PERMANENT MAGNETS FOR EFFICIENT ENERGY CONVERSION

Oliver Gutfleisch

Functional Materials, TU Darmstadt, Germany

oliver.gutfleisch@tu-darmstadt.de

- Magnets for NZE scenario
- Rare earth elements
- Hysteresis
- From intrinsic to extrinsic
- Nucelation and pinning magnets
- Future magnets
- Recycling

Embedded in…

TECHNISCHE UNIVERSITÄT DARMSTADT

- Material criticality in a net-zero CO_2 emissions (NZE) scenario
  - Finiteness of strategic metals and resource strategy

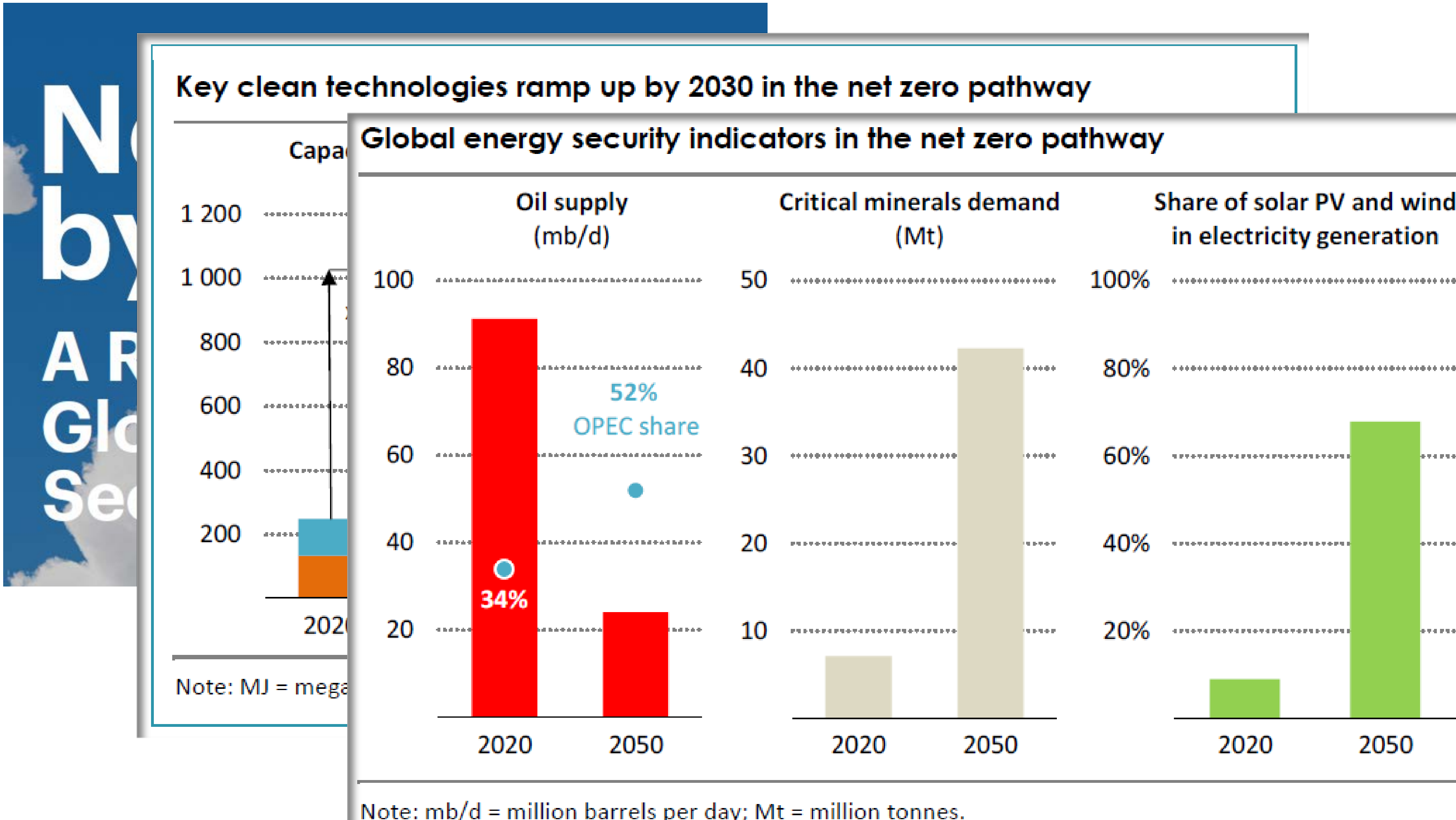
- Rational design of novel magnetic materials
  - Mastery of hysteresis
  - Permanent magnets for E-mobility and wind turbines
  - Magneto- and Multicaloric materials for solid state refrigeration
  - Reduction - Substitution - Recycling

- CRC/TRR 270 "*HoMMage*"

Hysteresis design of magnetic materials for efficient energy conversion

Global challenges

a pathway to a net-zero CO_2 emissions (NZE) scenario in 2050



IEA, Paris https://www.iea.org/data-and-statistics/charts/critical-minerals-demand-in-the-net-zero-pathway-2020-2050 and other graphs

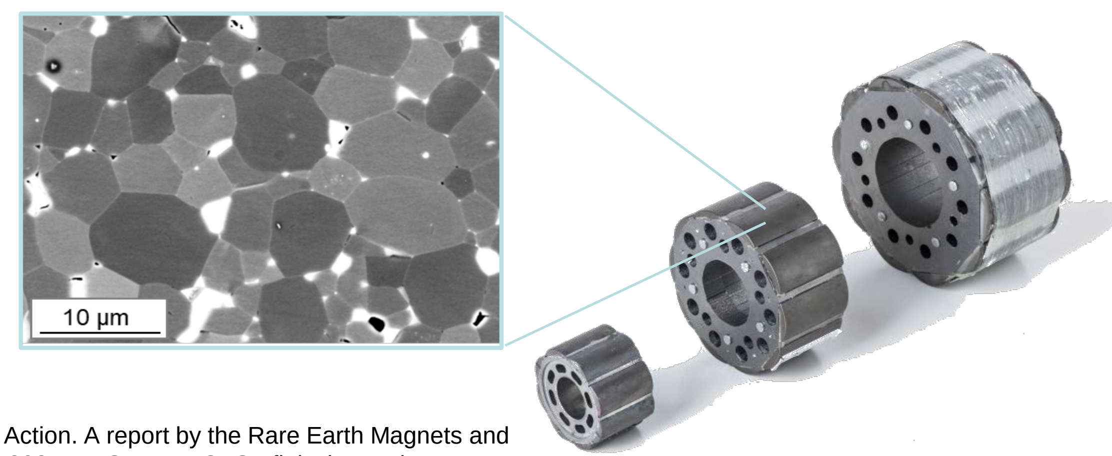
Rare earth elements for magnets and motors

TECHNISCHE UNIVERSITÄT DARMSTADT

➢ 95% of electric vehicles use rare earth drive motors: quantities required worldwide will grow from 5,000 tonnes in 2019 to approximately 40,000 - 70,000 tonnes per year by 2030.

➢ > 100,000 tonnes of rare earth permanent magnets are consumed each year in renewable energy, machine tools, robotics, loudspeakers, water pumps and mobile technology.

➢ < 1% recovery of rare earth permanent magnet scrap in Europe, which represents a large potential resource at a low carbon footprint.



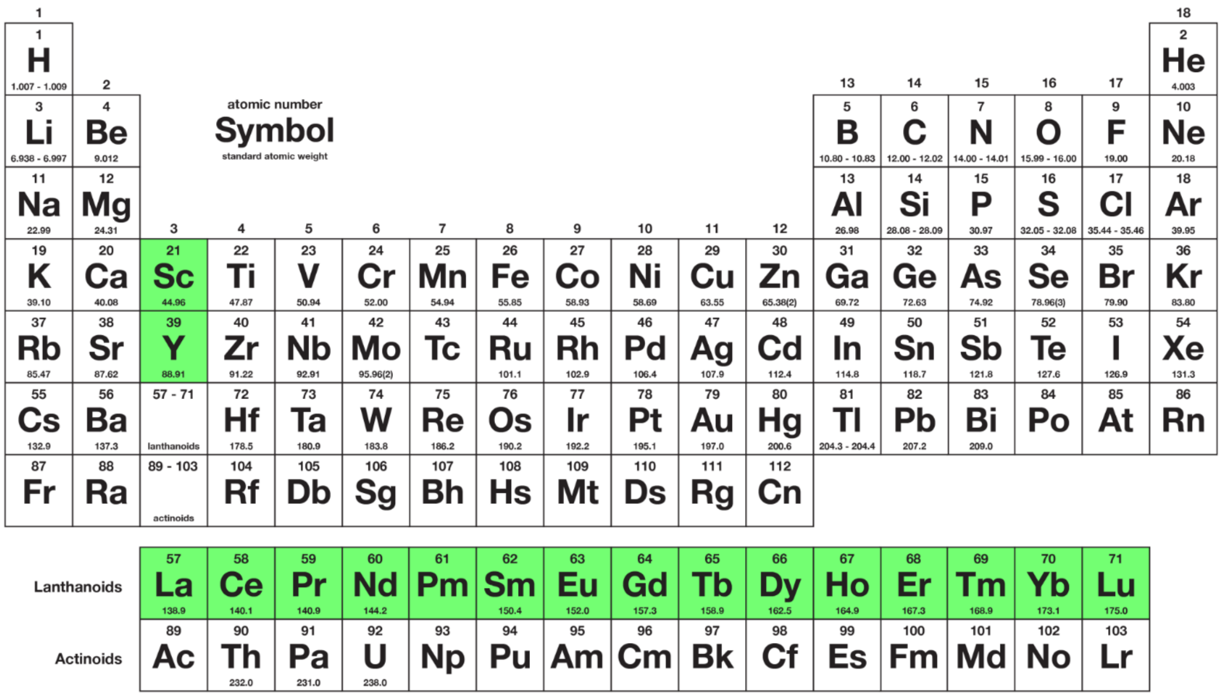
Images by TU Darmstadt and Fraunhofer IWKS

Source: Rare Earth Magnets and Motors: A European Call for Action. A report by the Rare Earth Magnets and Motors Cluster of the European Raw Materials Alliance. Berlin 2021, R. Gauss, ..O. Gutfleisch, et al.

General Context of the Rare-Earth Market

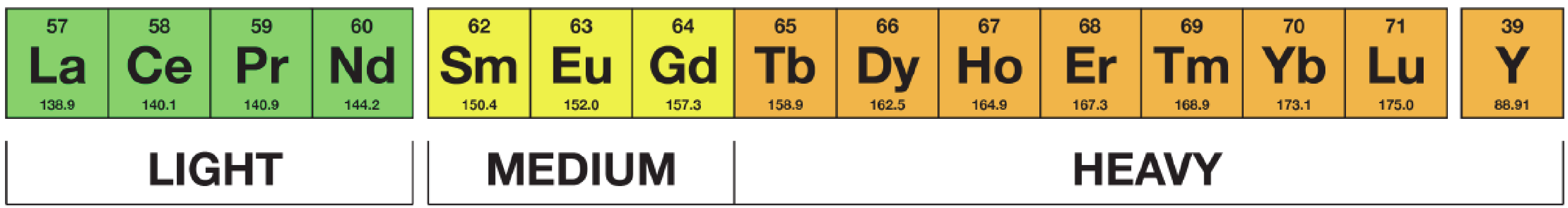
supply, criticality and applications

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, …)

The REs can be divided in subgroups

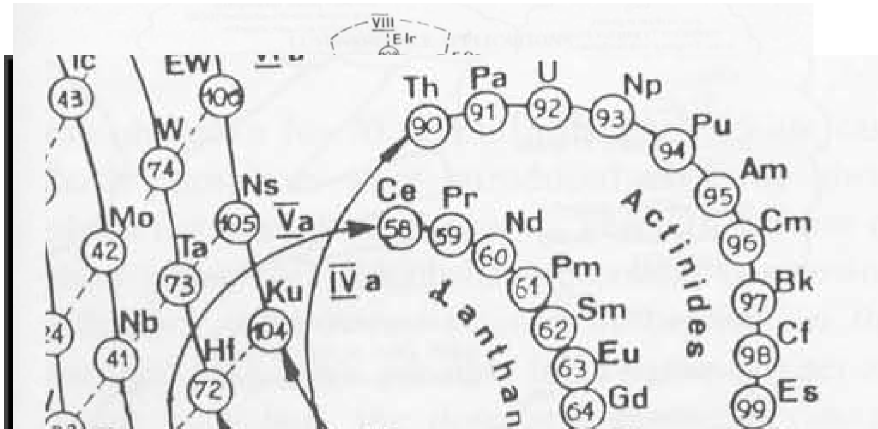


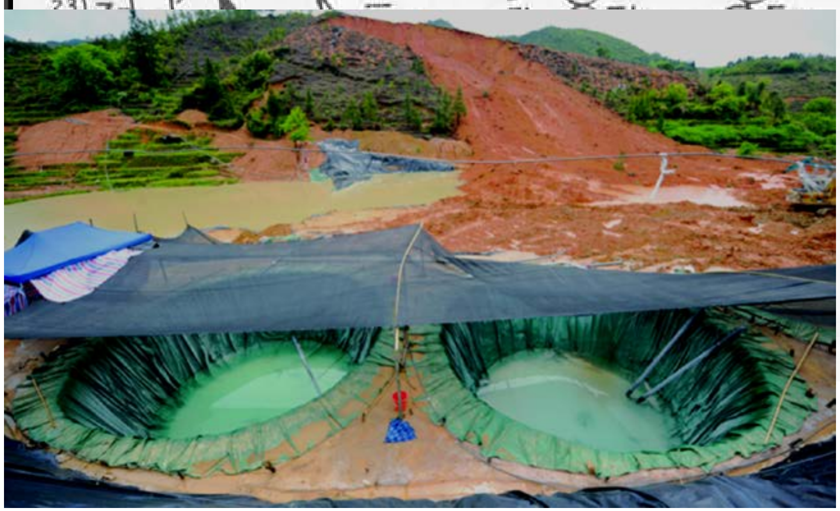
Source: Technology Metals Research

- Definitions relate to the processing of concentrates
- Used by metallurgists & flow-sheet engineers
- Not always used elsewhere in the industry
  - Sm frequently grouped with lights; Eu & Gd with the heavies
- Be sure to know which convention is being used
  - Make sure to compare “apples to apples”

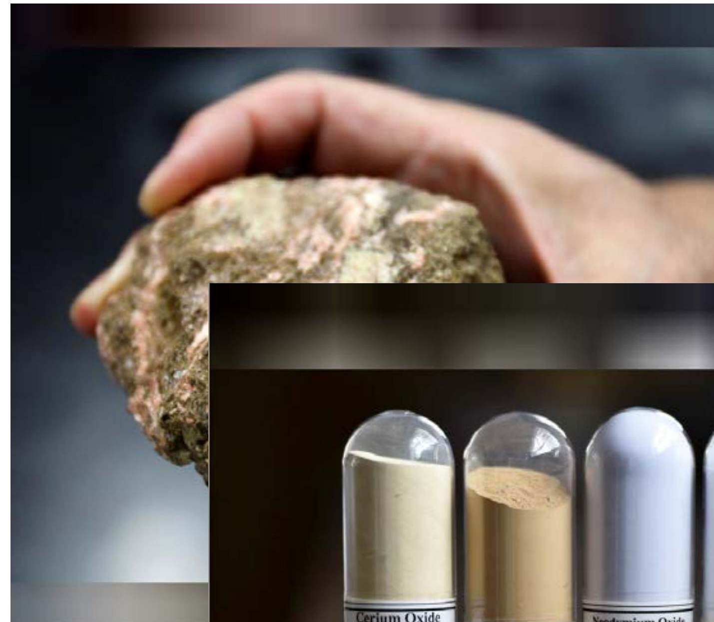
The element 60 – Neodymium

from critical metals to power-magnets for renewable energy





https://www.spiegel.de/wirtschaft/soziales/bild-1271097-1435707.html
6. Juni 2019



FILE PHOTO: A bastnaesite mineral containing r
2011. REUTERS/Yuriko Nakao/File Photo

FILE PHOTO: Samples of rare earth minerals from left, Cerium oxide, Bastnasite, Neodymium oxide and Lanthanum carbonate are on display during a tour of Molycorp's Mountain Pass Rare Earth facility in Mountain Pass, California June 29, 2015. REUTERS/David Becker/File Photo

Ce - 1803 – ***La*** - 1839 – ***Di*** - 1842 - ***Sm*** -1878 – ***Pr*** -1885 – ***Nd*** - 1885 – ***Eu*** - 1889

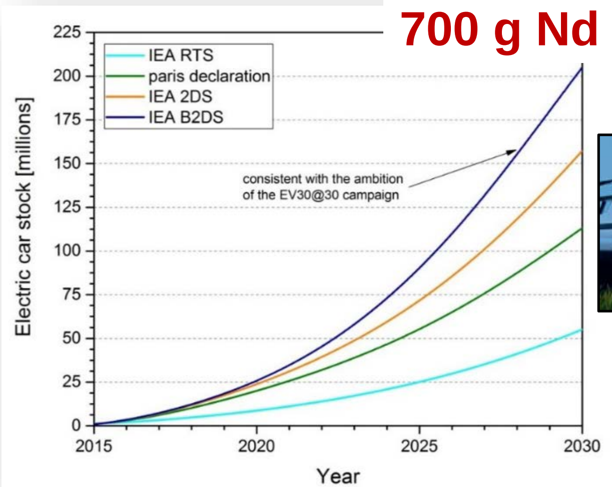
Magnets - key enablers in a NZE future

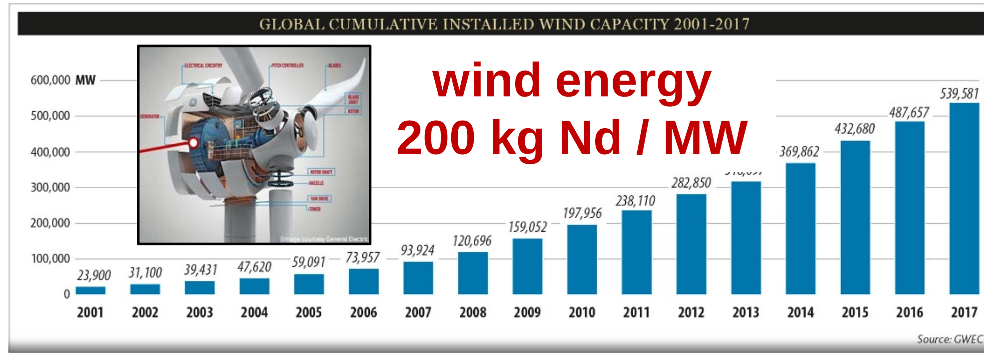
the criticality of the strategic elements in magnets

TECHNISCHE UNIVERSITÄT DARMSTADT

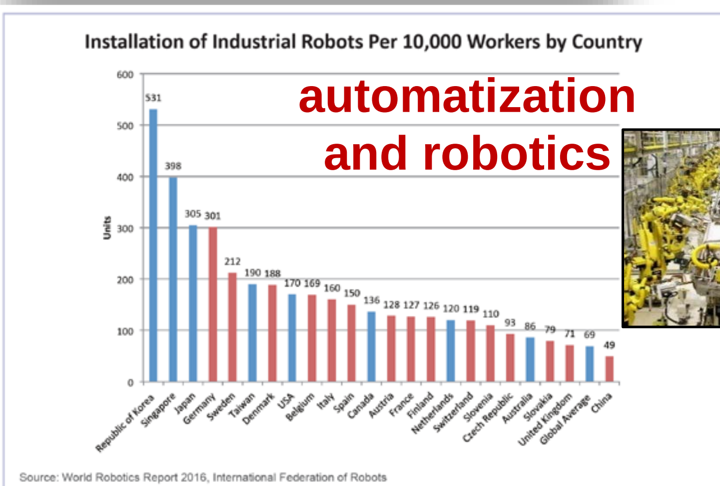
https://www.iea.org/reports/energy-technology-perspectives-2017

electro mobility
700 g Nd / Emotor

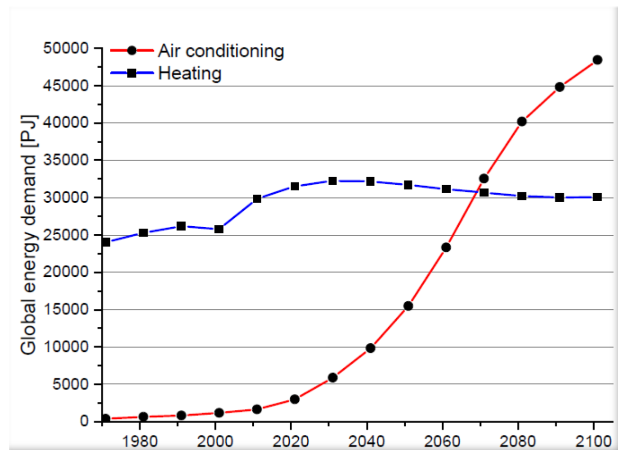




wind energy
200 kg Nd / MW



automatization
and robotics



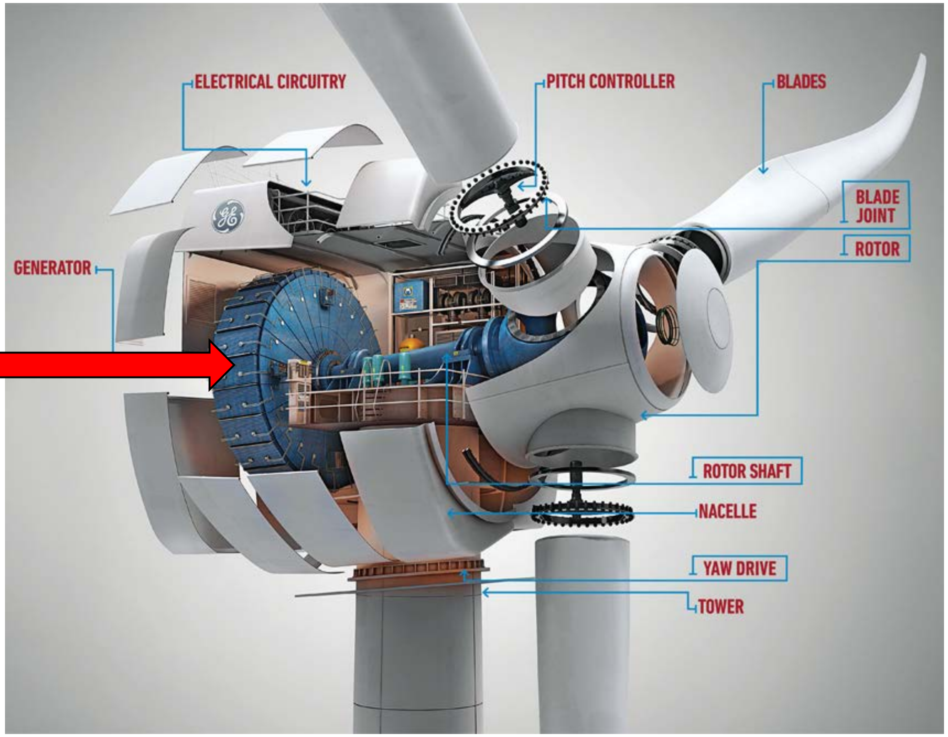
Adopted from M. Isaac, D. P. van Vuuren, Energy Policy 37 (2009) 507

cooling
1.5 kg Nd / kW

Direct drive wind turbine

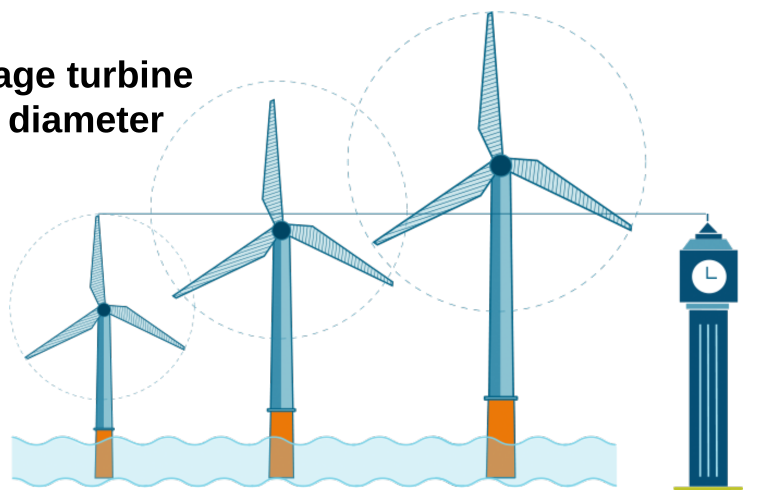
per 1 MW windpower

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



(image General Electric, Data: US DOE)

Average turbine rotor diameter

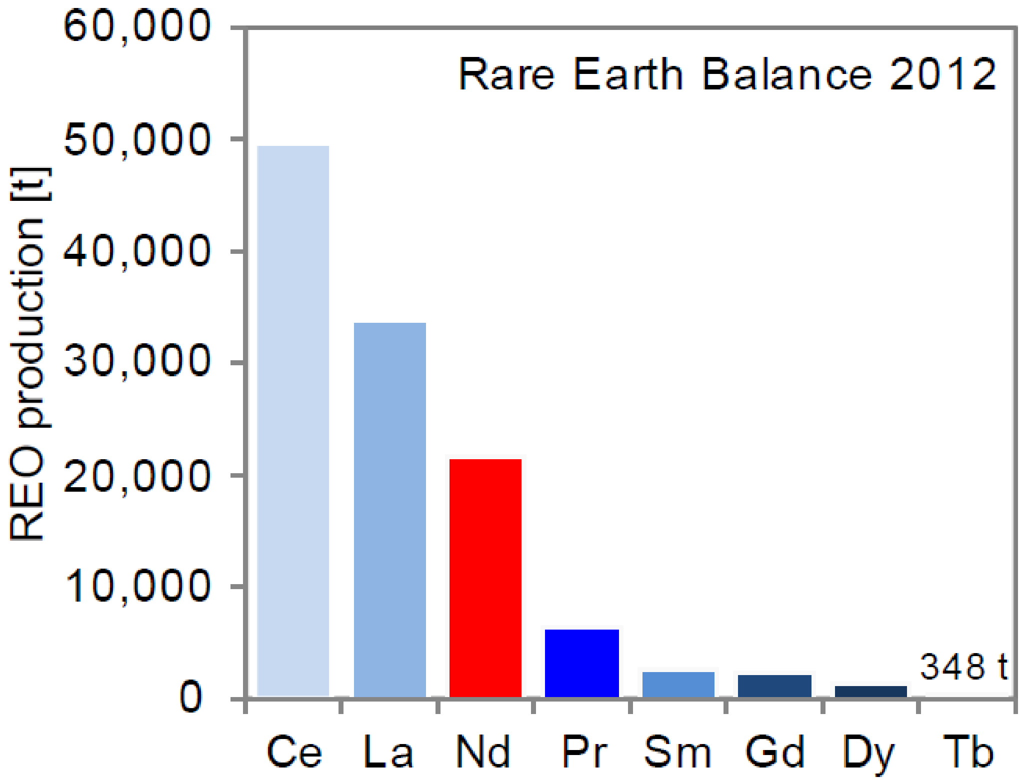


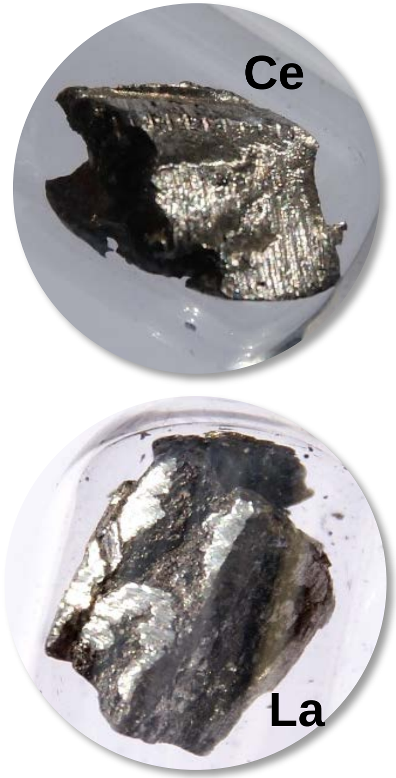
37m 1990 450kW	154m Today 6-8MW	240m 2020	94m Big Ben

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

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

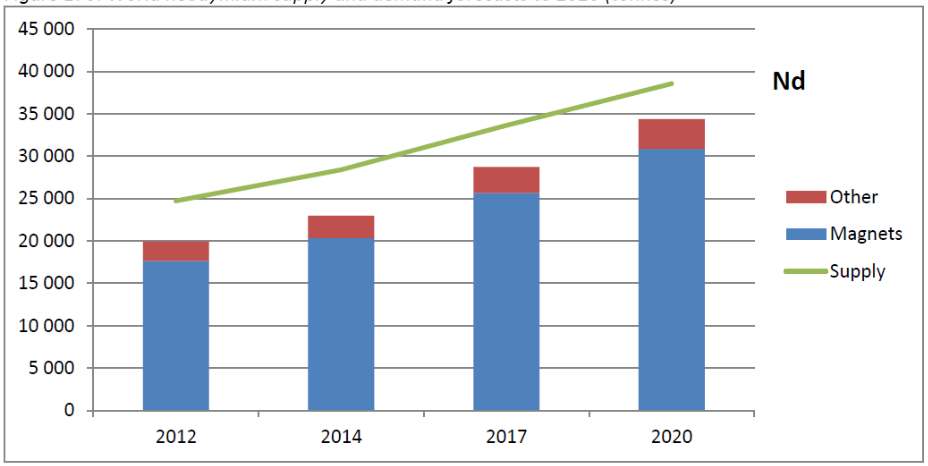
EU 2015: Critical raw materials for the EU
Gauss and Gutfleisch, The resource basis of magnetic refrigeration, J. of Industrial Ecology, 2016.
images: http://images-of-elements.com/ prices: metal pages

World REE supply and demand forecasts to 2020

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

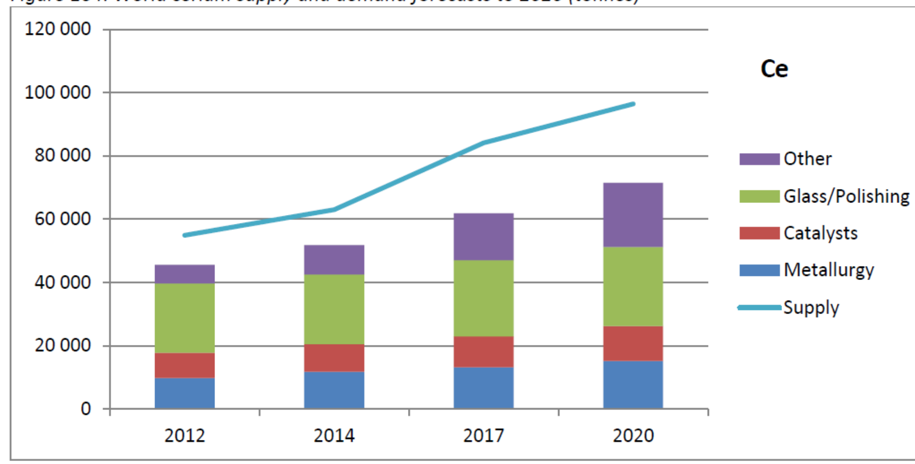
TECHNISCHE UNIVERSITÄT DARMSTADT

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



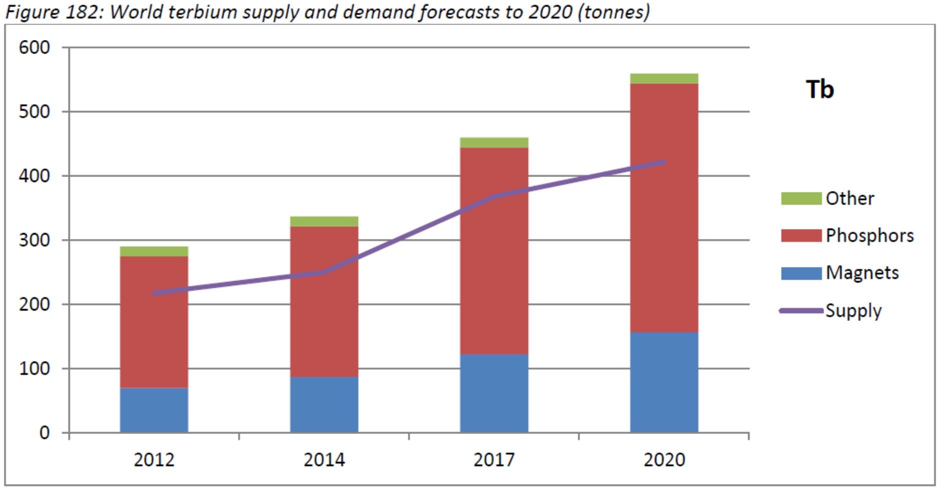
Sources: Roskill, IMCOA and Technology Metal Research Reports and Presentations (2012-2013)

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



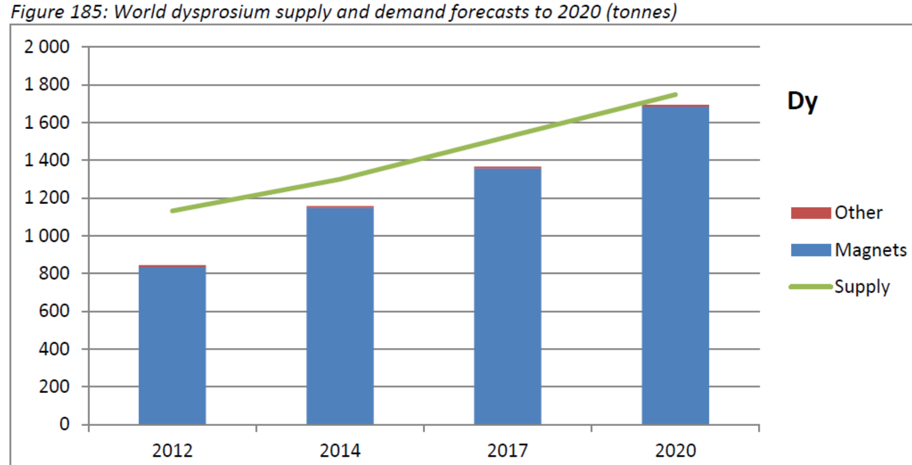
Sources: Roskill, IMCOA and Technology Metal Research Reports and Presentations (2012-2013)

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



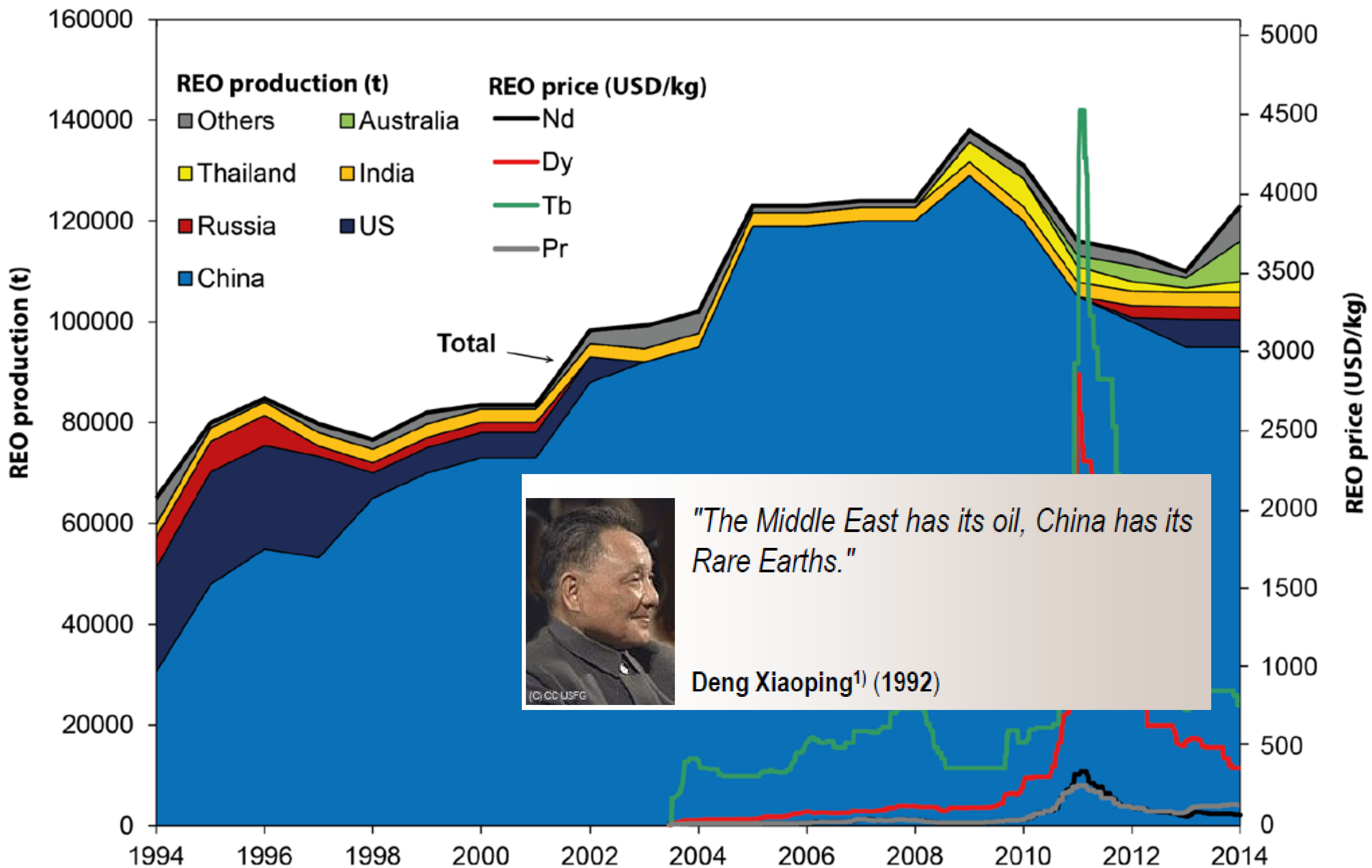
Sources: Roskill, IMCOA and Technology Metal Research Reports and Presentations (2012-2013)

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



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

Rare earth market and production



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, book in preparation.

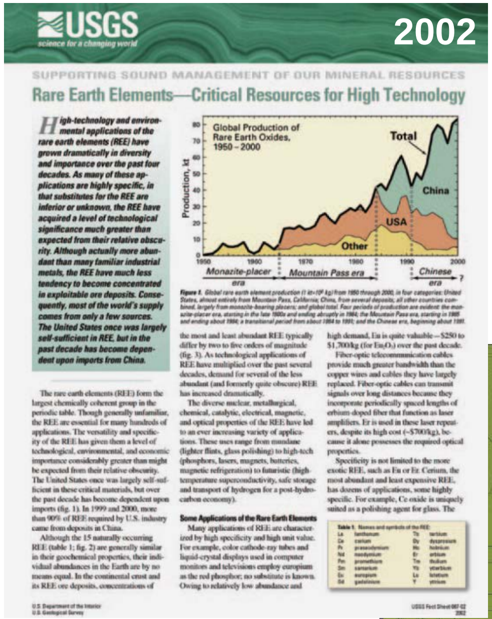
Rare earth crisis

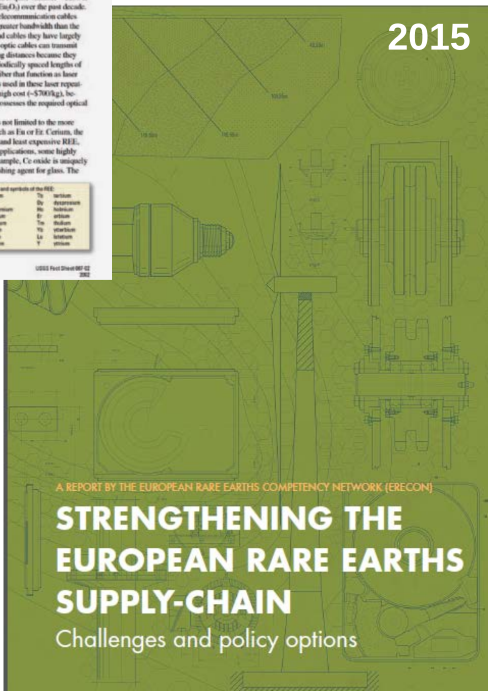
was not only predictable, it was also preventable

TECHNISCHE UNIVERSITÄT DARMSTADT

- USGS estimates proven reserves of REEs at 800 times of current demand.
- 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 would meet all Europe's current rare earth requirements.
- Import reliance rate of Europe is 100%.

EU communication on the 2017 list of Critical Raw Materials for the EU, Brussels, 13.9.2017





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

From where does the supply for REs originate?

21.06.2017 Roskill:

Molycorp declared bankruptcy in 10/2015.

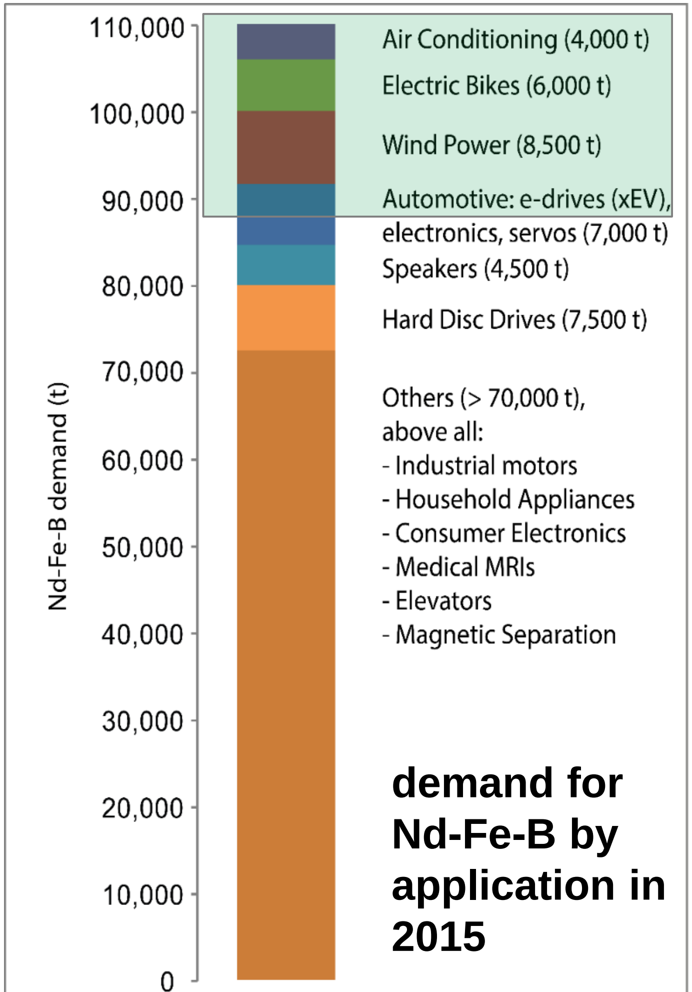
Mountain Pass had a design capacity to produce 16.1ktpy REO with reserves of 17.8Mt grading 8.10% REO.

Mountain Pass rare earths mine and processing facility previously operated by Molycorp was purchased by MP Mine Operations LLC for US$20.5M.

→ move by Chinese processing companies to secure raw materials from non-Chinese sources

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

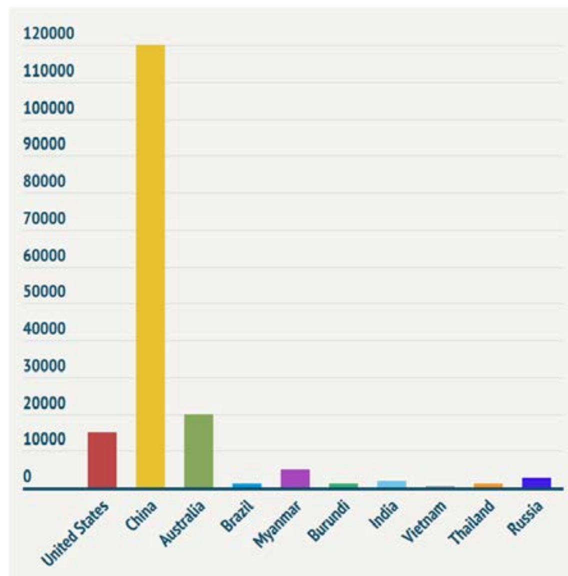
Supply and demand – permanent magnets



K.-H. Müller, S. Sawatzki, R. Gauss, O. Gutfleisch, Permanent Magnetism, in Springer Handbook of Magnetism, ed. by Coey and Parkin, 2021

China is the world leader in the rare earth elements production followed by the US and Australia.

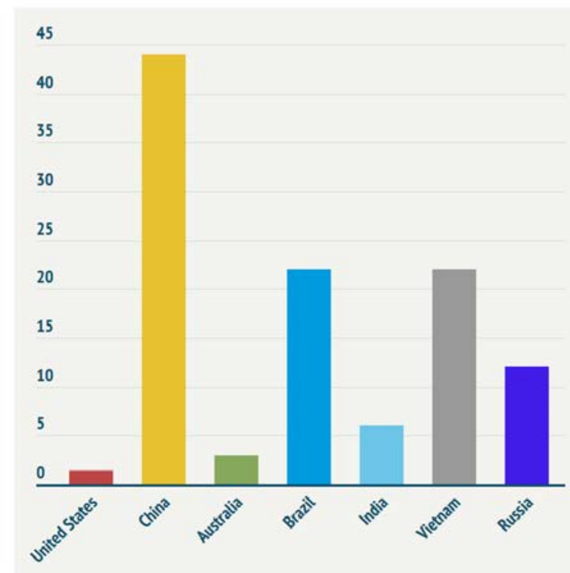
Source: U.S. Geological Survey, Mineral Commodity Summaries, February 2019



In metric tonnes REO

China is home to the biggest reserves of rare earth metals in the world, followed by Brazil and Vietnam, which have important deposits despite their low production.

Source: U.S. Geological Survey, Mineral Commodity Summaries, February 2019



In millions metric tonnes REO

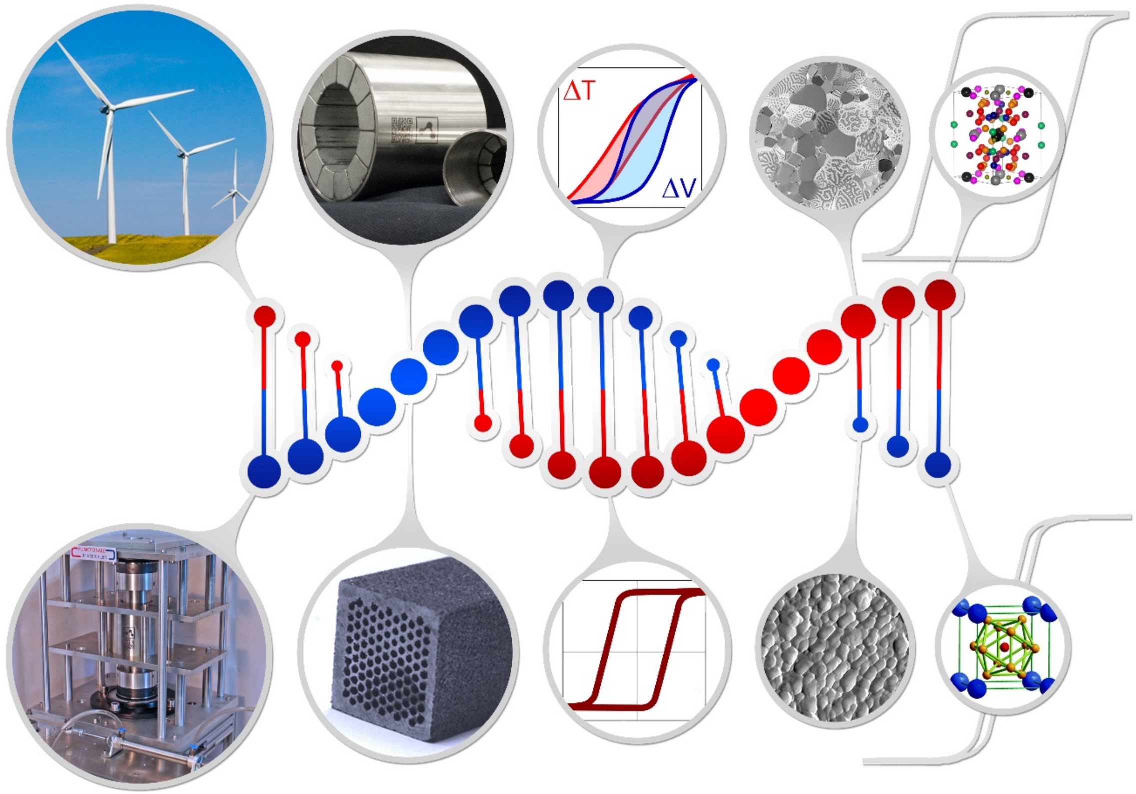
Mitigation strategies to address REEs criticality

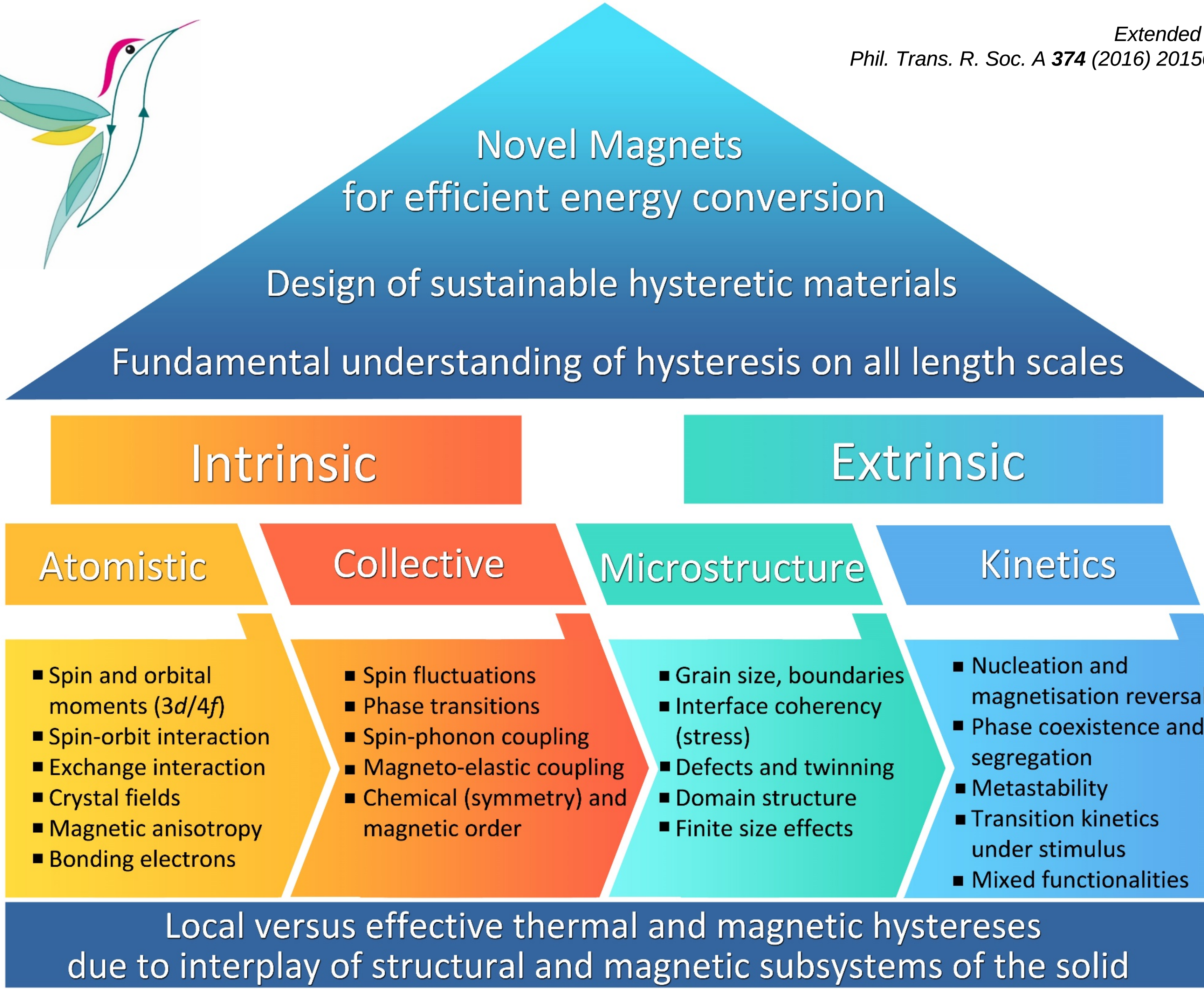
- **Diversify** primary mining and make it sustainable
- **Reduce the utilization** of critical materials by Material Science advances (GBDP and AM)
- **Recycling** will make use of the urban mine (technosphere)
- **Substitute** strategic metals by (more) earth abundant elements

Maximum Hysteresis for
Permanent Magnets
→ **Spin-orbit coupling**

electron, lattice, and spin degrees of freedom

Minimum Hysteresis for
Magnetocalorics
→ **Spin-phonon coupling**





Extended from
Phil. Trans. R. Soc. A ***374*** *(2016) 20150308*

Intrinsic and extrinsic magnetic properties

intrinsic properties + **microstructure** ⇒ **extrinsic properties**

microstructure

100 µm > l > 1 nm

↔ fit µ-magnetic length scales

„Magnetic hardening“

saturation magnetisation, M_s

anisotropy field, H_A

Curie temperature, T_C

remanence, J_r

coercivity, H_c

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

→

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

critical single domain particle size, D_c

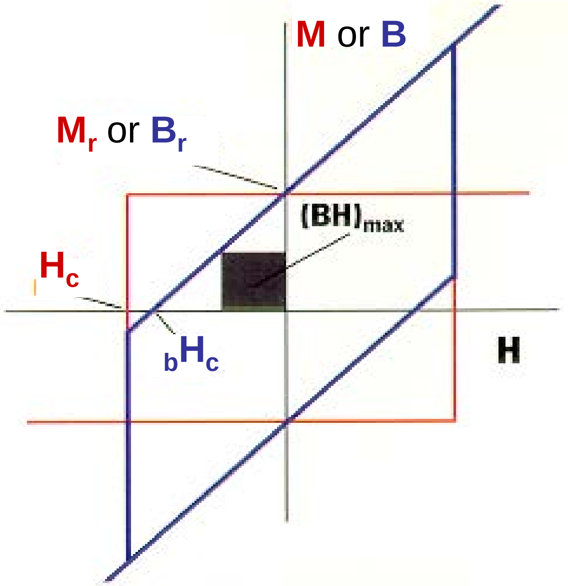
exchange stiffness, **A**

domain wall width δ_w and energy γ

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

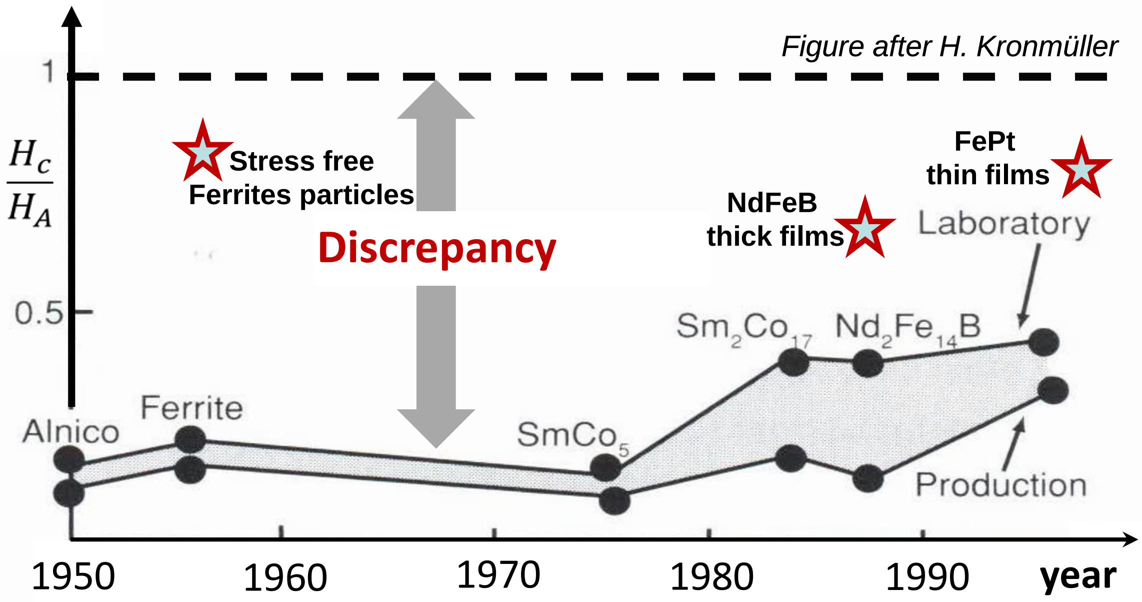
$$H_A = (2K_1 + 4K_2)/\mu_0 M_S$$

$$H_C = \alpha \frac{2K_1}{\mu_0 M_s} - N_{eff} M_s$$



BUT – the Brown paradox
in practice only 20% of H_A is achieved with H_c

TECHNISCHE UNIVERSITÄT DARMSTADT



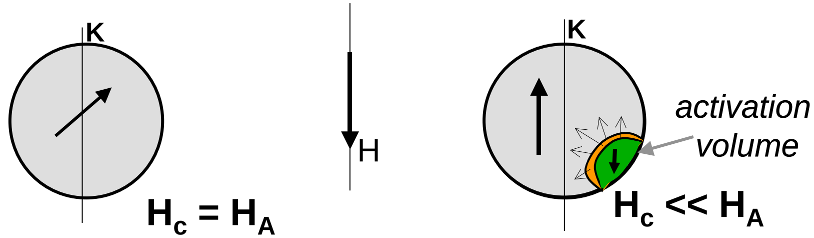
- W.F. Brown, Rev. Mod. Phys. 17 (1945) 15.
- W.F. Brown Jr, Micromagnetics, Interscience Publishers, New York, 1963, p. 68.
- E.C. Stoner, E.P. Wohlfarth, Philos. Trans. R. Soc. London 240A (1948) 599.
- H. Kronmüller, K.-D. Durst, M. Sagawa, J. Magn. Magn. Mater. 74 (1988) 291.
- **D. Givord** et al., J. Magn. Magn. Mat. 258–259 (2003) 1

SW-model

Perfect materials:
Coherent rotation

the real material

Defects :
Nucleation + propagation



It is theoretically impossible to reverse magnetization in a homogeneous sample in a field smaller than the magneto-crystalline anisotropy field.

BUT: an order of magnitude discrepancy between rigorous micromagnetic theory and experiment.

Magnetisation reversal in sintered NdFeB

… is governed by **nucleation → passage → expansion → depinning mechanisms**, each one occurring within a local critical volume under an effective critical field (H_n, H_{pass}, H_{expans} and H_{depin})

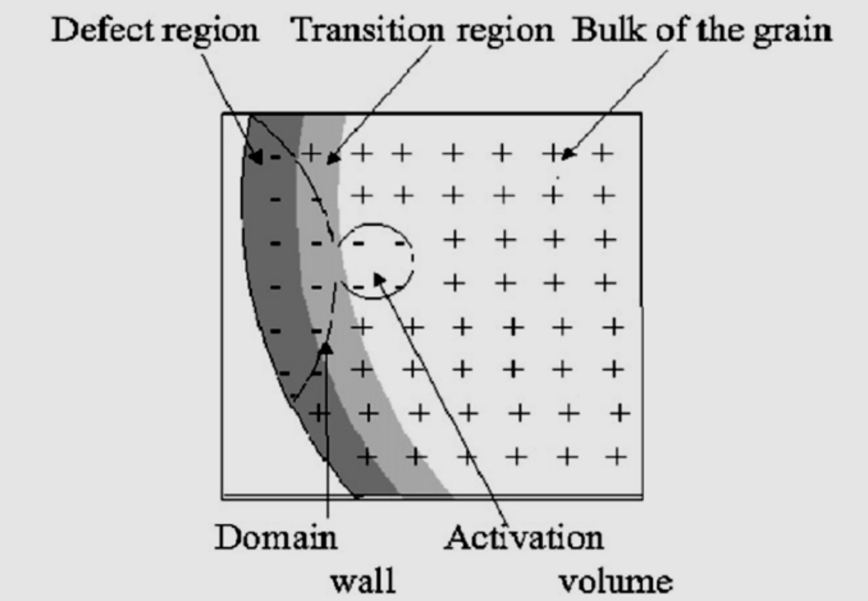


Fig. 4. Scheme of proposed determinant magnetization reversal process in ferrite or NdFeB magnets. The critical phenomenon is propagation/passage, it succeeds true nucleation at the grain surface, which is not determinant for reversal

D. Givord et al., J. Magn. Magn. Mat.258–259 (2003) 1

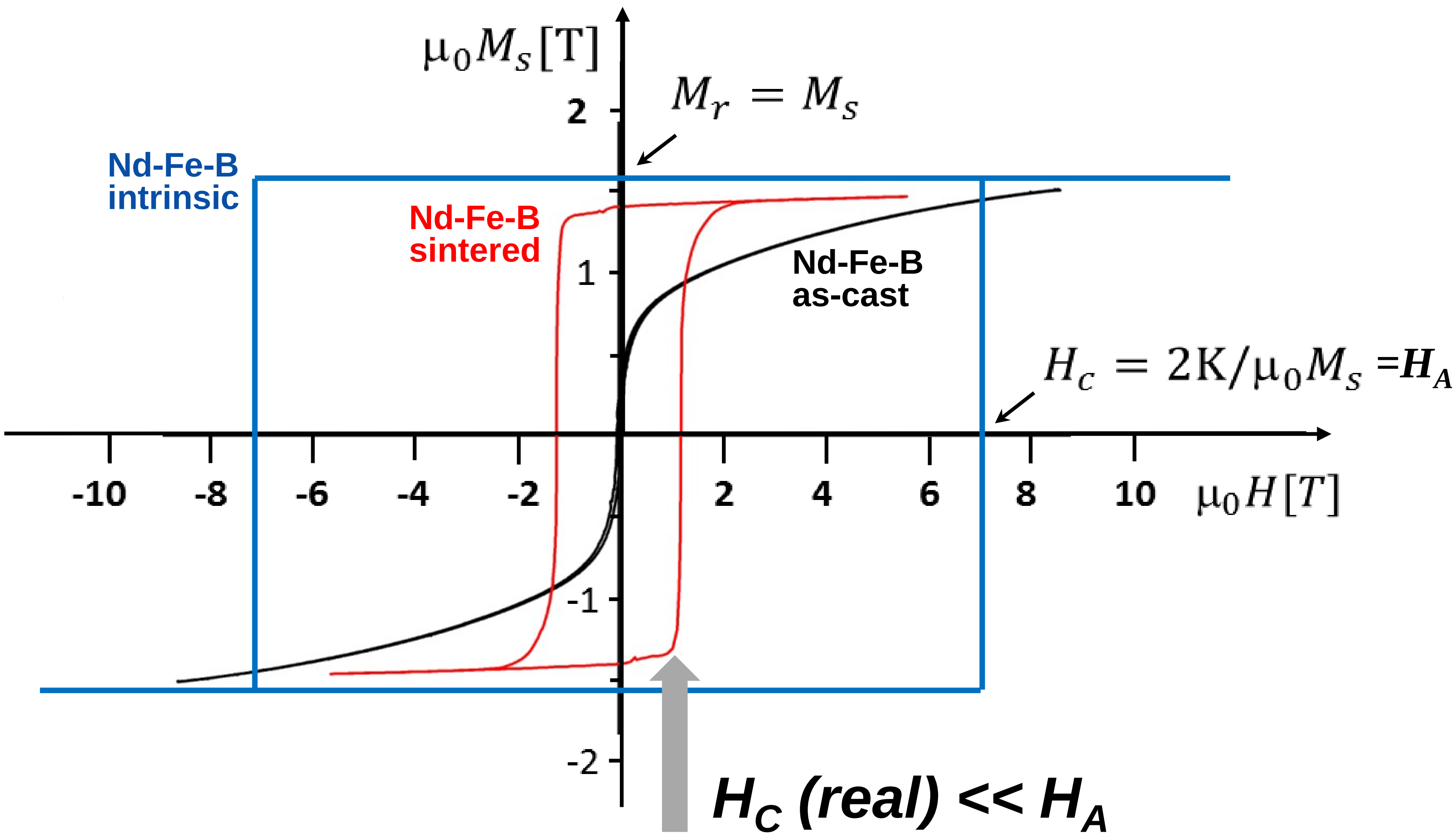
Reduction is principally attributed to chemical, structural or geometrical irregularities.
These heterogeneities lead to **local "magnetic softening",** i.e. spatial variations in anisotropy and exchange and thus small critical volumes where magnetization reversal is nucleated.

→ Identify **the weak link** in a complex multiphase microstructure by theory and experiment

→ **Multiscale** modelling and characterisation

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

- an unsolved problem in physics -



Reduction is principally attributed to **local "magnetic softening"** by chemical, structural or geometrical irregularities.

PERMANENT MAGNETISM

in High Magnetic Fields – Science and Technology, vol. 3, ed. F. Herlach and N. Miura, World Scientific Publ. Co. Pte. Ltd. Singapore, 2006, pp. 149-183.

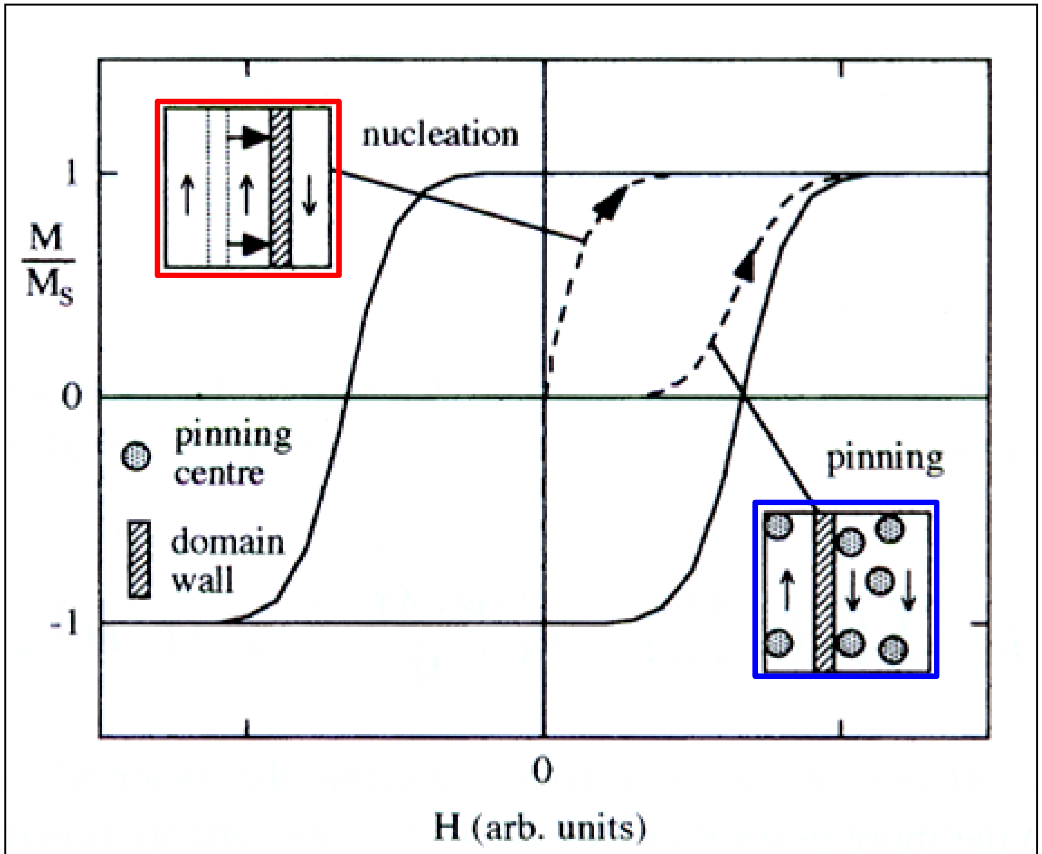
K.-H. MÜLLER, G. FUCHS and O. GUTFLEISCH
Leibniz Institute for Solid State and Materials Research Dresden,
POB 270116, D-01171 Dresden, Germany
E-mail: khm@ifw-dresden.de

$$_JH_c = \alpha H_A - N_{\text{eff}} M_s \tag{16}$$

where α and N_{eff} include the influence of microstructure [19,20,42,43]. In particular, α (with $0 < \alpha < 1$) describes the "softening" of ideal activation of homogeneous demagnetization modes and the effective demagnetization factor N_{eff} is a measure of local stray fields. It should be noted that, different from the true demagnetization factor, N_{eff} is not limited by Eq. (7). The terms "hard magnetic" or "permanent magnet material" should only be used if $_JH_c$ is not much smaller than M_s. Sometimes, these names are also used for magnetically highly anisotropic phases characterized by $H_A \gg M_s$ [40]. However, in accordance with Brown's paradox, for non-optimized microstructures $_JH_c \ll M_s \ll H_A$ can apply. It is of interest to note that the highest value of $_JH_c/H_A$ achieved so far is $\approx$ 20 % for commercial magnets and $\approx$ 40 % for laboratory magnets [42].

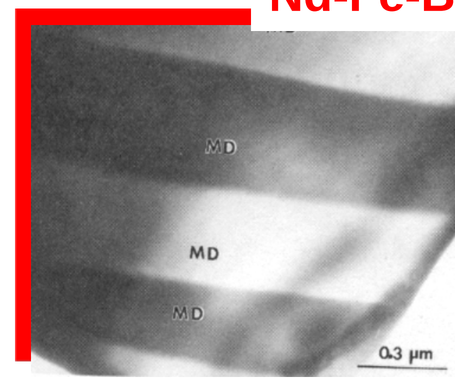
Fundamental coercivity mechanism

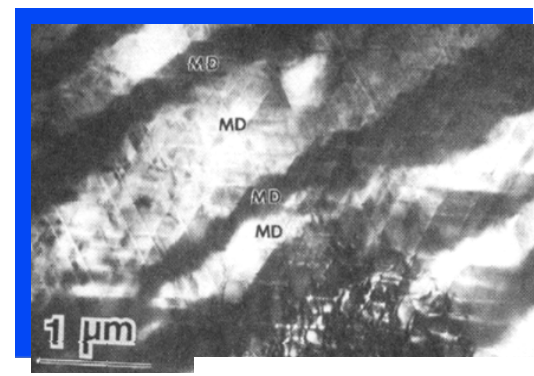
Initial magnetisation curve and field dependence of coercivity in nucleation and pinning-type magnets



Skomski and Coey 1999

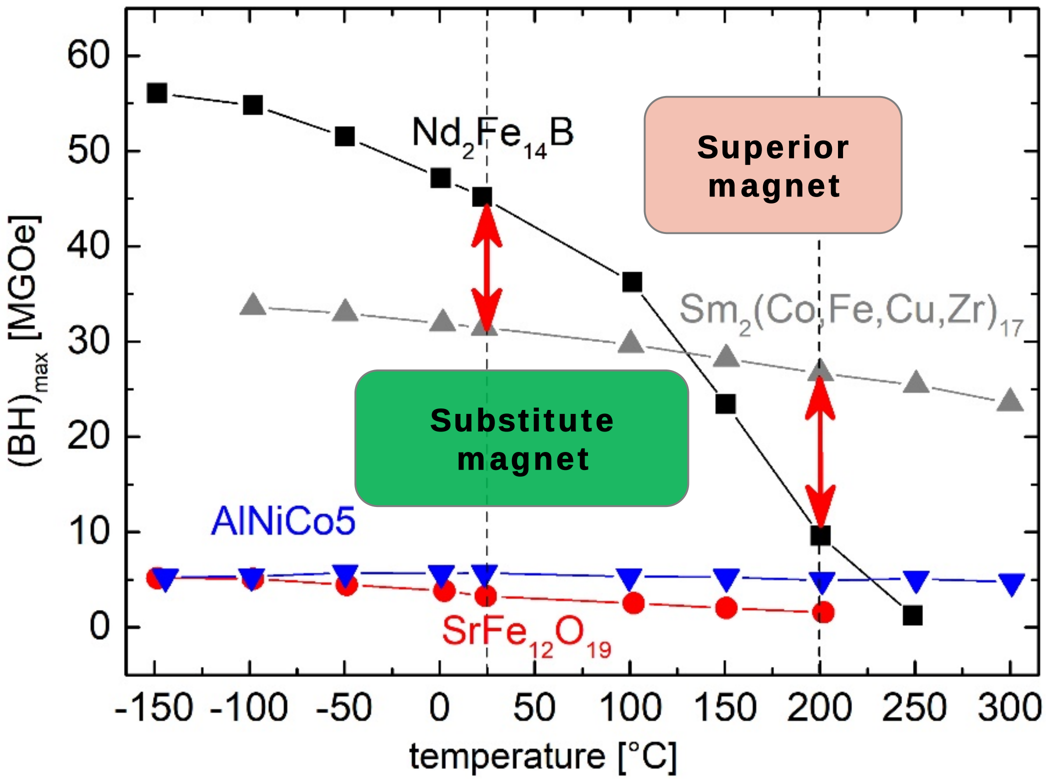
Nd-Fe-B





$Sm(CoFeCuZr)_z$

Sustainable bulk magnetic materials at their physical limits



→ **“new” magnets with secondary functionalities such as complex geometry by (nano-) additive manufacturing, local vs. effective anisotropy and exchange, mechanical, thermal and electrical properties**

Figure adapted from Magnetic Materials and Devices for the 21st Century, Review in Adv. Mat. 23 (2011) 821 and *Heavy rare earth free, free rare earth and rare earth free magnets*, Scripta Mat, View point 154 (2018) 289

Magnetic hardness kappa κ

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

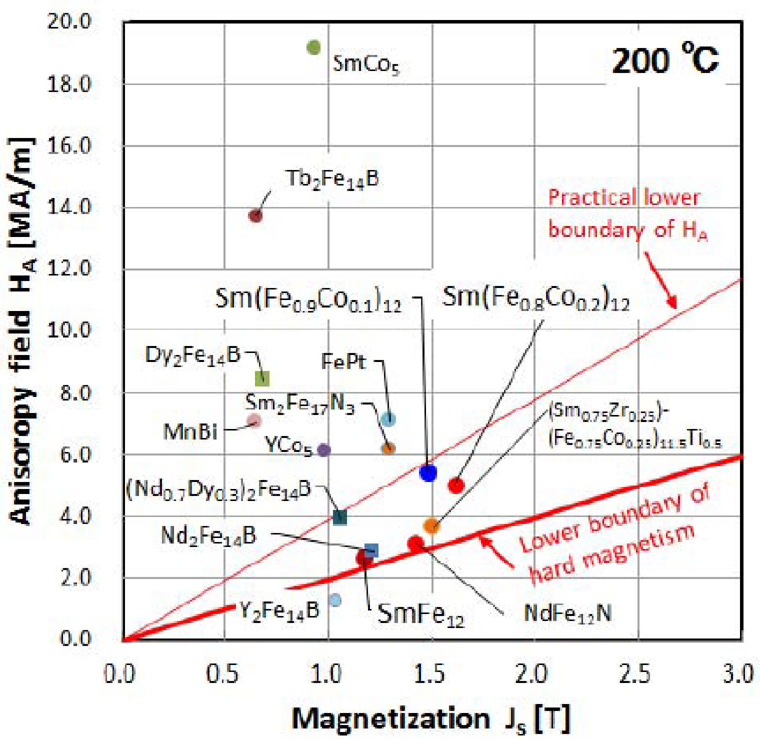


Fig. 1. Intrinsic magnetic properties of hard magnetic compounds at 200 °C based on various studies. This temperature is chosen as symbolic because high power-density machine inevitably operates at unfavorably high temperatures for permanent magnets. Red lines: lower boundary of hard magnetism corresponding to magnetic hardness factor (κ) of unity and the practical lower boundary for H_A corresponding to $\kappa = \sqrt{2}$.

Hirosawa. IEEE TRANSACTIONS ON MAGNETICS, VOL. 55, NO. 2, FEBRUARY 2019

NdFeB Permanent Magnets

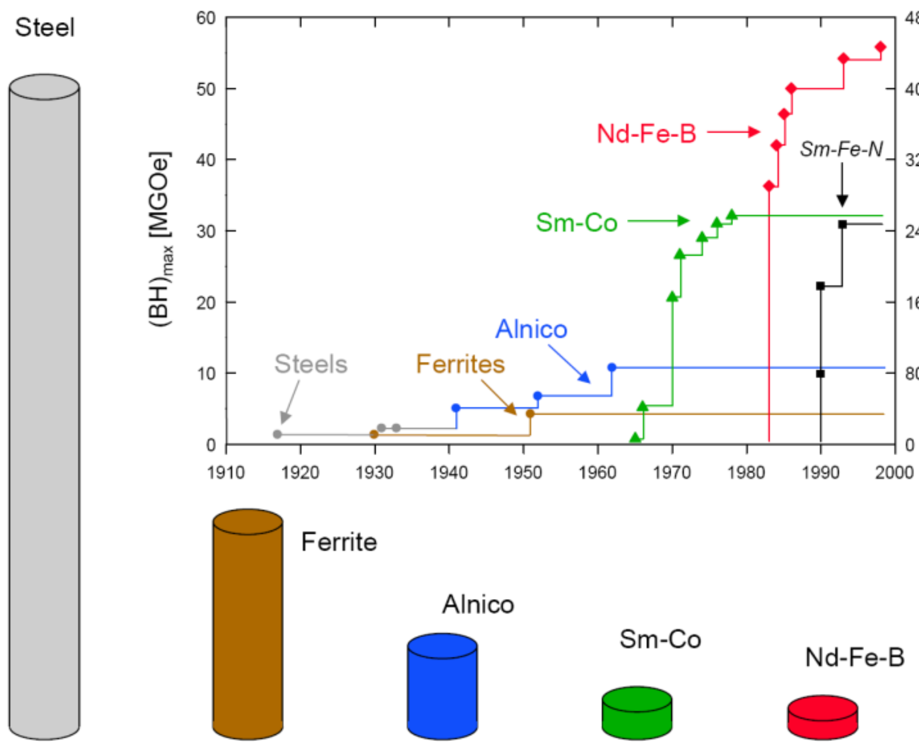
from intrinsic to extrinsic

towards mastery of coercivity

the strongest magnet

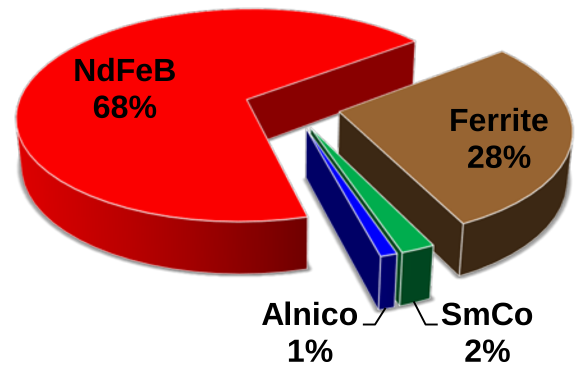
going even further in design and processing

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

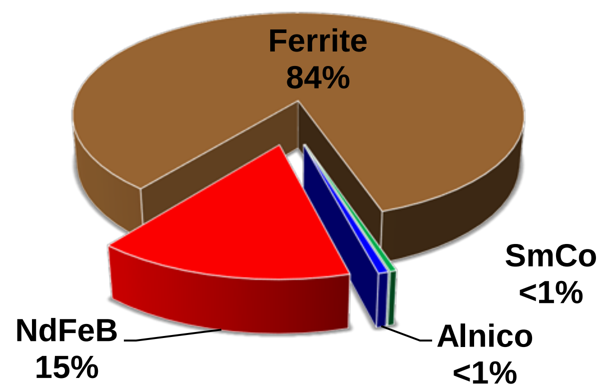


Adv. Mat. (Review) 23 (2011) 821

Market shares by value, 2016*



Market shares by mass, 2016*



*2016 forecast estimates
Constantinides, Magnetics Conference 2016

energy stored in permanent magnets

© Functional Materials

Sarmale cu mamaliga si carnati

Permanent magnet selection guidelines

Developing a new magnetic design and choosing a magnet:

- What are your requirements for the magnet?
- What maximum and minimum temperatures the magnet will be exposed to?
- Physical requirements and chemical environment in the application / of the material?
- Geometry (and the shaping for it), mass, volume, air gap, magnetic flux closure requirements?
- Price: low cost/low performance vs high cost/high performance application

- Sourcing/tracing your constituents of the magnets
- Check your value chain, your LCA, your LCC
- The recycling potential /design FOR recycling

Neodymium-Iron-Boron Magnet Grades
Summary Product List & Reference Guide
Basic Grades

	Properties	B_r		H_{cB}		H_{cJ}		$(BH)_{max}$		Temp. Coef.		T_w
	Grade**	Typical mT	Typical gauss	min kA/m	min oersteds	min kA/m	min oersteds	Typical kJ/m^3	Typical MGOe	$\alpha(B_r)$ %/°C	$\alpha(H_{cJ})$ %/°C	max °C
5	N30	1105	11050	796	100000	955	12000	235	30	-0.12	-0.750	80
6	N33	1150	11500	836	10500	955	12000	259	33	-0.12	-0.750	80
7	N35	1210	12100	860	10800	955	12000	0	0	-0.12	-0.618	80
8	N38	1260	12600	860	10800	955	12000	306	38	-0.12	-0.618	80
9	N40	1285	12850	923	11600	955	12000	318	40	-0.12	-0.618	80
10	N42	1315	13150	860	10800	955	12000	334	42	-0.12	-0.618	80
11	N45	1350	13500	860	10800	955	12000	350	44	-0.12	-0.618	80
12	N48	1400	14000	836	10500	875	11000	374	47	-0.12	-0.618	80
13	N50	1425	14250	836	10500	875	11000	390	49	-0.12	-0.618	80
14	N52	1450	14500	836	10500	875	11000	406	51	-0.12	-0.618	60
15	N55	1490	14900	716	9000	876	11000	430	54	-0.15	-0.618	60
16	N33M	1175	11750	836	10500	1114	14000	267	34	-0.12	-0.595	100
17	N35M	1210	12100	868	10900	1114	14000	283	35	-0.12	-0.595	100
18	N38M	1260	12600	899	11300	1114	14000	307	39	-0.12	-0.595	100
19	N40M	1285	12850	923	11600	1114	14000	322	40	-0.12	-0.595	100
20	N42M	1315	13150	955	12000	1114	14000	338	42	-0.12	-0.595	100
21	N45M	1350	13500	971	12200	1114	14000	354	44	-0.12	-0.595	100
22	N48M	1395	13950	995	12500	1114	14000	378	48	-0.12	-0.595	100
23	N50M	1415	14150	1035	13000	1114	14000	390	49	-0.12	-0.675	100
24	N52M	1445	14450	995	12500	1035	13000	406	51	-0.12	-0.675	100
25	N30H	1105	11050	796	10000	1353	17000	235	30	-0.12	-0.572	120
26	N33H	1175	11750	836	10500	1353	17000	267	34	-0.12	-0.572	120
27	N35H	1210	12100	868	10900	1353	17000	283	35	-0.12	-0.572	120
28	N38H	1260	12600	899	11300	1353	17000	307	39	-0.12	-0.572	120
29	N40H	1285	12850	923	11600	1353	17000	322	40	-0.12	-0.572	120
30	N42H	1300	13000	955	12000	1353	17000	330	41	-0.12	-0.572	120
31	N45H	1350	13500	971	12200	1353	17000	354	44	-0.12	-0.572	120
32	N48H	1390	13900	1011	12700	1273	16000	378	48	-0.12	-0.572	120
33	N50H	1415	14150	1035	13000	1274	16000	390	49	-0.12	-0.605	120

Randomly picked one of many manufacturers,
I declare no competing interests….

ARNOLD MAGNETIC TECHNOLOGIES
770 Linden Ave. • Rochester, NY 14625-2764 USA
Tel: 800-593-9127 • (+1) 585-385-9010 • Fax: (+1) 585-385-5625
Email: info@arnoldmagnetics.com
www.arnoldmagnetics.com

©2019 Arnold Magnetic Technologies

Permanent magnet selection guidelines

TECHNISCHE UNIVERSITÄT DARMSTADT

Sintered Neodymium-Iron-Boron Magnets

These are also referred to as "Neo" or NdFeB magnets. They offer a combination of high magnetic output at moderate cost. Please contact Arnold for additional grade information and recommendations for protective coating. Assemblies using these magnets can also be provided.

	Characteristic	Units	min.	nominal	max.
Magnetic Properties	**Br**, Residual Induction	Gauss	13,200	13,500	13,800
		mT	1320	1350	1380
	H_{cB}, Coercivity	Oersteds	12,200	12,700	13,200
		kA/m	971	1011	1050
	H_{cJ}, Intrinsic Coercivity	Oersteds	17,000		
		kA/m	1,353		
	BHmax, Maximum Energy Product	MGOe	42	45	47
		kJ/m^3	334	354	374

	Characteristic	Units	C //	C ⊥
Thermal Properties	Reversible Temperature Coefficients [1]			
	of Induction, α(Br)	%/°C	-0.120	
	of Coercivity, α(Hcj)	%/°C	-0.605	
	Coefficient of Thermal Expansion [2]	ΔL/L per °C$\times10^{-6}$	7.5	-0.1
	Thermal Conductivity	W / (m • K)	7.6	
	Specific Heat [3]	J / (kg • K)	460	
	Curie Temperature, Tc	°C	310	
Other Properties	Flexural Strength	psi	41,300	
		MPa	285	
	Density	g/cm^3	7.5	
	Hardness, Vickers	Hv	620	
	Electrical Resistivity, ρ	μΩ • cm	180	

Notes: (1) Coefficients measured between 20 and 120 °C (2) Between 20 and 200 °C (3) Between 20 and 140 °C

Randomly picked one of many manufacturers,
I declare no competing interests….

ARNOLD MAGNETIC TECHNOLOGIES

770 Linden Ave. • Rochester, NY 14625-2764 USA
Tel: 800-593-9127 • (+1) 585-385-9010 • Fax: (+1) 585-385-5625
Email: info@arnoldmagnetics.com

www.arnoldmagnetics.com

©2019 Arnold Magnetic Technologies

Einsatztemperaturen von Neodym-Magneten

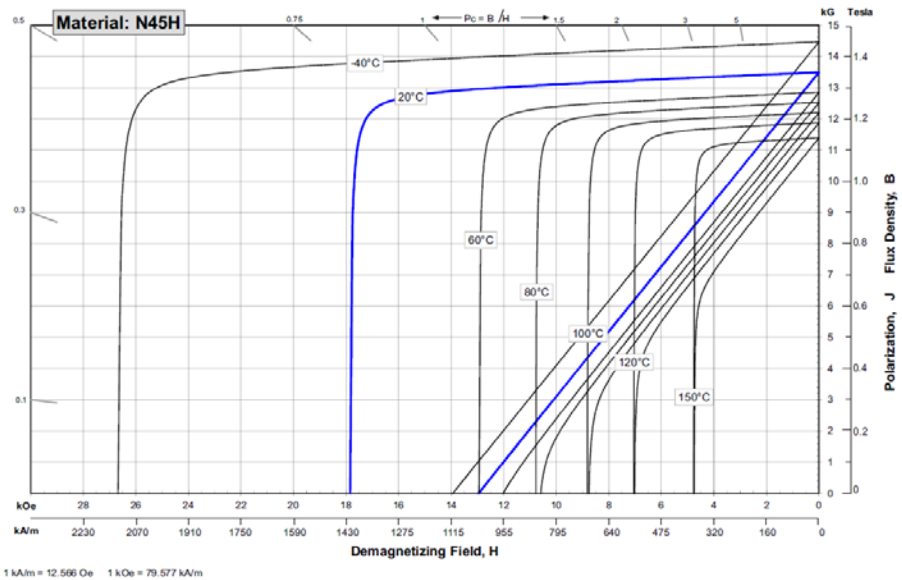
Überblick über die verschiedenen Temperaturtypen bei
Neodym-Magneten (übernommen von der Seite Physikalische Magnet-Daten).

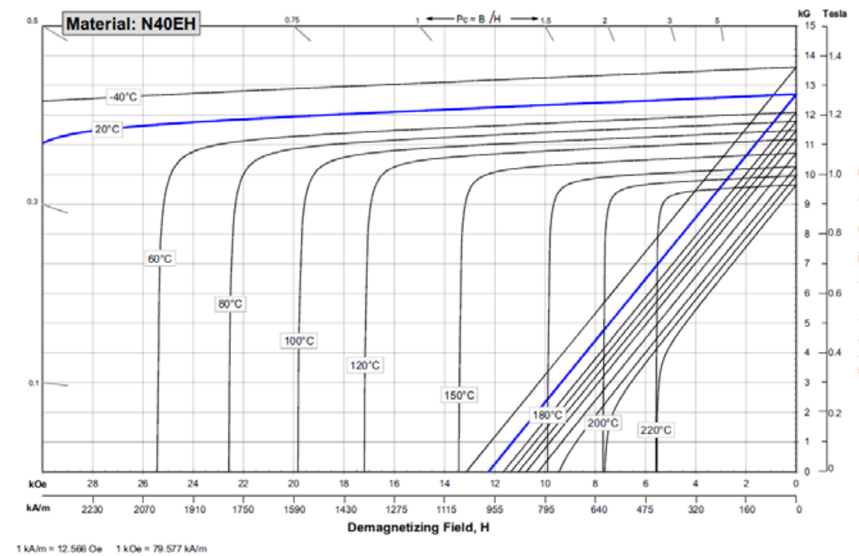
Temperaturtyp	Max. Einsatztemperatur	Curie-Temperatur
N	80 °C	310 °C
M	100 °C	340 °C
H	120 °C	340 °C
SH	150 °C	340 °C
UH	180 °C	350 °C
EH	200 °C	350 °C
AH	230 °C	350 °C

https://www.supermagnete.de/physical-magnet-data

Permanent magnet selection guidelines

N45H	1350	13500	971	12200	1353	17000	354	44	-0.12	-0.572	120





N40EH	1270	12700	915	11500	2388	30000	314	39	-0.12	-0.420	200

ARNOLD MAGNETIC TECHNOLOGIES
www.arnoldmagnetics.com

Randomly picked one of many manufacturers,
I declare no competing interests….

Permanent magnet selection guidelines

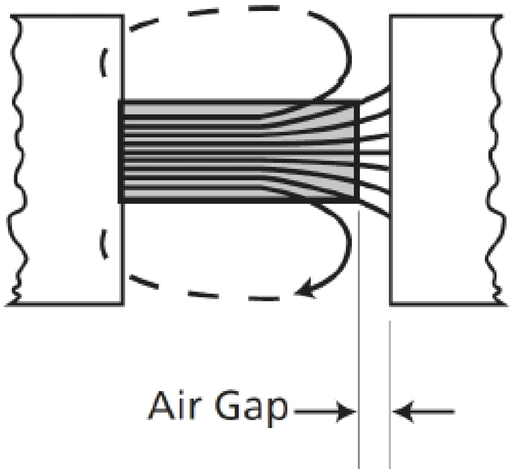


Figure 8: Air gap influence.

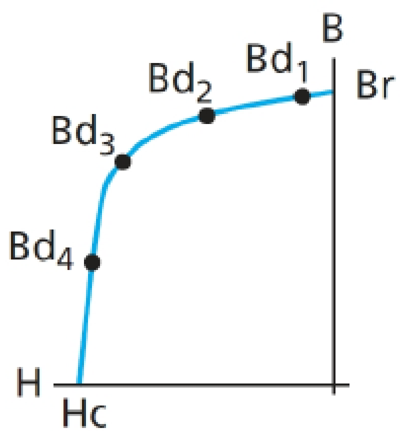


Figure 9: Bd (flux density) versus air gap size.

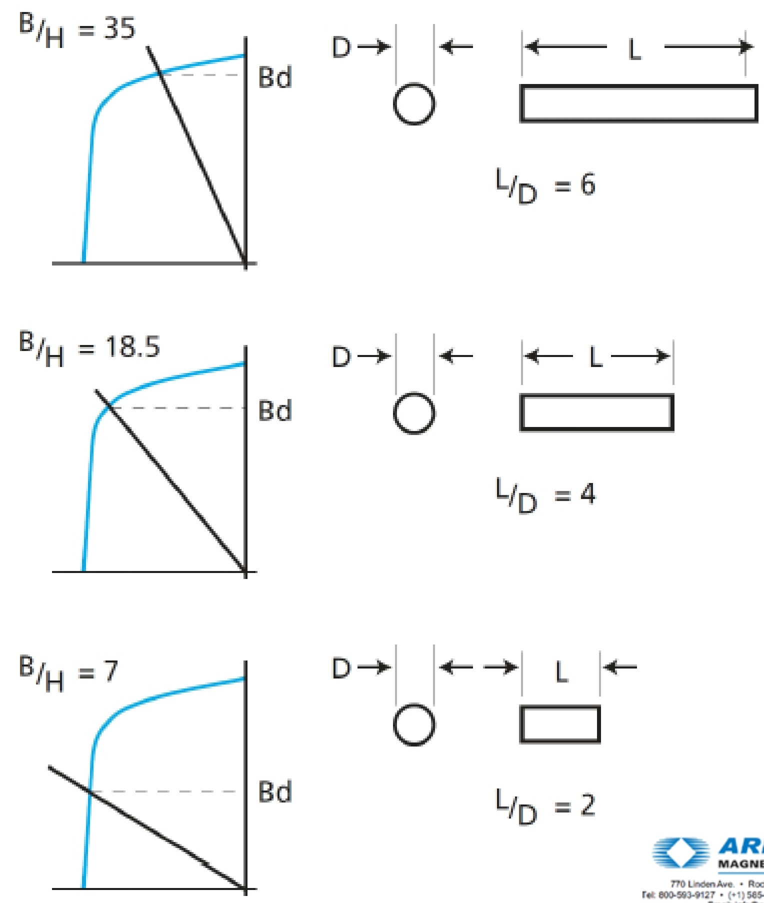


Figure 10: Open circuit conditions.

ARNOLD MAGNETIC TECHNOLOGIES
www.arnoldmagnetics.com

Permanent magnet selection guidelines

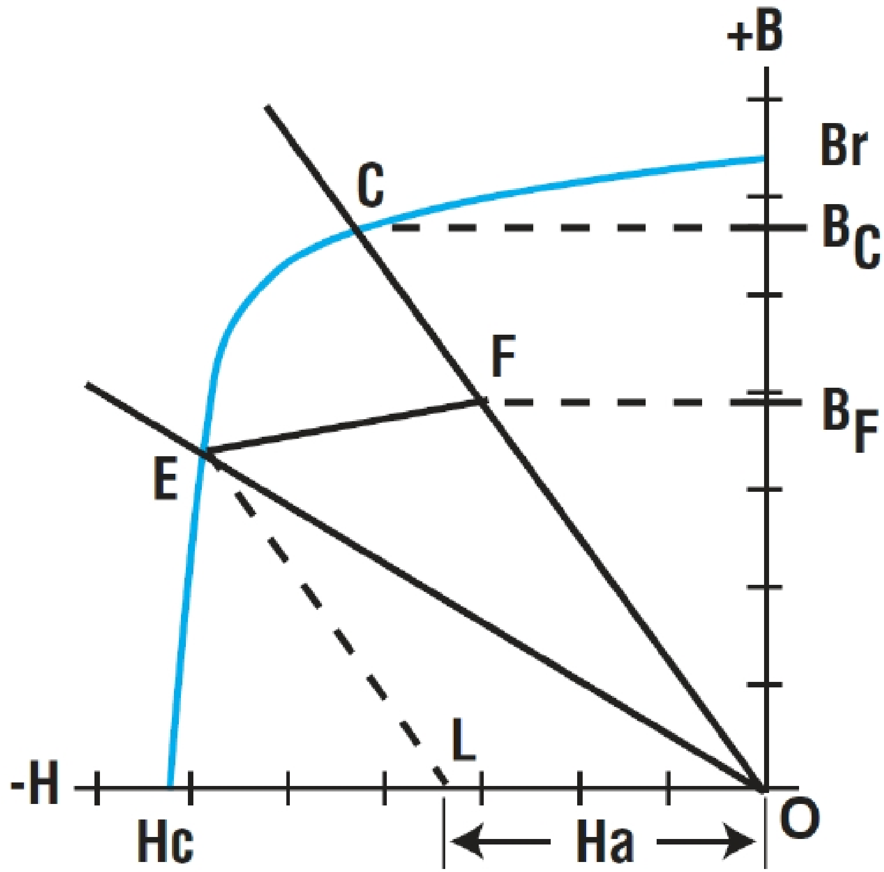
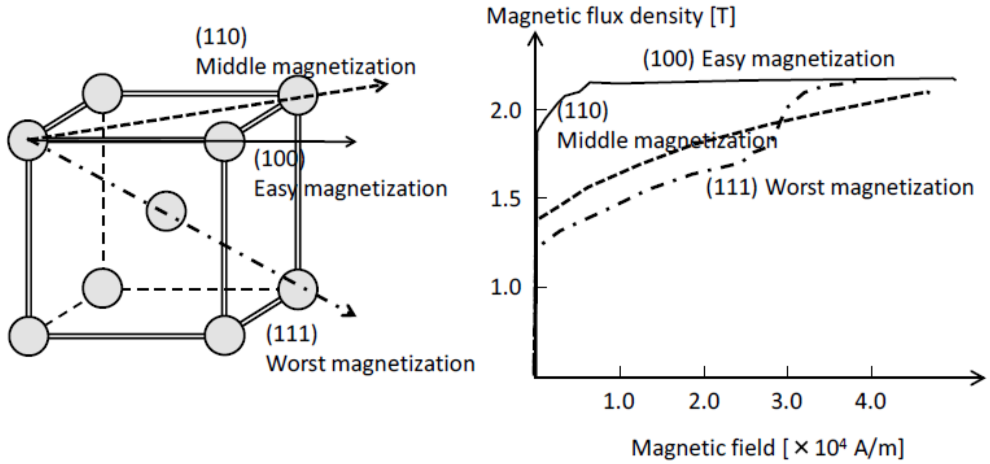


Figure 15: Externally applied field, Ha.

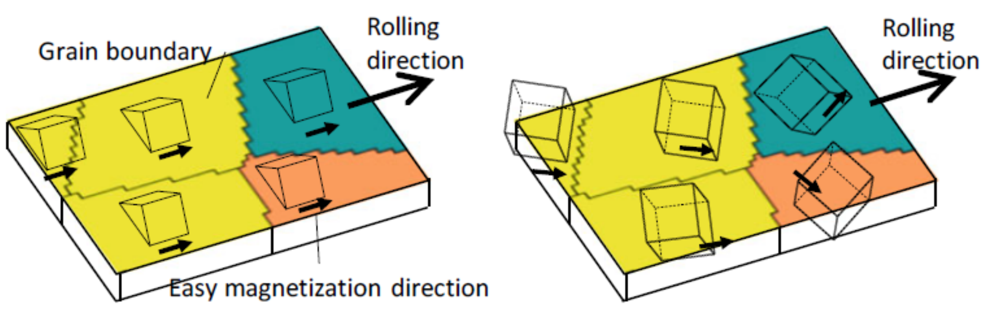
ARNOLD
MAGNETIC TECHNOLOGIES
770 Linden Ave. • Rochester, NY 14625-2764 USA
Tel: 800-593-9127 • (+1) 585-385-9010 • Fax: (+1) 585-385-5625
Email: info@arnoldmagnetics.com
www.arnoldmagnetics.com
©2019 Arnold Magnetic Technologies

easy magnetization axis



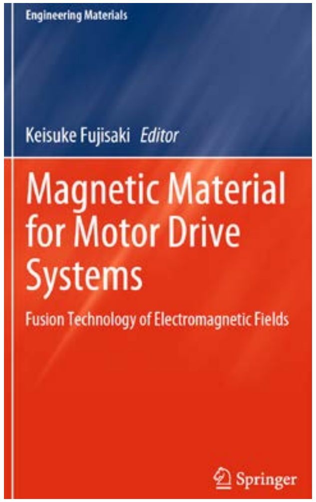
https://doi.org/10.1007/978-981-32-9906-1

Fig. 1 bcc-structure of iron and its crystal orientation (left) and its magnetization (right)

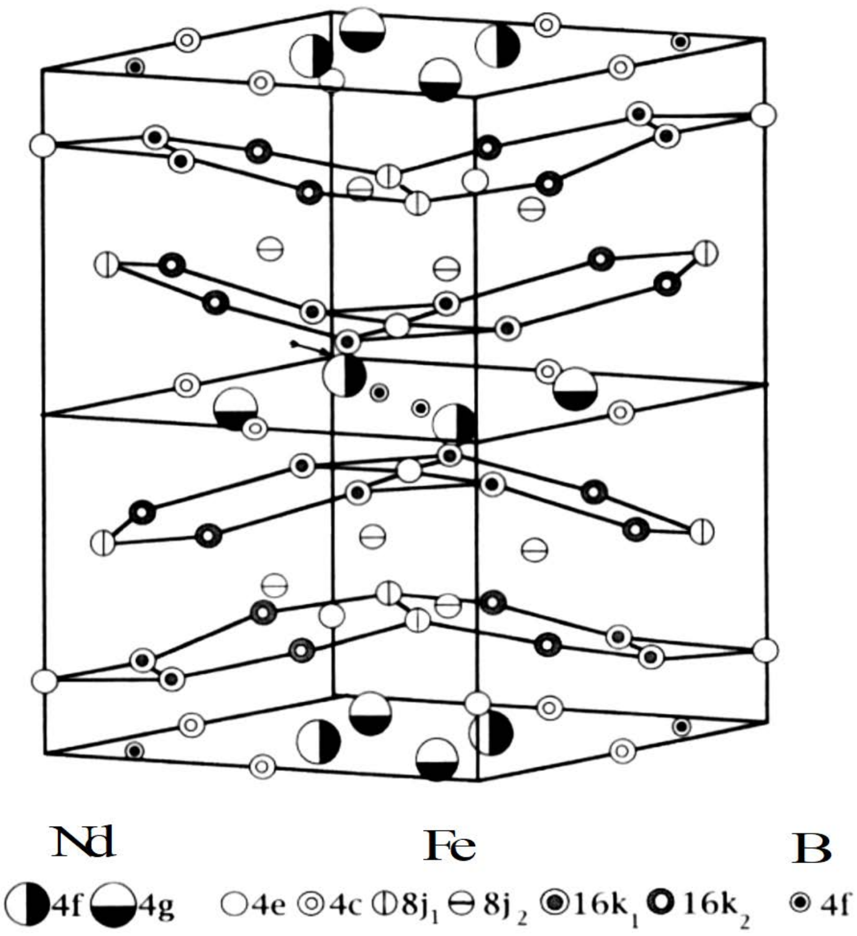


(a) Grain-Oriented steel (GO material) (b) Non-Oriented steel (NO material)

Fig. 2 Electrical steel with texture in some orientations of crystals



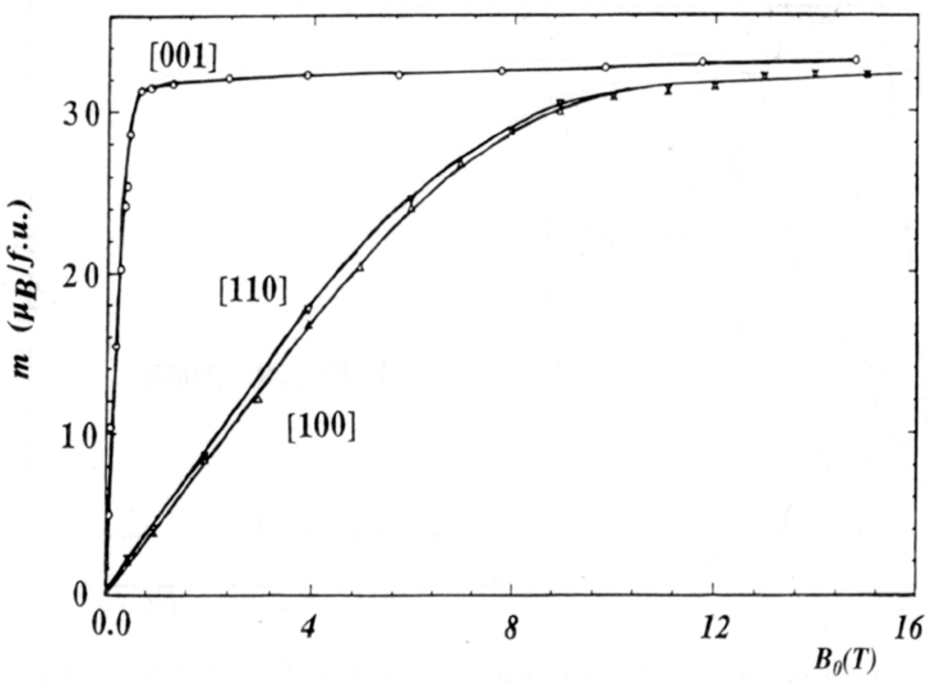
$Nd_2Fe_{14}B$



- $Nd_2Fe_{14}B$ 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*)

M_s = 1.61 T
μ_0H_A = 6.7 T
T_C = 585 K

A = 6.6 pJ m^{-1}
K = 4.3 MJ m^{-3}
l_{ex} = 1.2 nm
κ = 1.54
D_c = 200-300nm

Magnetism in $Nd_2Fe_{14}B$

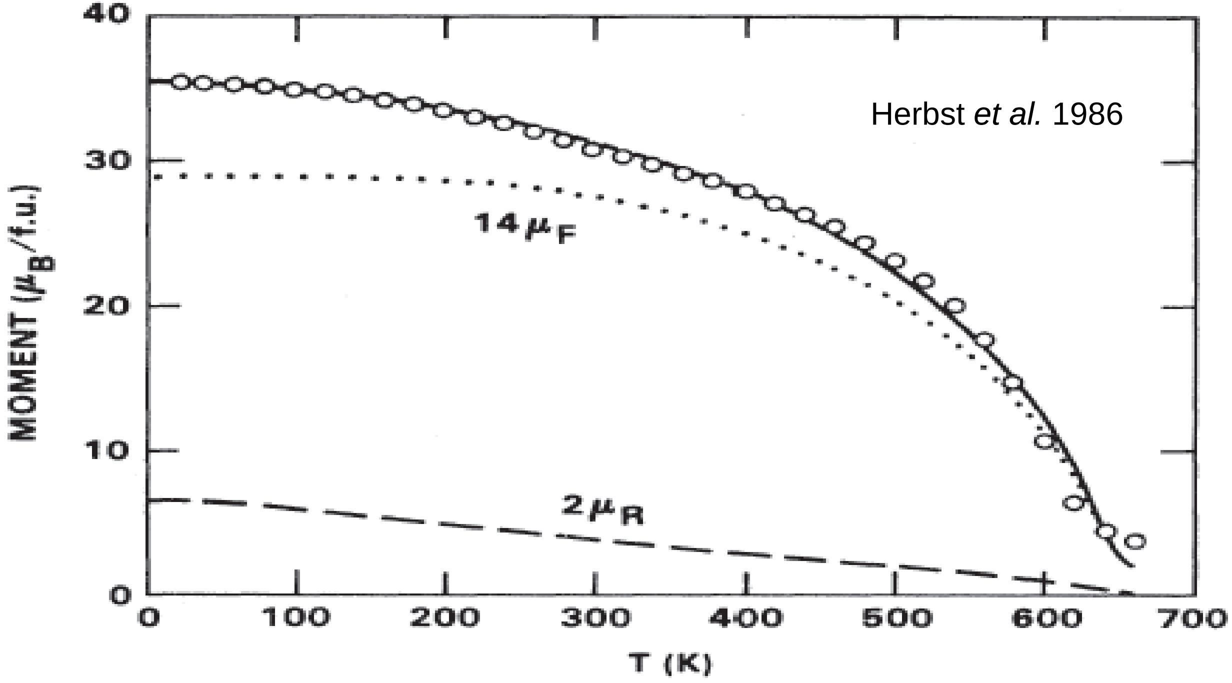


FIG. 11. Molecular-field analysis for $Nd_2Fe_{14}B$ (Fuerst *et al.*, 1986). Open circles denote the measured moment per formula unit. The solid line is the calculated total moment, which is the sum of the iron (dotted line) and neodymium (dashed line) contributions.

From intrinsic to extrinsic

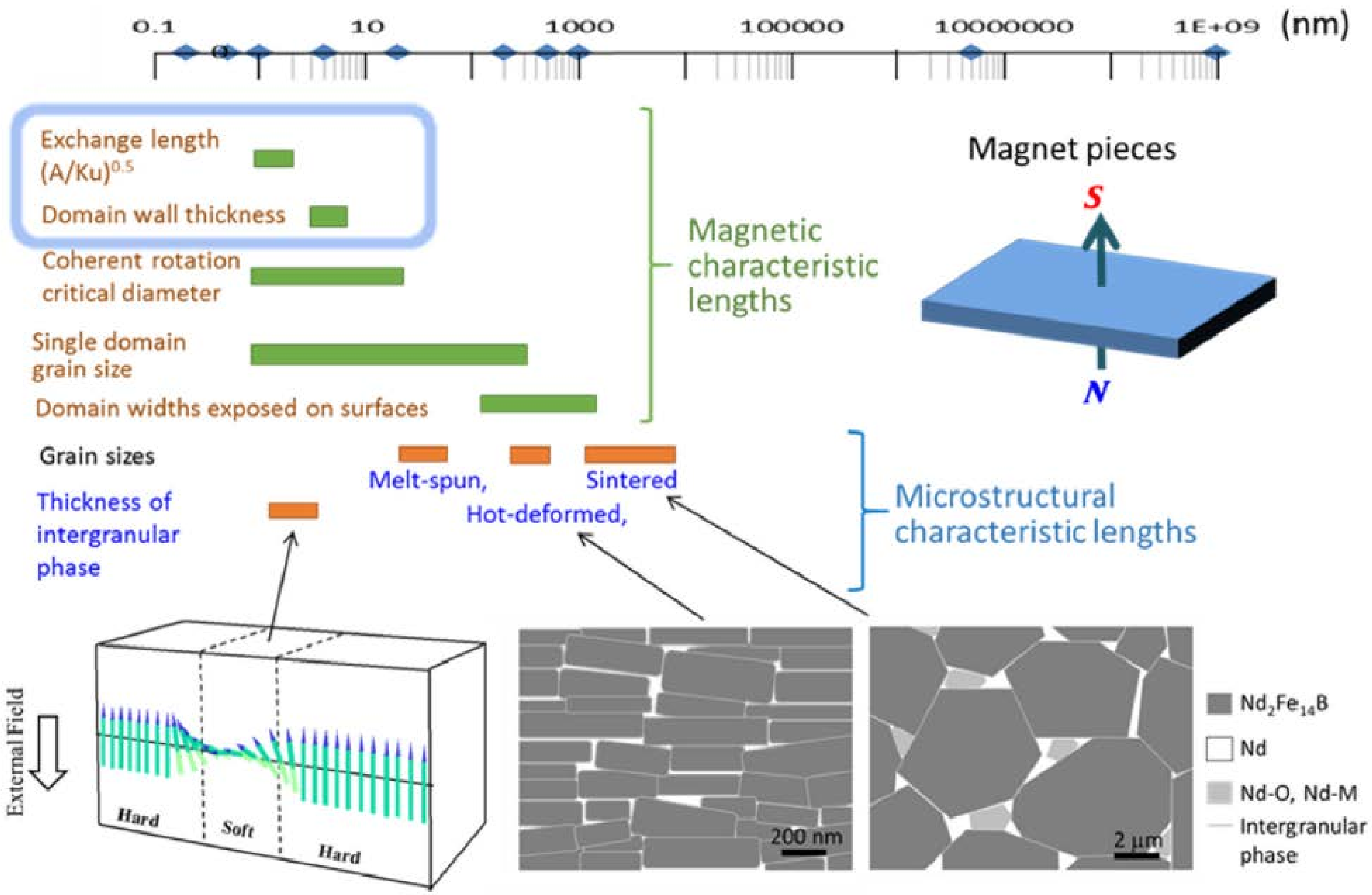


Figure 1. Magnetic characteristic lengths and illustration of typical microstructures in permanent magnets (anisotropic Nd–Fe–B magnets).

Hirosawa et al, Adv. Nat. Sci.: Nanosci. Nanotechnol. **8** (2017) 013002

From intrinsic to extrinsic

crystal electric field (CEF) Hamiltonian: $$\mathcal{H}^{J}_{CEF} = \sum_{l,m} \Theta_l A_l^m \langle r^l \rangle \widehat{O}_l^m$$

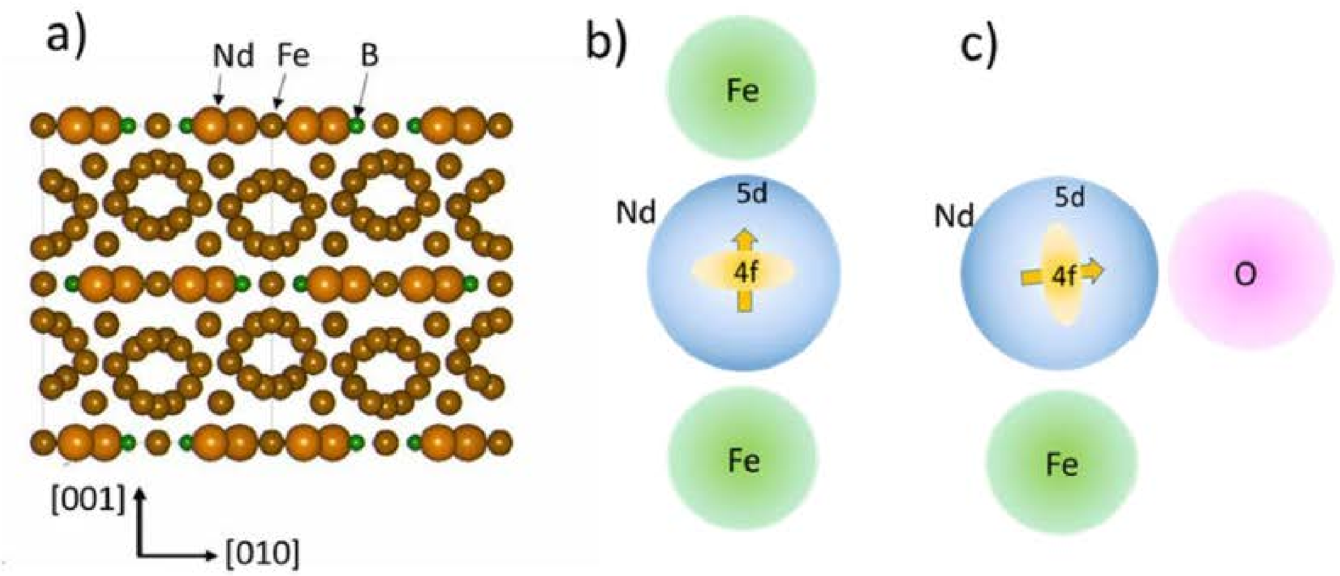
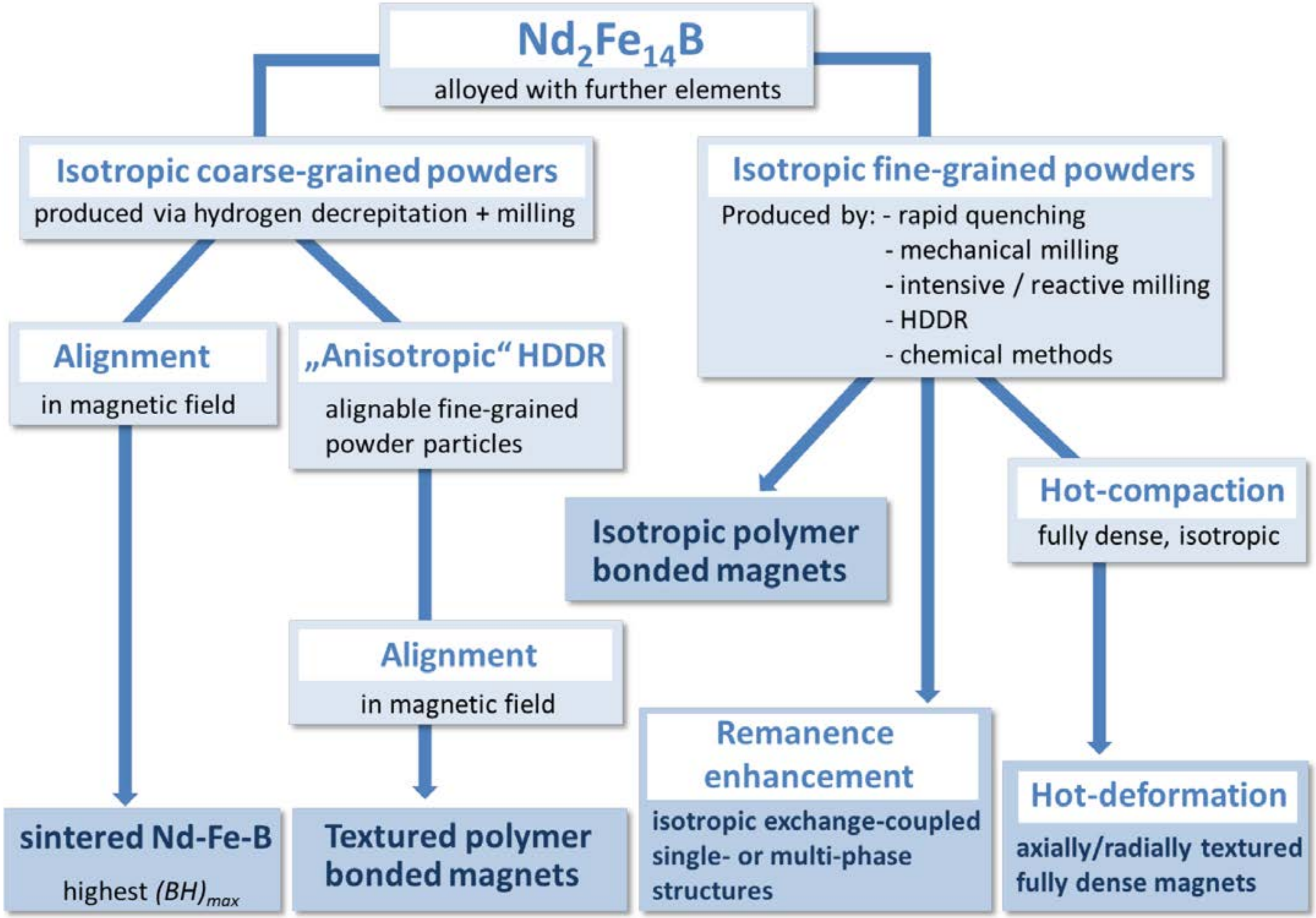


Figure 2. Illustrations of atomic arrangements in the $Nd_2Fe_{14}B$ crystal structure viewed along the [1 0 0] axis (a), the pancake-shaped 4f orbitals of an Nd ion sitting in an aspherical distribution of valence electrons which has larger density along the principal axis of symmetry of the $Nd_2Fe_{14}B$ lattice (b), and a hypothetical situation at an interface with a sub-phase containing oxygen in which the Nd valence electrons moved toward the oxygen atom for bonding.

Hirosawa et al, Adv. Nat. Sci.: Nanosci. Nanotechnol. **8** (2017) 013002

Principal processing routes of Nd-Fe-B magnets

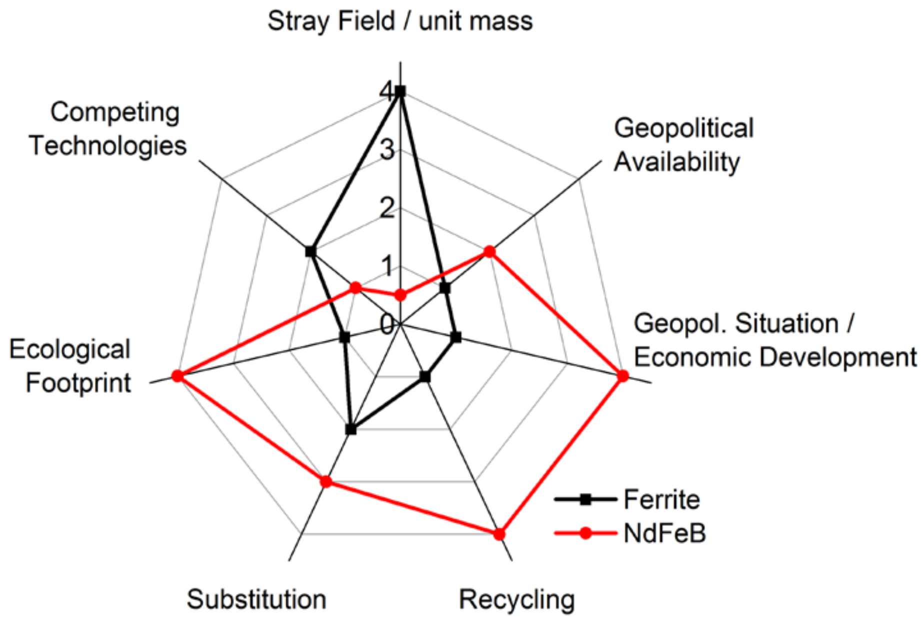
based on coarse grained and nanocrystalline powders



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.

Our playground – permanent magnets

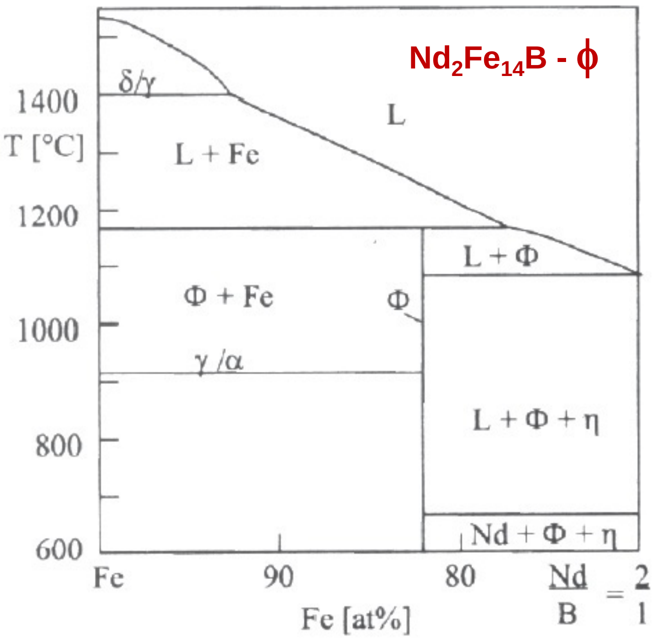
- heavy rare earth free:
  ~~Dy and Tb~~
- rare earth lean:
  $(Nd/Ce/Sm)Fe_{12}$
- free rare earth:
  Ce/La based
- rare earth free magnets:
  MnAl, FeSn, ..



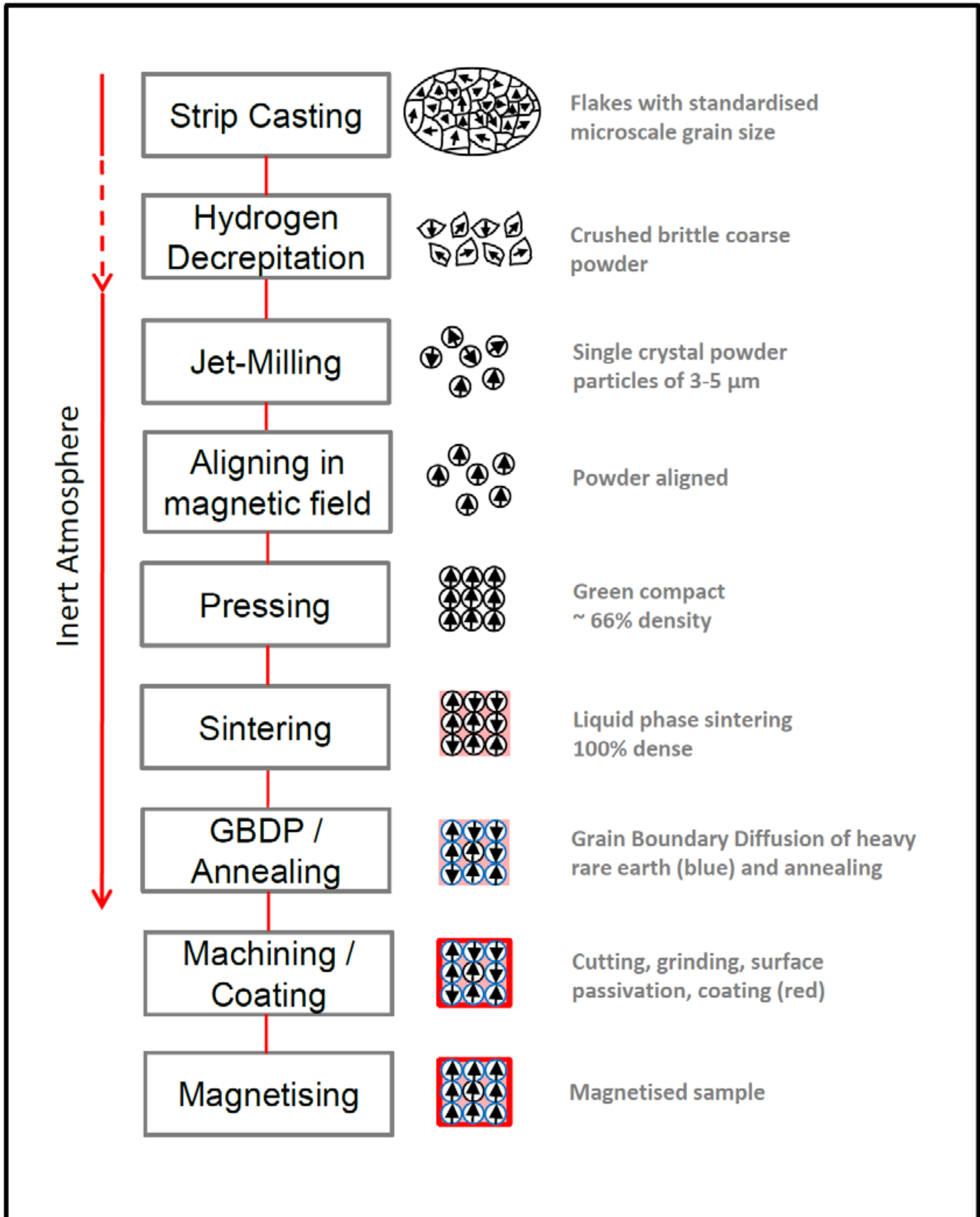
Criticality of strategic metals

Heavy rare earth free, free rare earth and rare earth free magnets,
Scripta Mat, View point 154 (2018) 289

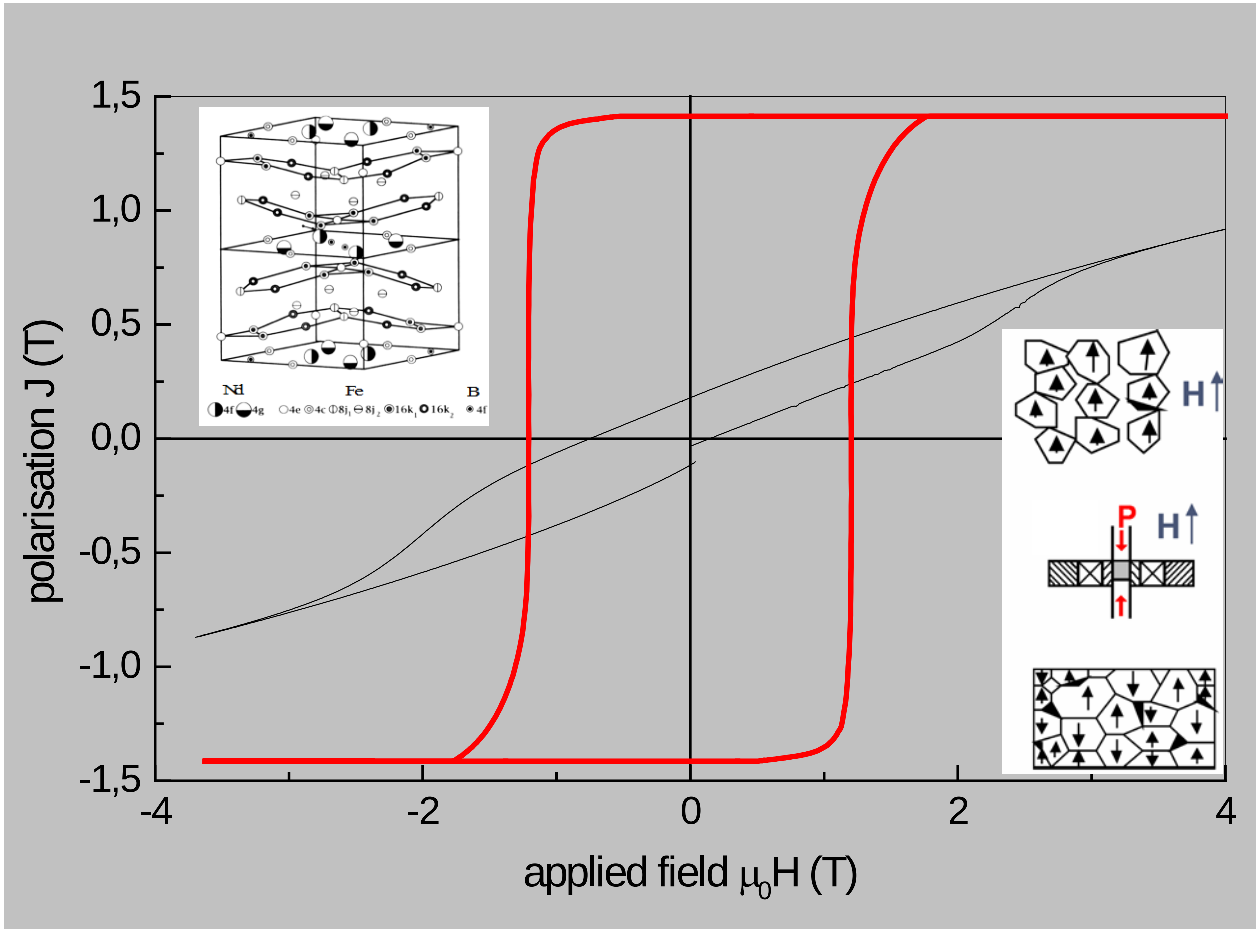
NdFeB sintered magnets

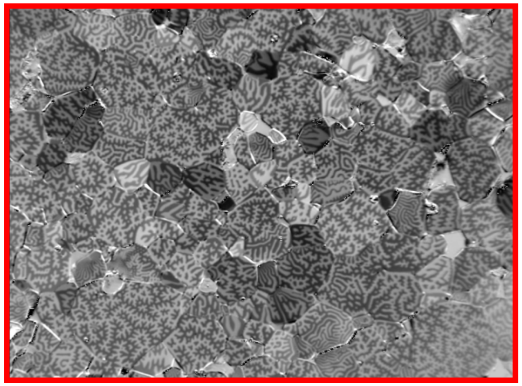


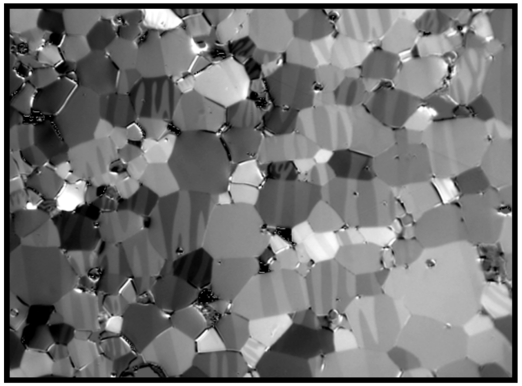
[redacted]



NdFeB sintered magnets

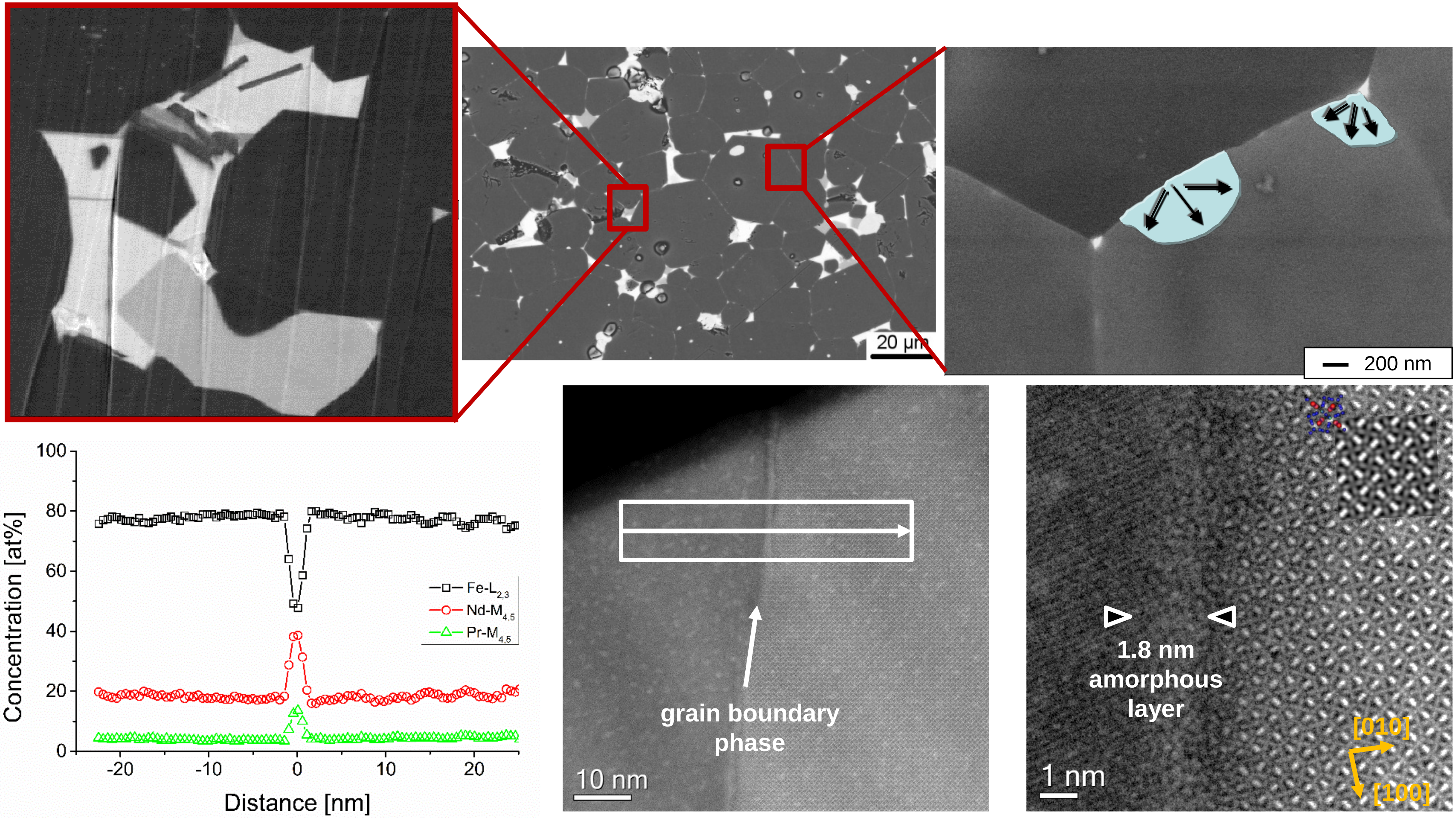






5μm

Microstructure of sintered NdFeB – the weak link



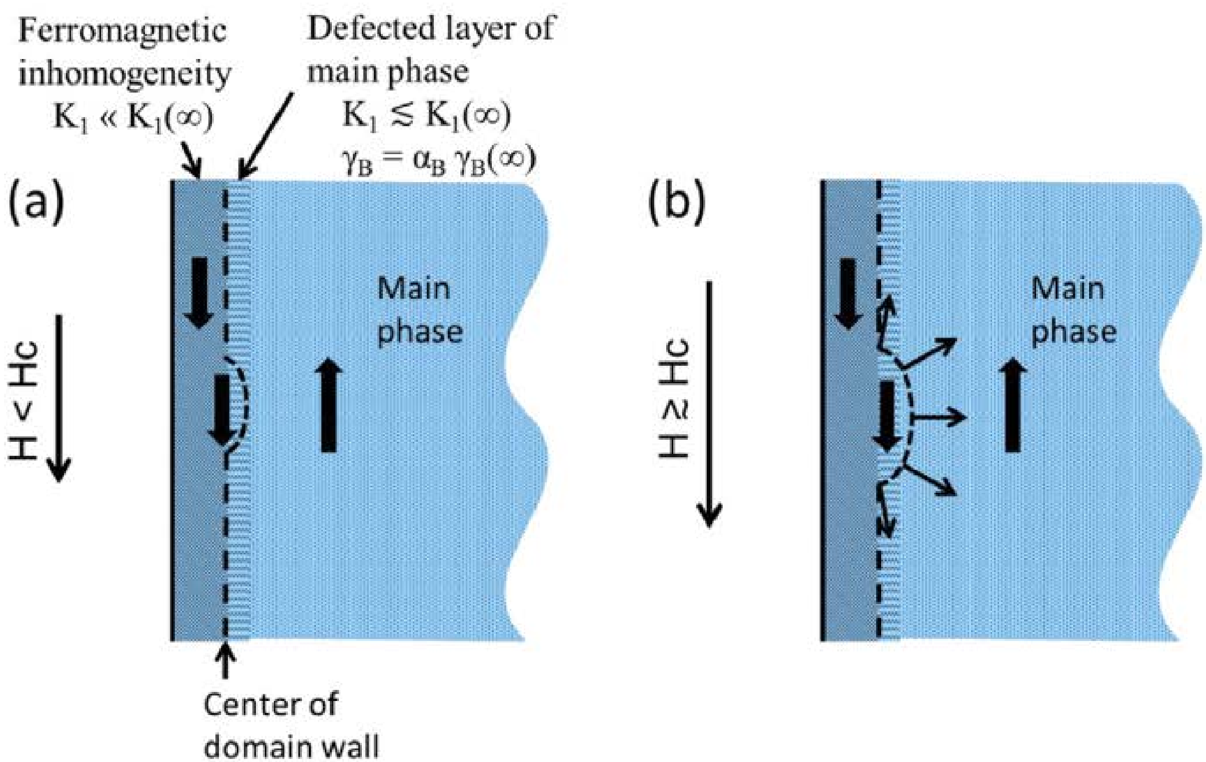


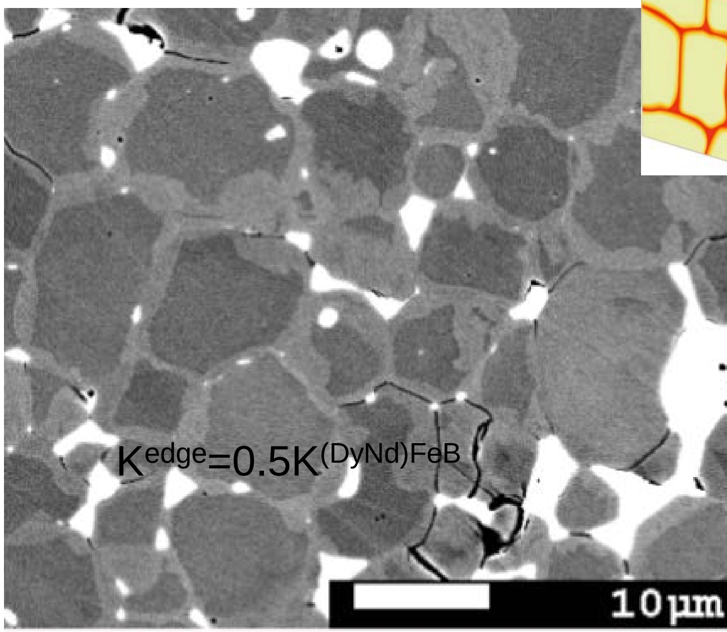
Figure 3. Illustrations of thermally activated 3D process of local depinning of a domain wall from a magnetic inhomogeneity into the matrix of a hard magnetic phase, before depinning (a) and a depinning incidence (b).

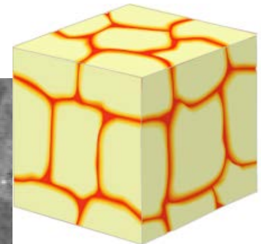
Hirosawa et al, Adv. Nat. Sci.: Nanosci. Nanotechnol. **8** (2017) 013002

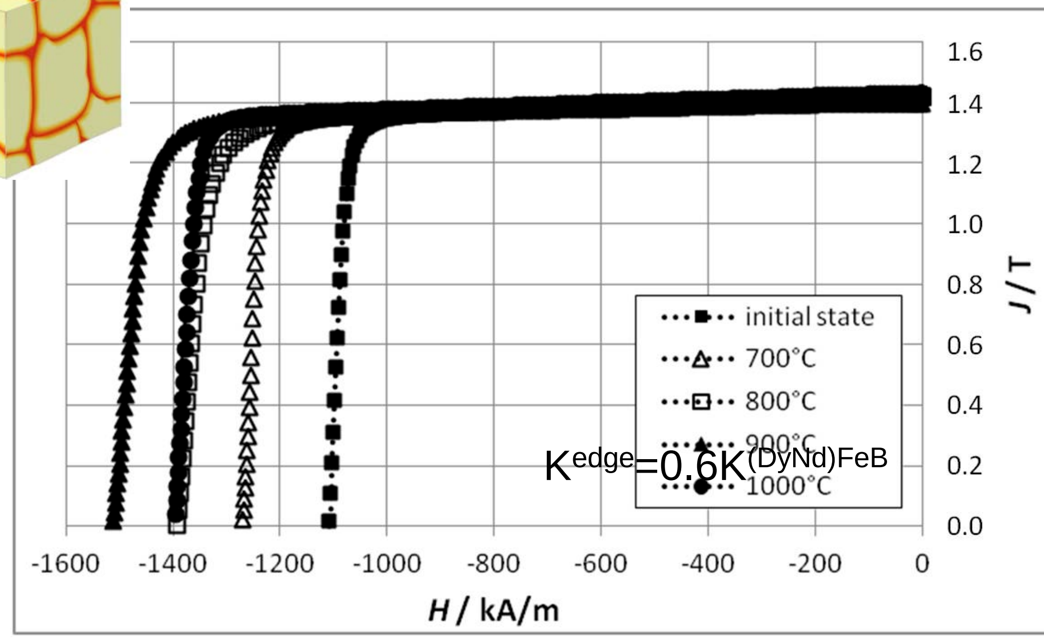
Grain boundary diffusion processes (GBDP)

Efficient utilization of heavy rare earth Dy or Tb

TECHNISCHE UNIVERSITÄT DARMSTADT







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

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

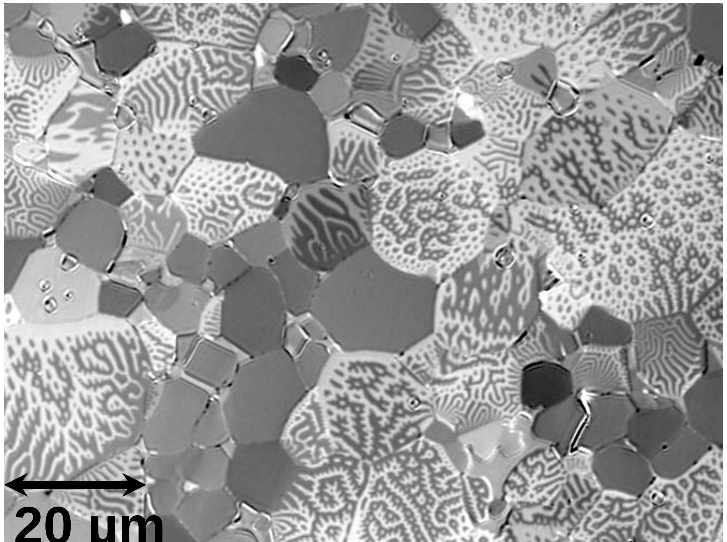
Hirosawa et al. J. Appl. Phys. 59 , 873, 1986

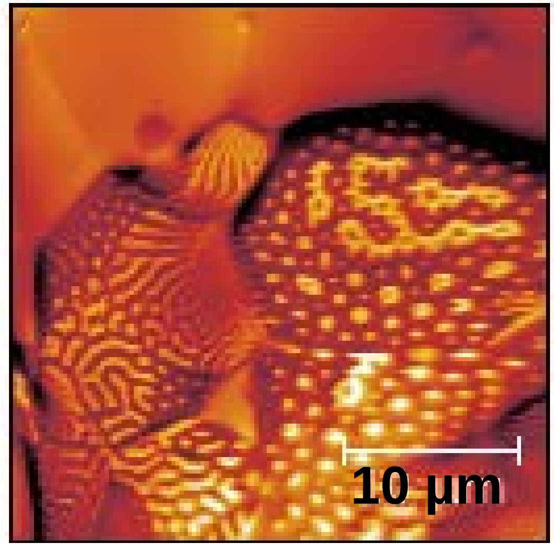
Acta Materialia 83 (2015) 248

Acta Materialia 127 (2017) 498
Physical Rev. Appl. 8 (2017) 014011

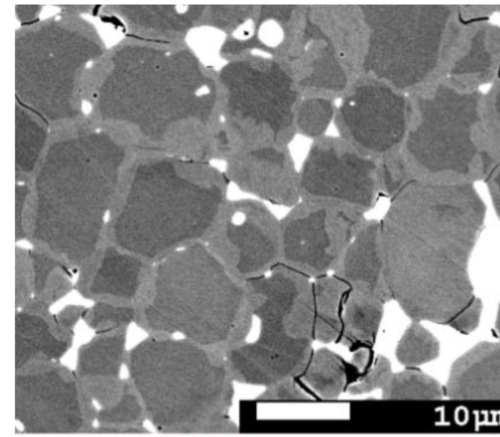
In-situ Magnetisation reversal

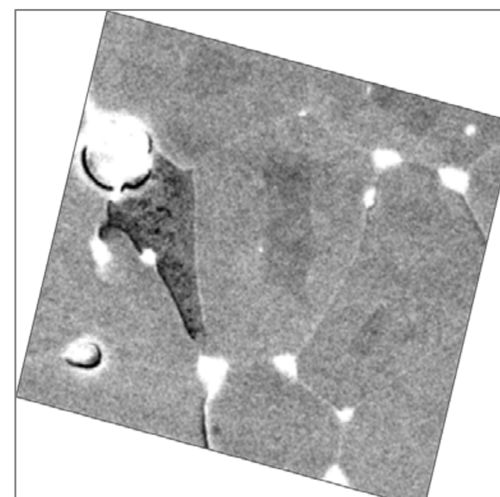
in GBDP processed sintered Nd-Fe-B magnets



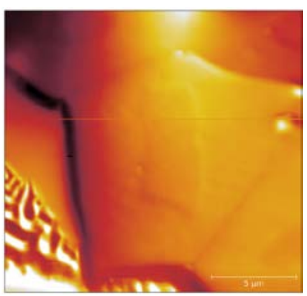


Remanent State (0 Tesla)
local switching by Kerr vs MFM

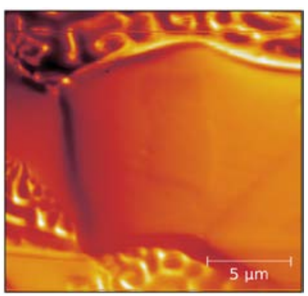




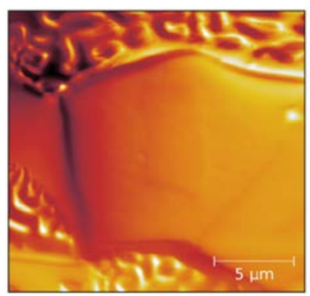
0 T



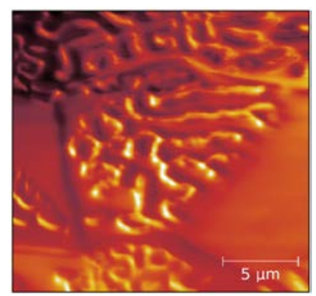
-0.1 T



-0.2 T



-0.3 T



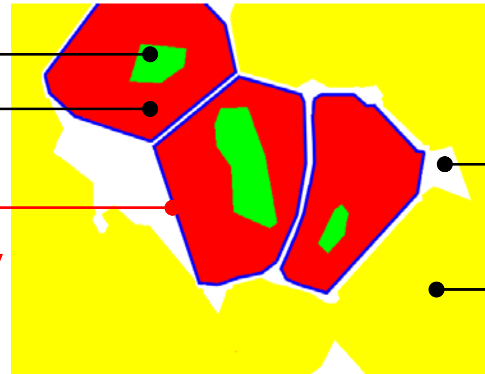
Acta Materialia 127 (2017) 498

Micromagnetic simulation of reversal process

NdFeB core

(DyNd)FeB shell

edge layer
with anisotropy
K^{edge}

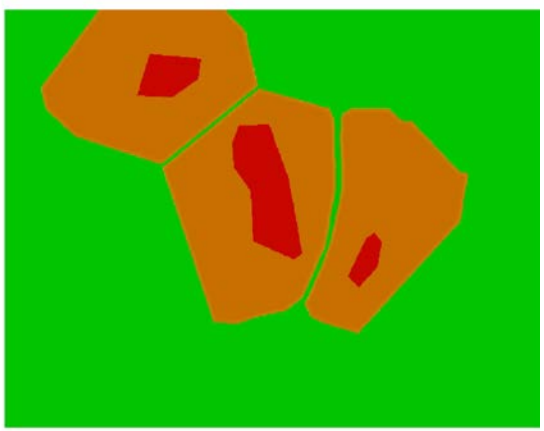


nonmagnetic material

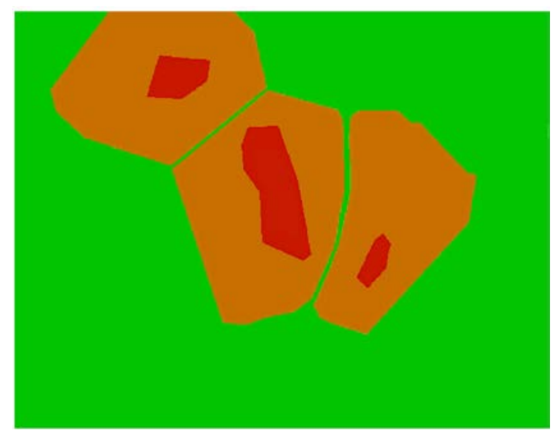
reversal region at remanent state (nonmagnetic material)

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

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



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



$\Rightarrow$ K^{edge} defines position of nucleation site

Acta Materialia 127 (2017) 498

SmCo Permanent Magnets

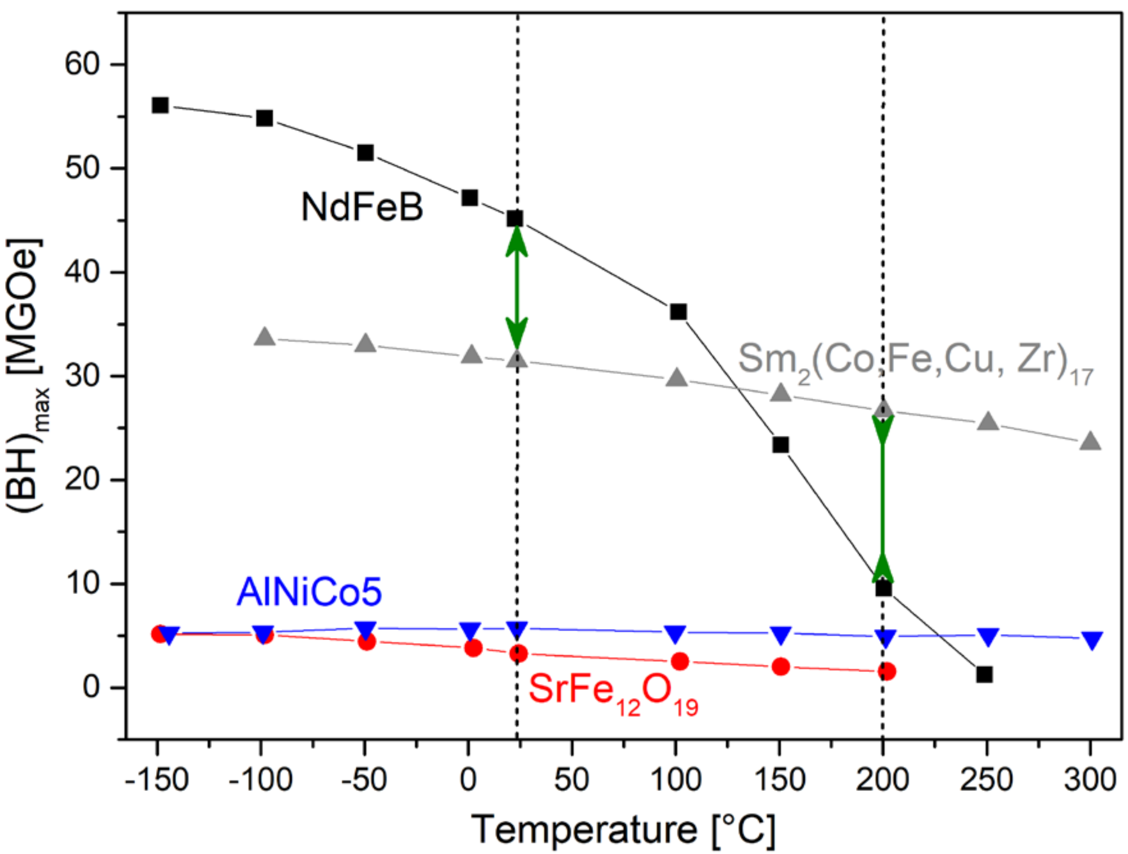
pinning type magnets

high temperature stability

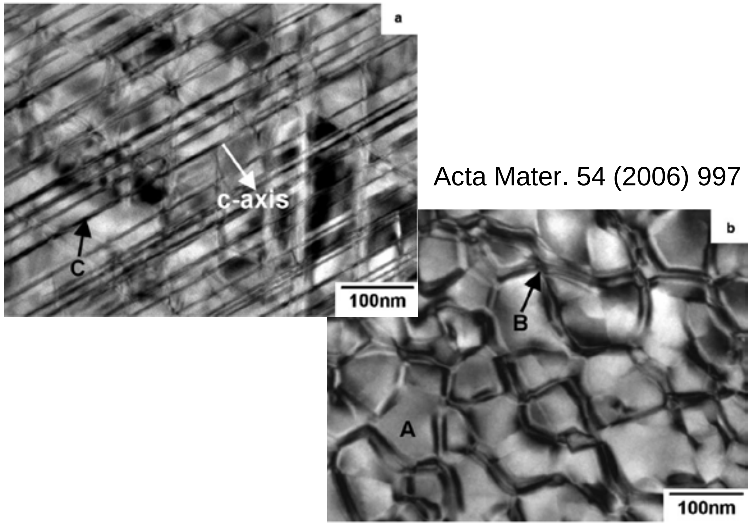
searching for the perfect defect

going beyond: Voltage-induced modification of magnetism

High temperature SmCo pinning magnet

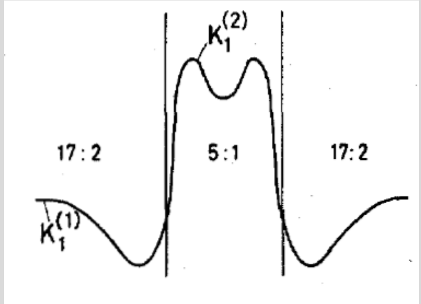


Adapted from Adv. Mat. (Review) 23 (2011) 821



Acta Mater. 54 (2006) 997

Pinning strength of 1:5 cell boundary

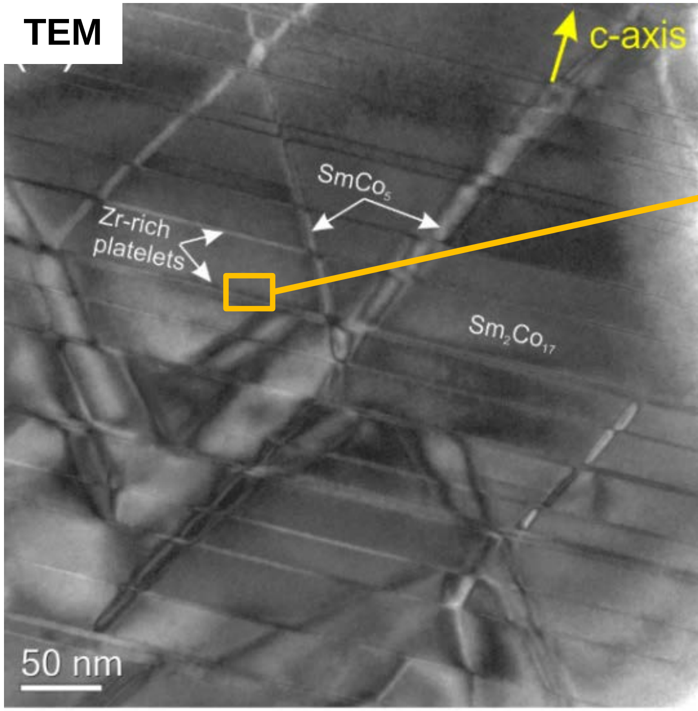


Kronmüller *et al.* IEEE Trans. Magn. 20 (1984) 1569

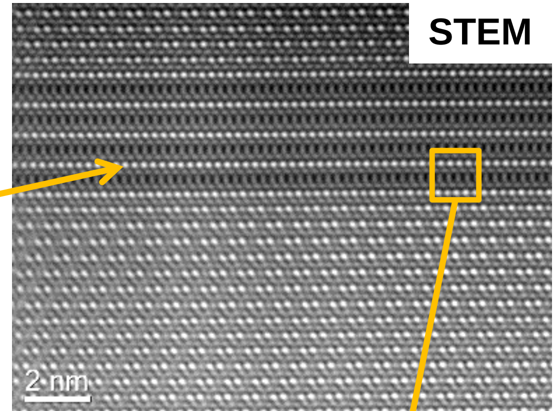
High temperature SmCo pinning magnet

Atomic scale characterisation with STEM, EELS, 3DAP and Modelling

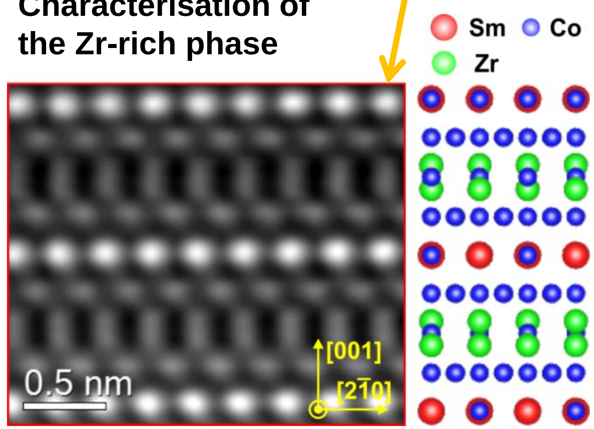
TEM



STEM

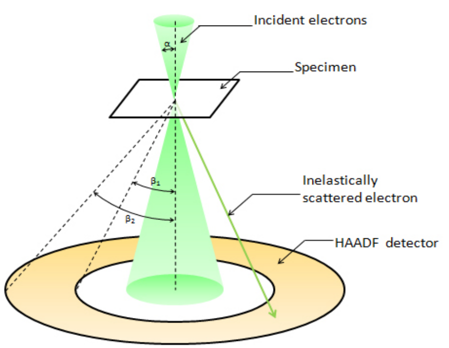


Characterisation of the Zr-rich phase

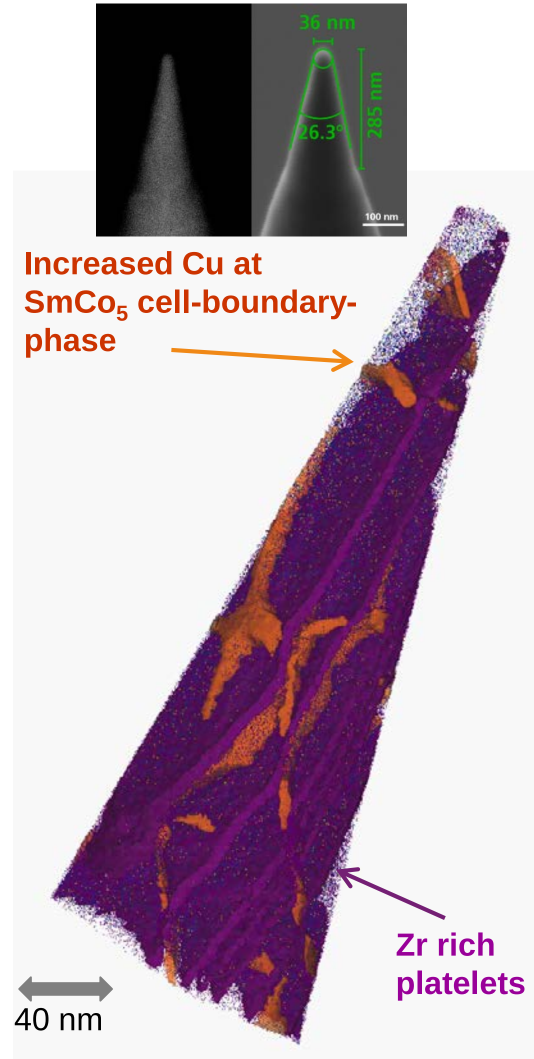


HAADF-STEM

$I \sim Z^2$



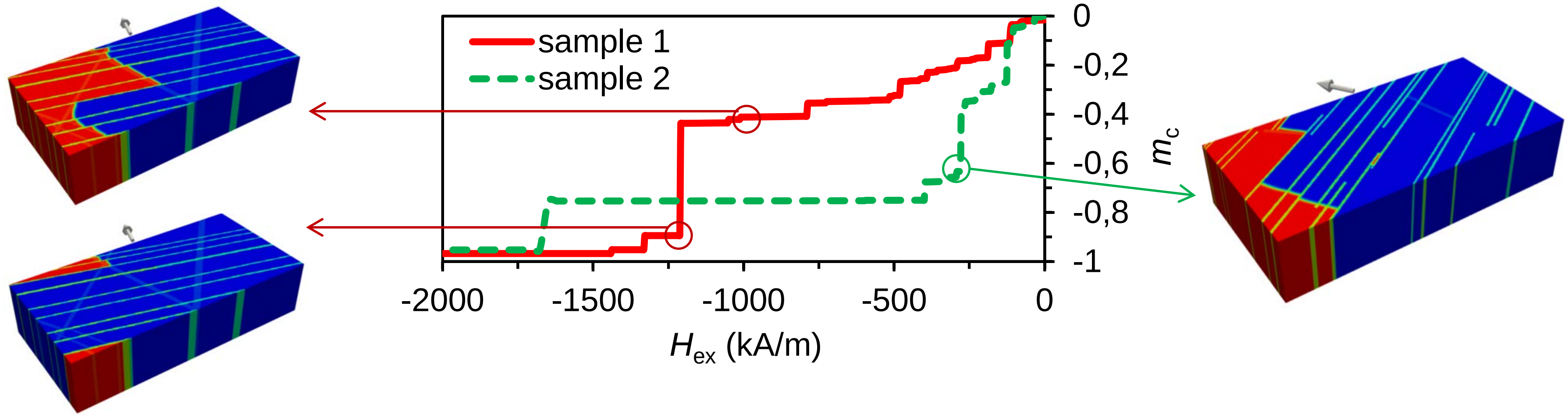
Nature Communications, 2017
Acta Materialia, 2017

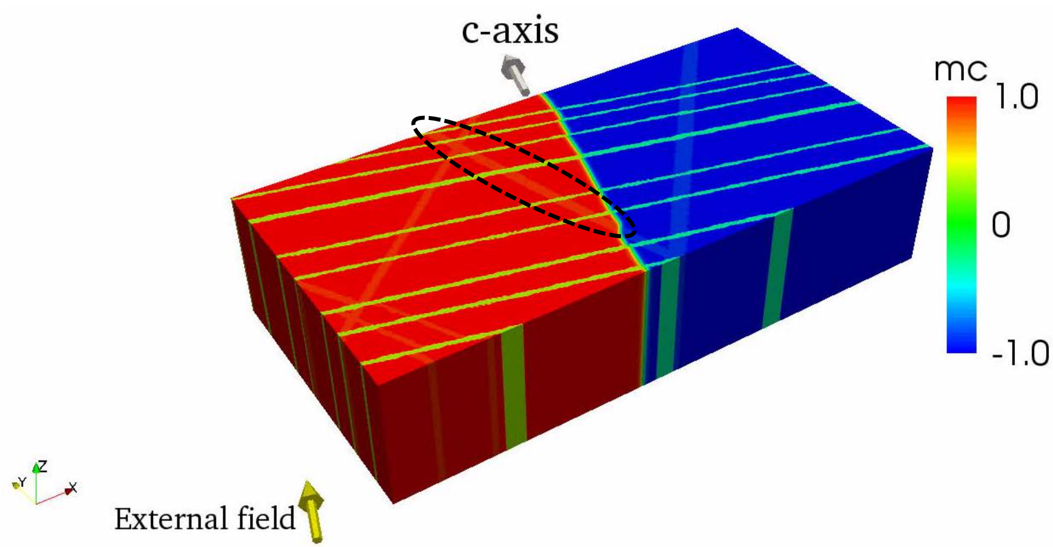


High temperature SmCo pinning magnet

Atomic scale characterisation with STEM, EELS, 3DAP and Modelling

TECHNISCHE UNIVERSITÄT DARMSTADT





Strongest pinning sites where 1:5 phase intersects with Zr-rich phase

→ Searching for perfect defects !

Nature Communications, 2017

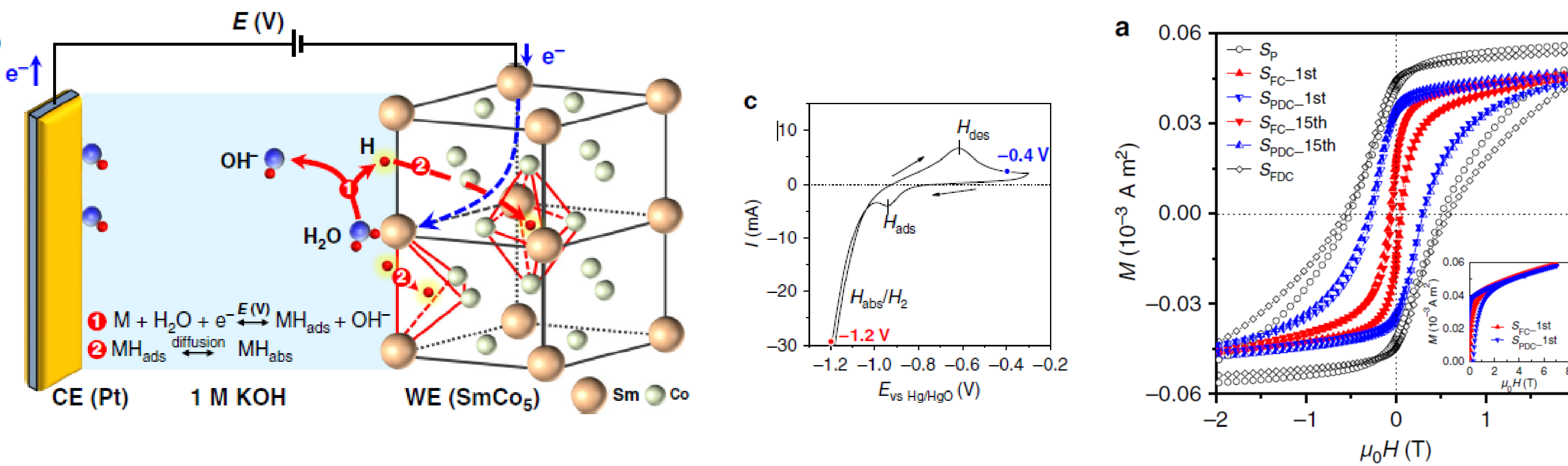
Voltage induced modification of permanent magnetism

Hydrogen as a tool and sensor

Voltage-induced modification of magnetism in $SmCo_5$ particles by hydrogen charging

TECHNISCHE UNIVERSITÄT DARMSTADT

in cooperation with Institute of Nanotechnology, KIT: X. Ye, H. Hahn, R. Kruk



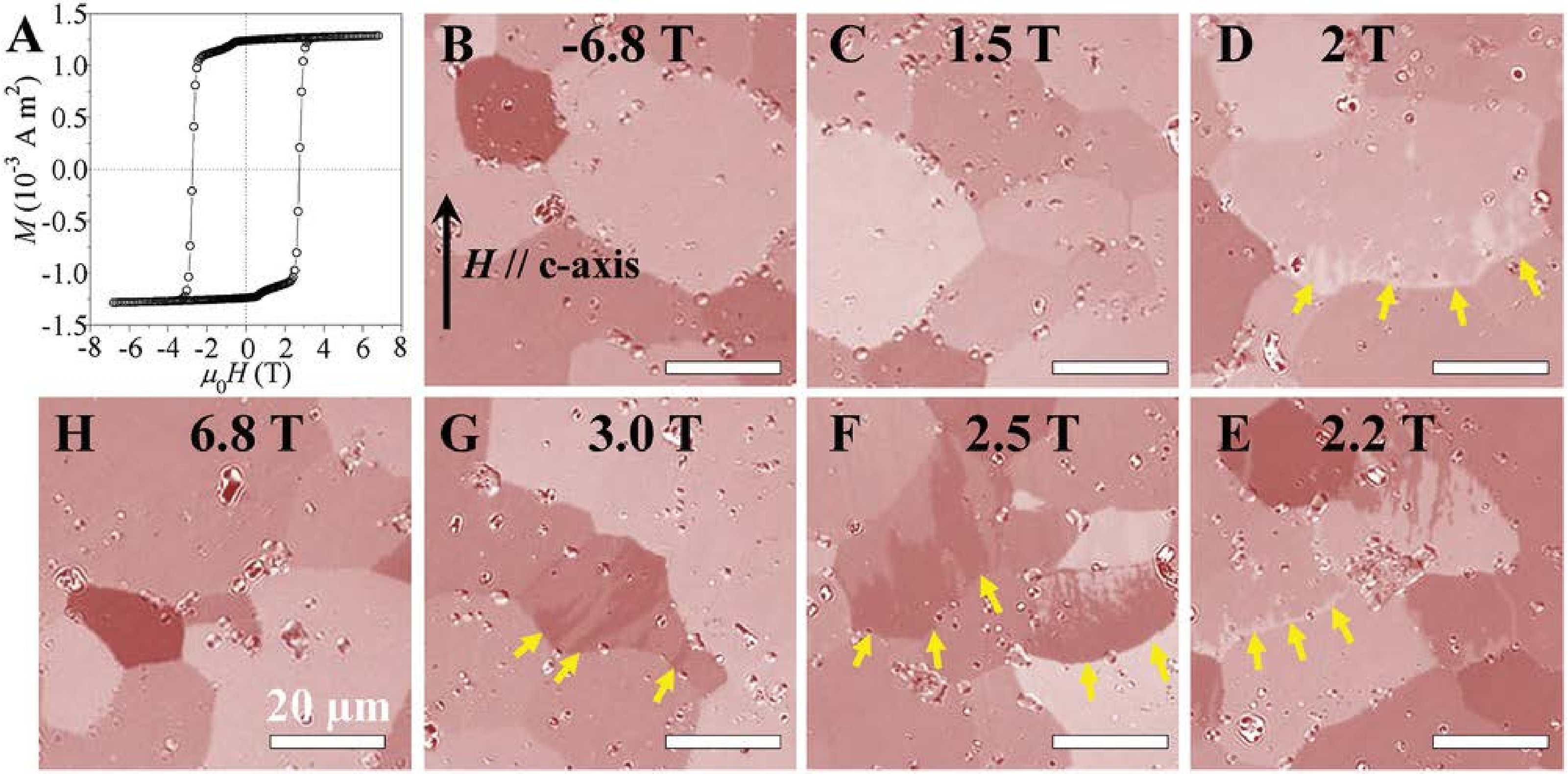
- modulate the coercivity of the whole volume of the particle by only charging and discharging the near-surface region enables the kinetically fast control
- nucleation and growth of the reversed magnetic domains from surface defects where local gradient of K_1 is capable of significantly lowering the nucleation field

Nat Commun **11** (2020) 4849

Magnetoelectric Tuning of Pinning-Type Sm_2Co_{17} through Atomic-Scale Engineering of Grain Boundaries

TECHNISCHE UNIVERSITÄT DARMSTADT

in cooperation with Institute of Nanotechnology, KIT, and MPI Eisenforschung Düsseldorf
X. Ye,, H. Hahn, D. Raabe, B. Gault, R. Kruk



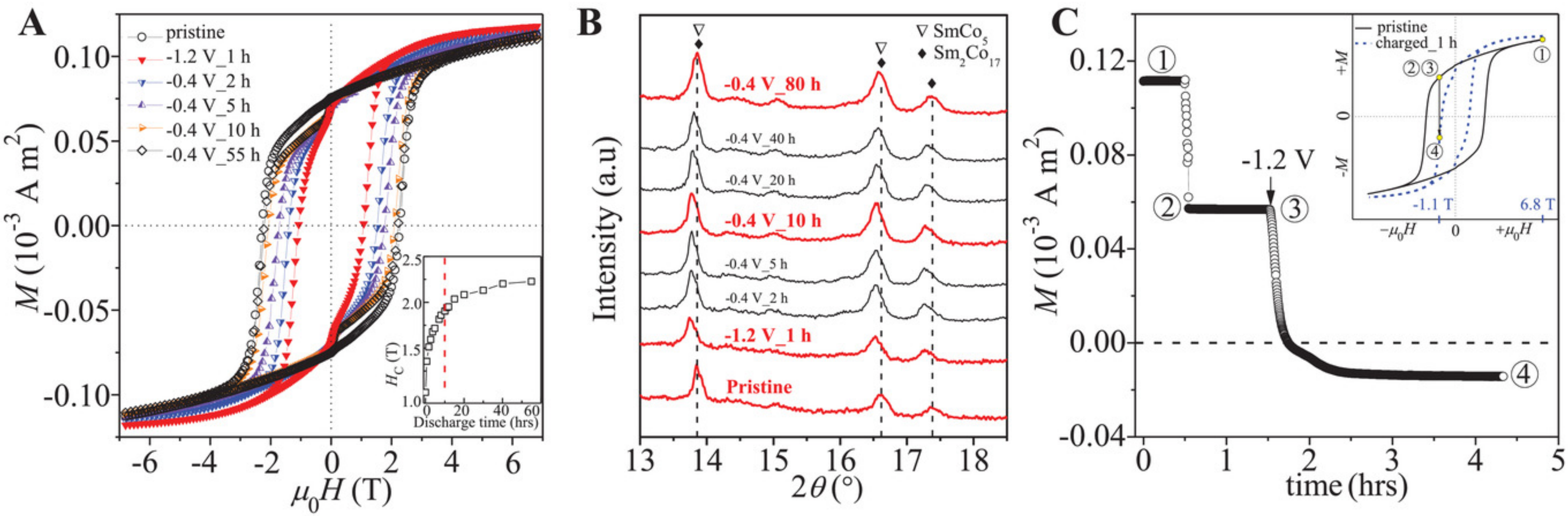
→ Disentangle the roles of grain-interior nanostructure and grain boundaries in controlling coercivity by magnetoelectric manipulation

Advanced Materials (2020) 2006853

Magnetoelectric Tuning of Pinning-Type Sm_2Co_{17} through Atomic-Scale Engineering of Grain Boundaries

in cooperation with Institute of Nanotechnology, KIT, and MPI Eisenforschung Düsseldorf
X. Ye,, H. Hahn, D. Raabe, B. Gault, R. Kruk

→ voltage-controlled reversible and fast hydrogen insertion/extraction



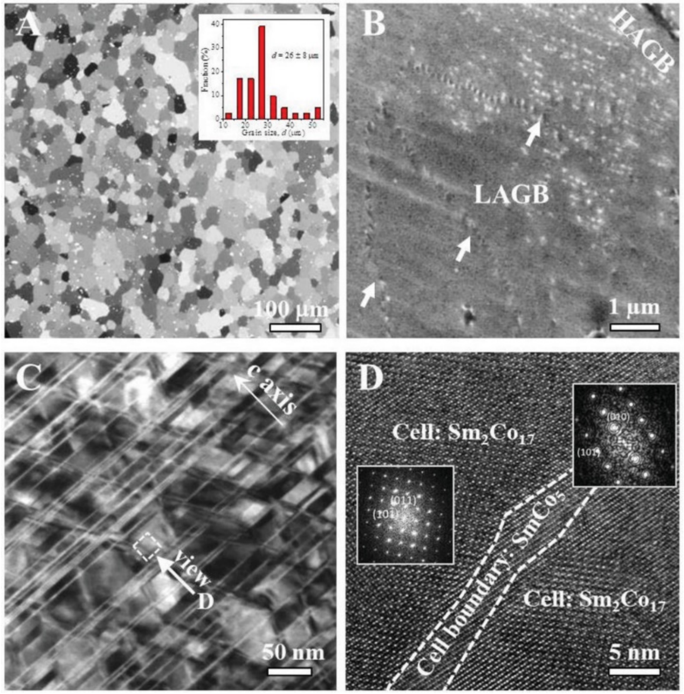
→ response of the coercivity of the sample to hydrogen charging/discharging was explored in-situ using a miniaturized electrochemical cell in the SQUID

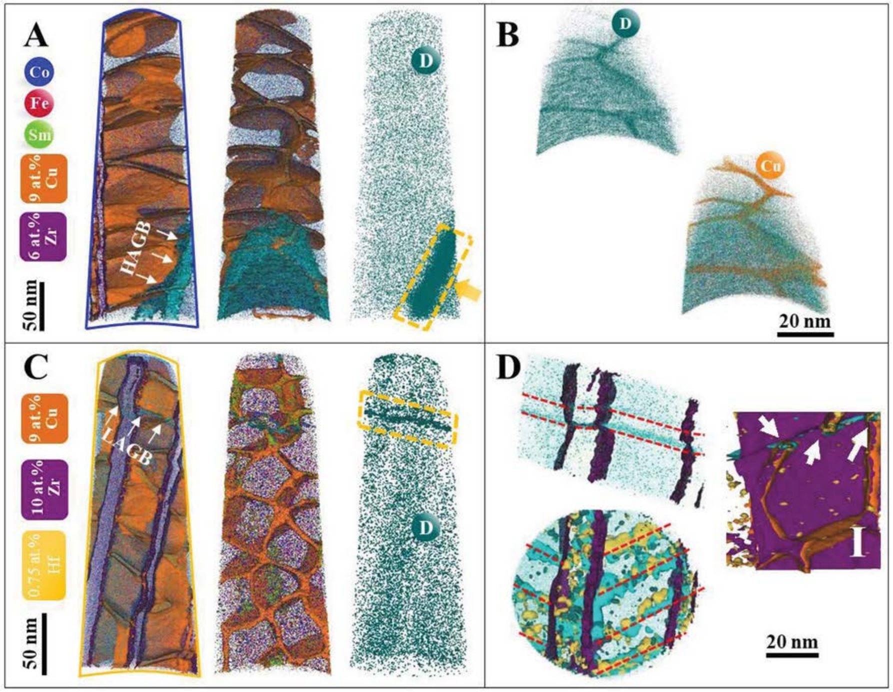
Advanced Materials (2020) 2006853

Magnetoelectric Tuning of Pinning-Type Sm_2Co_{17} by Atomic-Scale Engineering of Grain Boundaries

TECHNISCHE UNIVERSITÄT DARMSTADT

in cooperation with Institute of Nanotechnology, KIT, and MPI Eisenforschung Düsseldorf
X. Ye,, H. Hahn, D. Raabe, B. Gault, R. Kruk





→ **atomic-scale tracking of hydrogen atoms reveal that the segregation of hydrogen atoms at the grain boundaries dominates the reversible H_c change**
→ **near GBs: disintegrated cellular structure and different microchemistry**

Advanced Materials (2020) 2006853

Future magnets…?

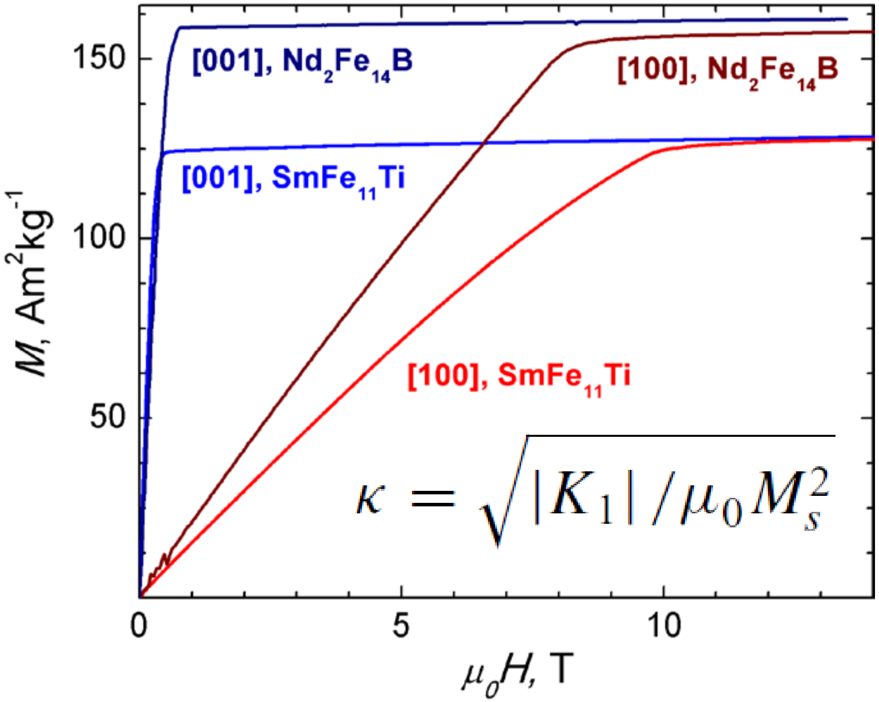
Searching for the perfect defect

Identifying and avoiding the weak link

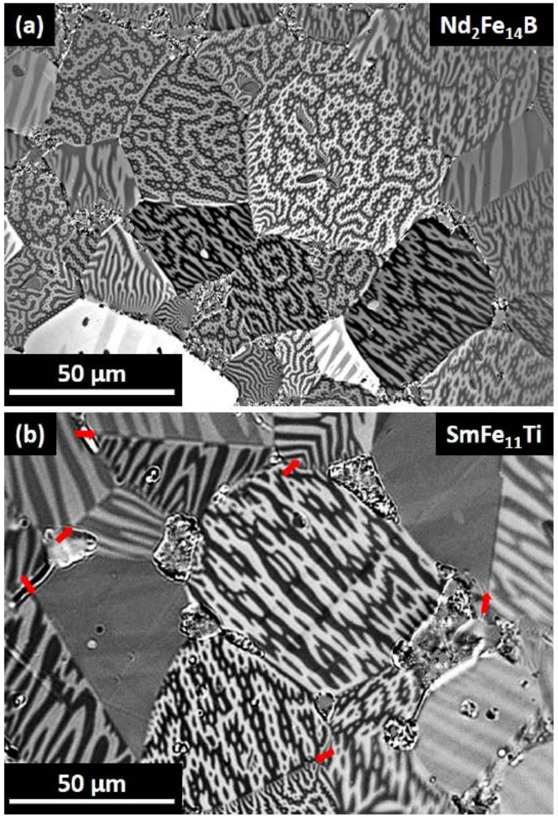
in 1:12; in MnAl

Dual phase strong soft magnets…

$SmFe_{11}Ti$: rare earth lean and high uniaxial anisotropy, BUT…



$$\kappa = \sqrt{|K_1| / \mu_0 M_s^2}$$



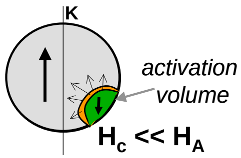
from single crystals to and new magnetic hardening mechanisms

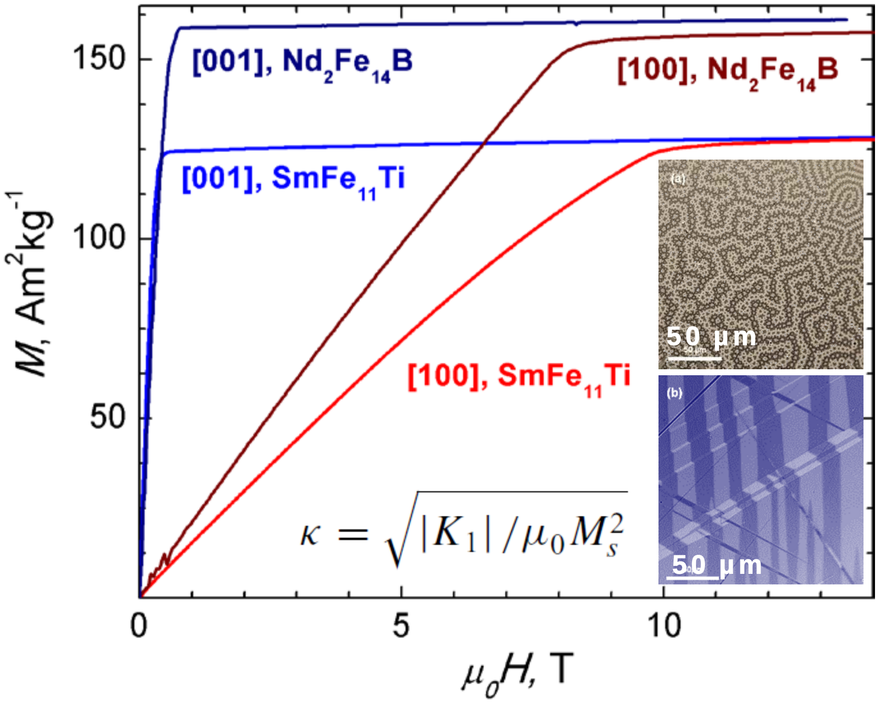
Scripta 2018, Acta Mat 2019, PRM 2020
Acta Materialia 214 (2021) 116968

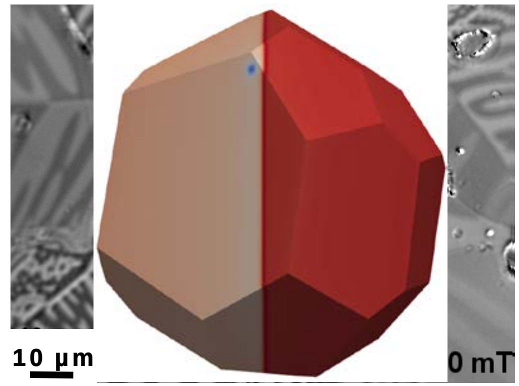
Talk Ener
Poster Maccari

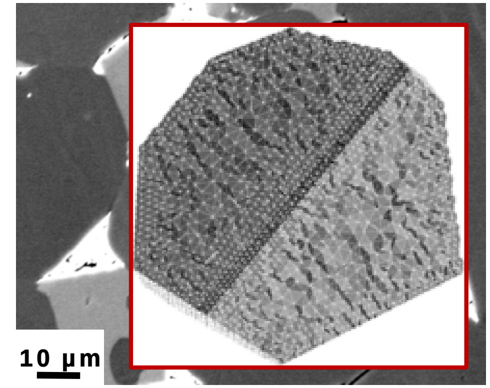
SmFe$_{11}$Ti: rare earth lean and high uniaxial anisotropy, BUT…

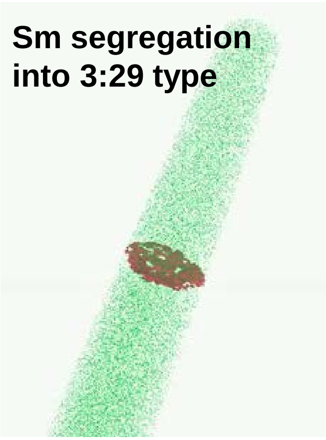
TECHNISCHE UNIVERSITÄT DARMSTADT

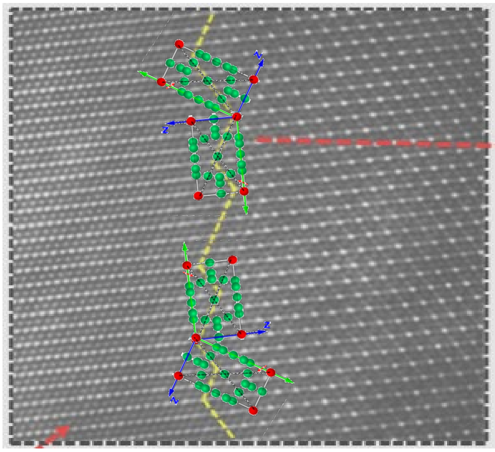












from single crystals to the search for *perfect defects* and new magnetic hardening mechanisms

Partners: Schrefl, Danube Uni; Gault, Raabe, MPIE; Dempsey, CNRS; Hrkac, Exeter; TMC

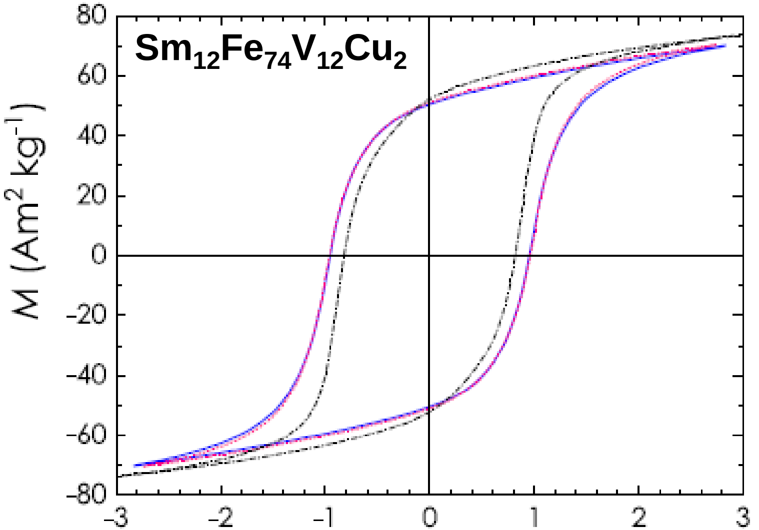
Physical Rev. Mat. 4 (2020) 054404
Acta Materialia 180 (2020) 15-23
Acta Materialia 214 (2021) 116968

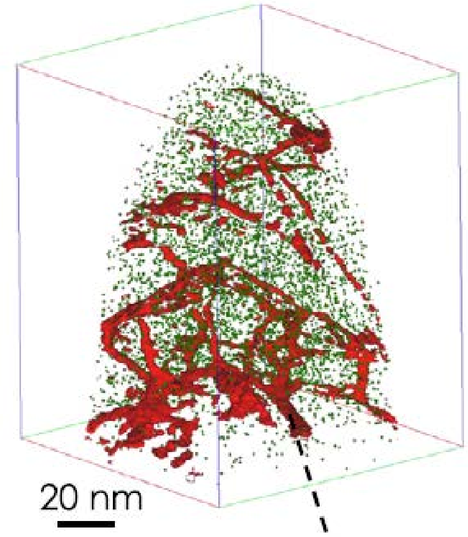
Nanocrystalline $SmFe_{11}V$ with high H_c

- Formation of twin boundaries in grains larger than 1µm can be attributed to the accumulation of internal stresses during solidification, where twin formation is favoured over the formation of specific grain boundaries
- Three approaches:

Acta Materialia 214 (2021) 116968

1. substitutional compositional modification to increase twin formation energy
2. heat treatment under stress → energy dissipation by dislocation activity
3. grain size reduction → change of volume-to-surface energy ratio decreases the need for stress relief via twin formation





$Sm_{20}Fe_{70}Ti_{10}$

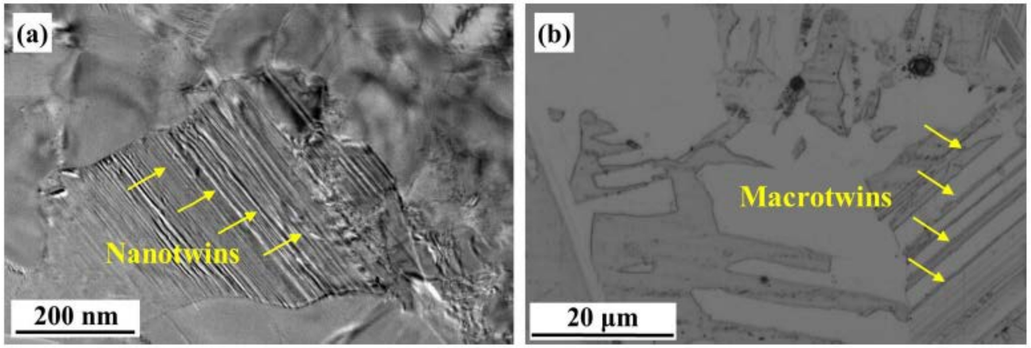
Partners:
Delaware,
BCM Bilbao,
Danube
MPIE

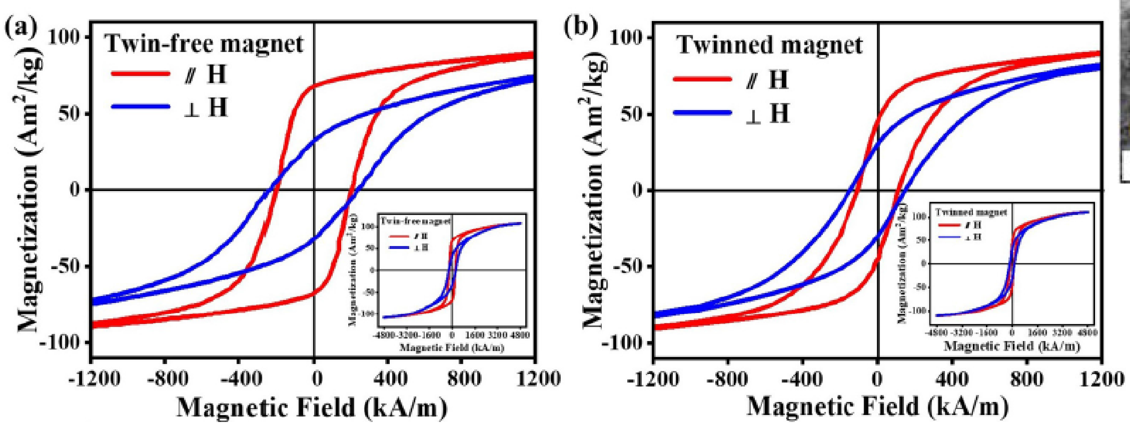
Talk Schönhobel

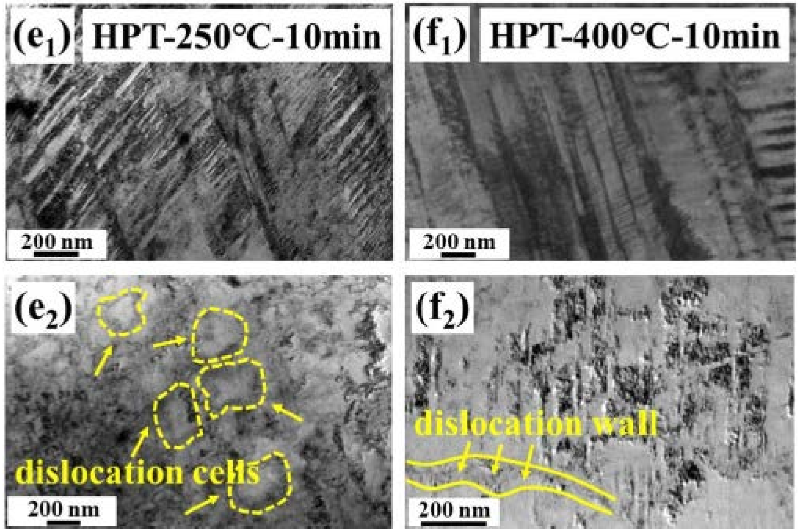
Acta Materialia 200 (2020) 652

$L1_0$ rare-earth-free permanent magnets: twinning vs dislocations in Mn-Al magnets

- “negative” effect of twin structure: nucleation of magnetization reversal
- “positive” effect of dislocations on H_c: acting as pinning center, and a high density of dislocations can modify the dominant coercivity mechanism from nucleation to pinning in severely deformed MnAl magnets







Partners:
Yuxiao Jia, Yuye Wu et al
Beihang University

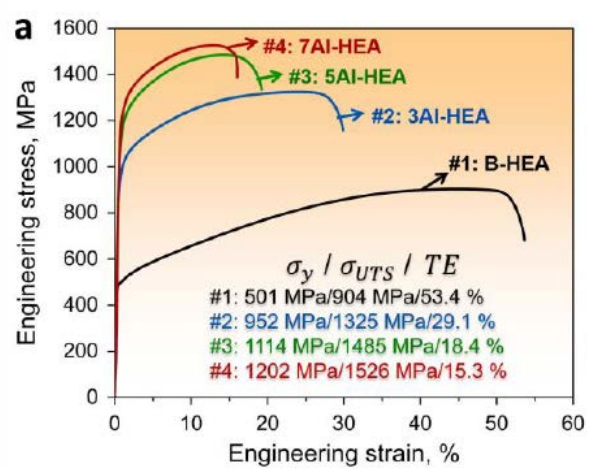
Poster Müller
Poster Staab

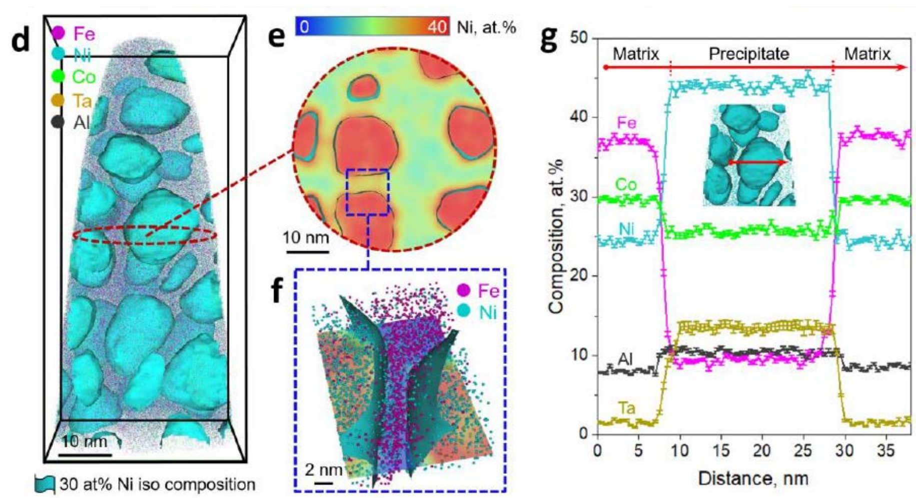
Phys. Rev. Mat. **4**, 094402 (2020)

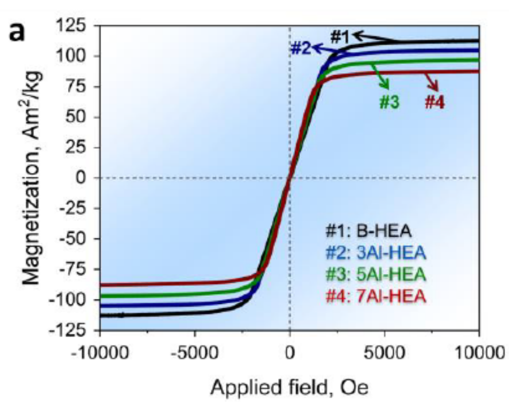
Ultrastrong and ductile soft magnetic high-entropy alloys via coherent ordered nanoprecipitates

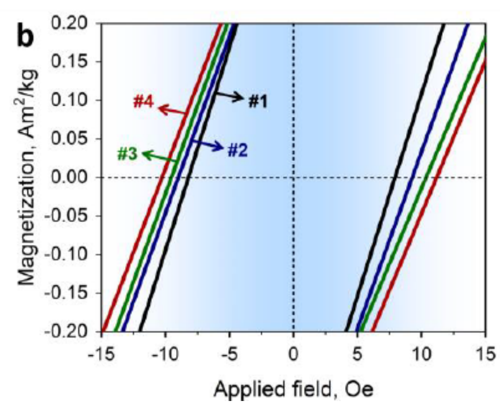
TECHNISCHE UNIVERSITÄT DARMSTADT

- strengthening and toughening of **soft magnetic materials difficult as props deteriorate due to Bloch wall interactions with the defects**
- **coherent and ordered nanoprecipitates (< 15 nm) dispersed homogeneously within a face-centered cubic matrix of a non-equiatomic CoFeNiTaAl high-entropy alloy HEA)**









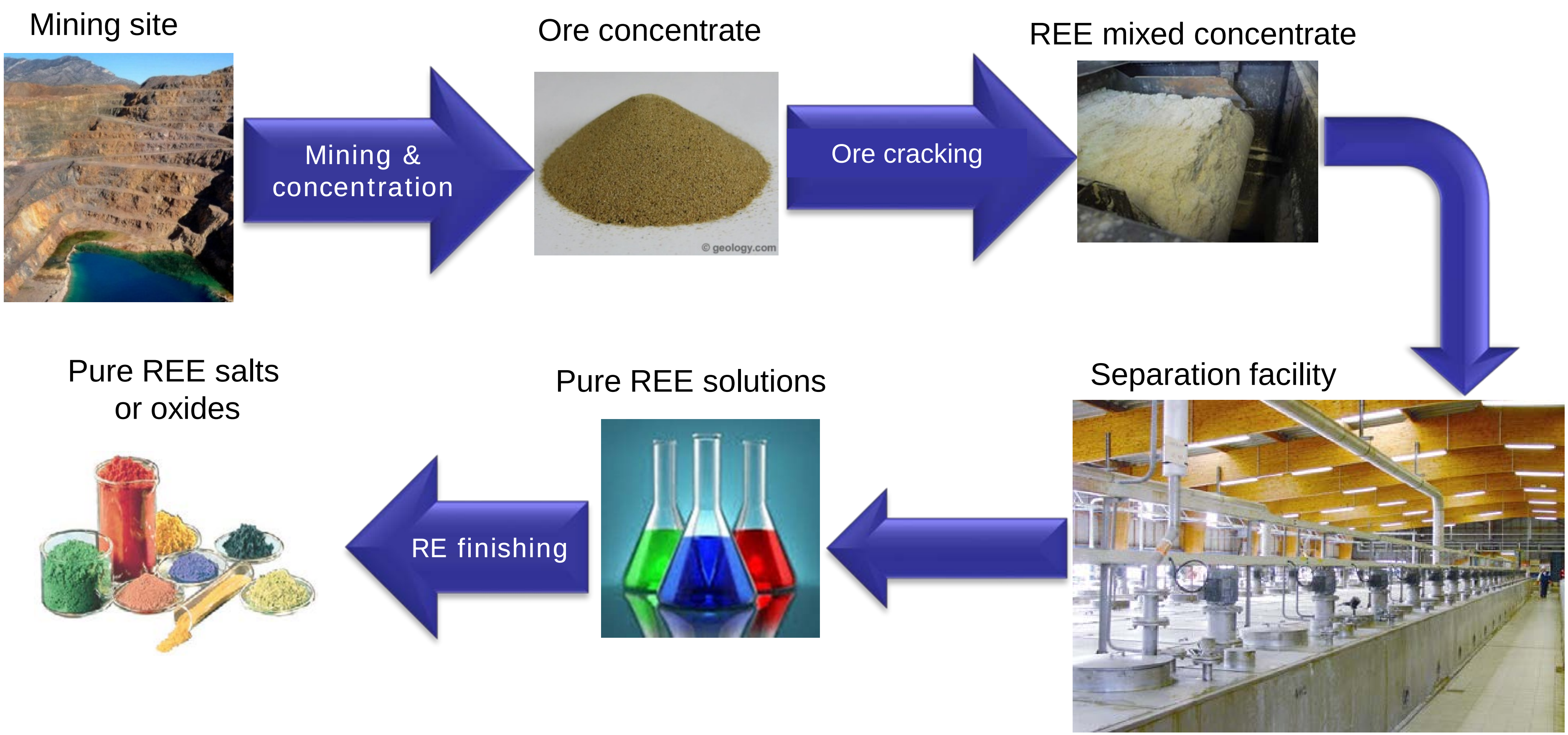
Work driven by L. Han, Raabe, MPIE and Z. Li, Central South Uni China

Advanced Materials, accepted

REE Recycling

The Integration of Recycling into the REE Supply Chain

A long value chain from the ore to the pure REE oxides, REE separation is the key step



Solvent extraction is the only industrial process used commercially for REE separation

Acknowledge A. Rollat

From EOL products to the pure RE oxides

Technische Universität Darmstadt

Almost same long value chain with some important differences !

Acknowledge A. Rollat

Collecting & Sorting

Sorted product cracking

RE mix concentrate

RE Separation

Pure RE solutions

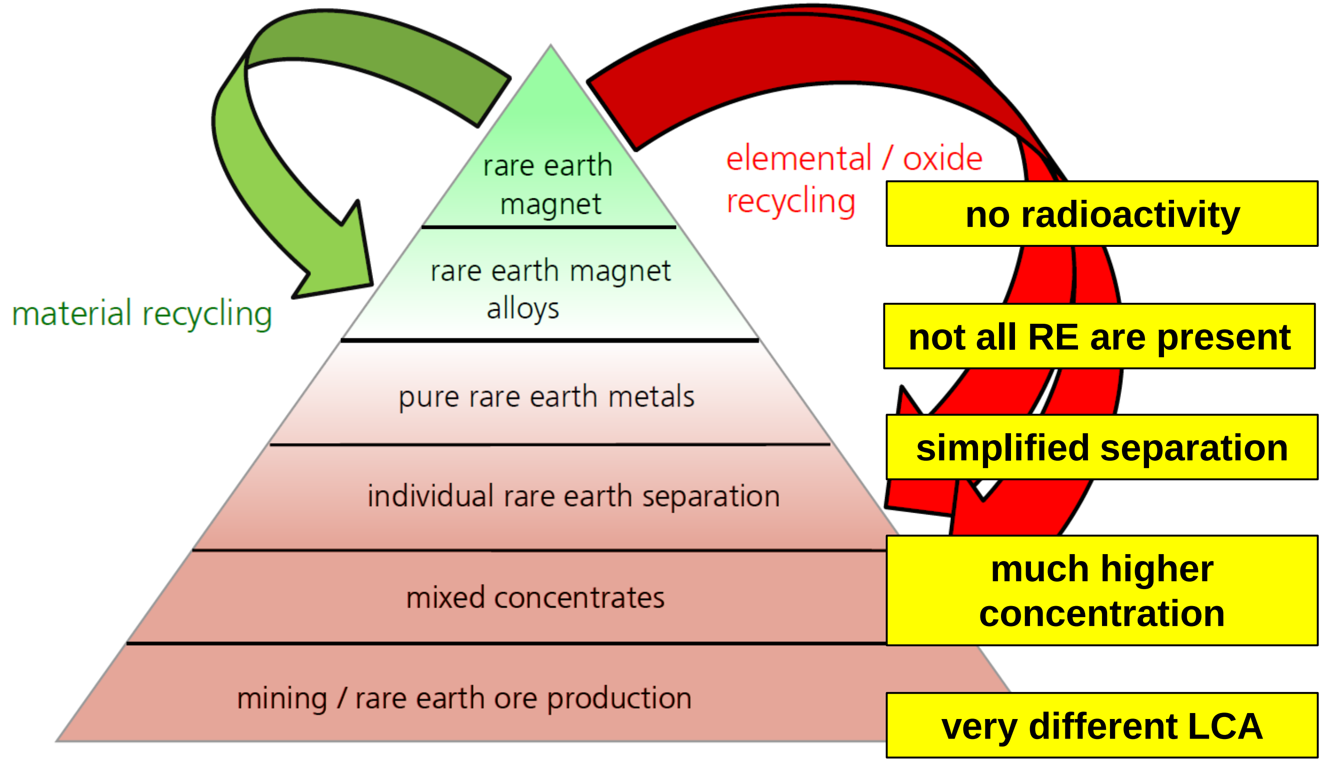
RE finishing

Pure RE salts or oxides

Rare earth value chain for magnets

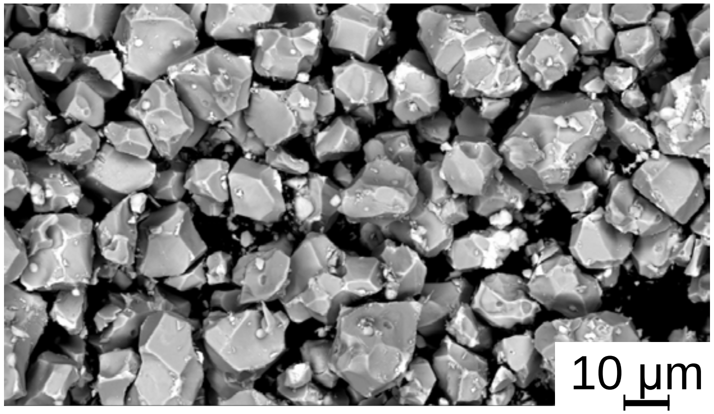
Advanced Functional Recycling of EoL products

TECHNISCHE UNIVERSITÄT DARMSTADT



R. Gauß und O. Gutfleisch,
„Magnetische Materialien – Schlüsselkomponenten für neue Energietechnologien"
Springer Spektrum Verlag, 2016

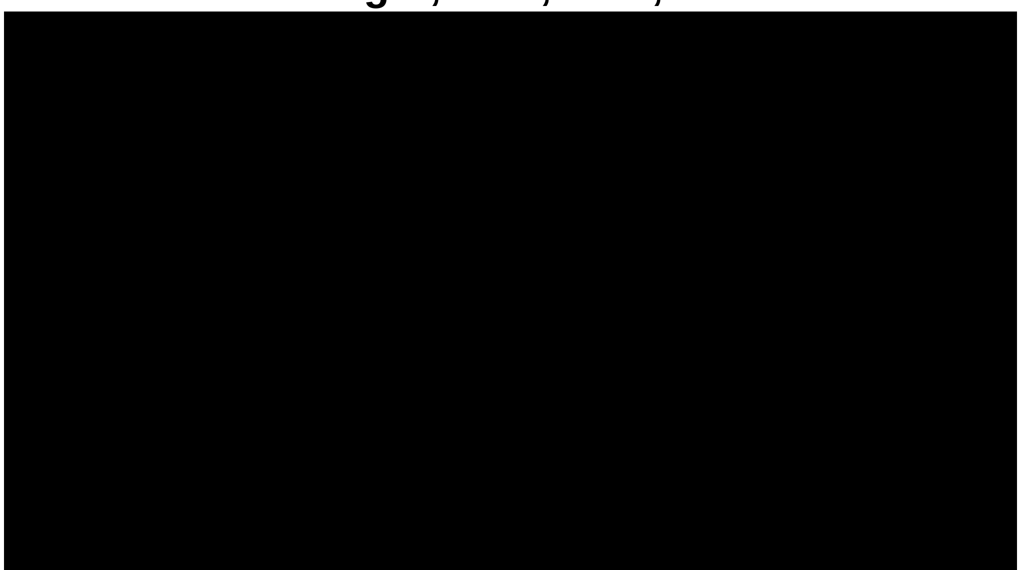
Recycling using Hydrogen Decrepitation (HD) of Nd-Fe-B



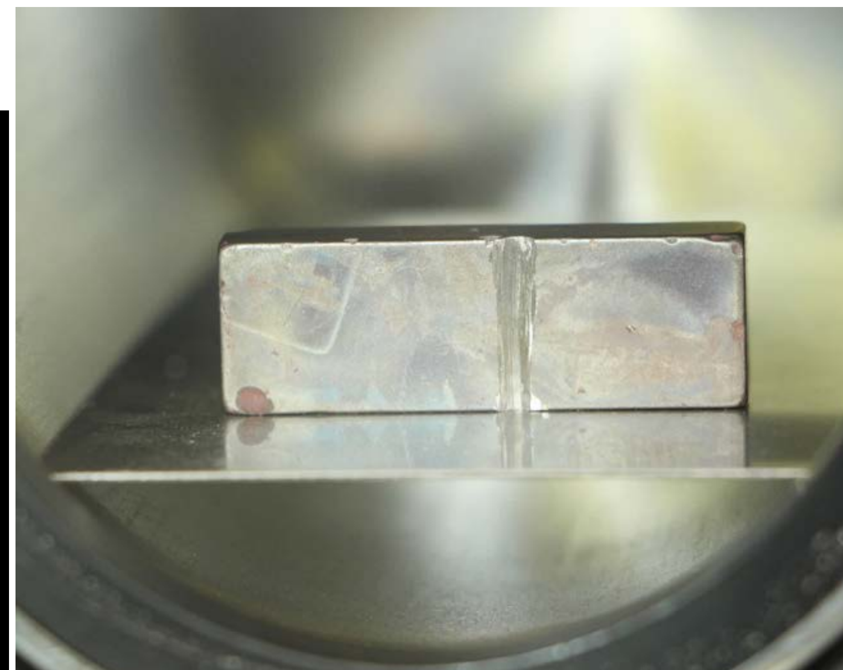
after HD

Advanced Energy Materials ***3*** *(2013) 151*

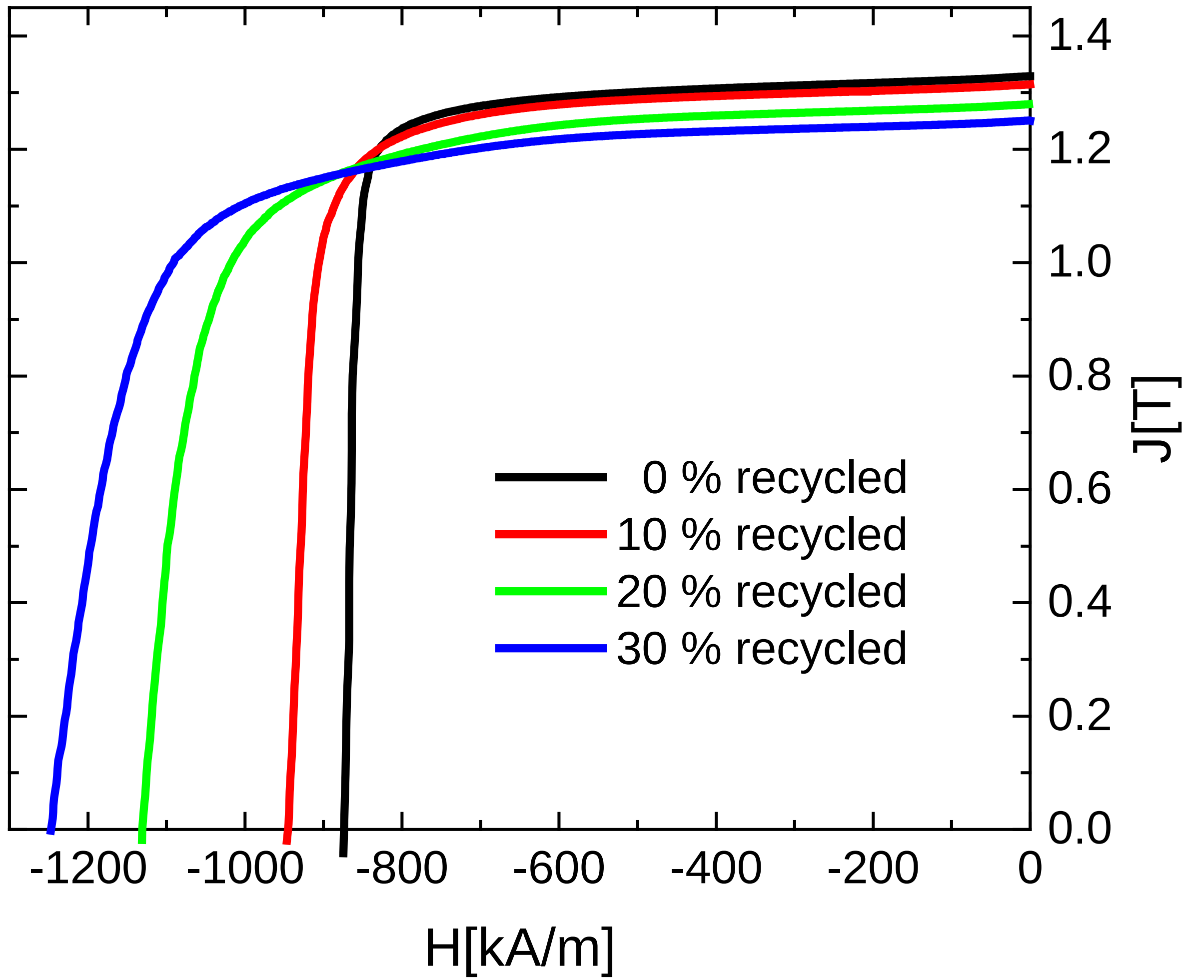
cast ingot, t x 4, 1bar, RT



sintered magnet, t x 90, 1bar, RT



Anisotropic sintered NdFeB magnets with X % recycled material



Searching for the perfect defect

TECHNISCHE UNIVERSITÄT DARMSTADT

- **current materials are not at their physical limit:**
  the Brown paradox remains unsolved
  search for perfect defects vs eliminating the weak link
- **Duality of defects - altering local anisotropy can**
  - serve as a nucleation site or act as a pinning site
  - softening vs step or gradient in K
  - electrostatic potential, size, symmetry, coherency, orientation, interfacial sharpness, population density, scale (gb vs cell boundary), embedment, synergy of…
- **multiscale characterization and modelling**
  insight into local and effective coercivity, magnetisation reversal
- **rational hysteresis (based on ML and AI?) design will enable new magnetic materials for efficient energy conversion,**
  explore digital twins
- **secondary functionalities and inverse stray field engineering by AM**

Conclusions

- big demands for high performance GREEN PMs, thus REEs, in E-mobility, wind turbines, 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, utilization of free rare earths
- environmental indicators of a product would be drastically improved if recycled REPMs were used → magnetic refrigeration

Acknowledgements

- University Duisburg-Essen
- CNRS Grenoble
- NIMS Tsukuba
- Universities of Barcelona, Seville, Parma
- Ames National Lab.
- HZDR and IFW Dresden, ESRF
- Universities Danube and Uppsala
- Max-Planck-Institut für Eisenforschung

- **Magnetic Materials and Devices for the 21st Century: Stronger, Lighter, and More Energy Efficient**
  Review in Adv. Mat. **23** (2011) 821
  Viewpoint Set in Scripta Mat. **67** (2012)
- **Towards high performance PMs w/o REs**
  J. Phys.: Condens. Matter **26** (2014) 064205;
  Scripta Mat View point (2018)
  Nature Com. 8:54 (2017)
  Phys. Rev. Mat. 4, 094402 (2020
- **Mastering hysteresis**
  Phil. Trans. R. Soc. A **374** (2016), Review in Energy Techn. 2018, Nature Com. (2018) 9:2680
  Nat Commun 11 (2020) 4849, Advanced Materials (2020) 2006853
- **Shaping and Additive manufacturing**
  J. Appl. Phys. 114 (2013) 043907, Adv. Mat. 22 (2010) 3735, Acta Materialia 127 (2017) 389
  Advanced Functional Materials (2021)