KAPITAŁ LUDZKI
NARODOWA STRATEGIA SPÓJNOŚCI

INSTYTUT METALURGII I INŻYNIERII MATERIAŁOWEJ im. Aleksandra Krupkowskiego Polskiej Akademii Nauk

UNIA EUROPEJSKA
EUROPEJSKI FUNDUSZ SPOŁECZNY

Ferromagnetyczne stopy z pamięcią kształtu do zastosowań w innowacyjnych „zielonych” technologiach chłodzenia

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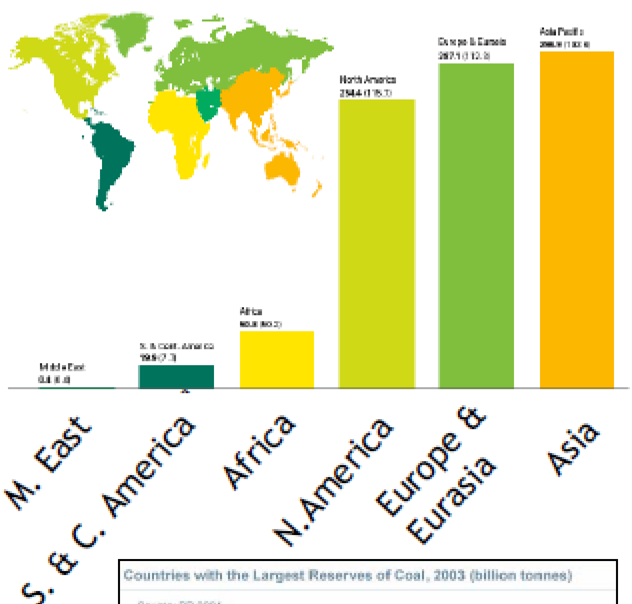
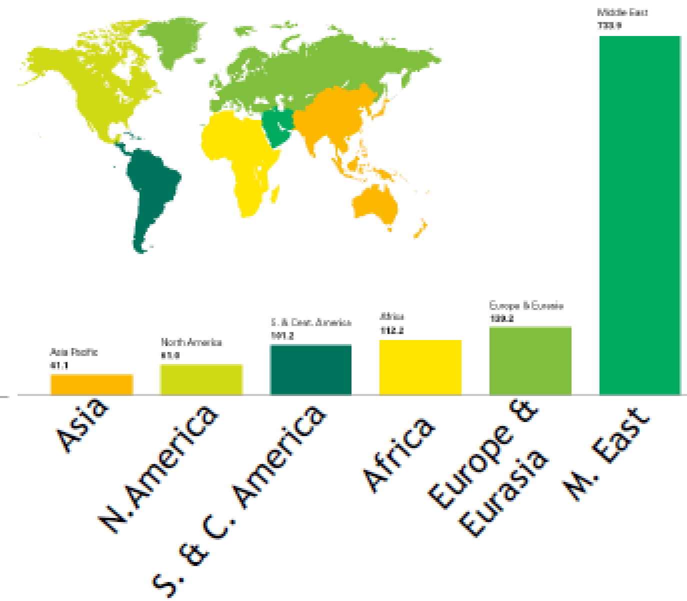
http://www.imim-phd.edu.pl/

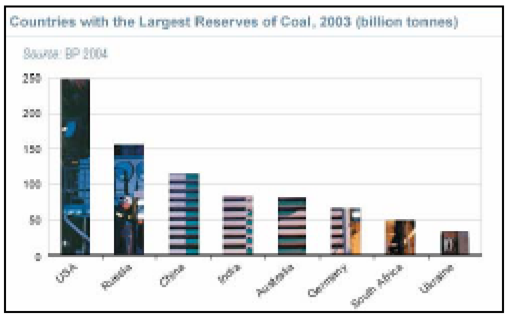
Global Fuel Reserves

Coal Reserves



Oil Reserves





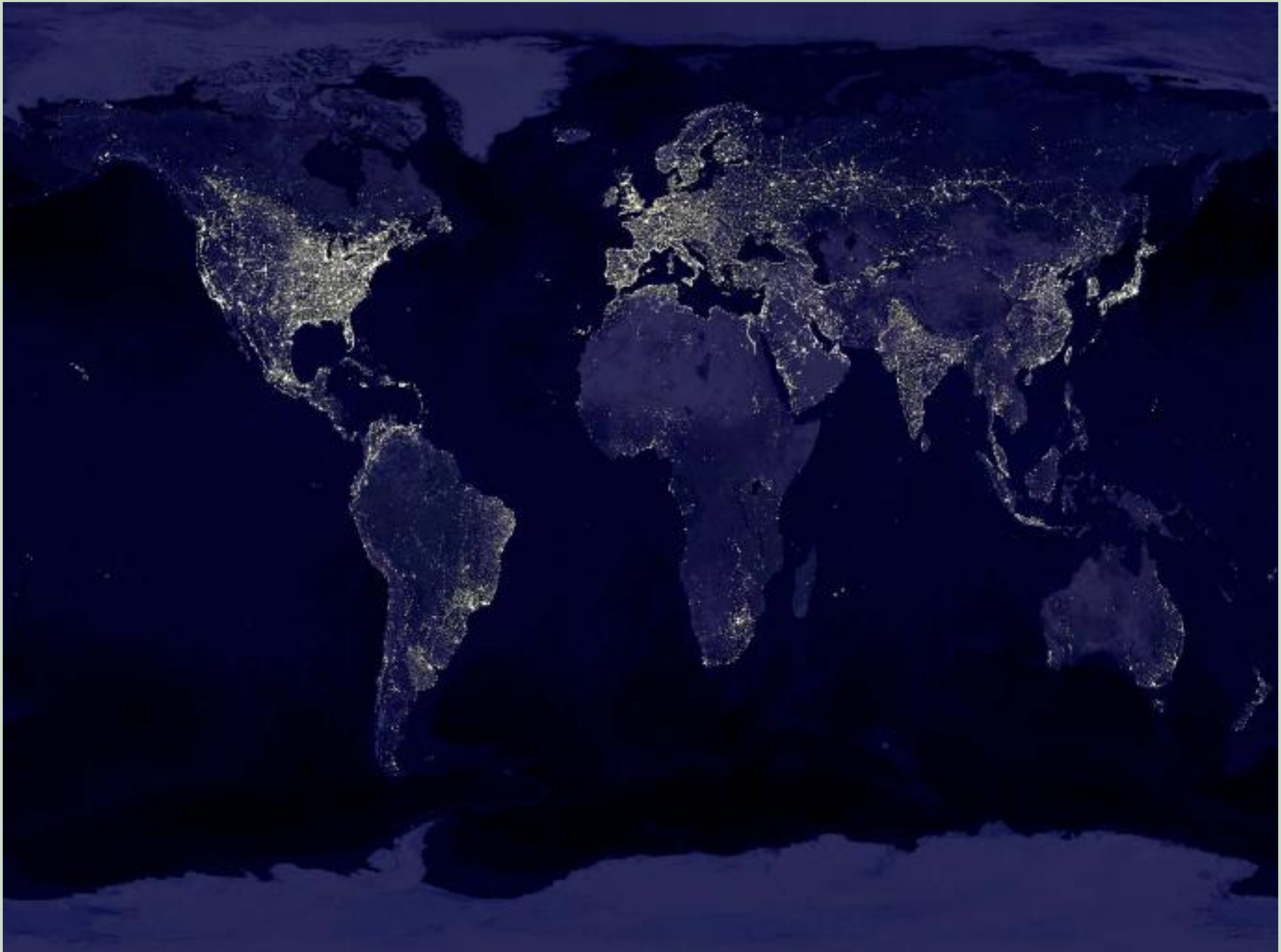
Source: John F. Bookout (President of Shell USA) ,"Two Centuries of Fossil Fuel Energy"
International Geological Congress, Washington DC; July 10,1985.
Episodes, vol 12, 257-262 (1989).

Source: BP Statistical Review of World Energy (2005)

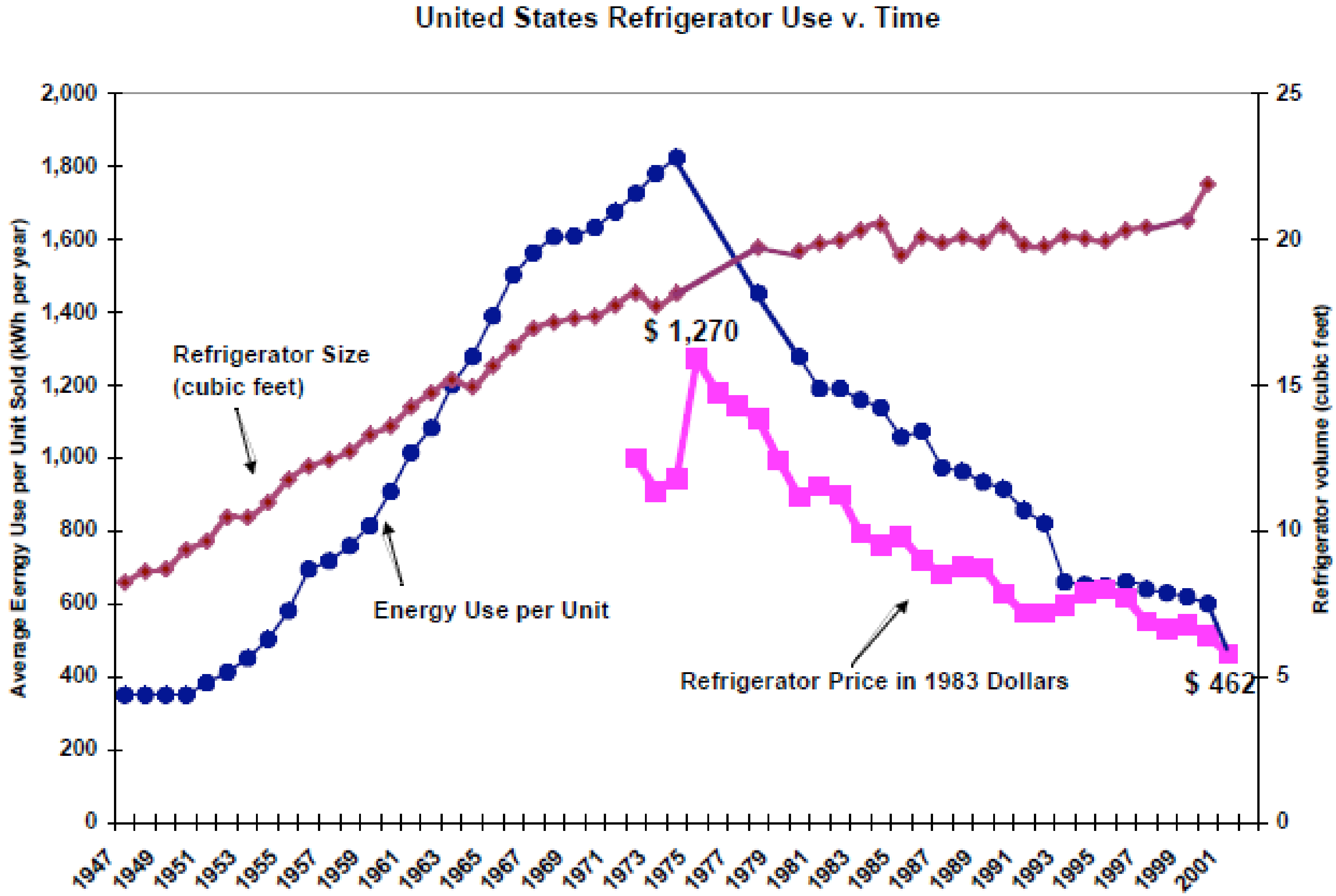
Demografia 2000 – 2050

- ✓Do 2050 populacja ludzi wzrośnie o 47%
- ✓Wzrost liczby ludności w najbliższych 50 latach będzie odpowiadał podwojonej liczbie mieszkańców Chin
- ✓Wzrost w krajach mniej rozwiniętych wyniesie 58%; 2% w krajach wysoko rozwiniętych,
- ✓99% ogólnego wzrostu populacji przypadnie na kraje mniej rozwinięte

A. Majumdar *Global Energy – Demand, Supply, Consequences, Opportuniteis.*
Lawrence Berkeley National Laboratory

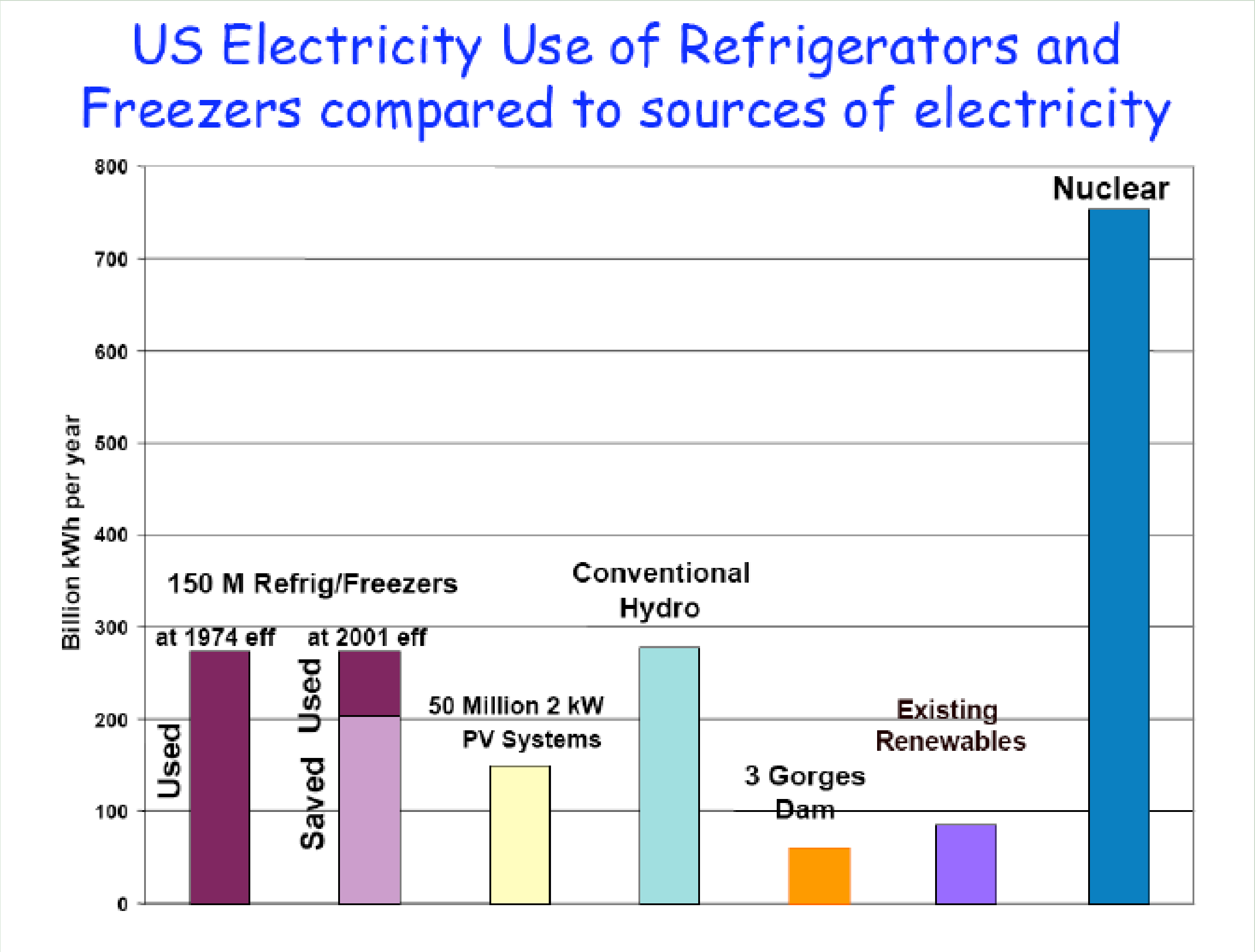


U.S. Refrigerator Energy Use vs. Time

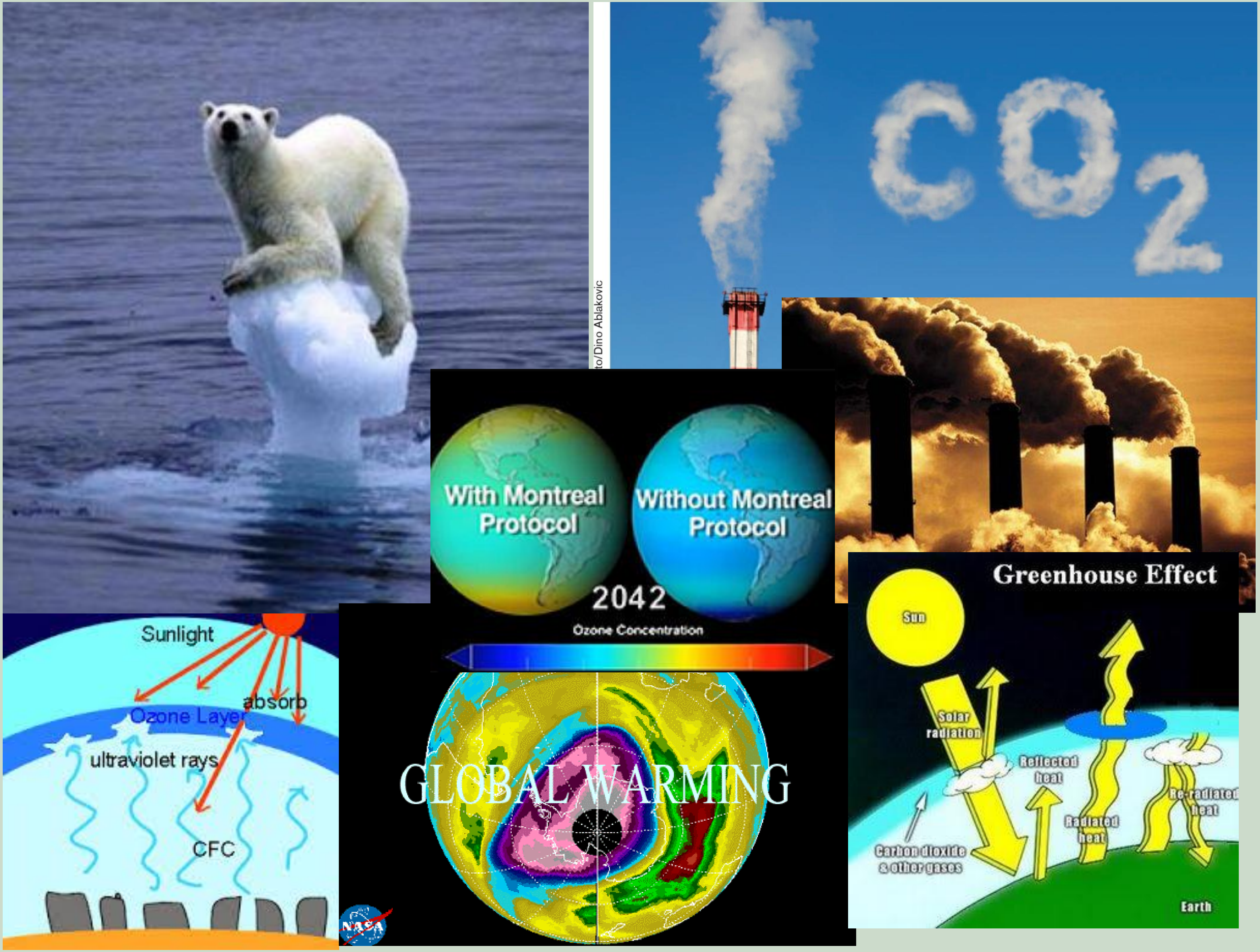


A. Majumdar *Global Energy – Demand, Supply, Consequences, Opportunities.*
Lawrence Berkeley National Laboratory

Lodówki w USA pochłaniają rocznie tyle energii ile produkuje 25 elektrowni
Odpowiada to 34% krajowego zużycia energii w USA
15% energii w skali globalnej pożerają chłodziarki

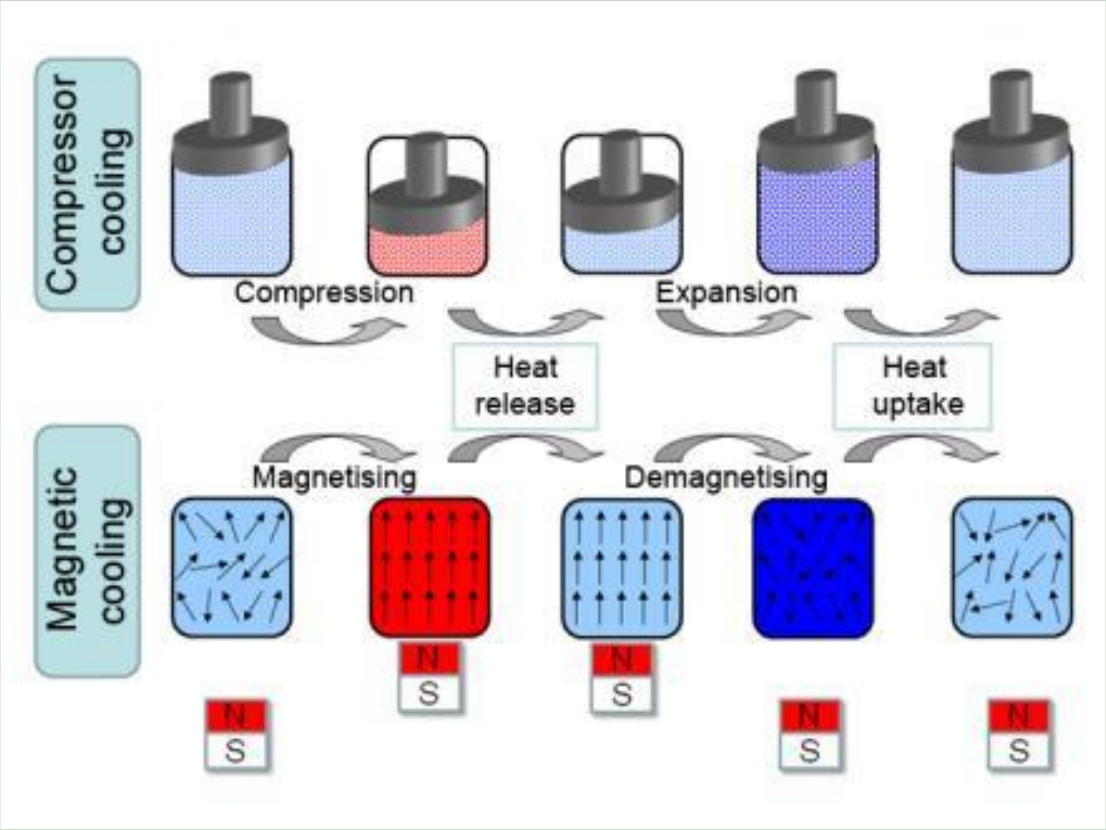


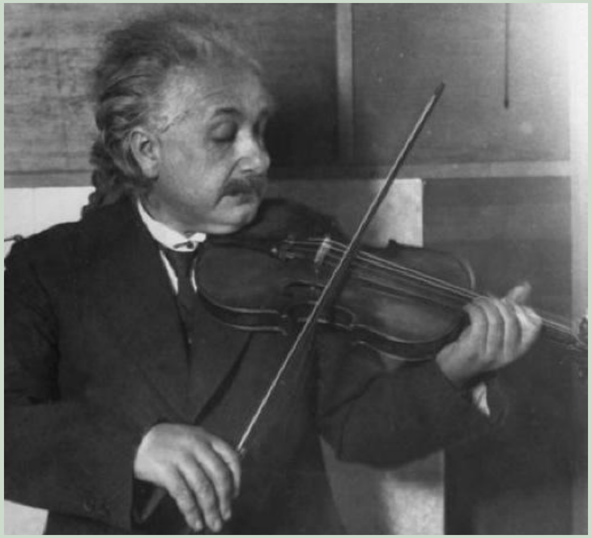
A. Majumdar *Global Energy – Demand, Supply, Consequences, Opportunities.* Lawrence Berkeley National Laboratory

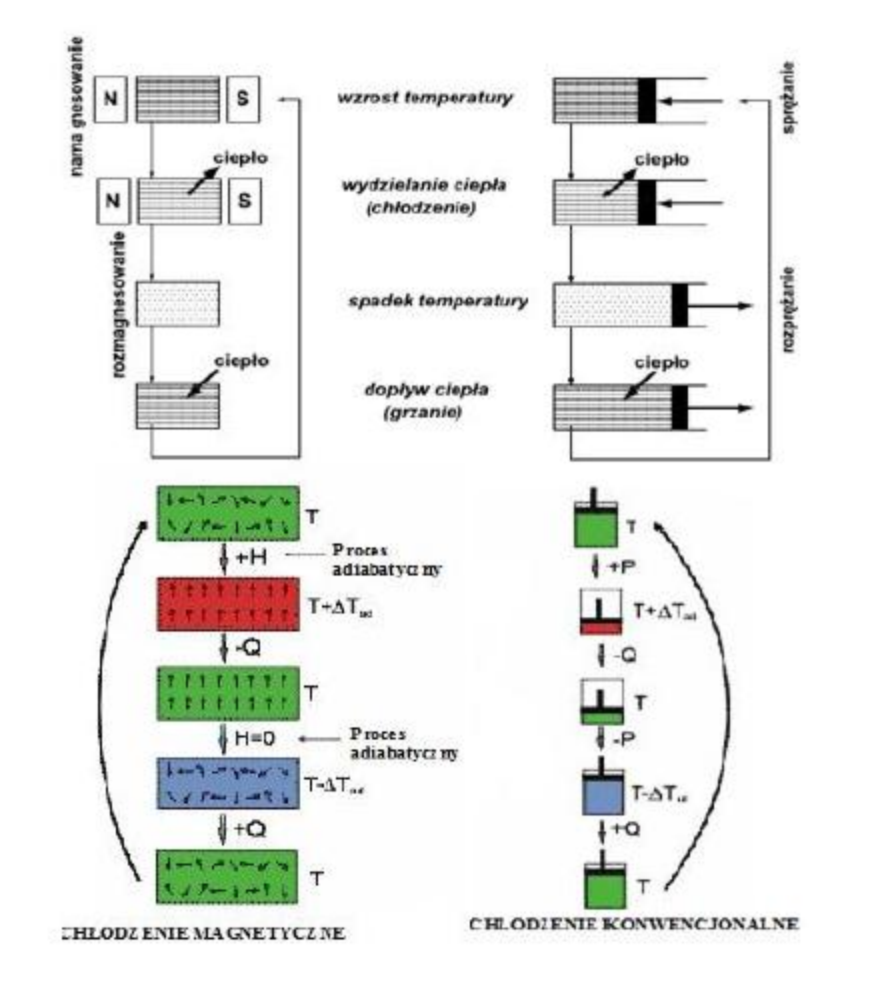

CO2
With Montreal Protocol
Without Montreal Protocol
2042
Ozone Concentration
Greenhouse Effect
Sun
Solar radiation
Reflected heat
Radiated heat
Re-radiated heat
Carbon dioxide & other gases
Earth
Sunlight
absorb
Ozone Layer
ultraviolet rays
CFC
GLOBAL WARMING
NASA


breaking
!
news

CHŁODZENIE MAGNETYCZNE!!!







namagnesowanie
rozmagnesowanie
N
S
ciepło
wzrost temperatury
wydzielanie ciepła
(chłodzenie)
spadek temperatury
dopływ ciepła
(grzanie)
sprężanie
rozprężanie
T
+H
Proces adiabatyczny
T+ΔT
-Q
H=0
T-ΔT
+Q
+P
-P
CHŁODZENIE MAGNETYCZNE
CHŁODZENIE KONWENCJONALNE

Camfridge

Materials Developers

Camfridge has built an extensive pan-European network of materials suppliers and researchers. We aim to ensure that we utilise the best refrigerants inside our technology.

By becoming a materials partner we offer a rigorous five step refrigerant evaluation process, advanced modeling and optimization of heat engine designs as well as a firm route to market for new materials.

Packaged Cooling Application Manufacturers

Camfridge is working with leading manufacturers of packaged cooling applications to embed Camfridge's gas-free high-efficiency technology in end-user applications.

By joining our manufacturer partner framework we provide resources and expertise in advanced cooling for your application area as well as privileged access to our intellectual property.

Contacts

For partnership details please contact us at:
partners@camfridge.com

Some of our partners

Whirlpool
arçelik
CLIVET
VAC VACUUMSCHMELZE

UNIVERSITY OF CAMBRIDGE
Imperial College London
INRiM ISTITUTO NAZIONALE DI RICERCA METROLOGICA
SINTEF

CNRS
SATIE
CMPE
iif iir

IFW
Leibniz Institute for Solid State and Materials Research Dresden

Whirlpool EUROPE

CONTACTS

Communications & Corporate Relations
Whirlpool Europe

Bracken Darrell, president, Whirlpool Europe, said: "Innovation is the lifeblood of Whirlpool, especially when it goes hand-in-hand with sustainability. Whirlpool is proud of being part of this project as an industrial partner. We are also delighted with the support from the Carbon Trust. We are still in an exploratory phase, but this technology looks very promising, and we are looking forward to offering millions of consumers worldwide this major, unprecedented revolution in their own kitchen."

WHIRLPOOL TO EXPLORE REVOLUTIONARY MAGNETIC REFRIGERATION CONCEPT

Highly efficient, environmentally friendly with reduced noise and vibration level: this ground-breaking, new technology might change cool industry forever

Comerio, Varese, October 10th, 2009. Whirlpool Europe is the principal partner of **Camfridge Ltd.** (British Company originally born as a spin-off of Cambridge University) for a project to deliver a domestic refrigerator based on "magnetic refrigeration" technology. The project that recently won funding from the UK government's agency the Carbon Trust, aims at validating a revolutionary technology that might change the way we have thought about refrigeration for the past 50 years. Magnetic refrigeration can free future refrigerators from heavy, noisy and heat-producing compressors, offering a high-efficiency, cool and gas-free solution to the industry and to millions of consumers.

Reduced-scale, laboratory testing conducted so far has proven successful and is looking very promising. The project is now moving on to a real-scale level to prove that this technology can effectively be applied to commercial products in a not-so-distant future. The project officially started in mid 2009, and is due for completion in 2012, when a prototype will be displayed during London 2012 Olympic Games.

The scientific principle behind magnetic cooling is based on the discovery that certain materials, when exposed to a magnetic field, exhibit a temperature change. When the magnetic field is removed, the materials will cool below their original temperature. Compared with gas refrigeration based on the use of compressors, this technology is more efficient and makes no use of environmentally harmful gases.

Bracken Darrell, president, Whirlpool Europe, said: "Innovation is the lifeblood of Whirlpool, especially when it goes hand-in-hand with sustainability. Whirlpool is proud of being part of this project as an industrial partner. We are also delighted with the support from the Carbon Trust. We are still in an exploratory phase, but this technology looks very promising, and we are looking forward to offering millions of consumers worldwide this major, unprecedented revolution in their own kitchen."

Caloric Effects in Ferroic Materials: New Concepts for Cooling

DFG Priority Programme 1599

Ferroic Cooling
A DFG PRIORITY PROGRAMME

Refrigeration is one of the main sinks of the German and European electricity consumption and accordingly contributes to worldwide CO_2 emissions. High reduction potentials are envisaged if caloric effects in solid materials are utilized. The recent discovery of giant entropy changes associated with ferroelastic phase transformations promises higher efficiency. Ferroic transitions enhance the entropy change of magneto-, elasto-, baro- and electro-caloric effects. Furthermore, because the refrigerant is in a solid state, the technology completely eliminates the need for high global-warming potential halofluorocarbon refrigerants. The smaller footprint for operation and the scalable mechanism open up further applications such as cooling of microsystems. While the principal feasibility of magnetocaloric refrigeration is already evident, the requirement of a large magnetic field (> 2 T) hampers wide industrial and commercial applications. It is expected that this obstacle can be overcome by materials with lower hysteresis and by using other types of fields (stress, electric).

In order to accelerate research on ferroic cooling DFG decided to establish the priority program SPP 1599 in April 2011. This SPP will address the following major challenges for introducing ferroic materials in practical cooling applications: Understanding of the underlying mechanisms, energy efficiency, effect size, fatigue, and system integration.

Projects proposals are required to cover one of the following "ferroic-caloric" material classes or combinations thereof: ferroelastic, ferromagnetic and ferroelectric materials. Proposals have to focus on basic or applied aspects of solid-state cooling processes.

In detail, the research programme of the priority programme will focus on four key problems related to ferroic cooling:

- *Which scheme is most efficient for solid state refrigeration?*
Giant caloric effects occur only in the vicinity of a first order transformation. For comparison experiments should focus on the direct adiabatic temperature change and cooling efficiency.

- *Which length and time scales are involved?*
Diffusionless transformations change the structure at the atomic scale. However, in real materials, the hysteretic transformation process creates complex microstructures spanning many length scales up to the macroscale. To understand hysteresis losses, collaborations should cover several length scales, consider coupling effects (thermo-mechanic-magnetic-electric) and, in particular, use suitable in-situ methods.

- *Which are the best materials and microstructures?*
Solid state cooling does not only require a maximized entropy change but also heat capacity and conductivity contribute to the cooling power. Hysteresis losses and fatigue, which are critical due to the high cycle numbers required for cooling demonstrators, should be addressed. Research should centre on environmentally friendly materials.

- *Which are competitive device concepts?*
The development of novel solid state cooling demonstrators is essential for the adaption of ferroic-caloric materials. Proposal should work out the advantage of the selected setup and consider the effort for the entire refrigeration system.

The complexity of ferroic cooling requires a close collaboration of materials scientists, engineers, physicists and mathematicians. The aim of this priority programme is to bring groups from these disciplines together to combine their complementary expertise from basic research to application. Therefore joint proposals or bundles of proposals are encouraged. The number of principal investigators should reflect the complementary scientific expertise needed for the proposed research. These proposals should aim at a comprehensive assessment of efficiency of solid-state refrigeration, addressing the route from materials fundamentals to demonstrators. Proposals addressing methodological aspects relevant for understanding solid-state refrigeration must give detailed plans for bilateral cooperation with particular partners.

Proposals considering liquid/ gaseous or thermoelectric refrigerants or focussing on actuation/sensor applications alone will not be funded. Also, concepts which aim on electric power generation will not be considered.

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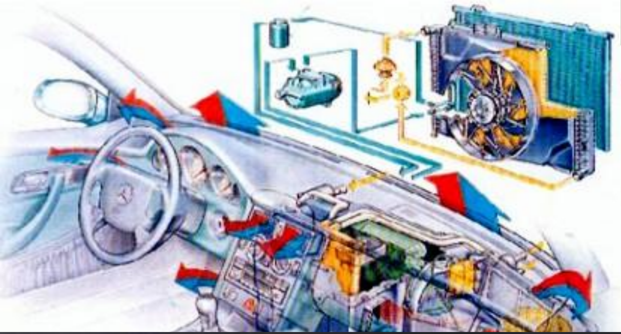
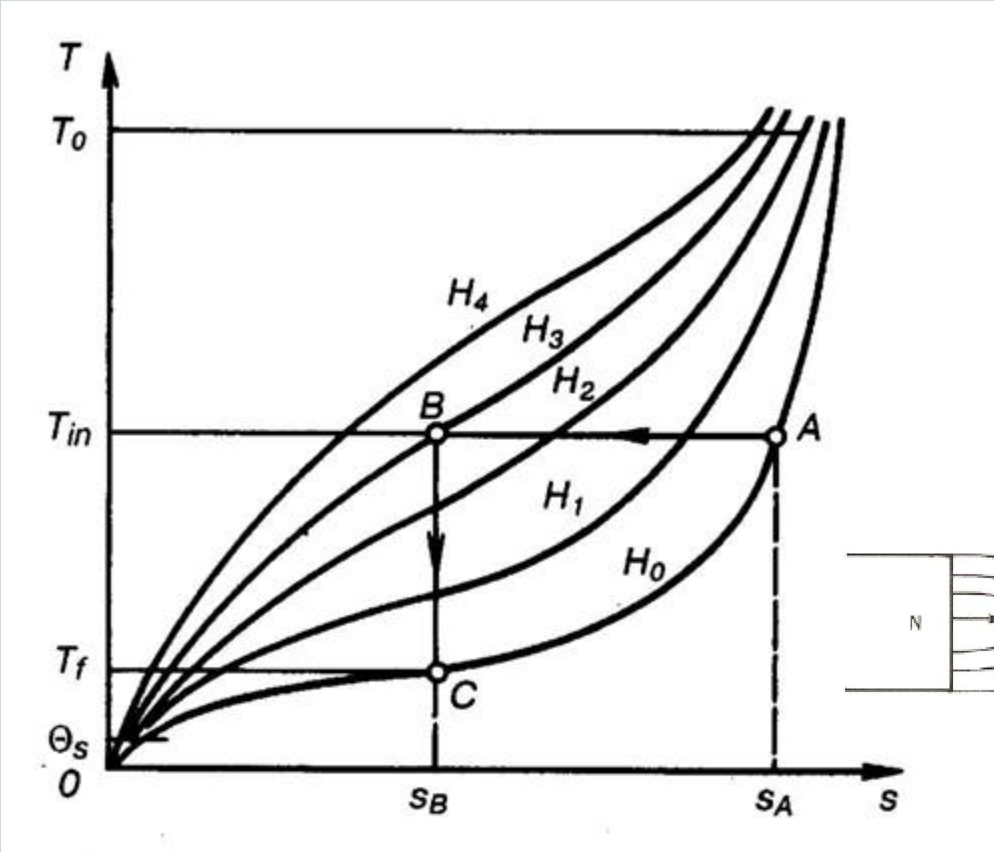
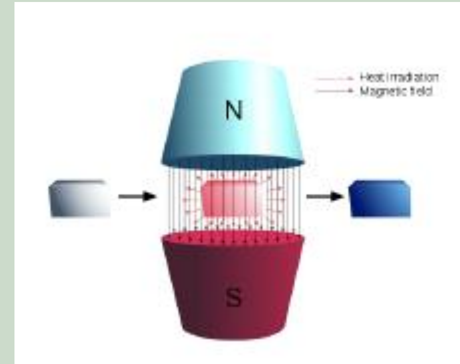
Zastosowania:

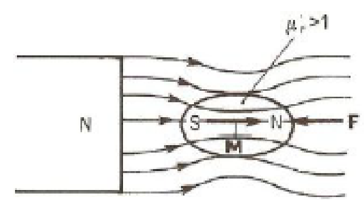


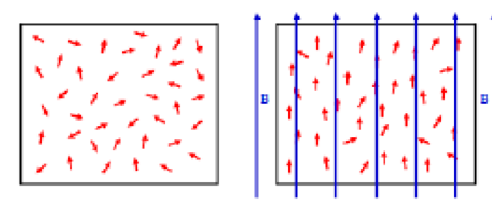

Klimatyzacja to podstawa
chmurak.pl

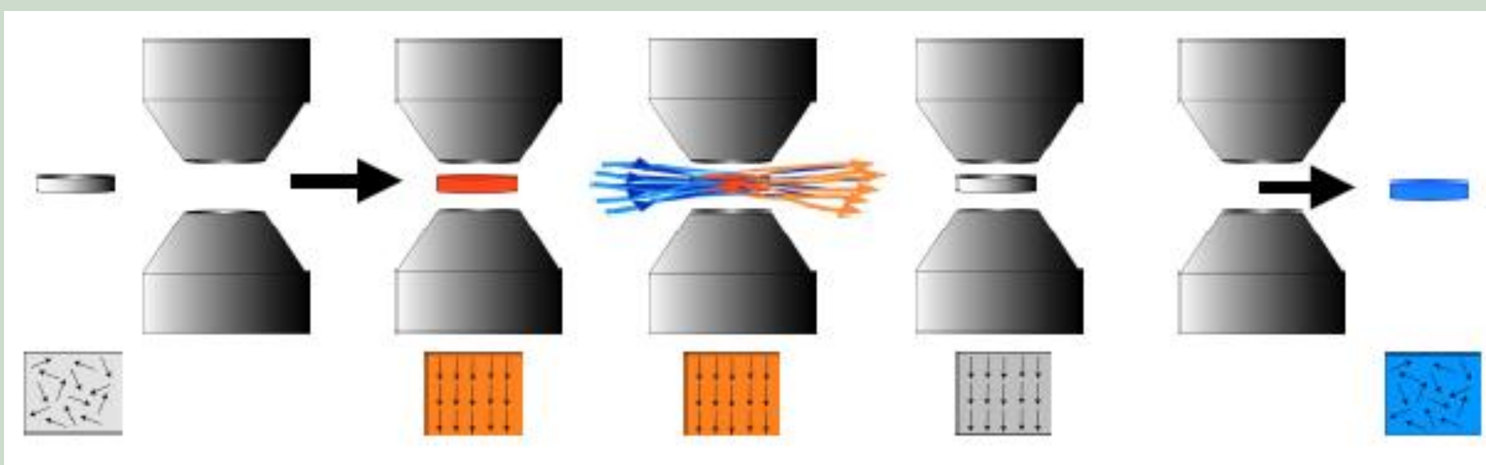
CHŁODZENIE MAGNETYCZNE?


T
T_0
H_4
H_3
H_2
H_1
H_0
B
A
T_{in}
T_f
C
Θ_S
0
s_B
s_A
s

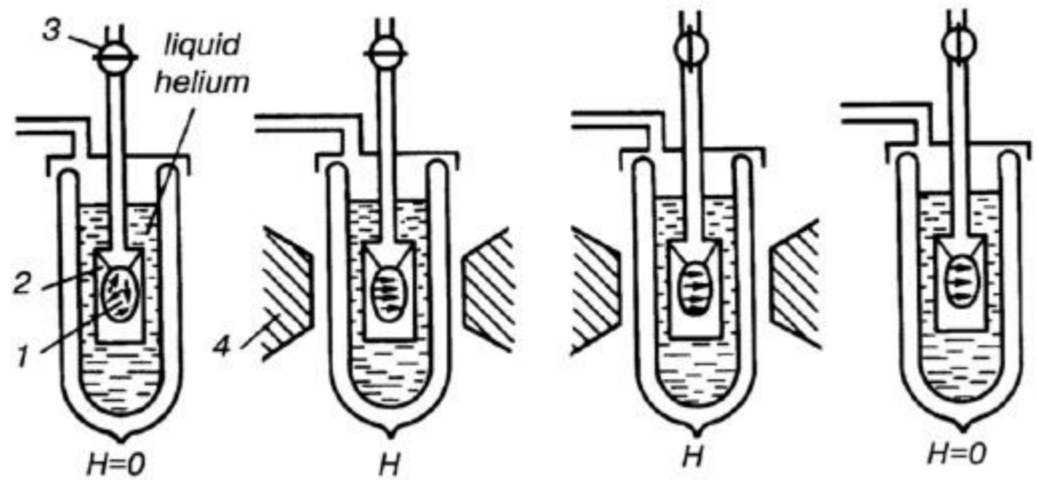

N
S
Heat irradiation
Magnetic field


N
S
N
F
M

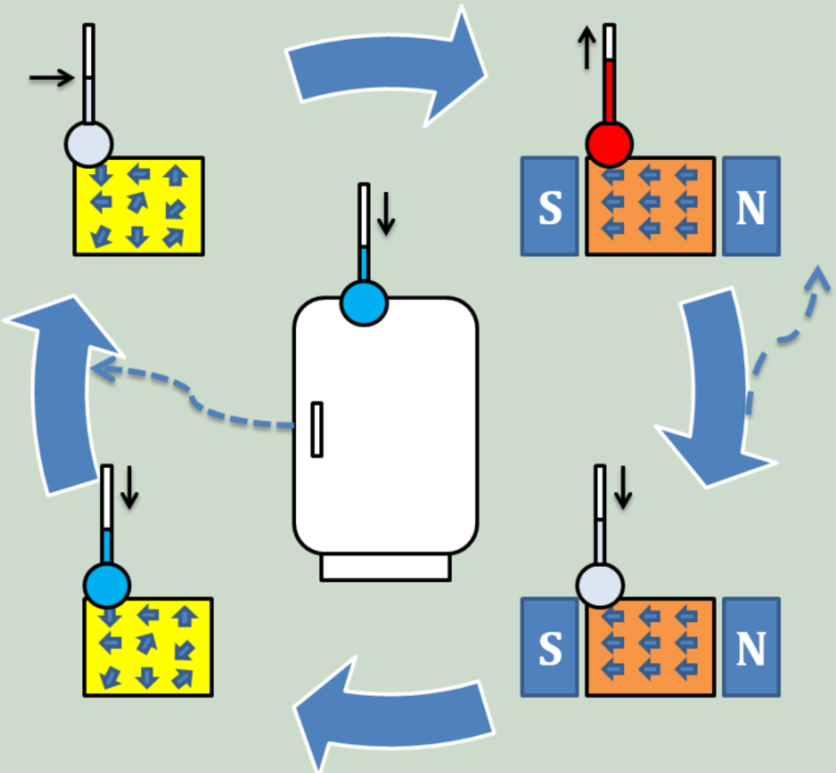

B
B

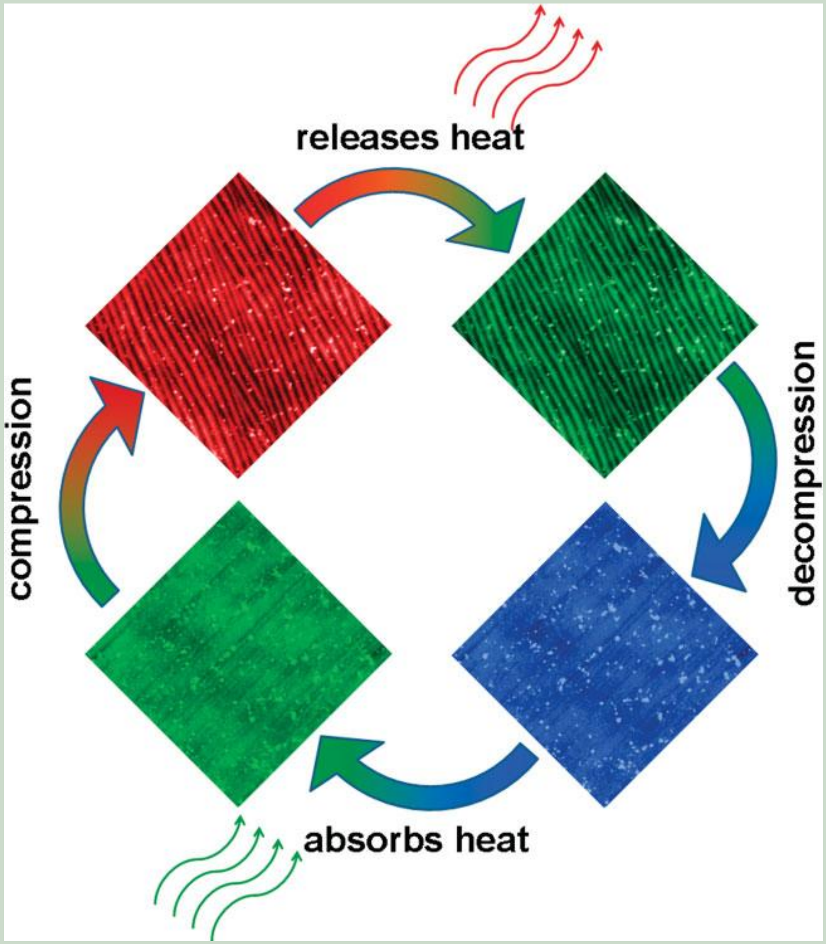


- Azotan cerowo magnezowy $CeMg_3(NO_3)_{12}$ $24H_20$
- Siarczan miedziowo potasowy $CuK_2(SO_4) \cdot 6H_2O$
- Ałun chromowo potasowy $KCr(SO_4)_2 \cdot 12H_20$
- Siarczan gadolinu $Gd_2(SO_4)_3 \cdot 8H_20$



- ✓ proces ten nie wymaga części mechanicznych ani stosowania gazów szkodliwych dla środowiska,
- ✓ aparatura wykorzystująca rozmagnesowanie adiabatyczne nie zużywa się,
- ✓ jest wydajniejsza o 40% od tradycyjnych metod i energooszczędna (stwarza nadzieje na oszczędność energii elektrycznej nawet do około 50%)
- ✓ zajmuje także mniej miejsca od sprężarek

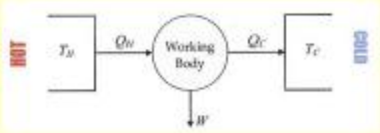




Magnetic Fields Magnetic Cooling - YouTube.flv

E. Bruck et al. J. Magn. Magn. Mater 310 (2007) 2793-2799.

Efficiency:

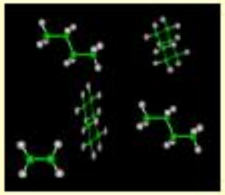


Solid-state: ~60% Carnot efficiency

Comp. gas: <40% (for the best ones!)

Environment + Power grid…

Environment:

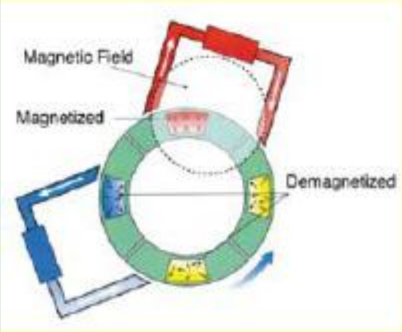


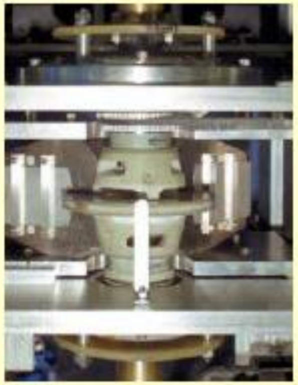
Reduces hydrocarbon emission (efficiency)

No Gaseous Refrigerants!

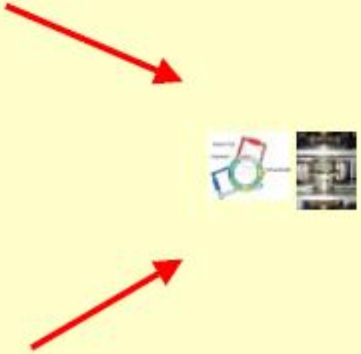
However, need to be careful with solid state materials too!!

Simple (in principle):



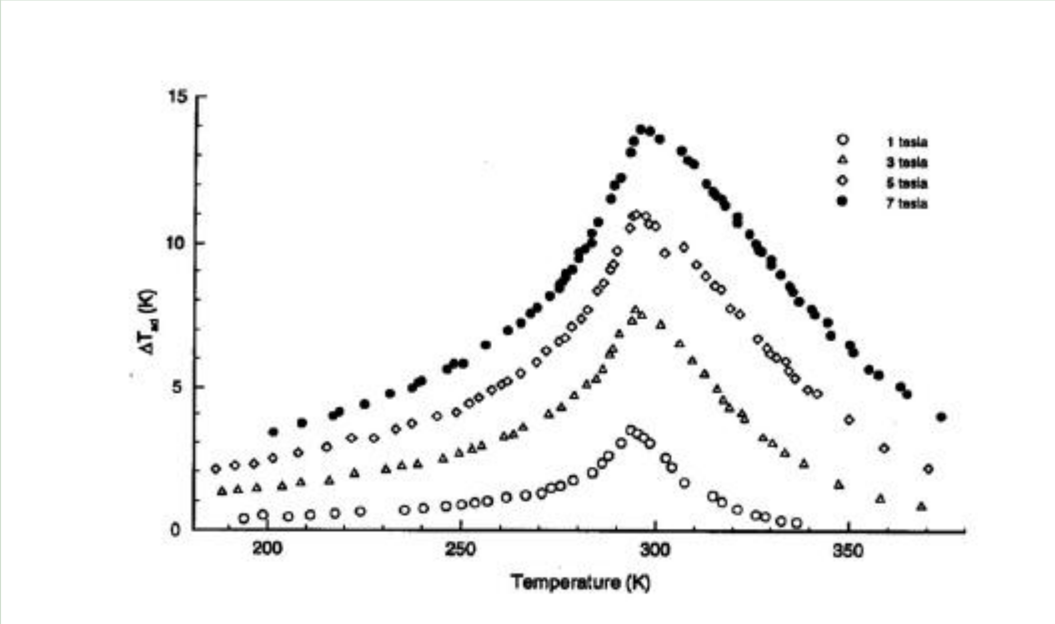


Scalable (in size and output):

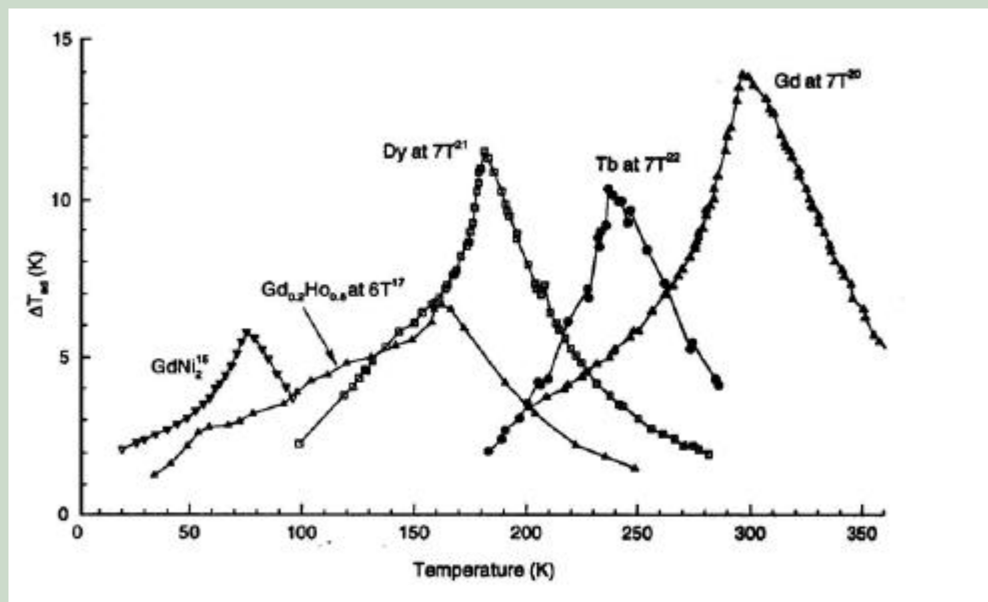


Idealny materiał:

- Intrinsic properties
  - Huge latent heat
  - High susceptibility to external fields (large ΔM, ΔV, Δu, ΔD)
  - T_M around room temperature (tunable)
- Extrinsic properties
  - Low hysteresis
  - Cycle stability
- Technological issues
  - Cost (Fe-based, FeRh)
  - Environmentally friendly (Pb, As)



1 tesla
3 tesla
5 tesla
7 tesla
ΔT_{ad} (K)
Temperature (K)



Gd at 7T[20]
Dy at 7T[21]
Tb at 7T[22]
$Gd_{0.2}Ho_{0.8}$ at 6T[17]
$GdNi_2$[15]
ΔT_{ad} (K)
Temperature (K)

Materiały:

- **$Gd_5Ge_2Si_2$**
- **$La(Fe,Si)_{13}$**
- **MnAs**
- **Stopy Heuslera**

Stopy Heuslera*

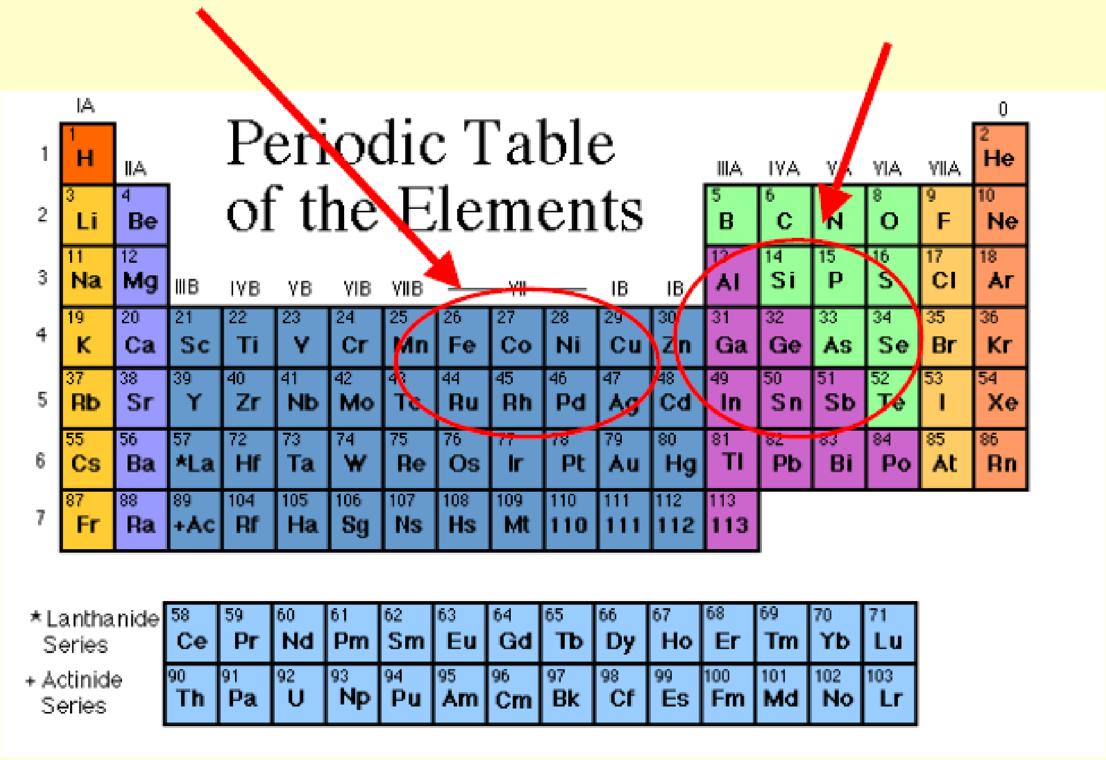
- ❑Stopy z pamięcią kształtu
- ❑Intermetaliki
- ❑Magnetooporność
- ❑Exchange bias
- ❑Efekt magnatokaloryczny

* Heusler, Verh. Dtsch. Phys. Ges. 5, 219 (1903)

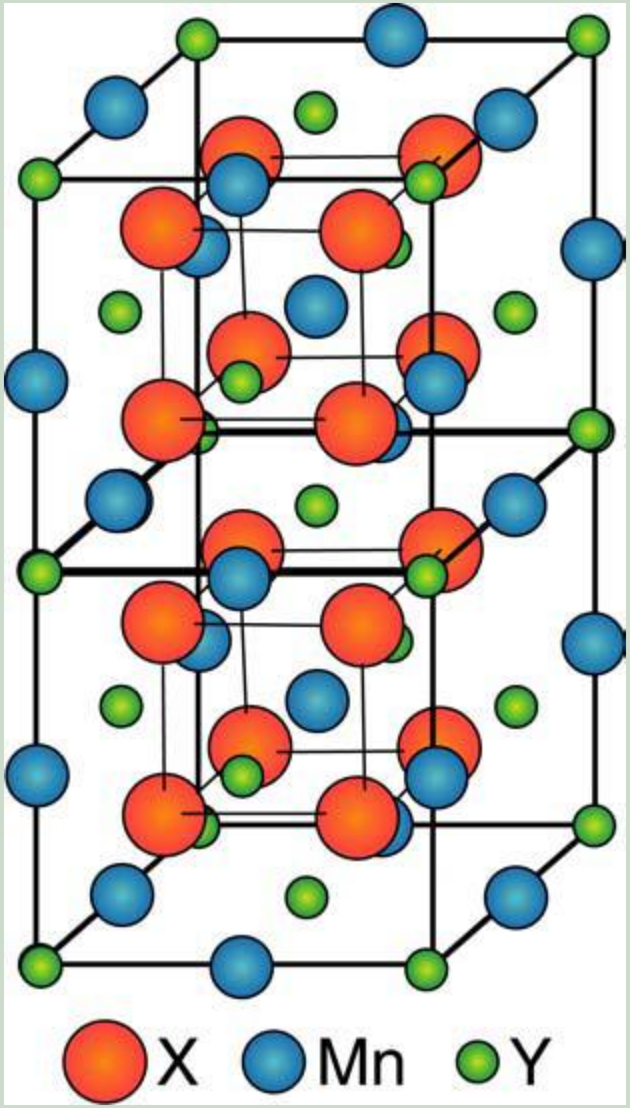
Full-Heusler Alloys: X_2MnY ($L2_1$ structure)

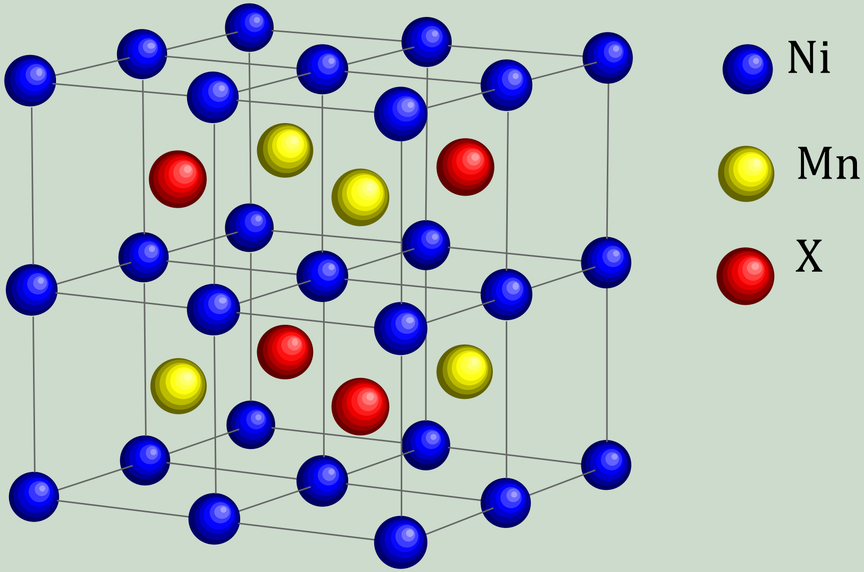
Half-Heusler Alloys: XMnY ($C1_b$ structure)

X = Transition metals **Y = Group IIIA, IVA, and VA elements**



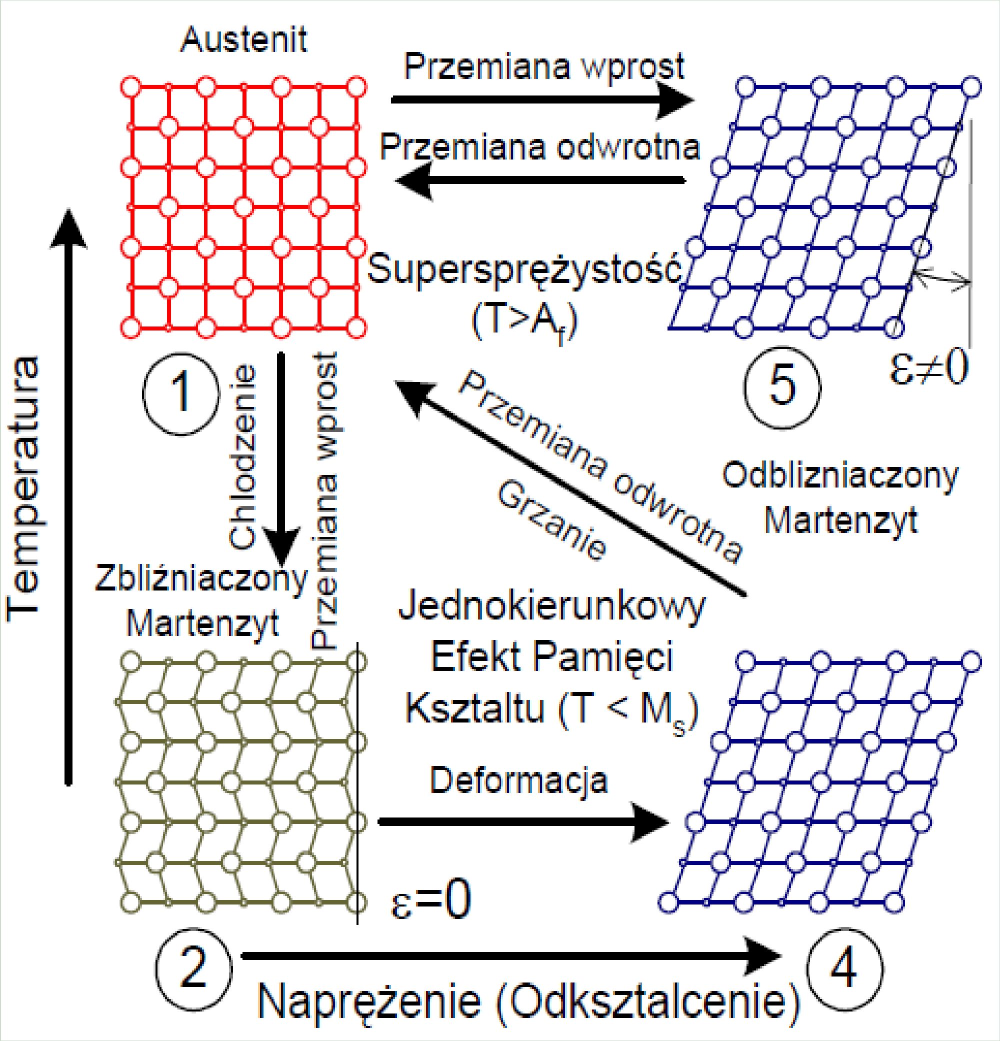
X_2YZ
NiMnX (X = Al, Ga, Sn, Sb, In)

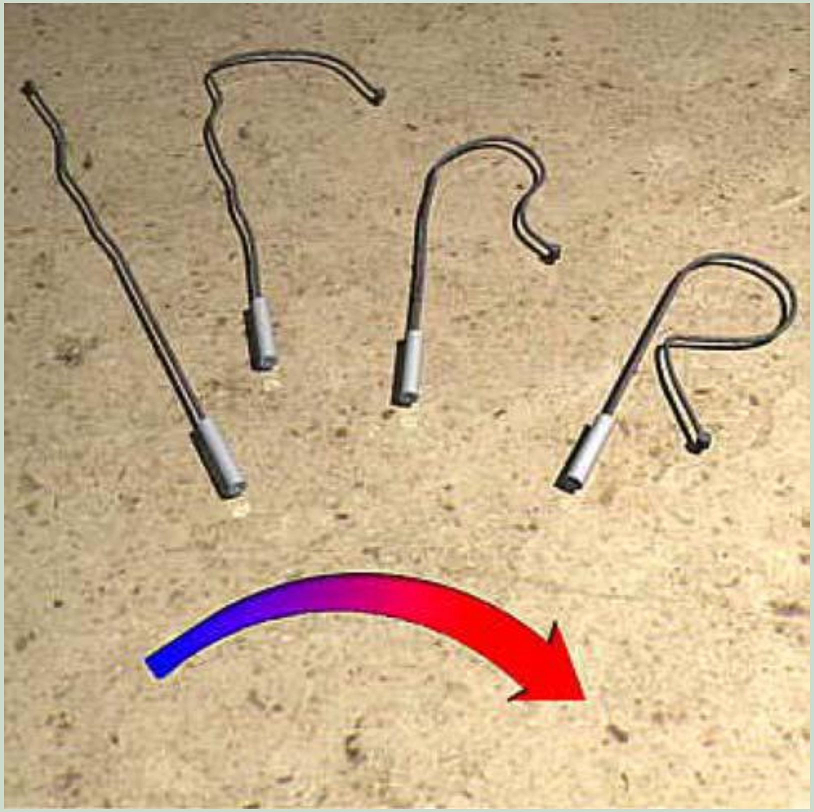




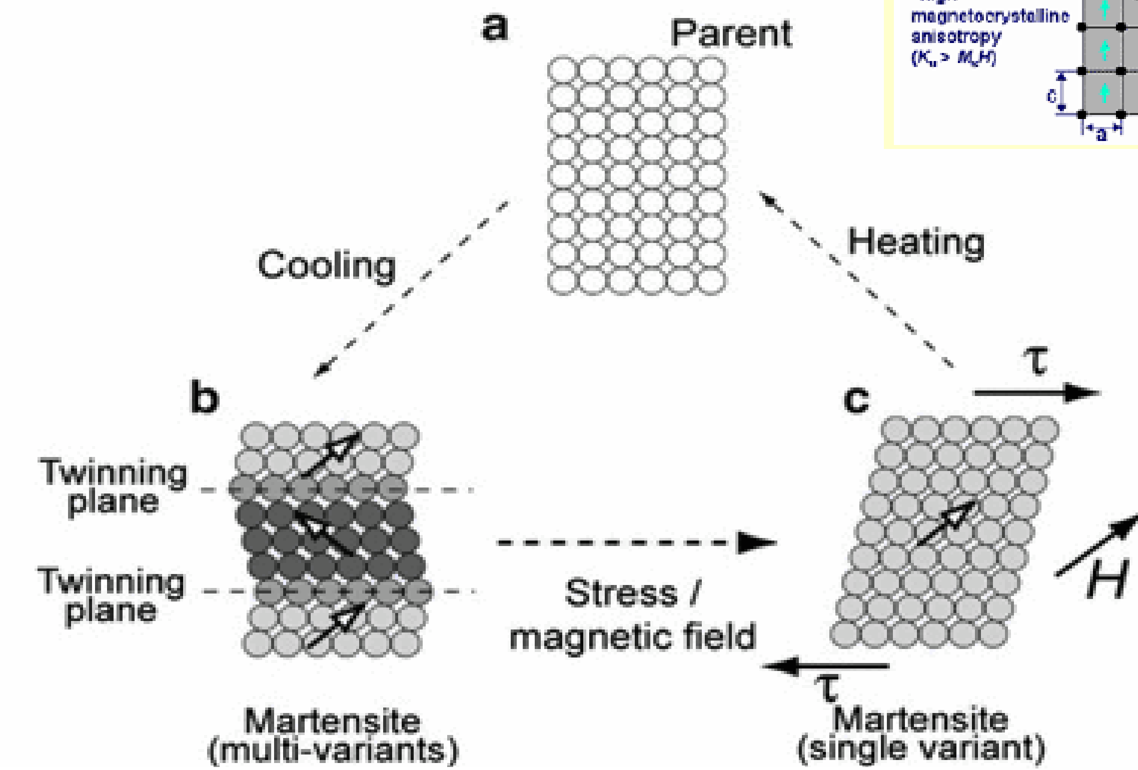
Ausetnit $L2_1$
Martenzyt 10M, 14M, $L1_0$…

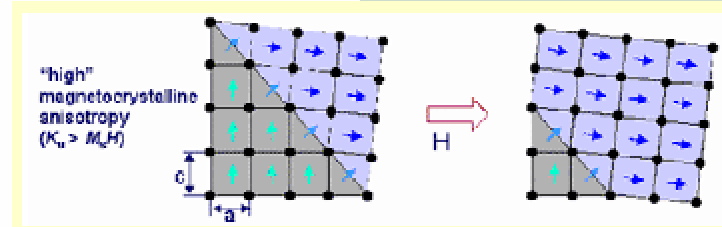
H. Luo, G. Liu, F. Meng et al. *Physica B* 405 (2010) 3092-3095.

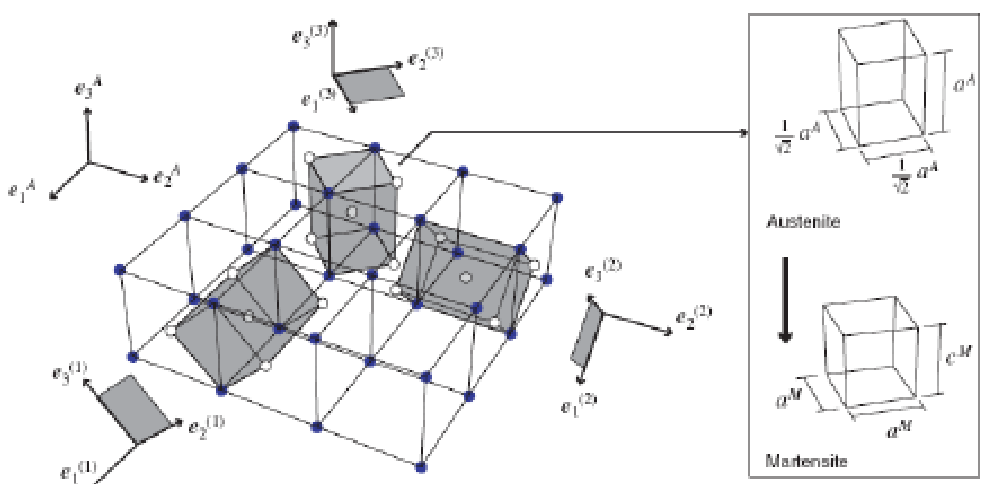




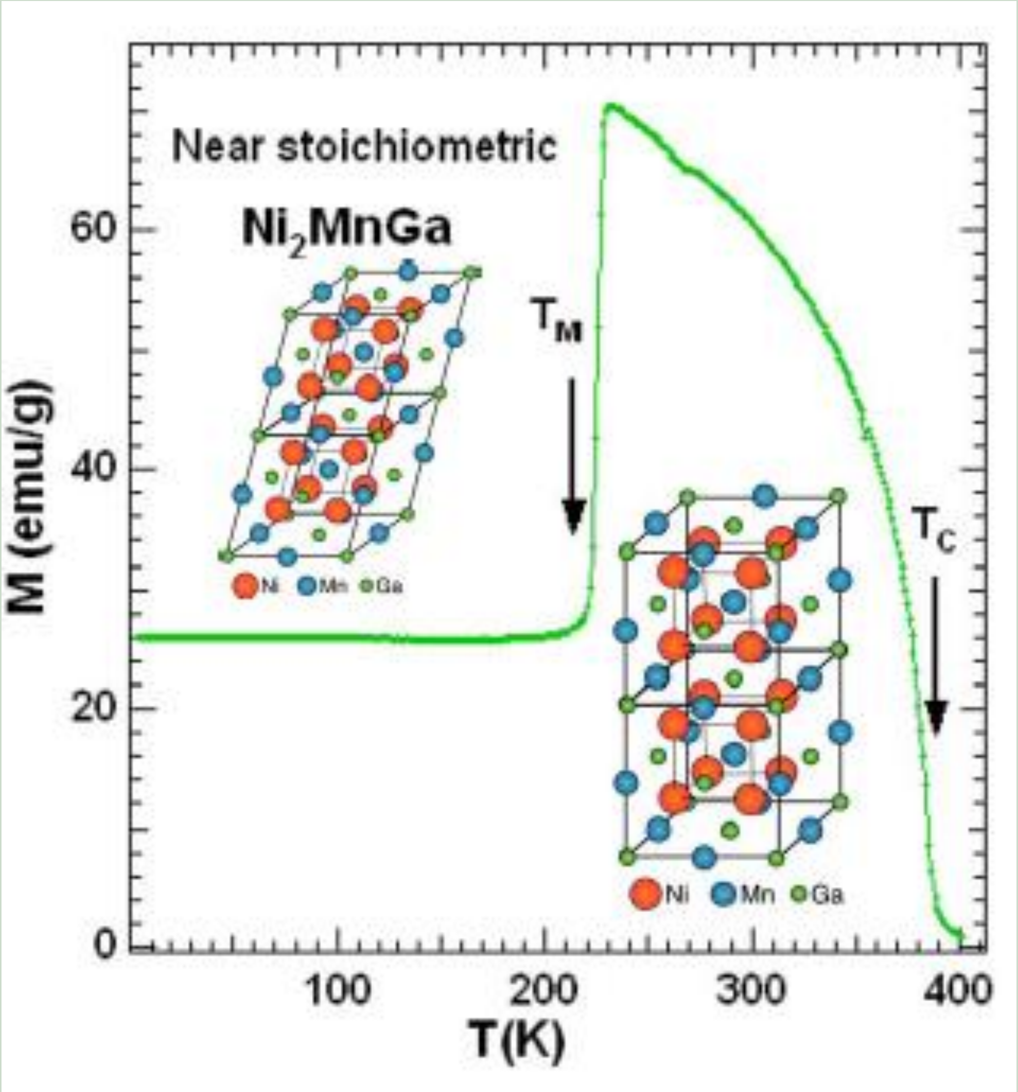
Pamięć kształtu



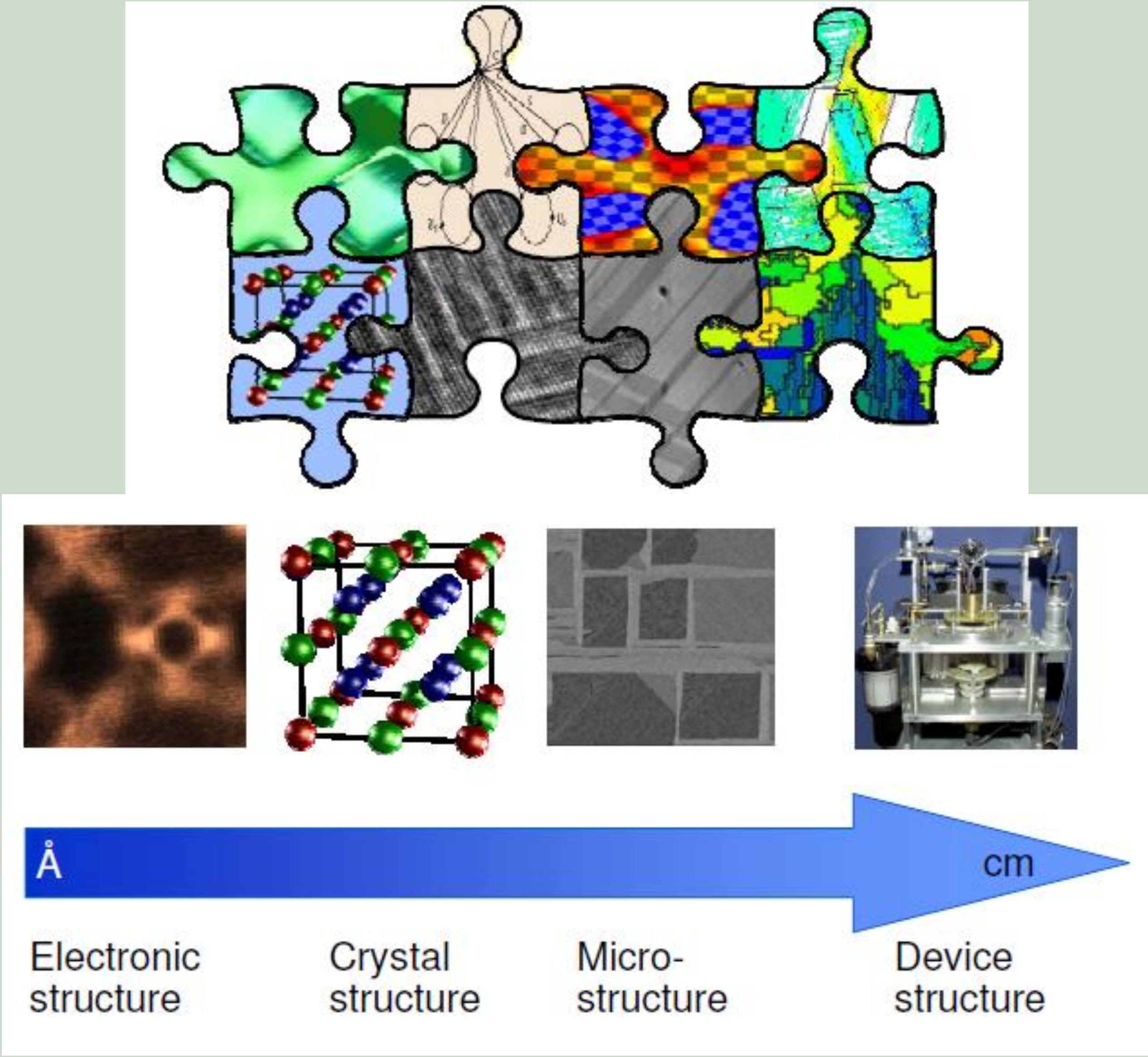




Sensory
Aktuatory
Tłumienie drgań itp.



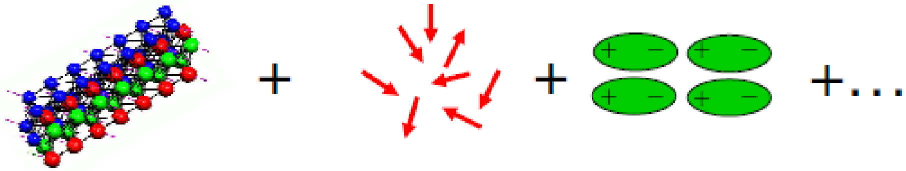
Near stoichiometric
Ni_2MnGa
T_M
T_C
Ni
Mn
Ga
Ni
Mn
Ga
M (emu/g)
0
20
40
60
100
200
300
400
T(K)



S. Fahler IFW Dresden Ferroic Cooling a DFG Priority Programme

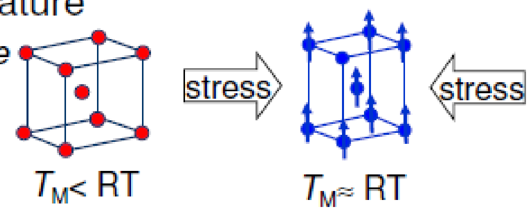
S. Fahler IFW Dresden Ferroic Cooling a DFG Priority Programme

- Summing up entropy changes of lattice, spin…

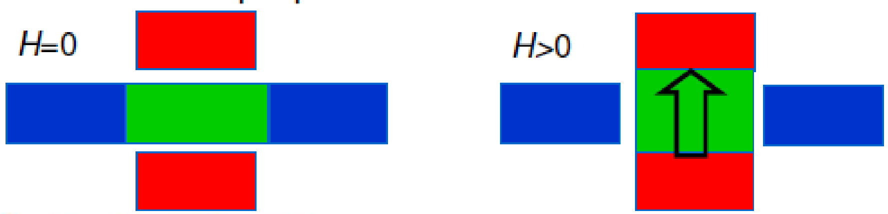


- Tuning of working temperature

e. g. Stress induced martensite

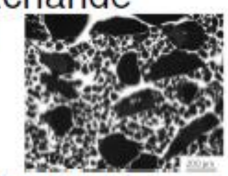


- Use of actuation properties to establish heat transfer



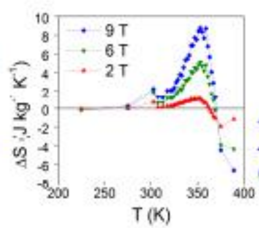
- Faster heat exchange

Foam



Chmielus et al. Nat. Mat. 8 (2009) 863

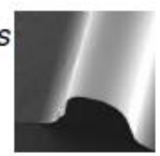
Films



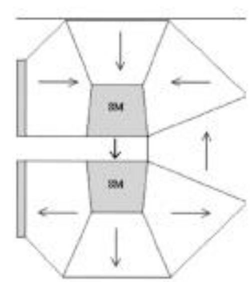
Niemann et al. APL 97 (2010) 222507

- Reduced conduction losses

Freestanding films

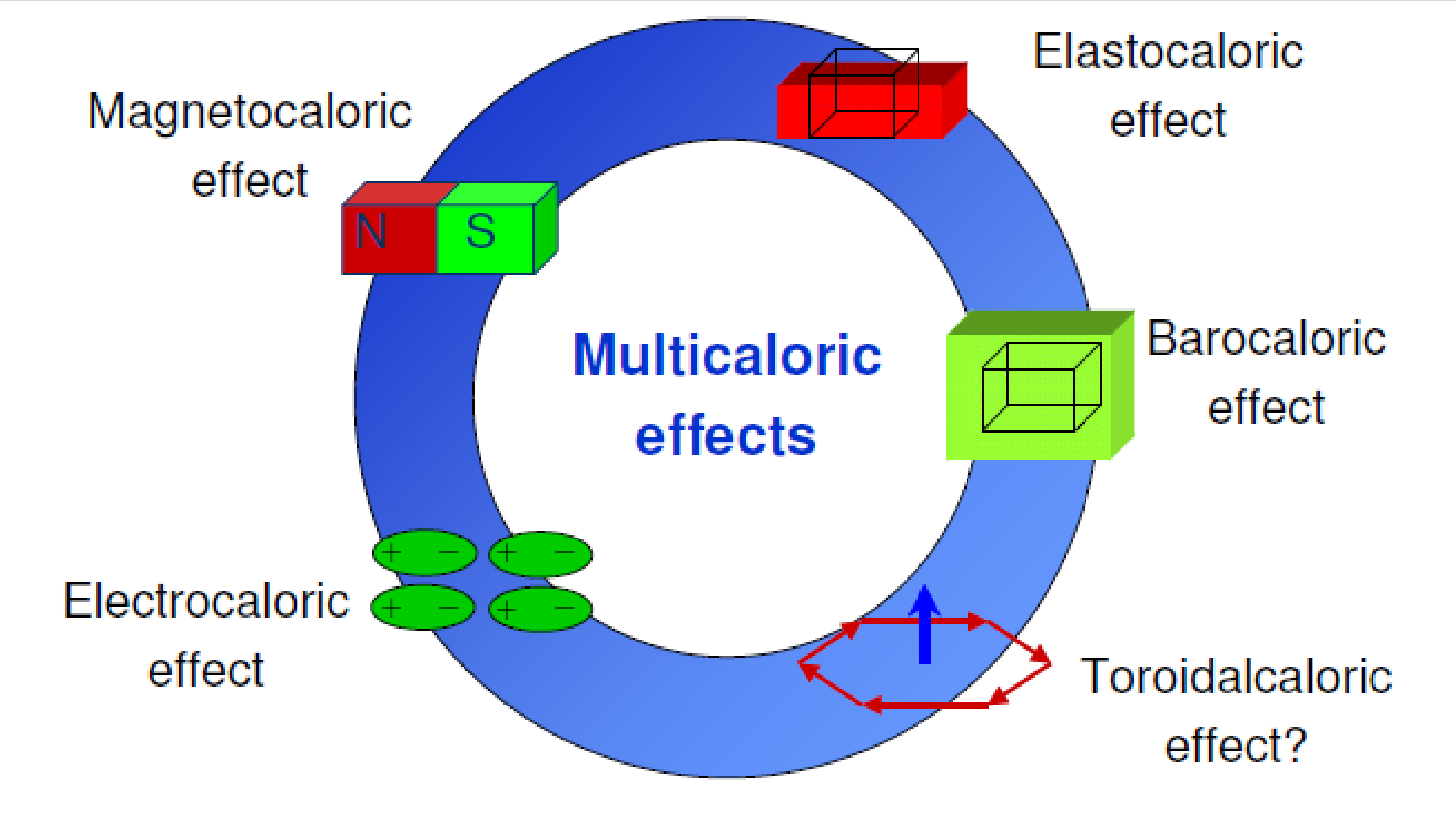


- Generation of sufficient driving fields

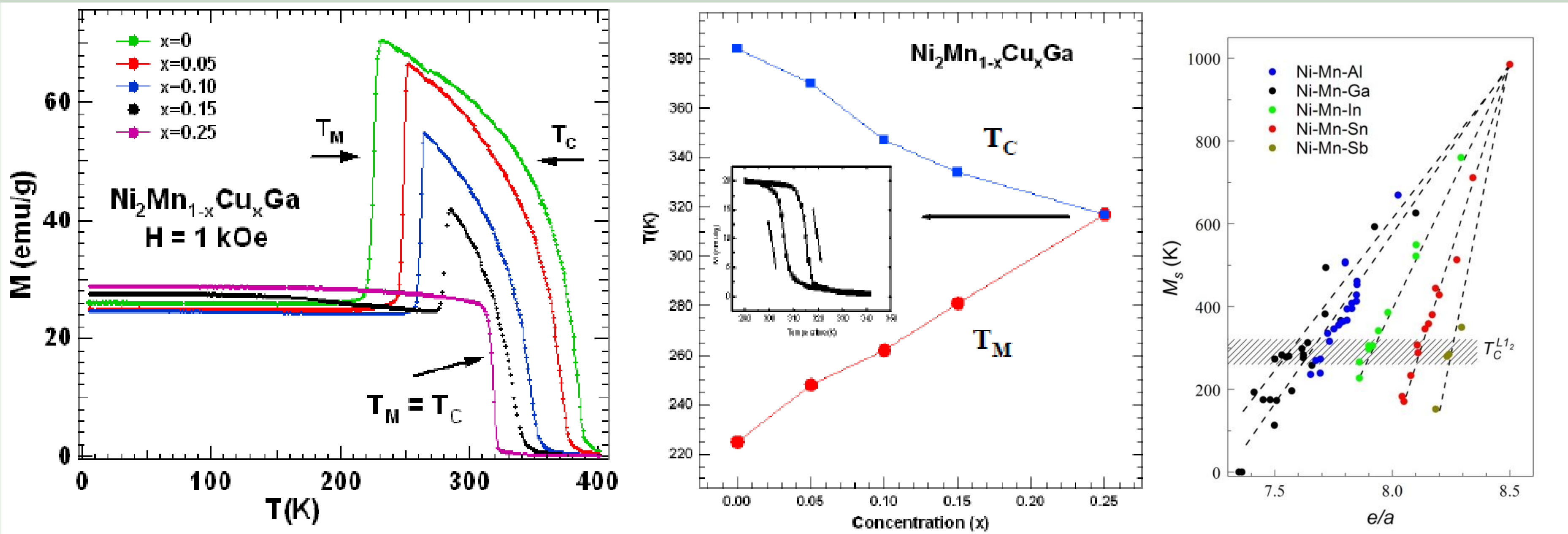


S. J. Lee, et al., J. Appl. Phys. 91, 8894 (2002)

- Innovative cooling system designs

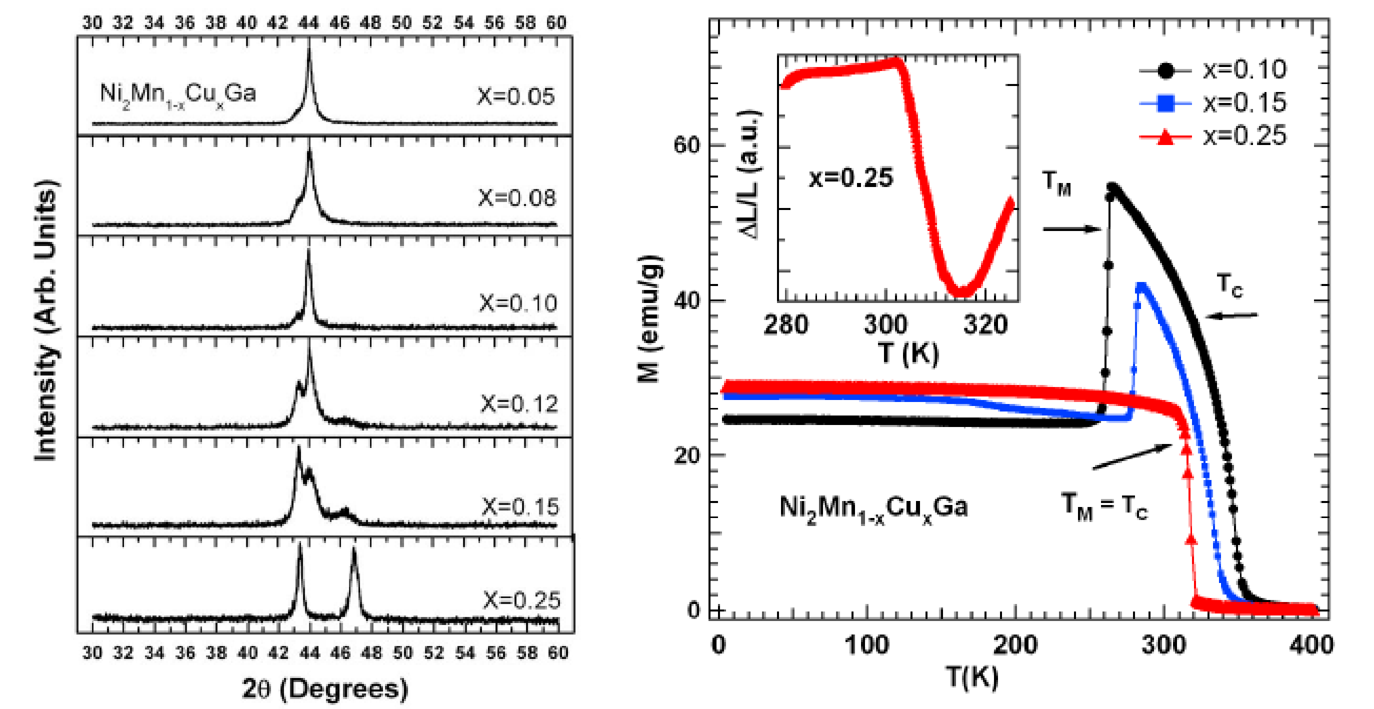


S. Fahler IFW Dresden Ferroic Cooling a DFG Priority Programme

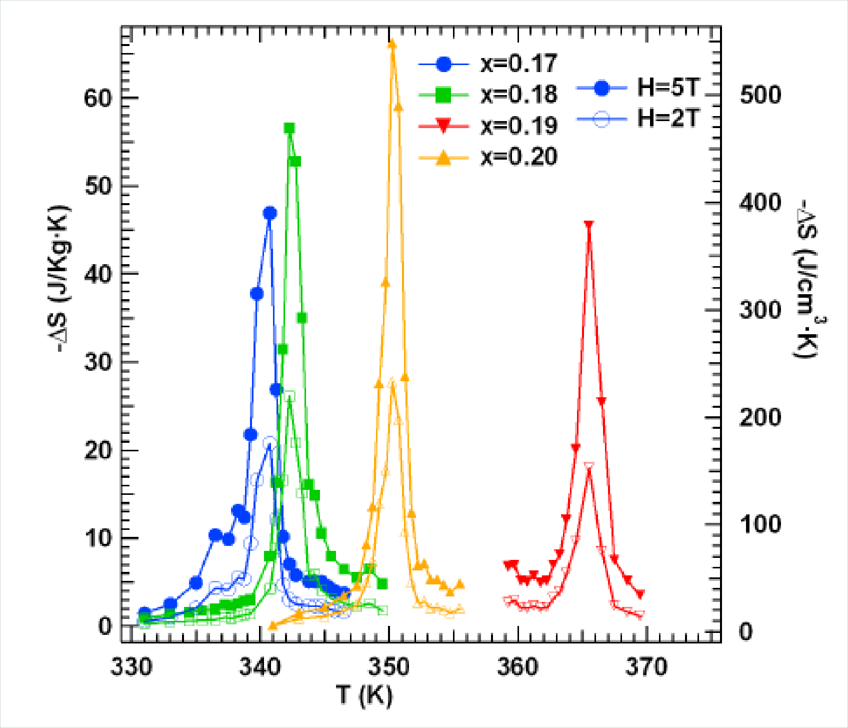


S. Stadler et al. Appl. Phys. Lett. 88, 192511 (2006)

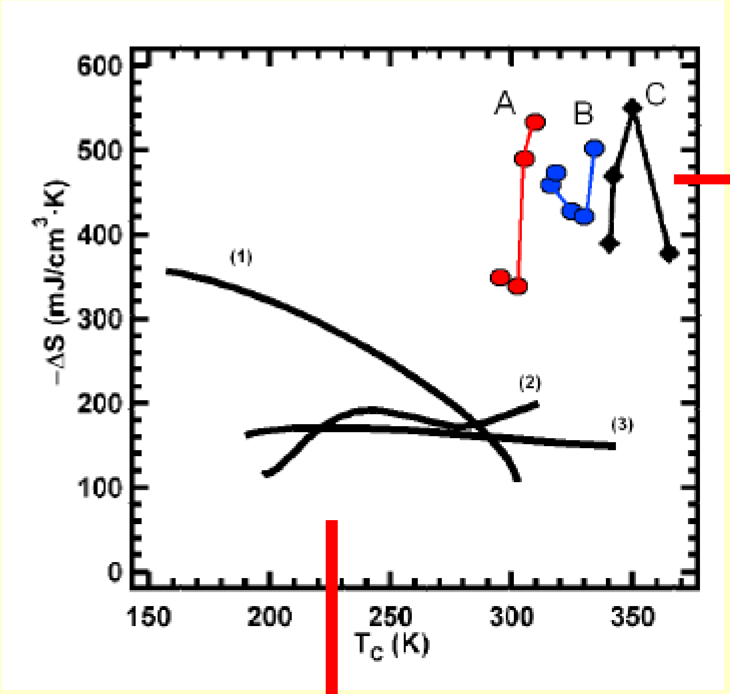
Krenke, M. Acet, E. F. Wassermann *Physical Review* B 73, 174413 (2006)



30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60
$Ni_2Mn_{1-x}Cu_xGa$
X=0.05
X=0.08
X=0.10
X=0.12
X=0.15
X=0.25
Intensity (Arb. Units)
2θ (Degrees)
x=0.10
x=0.15
x=0.25
ΔL/L (a.u.)
x=0.25
280
300
320
T (K)
T_M
T_C
$T_M = T_C$
$Ni_2Mn_{1-x}Cu_xGa$
M (emu/g)
0
20
40
60
100
200
300
400
T(K)



M. Khan et al. IEEE Trans. Mag. 42, 3108 (2006).



(A) $Ni_2Mn_{1-x}Cu_xGa$

(B) $Ni_2Mn_{0.75}Cu_{0.25-x}Co_xGa$

(C) $Ni_{2+x}Mn_{1-x}Ga$

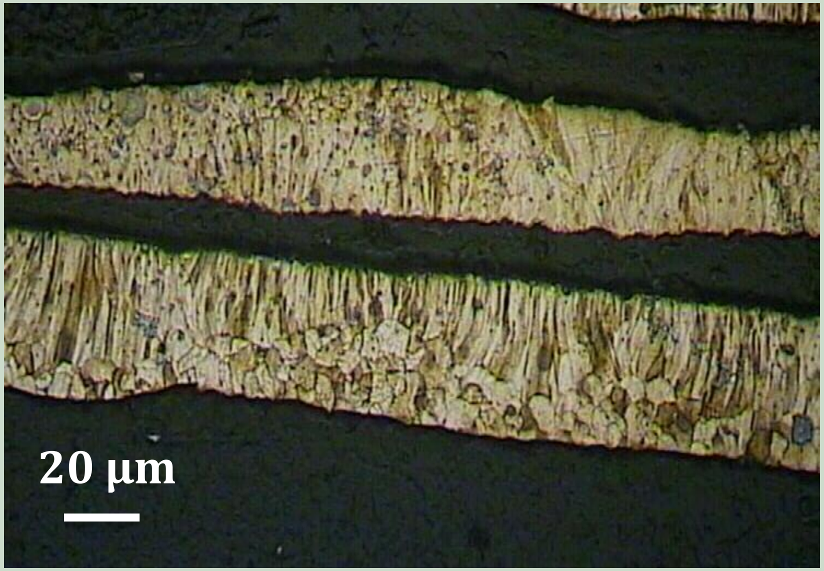
(1) $Gd_5(Si_{1-x}Ge_x)_4$

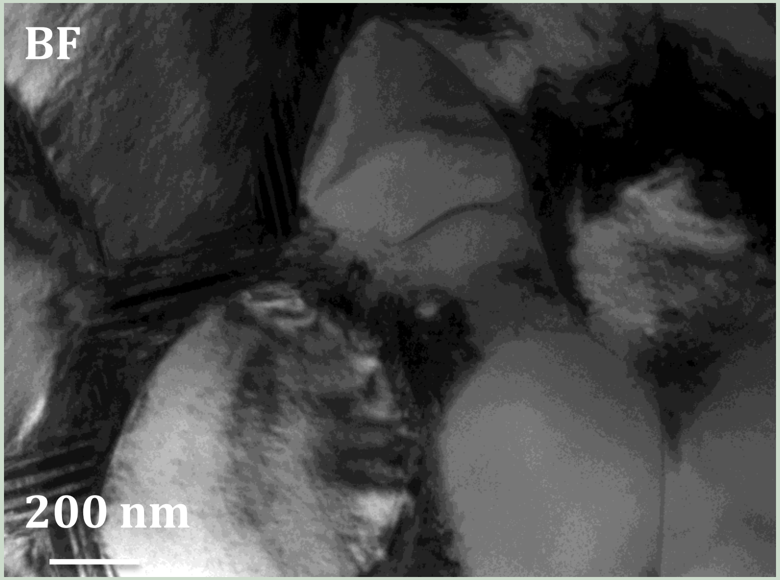
(2) $Mn(As_{1-x}Sb_x)$

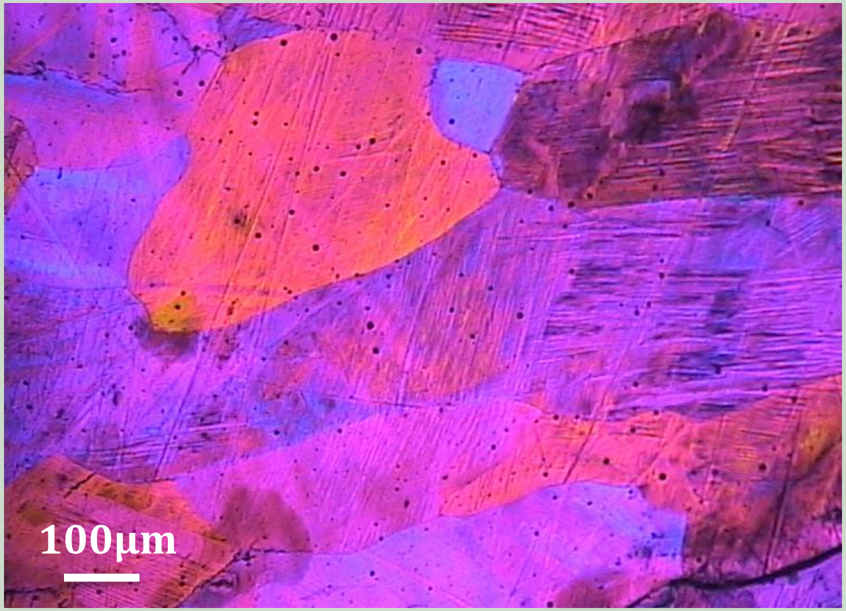
(3) $La(Fe_{13-x}Si_x)H_y$ (Ref. 17)

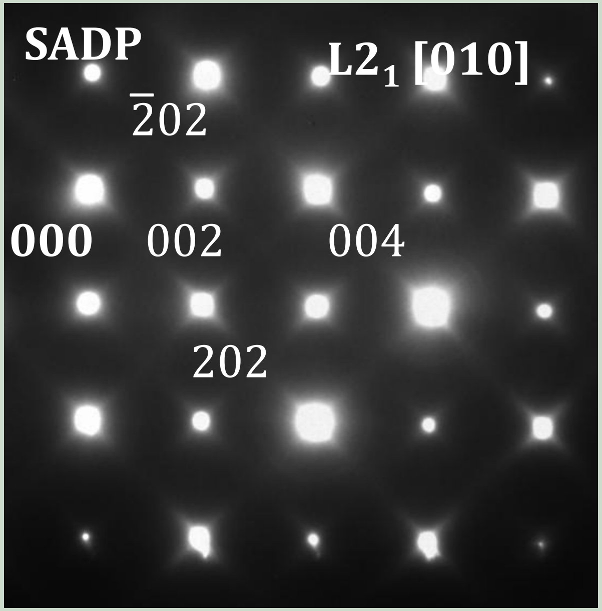
S. Stadler et al. *Magnetocaloric Effects in Mn Based Heusler Alloys.*

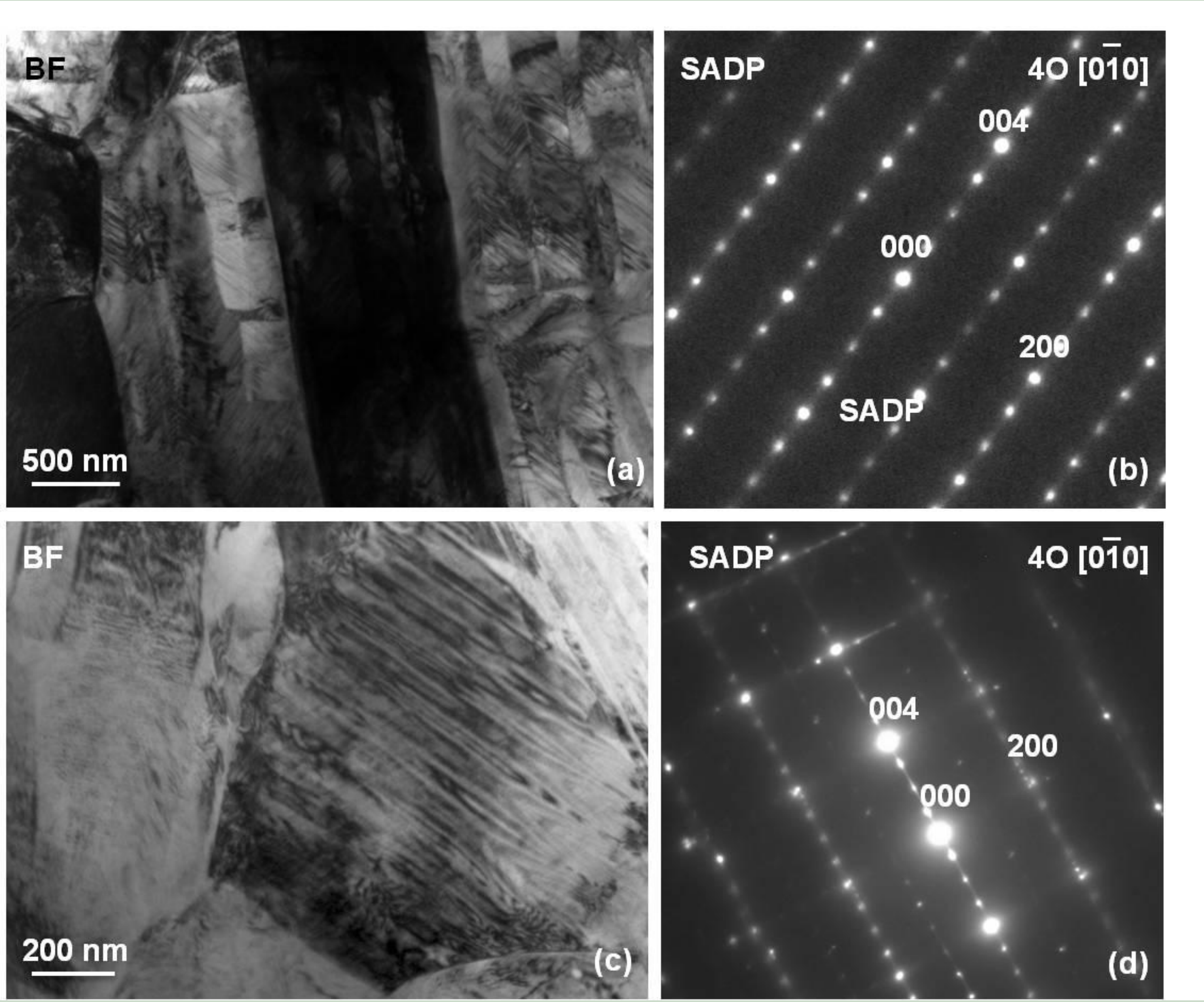
Mikrostruktura

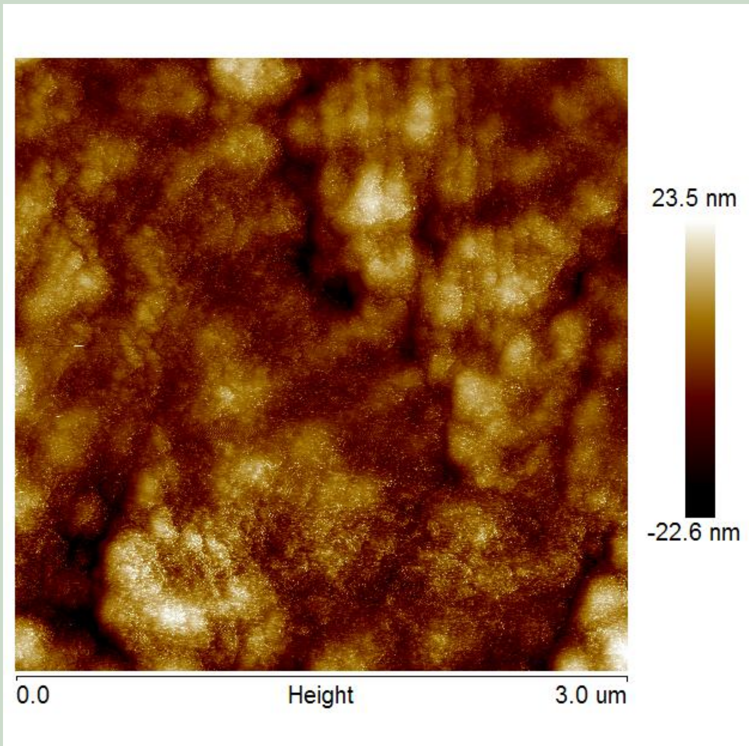


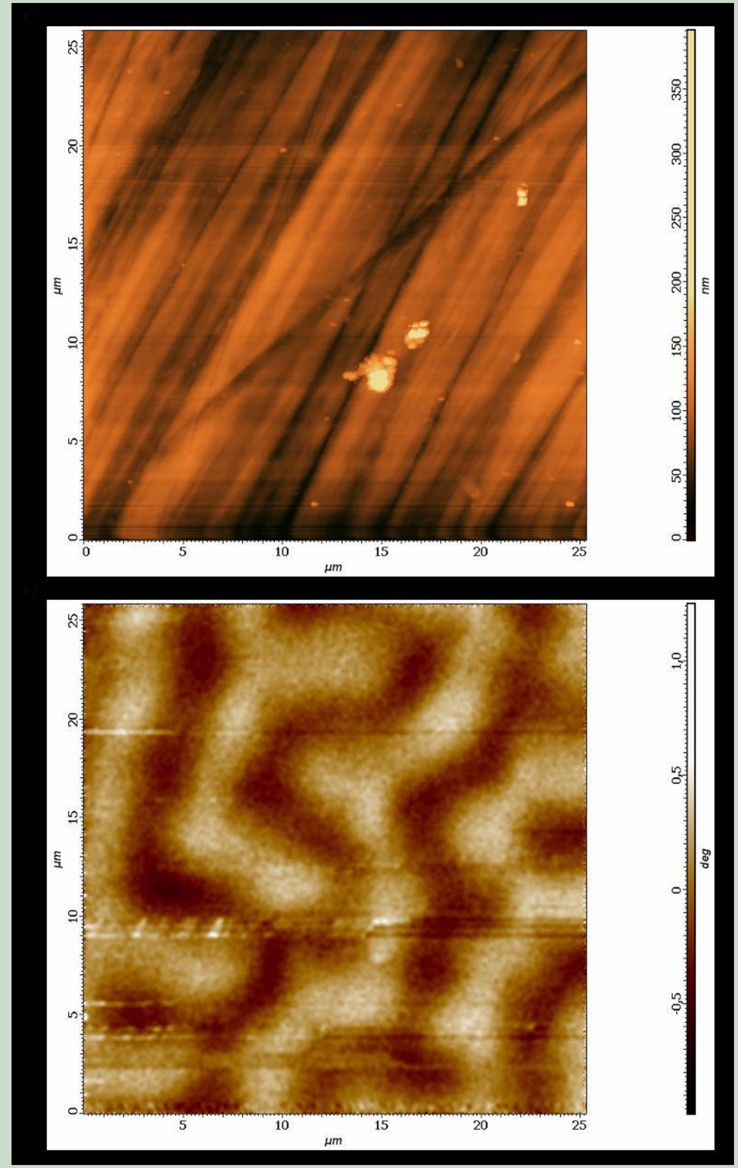


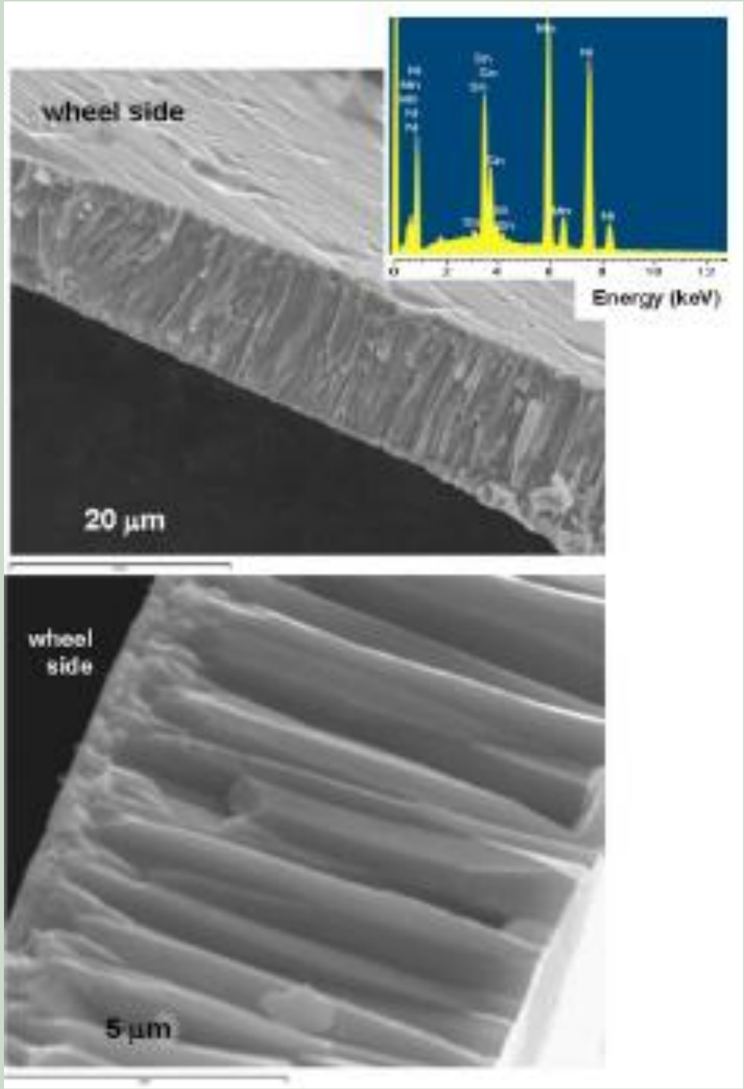




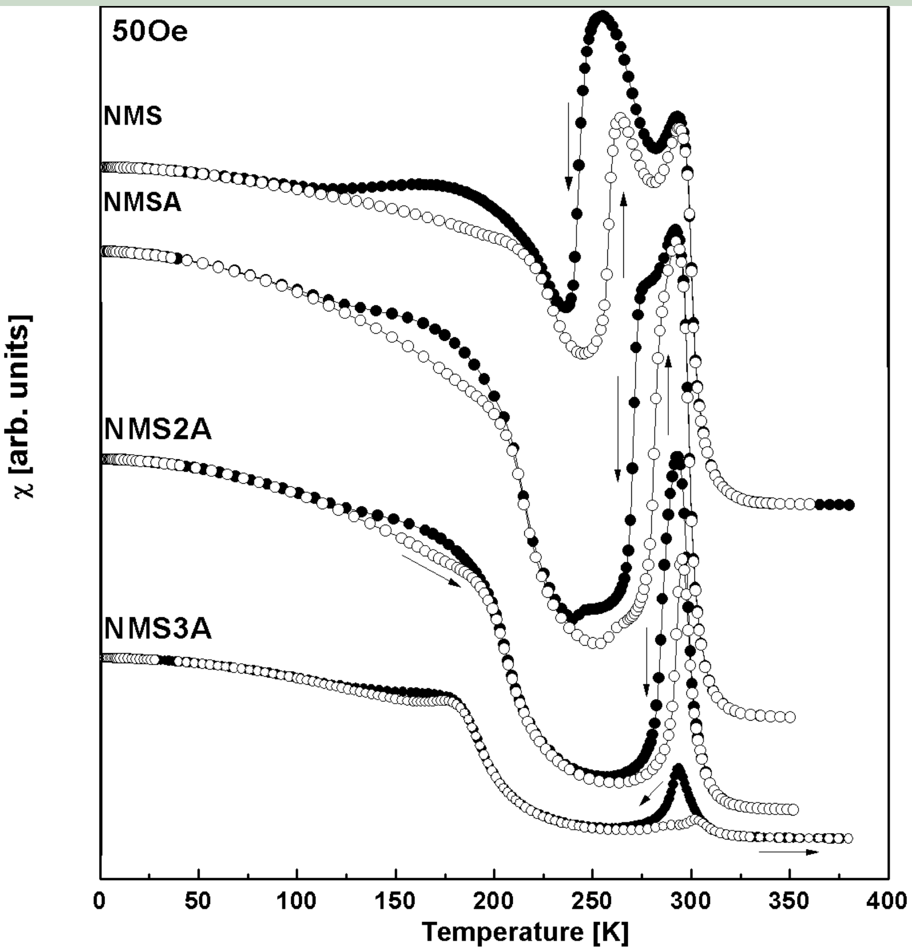

BF
500 nm
(a)
SADP
4O [0$\bar{1}$0]
004
000
200
SADP
(b)
BF
200 nm
(c)
SADP
4O [0$\bar{1}$0]
004
200
000
(d)

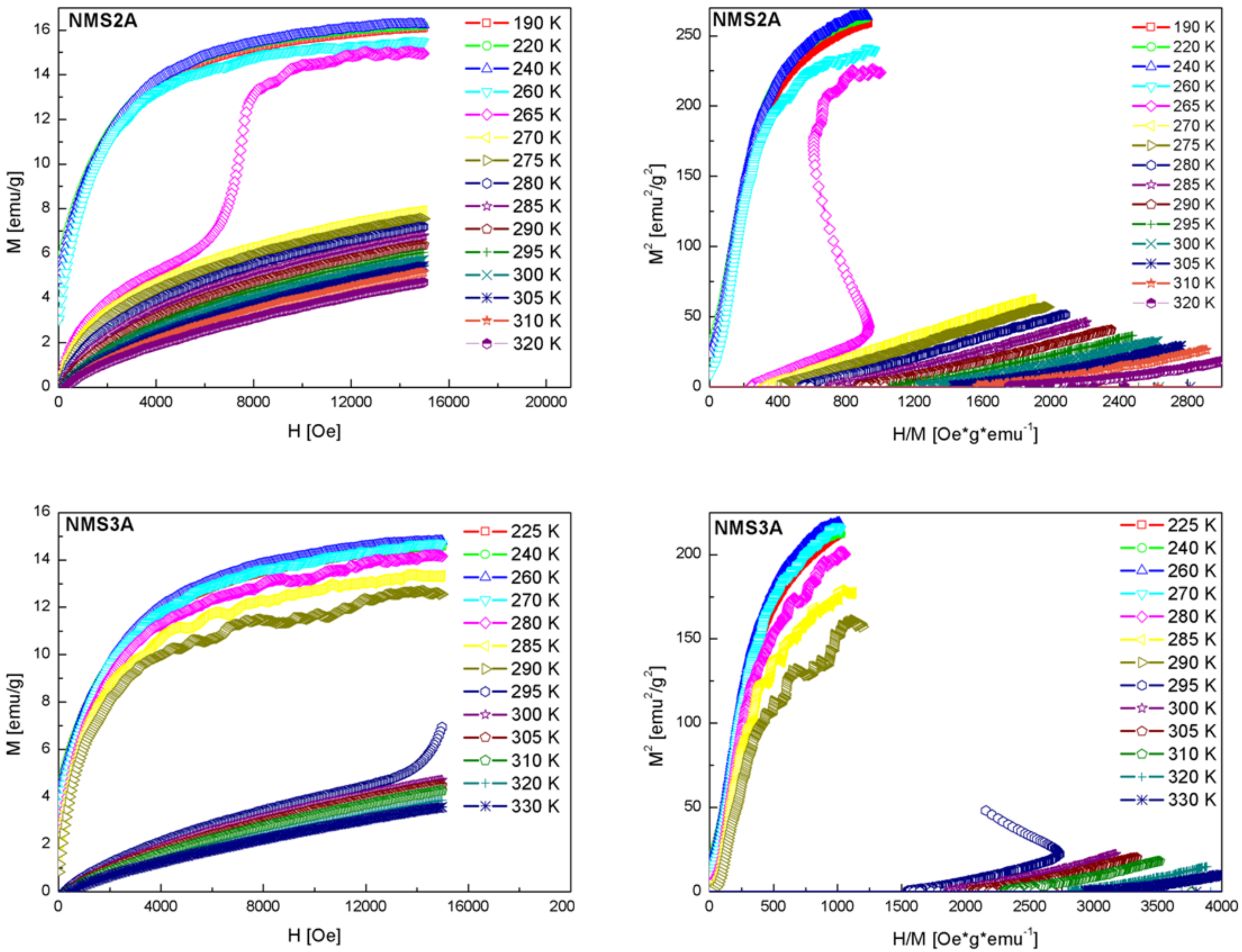

23.5 nm
-22.6 nm
0.0
Height
3.0 um


µm
0
5
10
15
20
25
nm
0
50
100
150
200
250
300
350
deg
-0,5
0
0,5
1,0

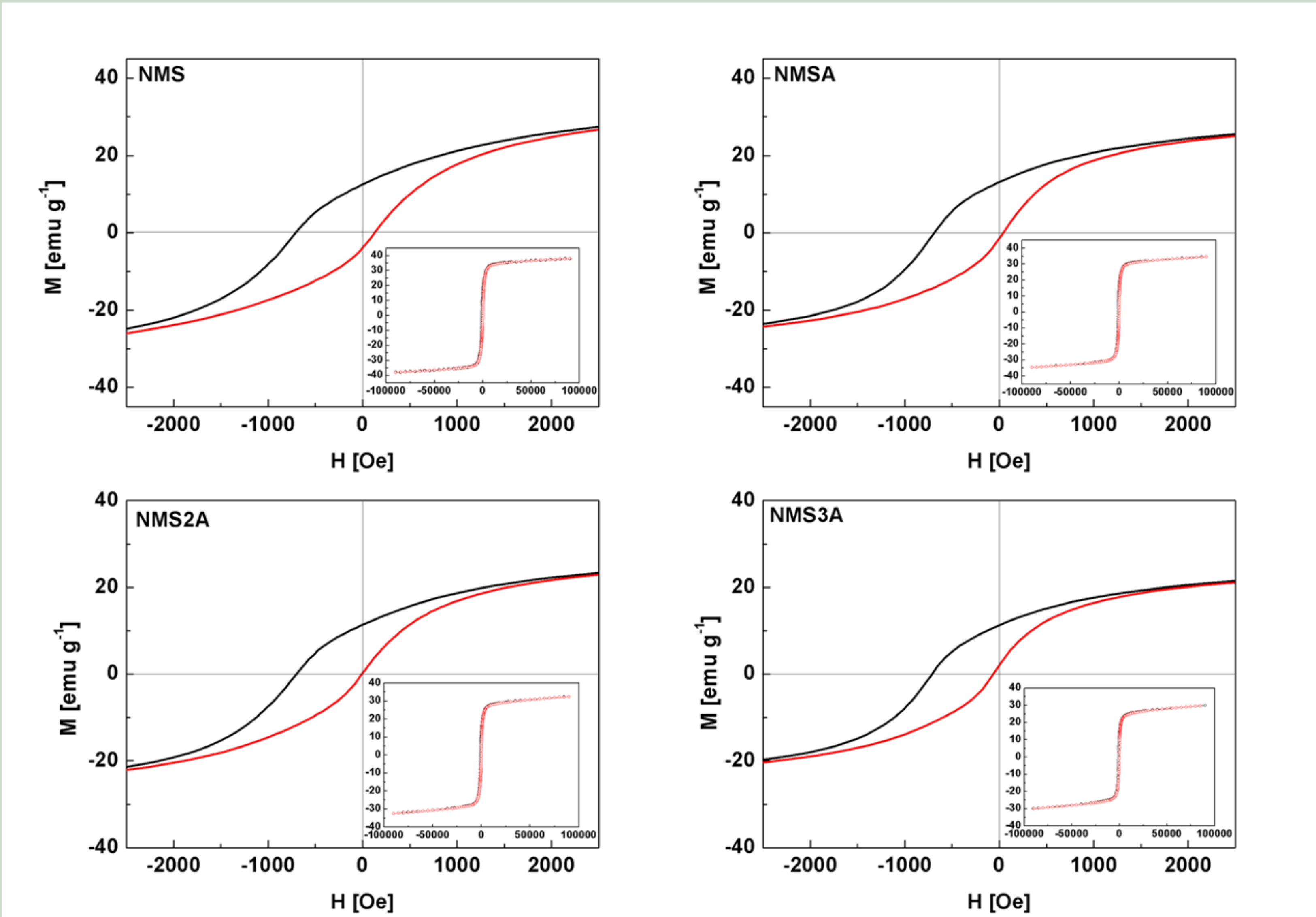


J. D. Santos et al. J. Appl. Phys. 103 07B326 (2008)

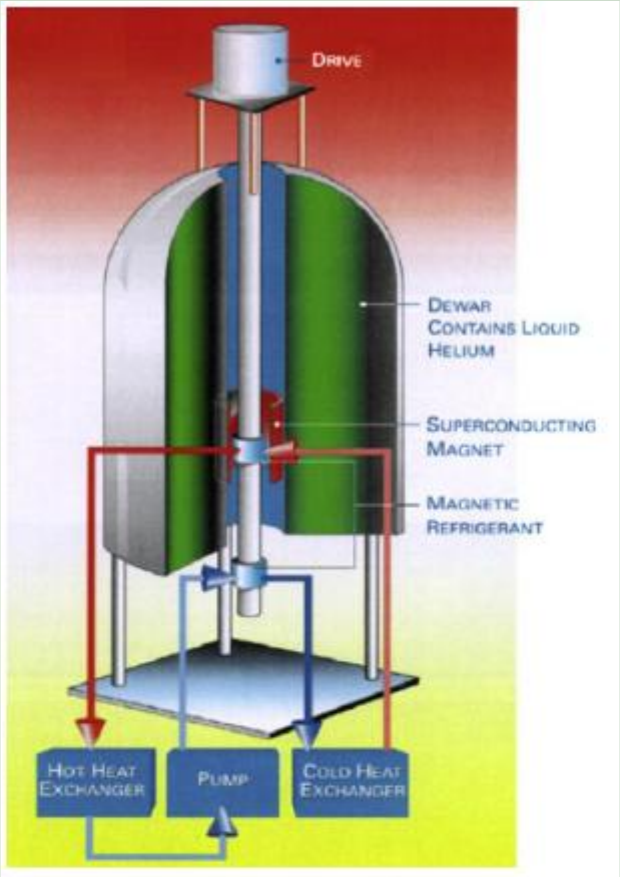

50Oe
NMS
NMSA
NMS2A
NMS3A
χ [arb. units]
0
50
100
150
200
250
300
350
400
Temperature [K]

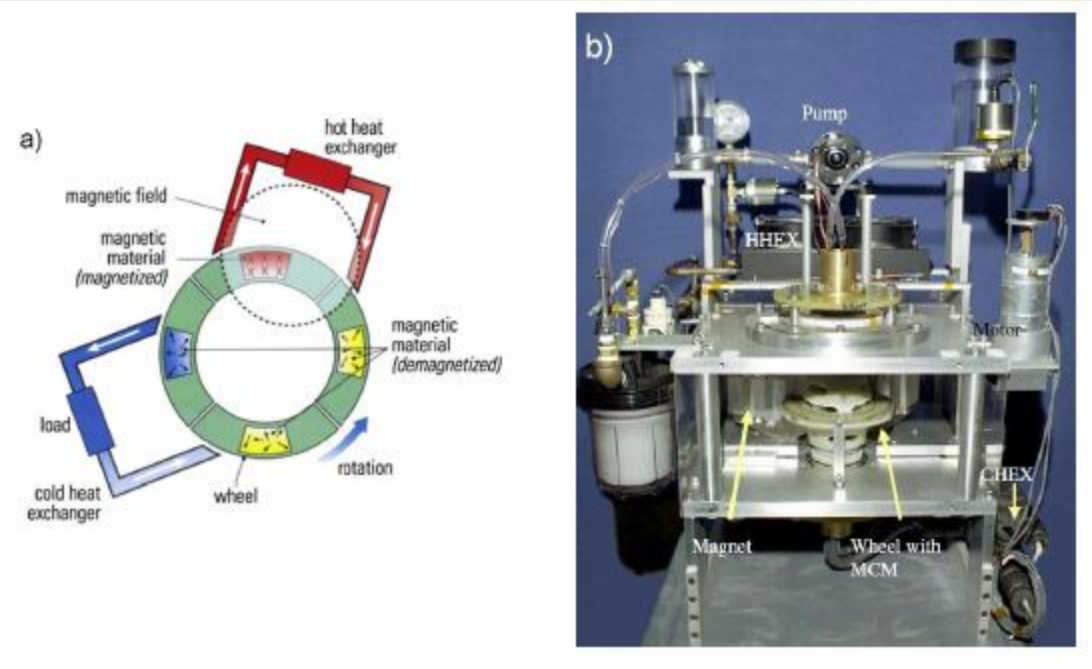


NMS2A
M [emu/g]
H [Oe]
0
2
4
6
8
10
12
14
16
4000
8000
12000
16000
20000
190 K
220 K
240 K
260 K
265 K
270 K
275 K
280 K
285 K
290 K
295 K
300 K
305 K
310 K
320 K
NMS2A
M² [emu²/g²]
H/M [Oe*g*emu⁻¹]
0
50
100
150
200
250
400
800
1200
1600
2000
2400
2800
190 K
220 K
240 K
260 K
265 K
270 K
275 K
280 K
285 K
290 K
295 K
300 K
305 K
310 K
320 K
NMS3A
M [emu/g]
H [Oe]
0
2
4
6
8
10
12
14
16
4000
8000
12000
16000
200
225 K
240 K
260 K
270 K
280 K
285 K
290 K
295 K
300 K
305 K
310 K
320 K
330 K
NMS3A
M² [emu²/g²]
H/M [Oe*g*emu⁻¹]
0
50
100
150
200
500
1000
1500
2000
2500
3000
3500
4000
225 K
240 K
260 K
270 K
280 K
285 K
290 K
295 K
300 K
305 K
310 K
320 K
330 K

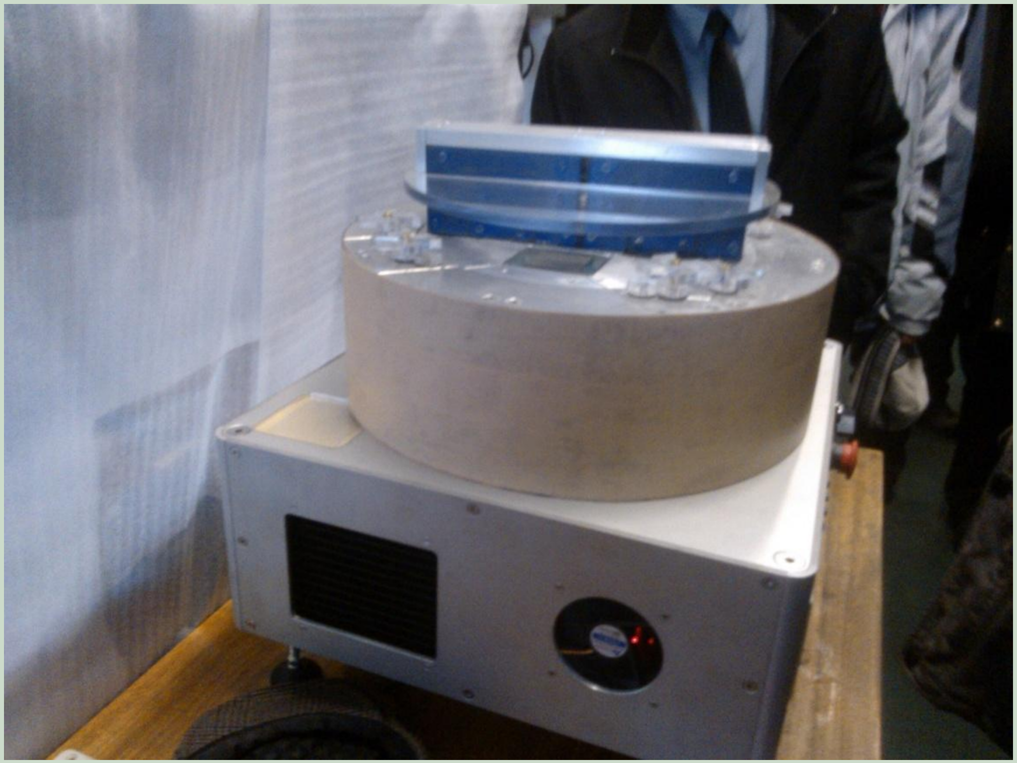


NMS
NMSA
NMS2A
NMS3A
M [emu g-1]
H [Oe]
40
20
0
-20
-40
-2000
-1000
0
1000
2000
-100000
-50000
50000
100000





J. Buh *The Magnetocaloric Effect and Magnetocaloric Materials* Univerza v Lubljani 2010.

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Modern society relies on the possibility to cool below ambient.

Ll. Manosa, ICOMAT 2011