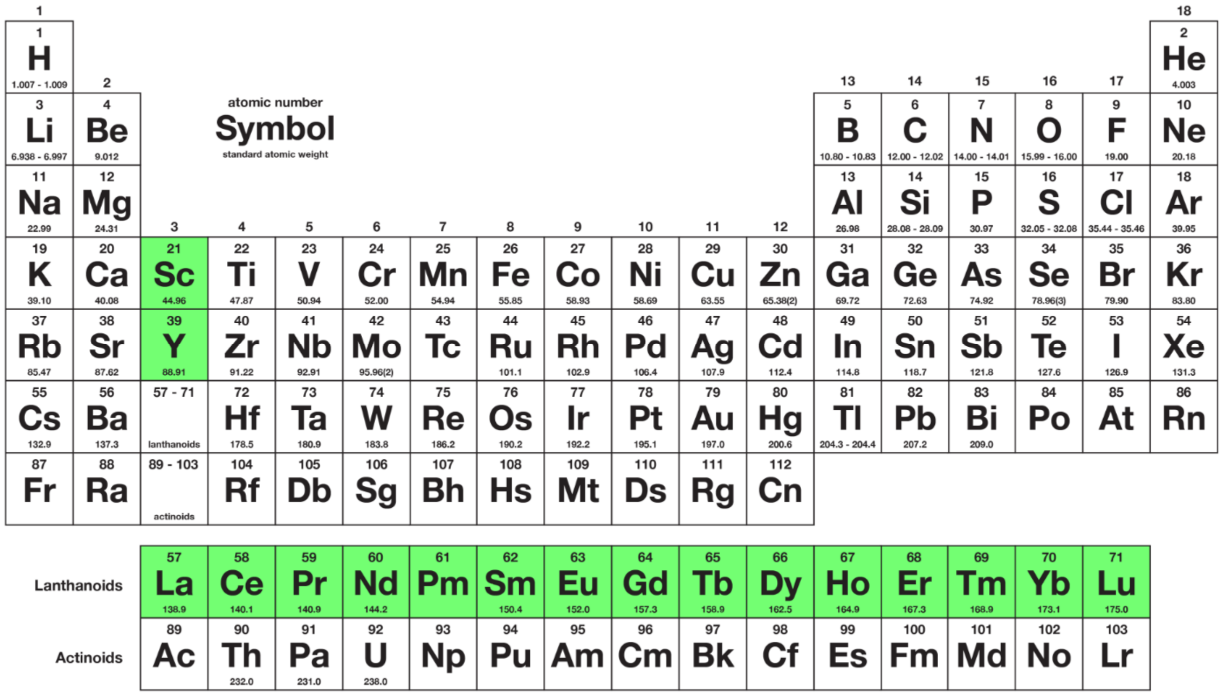
(Pricing, Offering, Demand)

Substitution, Recycling possible?

(possibly reduced cost and performance vs sustainability)

Criticality is dynamic !

Which are the 17 rare earths?



- Light and heavy rare earths
- lighter RE are more incompatible (as they have larger ionic radii) and therefore more strongly concentrated in the continental crust than the heavier RE
- RE with even atomic numbers (58Ce, 60Nd, …) have terrestrial abundances than adjacent RE with odd atomic numbers (57La, 59Pr, …)

Abundance of elements in the Earth crust per million of Si atoms

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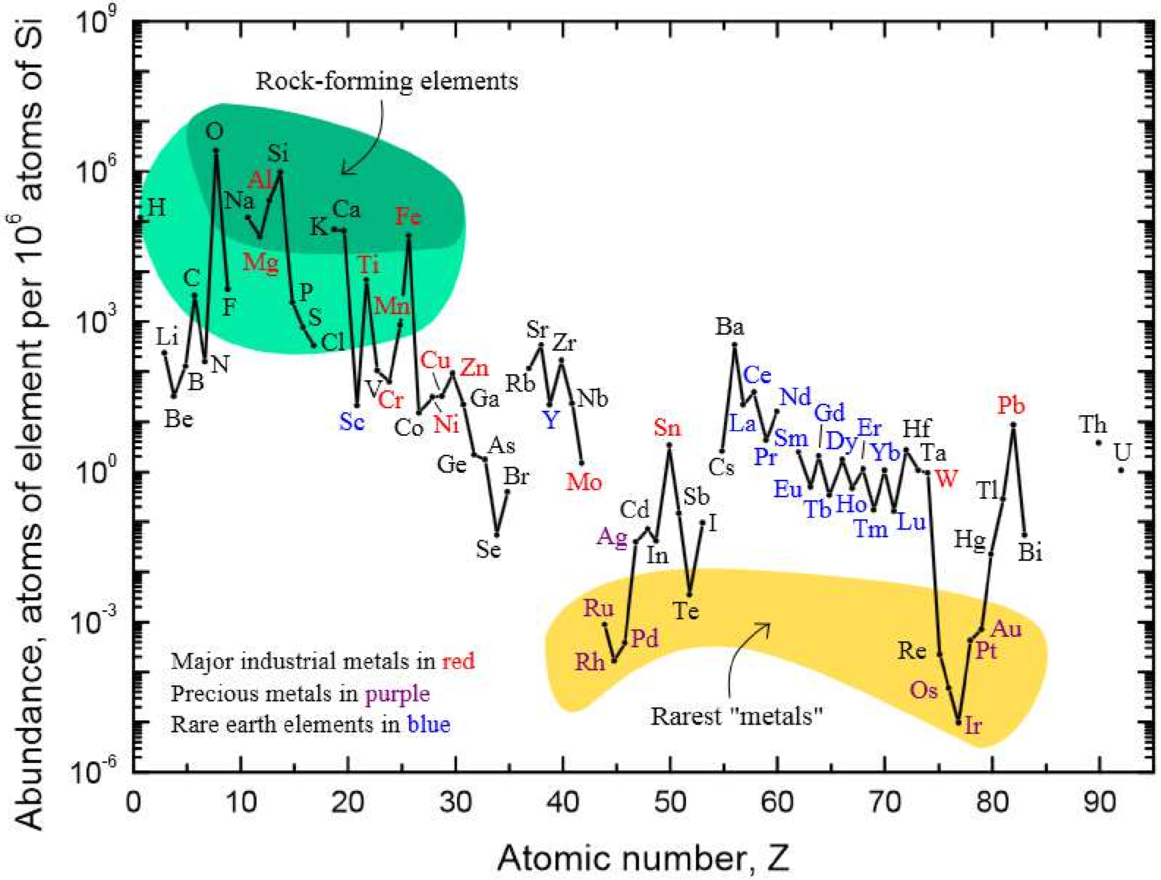


Abundance of the chemical elements in Earth's upper continental crust

(1) Rock-forming elements (major elements in green field and minor elements in light green field);
(2) Rare earth elements (lanthanides, La–Lu, and Y; labeled in blue);
(3) Major industrial metals (global production >~3×10^7 kg/year; labeled in red);
(4) Precious metals (purple);
(5) The nine rarest "metals"—the six platinum group elements plus Au, Re, and Te (a metalloid).

US Geological Survey

The periodic table of companionality

Nassar, Graedel, Harper Sci. Adv. 2015;1:e1400180 3 April 2015

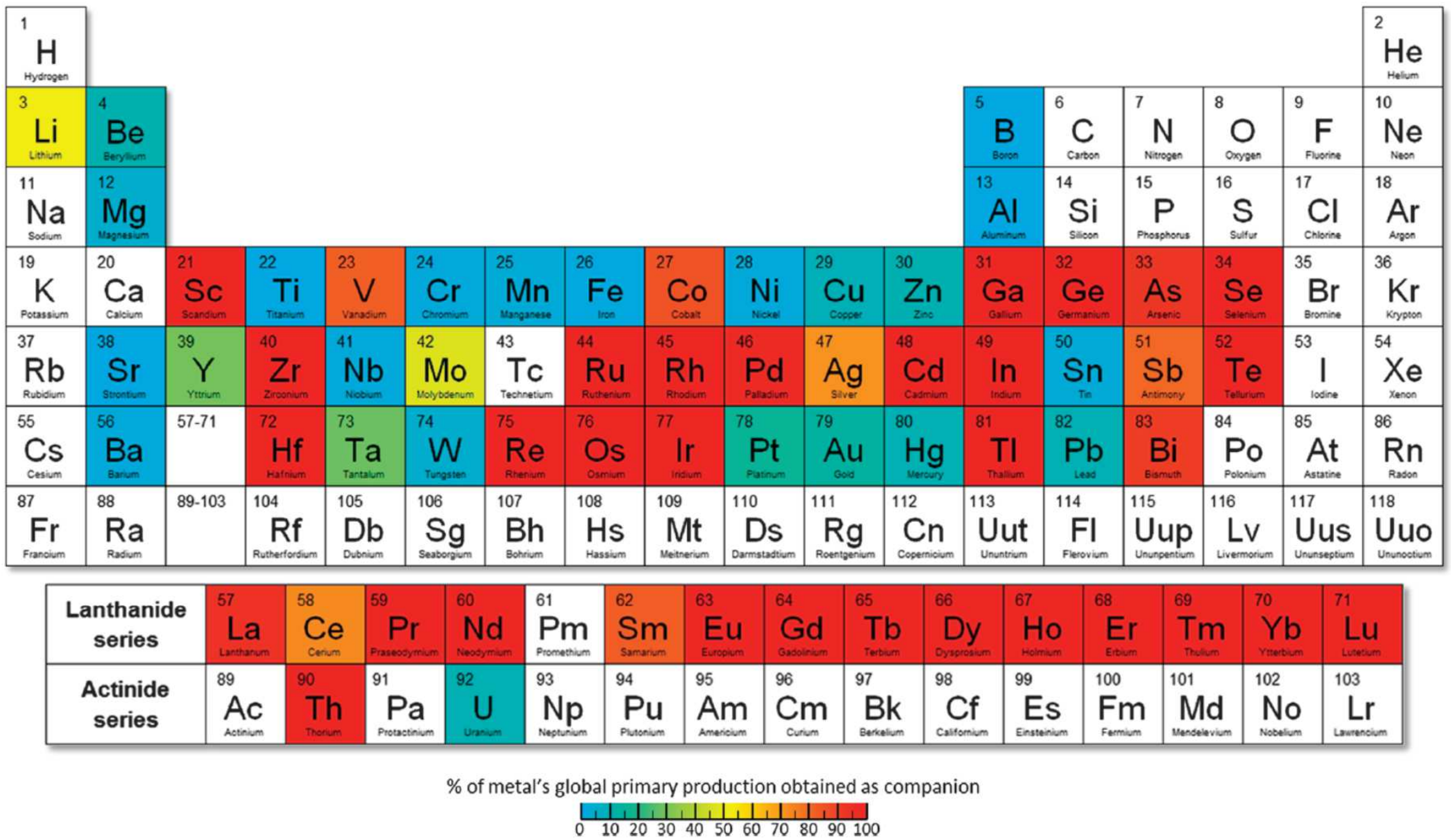
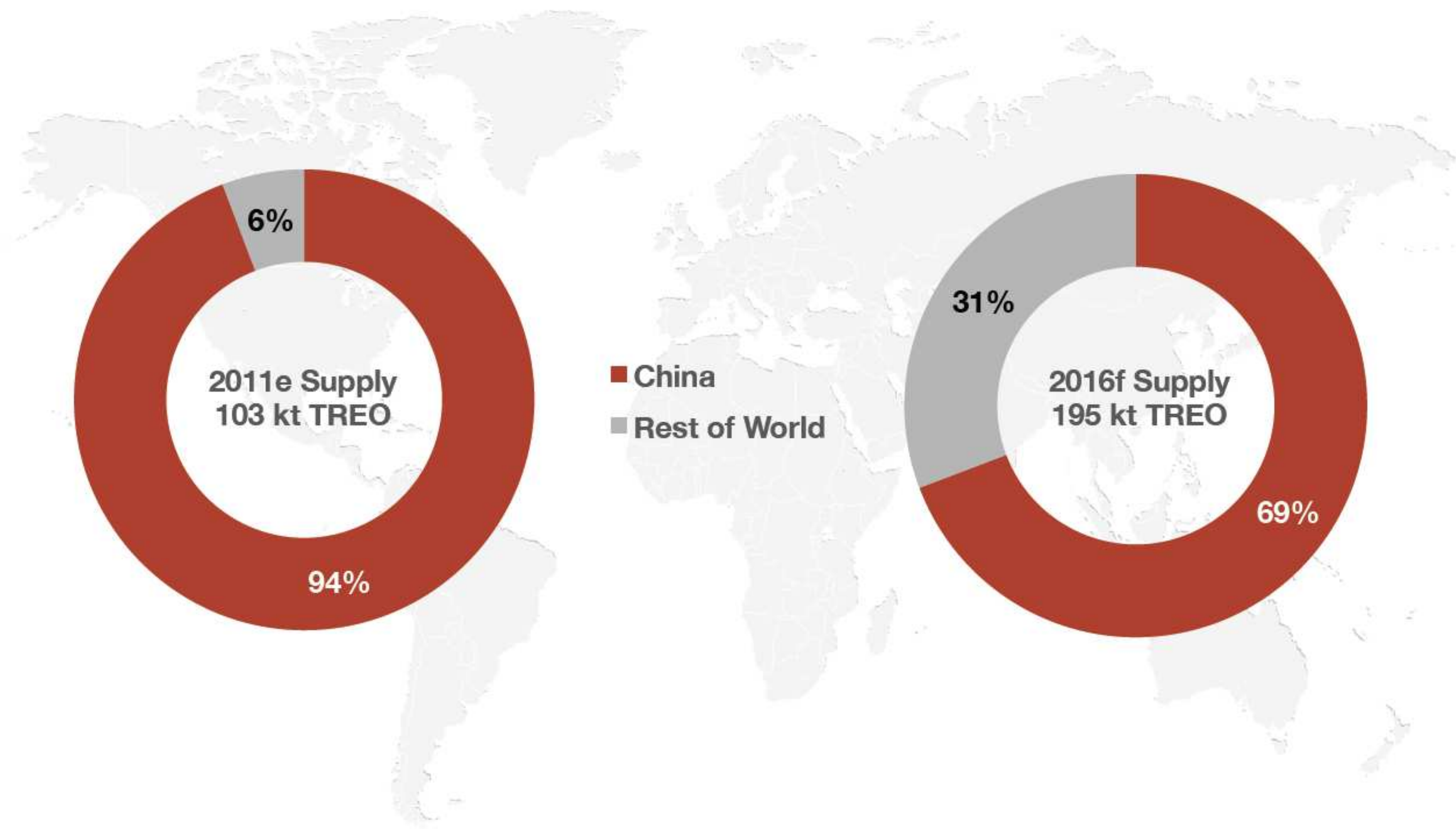


Fig. 1. The periodic table of companionality on a global basis for 2008. Metals that are mainly produced as hosts appear in blue, and those that are mainly produced as companions are in red. Details regarding data sources and assumptions are presented in the Supplementary Materials.

General Context of the Rare-Earth Market

supply, criticality and markets

From where does the supply for REs originate?



Sources: IMCOA, Chinese State Council Information Office, Technology Metals Research

Rare earth market and production

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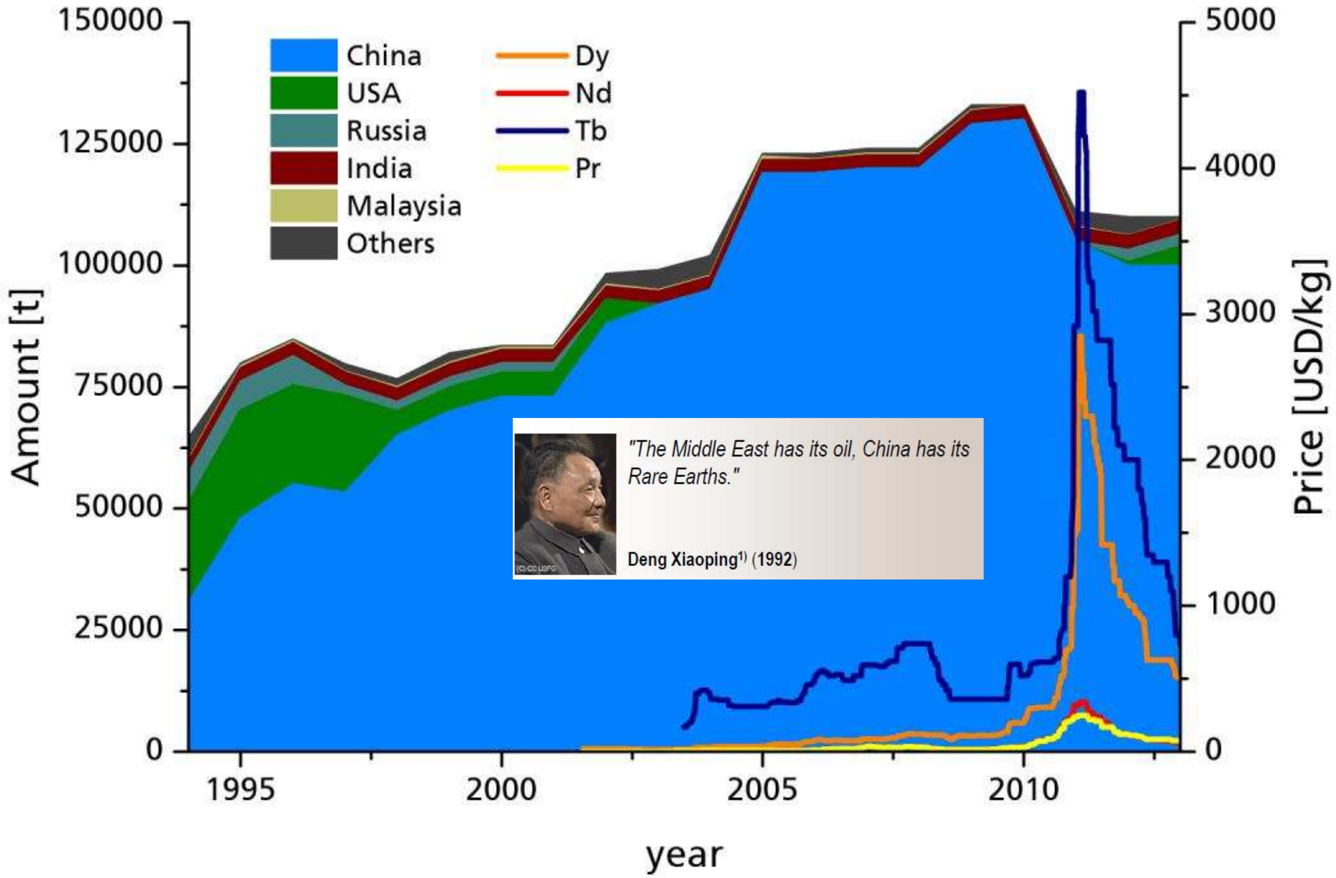

K.-H. Müller, S. Sawatzki, R. Gauss and O. Gutfleisch, Permanent magnetism, in Springer Handbook of Magnetism, ed. by J.M.C. Coey and S. Parkin, in preparation.

Rare earth crisis

was not only predictable, it was also preventable

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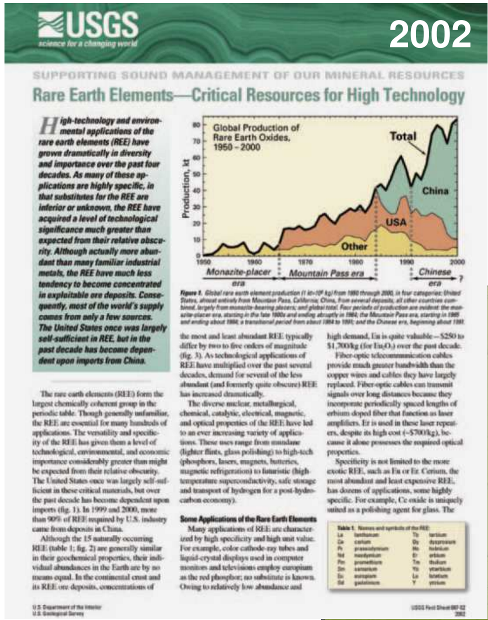
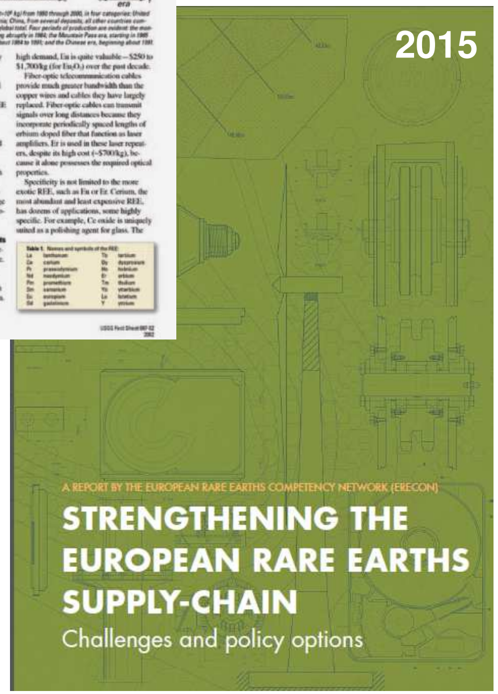
- The USGS estimates proven reserves of REEs at 800 times of current demand.
- The technologies for mining, beneficiation and separation of REE are available outside China.
- With an adequate, one-off investment, REE supply could have been diversified and supply security been guaranteed.
- A single REE mine is likely to meet all of Europe's current rare earth requirements, and a handful of mines could meet the world's demand outside of China.





*REPORT BY THE EUROPEAN RARE EARTHS COMPETENCY NETWORK (**ERECON**), 2015*

World REE supply and demand forecasts to 2020

REPORT ON CRITICAL RAW MATERIALS FOR THE EU CRITICAL RAW MATERIALS PROFILES, May 2014

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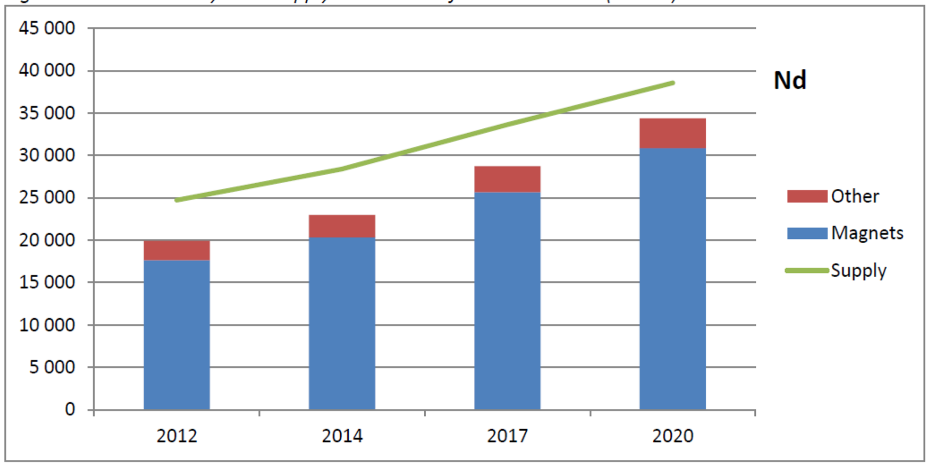
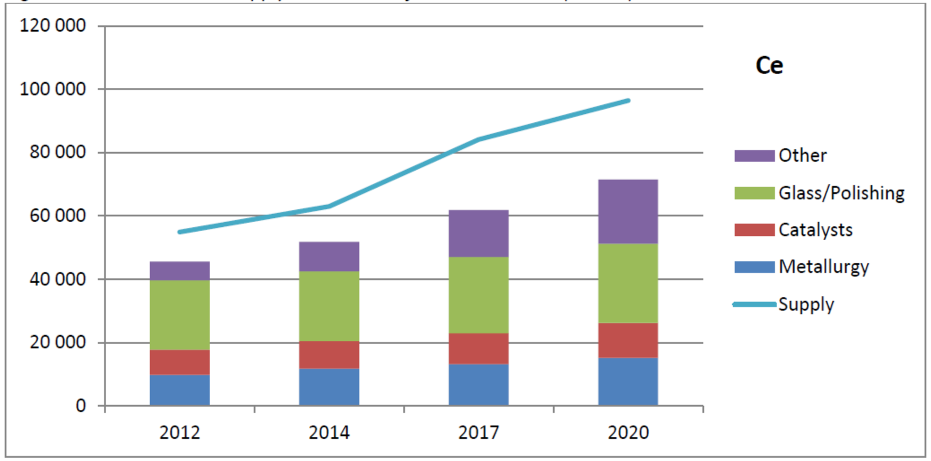
Figure 170: World neodymium supply and demand forecasts to 2020 (tonnes)



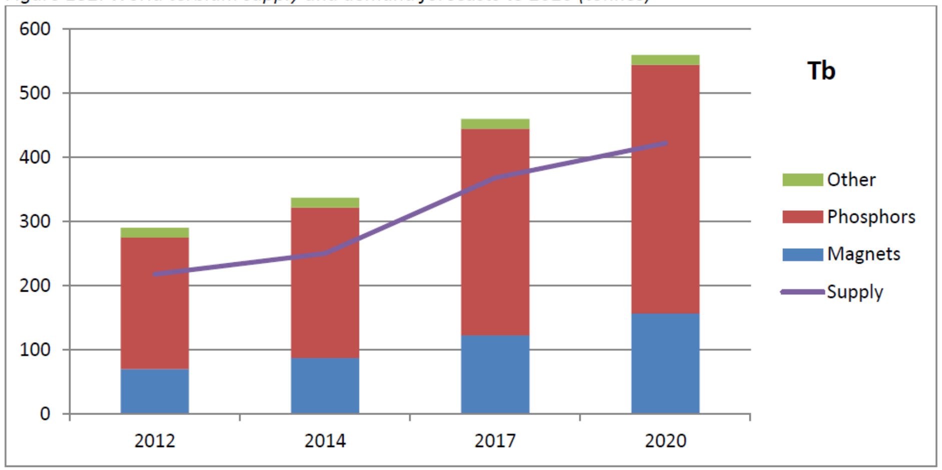
Sources: Roskill, IMCOA and Technology Metal Research Reports and Presentations (2012-2013)

Figure 164: World cerium supply and demand forecasts to 2020 (tonnes)



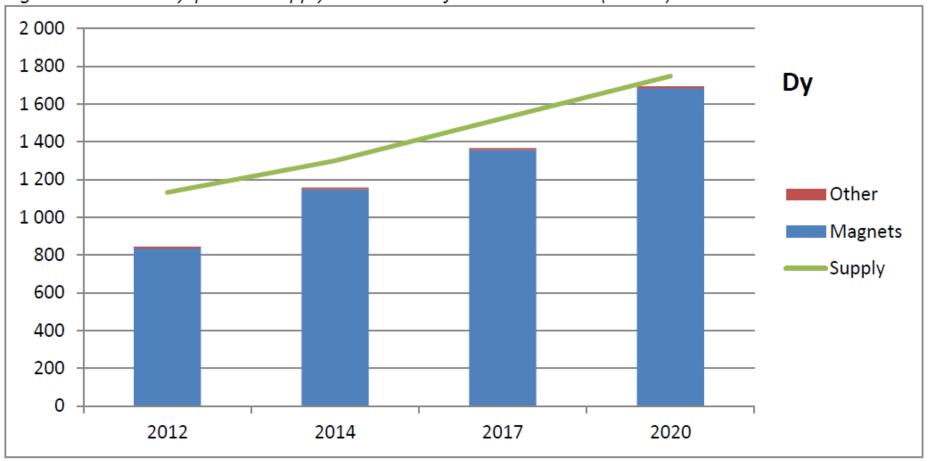
Sources: Roskill, IMCOA and Technology Metal Research Reports and Presentations (2012-2013)

Figure 182: World terbium supply and demand forecasts to 2020 (tonnes)



Sources: Roskill, IMCOA and Technology Metal Research Reports and Presentations (2012-2013)

Figure 185: World dysprosium supply and demand forecasts to 2020 (tonnes)



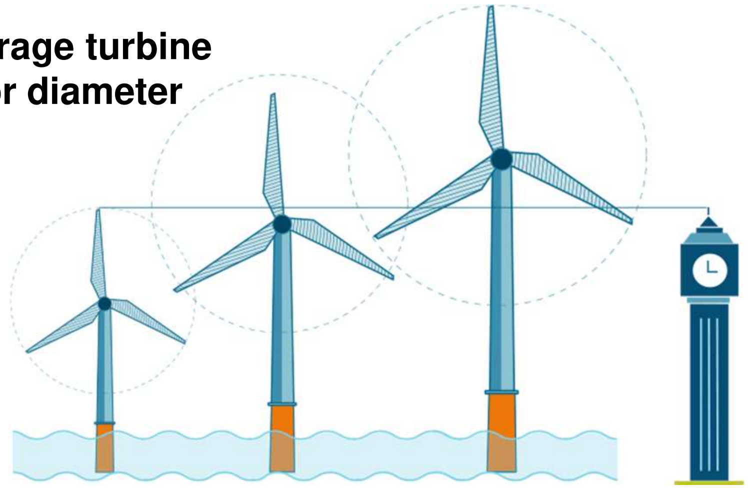
Sources: Roskill, IMCOA and Technology Metal Research Reports and Presentations (2012-2013)

Direct drive wind turbine

per 1 MW windpower

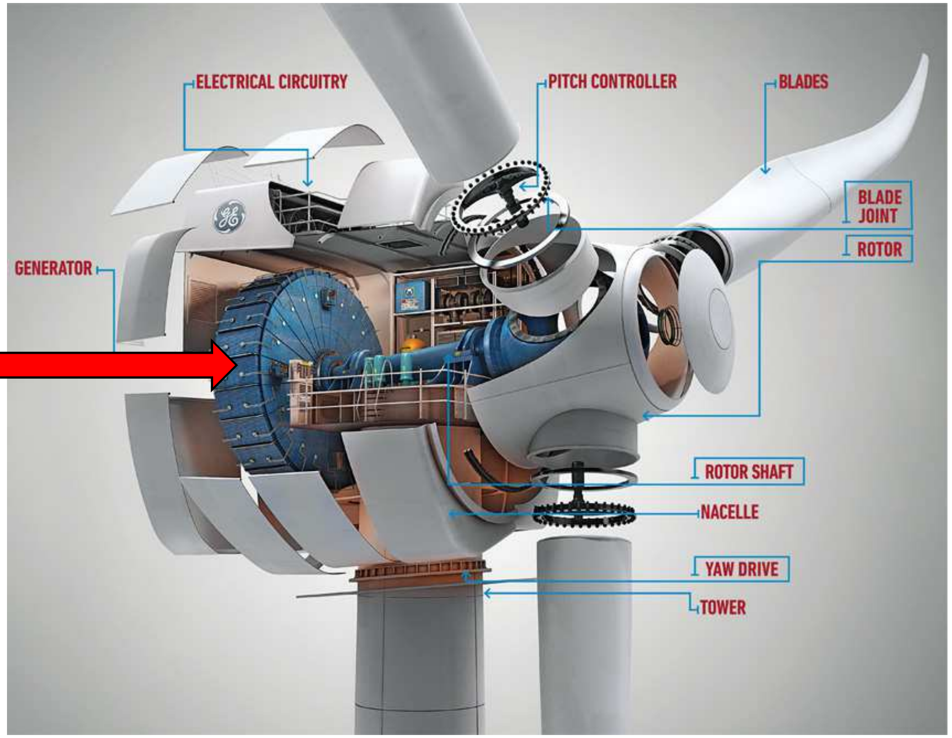
- **+/- 600 kg Nd-Dy-Fe-B**
- 4% Dy = 24 kg
- 28% Nd = 168 kg

Average turbine rotor diameter



37m 1990 450kW	154m Today 6-8MW	240m 2020	94m Big Ben height

https://www.siemens.com/global/en/home/markets/wind/offshore.html



(image General Electric, Data: US DOE)

Global refrigeration

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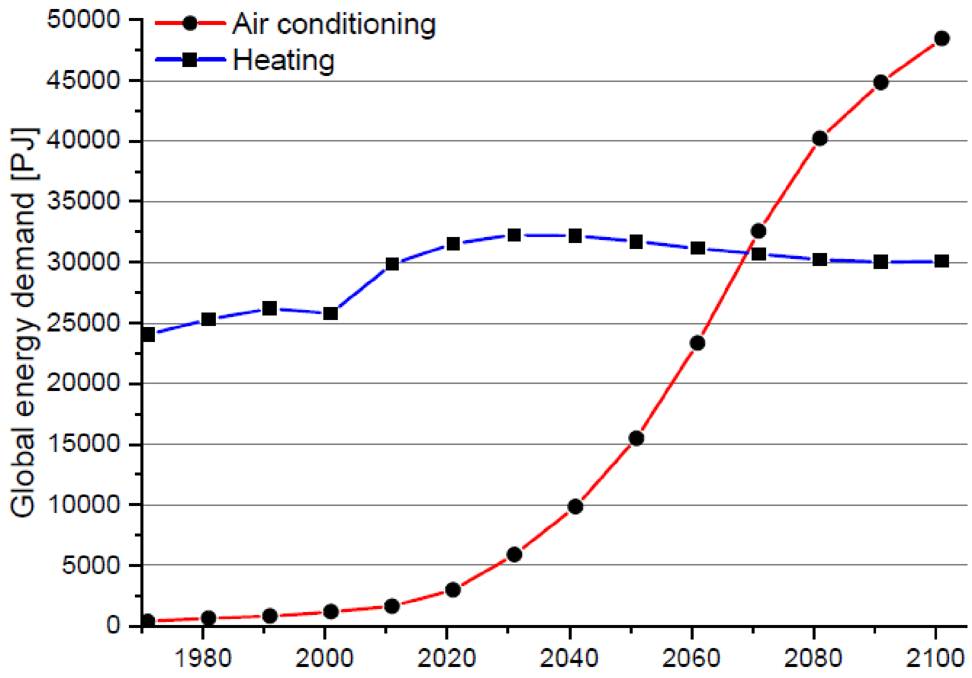
- **3 billion** refrigeration, air-conditioning and heat pump systems in operation worldwide
- **300 billion USD global** annual sales
- **12 million people** employed worldwide in the refrigeration sector
- **17% of the overall electricity** used worldwide consumed by refrigeration

IIR 29th Informatory Note on Refrigeration Technologies 02/12/2015

Global residential energy demand

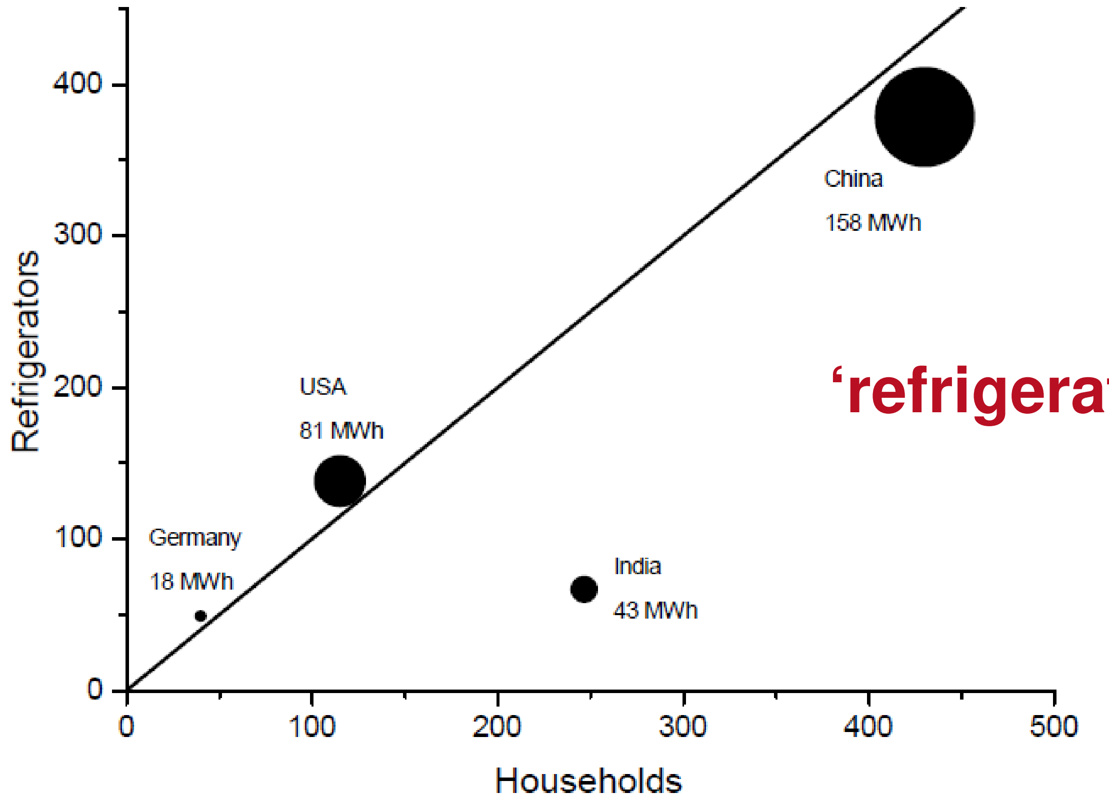


Heating versus cooling (air conditioning) reference scenario

as modelled by Isaak and van Vuuren 2009

Numbers of household versus numbers of refrigerators for Germany, USA, China and India (in million units)

The size of the spots correlates with the amount of energy spent for **domestic refrigeration** in each country per year (estimates for the years 2013/2014).



‘refrigeration revolution’

Gauss and Gutfleisch, The resource basis of magnetic refrigeration, J. of Industrial Ecology, 2016.

China - the factory of the world - I

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In 2015, it produced or assembled:

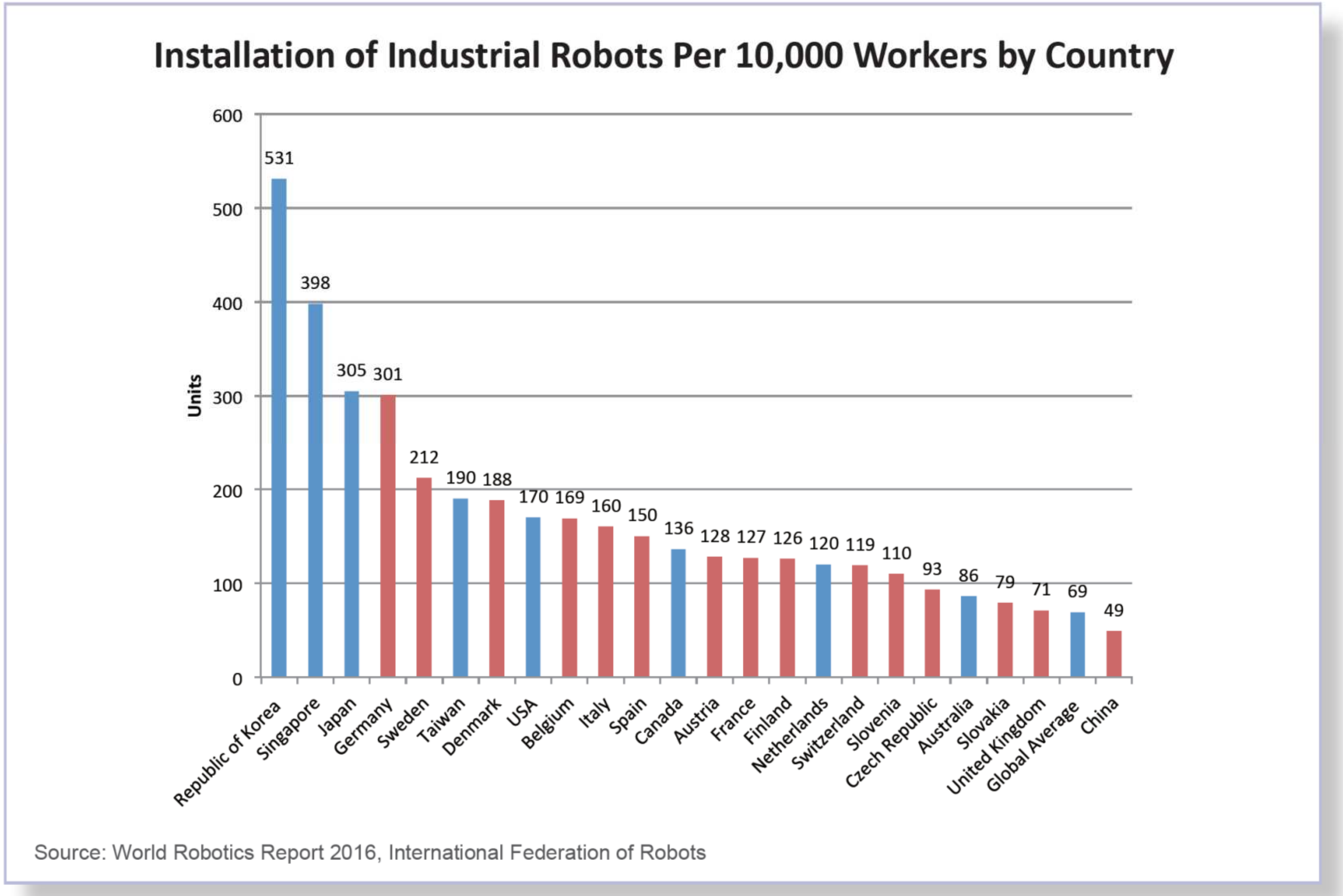
- 28% of the world's automobiles
- 41% of the world's ships
- 80%+ of the world's computers
- 90%+ of the world's mobile phones
- 60% of the world's colour TV sets
- 50%+ of the world's refrigerators
- 80% of the world's air-conditioners
- 24% of the world's power
- Half of the world's steel

strategy targets are all high-tech industries:

- Automotive
- Aviation
- Machinery
- Robotics
- high-tech maritime
- railway equipment
- energy-saving vehicles
- medical devices
- information technology

📖 China Manufacturing 2025
2017 by the European Union Chamber of Commerce in China

China - the factory of the world - III



World Robotics Report 2016: European Union Occupies Top Position in the Global Automation Race, International Federation of Robots, 29th September, 2016, viewed 2nd December, 2016, p. 2, <http://www.ifr.org/news/ifr-press-release/world-robotics-report-2016-832/>

How to tackle the REE supply risk?

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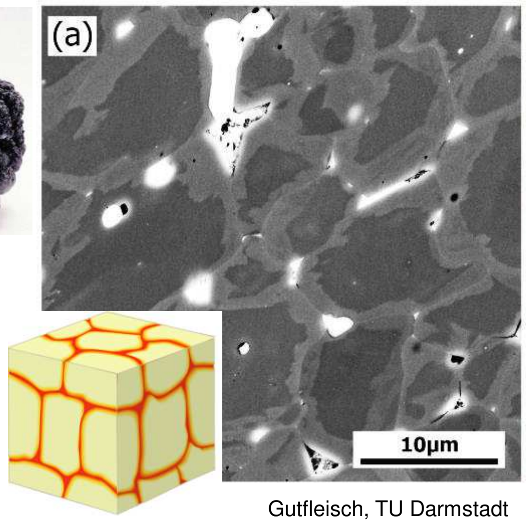
Mine & separate oxides → Purify metals → Alloys & magnet powders → Magnet manufacture → Components for motors & generators → Intallation & use → Disposal

Recycling

Note: Orange colour represents stages of the supply chain which take place in Europe

1. **Sustainable primary mining from old / new REE deposits**
2. **Reduce critical REEs by novel microstructures and processing routes**
3. **Substitute REEs altogether → REE-free magnets**
4. **Technospheric mining (Recycling)**

Kümpel, Wiedicke, BGR



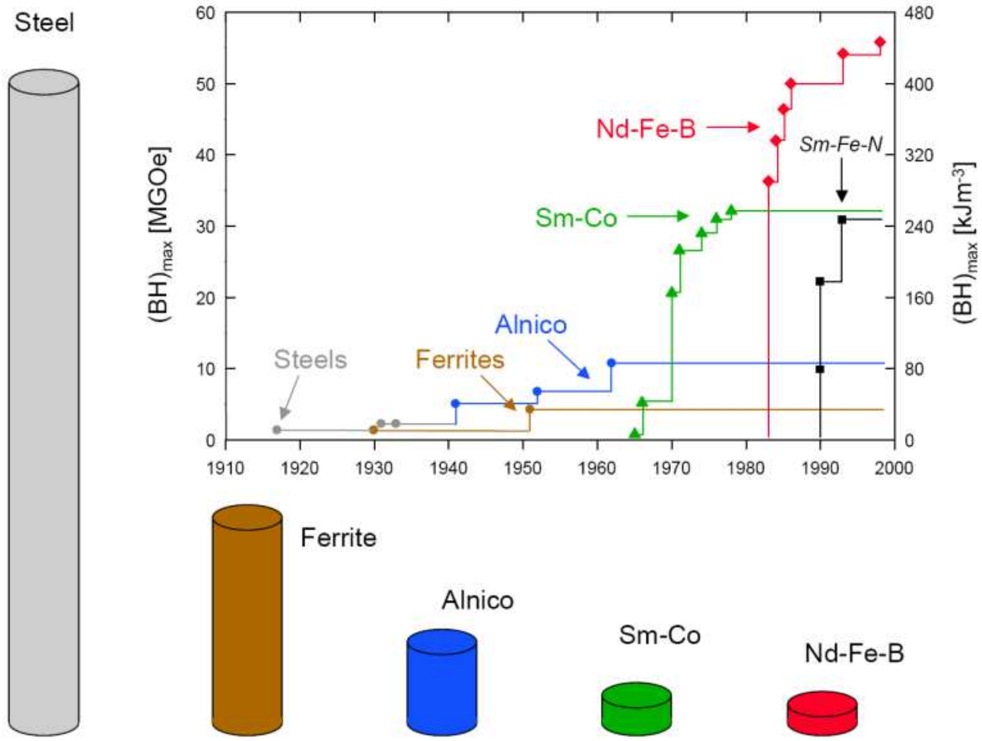
Gutfleisch, TU Darmstadt

Reller, Augsburg

REE Permanent Magnets

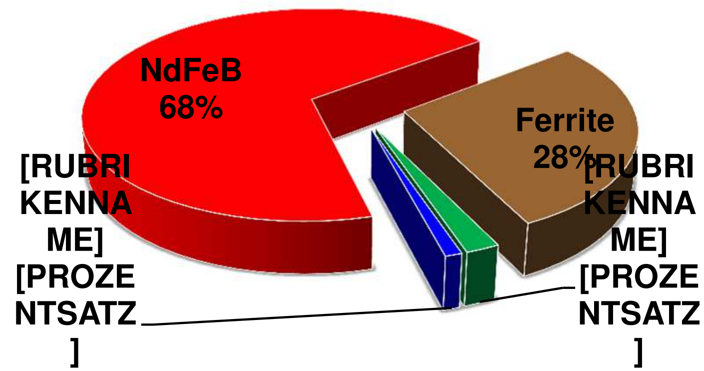
the value chain – towards mastery of coercivity

NdFeB magnets dominate the permanent-magnet market by value, ferrites dominate by mass

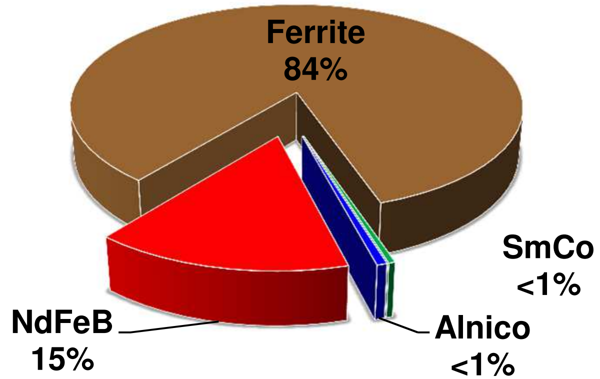


Adv. Materials 23, 2011

Market shares by value, 2016*

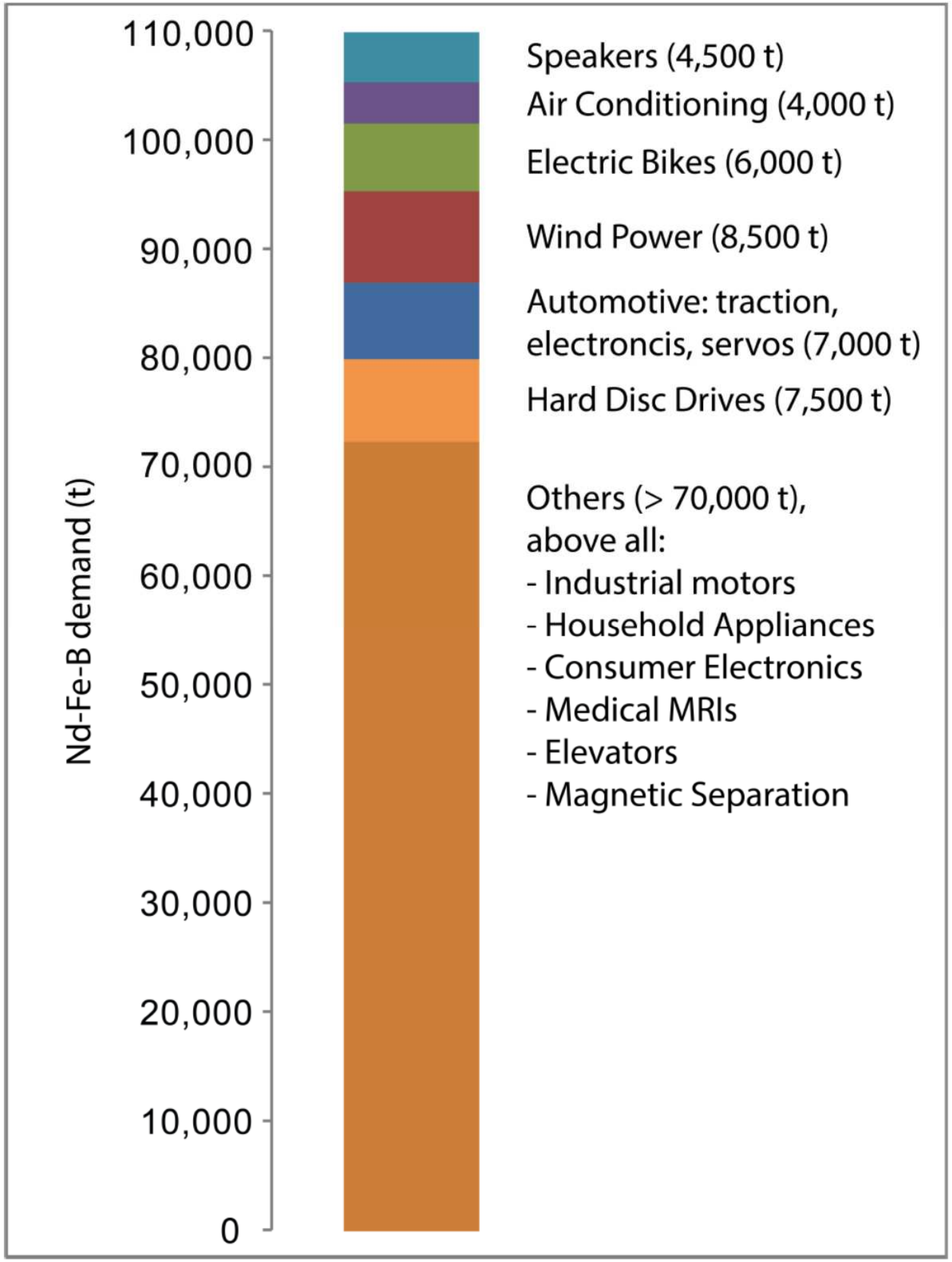


Market shares by mass, 2016*



*2016 forecast estimates
Constantinides, Magnetics Conference 2016

The demand for Nd-Fe-B by different applications in 2015

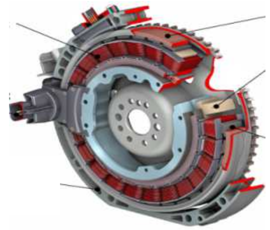


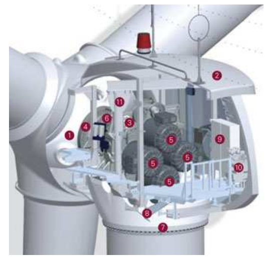
K.-H. Müller, S. Sawatzki, R. Gauss and O. Gutfleisch,
Permanent magnetism,
in Springer Handbook of Magnetism,
ed. by J.M.C. Coey and S. Parkin, in preparation.

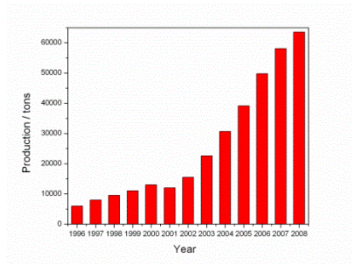
FUNKTIONALE MATERIALIEN

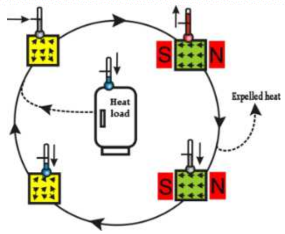
Permanent Magnet Growth

- **World production of sintered NdFeB in 2012: ~100.000 t (estimated 80% China, ~18%Japan, 2%Europe)**
- The **motor/generator in a hybrid electric vehicle contains 1 kg of NdFeB**. Set to grow to between 10 million and 20 million vehicles by 2018.
- New **designs of wind generators use NdFeB magnets at a rate of ~600 kg per mega-watt**. This application alone has potential to increase RE demand by 25% per year above current production.
- Hard disc drives cannot function without RE permanent magnets. Formerly 70% of the NdFeB market this is now diluted by the other major applications.
- Solid state energy efficient cooling: **Magnetocalorics 1kg MCE and 4 kg NdFeB per kilo-watt cooling power**









***Adv. Mat. (Review)* 23 (2011) 821**

Intrinsic and extrinsic magnetic properties

intrinsic properties + **microstructure**

100µm > l > 1nm

↔ fit µ-magnetic length scales

⇒ **extrinsic properties**

saturation magnetisation, M_s

anisotropy field, H_a

Curie temperature, T_C

→

exchange length, l_k $$l_\kappa = \sqrt{\frac{A}{K_1}}$$

critical single domain particle size, D_c

exchange stiffness, **A**

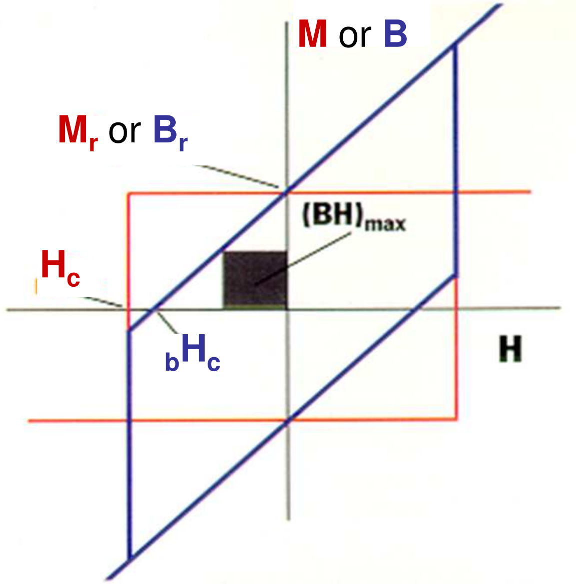
domain wall width δ_w and energy γ

hardness parameter κ $$\kappa^2 = \frac{K_1}{\mu_0 M_s^2}$$

remanence, J_r

coercivity, H_c

energy density, $(BH)_{max}$



Intrinsic magnetic properties

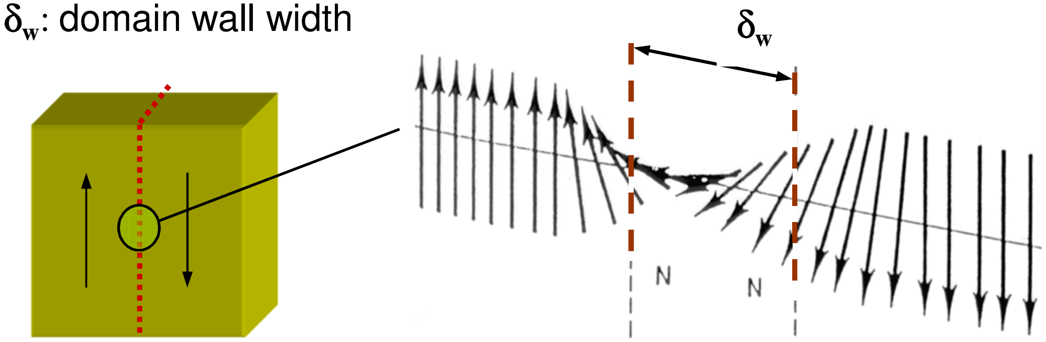
compound	T_C , K	$\mu_0 M_s$, T	K_1, MJ/m³	D_c, nm	δ_w
$Nd_2Fe_{14}B$	585	1.60	5	214	4
$SmCo_5$	993	1.05	17	1700	3.7
Sm_2Co_{17}	1100	1.30	3.3	490	8.6
α-Fe	1043	2.16	0.046*	7	30

D_c: critical single-domain particle size

δ_w: domain wall width

$$D_c = 72\, l_K \kappa^2 = 72 \frac{\sqrt{AK_1}}{\mu_0 M_s^2}.$$

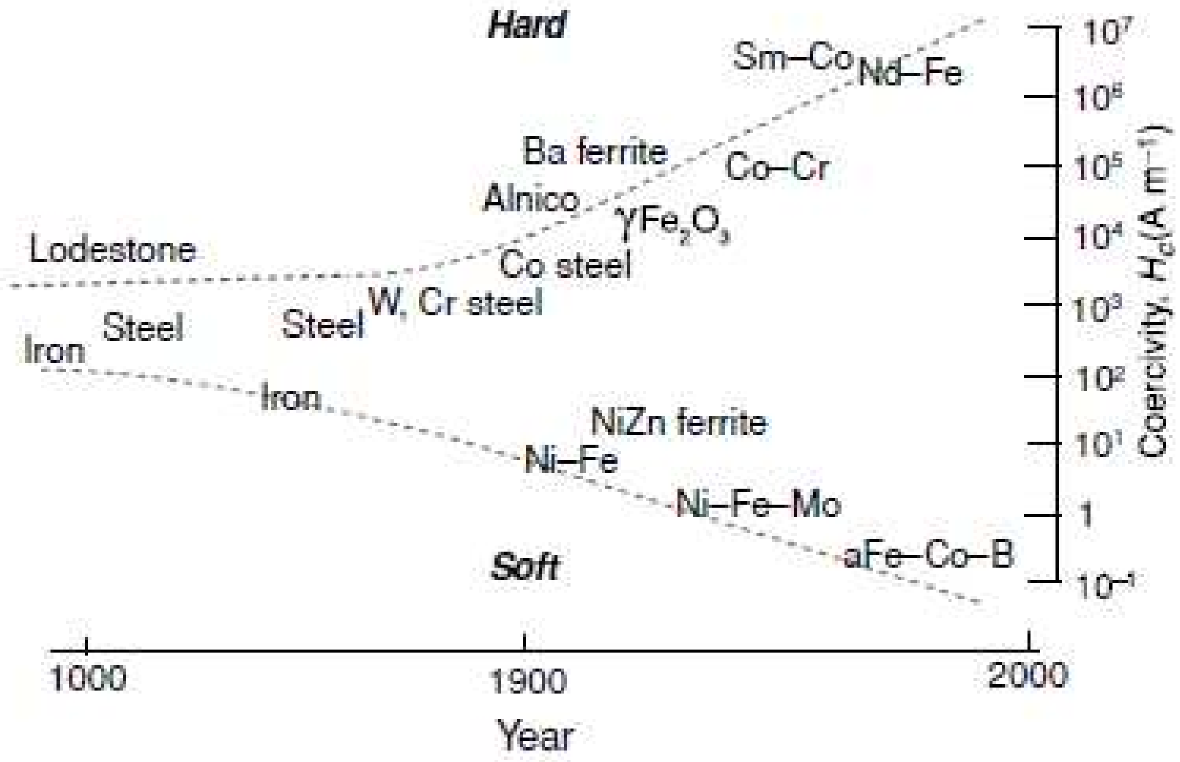
$$\delta_w = \pi l_K = \pi \sqrt{\frac{A}{K_1}}$$



Progress in coercivity

Figure 1.5

Progress in expanding the range of coercivity of magnetic materials during the twentieth century.



J. M. D. Coey,
Magnetism and Magnetic Materials,
Cambridge University Press 2010

Brown's paradox (W.F. Brown, 1945)

- an unsolved problem in physics -

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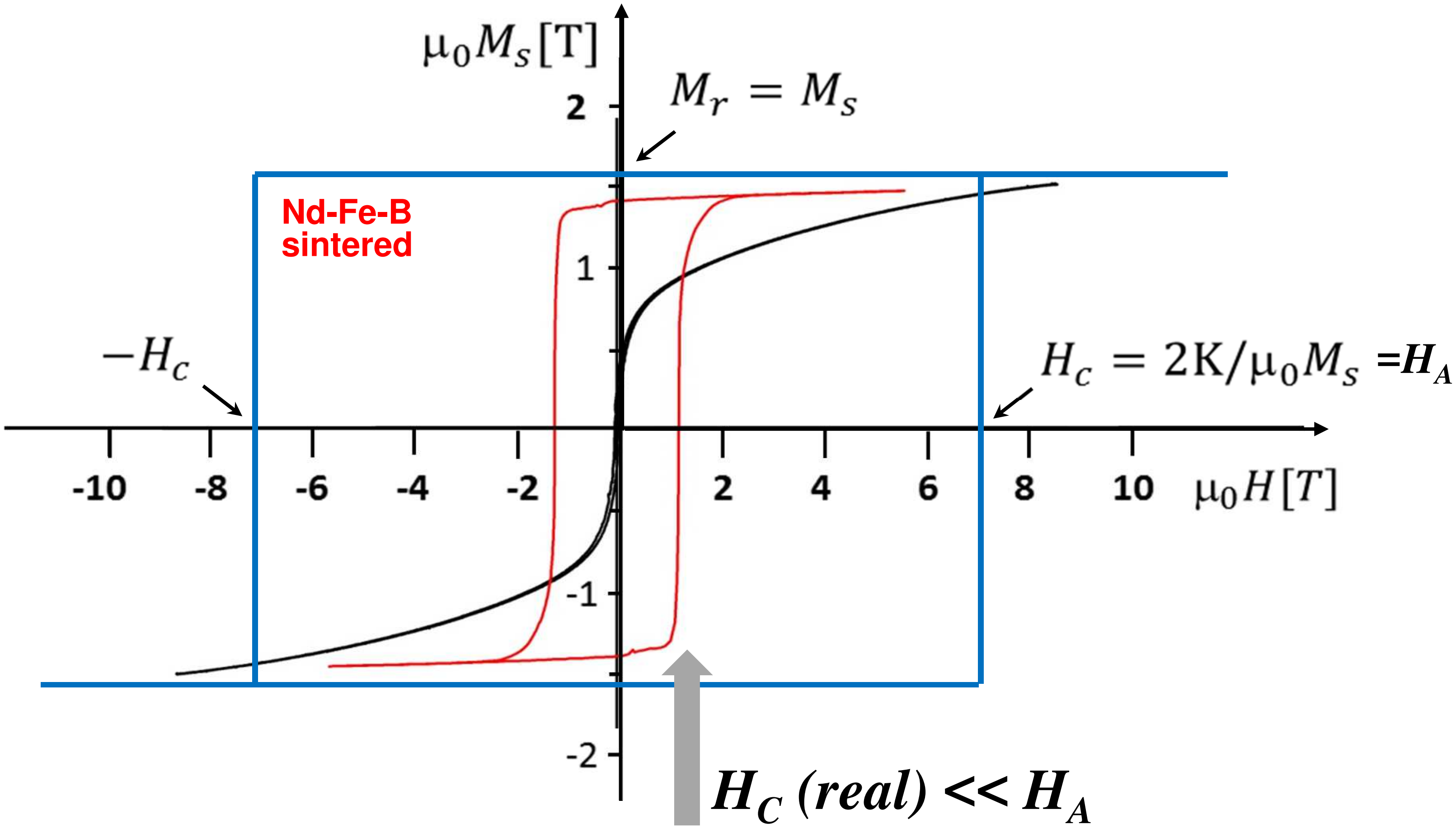
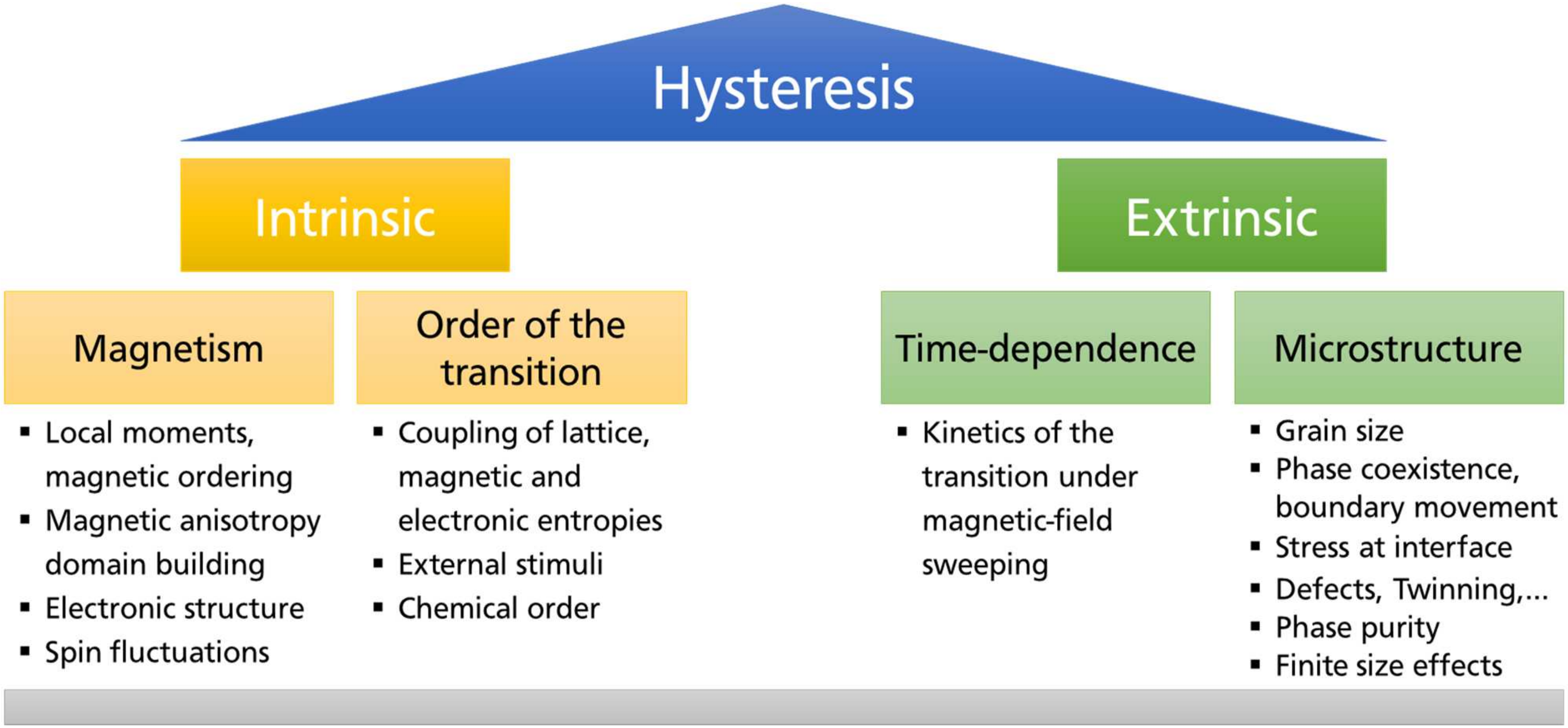


$H_C\ (real) \ll H_A$

This reduction is principally attributed to microstructural effects or local "magnetic softening" by chemical, structural or geometrical irregularities.

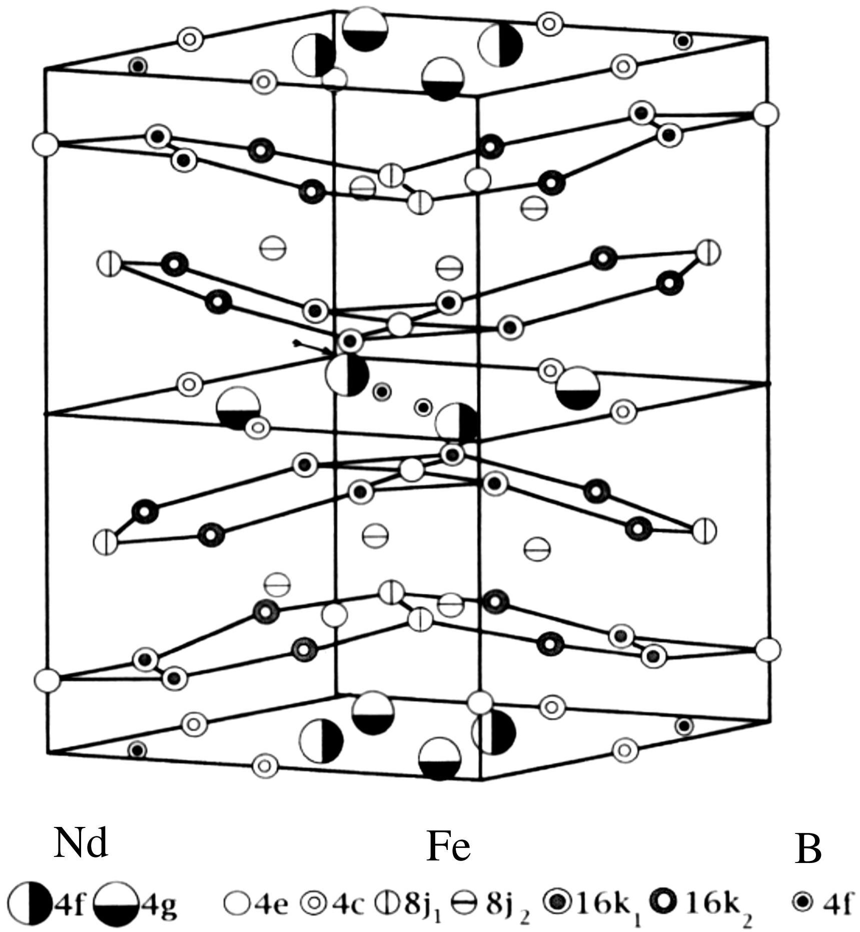
Origin of hysteresis

Mastering hysteresis → efficiency and reversibility



Phil. Trans. R. Soc. A, 374: 20150308 (2016)

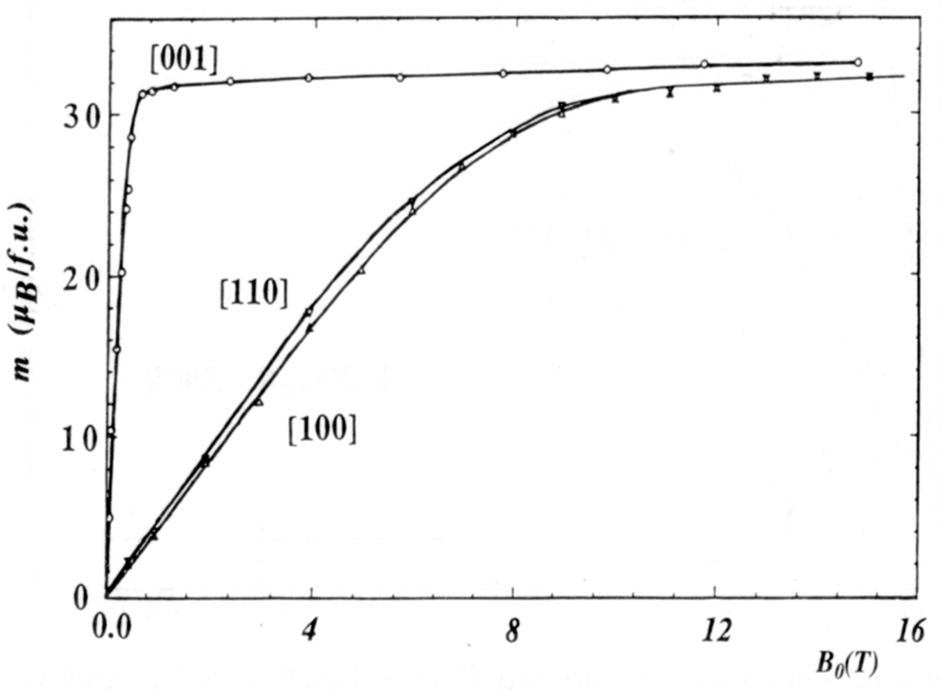
$Nd_2Fe_{14}B$



- $Nd_2Fe_{14}B$ structure has a tetragonal crystal structure.
- It is largely composed of Fe which is abundant and has a large FM moment.
- Relatively small amount of abundant light rare earth provide anisotropy.
- Tetragonality stabilised by B occupying only 2 vol. %
- alternating layers of soft and hard

Magnetism in $Nd_2Fe_{14}B$

Element	M_S	K_1	T_C
Fe 3d	high	low	high
Nd 4f	low	high	low



Magnetisation curves for a $Nd_2Fe_{14}B$ single-crystal at room temperature (from *Chikazumi 1997*)

Magnetismus in $nd_2fe_{14}b$

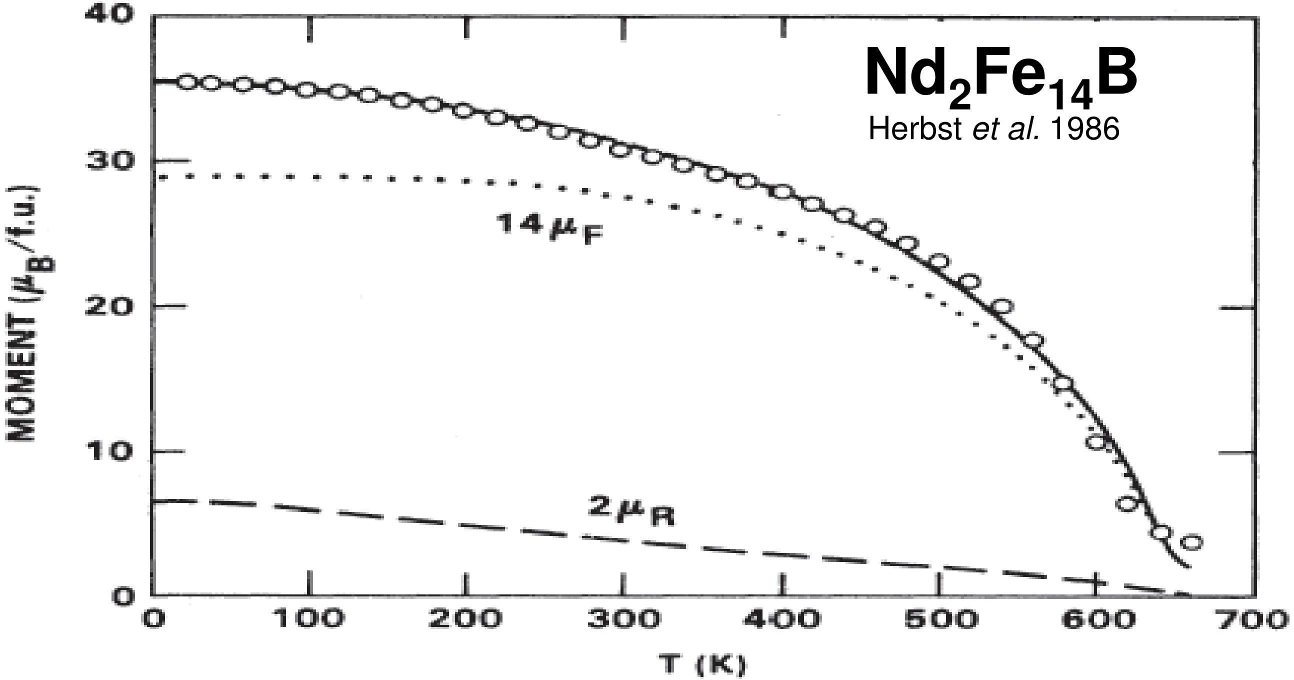
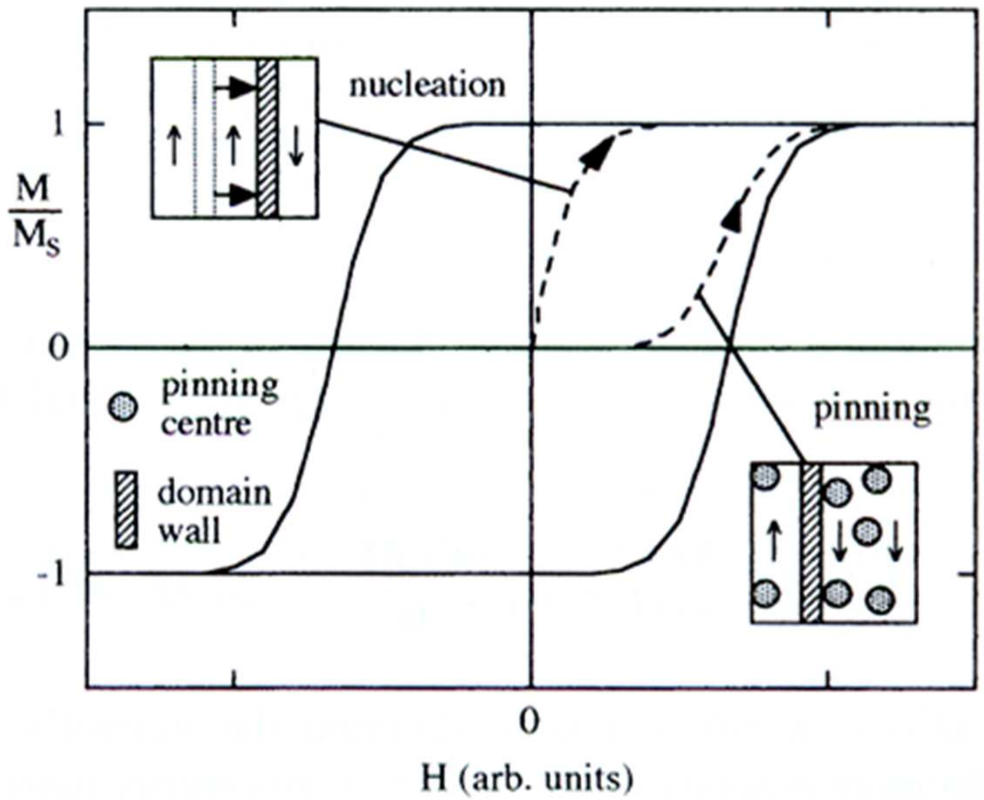


FIG. 11. Molecular-field analysis for $Nd_2Fe_{14}B$ (Fuerst *et al.*, 1986). Open circles denote the measured moment per formula unit. The solid line is the calculated total moment, which is the sum of the iron (dotted line) and neodymium (dashed line) contributions.

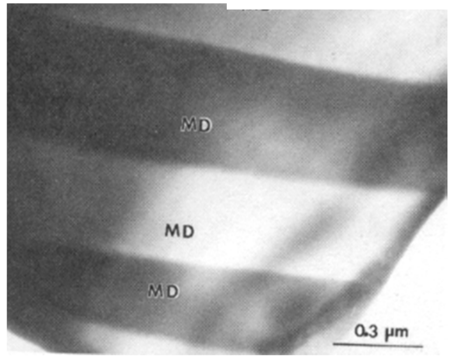
Initial magnetisation curve and field dependence of coercivity

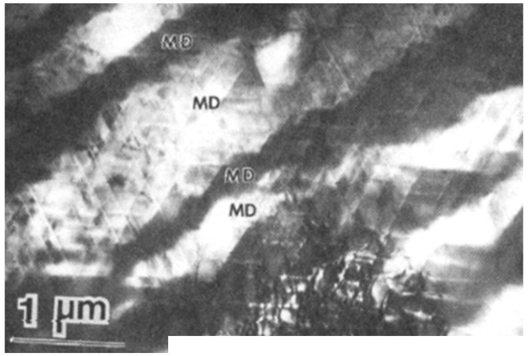
in nucleation and pinning-type magnets



Skomski and Coey 1999

Nd-Fe-B



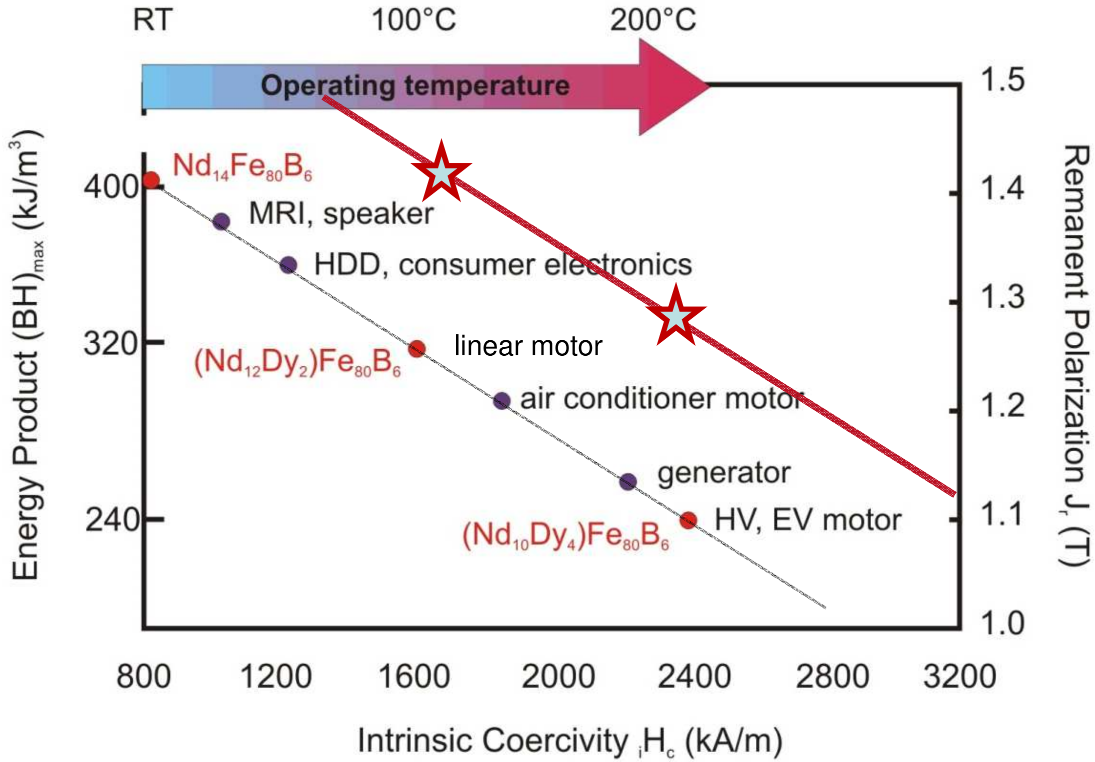


$Sm(CoFeCuZr)_z$

Sintered NdFeB magnets for electro motors

- **Design light-weight, high torque-to-weight ratio motors, using permanent magnets with adequate temperature stability**

  → torque scales linearly with remanence

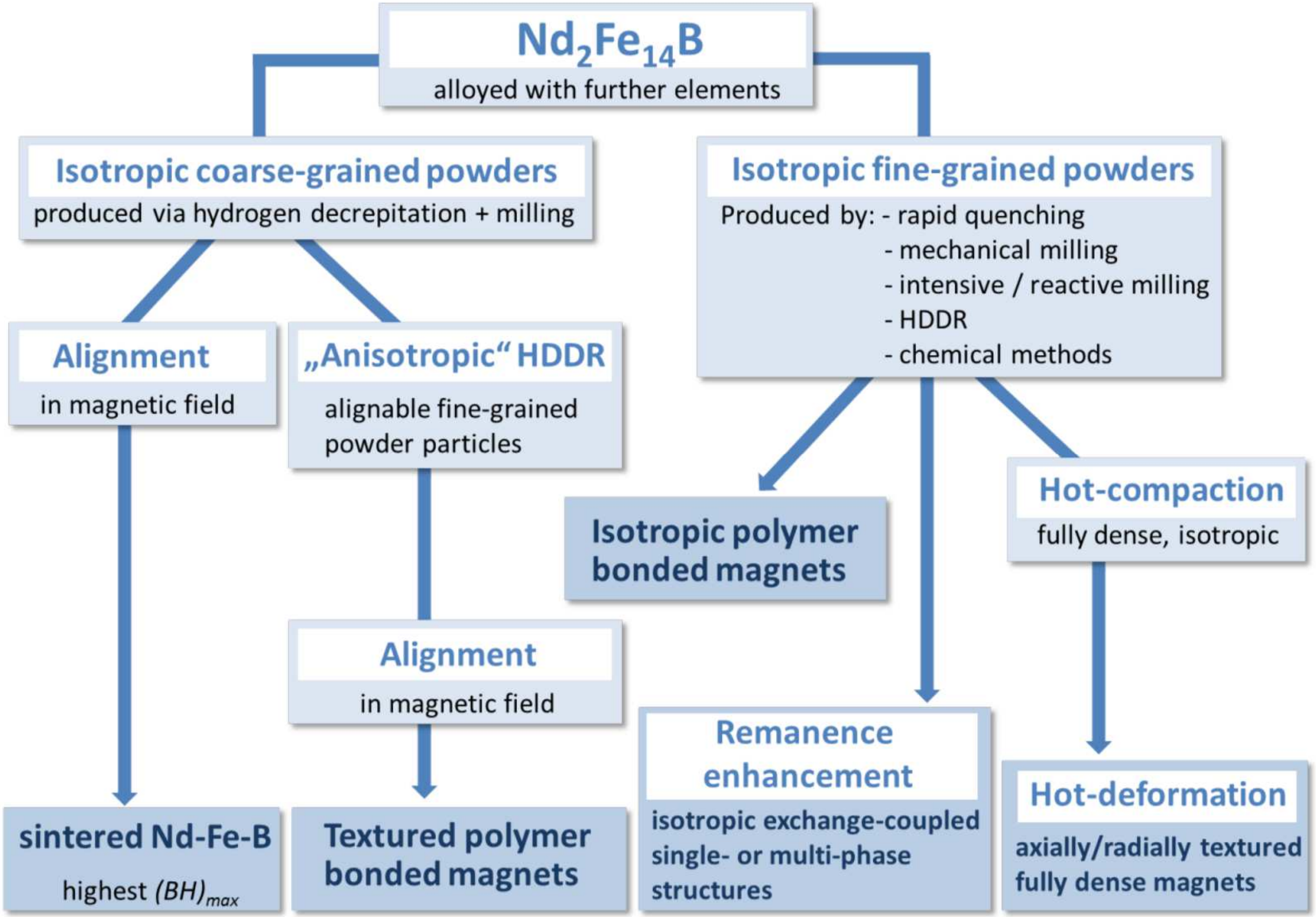


Hirosawa et al. J. Appl. Phys. 59 , 873, 1986

Crystal	M_s at 300K / μ_B/f.u.	H_a at 300K / kOe	T_c / K
$Nd_2Fe_{14}B$	32.5	67	585
$Dy_2Fe_{14}B$	14.0	150	598
$Pr_2Fe_{14}B$	31.9	87	569

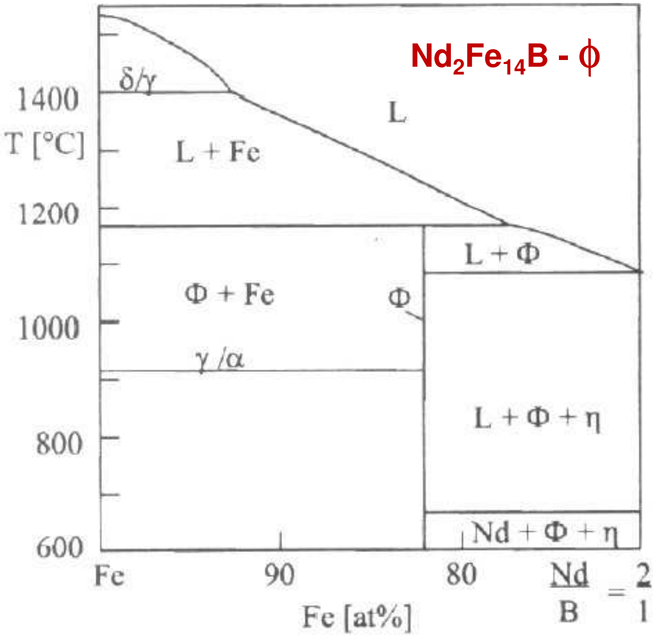
Adv. Mat. 23 (2011) 821

Principal processing routes of Nd-Fe-B magnets
based on coarse grained and nanocrystalline powders

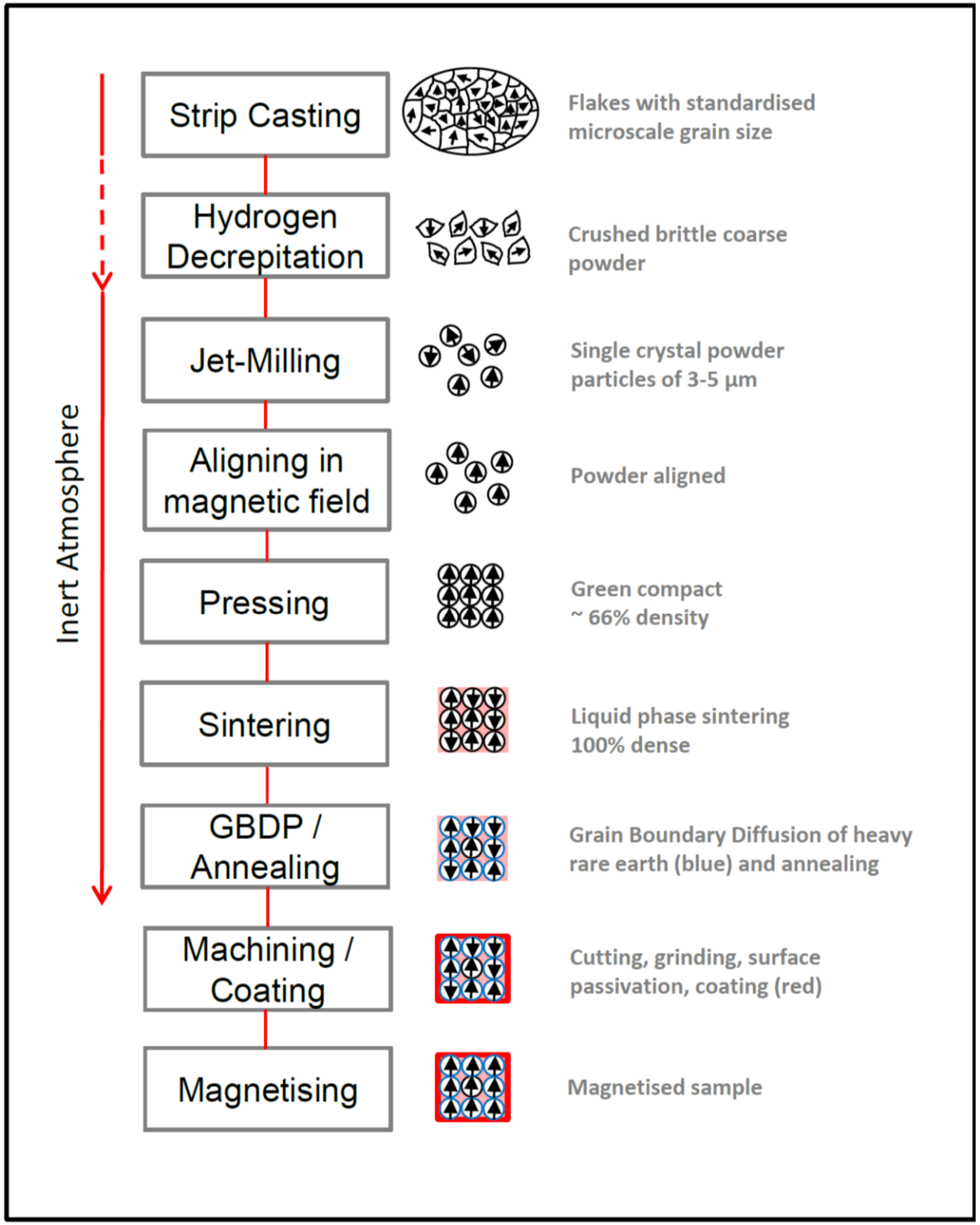


K.-H. Müller, S. Sawatzki, R. Gauss and O. Gutfleisch, Permanent magnetism,
in Springer Handbook of Magnetism, ed. by J.M.C. Coey and S. Parkin, in preparation.

NdFeB sintered magnets



VIDEO hydrogen decrepitation



FUNKTIONALE MATERIALIEN

NdFeB sintered magnets

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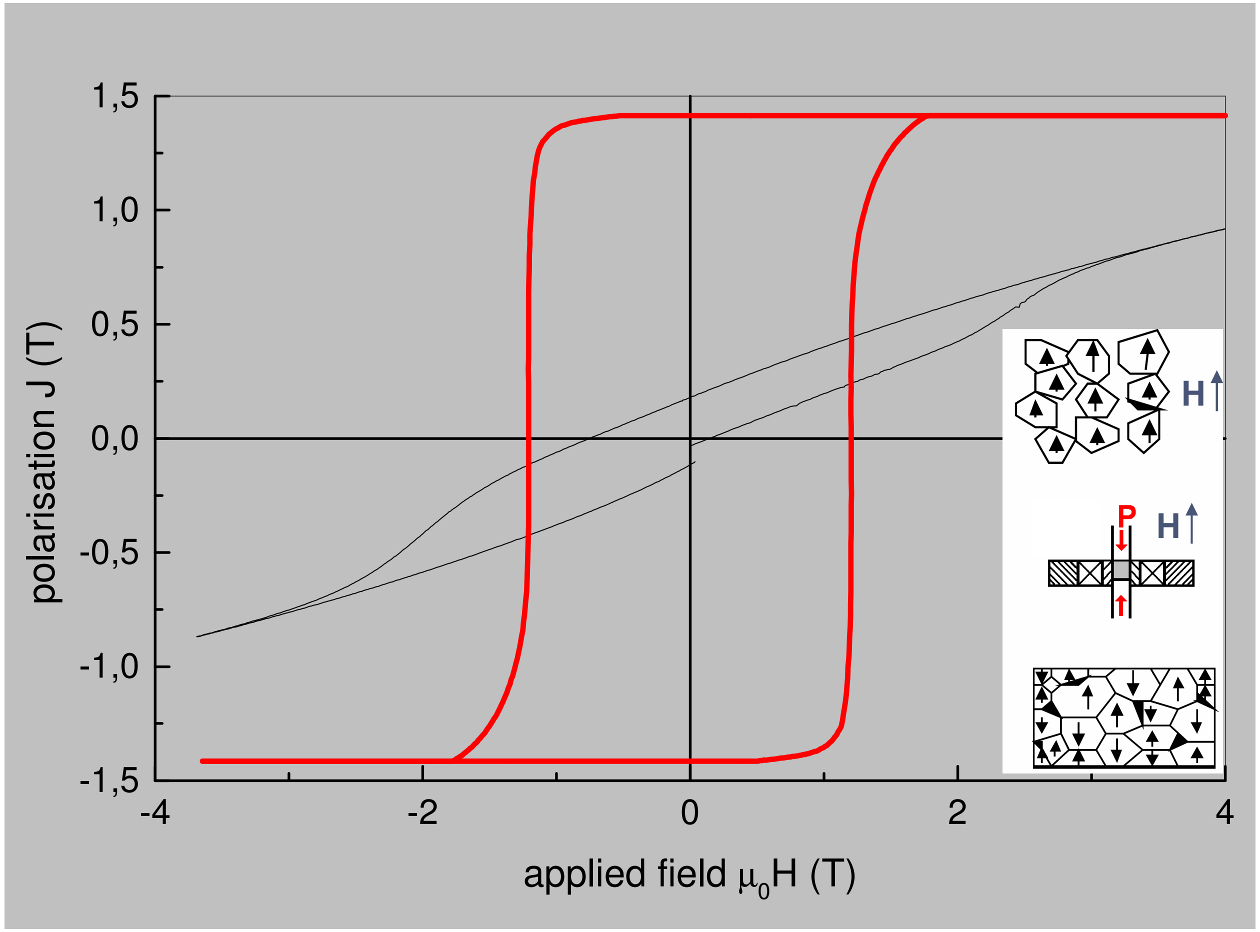
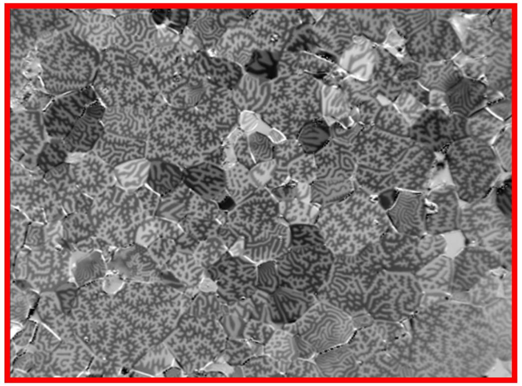
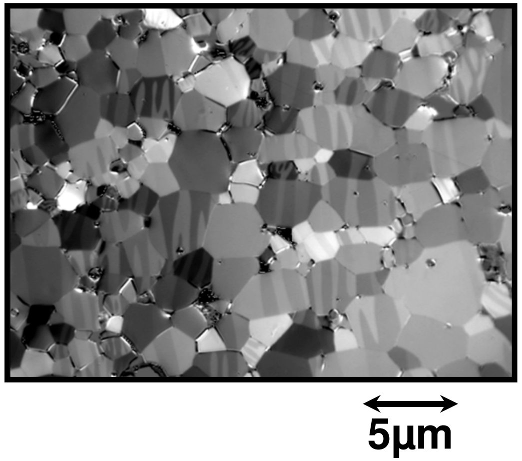
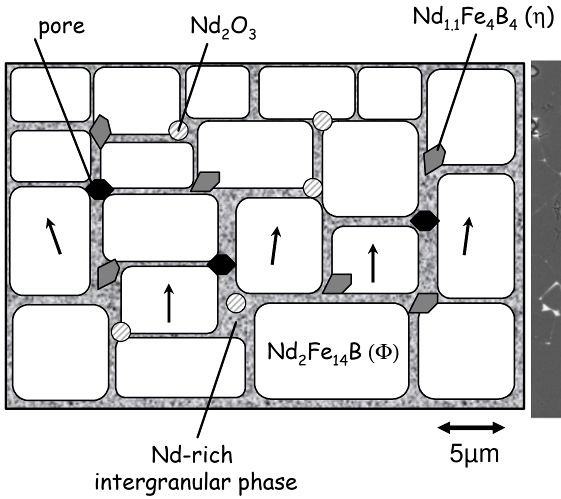
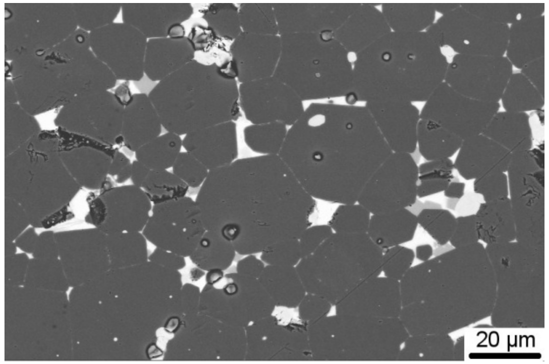




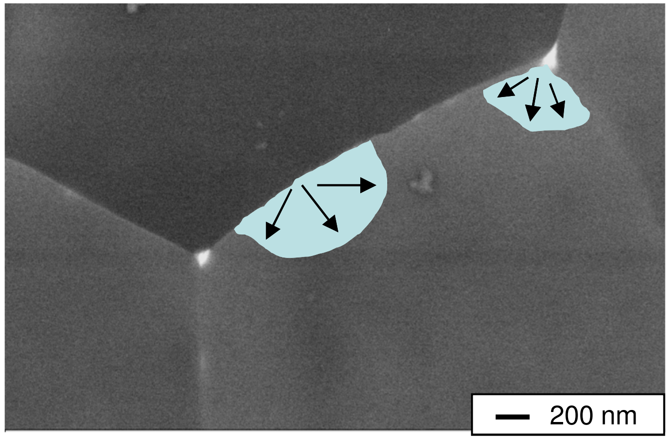


Magnetisation reversal in sintered NdFeB





the weak link



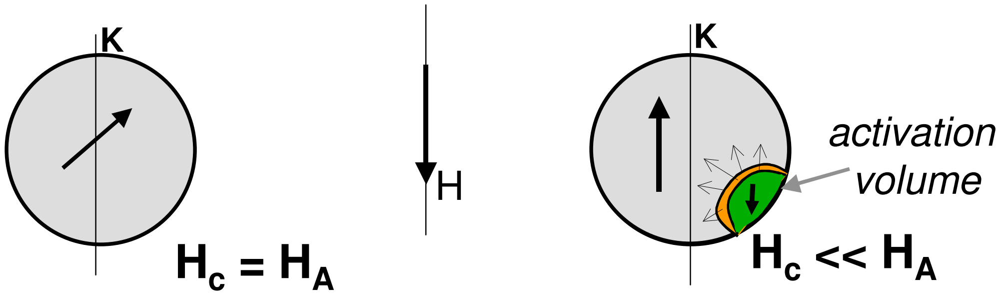
crystalline or amorphous
metallic or oxidic
FM or PM
microchemistry, structural defects
continuous or discontinuous

??

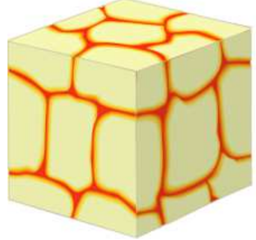
Nucleation-type magnet

Perfect materials:
Coherent rotation

Defects :
Nucleation + propagation



$$v_a = \frac{k_B T}{\mu_0 S_v M_s}$$

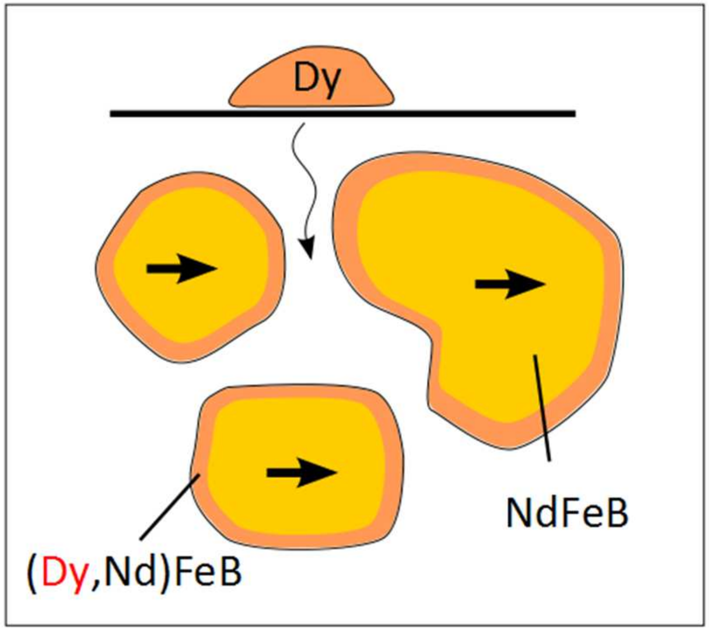


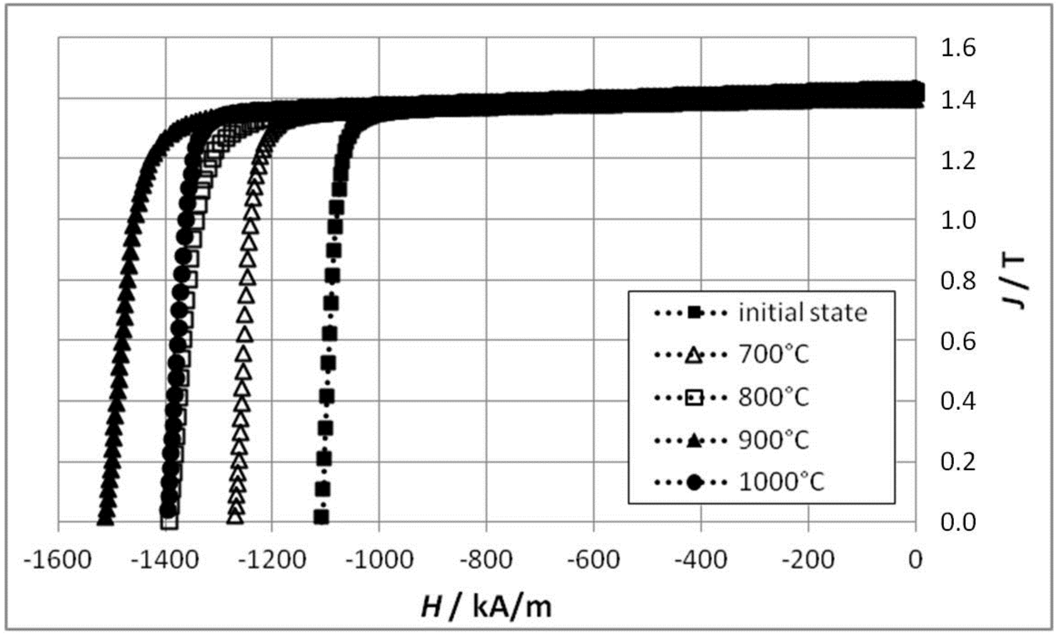
efficient use of Dy
grain boundary diffusion process

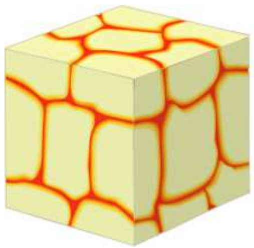
Grain boundary diffusion processes (GBDP)

in sintered Nd-Fe-B magnets

Park et al. REPM proc. (2000) 257





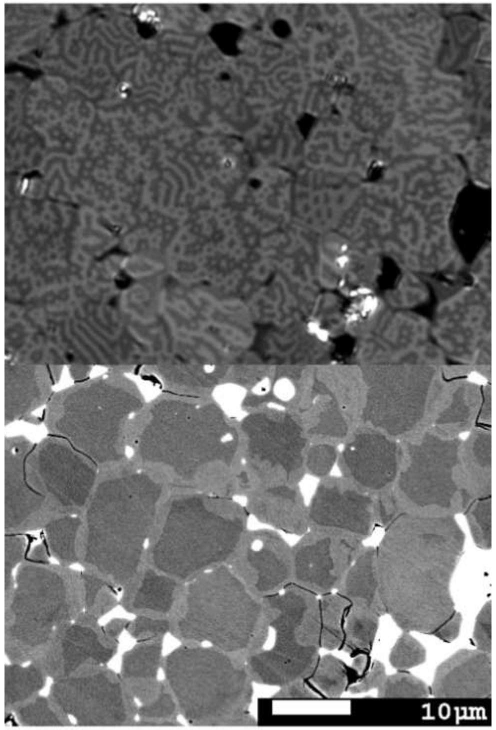


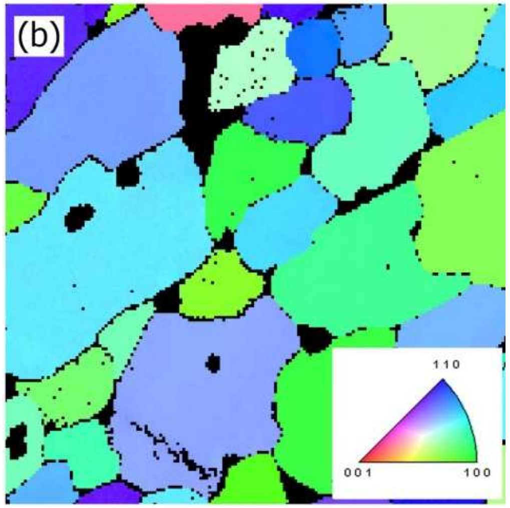
Increase by 420 kA/m (0.52 T) at 0.11 wt.% Dy

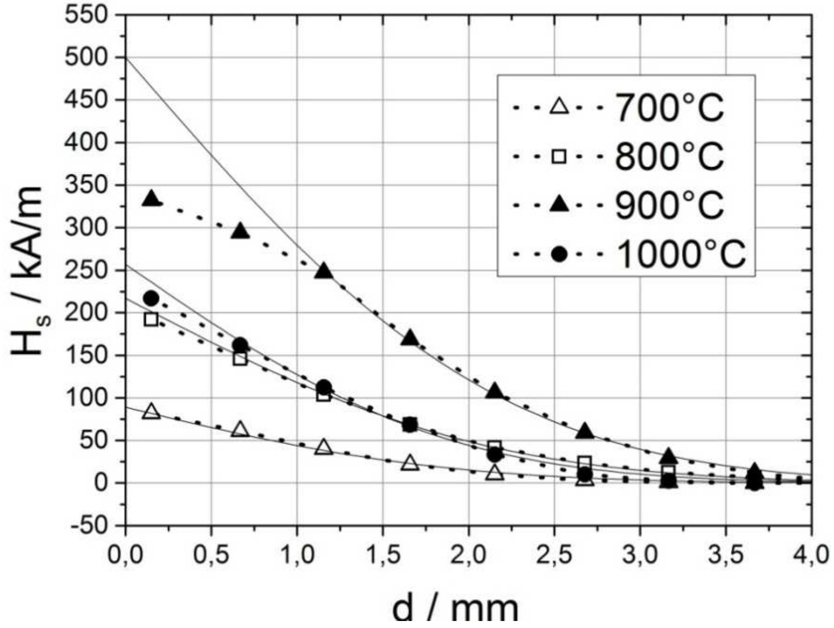
Acta Mater. 83 (2015) 248-255

Grain boundary diffusion processes (GBDP)

Coat with Dy slurry and anneal of sintered Nd-Fe-B magnets







Penetration depth of Dy limits the size of the magnet

Dy-shells do not affect the domain pattern nor the local orientation

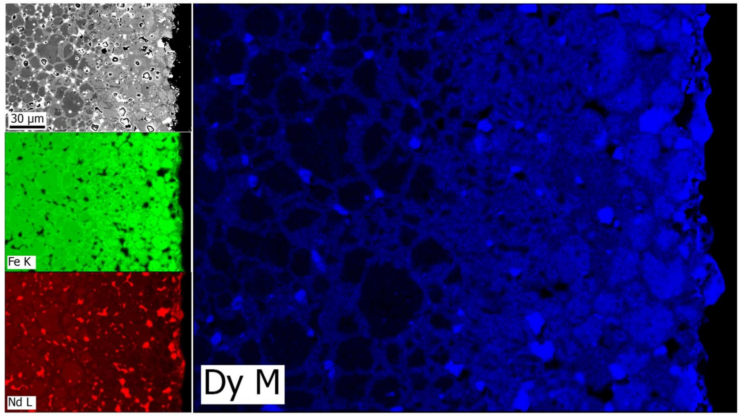
→ **Dy shells grows epitactically on the surface of the $Nd_2Fe_{14}B$ grains**

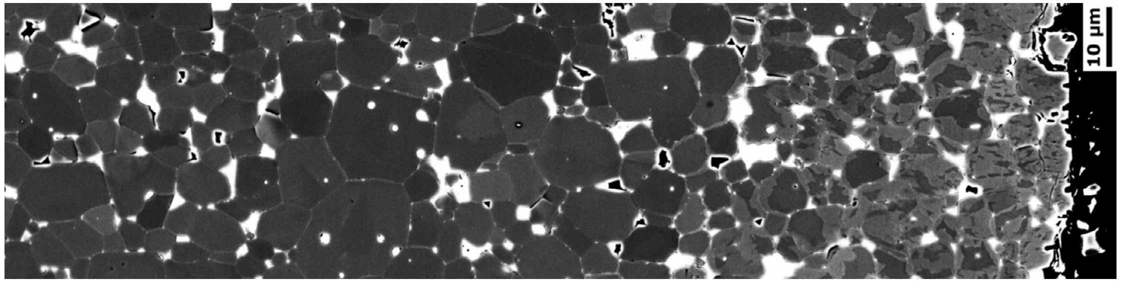
by substitution of Nd with Dy

Acta Mater. 83 (2015) 248-255

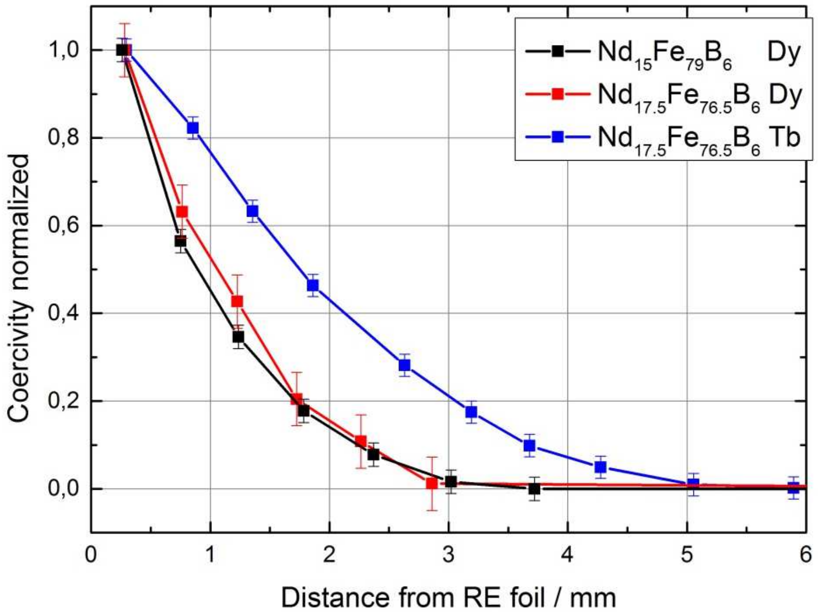
Grain boundary diffusion processes (GBDP)

Coat with Dy slurry and anneal of sintered Nd-Fe-B magnets



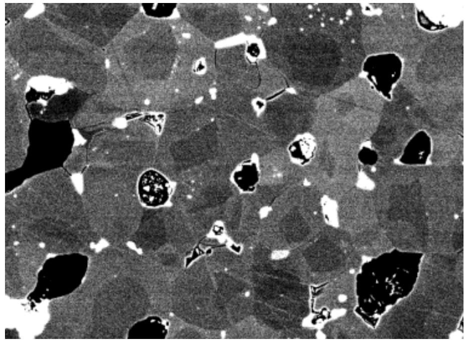


Loewe et al. Acta Mater. 83 (2015) 248-255



→ **two powder method**

Magnet 10 x 8 x 7 mm: image from the center



Tb leads to higher increase in coercivity and a deeper penetration depth compared to Dy

In-situ Magnetisation reversal
in GBDP processed sintered Nd-Fe-B magnets

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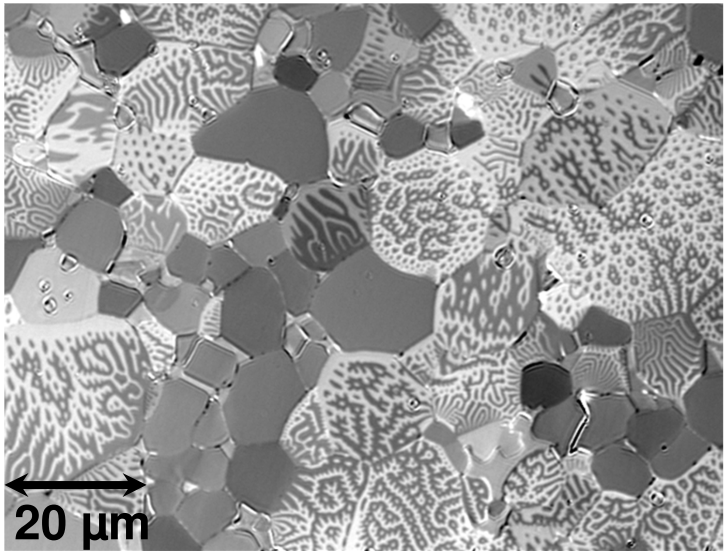
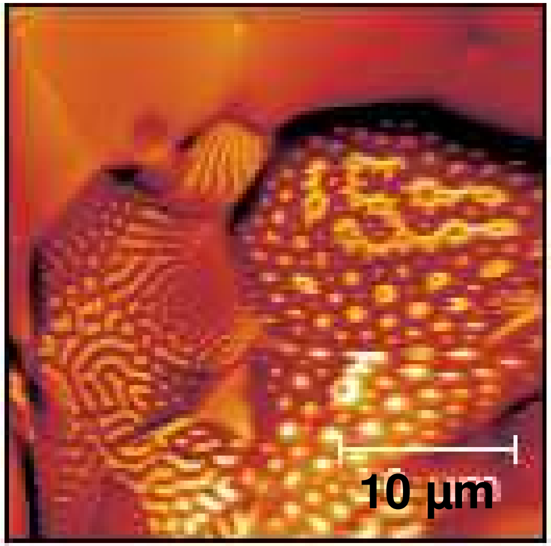
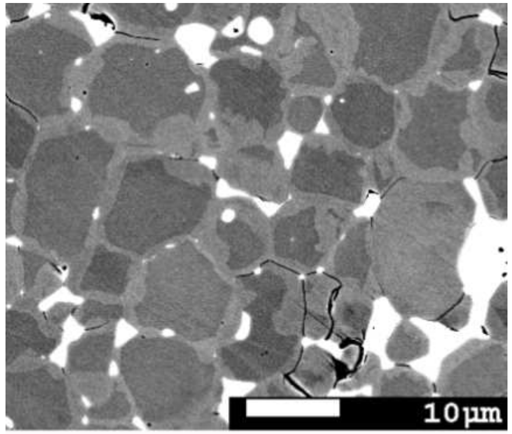
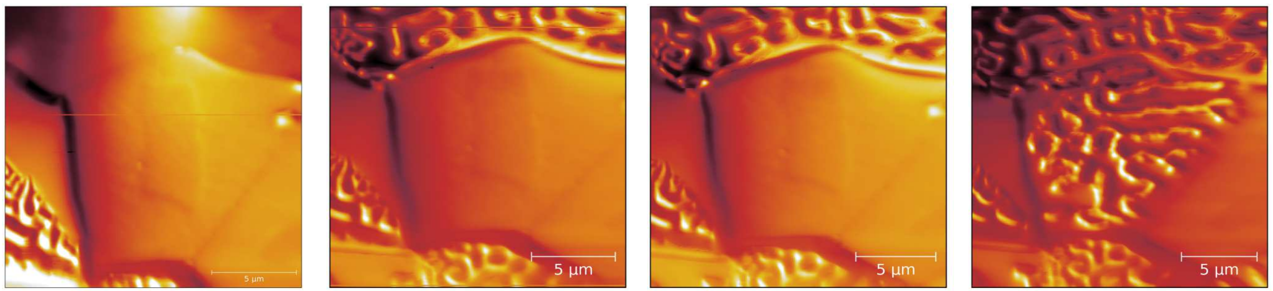


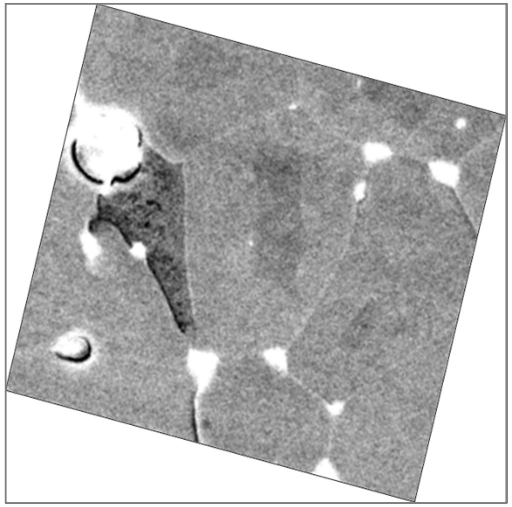


Remanent State (0 Tesla)
Kerr vs MFM



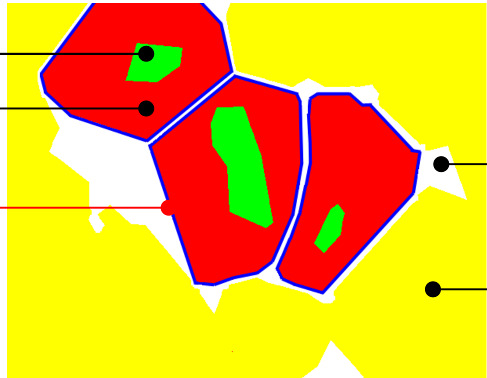
0 T | -0.1 T | -0.2 T | -0.3 T





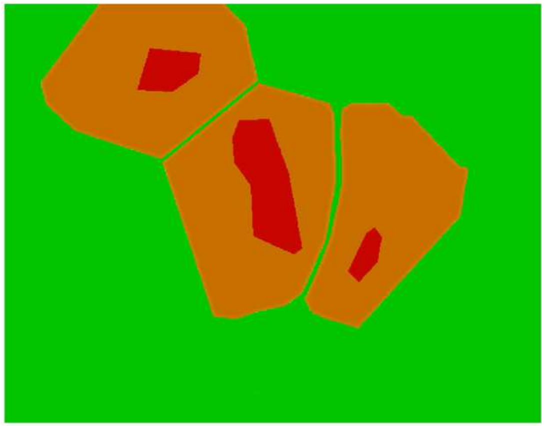
Local switching in a grain boundary diffused sintered magnet is homogeneous on the observable time scale

Micromagnetic simulation of reversal process

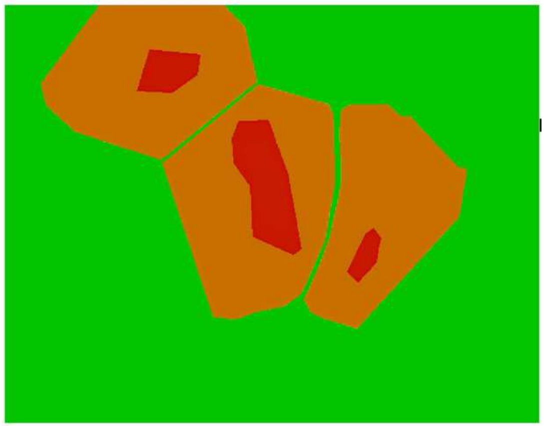


$3100 \times 2420 \times 2\ \mathrm{nm}^3$

K^{edge}=0.5$K^{(DyNd)FeB}$



K^{edge}=0.6$K^{(DyNd)FeB}$



⇒ K^{edge} defines position of nucleation site

Acta Materialia 127 (2017) 498

Principal processing routes of Nd-Fe-B magnets

based on coarse grained and nanocrystalline powders

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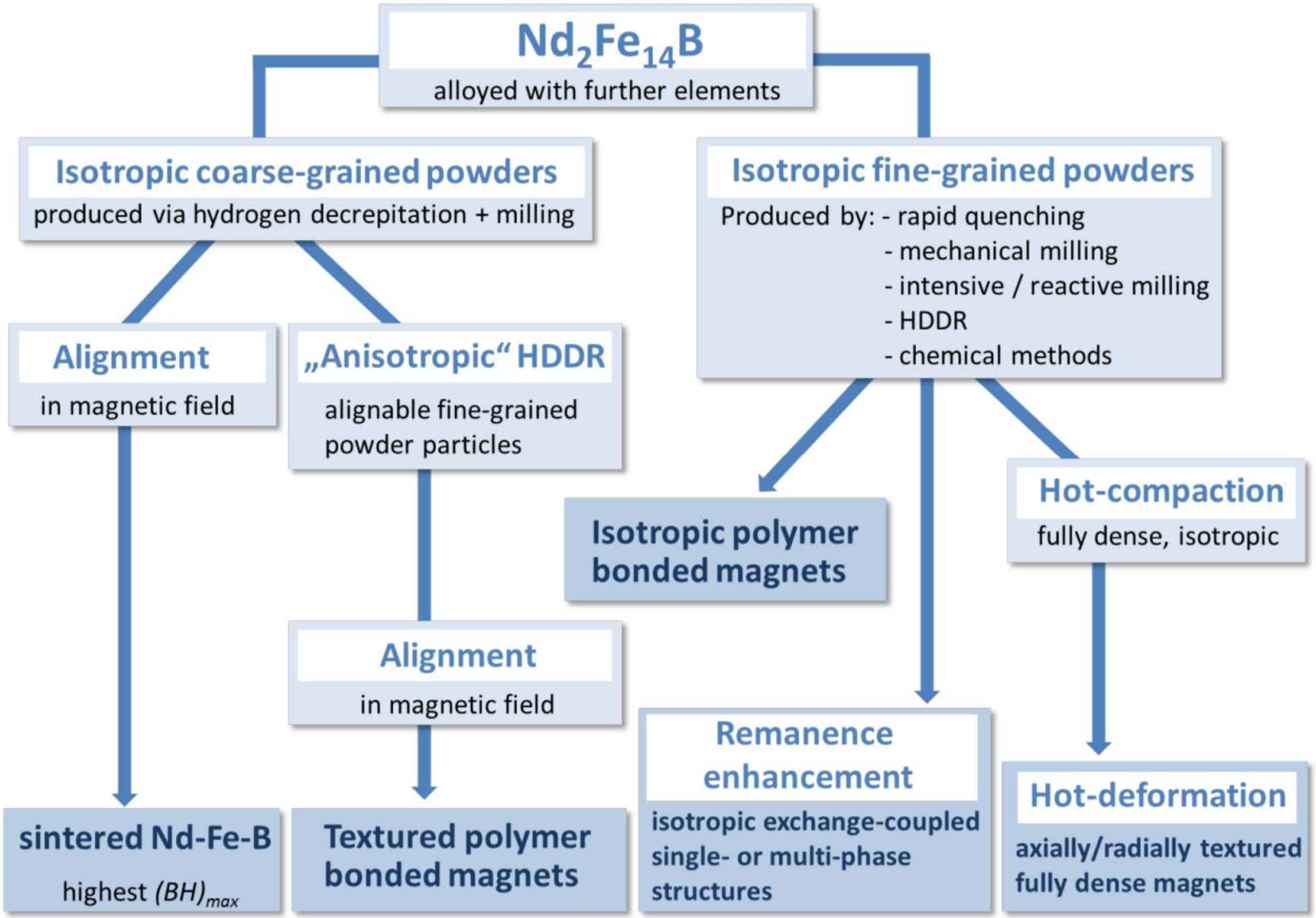
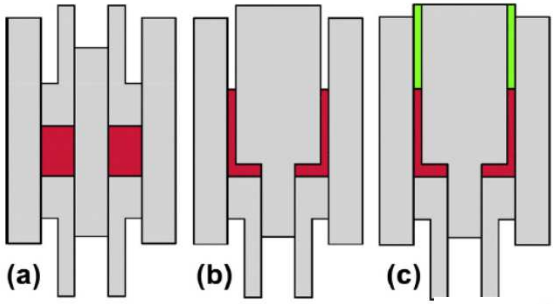
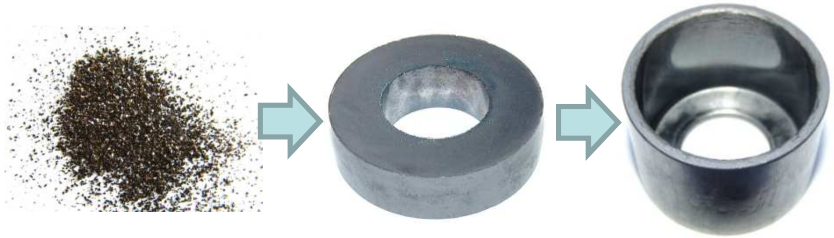
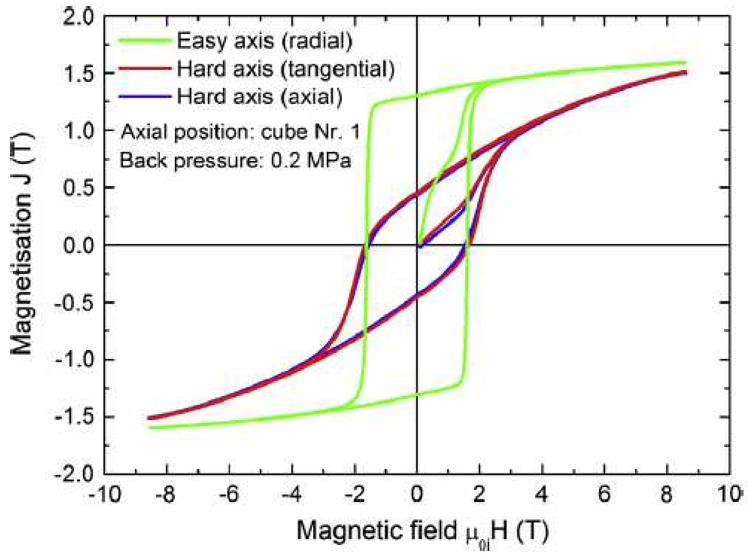


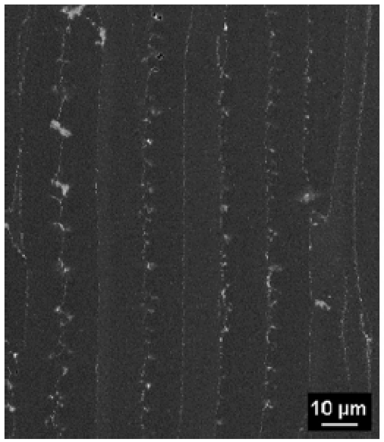
K.-H. Müller, S. Sawatzki, R. Gauss and O. Gutfleisch, Permanent magnetism, in Springer Handbook of Magnetism, ed. by J.M.C. Coey and S. Parkin, in preparation.

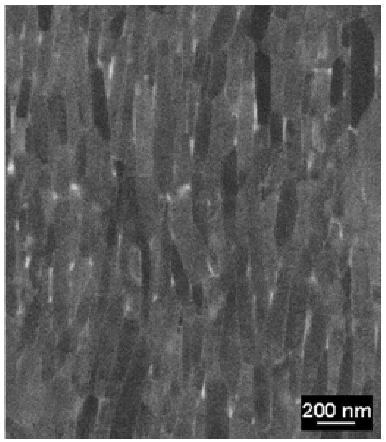
Net-shape and crack-free production of Nd–Fe–B magnets by hot deformation

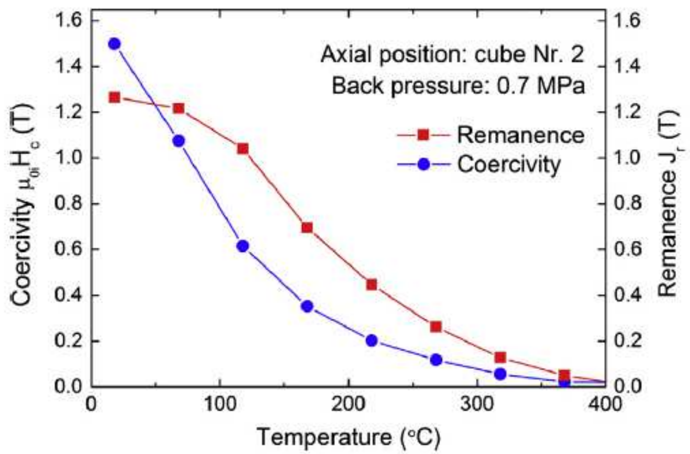




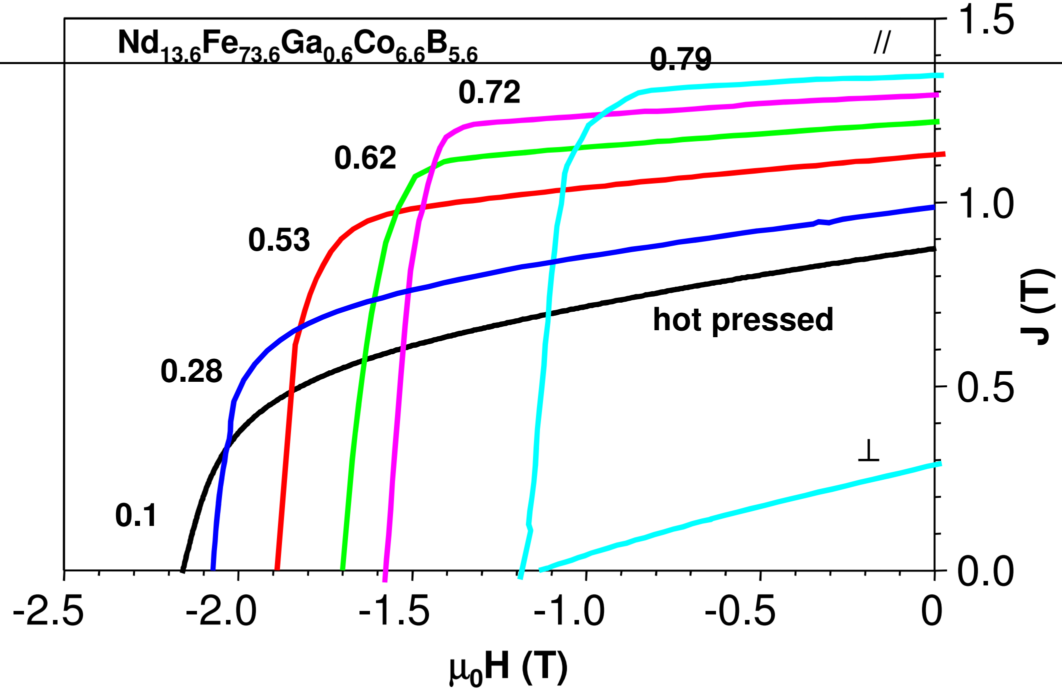


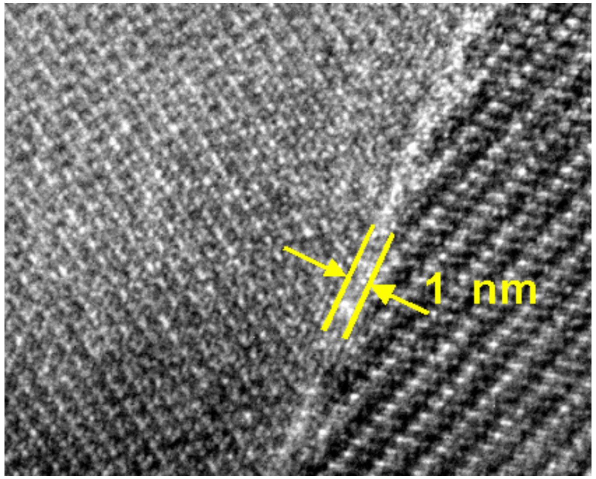


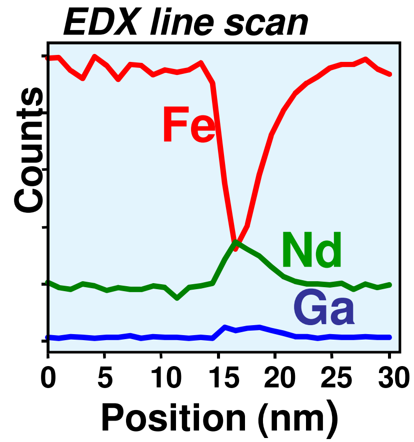


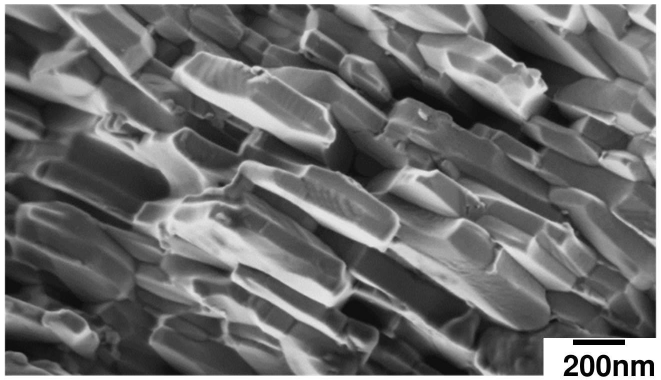


Texture in fine grained NdFeB magnets

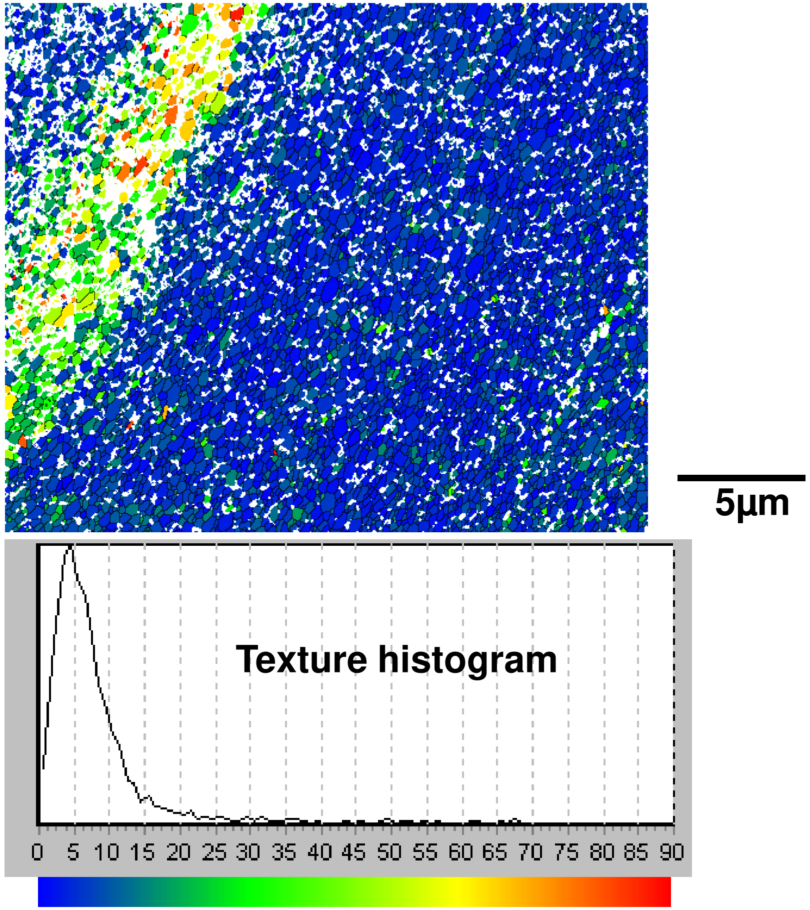


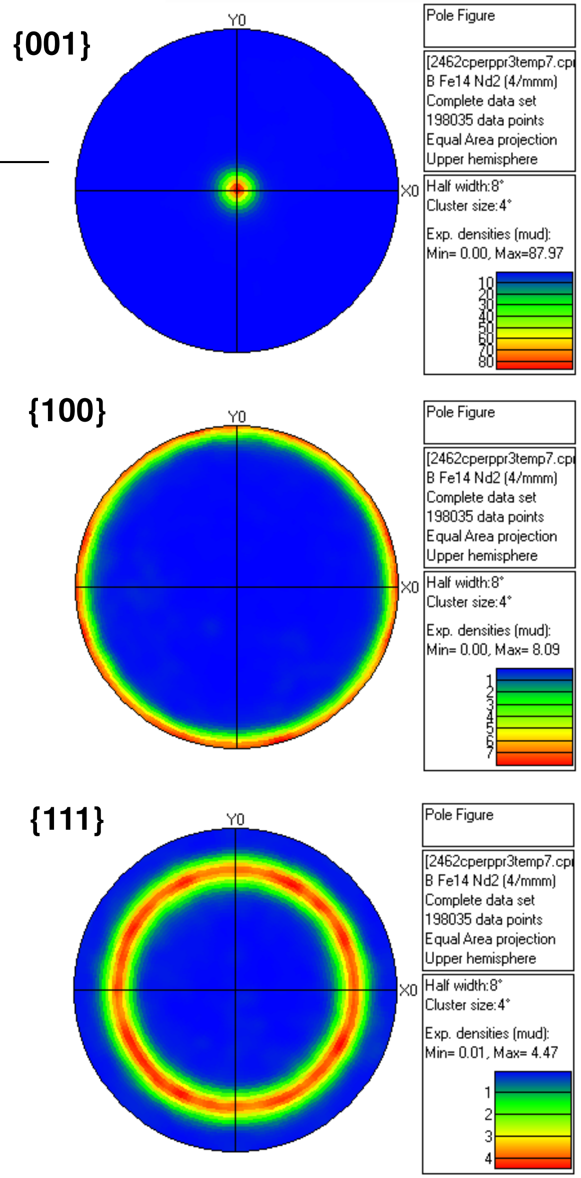






Texture in fine grained NdFeB magnets

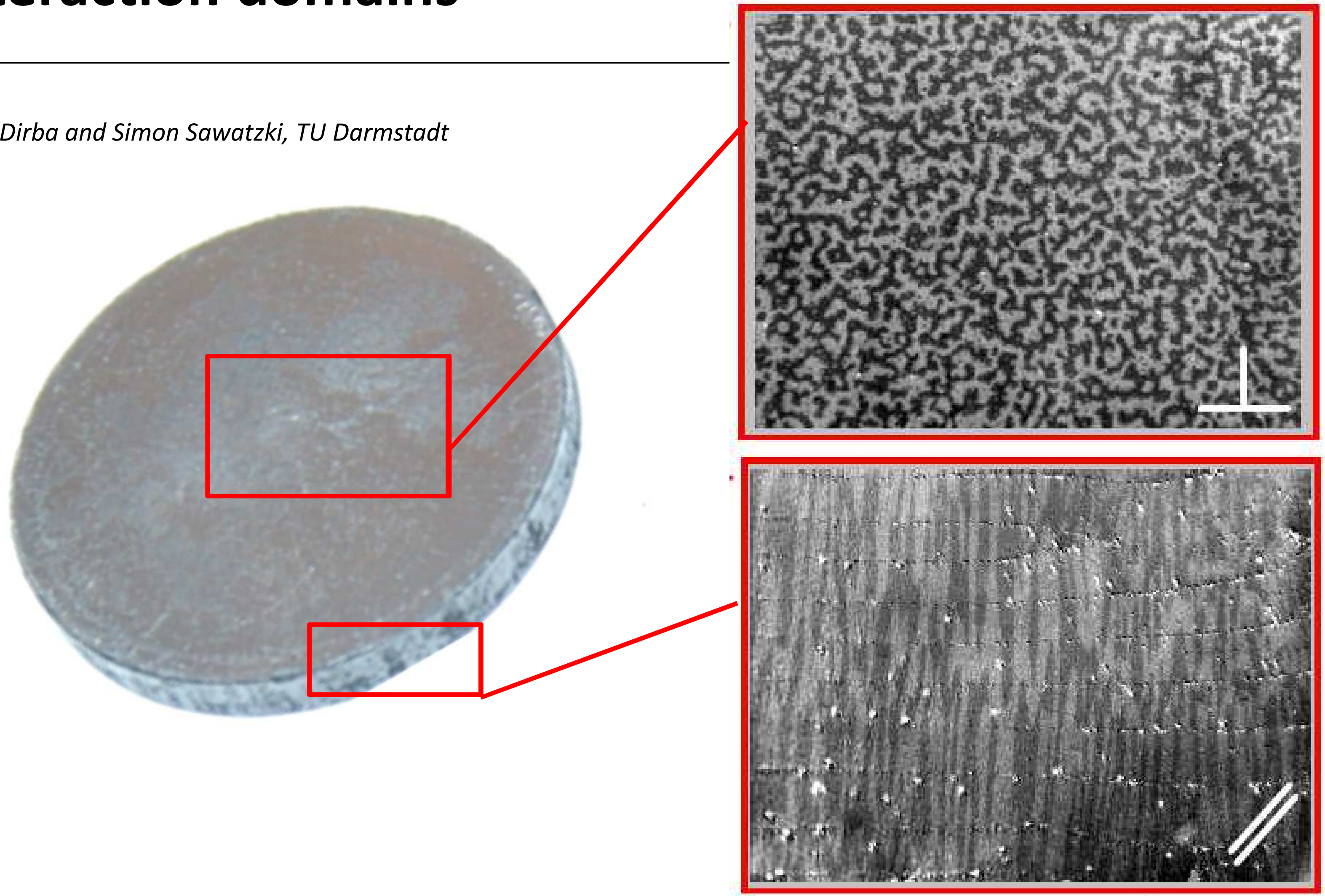




K. Khlopkov, O. Gutfleisch, D. Hinz, K.-H. Müller, L. Schultz, J. Appl. Phys. 102, 023912 (2007)

Interaction domains

Imants Dirba and Simon Sawatzki, TU Darmstadt

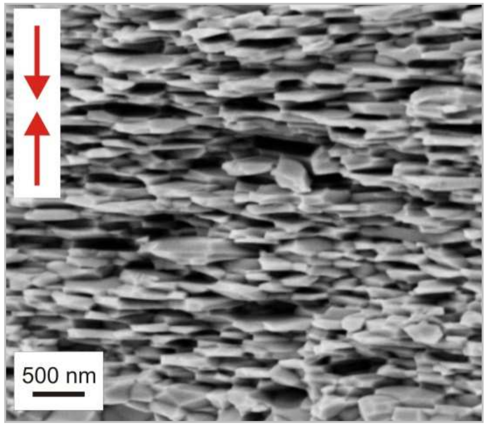


K. Khlopkov, O. Gutfleisch, D. Hinz, K.-H. Müller, L. Schultz, J. Appl. Phys. 102, 023912 (2007)

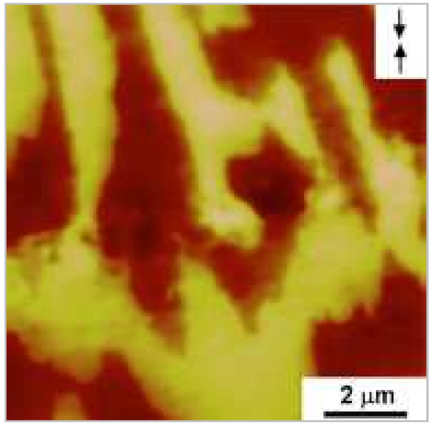
90μm

Interaction domains

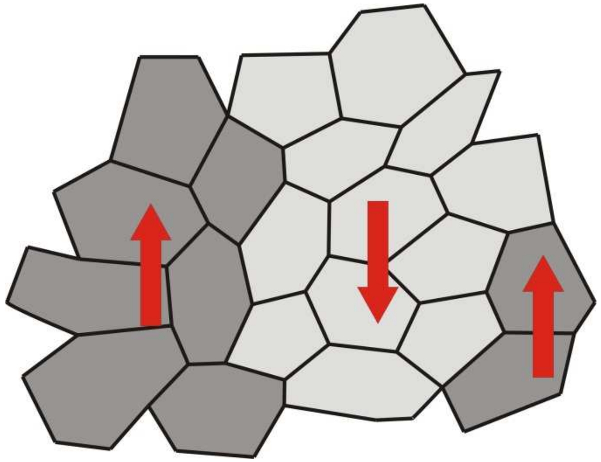
in die-upset magnets consisting of only melt-spun NdFeB ribbons



fractured surface:
plate-like grains with thickness of 100…200 nm and lateral expansion of 400…500 nm



MFM picture of interaction domains in die-upset NdFeB magnet



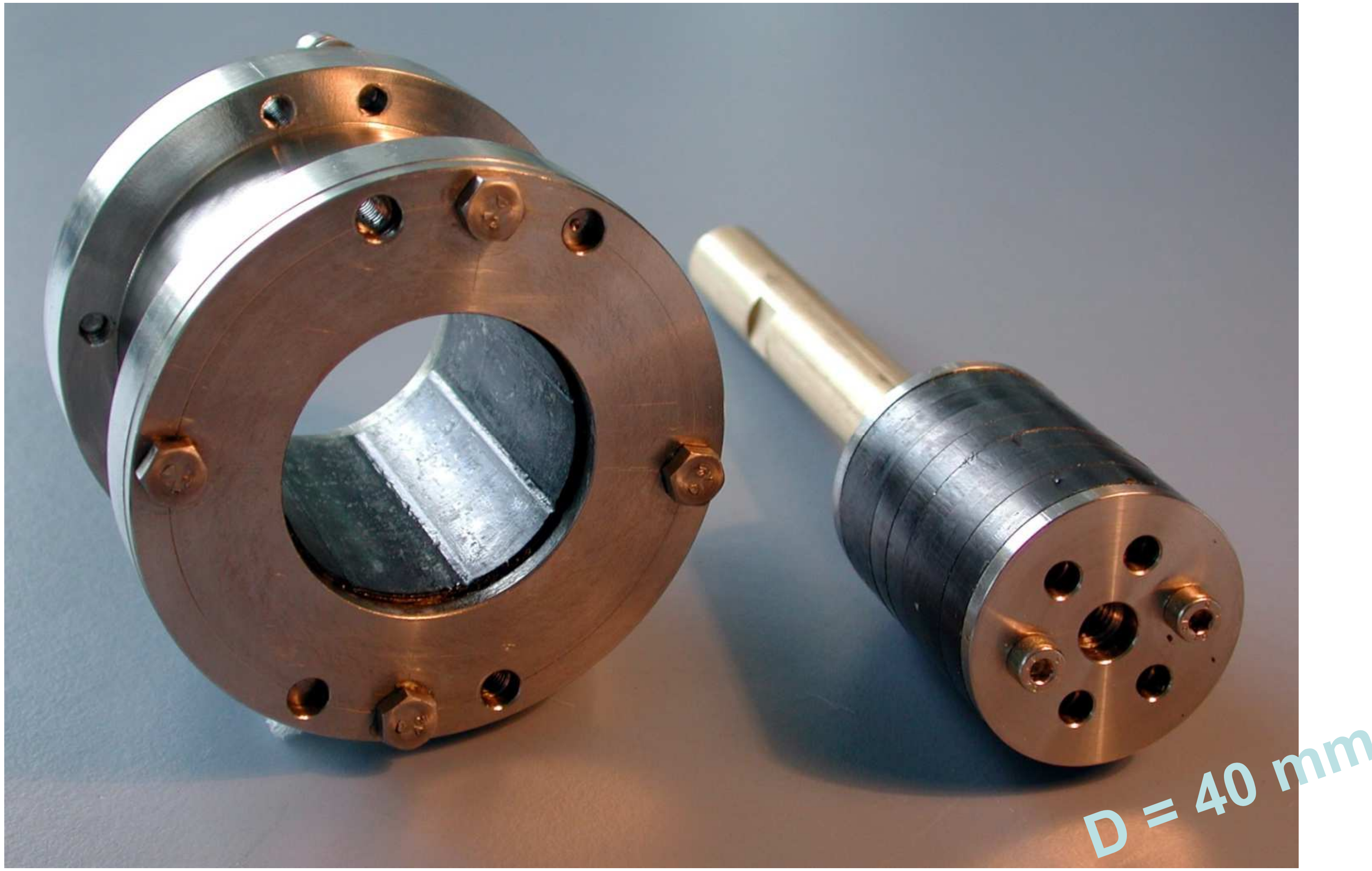
interaction domains encompass several grains

D. J. Craik and E. D. Isaac, Proc. Phys. Soc. 76, 160 (1960)

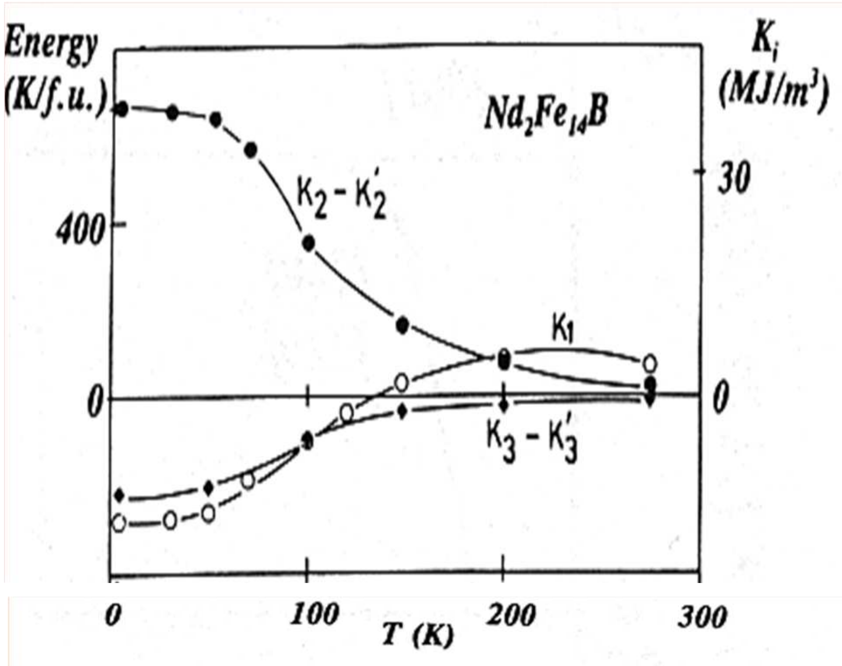
L. Folks, R. Street, R.C. Woodward, Appl. Phys. Lett. 65 (7), (1994)

K. Khlopkov, O. Gutfleisch, D. Hinz, K.-H. Müller, L. Schultz, J. Appl. Phys. 102, 023912 (2007)

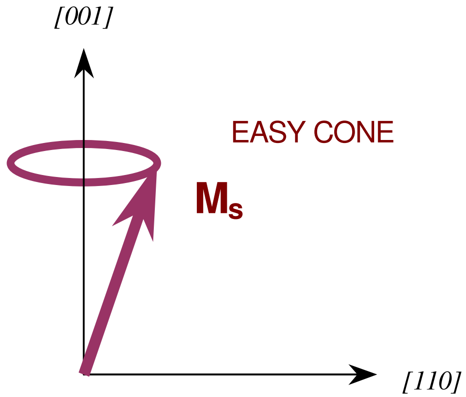
Bearings with superconducting YBCO and hard magnetic PrFeB

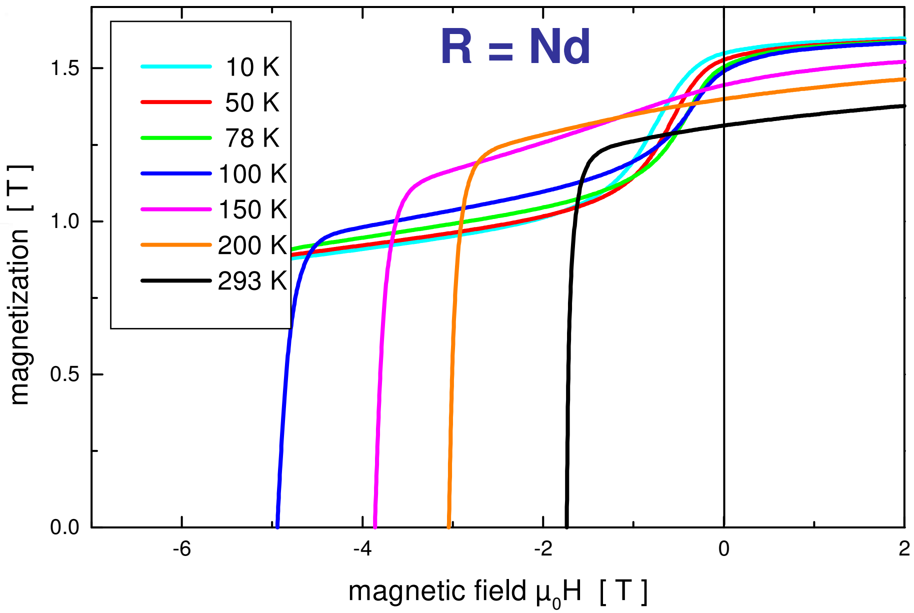


Spin reorientation in $Nd_2Fe_{14}B$ for T < 135 K



Anisotropy constants of
$Nd_2Fe_{14}B$
in dependence on temperature

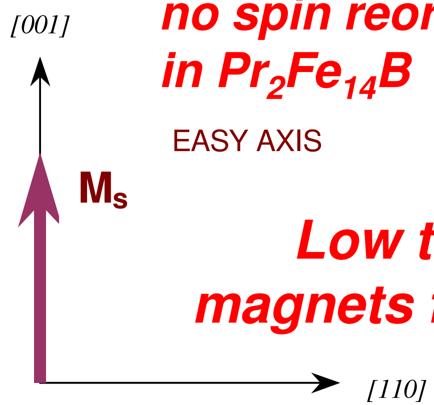




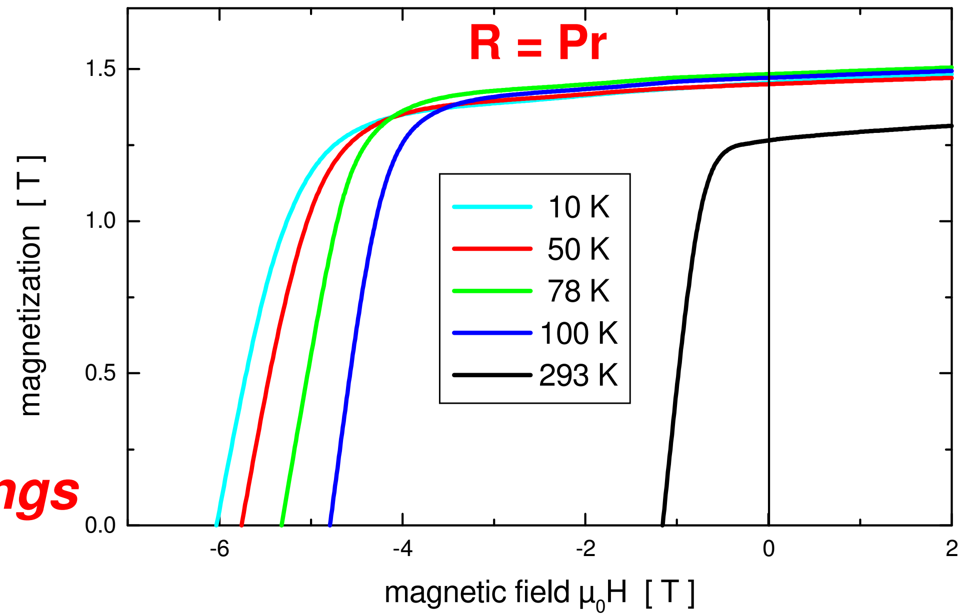
$Nd_2Fe_{14}B$ vs. $Pr_2Fe_{14}B$

Compound	T_C (K)	μ_0H_A (T)	K_1 (MJm^{-3})	μ_0M_S (T)	$(BH)_{max}$ (kJm^{-3})	δ_w (nm)	d_c (nm)
$Nd_2Fe_{14}B$	585	6.7	4.9	1.60	516	4.2	300
$Pr_2Fe_{14}B$	565	8.7	5	1.56	484	~ 4	~300

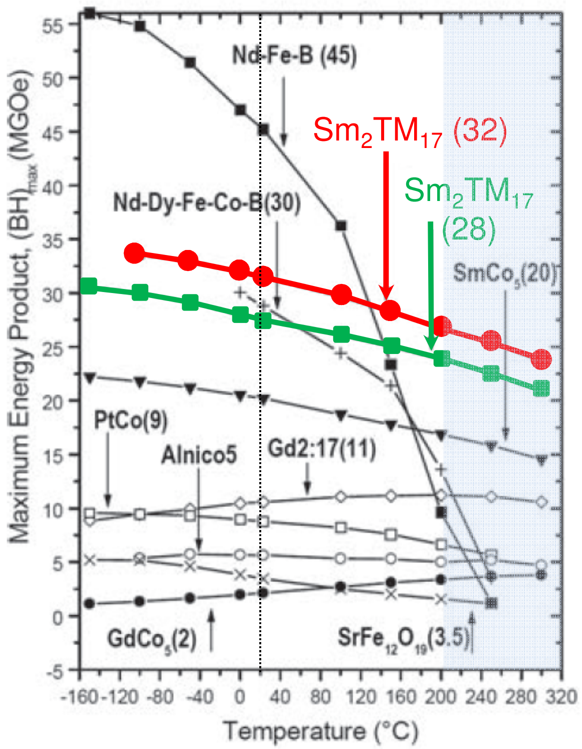
no spin reorientation in $Pr_2Fe_{14}B$

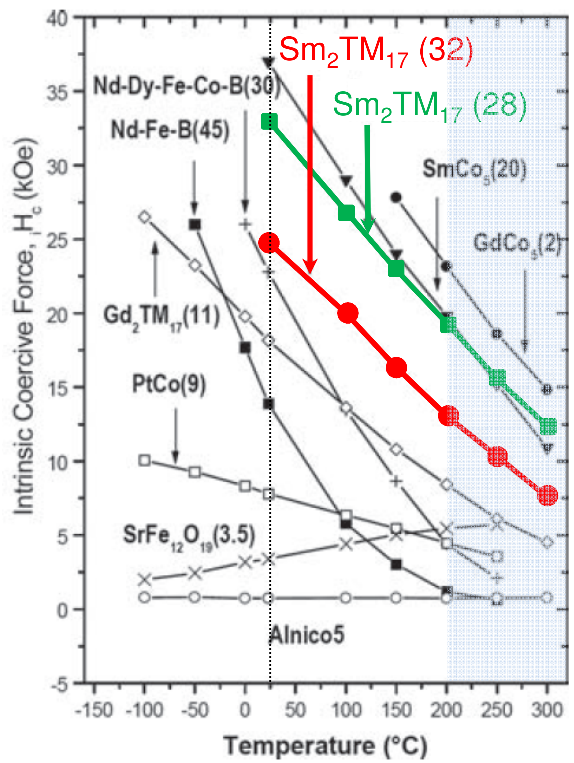


Low temperature magnets for SC bearings



Sm2TM17 pinning magnets





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

K. J. Strnat *et al.* J. Magn. Magn. Mater. 100 (1991) 38.
R. K. Mishra *et al.* J. Appl. Phys. 52 (1981) 2517.
Y. Horiuchi *et al.* Mater. Trans. 55 (2014) 482.

	Sm_2Co_{17}-type sintered magnet	Nd-Fe-B type sintered magnet
β (%/℃)	≈ -0.2 to -0.3	≈ -0.45 to -0.60

Sm2TM17 pinning magnets

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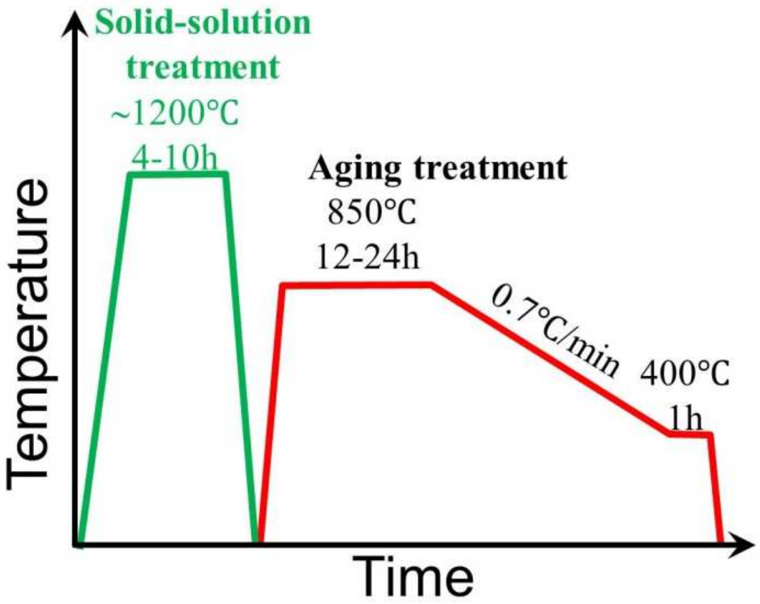
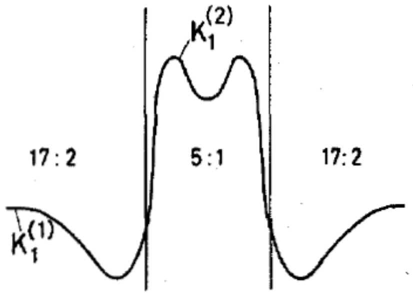
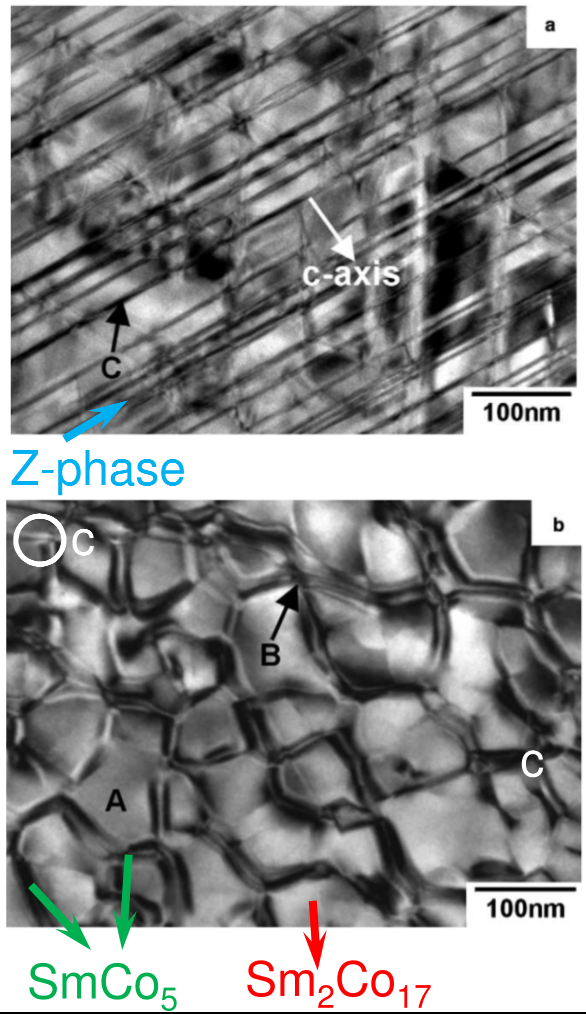


Pinning strength of 1:5 cell boundary



Kronmuller *et al.* IEEE Trans. Magn. 20 (1984) 1569.

O. Gutfleisch *et al.* Acta Mater. 54 (2006) 997.



Atomic-Scale Characterisation and modelling

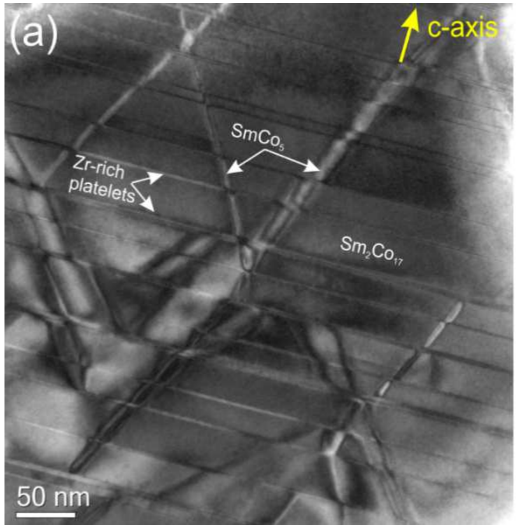
TEM and analysis of SmCo pinning magnet

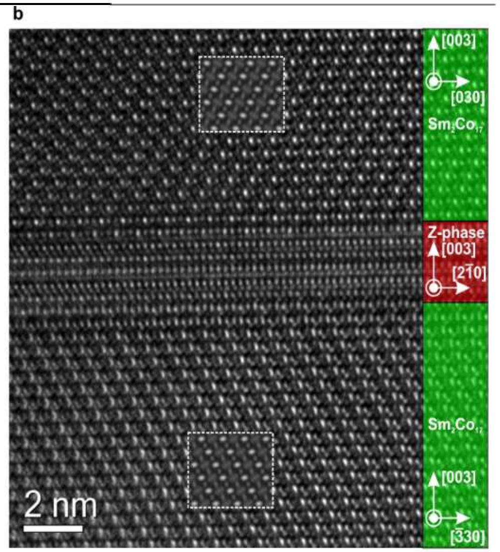
Increased Cu at $SmCo_5$ cell-boundary-phase

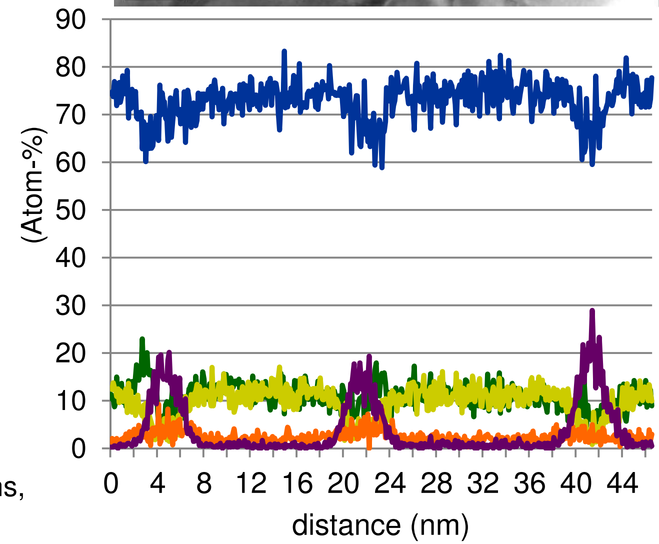
VIDEO **3D Atomprobe**

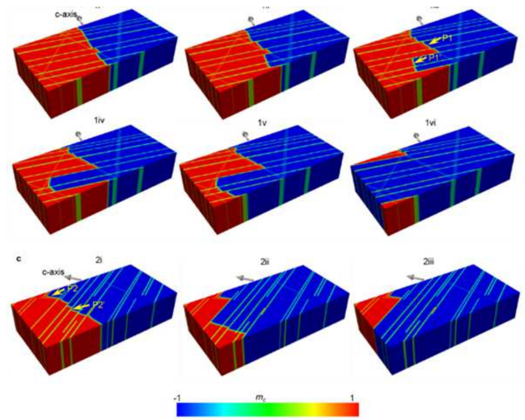
Zr rich platelets

40 nm Sm_2Co_{17}









Nature Communications, accepted

Additional properties for application

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Table 6. Comparison of the specific electrical resistivity ρ and the temperature coefficients of remanence α and coercivity β. The data are taken from (1) [9], (2) [197], (3) [87], (4) [198], (5) [199] and (6) [200]

material	ρ ($\mu\Omega m$)	α (%/K)	β (%/K)
$SrFe_{12}O_{19}$ sintered(1)	10^8	-0.20	0.45
$SrFe_{12}O_{19}$ polymer bonded(1)		-0.02	0.45
Alnico 5 cast(1)	0.5	-0.02	0.03
$SmCo_5$ sintered(1,2)	0.6	-0.04	-0.31
Sm_2Co_{17} sintered(1,2)	0.9	-0.03	-0.20
$Nd_2Fe_{14}B$ sintered(1,3)	1.5	-0.13	-0.60
$Nd_2Fe_{14}B$ die-upset(4,5)	1.2	-0.09	-0.60
$Nd_2Fe_{14}B$ HDDR polymer bonded(1,6)	200	-0.10	-0.55

K.-H. Müller, S. Sawatzki, R. Gauss and O. Gutfleisch, Permanent magnetism,
in Springer Handbook of Magnetism, ed. by J.M.C. Coey and S. Parkin, in preparation.

REE Recycling

The Integration of Recycling into the REE Supply Chain

Global estimates of end-of-life **recycling** rates for 60 metals and metalloids (2008)

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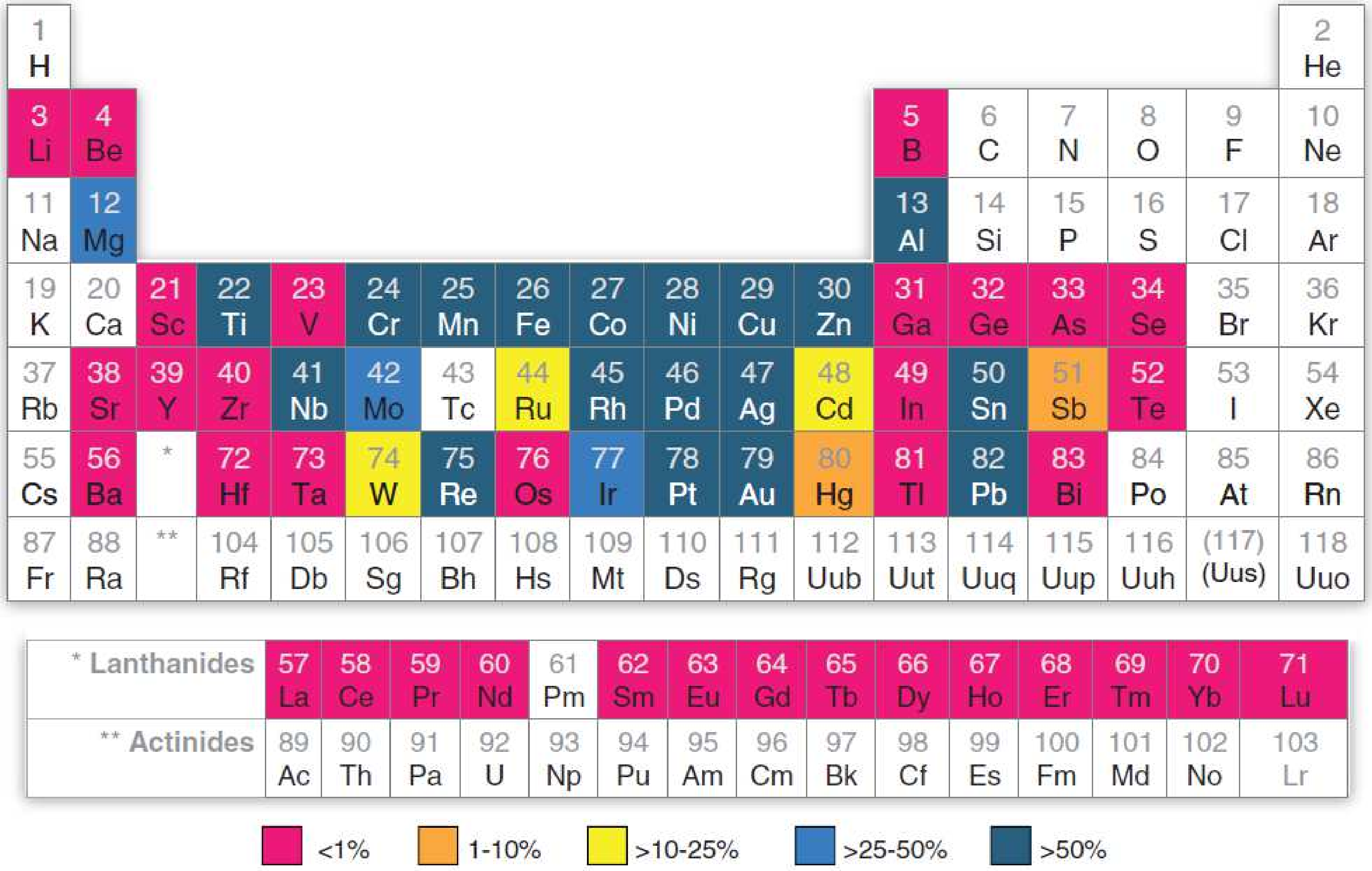
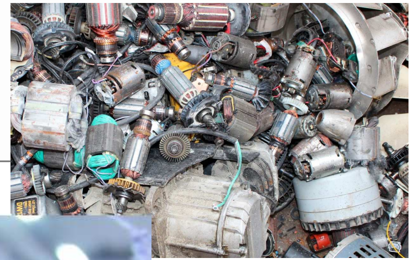
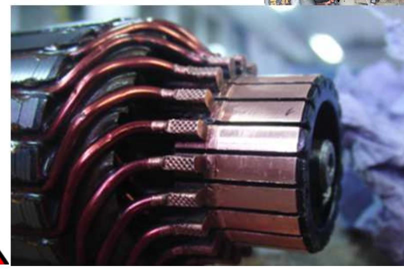


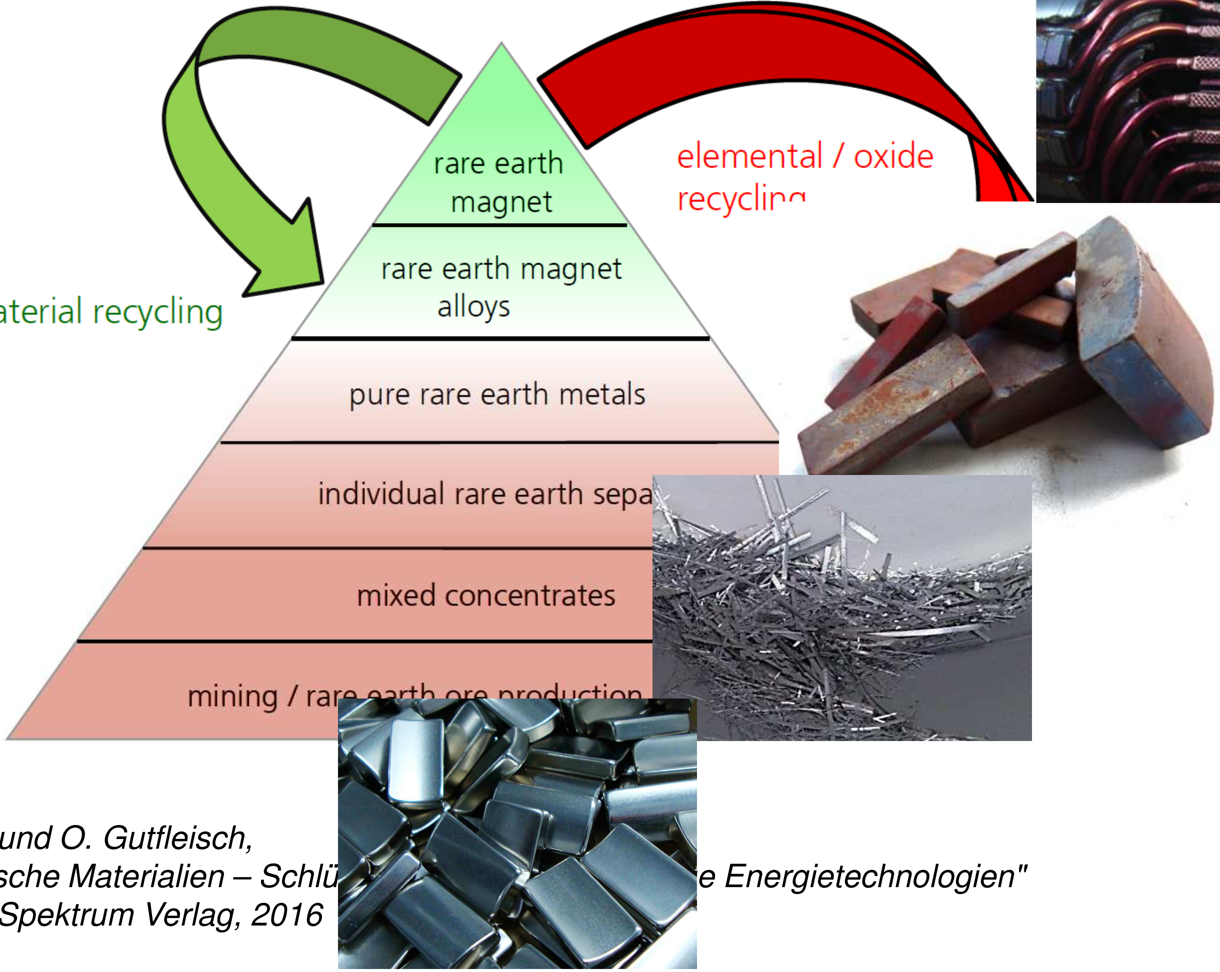
T. E. Graedel et al., J. Ind. Ecol. 15, 355 (2011).

Rare earth value chain for magnets

Advanced Functional Recycling



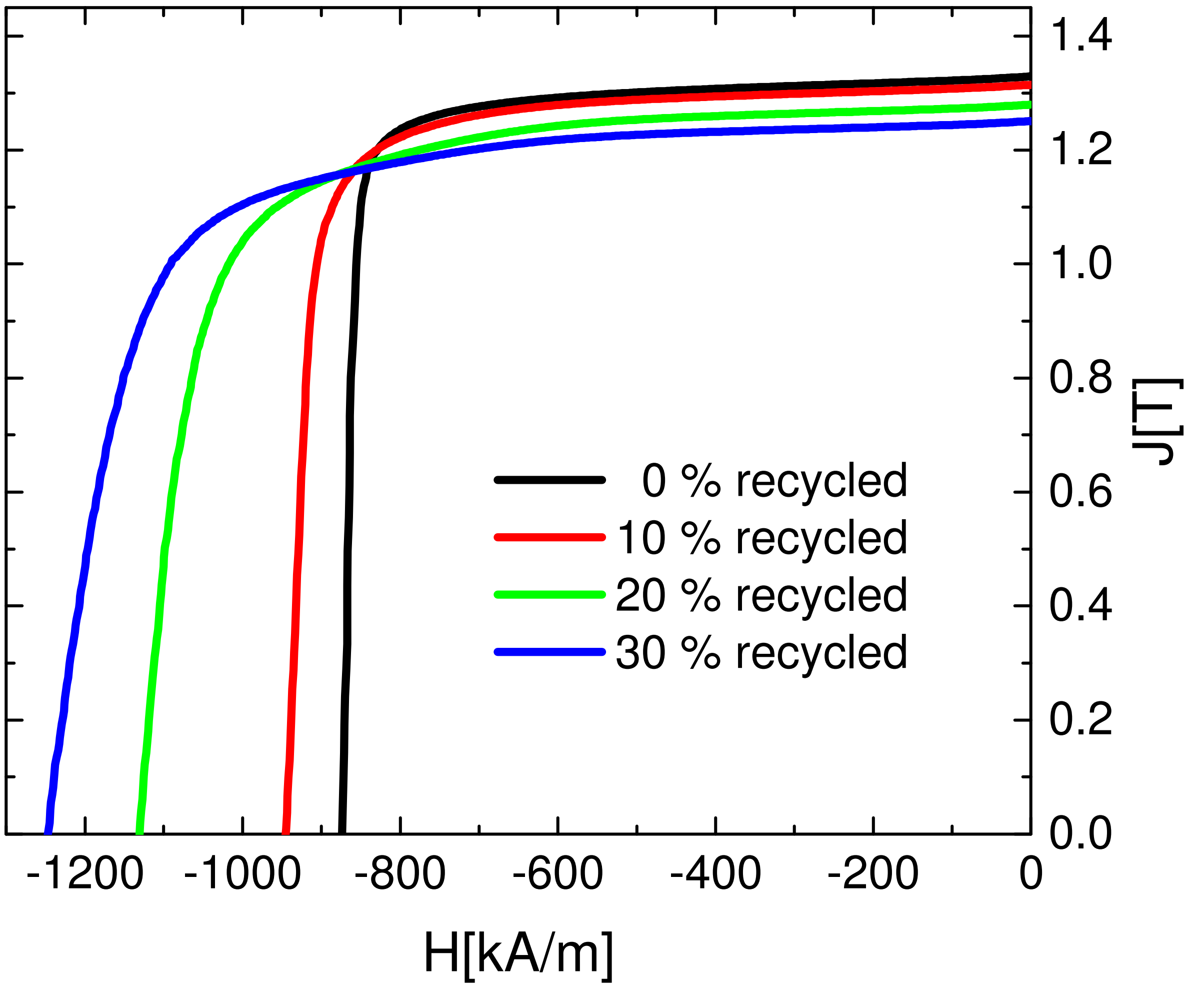




Urban mine to market

R. Gauß und O. Gutfleisch,
„Magnetische Materialien – Schlü e Energietechnologien"
Springer Spektrum Verlag, 2016

Anisotropic sintered NdFeB magnets with X % recycled material

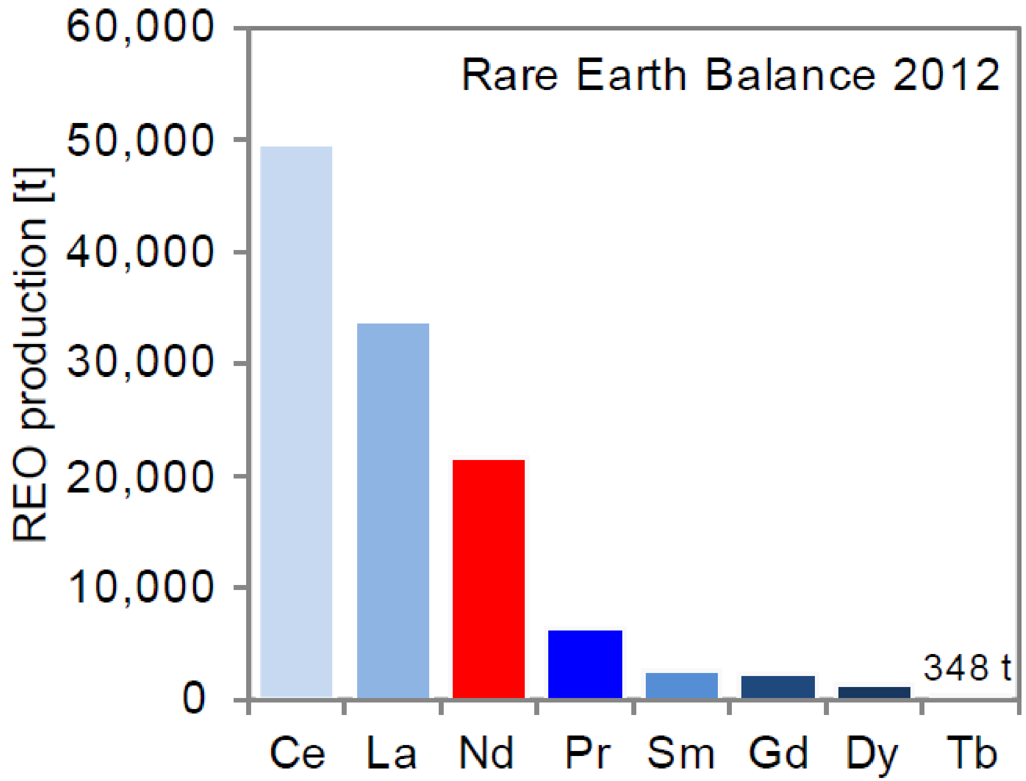


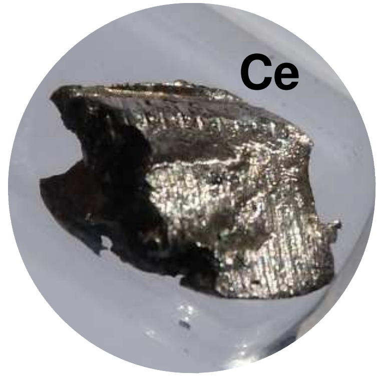
Free rare earth or rare earth free magnets

Vision and reality

I Rare earth balance

Utilisation of earth abundant rare earths



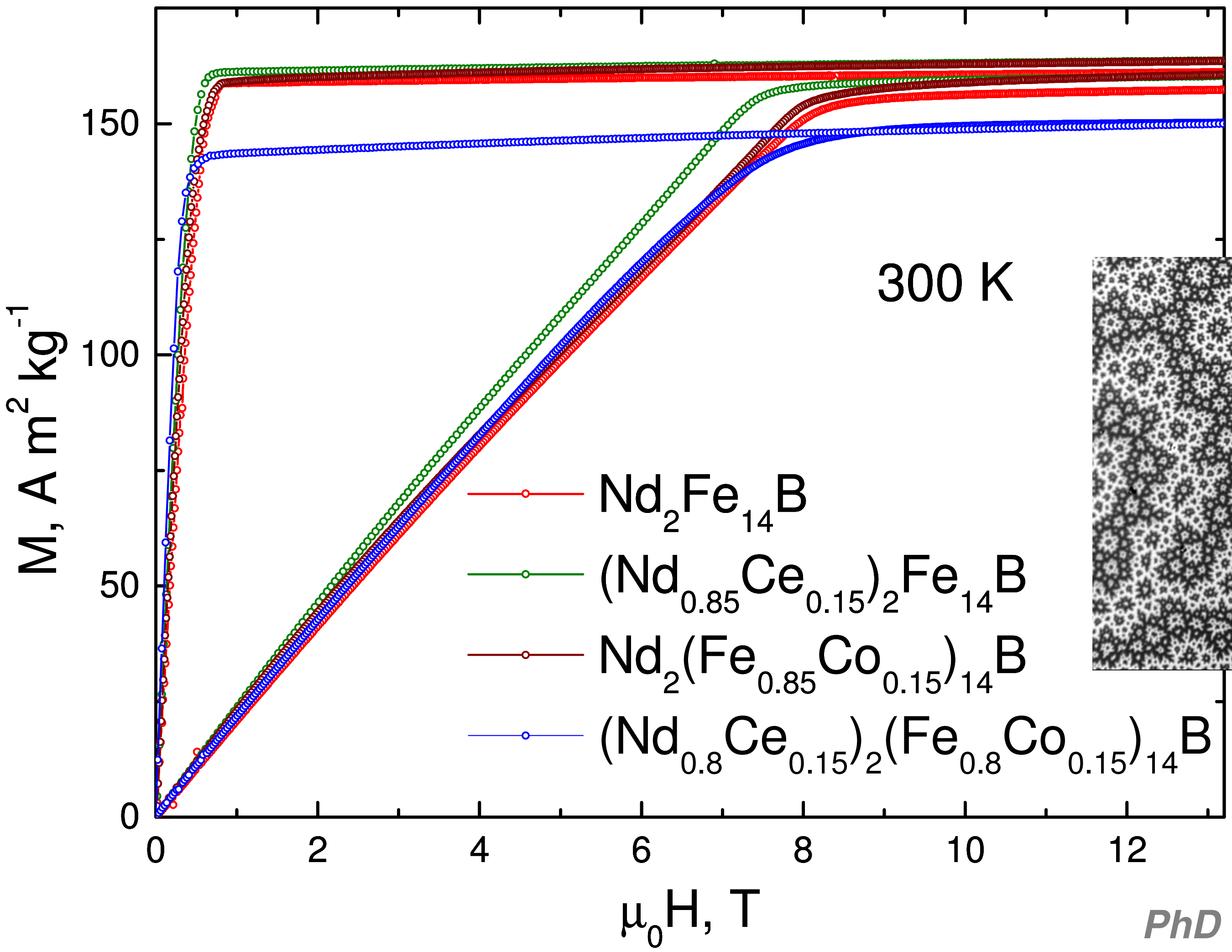


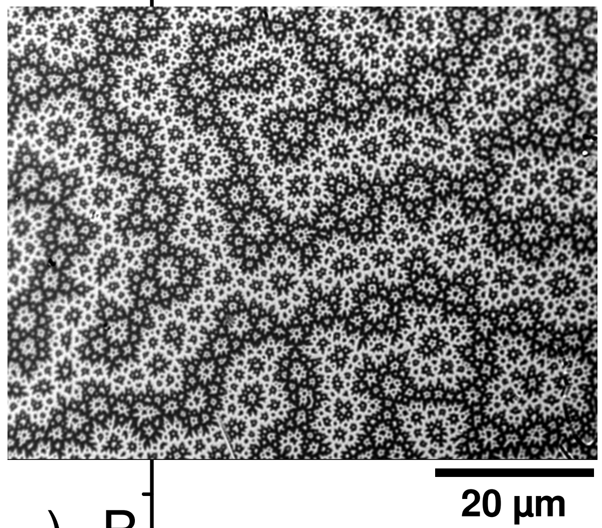
Production 2020: every kg Nd yields 1.5 kg La and 2.5 kg Ce

China FOB 4Q2016: Nd US$ 40, La US$ 2, Ce US$ 1, Dy US$ 185, Tb US$ 425

EU 2015: Critical raw materials for the EU
Gauss and Gutfleisch, The resource basis of magnetic refrigeration, J. of Industrial Ecology, 2016.
images: http://images-of-elements.com/ prices: metal pages

$(Nd_{1-x}Ce_x)_2(Fe_{1-y}Co_y)_{14}B$ single crystals





PhD work Bahar Fayyazi

Free Rare Earth Magnets using Ce and La

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- Target compositions:

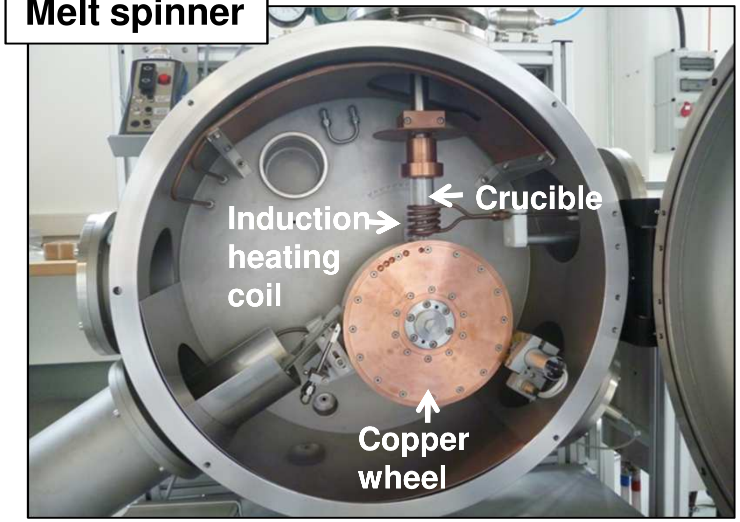
Melt-spinning → $(Nd_{1-x}Ce/La_x)_{13.6}Fe_{73.6}Co_{6.6}Ga_{0.6}B_{5.6}$ → hot-pressing/deformation

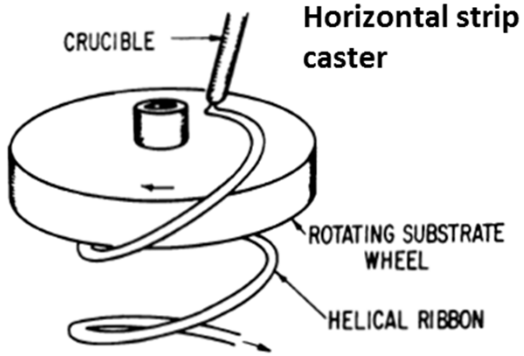
Strip-casting → $(Nd_{1-x}Ce_x)_{15}Fe_{79}B_6$ → H_2 treatments (HD, HDDR)

- Phase composition, Microstructure, Magnetic properties

Arc melter

Melt spinner





PhD work Iuliana Poenaru

EREAN
EU FP7 Marie-Curie Initial Training Network

IOP Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **26** (2014) 064205 (5pp) doi:10.1088/0953-8984/26/6/064205

Towards high-performance permanent magnets without rare earths

M D Kuz'min[1], K P Skokov[1], H Jian[1], I Radulov[1] and O Gutfleisch[1,2]

- Achieving a very strong magnetic anisotropy in a 3d material is a difficult, but not an impossible task.
- It is difficult because there is no general recipe (necessary condition) for a strong anisotropy in a band magnet.
  - **Induced non-cubicity**
  - **Volume expansion**
  - **3d–5d binaries**
  - **Searching for new compounds**

Ways of enhancing magnetocrystalline anisotropy in 3d magnets:

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1. **Induced non-cubicity**
2. **Volume expansion**
3. **3d–5d binaries**
4. **Searching for new compounds**

Avoidance of cubic structures is a general principle of searching for strongly anisotropic magnetic materials.
Bcc Permendur is unsuitable for permanent magnet applications. Fe–Co alloys are of interest, provided the lattice symmetry is artificially reduced to e.g. tetragonal.
As a more general case one can regard the body centered tetragonal lattice, the so-called tetragonal Bain path.
The shape of such a lattice is described by a single parameter — the aspect ratio a/c. There are two special cases corresponding to the cubic symmetry: a/c=1 (body centered cubic) and a/c = $\sqrt{2}$ (face centered cubic).
The second-order anisotropy energy must vanish at both points. Therefore, there should be a maximum in between, at a/c ~ 1.2.

J. Phys.: Condens. Matter 26 (2014) 064205

Magnetic refrigeration

From fundamentals to application

Magnetocaloric refrigeration

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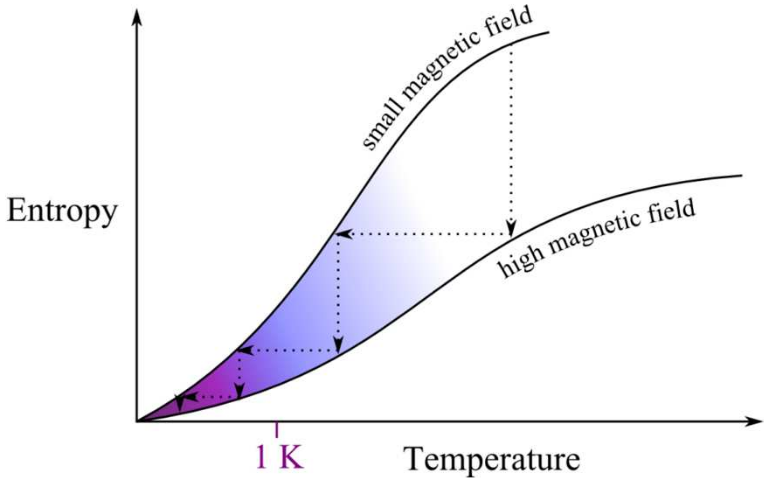
- First described in 1917 by P. Weiss
- Used to reach temperatures below 1 K
  → Nobel Prize for Chemistry 1949
- Todays objective:
  Magnetic refrigeration close to room temperature



- 20% of worldwide consumption of electricity caused by refrigeration and air-conditioning

Magnetic refrigeration as an alternative ?

Potentially higher efficiency than conventional technology but still many problems to be solved

COMPARISON OF COOLING TECHNOLOGIES

Technology	Conventional gas compression	Gas absorption	"Peltier" electric coolers	Thermoacoustic coolers	Magnetic cooling engine
Change of state	Liquid↔Gas	Liquid↔Gas	Electron↔ Hole states	High pressure gas↔Low pressure gas	Different magnetic states
Max. efficiency	**45%**[2]	30%[3]	<10%[4]	40%[5]	**60%**[6]

[2] www.coolchips.gi
[3] www.coolchips.gi, www.healthgoods.com
[4] F.J. DiSalvo, Science, **285** 703 (1999) and references therein
[5] D.L. Gardner and G.W. Swift, J. Acoust. Soc. Am., **114** 1905 (2003)
[6] C. Zimm et al., Adv. Cryog. Eng. **43** 1759 (1998)

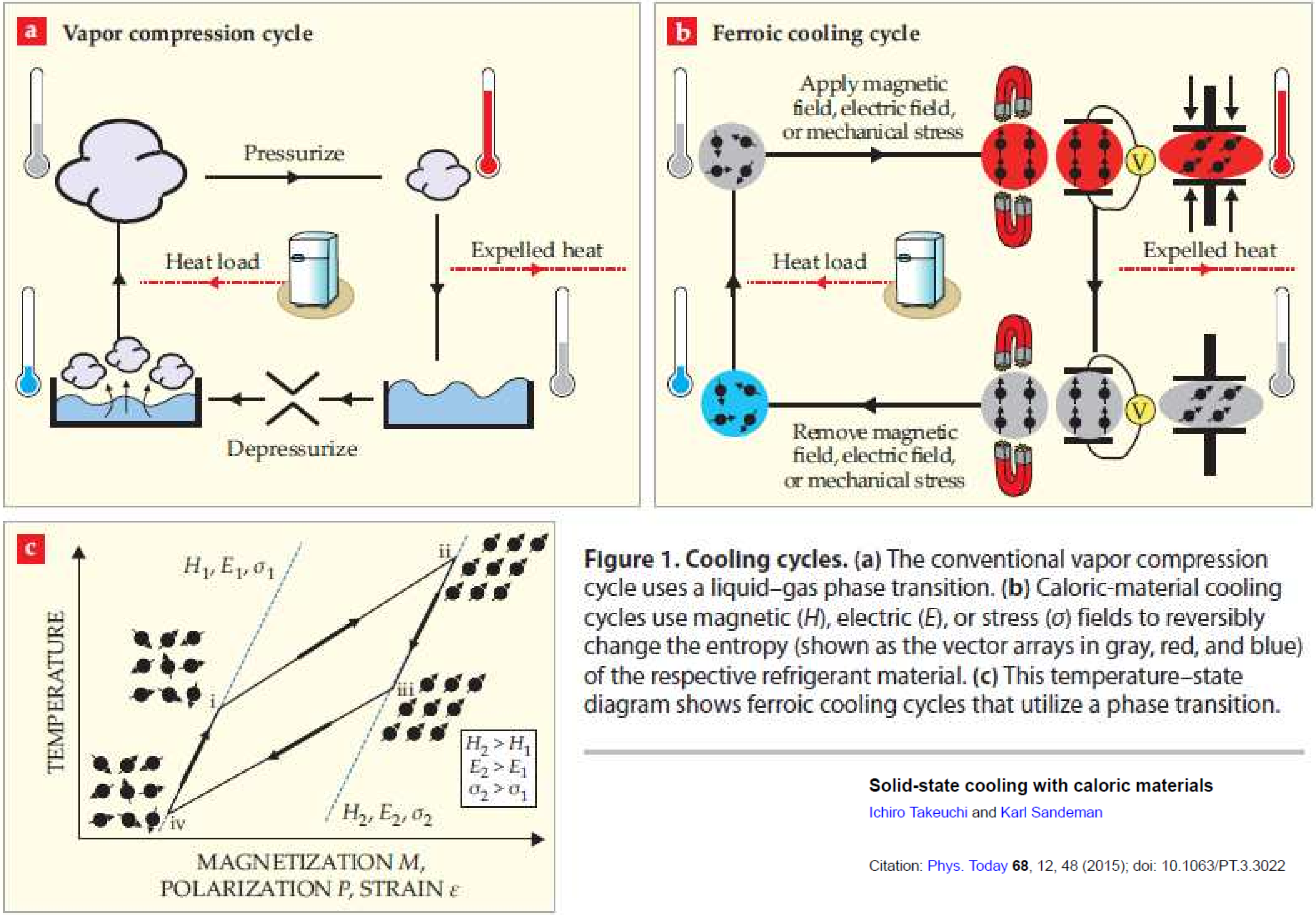


Figure 1. Cooling cycles. (a) The conventional vapor compression cycle uses a liquid–gas phase transition. **(b)** Caloric-material cooling cycles use magnetic (H), electric (E), or stress (σ) fields to reversibly change the entropy (shown as the vector arrays in gray, red, and blue) of the respective refrigerant material. **(c)** This temperature–state diagram shows ferroic cooling cycles that utilize a phase transition.

Solid-state cooling with caloric materials

Ichiro Takeuchi and Karl Sandeman

Citation: Phys. Today **68**, 12, 48 (2015); doi: 10.1063/PT.3.3022

The specific entropy *s* in a magnetocaloric material
is a combination of

- specific magnetic entropy $s^{(m)}$,
- specific lattice subsystem entropy $s^{(l)}$ and
- specific entropy of the conduction electrons $s^{(e)}$.

If we consider *s* as a function of *T* and H_0, it follows:

$$s(T,H_0) = s^{(\mathrm{m})}(T,H_0) + s^{(\mathrm{l})}(T,H_0) + s^{(\mathrm{e})}(T,H_0)$$

Magnetocaloric effect

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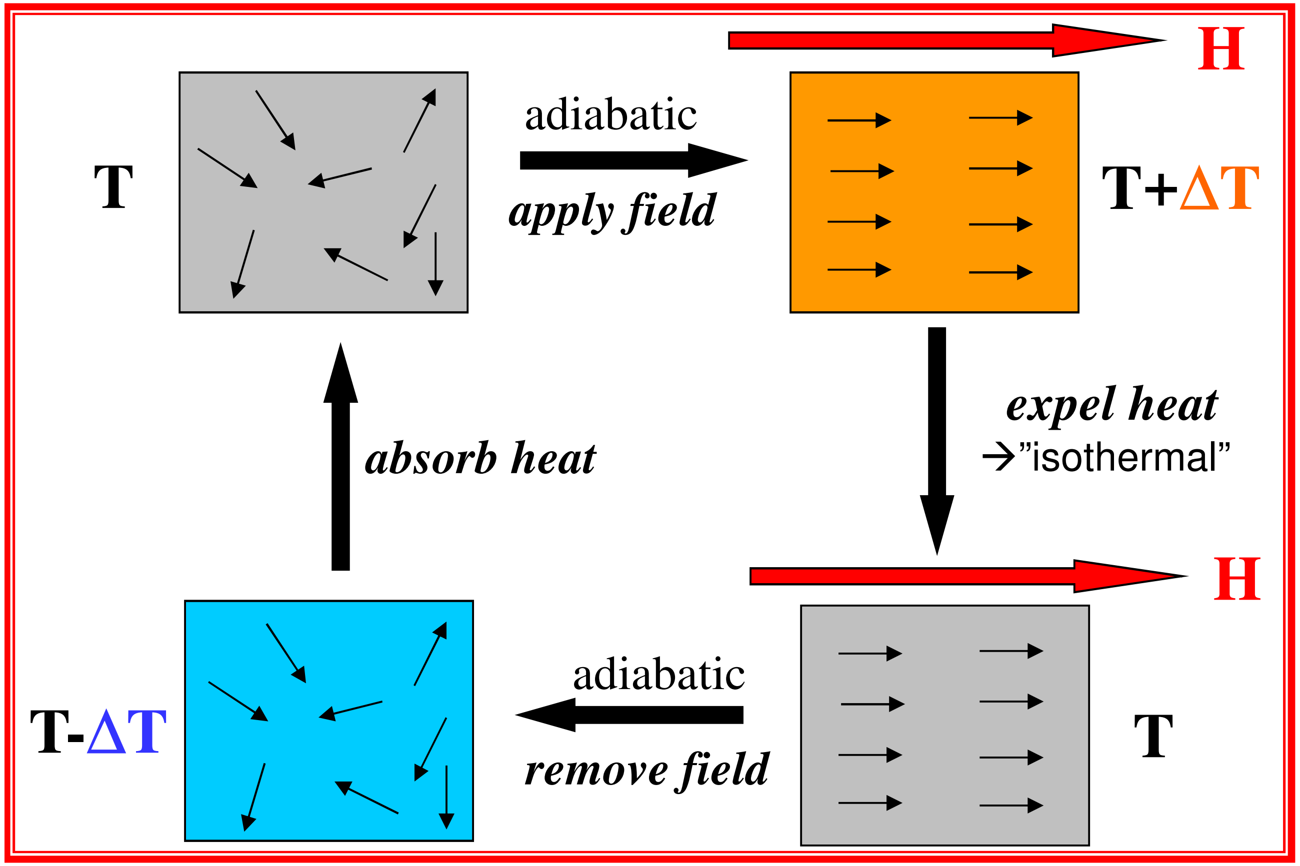


$$\Delta S_m = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH$$

$$\Delta T = -\int_0^H \frac{T}{C_{H,p}} \left(\frac{\partial M}{\partial T}\right)_{H,p} dH$$

Large H

Large $\left(\frac{\partial M}{\partial T}\right)_H$

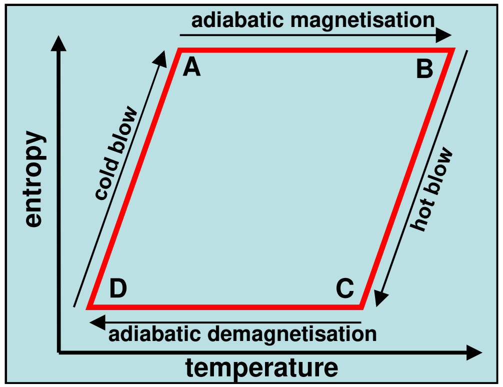
Small $C_{H,p}$

} **Large MCE**

- **Maxwell equation applies to equilibrium thermodynamics**
- **coupled magnetostructural transitions, related latent heat, hysteresis**
- $\Delta S_{iso} = \Delta S_{mag} + \Delta S_{lat} + \Delta S_{el}$

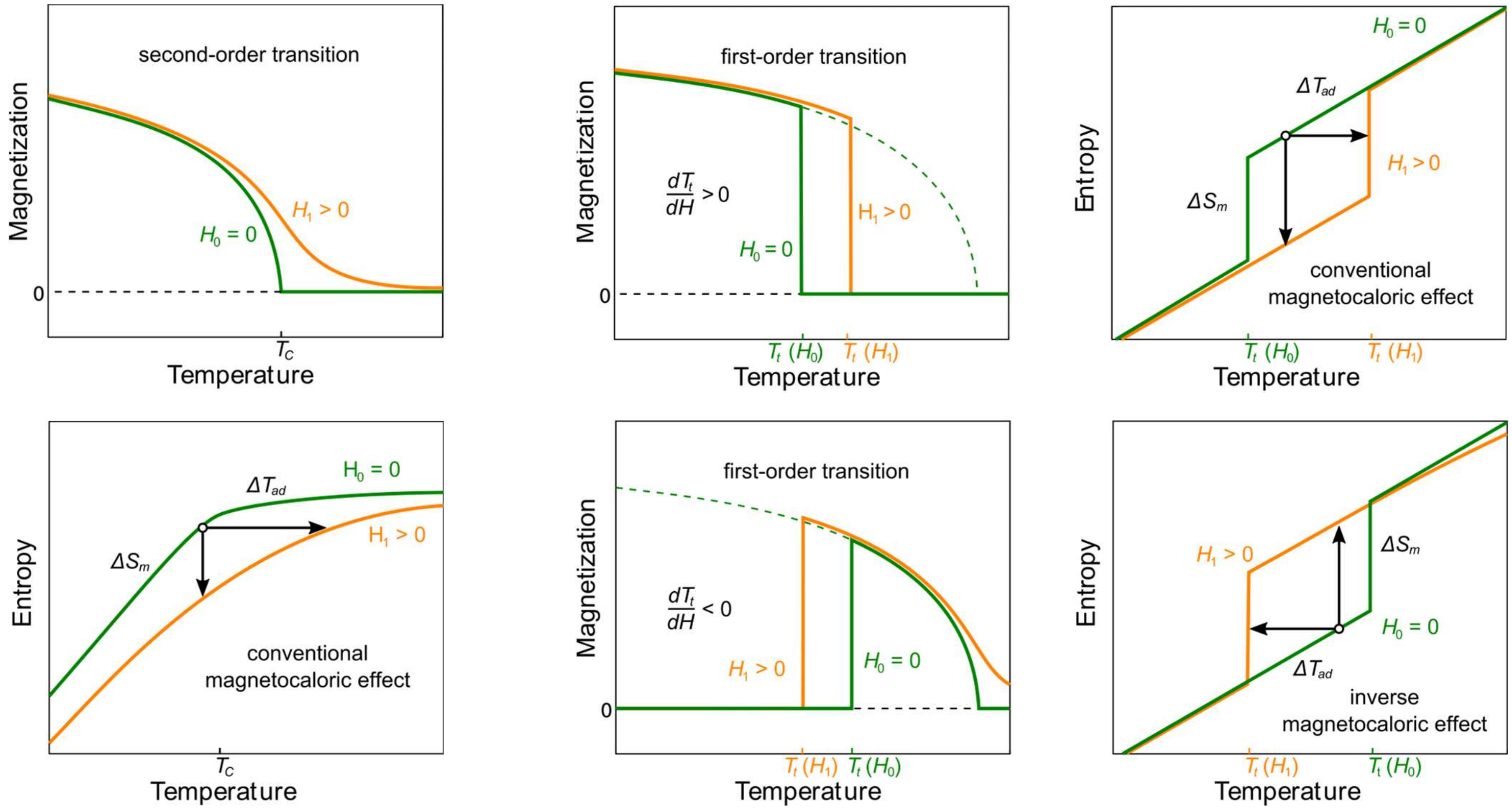
Active Magnetic Regenerator

VIDEO AMR animation



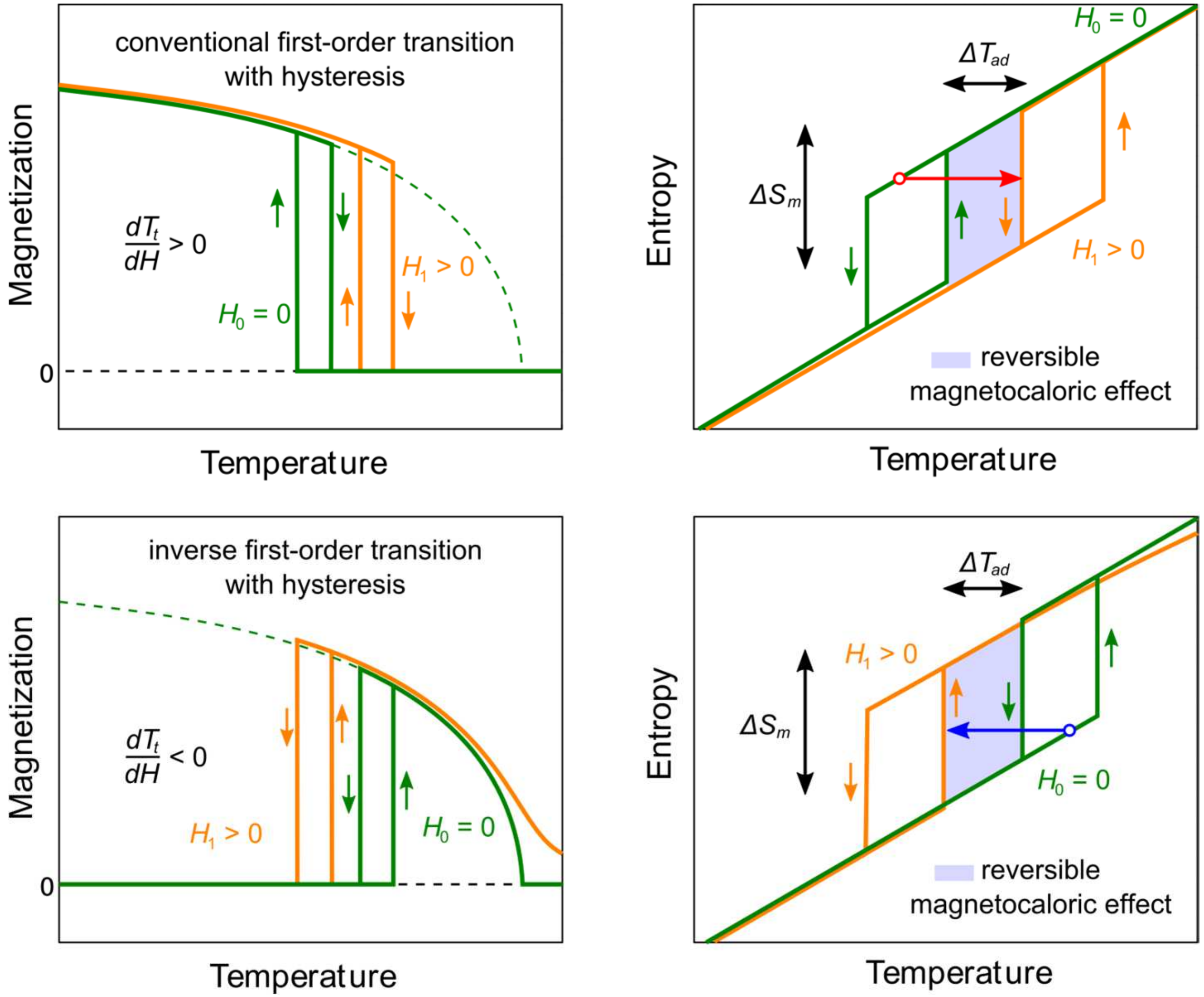
AMR first proposed by J.A. Barclay,1982

Classification of MCE materials I



Gutfleisch et al., Phil. Trans. R. Soc. A, (2016)

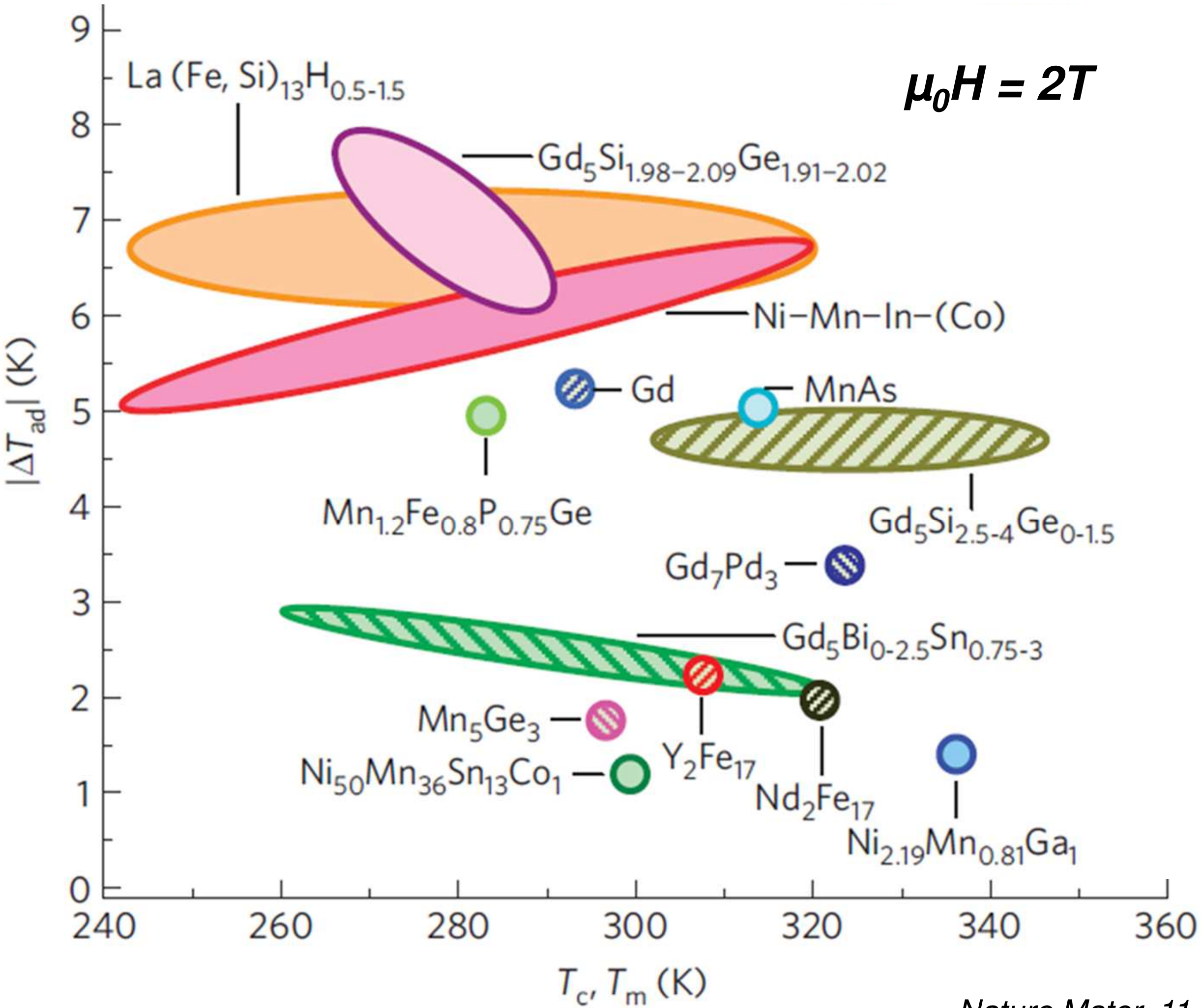
Classification of MCE materials II



→ Thermal hysteresis reduces the reversibility of the magnetocaloric effect

→ Shift of transition temperature in magnetic fields is the driving force of MCE

Gutfleisch et al., Phil. Trans. R. Soc. A, (2016) 1st order transition 2nd order transition



Nature Mater. 11 (2012) 620

La-Fe-Si based compounds

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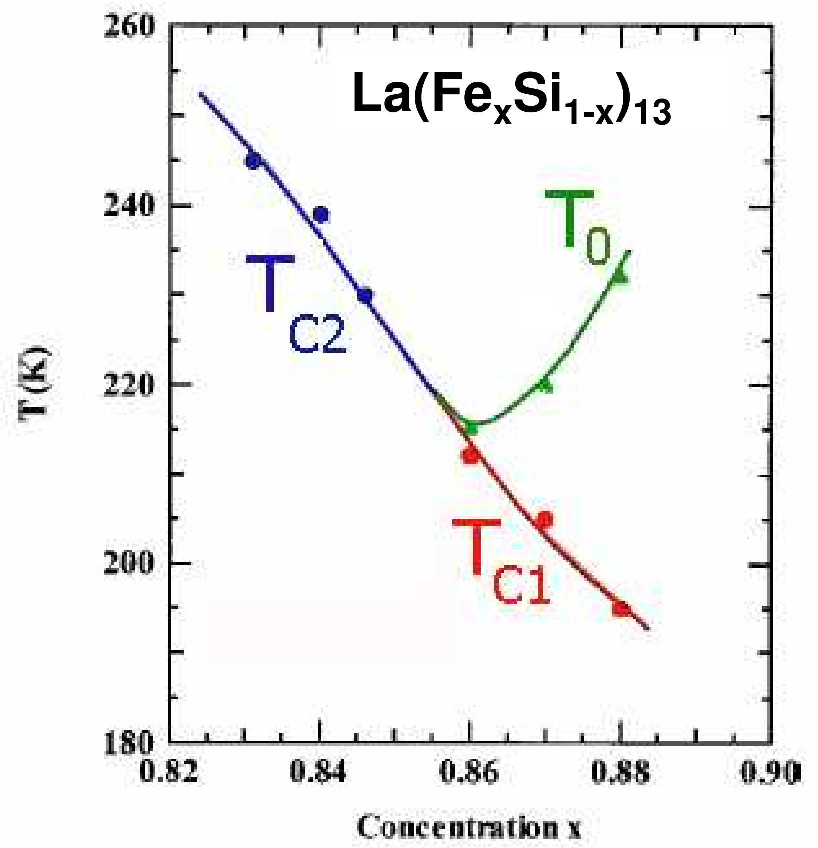
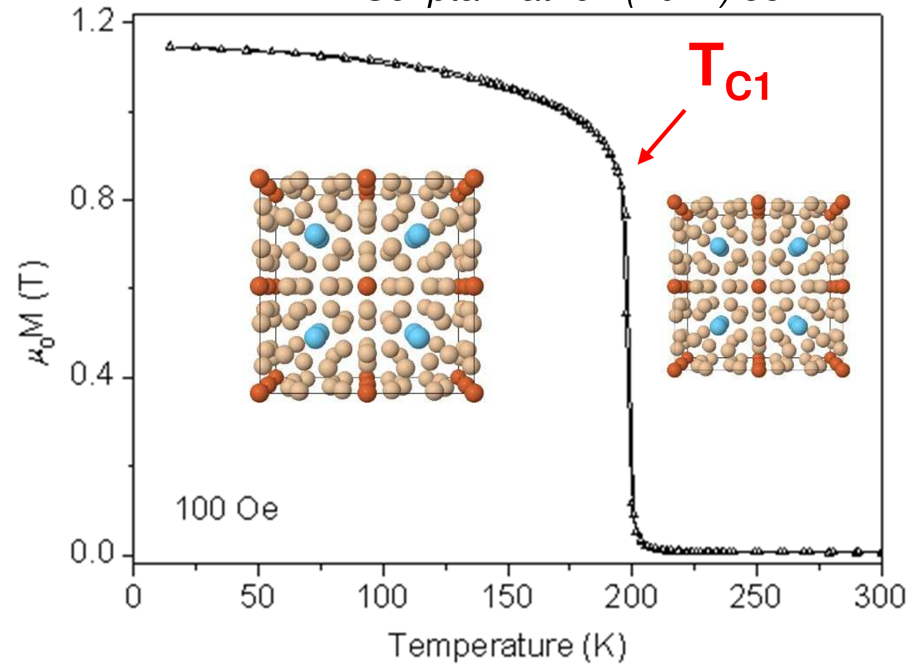


T_{C1}: 1st order FM ↔ PM transition
T_{C2}: 2nd order FM ↔ PM transition
T_0 : Itinerant electron metamagnetic (IEM) transition

Phase Transition in $LaFe_{11.6}Si_{1.4}$
*Scripta Mat. **67** (2012) 584*



F.X. Hu et al, Chinese Phys. 2000, 9, 550; APL 78, 3675 (2001)
S. Fujieda et al, PRB 2001, 65, 014410, APL 2002, 81, 1276

Tailoring of ΔS_m , ΔT_{ad} and ΔV: Addition of Co

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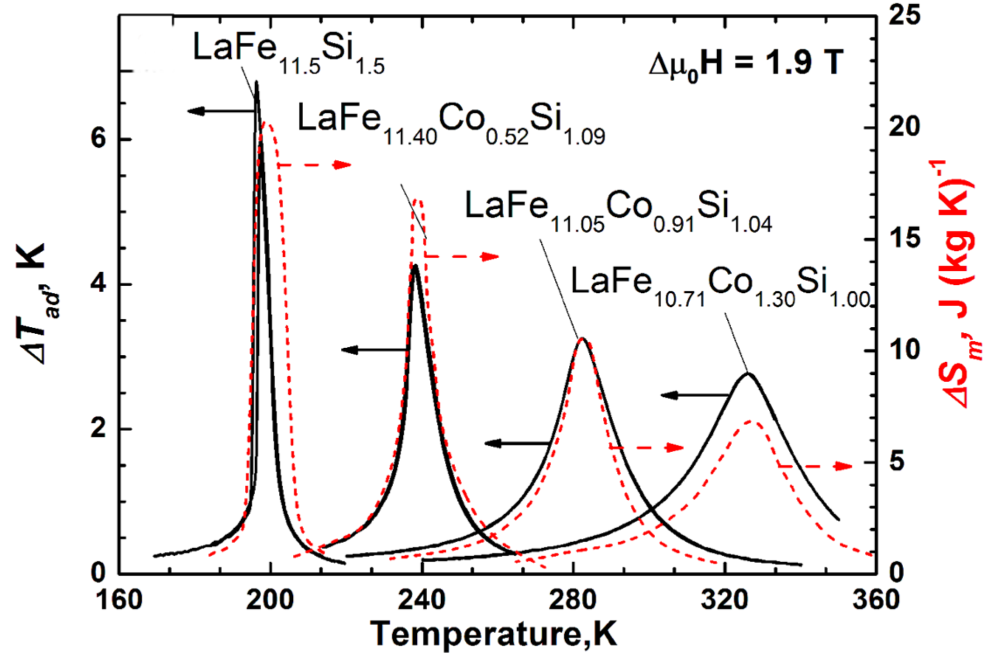
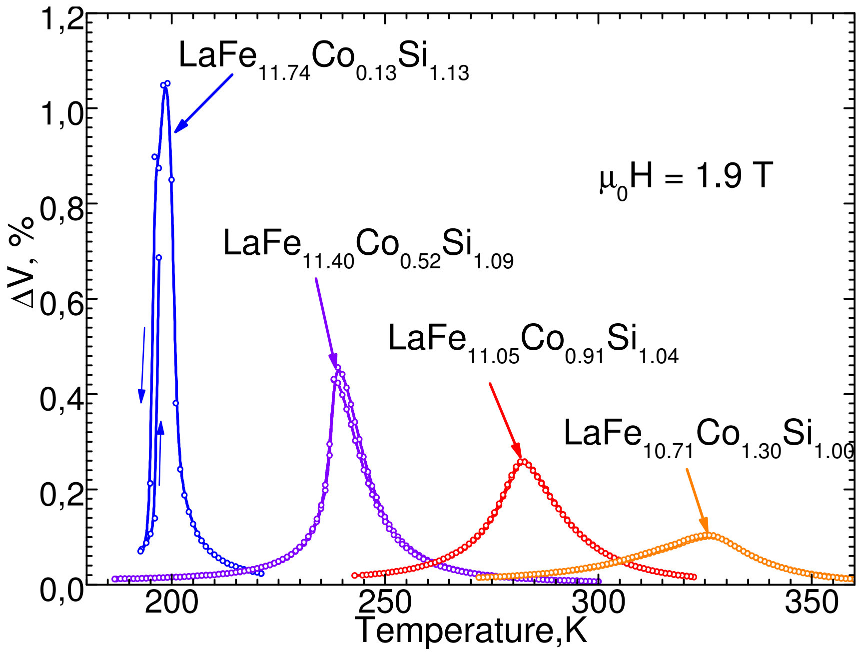
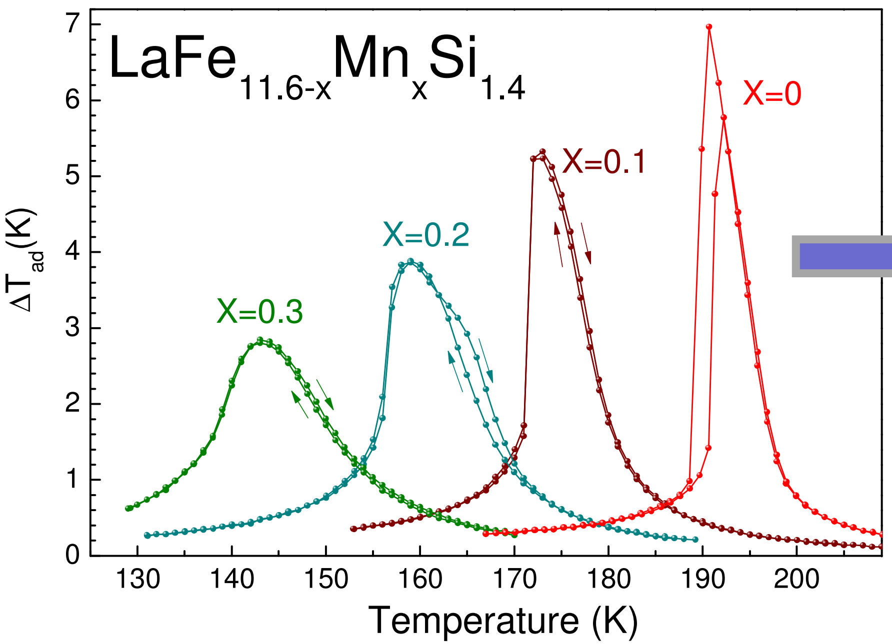
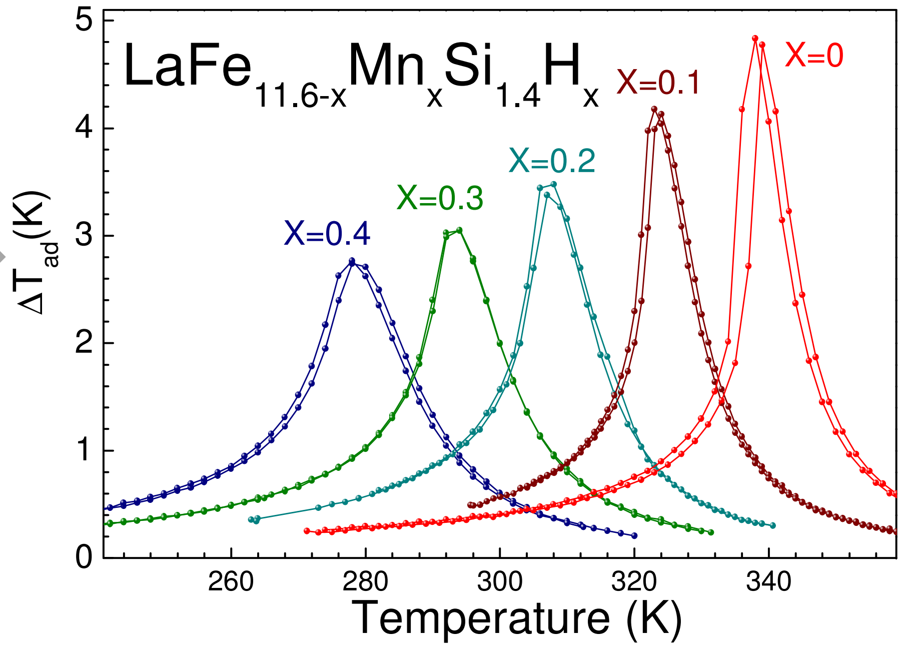




Acta Mat. ***59*** *(2011) 3602*
Scripta Mat. ***67*** *(2012) 584*

Tailoring of T_C II: Addition of Mn and H

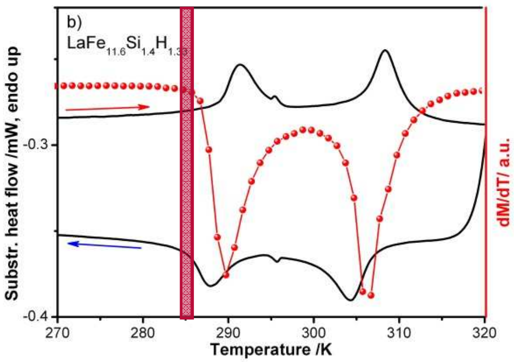




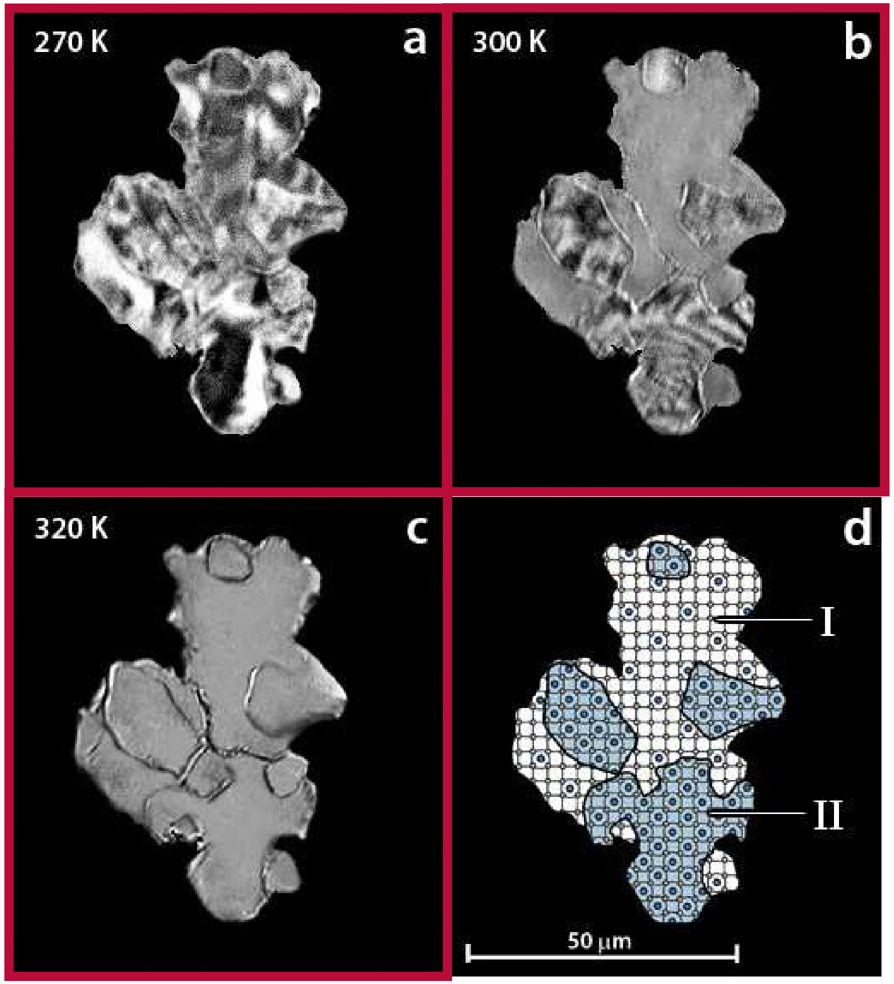
- **Hydrogenation shifts transition temperature to room-temperature region**
- **Gradual decrease in T_c with increasing x**
- **Increasing Mn content weakens first-order nature of magnetic transition**

J. Appl. Phys. ***111*** *(2012) 083918*
J. Alloys and Comp. ***598*** *(2014) 27*
J. Appl. Phys. ***115*** *(2014) 203905*

Introducing hydrogen



- **Magneto-volume effects**
- **DOS at EF**
- **phase co-existence**
- **hydrogen embrittlement**



J. Appl. Phys. **111** (2012) 083918

ΔT_{ad} of La(FeMnSi)$_{13}$H$_{1.53}$

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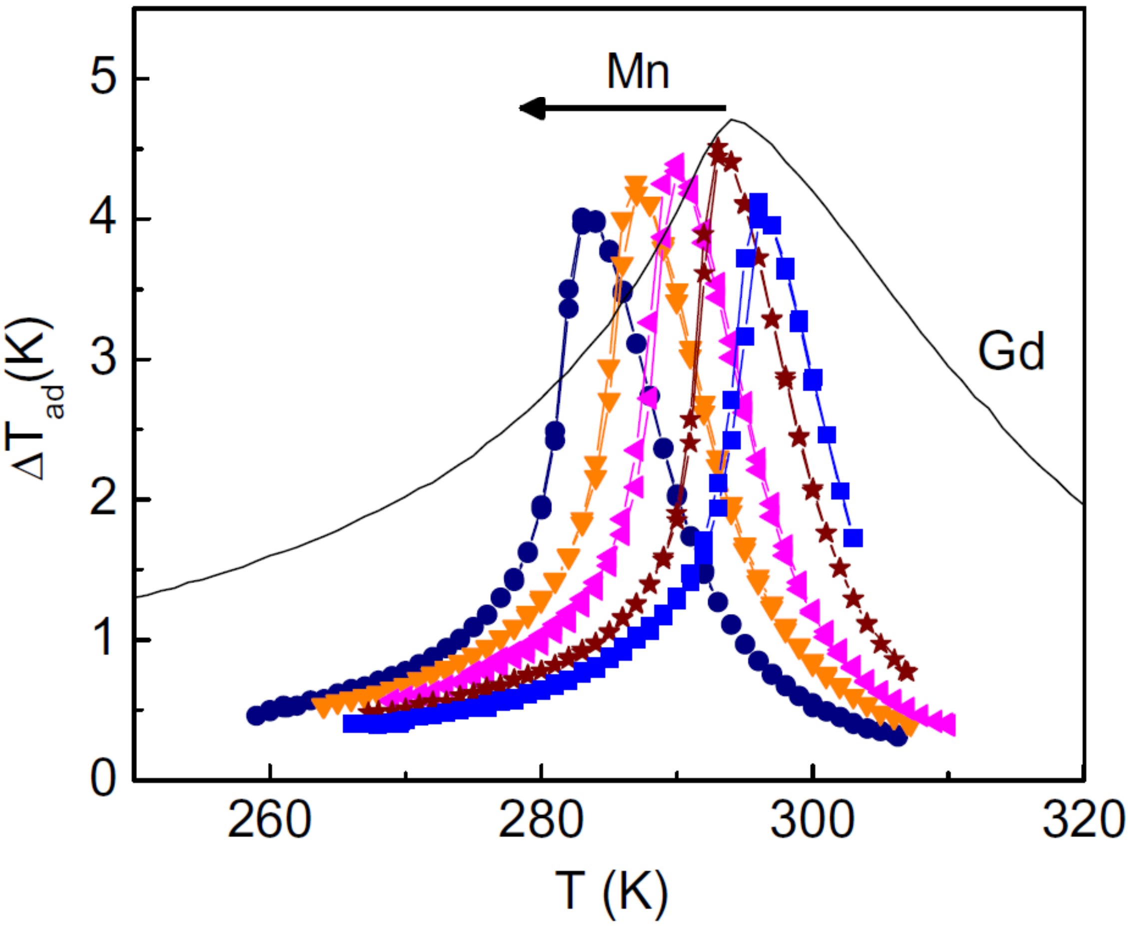
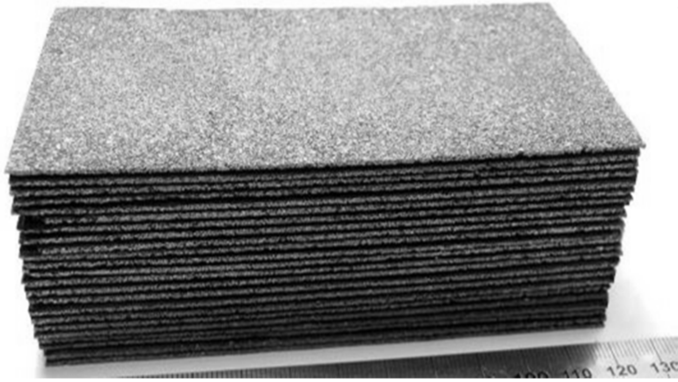


μ_0H = 1.93 T

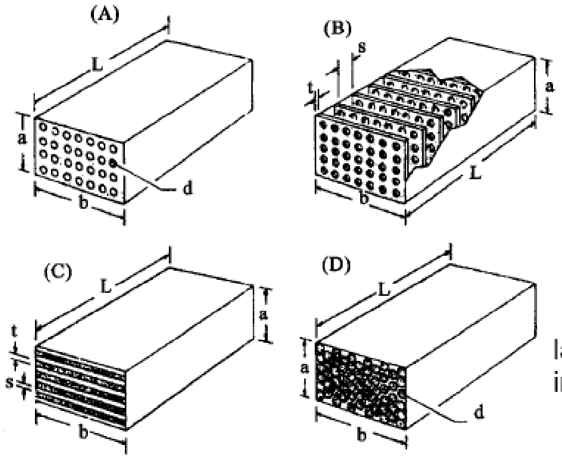
Scripta Mat. **67** (2012) 584
Cooperation Vacuumschmelze Hanau

Shaping

J. Magn. Magn. Mater. 396 (2015) 228



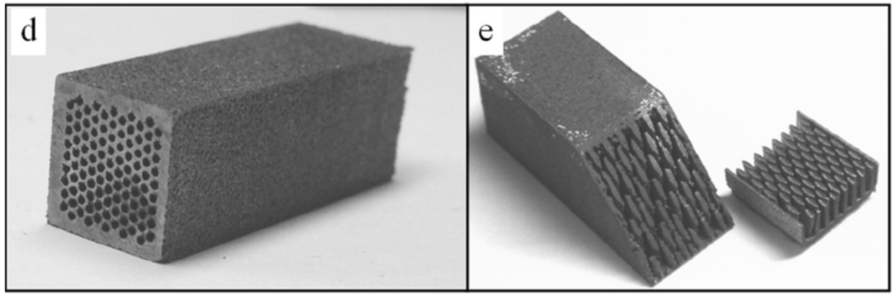
Designs for active magnetic regenerators



large pressure drops in powder beds?

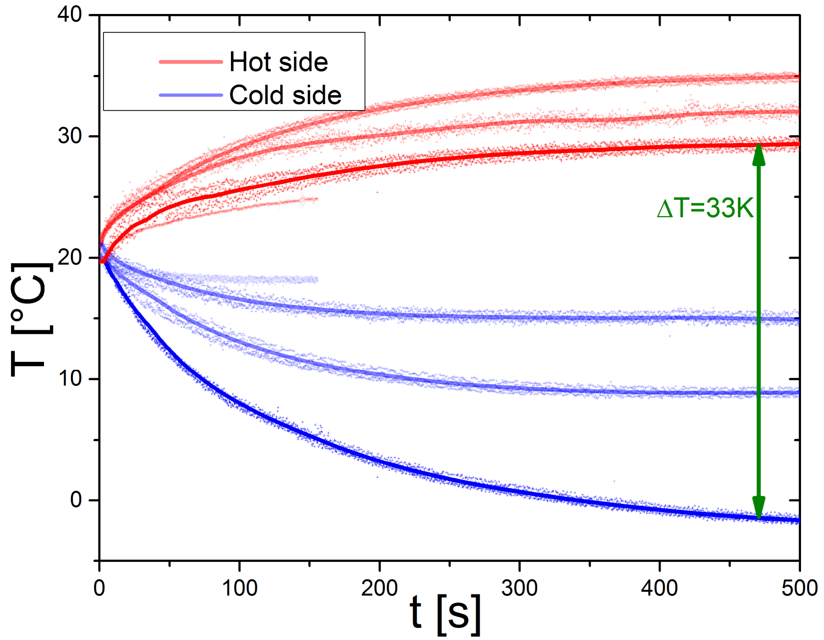
J.A. Barclay and S. Sarangi 1984 in A.M. Tishin and Y.I. Spichkin 2003

JAP114 (2013)



Acta Mat (2017)

Demonstrator – 2nd generation



$\Delta\mu_0 H$:	1.1 T
Mass of magnet:	3.9 kg
Active Volume:	63.6 cm³
Frequency:	up to 5 Hz
Fluid:	water
Temperature span:	26 K
Gd mass:	76 g
Sphere diameter:	250-355 µm

- Use of **recycled** $Nd_2Fe_{14}B$
- Less permanent magnet mass
- 124% higher active volume
- 18% higher magnetic field change
- 50% lower torque → smaller motor
- Less heating of magnets
- 50% higher maximum thermal span

Permanent magnet assemblies

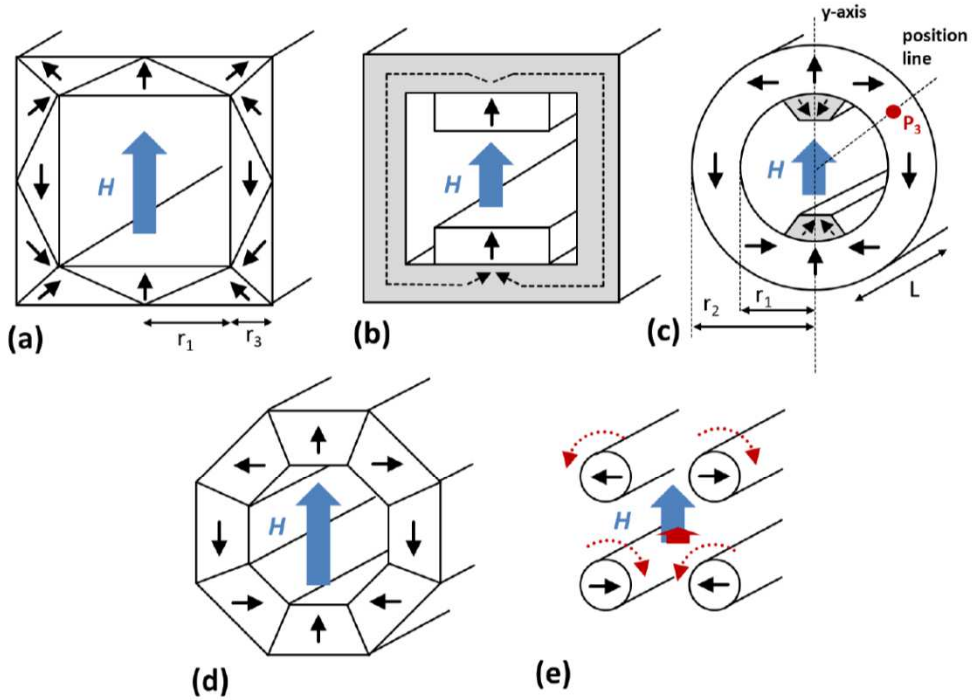
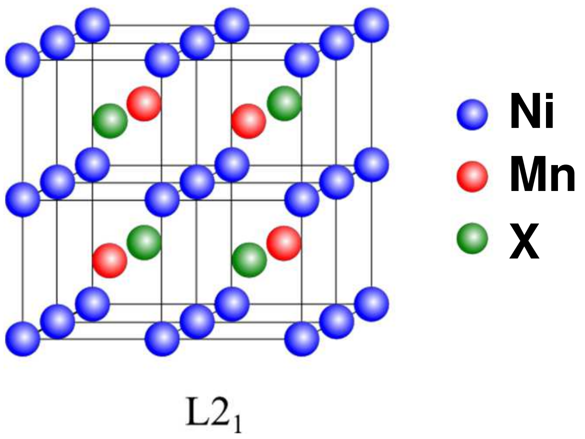
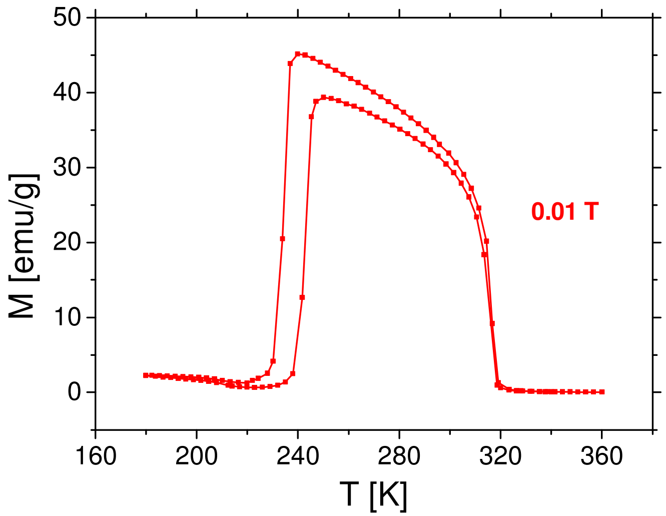


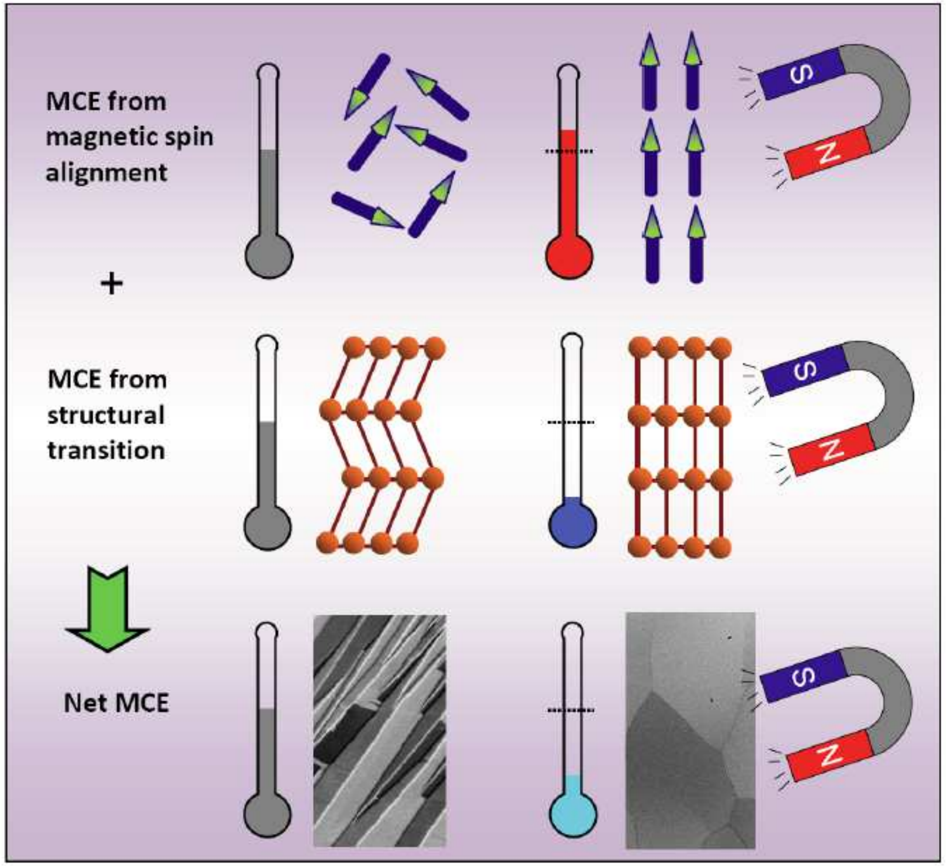
Fig. 27. Cross sections of some permanent magnet assemblies which create a uniform magnetic field along the blue arrows **(a)** from wedge segments, **(b)** with soft iron return path, **(c)** from Halbach array with soft iron pole-shoes **(d)** from segmented Halbach array, and **(e)** from a magnetic mangle, respectively, modified after [196]. The black solid and the black dashed arrows indicate the direction of magnetization in the permanent magnet as well as in the soft iron. The red dotted arrows show the sense of rotation

K.-H. Müller, S. Sawatzki, R. Gauss and O. Gutfleisch, Permanent magnetism,
in Springer Handbook of Magnetism, ed. by J.M.C. Coey and S. Parkin, in preparation.

Ni-Mn based Heusler compounds







→ dilemma of inverse magnetocaloric materials

Coupled structural transitions and associated giant cooling effect in Ni–Mn–In–(Co)

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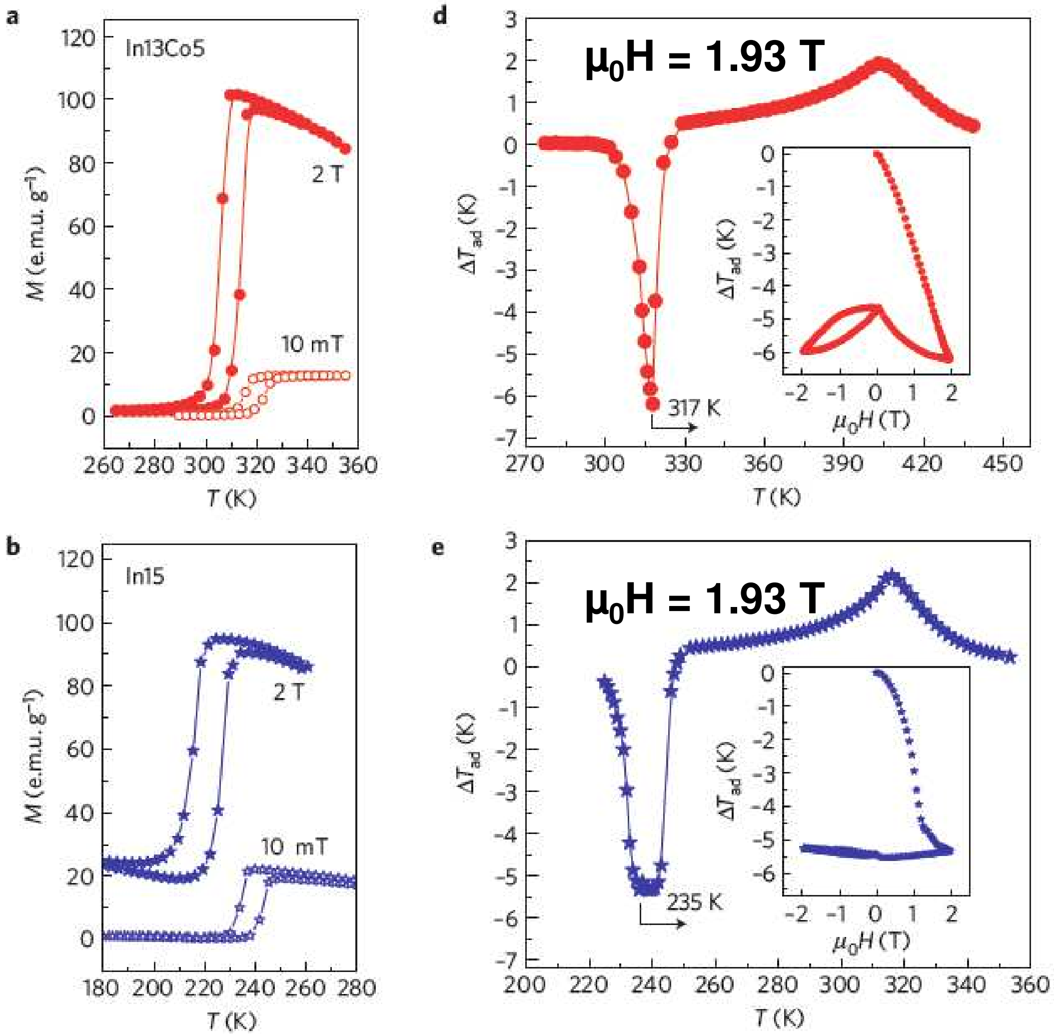
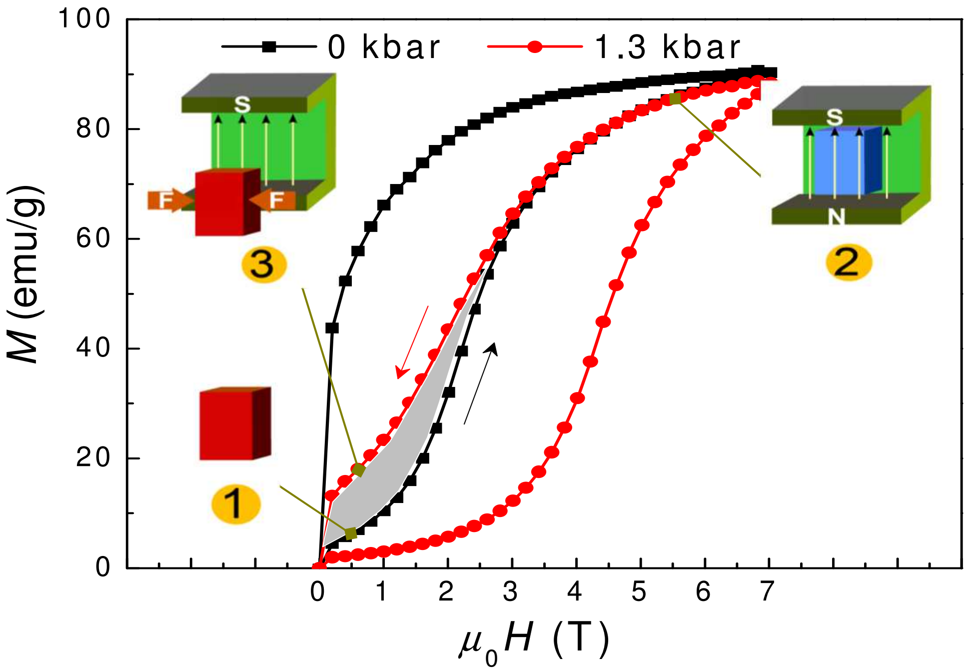
$Ni_{45}Mn_{37}In_{13}Co_5$

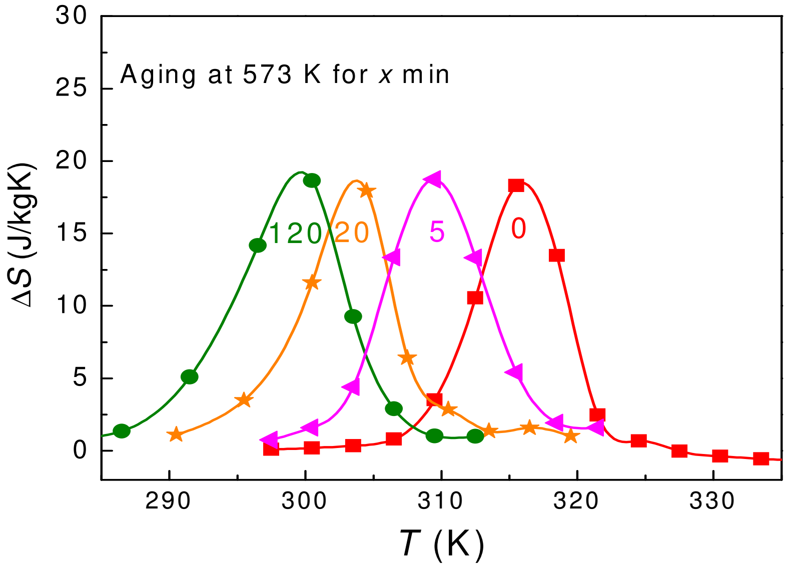
$Ni_{50}Mn_{35}In_{15}$



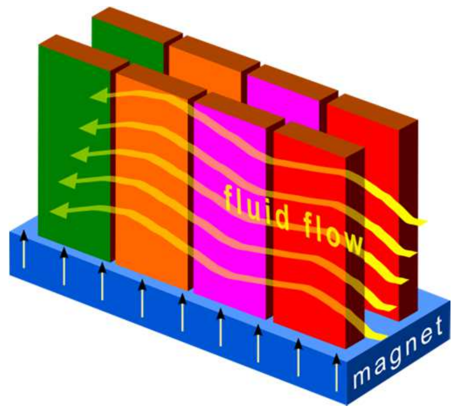
Nature Mater. 11 (2012) 620

Mastering hysteresis in NiMnInCo





- **Adjusting the transition temperature**
- **Increasing the operating range**



Large thermal irreversibility can be overcome by the combination of magnetic and mechanical forces

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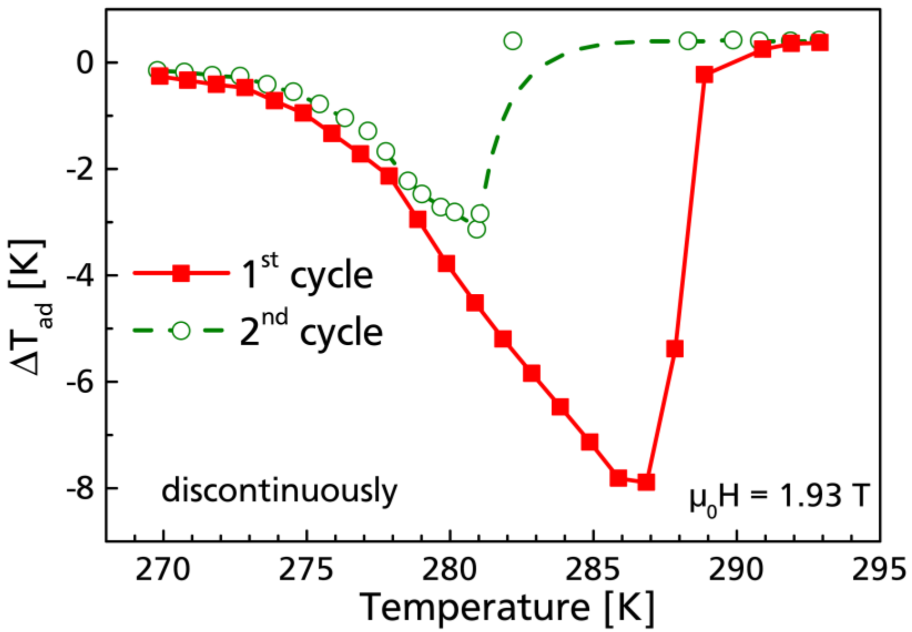
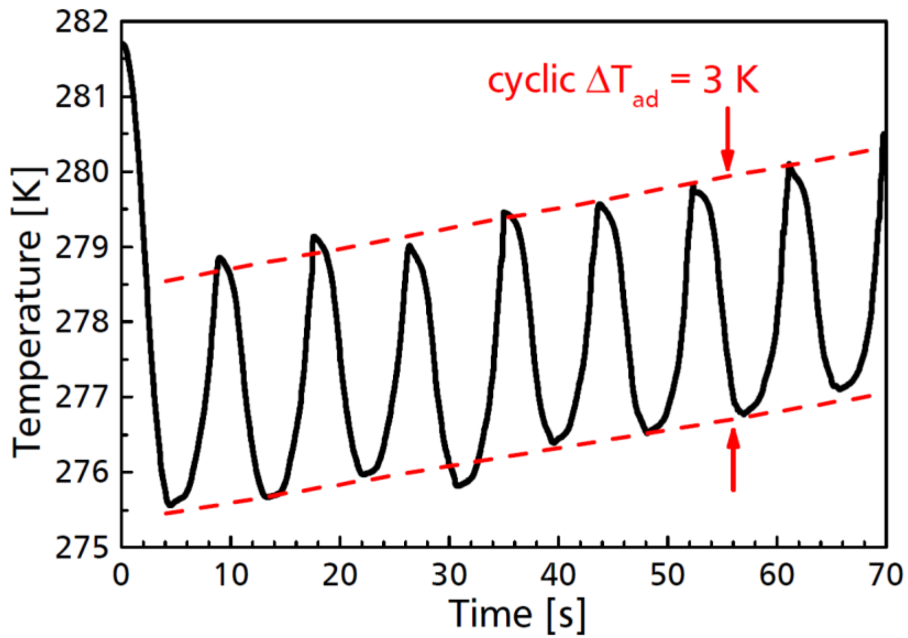
Reversibility of MCE



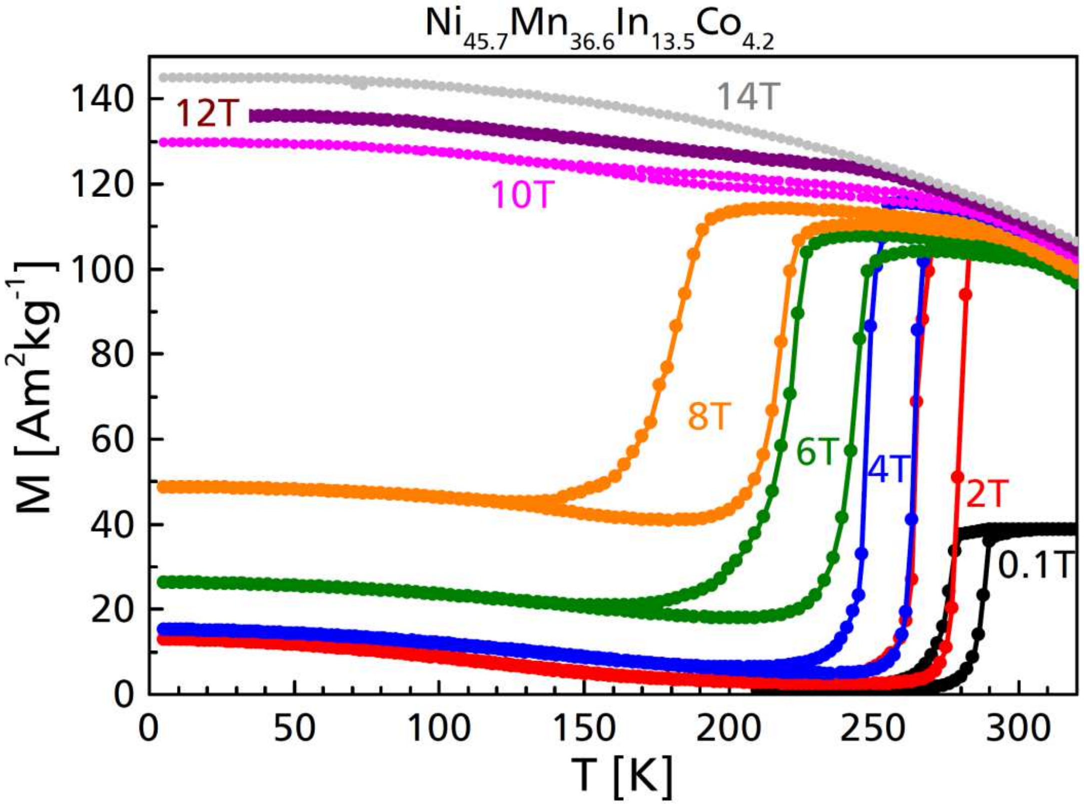


- Applying minor loops of magnetisation

→ Large reversible ΔT_{ad} despite significant thermal hysteresis

Gottschall et al., Appl. Phys. Lett. 106, 021901 (2015)

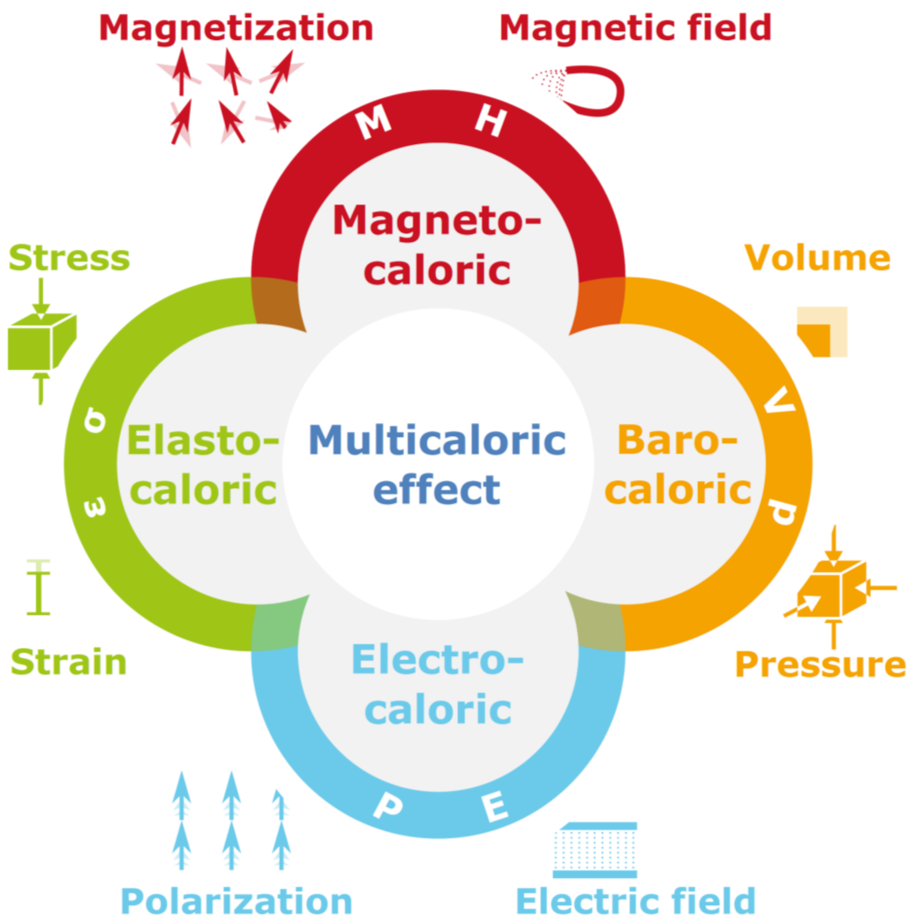
The transition in higher fields



- magnetic field of ≥ 6T:
  → thermal hysteresis increases and transition is partly suppressed (→ T_{comp})
- in 14T pure austenite remains, linear shift not valid for higher fields

Phys. Rev. B 93, 184431 (2016)

Solid-state caloric effects



Advanced Functional Material, in press

Conclusions

TECHNISCHE UNIVERSITÄT DARMSTADT

- Post-fossil society is not possible without rare metals
- REPM based motors are the best technological solution
- big demands in E-mobility, wind turbines, maybe magnetic refrigeration are still to come
- currently no equivalent substitutes for Nd-Fe-B magnets in many applications; a new RE free PM would be technologically disruptive
- RE balance needs to be explored, utilisation of free rare earths
- environmental indicators of a product would be drastically improved if recycled REPMs were used → magnetic refrigeration
- FORWARD by high through-put modelling → materials database → rational synthesis → advanced characterisation → identification of replacement material (earth abundant materials)

THANKS to ….

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- University of Torino
- IFW Dresden
- Unis Vienna and Exeter

- DFG
- BMBF
- EU 7th FP
- AiF
- MagHem
- industrial partners
- HMWK LOEWE

Read more in:

- **Magnetic Materials for Energy,**
  Viewpoint Set in *Scripta Mat.* ***67*** *(2012)*
- **Magnetic Materials and Devices for the 21st Century: Stronger, Lighter, and More Energy Efficient**
  Review in *Adv. Mat.* ***23*** *(2011) 821*
- **Towards high performance PMs w/o REs**
  Viewpoint in *J. Phys.: Condens. Matter* ***26*** *(2014) 064205*
- **Giant magnetocaloric effect driven by structural transition**
  Nature Mat. 11 (2012) 620