Magnetic Materials in Sustainable Energy

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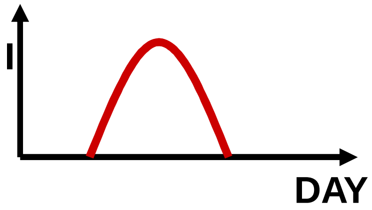
from 01.02.2012 @ Technical University of Darmstadt AND Fraunhofer Group Substitutional Materials Hanau

- **Materials for Energy Applications**
- **Magnetism and Energy:**
  - **Permanent magnets for E-mobility and wind turbines**
  - **Rare earth metals, recycling**
  - **Magnetocaloric materials for novel refrigeration technology**
- **Description of structure, dynamics of phase transitions and function on all length scales**

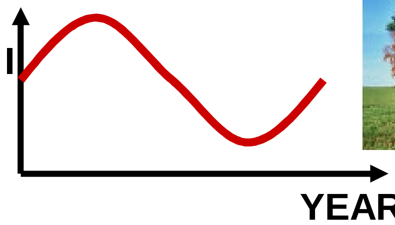
Adv. Mat. (Review) **23 (2011) 821-842**

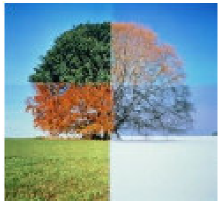
Renewable Energy is intermittent in nature

DAY - NIGHT CYCLE

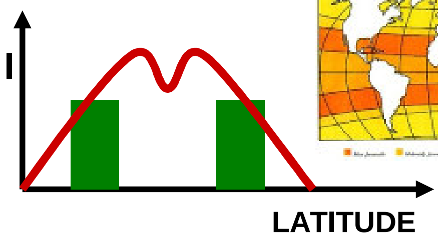


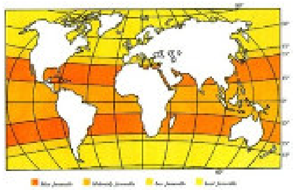
SEASONAL CYCLE



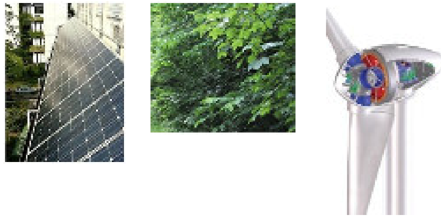


Geographical ENERGY DISTRIBUTION of WWS

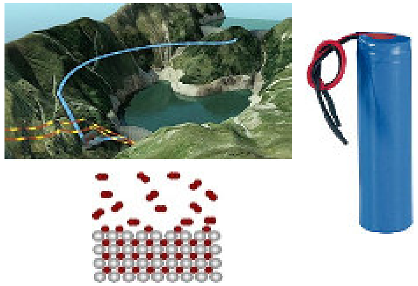




CONVERSION of WWS

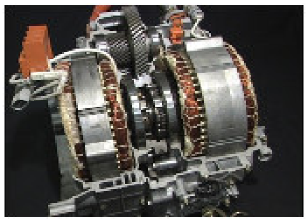


STORAGE



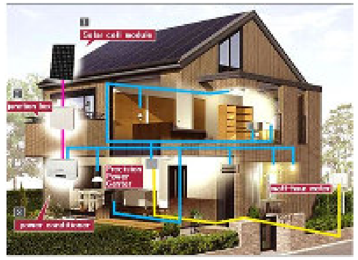
TRANSPORT

CONVERSION into …



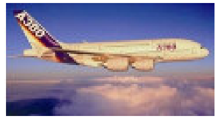
RESIDENTIAL

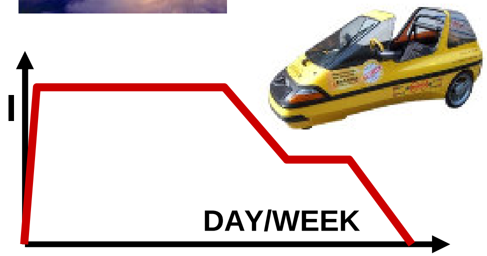
Heat



MOBILITY

Work





INDUSTRY

Heat & Work

adapted from A. Züttel

Materials for sustainable energy

commodity materials
disposible fuels
gas CH_4
oil CH_2
coal $CH_{0.8}$

→ combustion → heat → useful work

sunlight
wind
water
geothermal
biomass

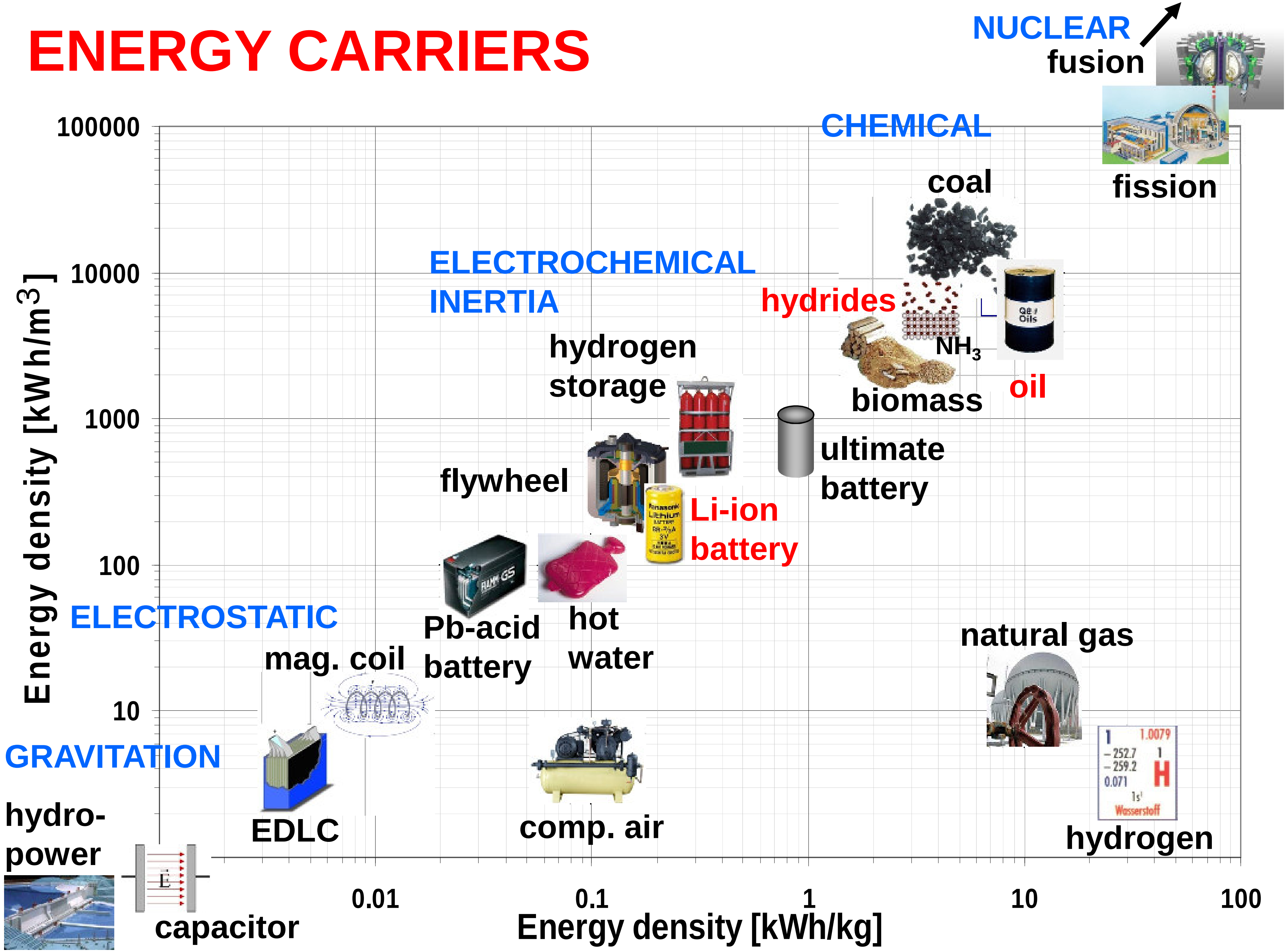
→ Direct conversion → electricity, biofuel, hydrogen, chemical fuel → useful work

material + chemistry
ultra-small and -fast

← BUT: critical metals

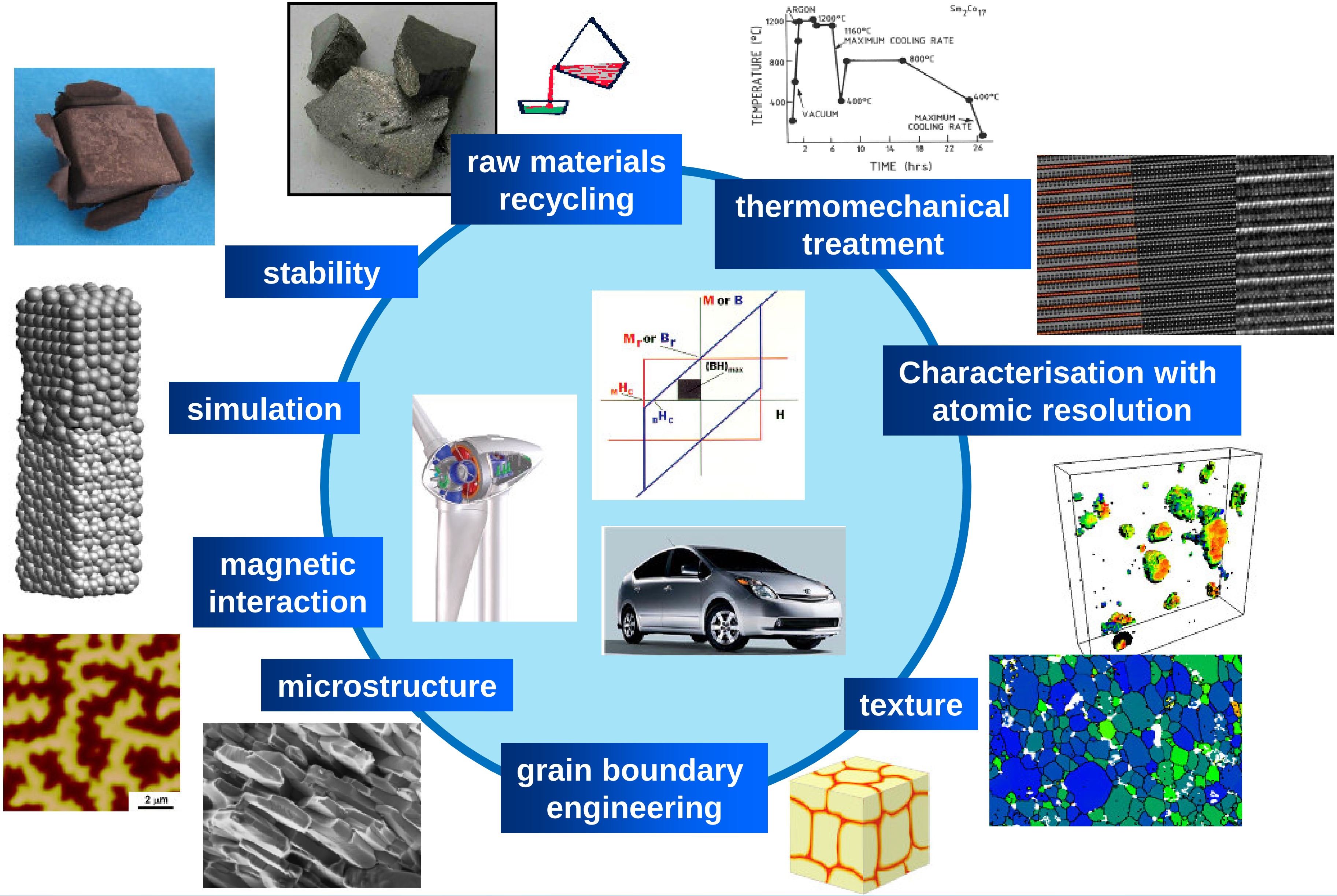
modelling | nano-science | complex materials

ENERGY CARRIERS



A. Züttel et al. , Phil. Trans. R. Soc. A (2010)

Permanent magnets for e-mobility and wind turbines



Intrinsic and extrinsic magnetic properties

intrinsic properties + **microstructure**

100µm > l > 1nm

↔ fit µ-magnetic length scales

⇒ **extrinsic properties**

saturation polarisation, $\boldsymbol{J_s}$

anisotropy field, $\boldsymbol{H_a}$

Curie temperature, $\boldsymbol{T_C}$

remanence, $\boldsymbol{J_r}$

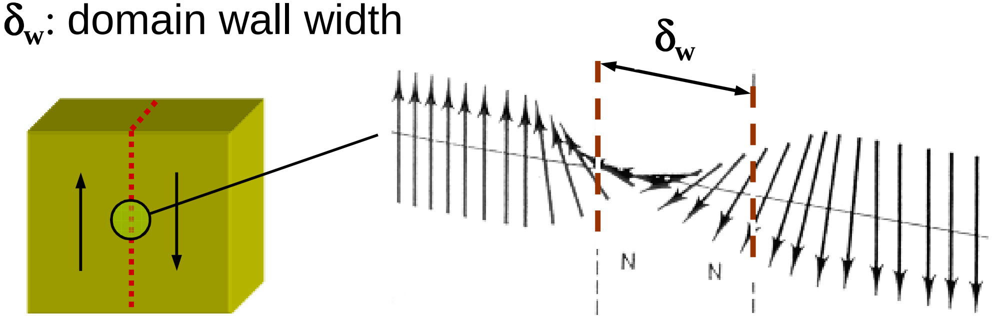
coercivity, $\boldsymbol{H_c}$

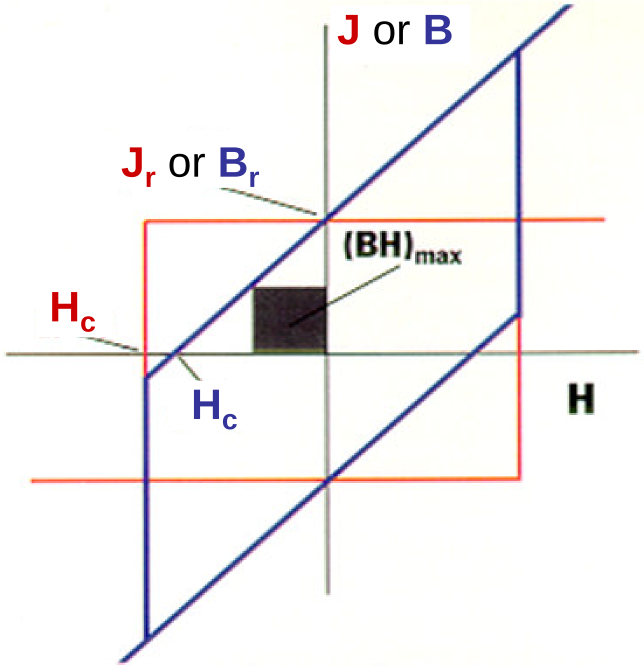
energy density, $\boldsymbol{(BH)_{max}}$

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



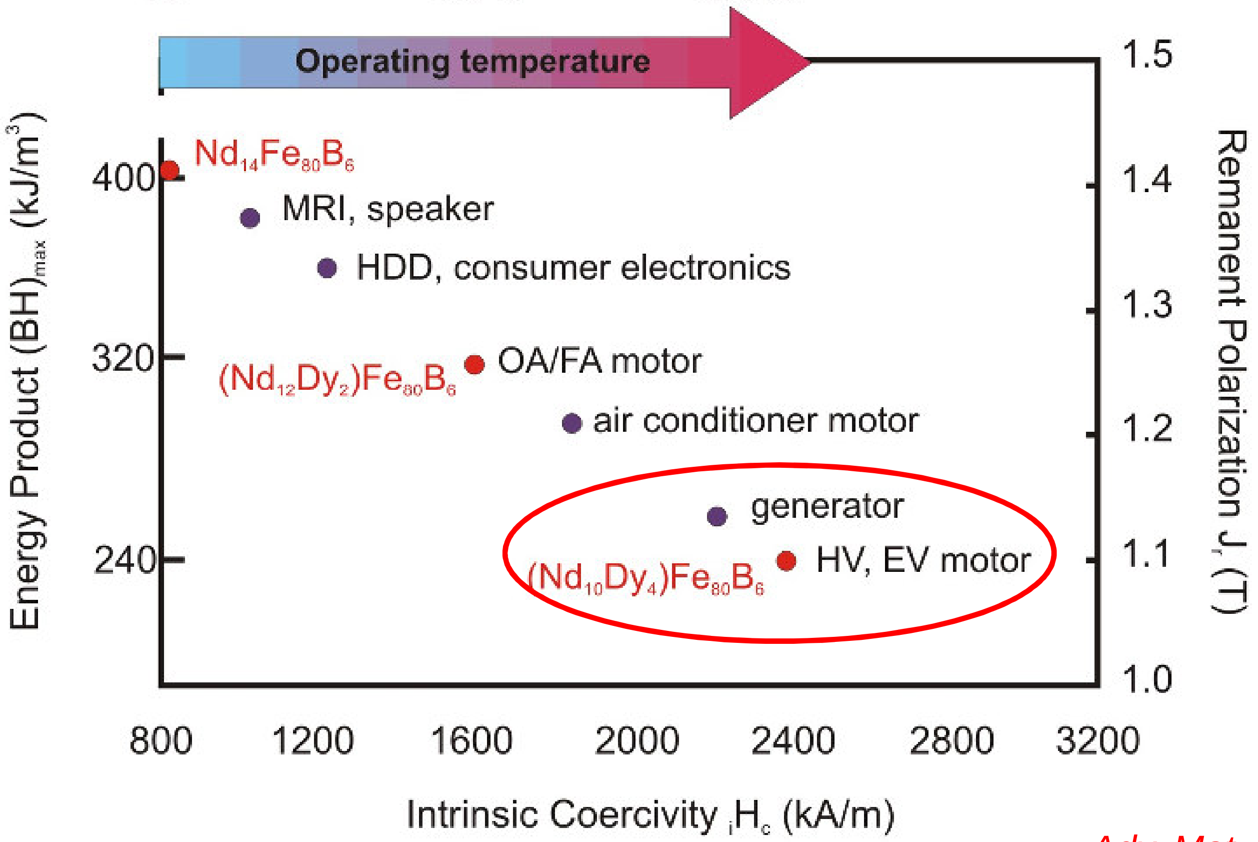


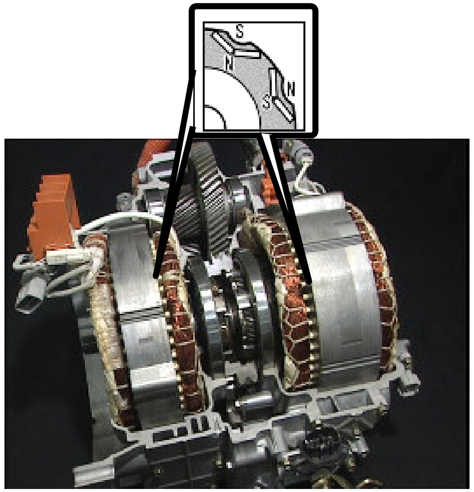
J. Phys. D: Appl. Phys. **33** *(2000) R157-R172*

Sintered NdFeB magnets for electro motors

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

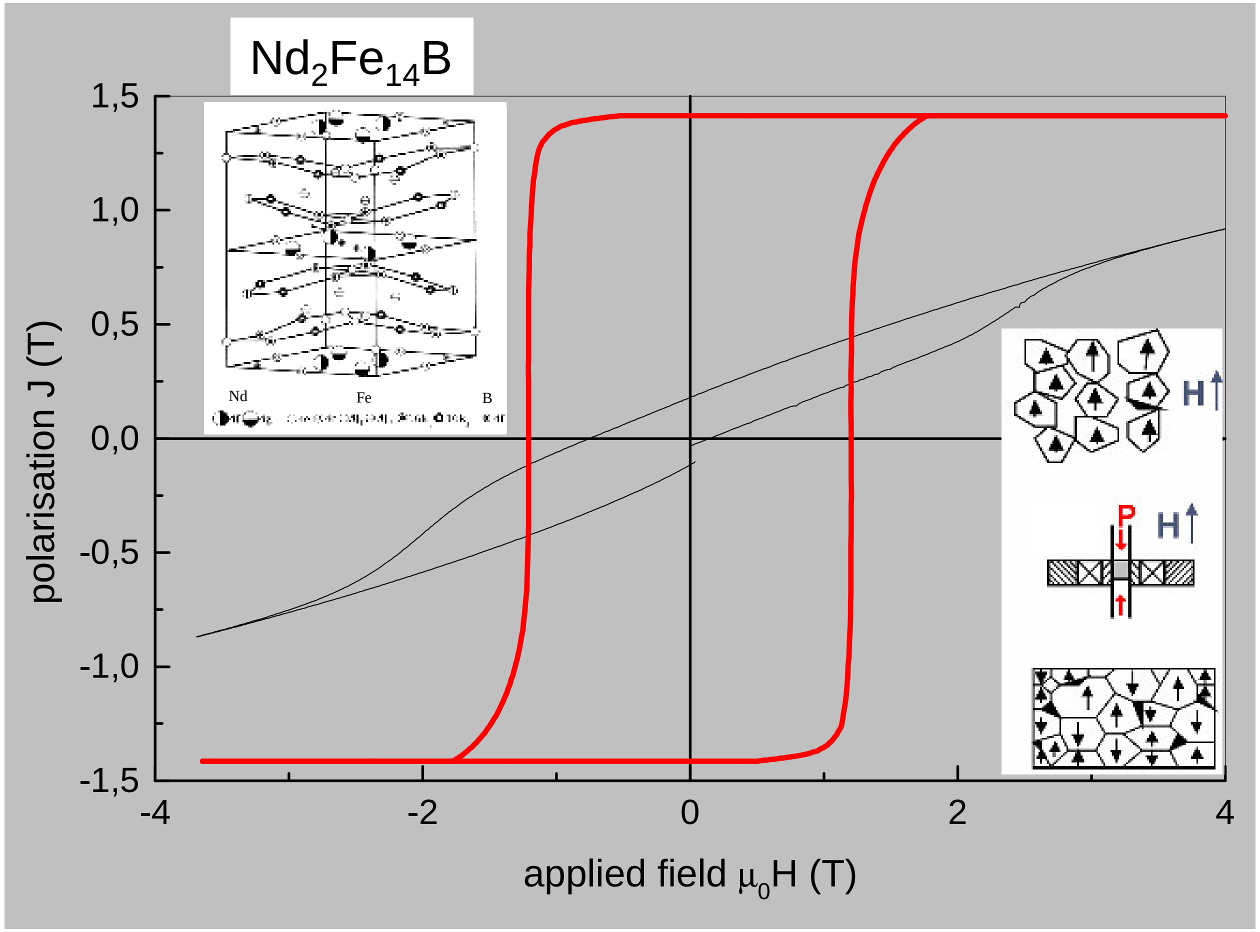
→ torque scales linearly with remanence

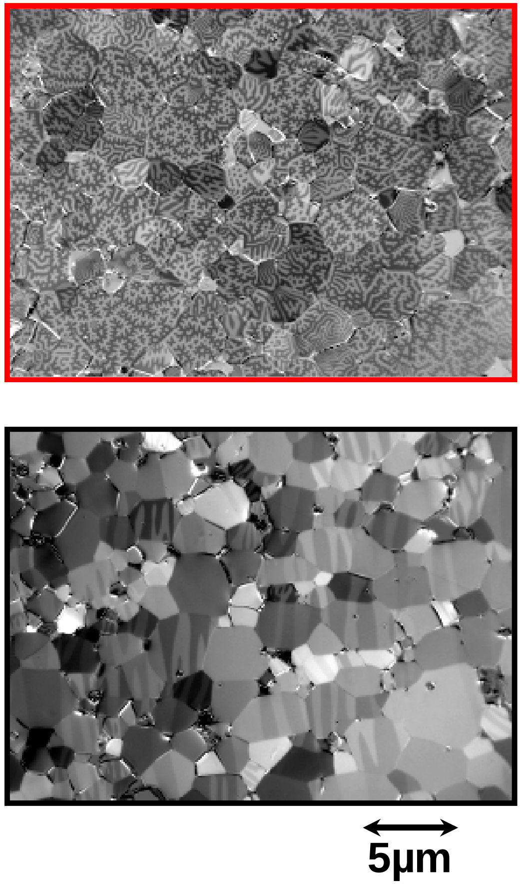




Courtesy: Toyota Motor Corporation

Adv. Mat. (Review) 23 (2011) 821-842

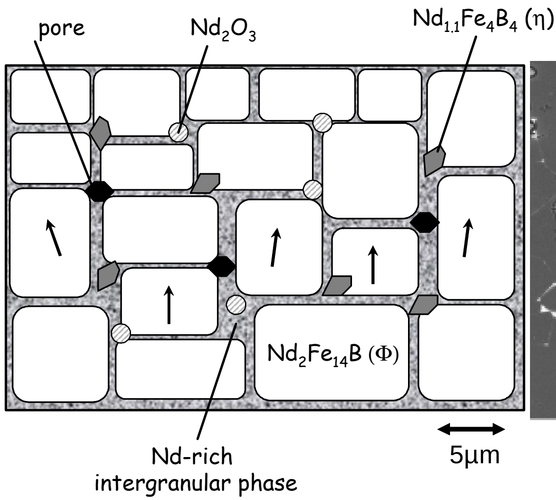


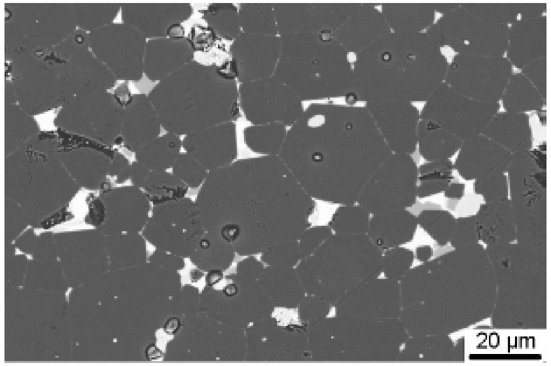


macrotexture ↔ microtexture

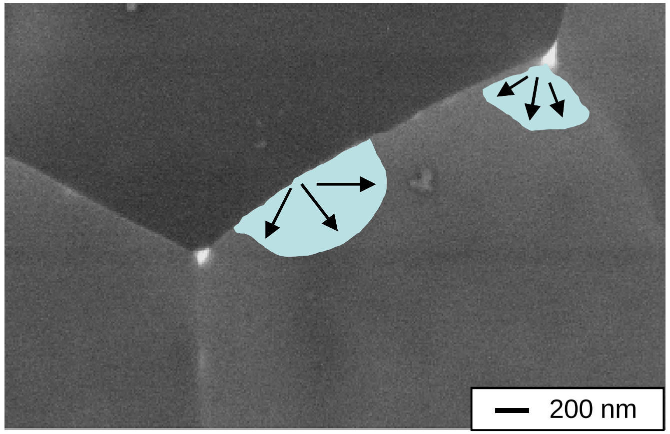
magnetic measurements ↔ Kerr microscopy

Magnetisation reversal in sintered NdFeB





the weak link



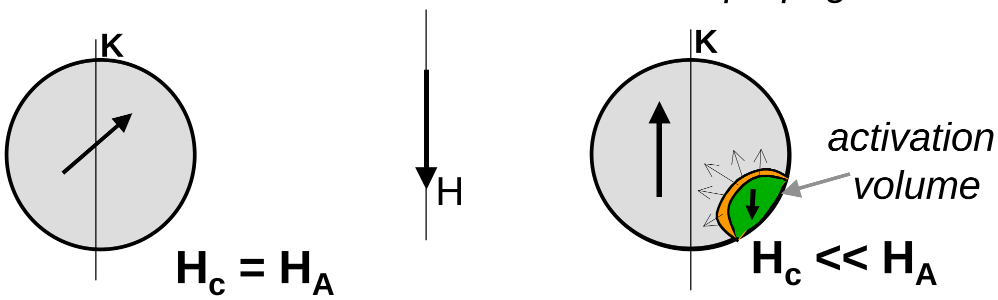
crystalline or amorphous
metallic or oxidic
FM or PM
microchemistry, structural defects
continuous or discontinuous

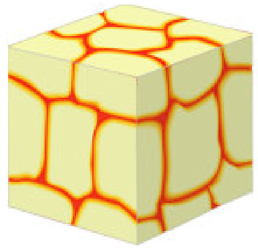
??

Nucleation-type magnet

Perfect materials:
Coherent rotation

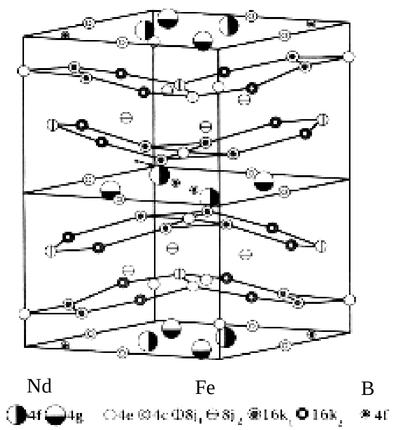
Defects :
Nucleation + propagation

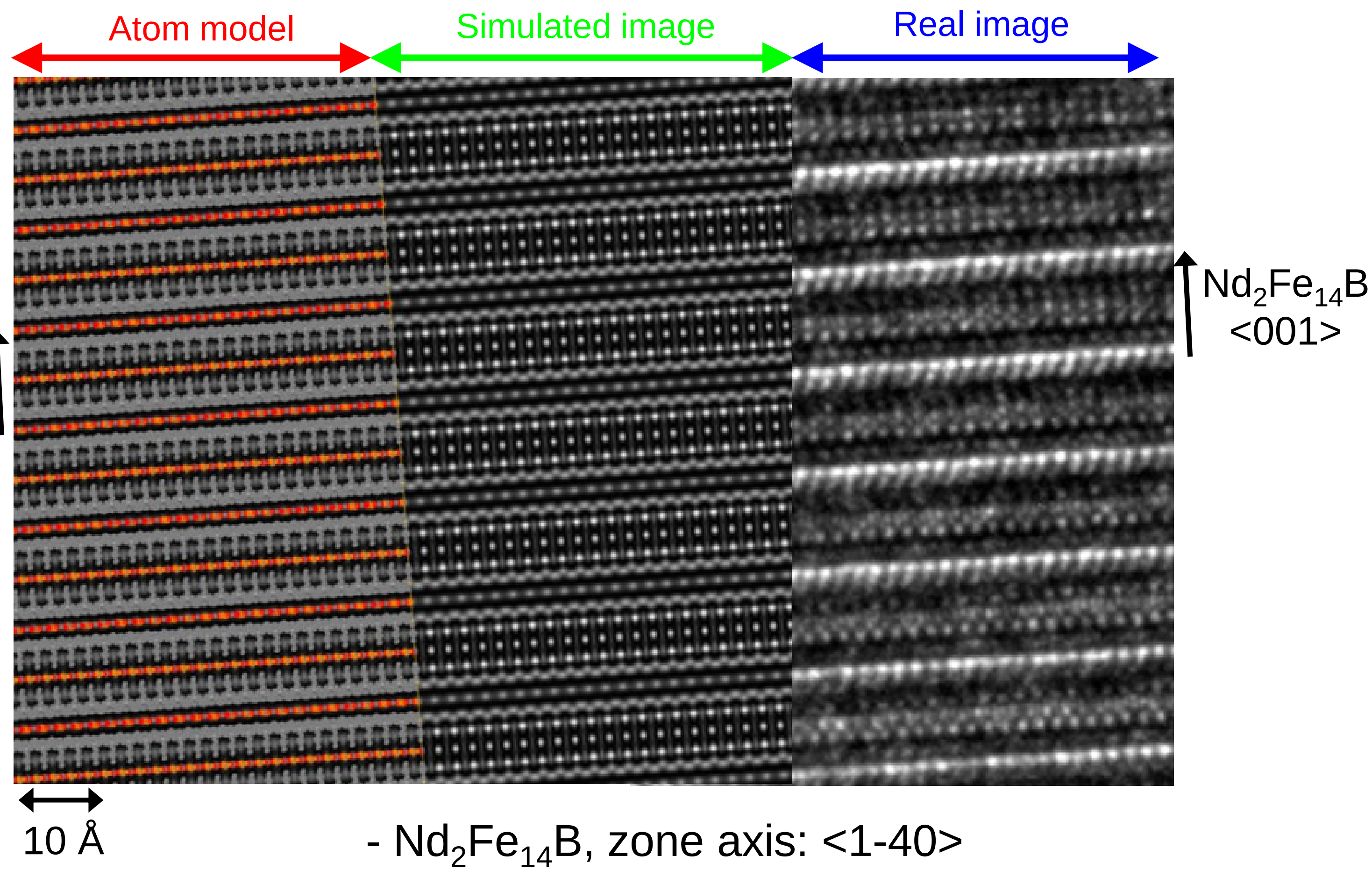




efficient use of Dy by
grain boundary diffussion process
coating

1Å resolution by C_s aberration corrected HRTEM



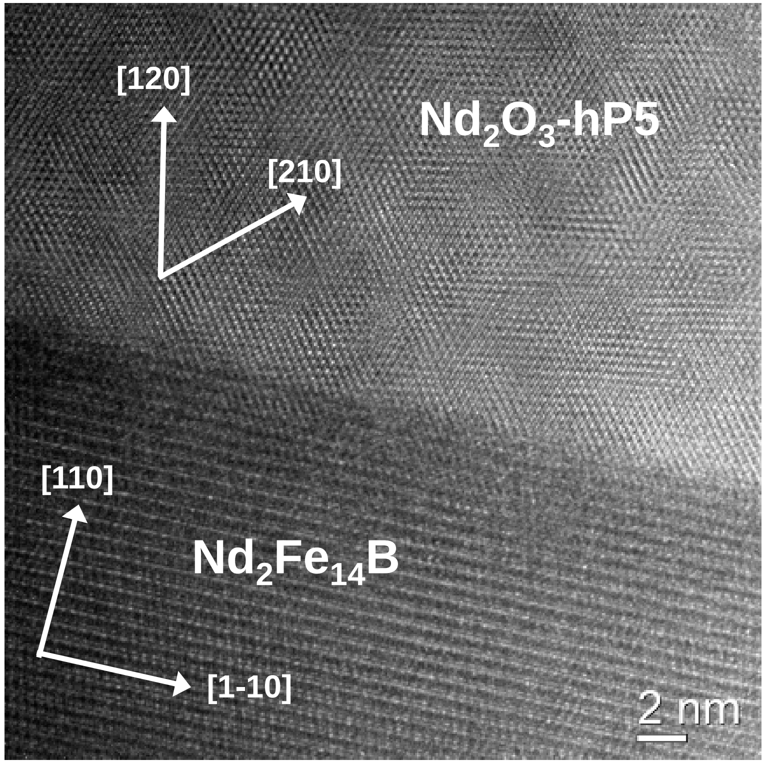


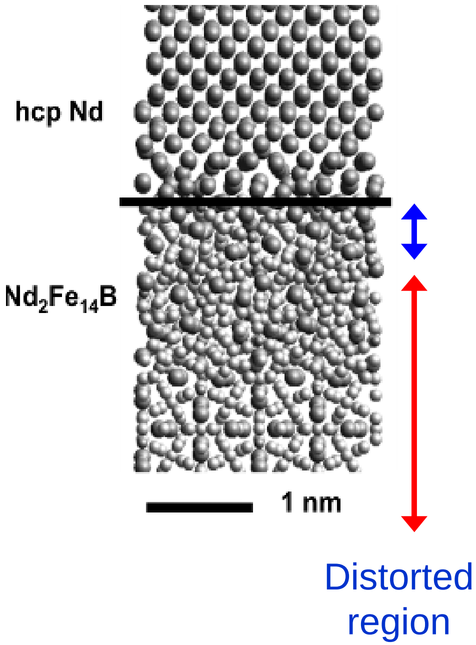
- $Nd_2Fe_{14}B$, zone axis: <1-40>

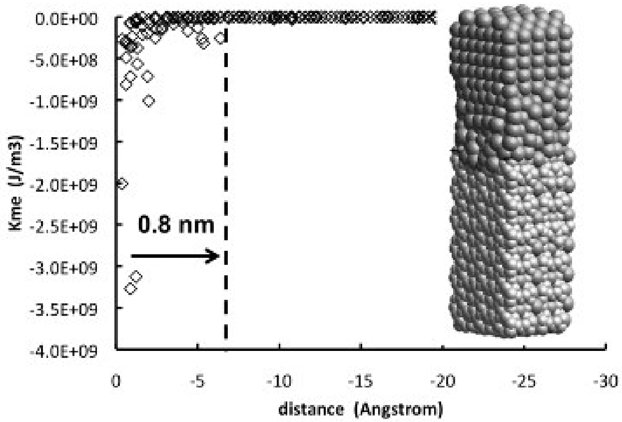
Sample thickness: 15 nm

Atomistic simulation of Nd-rich phase / $Nd_2Fe_{14}B$ interface

Fourier enhanced HR-image







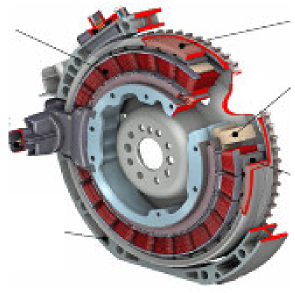
Magnetoelastic anisotropy as function of distance for $Nd_2Fe_{14}B$ (100) surface cut, c-axis parallel to interface to a fcc Nd (011) surface, the plane orientation is in respect to the interface.
Inset: Top layer is the fcc Nd rich phase, bottom layer is the $Nd_2Fe_{14}B$ phase.

→ Thickness of region with reduced anisotropy varies with phase and orientation

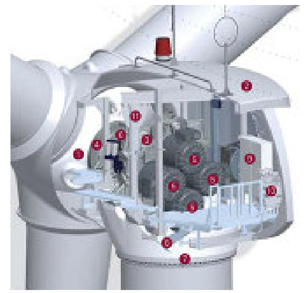
Appl. Phys. Lett. **97** (2010) 232511, cooperation Uni Sheffield

Permanent Magnet Growth

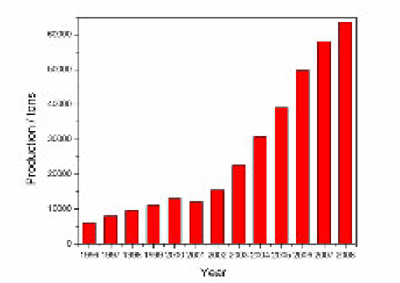
- The **motor/generator in a hybrid electric vehicle contains 2 kg of NdFeB**. This application is set to grow to between 10million and 20million vehicles by 2018. (now: 2.5 out of 850 million vehicles are hybrids worldwide)



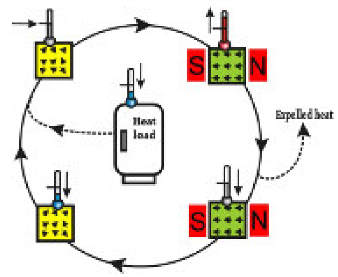
- New **designs of wind generators use NdFeB magnets at a rate of ~700 kg per mega-watt**. This application alone has potential to increase RE demand by 25% per year above current production.



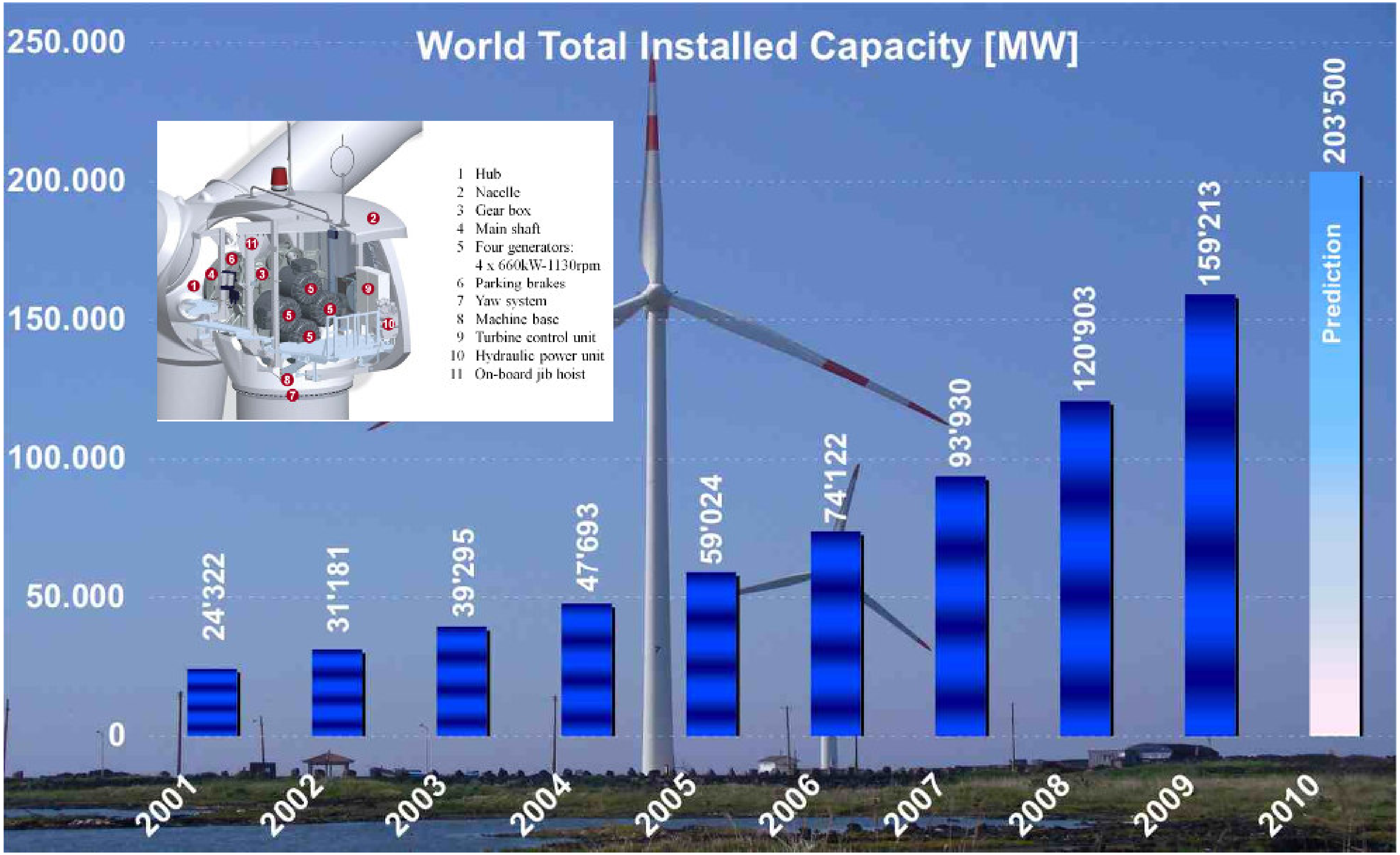
- Hard disc drives cannot function without RE permanent magnets. Formerly 70% of the NdFeB market this is now diluted by the other major applications.
- World production of sintered NdFeB in 2011: **~100.000 t**



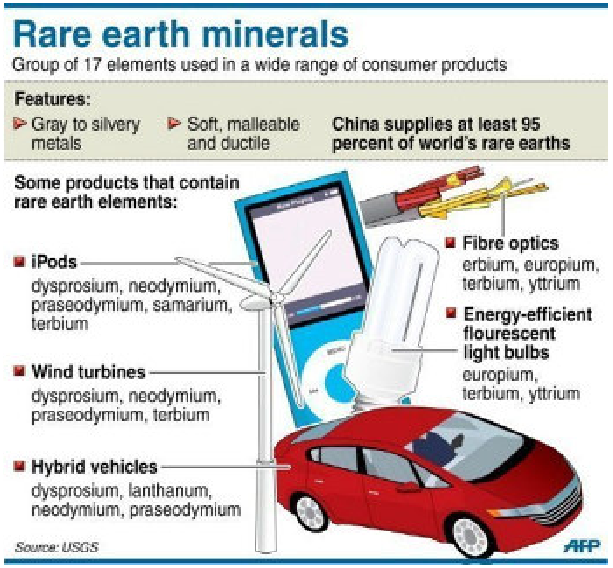
- Solid state energy efficient cooling: **Magnetocalorics**



Installed wind power doubles every three years…



References in Adv. Mat. (Review) 23 (2011) 821-842



Rising Demand for RE Materials (REO t)

REE Application	REO	2008 Demand	2015f Demand
Permanent Magnets	Nd, Pr, Dy, Tb, Sm	26,500	48,000
NiMH Batteries	La, Ce, Pr, Nd	22,500	35,000
Catalysts	Ce, La, Pr, Nd	23,000	28,500
Phosphors	Eu, Y, Tb, La, Dy, Ce, Pr, Gd	9,000	13,000
Polishing Powders	Ce, La, Nd, mixed	15,000	30,500
Glass Additives	Ce, La, Nd, Er, Gd, Yb	12,500	11,000
Ceramics, other	Mixed	15,500	19,000
Total		**124,000**	**185,000**

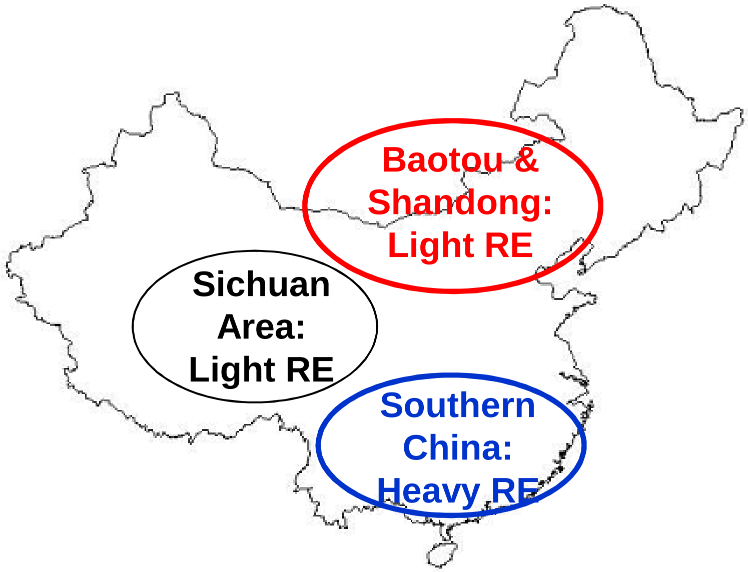
Source: IMCOA 2010

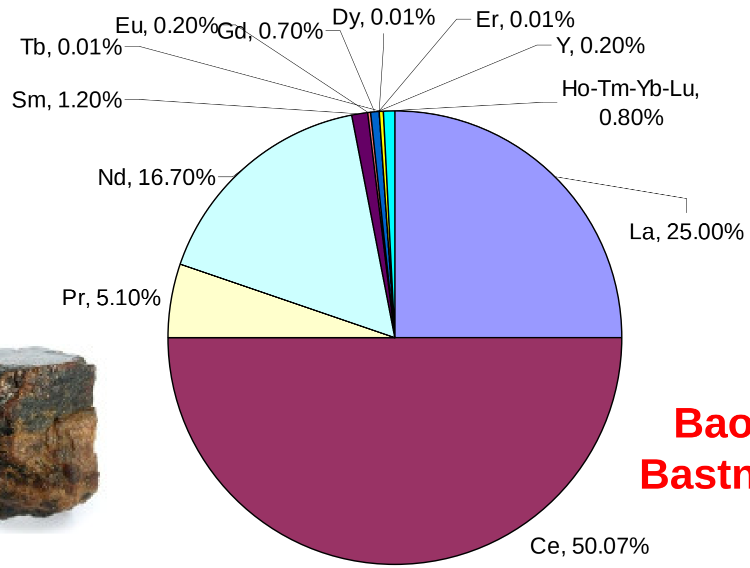
Science News, August 27, 2011

Rare Earth Elements in Automotive

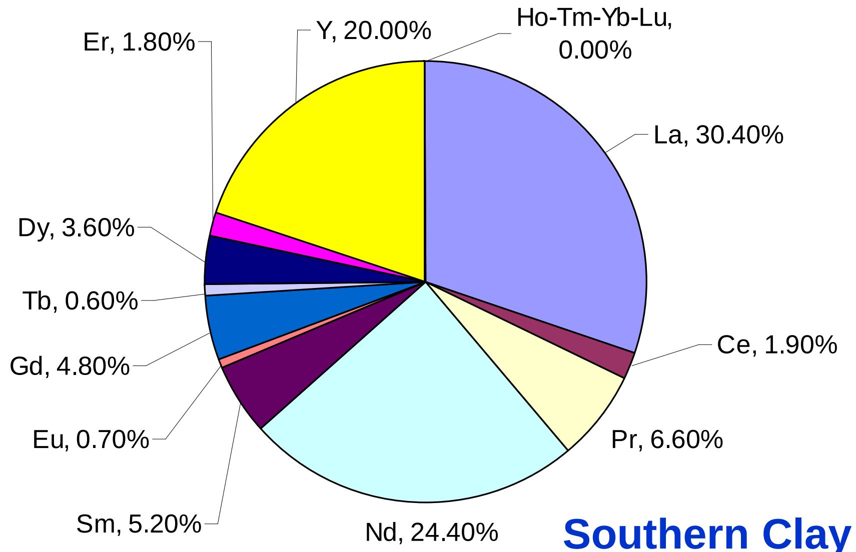
Science News, August 27, 2011

Rare earth oxides in China





Baotou Bastnasite

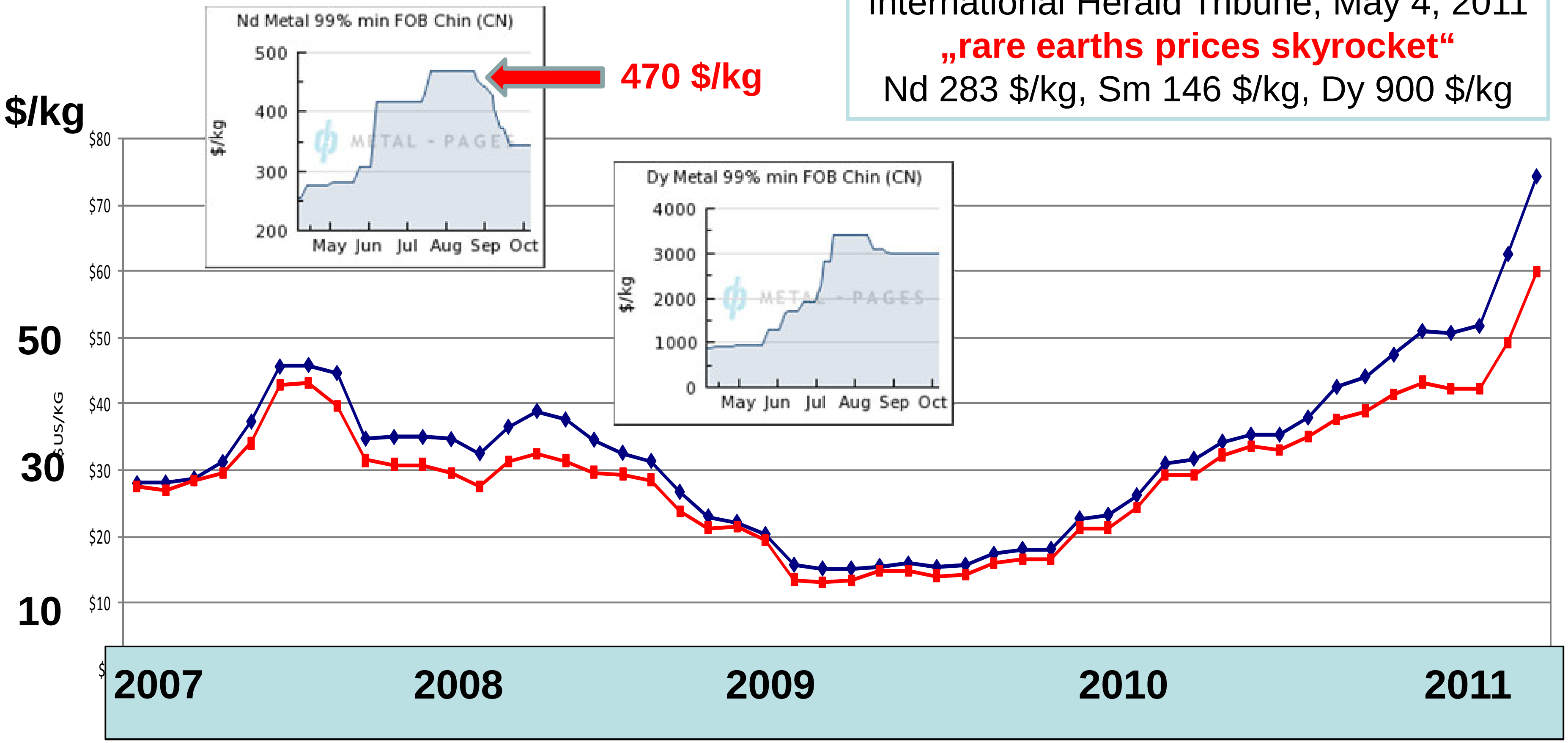


Southern Clay

Raw Materials: Nd and Pr-Nd metal

(Asian Metal and metal-pages)

International Herald Tribune, May 4, 2011
„rare earths prices skyrocket“
Nd 283 $/kg, Sm 146 $/kg, Dy 900 $/kg



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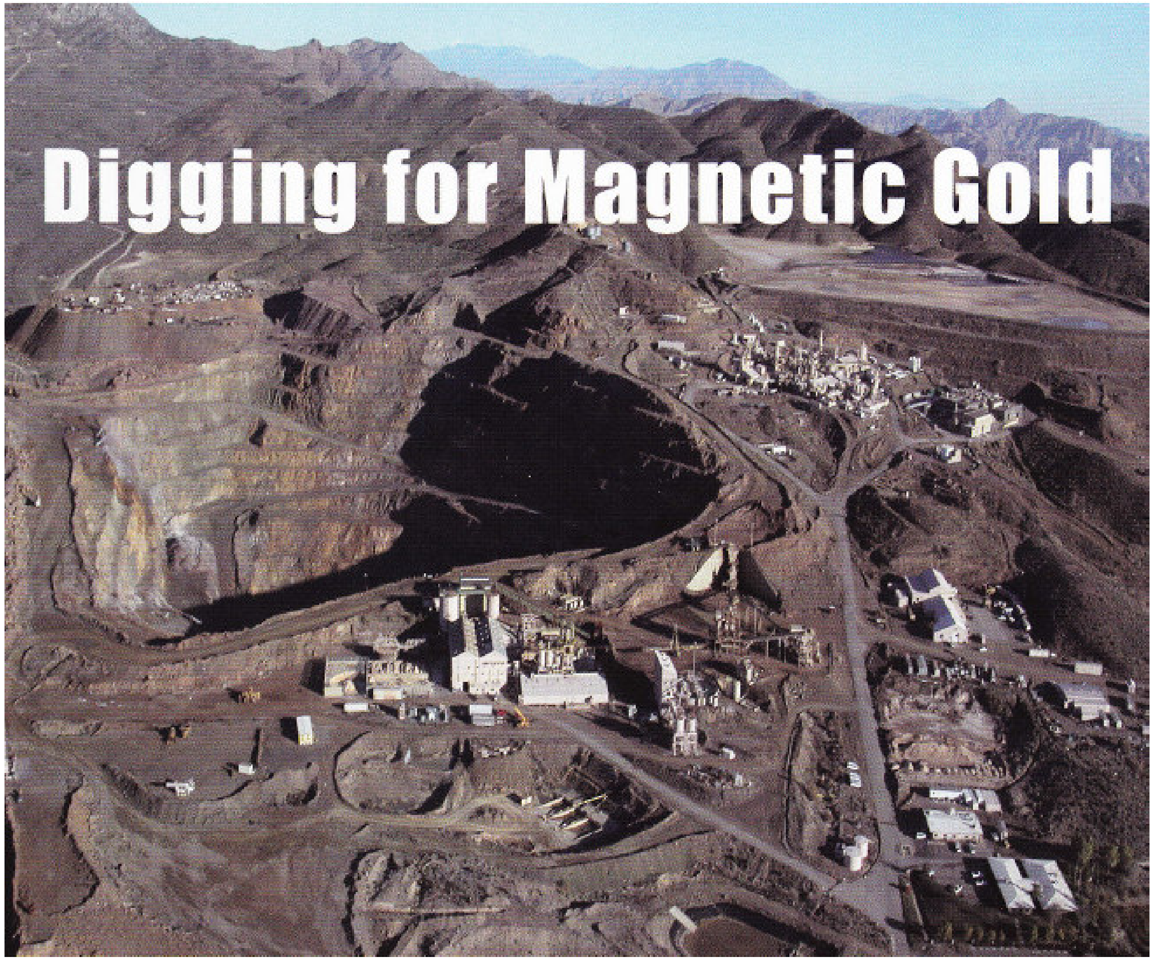
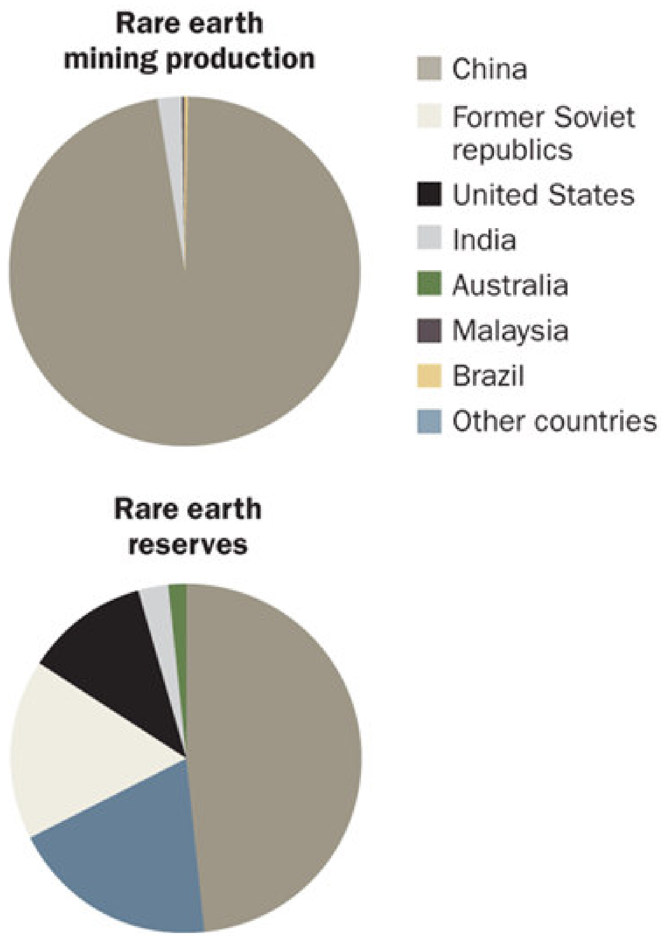
Nd Metal	$28	$28	$28	$31	$37	$45	$45	$44	$34	$35	$35	$34	$32	$36	$39	$37	$34	$32	$31	$26	$23	$22	$20	$15	$15
Pr-Nd Metal	$27	$27	$28	$29	$34	$43	$43	$39	$31	$30	$30	$29	$27	$31	$32	$31	$29	$29	$28	$23	$21	$21	$19	$13	$13

	Feb-09	Mar-09	Apr-09	May-09	Jun-09	Jul-09	Aug-09	Sep-09	Oct-09	Nov-09	Dec-09	Jan-10	Feb-10	Mar-10	Apr-10	May-10	Jun-10	Jul-10	Aug-10	Sep-10	Oct-10	Nov-10	Dec-10	Jan-11	Feb-11
Nd Metal	$15	$15	$16	$15	$15	$17	$18	$18	$22	$23	$26	$31	$31	$34	$35	$35	$38	$42	$44	$47	$51	$50	$51	$62	$74
Pr-Nd Metal	$13	$14	$14	$14	$14	$16	$16	$16	$21	$21	$24	$29	$29	$32	$33	$33	$35	$37	$39	$41	$43	$42	$42	$49	$60



UK Magnetics Society Newsletter Cover Winter 2010



Science News, August 27, 2011

Rare metals in electro mobility

- Meeting in 09/2010 at the German Ministry for Environment, a priority list for critical materials was determined.
  First Priority was given to:
  - **Dy**
  - **Nd**
  - **Tb**
  - **Pr**
  - Ga (Magnets 0.1%, Power Electronics, DC/AC Converter)
  - In (Heating/Cooling, Electronics, Displays)
  - Pd (Fuel Cell, Cat., Power Electronics, Battery-Management-System)
  - Pt (Fuel Cell, Cat., Power Electronics, Battery (Au-Pt Cat. In Li-Air Batt.))
  - Au (Fuel Cell, Cat., Power Electronics, Battery (Au-Pt Cat. In Li-Air Batt.))
  - Cu (Electronics, Cables, Battery, Cooling/Heating,…)
  - Ru (Semi-Conductors, Capacitor, Fuel Cell, Battery) – all in mg volumes

- Dy was described to become the most critical element of all because of single source in the Chinese region and extremely low content in the mines of Molycorp and Lynas.
- **After 2014 a sufficient amount of RE (beside Dy) can be expected in the global market.**
- **Dy will NOT suffice !**

Recycling of scrap sintered NdFeB by hydrogen processing

(1) HD – hydrogen decrepitation

and

(2) HDDR – hydrogenation disproportionation desorption recombination

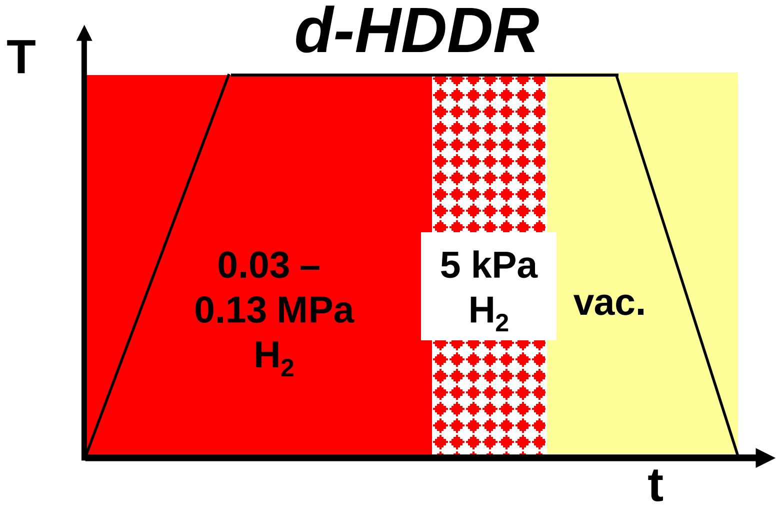
Issues

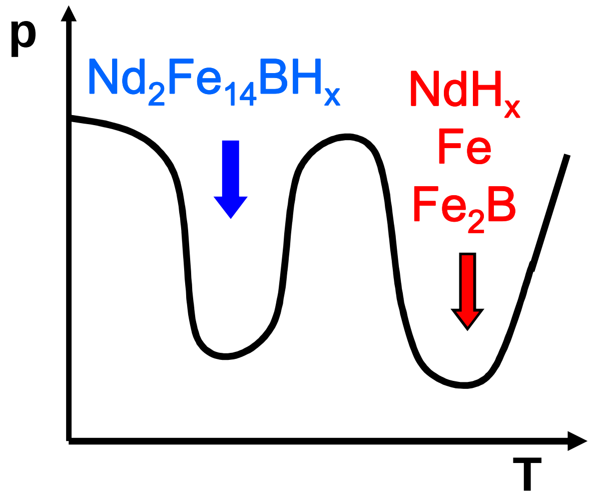
- Removal of brittle intermetallics imbedded with epoxy in assemblies
- Powders are very reactive
- Organics from machining, coatings and epoxies
- Coatings (e.g. Ni) for corrosion protection

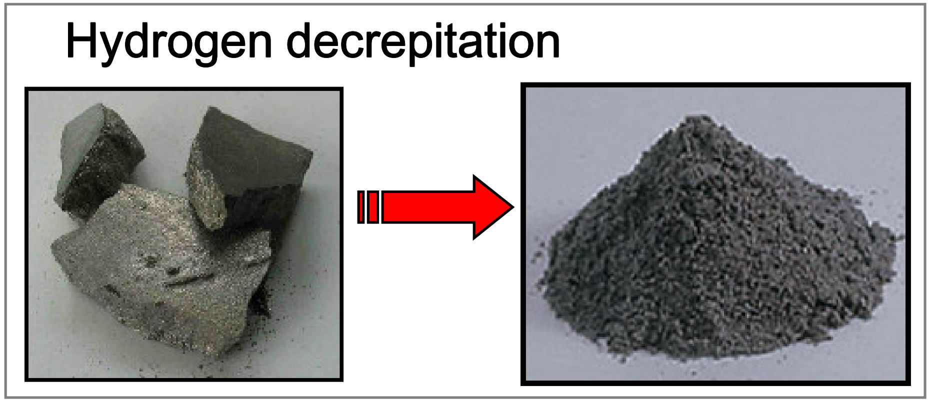
HDDR

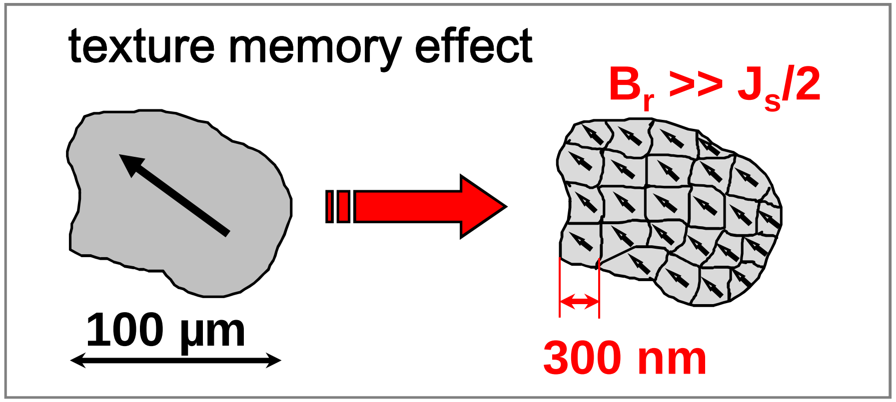
$Nd_2Fe_{14}B + \frac{1}{2} xH_2 \Leftrightarrow Nd_2Fe_{14}BH_x \pm \Delta H_1$ (HD)

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



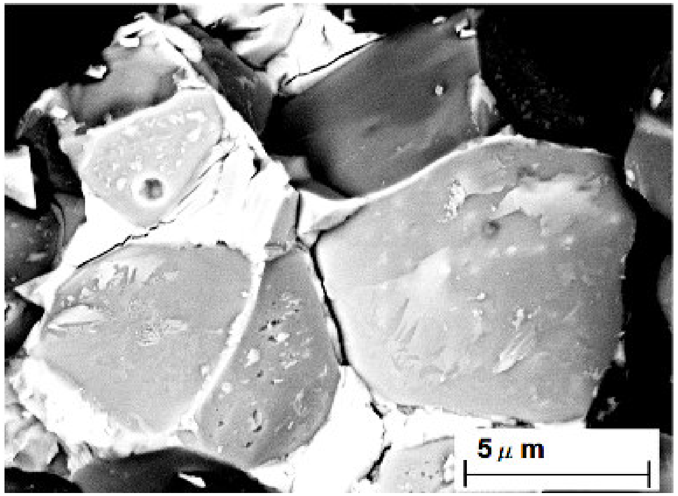






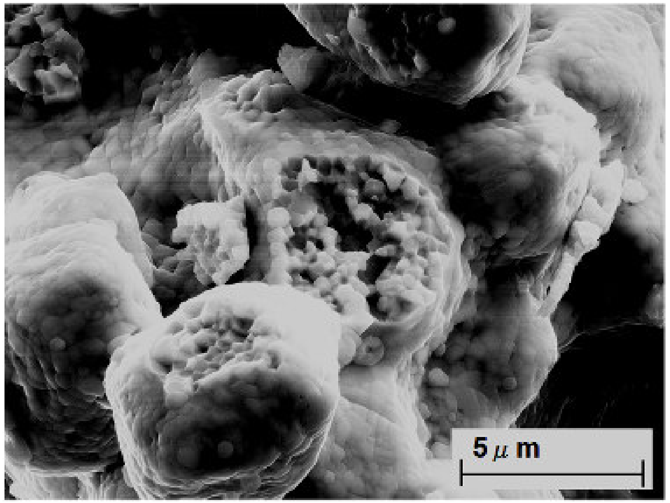
Morphology of hydrogen recycled magnet

after HD

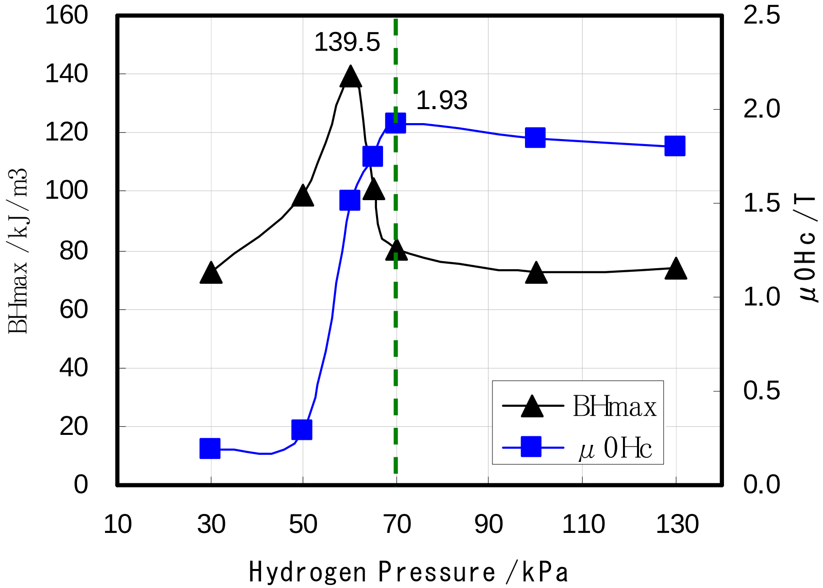


Polyhedron single crystal particle

after d-HDDR



ultrafine grained structure ～300nm



Energy saving by size reduction

conventional seat motor using ferrite magnet	new seat motor using anisotropic polymer bonded HDDR magnet	latest motor using anisotropic polymer bonded HDDR magnet

photos courtesy Aichi Steel

Weight: 465 g	Weight: 295 g (-37%)	Weight: 140 g (-53%)
Volume: 110 cm^3	Volume: 54.5 cm^3 (-51%)	Volume:
Motor power: 50 W	Motor power: 50 W	Motor power: 50 W
Magnet weight : 80g	Magnet weight : 20g	Magnet weight : 8g

Adv. Mat. (Review) 23 (2011) 821-842

How to move forward ?

PATH 1 – use of existing phases

- **Dy-less magnets** – GBDP, grain refinement, interfacial control
- **Textured nanocomposites** (bottom-up approaches incl. the consolidation of nanoparticles, core-shell particles, etc)

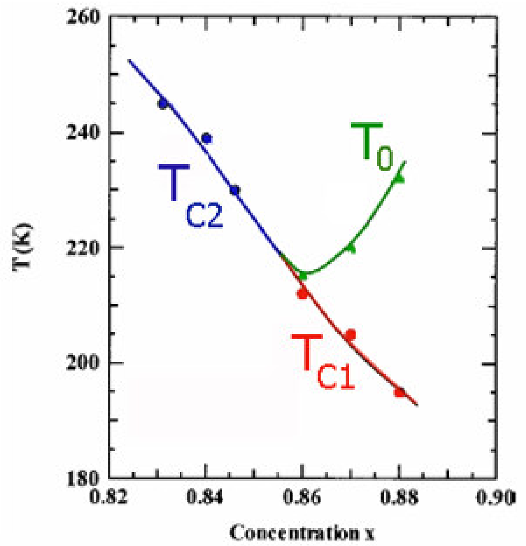
→ **Reduction, Substitution and Recycling of RE-TM magnets, reduce losses**

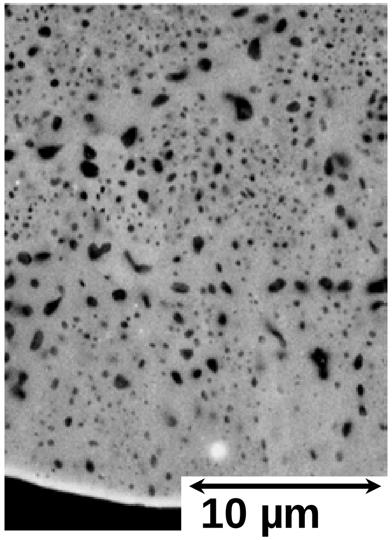
on-going cooperations between us and Japanese partners

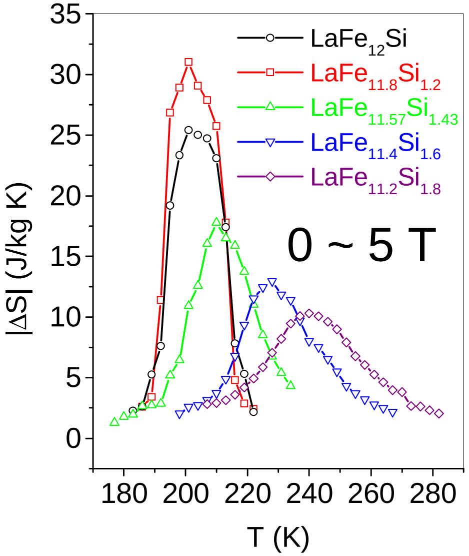
PATH 2 – “new” better “alternative” phases

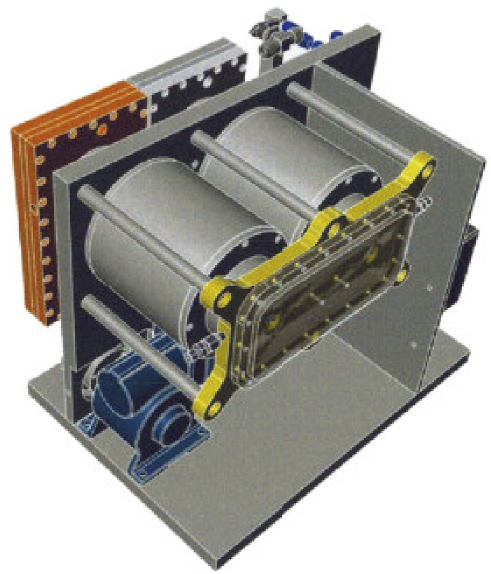
- **Search for new phases** (Heusler, Mn_3Ga, MnBi, $Fe_{16}N_2$, etc)
- **FeCo** (or similar, induce tetragonality or other lower symmetry, explore shape anisotropy)
- **from metastability to volume samples**

→ **Aim to be (much) better than best hard ferrites with good thermal stability but without RE**









compact, solid state, silent and energy efficient heat pump

Magnetic Materials and Devices for the 21st Century: Stronger, Lighter, and More Energy Efficient

Adv. Mat. (Review) 23 (2011) 821-842

Solid state energy efficient magnetic cooling

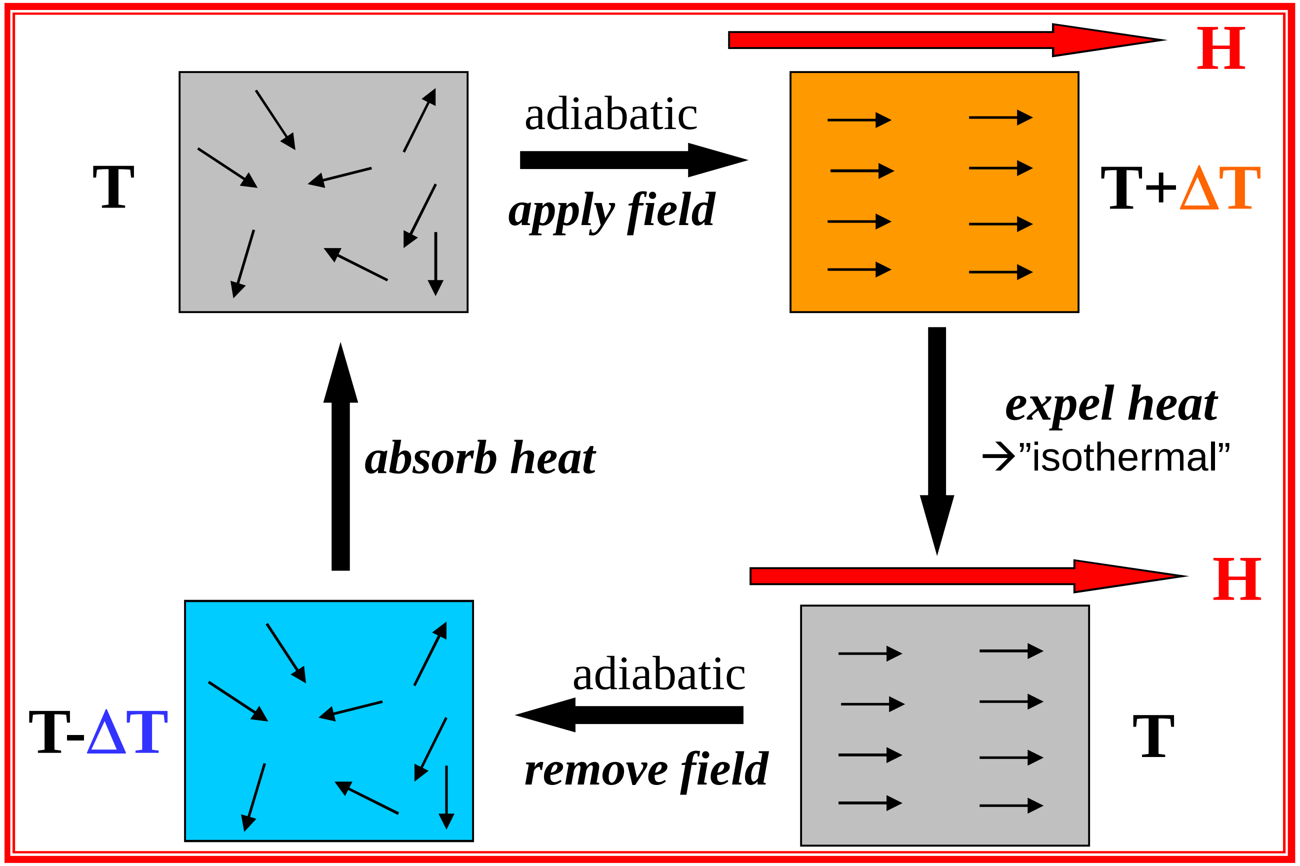
All refrigeration technologies have one thing in common:
they contain a refrigerant which changes state, and in doing so, changes temperature. The changes in temperature of the refrigerant are relayed to the body to be cooled by means of one or more heat exchangers.

Magnetic refrigeration is the only alternative technology which would simultaneously eliminate the need for harmful refrigerant gases and reduce the energy requirements, and hence carbon dioxide emissions.

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)

Magnetocaloric effect & Magnetic refrigeration



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

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

Large H

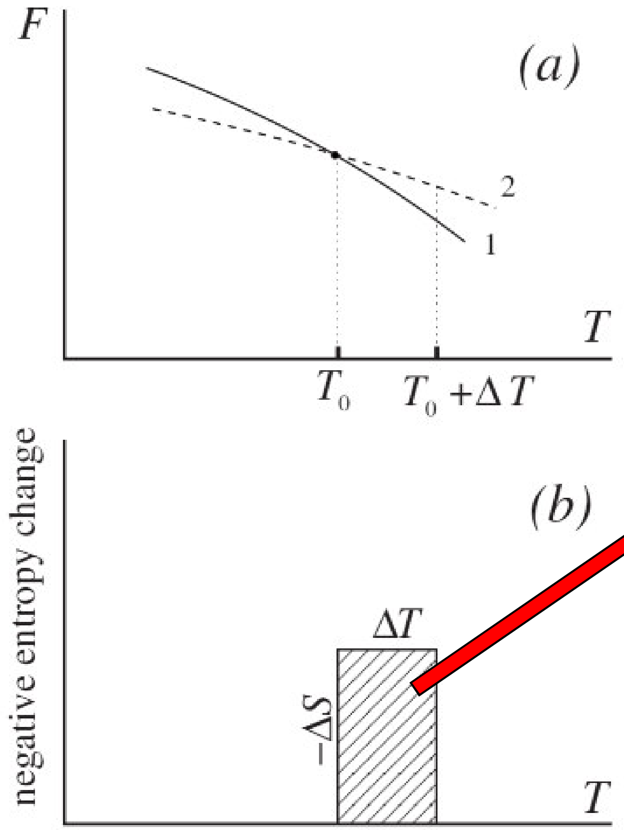
Large $\left(\frac{\partial M}{\partial T}\right)_H$

Small $C_{H,p}$

} **Large MCE**

- **Maxwell equation applies to equilibrium thermodynamics**
- **δM / δT finite or infinite during a first-order magnetic phase transition ?**
- **hysteresis**
- **coupled magnetostructural transitions and related latent heat**
- **comparison with c_p (H) measurements**

Relative cooling power RCP



Magnetic refrigerant undergoing a 1st phase transition:
(a) free energies of the two phases in the absence of magnetic field
(b) field-induced entropy change plotted against T.

with $M_2 > M_1$
and
$\Delta T (S_1 - S_2) = B(M_2 - M_1)$

$RCP = B(M_2 - M_1)$ per refrigeration cycle

Actual cooling power [W/m³]:
RCP x operating frequency f
Inertia of heat exchange
→ upper limit 200 Hz
and
dynamics of the 1st-order phase transition

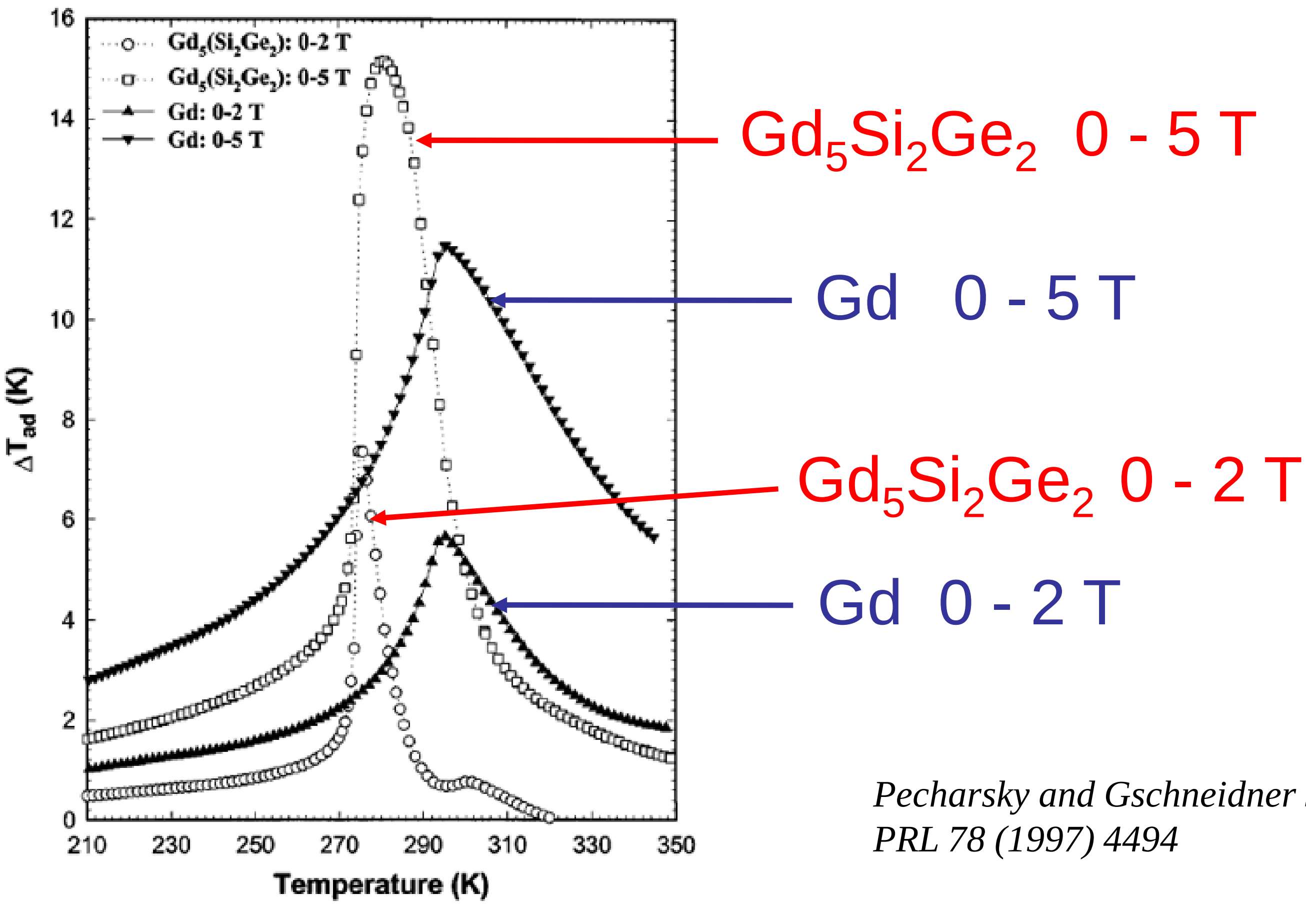
Phys. Rev. B 76, 092401 (2007)
APL 90, 251916 (2007)
Cooperation with IFW theory group M. Richter

Requirements and Challenges

- strong temperature dependence of magnetisation, large entropy jump at T_C, large field dependence of T_C
- large $\Delta T_{ad} / \Delta H$ → driven by moderate magnetic field (RPMs) at a tailored operating temperature
- small thermal and magnetic hysteresis, dynamics
- material cost (e.g. Gd), non-toxic (e.g. As)
- high thermal and small electrical conductivity
- mechanical and chemical stability, high ductility

Giant magnetocaloric materials

alloy	T_c (K)	structure	ΔV	problems
$Gd_5(Si_{1-x}Ge_x)_4$	130-270	orthorhombic⇔ monoclinic	0.5 %	high purity Gd



Pecharsky and Gschneidner Jr., PRL 78 (1997) 4494

Giant magnetocaloric materials

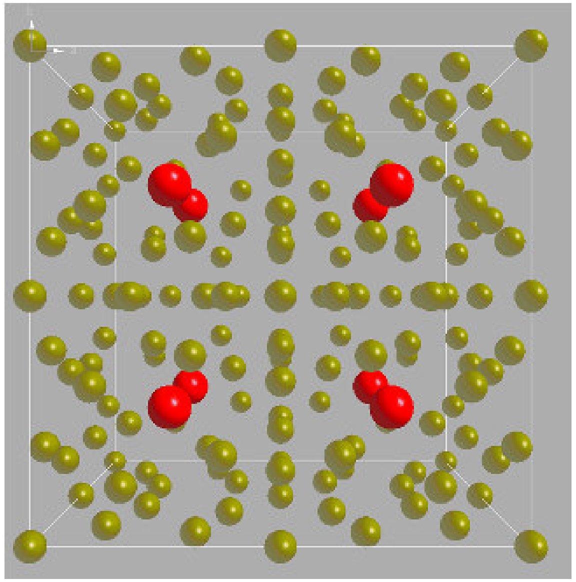
alloy	T_c (K)	structure	ΔV	problems
$Gd_5(Si_{1-x}Ge_x)_4$	130-270	orthorhombic⇔ monoclinic	0.5 %	high purity Gd
$La(Fe,Si)_{13}H_x$ **also Si or Co**	**200-330**	**cubic → cubic ($NaZn_{13}$)**	**1.5 %**	**α Fe**
MnFe(P,As) MnFe(P,Ge)	150-340 250-580	hex → hex (Fe_2P)	0.1 %	toxic
MnAs Mn(As,Sb)	317 reduced hysteresis	hex → ortho (NiAs→MnP)	2.2% 0.7 %	toxic
$Ni_{55.2}Mn_{18.6}Ga_{26.2}$ NiMnInCo	315 various	$L2_1$ ⇔ 5M martensitic trans.	0	large strain, hysteresis

in red: research @ IFW Dresden

3d intermetallic compounds as an alternative to heavy rare earths containing compounds ??
(high abundance, relatively high magnetic moment, coupling to lattice)

$La(FeSi)_{13}$

$NaZn_{13}$-type structure stabilised by Si or Al



La: 8a sites Fe/Si: 8b and 96i

$$(Fm\bar{3}c)$$

Research @ IFW Dresden

(1) What is special about $La(Fe,Si)_{13}$

(2) Synthesis

(3) Tailoring hysteresis and operating temperature

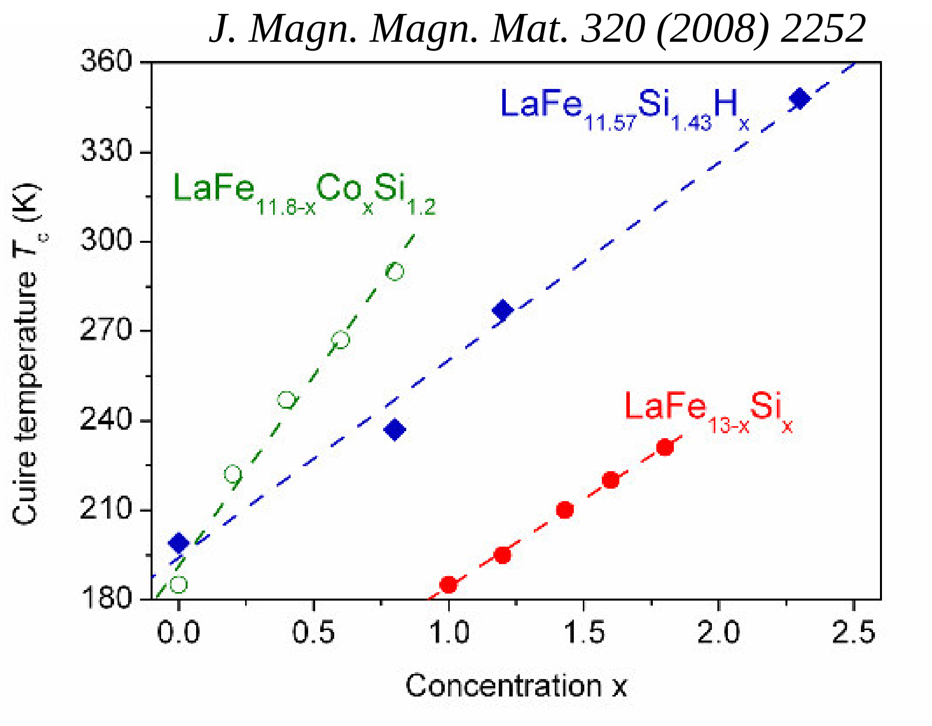
(4) Magnetovolume, hybridisation and cooling power

(5) Strain related effects

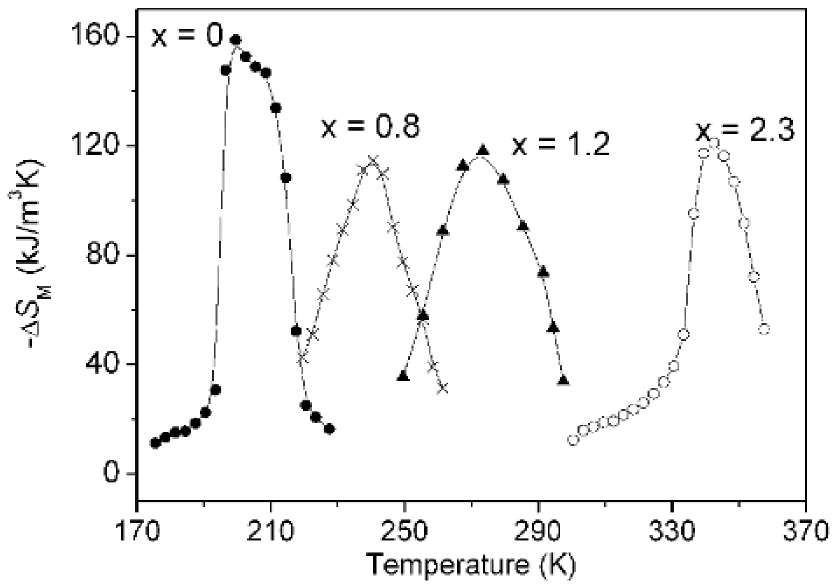
(6) Layered beds

Tailoring T_c by interstitial hydrogen

J. Magn. Magn. Mat. 320 (2008) 2252



La(Fe,Si)$_{13}$H$_x$



JAP 102 (2007) 053906

Co substitution

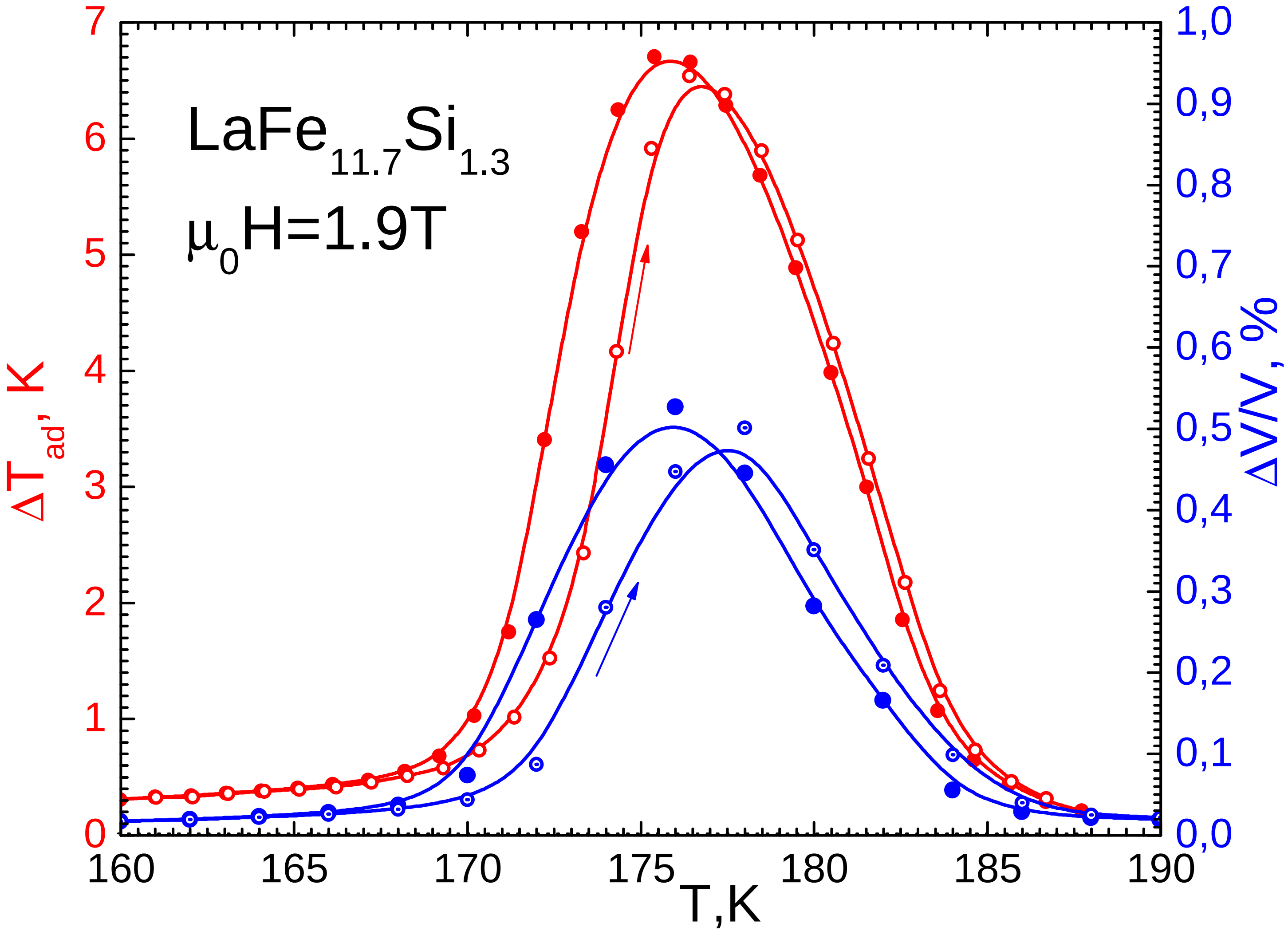
- **T_c ↑**
- **gradual transition to 2nd order – ↓ ΔS_{max}**

Hydrogen insertion

- **T_c ↑**
- **1st order transition preserved – large ΔS_{max}**

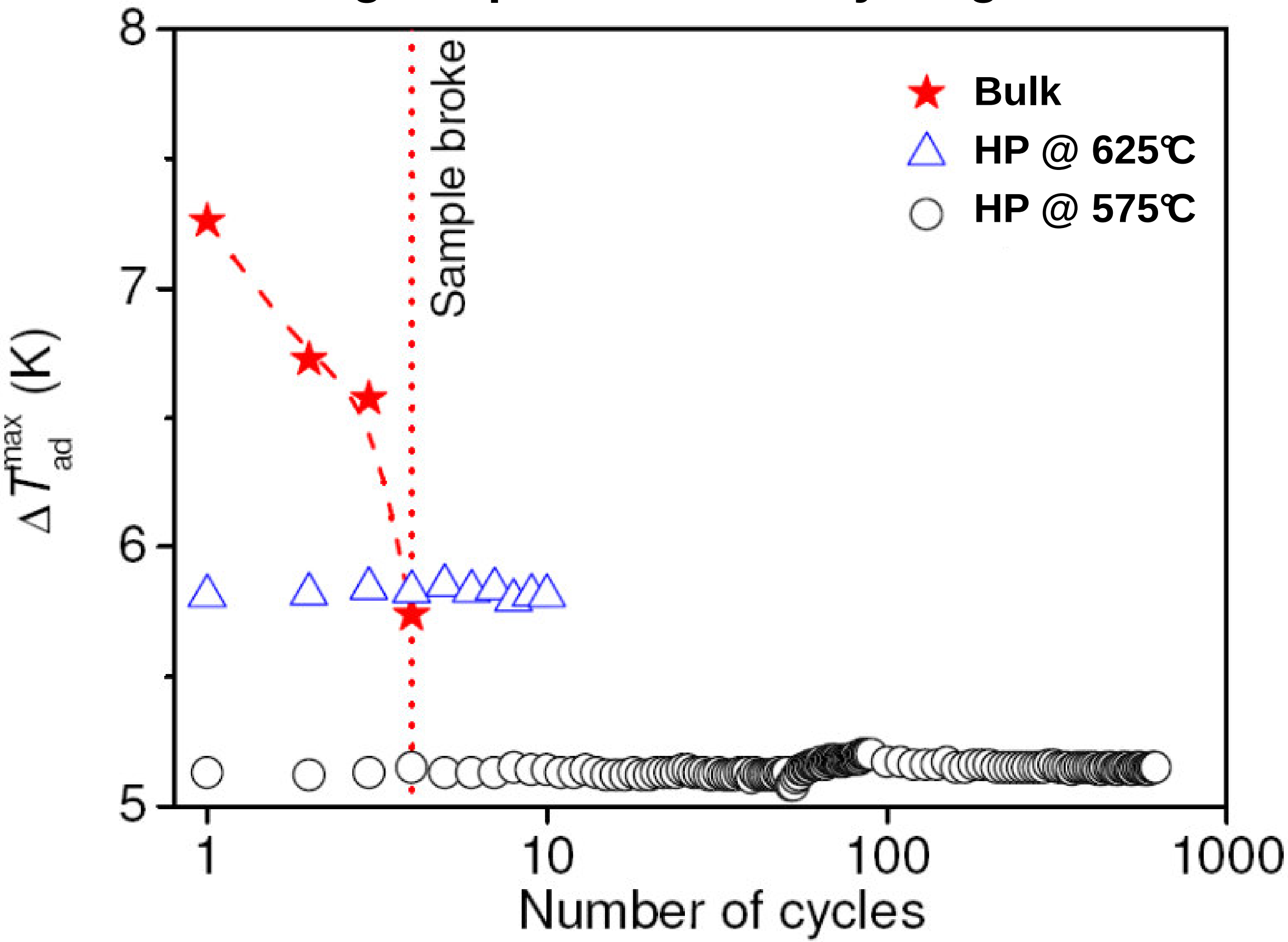
ΔT_{ad} and $\Delta V/V$ of $LaFe_{11.7}Si_{1.3}$

adiabatic temperature change and related magnetovolume effects



New porous morphology of $LaFe_{11.6}Si_{1.4}$

Hot pressed porous compacts retain mechanical integrity during temperature-field cycling

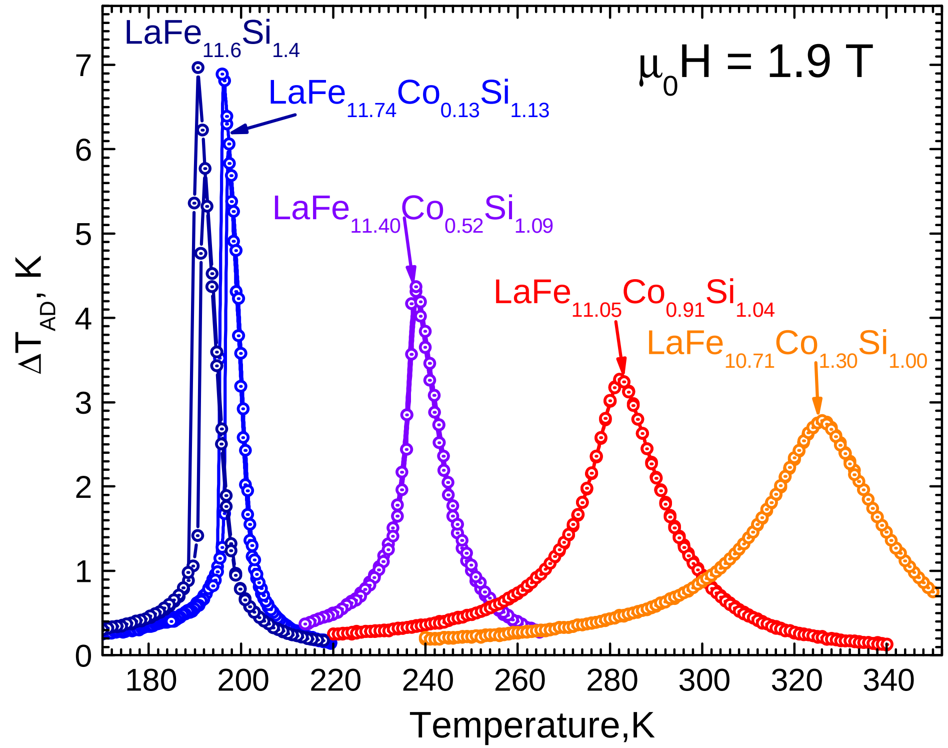


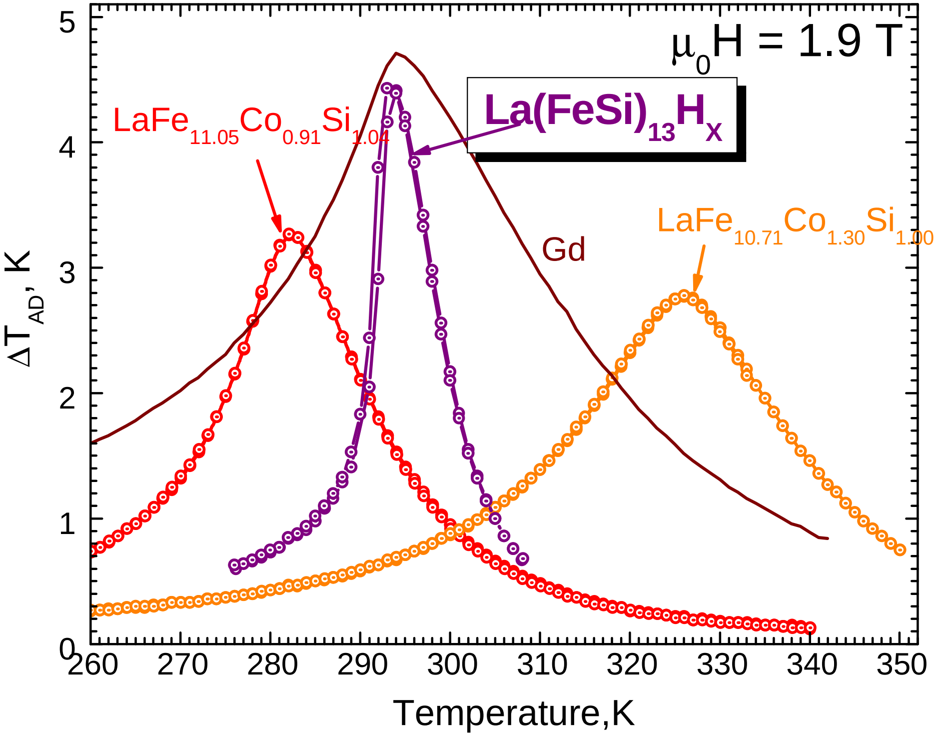
Adv. Mat. 22 (2010) 3735, Patent filed.

Comparison of ΔT_{ad}

1st vs. 2nd order type materials

EU project SSEEC, cooperation Vacuumschmelze Hanau



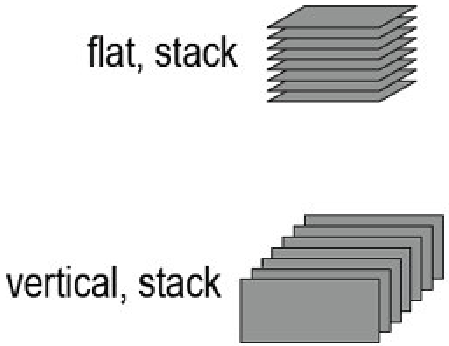


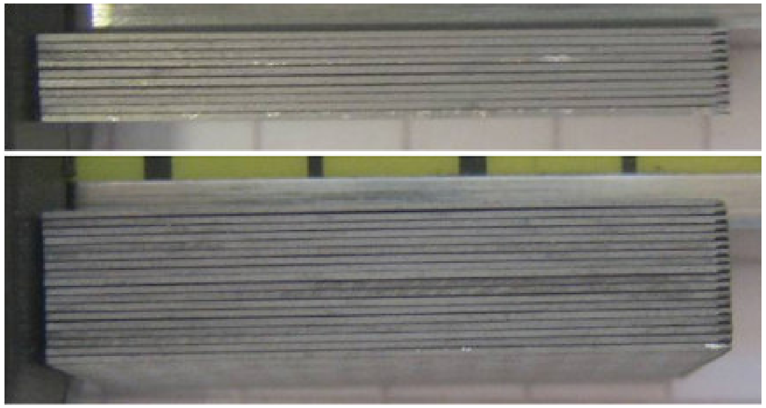
→ comparison in a realistically operating prototype device

refrigerant capacity $$q = \int_{T_{\text{cold}}}^{T_{\text{hot}}} \Delta S(T,P,\Delta H)_{P,\Delta H}\, dT$$

Towards application

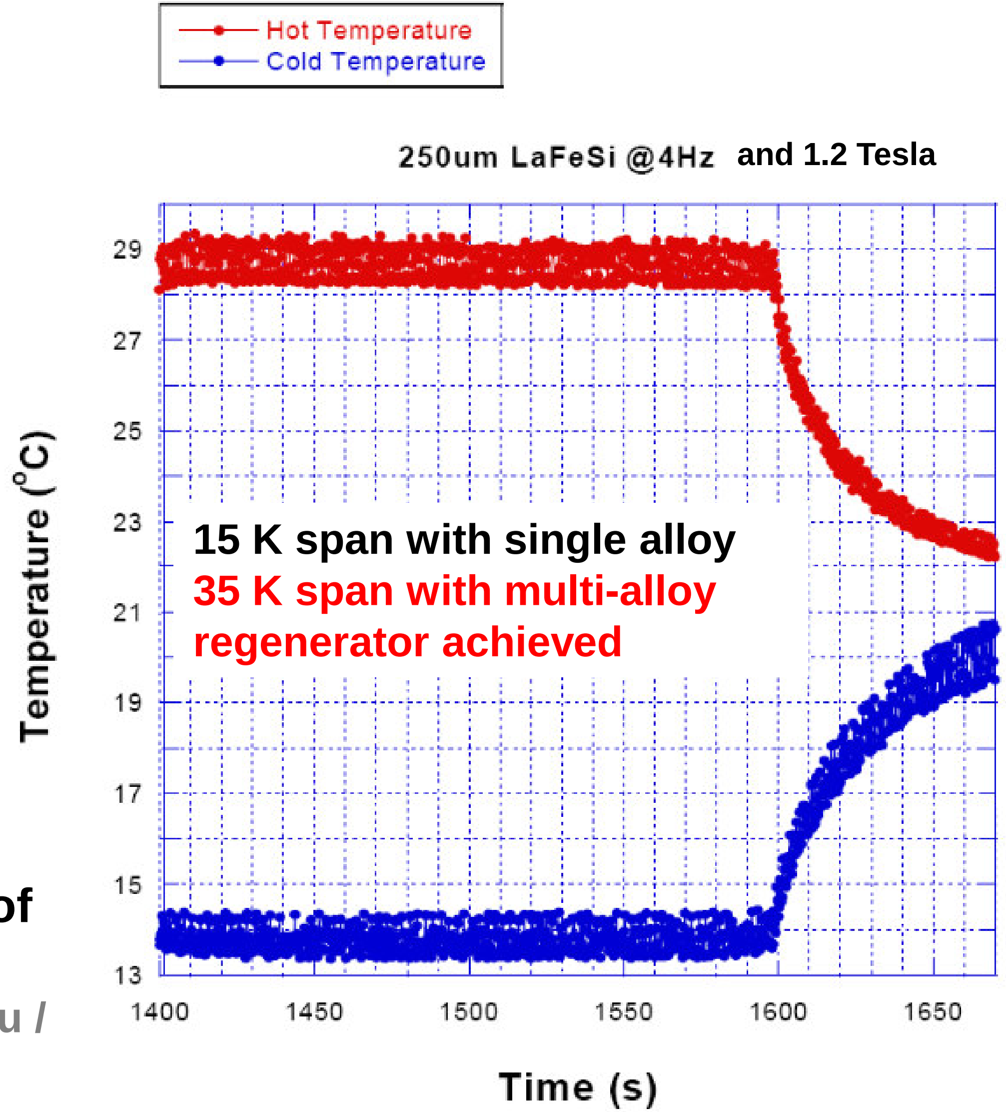
Prototype development in the SSEEC project (EU)





Plates of sintered $La(FeCoSi)_{13}$ of 0.25mm thickness

produced by Vacuumschmelze Hanau / System by Camfridge Ltd.



How to move forward ?

Generally, we have a number of parameters to maximize the MCE at a given magnetic field:

- **Lattice** (especially for low magnetic fields the way forward is to maximize the structural contribution; big shift of the magnetostructural transition with field (several Kelvin per Tesla))
- **Spins** (exploit chemical complexity to precisely tune magnetism)
- **Hysteresis** (maintain first-order character but minimize hysteresis)
- **µ-structure** (engineer (multiphase) nanostructure with stress generating/relieving features)
- **Metastability and non-equilibrium** (coexistence)

How to move forward ?

Drastically Reduced Rare Earth use in Applications of Magnetocalorics

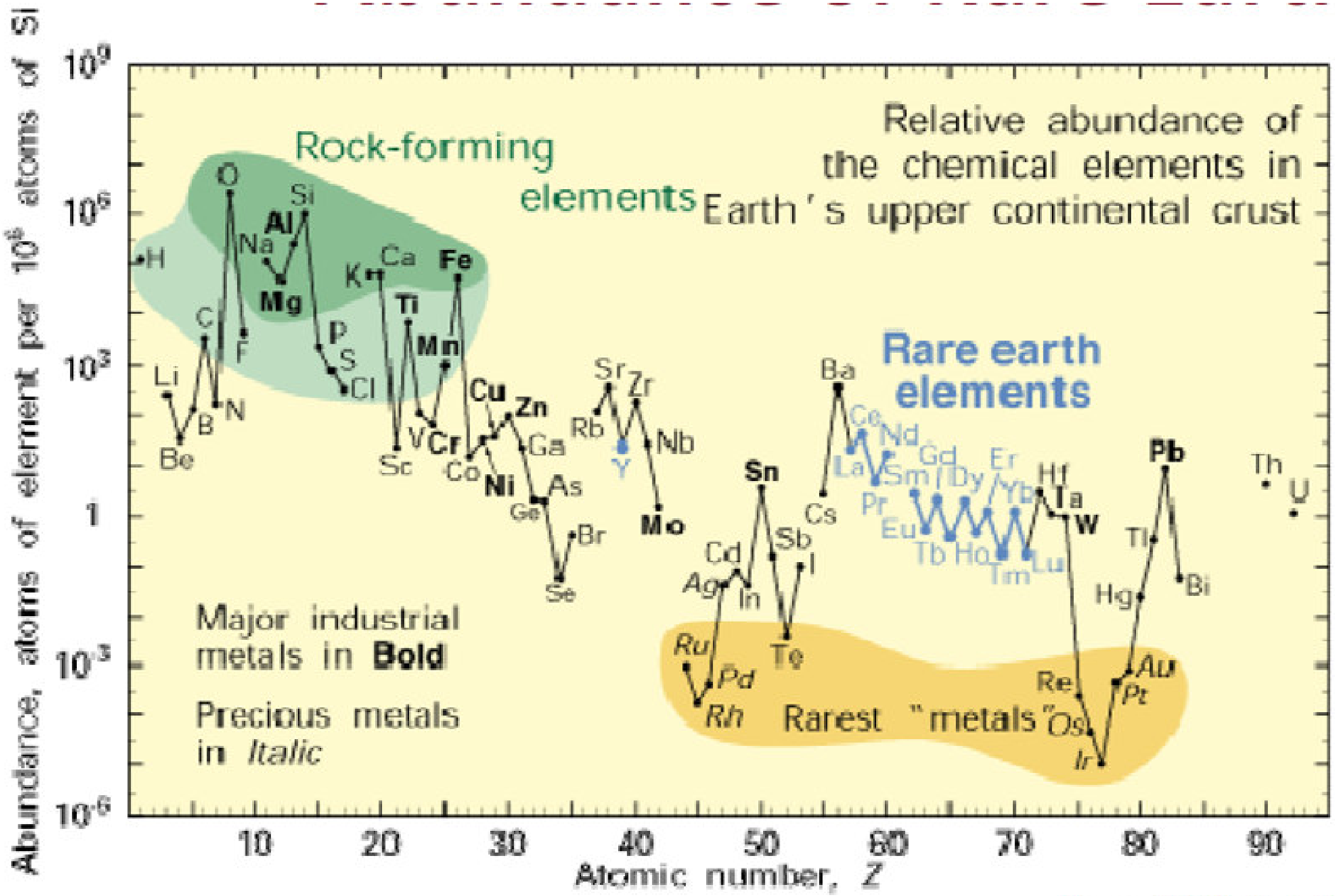
- minimise rare earth wastage through the efficient manufacture of large volumes of magnetocaloric material parts;
- drastically reduce the consumption of rare earth permanent magnets in end use through step-change improvements in the performance of magnetocaloric materials;
- investigate the fundamental properties of several rare earth-free magnetocaloric materials through theoretical modelling, resulting in improved understanding of magnetocaloric mechanisms and parallel benefits for thermomagnetic power generation.

Replacements – Long term - New systems (ARPA-E REACT Awards $24M plus)

Lead Research Organization (Partner Organizations)	Amount	Project Title
Case Western Reserve University	$1,000,000	Transformation Enabled Nitride Magnets Absent Rare Earths
Dartmouth College	$397,433	Nanocrystalline τ-MnAl Permanent Magnets
Northeastern University (Arnold Magnetic Technologies Corporation, Columbia University, General Motors Research and Development, University of Massachusetts Amherst, University of Nebraska – Lincoln)	$3,439,877	Multiscale Development of $L1_0$ Materials for Rare-Earth-Free Permanent Magnets
QM Power (Oak Ridge National Laboratory, Smith Electric Vehicles, University of Delaware)	$2,319,474	Advanced Electric Vehicle Motors with Low or No Rare Earth Content
Pacific Northwest National Laboratory (Ames Laboratory, Electron Energy Corp, United Technologies Research Center, University of Maryland, University of Texas at Arlington)	$2,344,299	Manganese-Based Permanent Magnet with 40 MGOe at 200°C
University of Alabama (University of California at San Diego, Mississippi State University)	$1,265,589	Rare-Earth-Free Permanent Magnets for Electrical Vehicle Motors and Wind Turbine Generators: Hexagonal Symmetry Based Materials Systems Mn-Bi and M-type Hexaferrite
Argonne National Laboratory (Electron Energy Corporation)	$2,965,904	Nanocomposite Exchange-Spring Magnets for Motor and Generator Applications
Baldor Electric Company (Arnold Magnetic Technologies Corp, ABB)	$2,942,867	Rare Earth-Free Traction Motor for Electric Vehicle Applications
Virginia Commonwealth University (Arnold Magnetic Technologies, Northeastern University, University of California - San Diego, Moog Inc., Bayer Technology Services)	$2,911,374	Discovery and Design of Novel Permanent Magnets using Non-strategic Elements having Secure Supply Chains
University of Minnesota (Oak Ridge National Laboratory)	$2,529,299	Synthesis and Phase Stabilization of Body Center Tetragonal (BCT) Metastable FE-N Anisotropic Nanocomposite Magnet - A Path to Fabricate Rare Earth Free Magnet
Ames Laboratory (General Motors, Molycorp, NovaTorque)	$2,202,545	Novel high energy permanent magnet without critical elements

October 2011

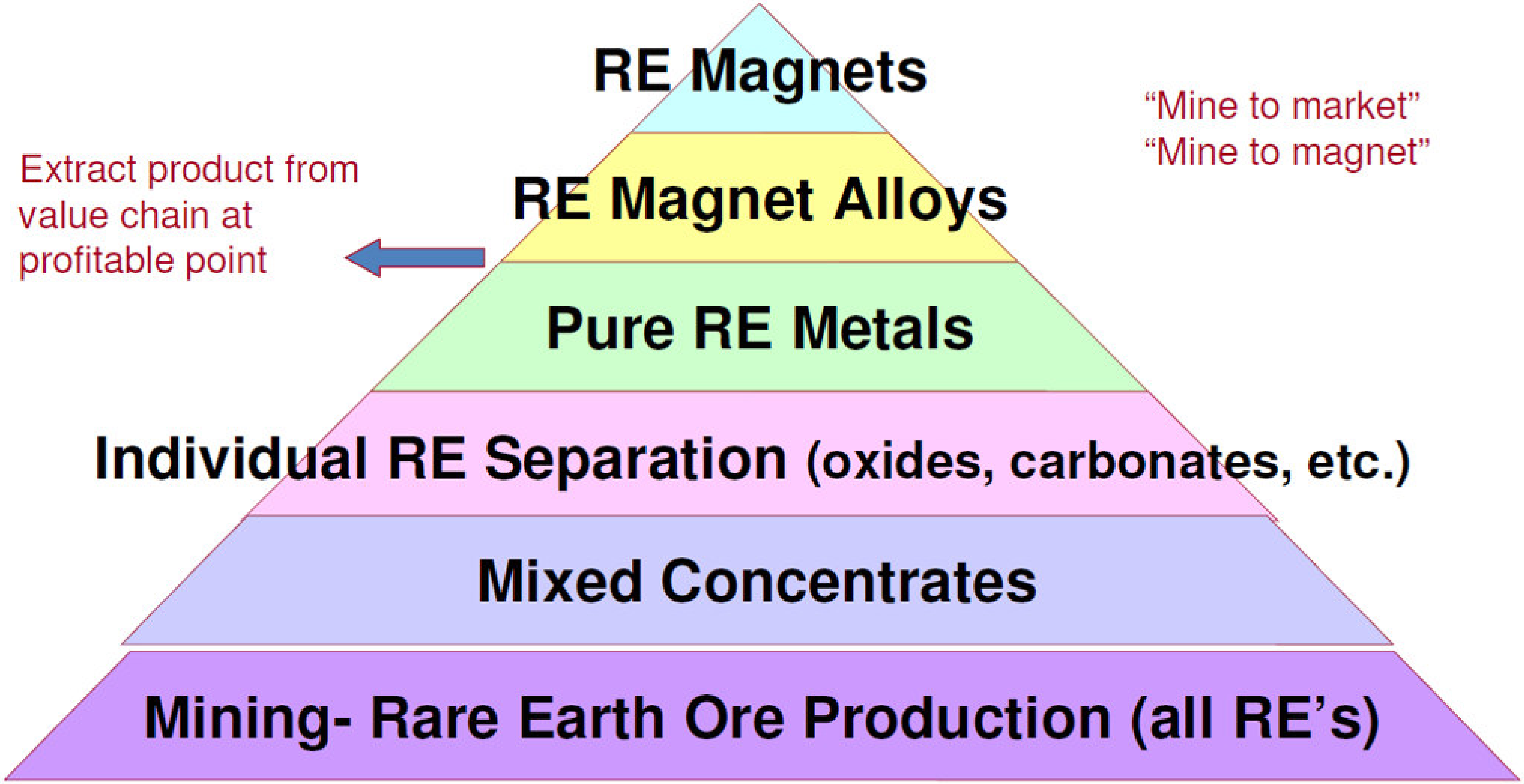
Abundance of rare earths



- **Figure 4.** Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number. Many of the elements are classified into (partially overlapping) categories: (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 >~3x107 kg/year; labeled in bold); (4) precious metals (italic); and (5) the nine rarest "metals"—the six platinum group elements plus Au, Re, and Te (a metalloid).

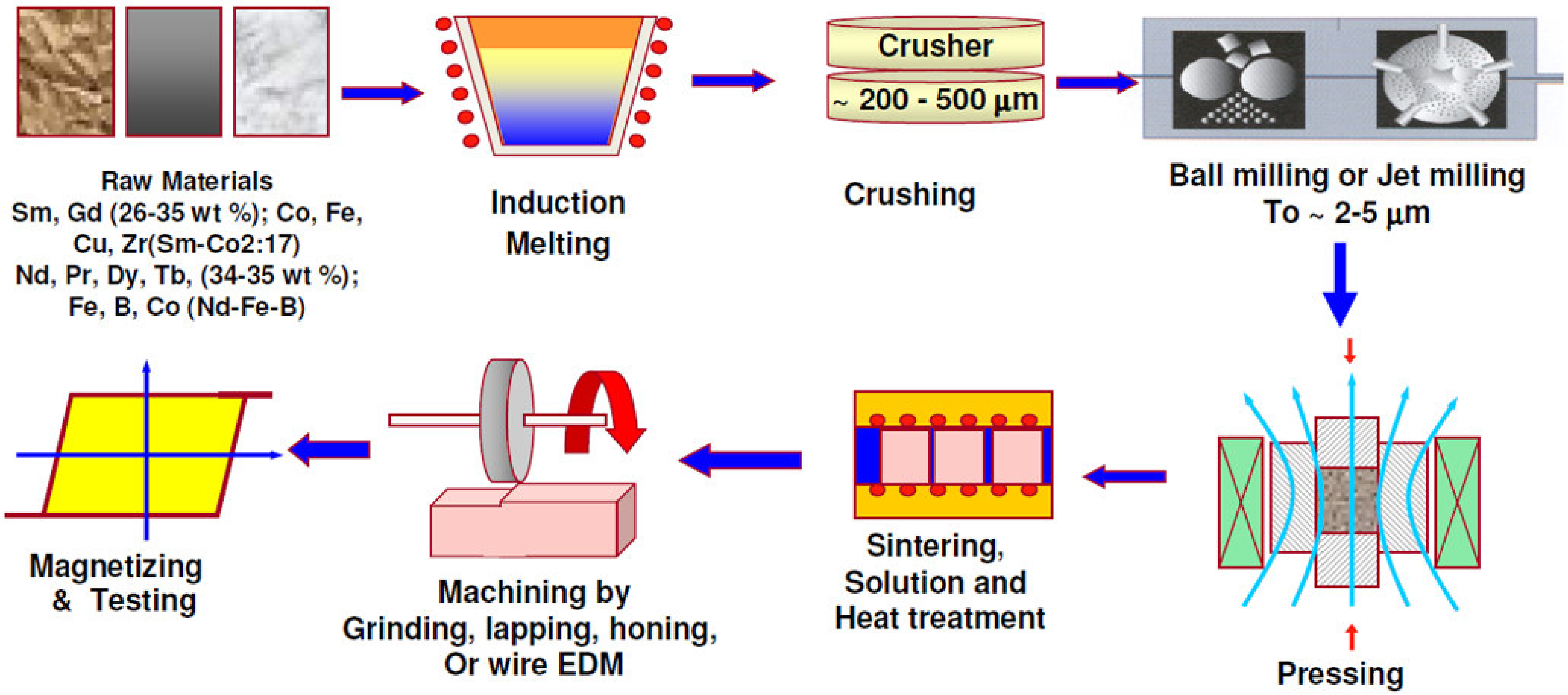
Source; U.S. Geological Survey Fact Sheet 087-02

Rare earth value chain



Courtesy P. Dent, MMM Conf. Nov. 2011

Manufacturing of sintered RE magnets



Courtesy P. Dent, MMM Conf. Nov. 2011