Introducing the Magnetocaloric Effect

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Master's degree: ADVANCED PHYSICS

TOC

Goals

The student will learnt:

- The Magnetocaloric Effect
  - Caloric effects
  - History of MCE
- Thermodynamic description
  - Relation with the phase transformation
- Experimental determination
  - Direct measures
  - Indirect measures
- The MCE in different materials
  - First-order phase transition materials
  - Second-order phase transition materials
  - Composites
- The use of MCE for magnetic refrigeration
  - Thermodynamic cycles
  - Prototypes

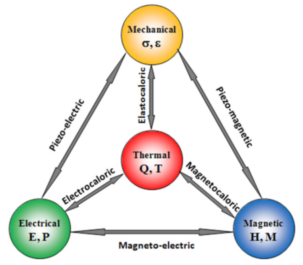
Bibliography:

- A.M. Tishin, Y.I. Spichkin, The magnetocaloric effect and its applications, IOP Publishing, Bristol, 2003
- A. Kitanovski, J. Tusek, U. Tomc, U, Plazinik, M. Ozbol, A. Poredos, Magnetocaloric Energy Conversion. From Theory to Applications, Springer, Londres, 2015
- V. Franco, J.S. Blázquez, J.J. Ipus, J.Y. Law, L.M. Moreno-Ramírez, A. Conde, Prog. Mater. Sci. 93 (2018) 112-232
- V.K. Pecharsky, K.A. Gschneidner, Int. J. Refrigeration 29 (2006) 1239-49
- V.K. Pecharsky, K.A. Gschneidner, A.O. Tsokol, Rep. Prog. Phys. 68 (2005) 1479-1539

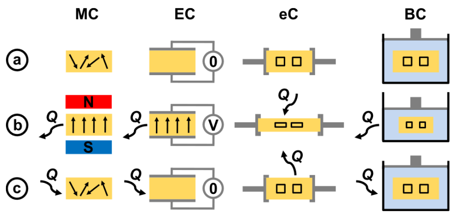
Introduction to the magnetocaloric effect

Caloric effects

We apply a field → Changes of entropy and temperature



M.M. Vopson, J. Phys. D: Appl. Phys. **46** (2013) 345304



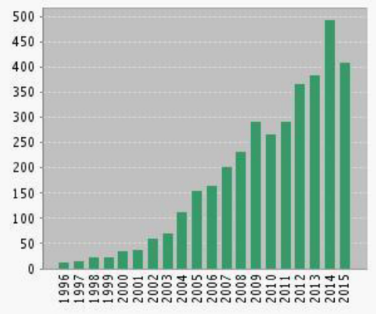
S. Crossley et al., AIP Advances **5** (2015) 067153

Introduction to the magnetocaloric effect

Historical development

- William Thomson (Lord Kelvin) in 1860: if magnetization decreases (increases) with temperature, the specimen heats up (cools down) with increasing (decreasing) magnetic field
- Pierre Weiss and Auguste Picard in 1921: reversible increment of 0.7 ℃ by applying a magnetic field of 1.5 T to Ni at 354 ℃
- Peter Debye in 1926 and William Fracis Giauque in 1927: ultra low temperatures can be reached ($< 1\,\mathrm{K}$) through paramagnetic salts ($Gd_2(SO_4)_3 8H_2O$)
  - Experimentalmente checked by Giauque (Nobel laureate, 1949) and MacDougall in 1933
- Brillouin and Iskendenian in the late 1950's: thermodynamic analysis of magnetocaloric power generation
- Greg Brown in 1976: magnetic refrigerator prototype at room temperature
- Carl Zimm in 1996: 3 kg of Gd generated up to $500 - 600\,\mathrm{W}$ of refrigeration power under a magnetic field of 5 T
- Vitalij K. Pecharsky and Karl A. Gschneidner Jr. in 1997: high MCE in $Gd_5Si_2Ge_2$

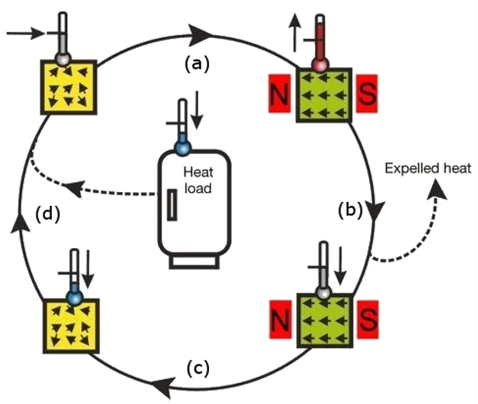
Introduction to the magnetocaloric effect



A.M. Tishin et al., Int. J. Refrig. **68** (2016) 177-186

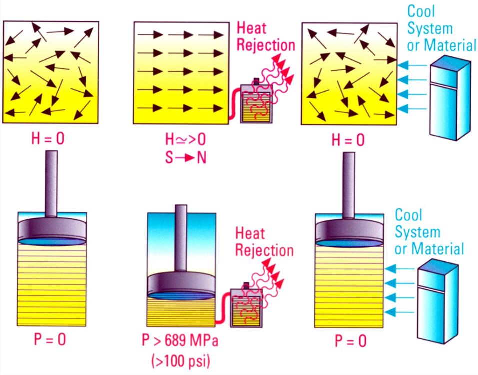
Introduction to the magnetocaloric effect

Magnetic refrigeration



Introduction to the magnetocaloric effect

Comparison with conventional refrigeration



Introduction to the magnetocaloric effect

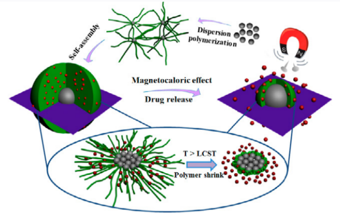
Advantages of the Magnetic Refrigeration

- Larger efficiency
  - 20-30% more efficient than the traditional refrigeration
  - Reduction in the fossil fuels consumption
- Technology more respectful with the environment
  - Less emission of CO_2
  - Use of clean fluids for heat exchange (water, antifreeze)
  - No direct emissions to the environment (no CFC, no HFC)
- Simple construction engines
  - Neither vibrations nor noises
  - Low maintenance cost

Introduction to the magnetocaloric effect

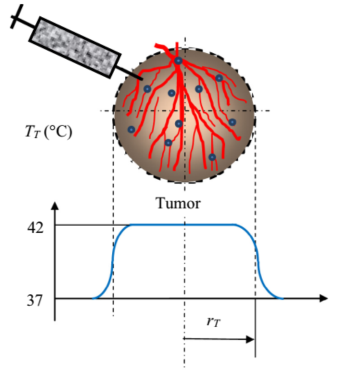
Other applications

- Magnetic heat pumps
- Power generation
- Drug delivery



J. Li et al., **23** (2012) 505706

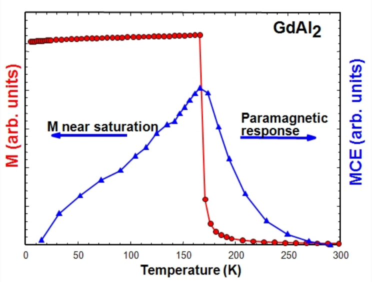
- Hyperthermia



A.M. Tishin et al., Int. J. Refrig. **68** (2016) 177-186

Thermodynamic description

Dependency of magnetization with temperature: relationship with the MCE



The MCE is maximum for
$T \rightarrow$ order temperature

Isothermal magnetic entropy change

Maxwell's relationship

$$\Delta S_M (T, H_2)_{P,\Delta H} = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T} \right)_{P,H} dH$$

Adiabatic temperature change

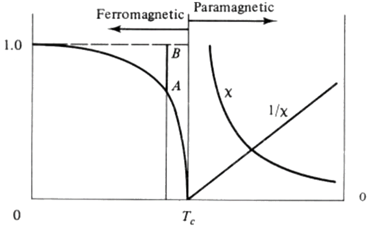
$$\Delta T_{ad} (T, H_2)_{P,\Delta H} = - \int_{H_1}^{H_2} \left(\frac{T}{C_P} \frac{\partial M}{\partial T} \right)_{P,H} dH$$

$$\Delta H = H_2 - H_1$$

Thermodynamic description

Phase transition: second order

- Purely magnetics
- Continuous change of magnetization
- Magnetic susceptibility divergency
- No thermal hysteresis



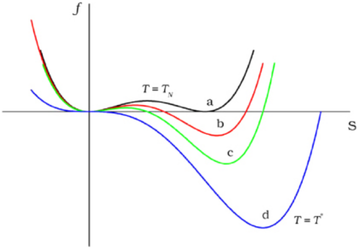
$$S(T,H) = S_L(T) + S_E(T) + S_M(T,H)$$

- S_L: entropy associated to the **crystal lattice vibrations**
- S_E: entropy associated to the **electrons**
- S_M: entropy associated to the **magnetic order**

Thermodynamic description

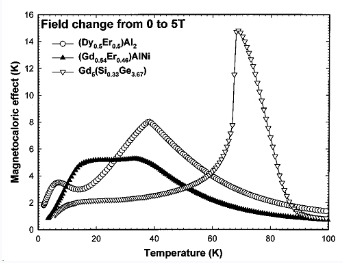
Phase transitions: first order

- Magnetostructural transitions → Volume change
- Coexistence of phases (minima in Gibbs free energy: $G = U + PV - TS$)
- Divergence in the magnetization
- Latent heat: heat absorption or release (constant T)
- Thermal hysteresis



Thermodynamic description

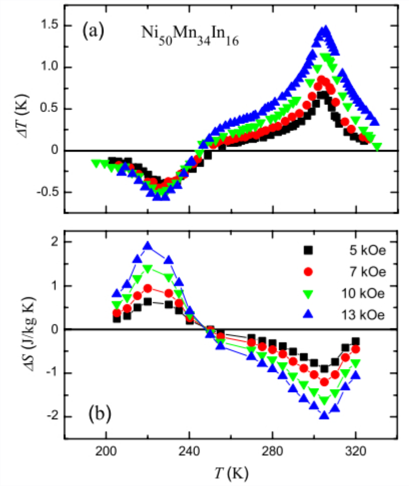
Shape of $\Delta S_M(T)$ and $\Delta T_{ad}(T)$ curves



K.A. Gschneidner et al., J. Appl. Phys. **85** (1999) 5365

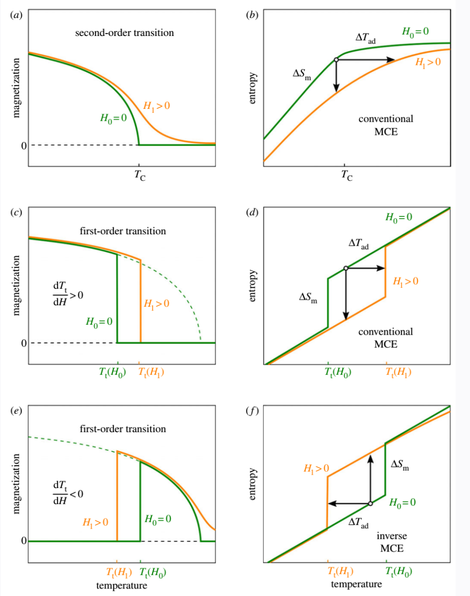
- Skyscraper-like → First order phase transitions. Large MCE elevado but confined in a small temperature range
- Caret-like (ˆ) → Second order phase transitions. Moderate MCE but in a large temperature range
- Table-like → MCE-composites. Constant MCE in a large temperature interval for certain magnetic field values

Temperature dependence of the MCE



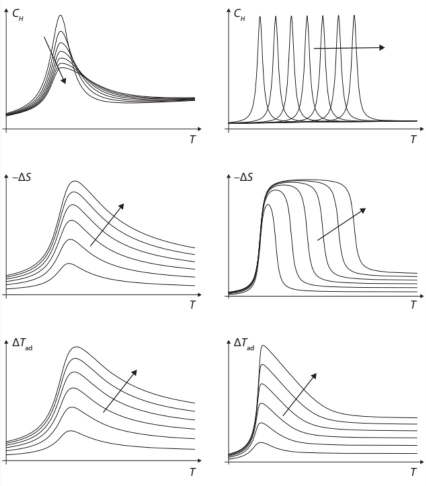
A. Planes et al., J. Phys.: Condens. Matter **21** (2009) 233201

Conventional and inverse MCE



O. Gutfleisch et al., Cl Philos. Trans. R. Soc. A-Math. Phys. Eng. Sci. **374** (2016) 20150308

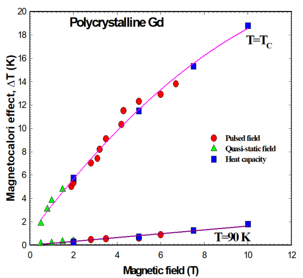
Dependency of the heat capacity with the temperature and the magnetic field: relation with the MCE

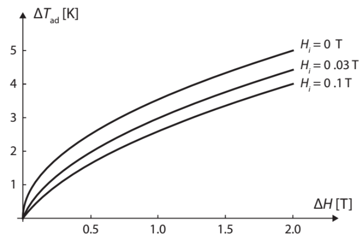


A. Smith, C.R.H. Bahl et al., Adv. Energy Mater. **2** (2012) 1288-1318

$$\Delta S_M\left(T,H_2\right)_{P,\Delta H}=\int_0^T\frac{C_P\left(t,H_2\right)-C_P\left(t,H_1\right)}{t}dt$$

Dependency of MCE with the magnetic field intensity





A. Smith, C.R.H. Bahl et al., Adv. Energy Mater. **2** (2012) 1288-1318

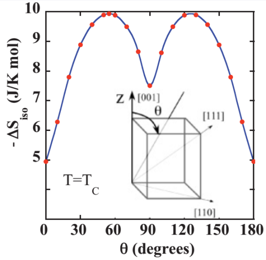
$\Delta S_M(H)$ for second order phase transition materials

$$\Delta S_M\,(H) \propto H^n$$

n: **Critical exponent**

For mean field: $n = 2/3$

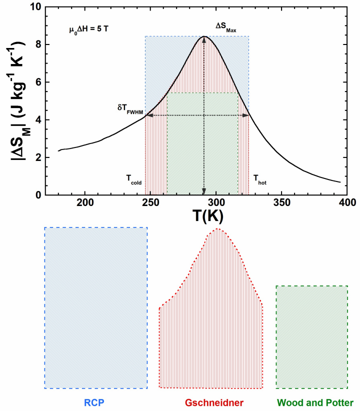
Dependenciy of MCE with the magnetic field direction



P. Álvarez et al., Phys. Rev. B. **84** (2011) 024412

Introduction to the magnetocaloric effect

Refrigeration capacity (RCP o RC)



A.A.E. Gendy, J.M. Barandiaran, and R.L. Hadimani, Magnetic Nanostructured Materials: From Lab to Fab, Elsevier (2018)

Refrigerant capacity estimation

$$RC_1(H) = |\Delta S_M^{Pico}(H)| \times \delta T_{FWHM}$$

$$RC_2(H) = \int_{T_C}^{T_H} |\Delta S_M(T,H)| \; dT$$

$$RC_3(H) = max\{|\Delta S_M(T_1,H)| \times (T_2 - T_1)\}$$

Magnetocaloric effect determination

Types of measures

- Direct measurements
- Indirect measurements
  - $M(T,H)$
  - $C_P(T,H)$

Isothermal magnetic entropy change

$$\Delta S_M\left(T,H_2\right)_{\Delta H} = Q/T$$

$$\Delta S_M\left(T,H_2\right)_{\Delta H} = \int_{H_1}^{H_2}\left(\frac{\partial M}{\partial T}\right)_H dH$$

$$\Delta S_M\left(T,H_2\right)_{\Delta H} = \int_0^T \frac{C_P\left(t,H_2\right)-C_P\left(t,H_1\right)}{t}dt$$

Adiabatic temperature change

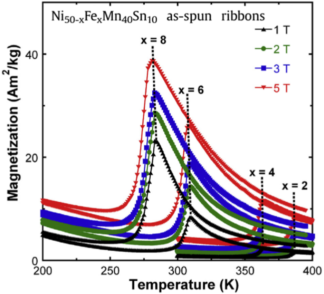
$$\Delta T_{ad}\left(T,H_2\right)_{\Delta H} = T(S,H_2)-T(S,H_1)$$

$$\Delta T_{ad}\left(T,H_2\right)_{\Delta H} = -\int_{H_1}^{H_2}\left(\frac{T}{C_P}\frac{\partial M}{\partial T}\right)_H dH$$

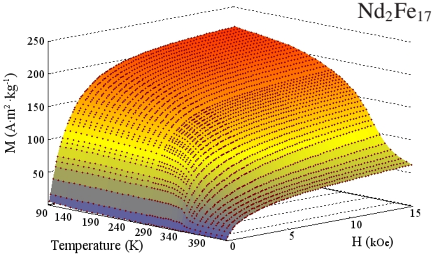
Indirect measurements

Magnetization measurement

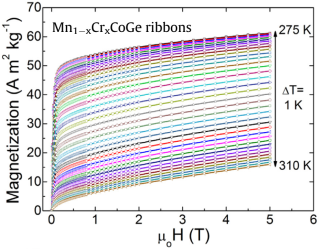
- Method more used for determining ΔS_M
- VSM, SQUID, magnetometers
- Devices available in many laboratories
    - Magnetic fields: 15 T
    - temperatures: 4 K-400 K
- Mass: 0.1-100 mg



C.O. Aguilar-Ortiz et al., Acta Mater. **107** (2016) 9



P. Alvarez et al., J. Phys.: Condens. Matter. **22** (2010) 216005

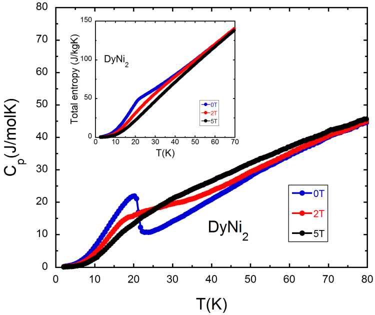


G. Daniel-Pérez et al.,J.Magn.Magn. Mater. 444 (2017) 263

Indirect measurements

Heat capacity measurements

- Determining ΔS_M and ΔT_{ad}
- *Intermitent heating* and *Continuous heating*
- More specialized (home-made)
  - Magnetic fields: 5 T
  - temperatures: 4 K-300 K
- Mass: 0.1-1000 mg



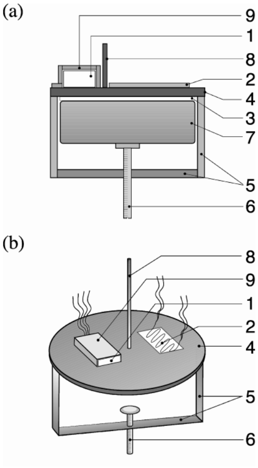


FIG. 7. A schematic drawing of the sample holder, showing its main parts (a) and 3-D view of sample holder top plate and frame (b). (1) CERNOX temperature sensor; (2) heater (a 350 Ω strain gauge); (3) a 50:50 (by volume) mixture of Apiezon-N grease and 10 μm Ag powder; (4) sample holder top plate (Cu, ~0.5 mm thick, 14 mm diameter; (5) sample holder frame (Cu, ~0.7 mm thick, 2.5 mm wide); (6) holding screw (Cu) with 0–40 threads; (7) sample; (8) heat switch (Cu, ~0.5 mm diameter); (9) temperature sensor holding clamp (0.012-mm-thick copper foil).

V.K. Pecharsky et al., Rev. Sci. Instrum. **68** (1997) 4196-4207

Indirect measurements

Heat capacity measurements

- Determining ΔS_M and ΔT_{ad}
- *Intermitent heating* and *Continuous heating*
- More specialized (home-made)
  - Magnetic fields: 5 T
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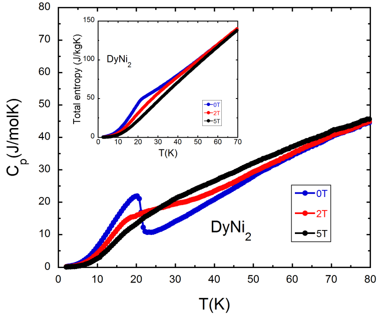
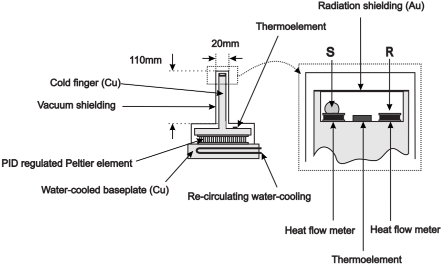


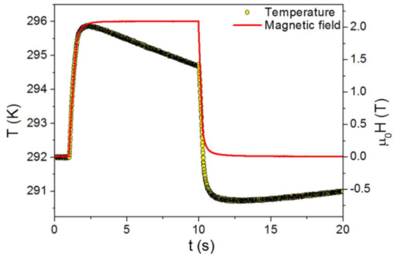


S. Jeppesen et al., Rev. Sci. Instrum. **79** (2008) 083901

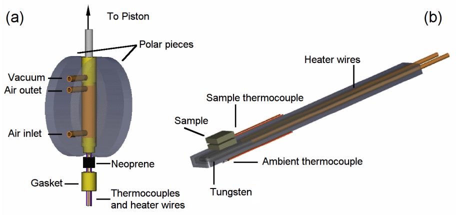
Direct measurements

Adiabatic temperature change measurement

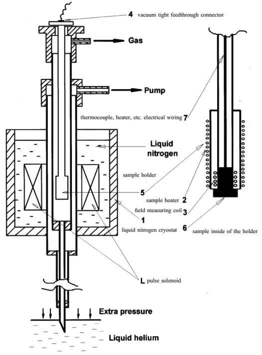
- *Static applied magnetic field* and *Variable applied magnetic field*
- Specialized equipments (home-made)
  - Magnetic field: up to 14 T
  - temperatures: 4 K-300 K
- Mass: 0.1-1000 mg



F. Cugini et al., Rev. Sci. Instrum. **85** (2014) 074902



P. Alvarez-Alonso et al., Key Eng. Mater. **644** (2015) 215-218



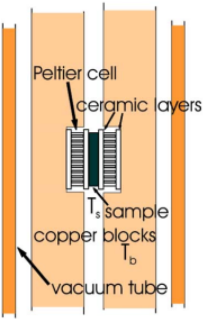
S.Y. Dan'kov et al., Rev. Sci. Instrum. **68** (1997) 2432

Direct measurements

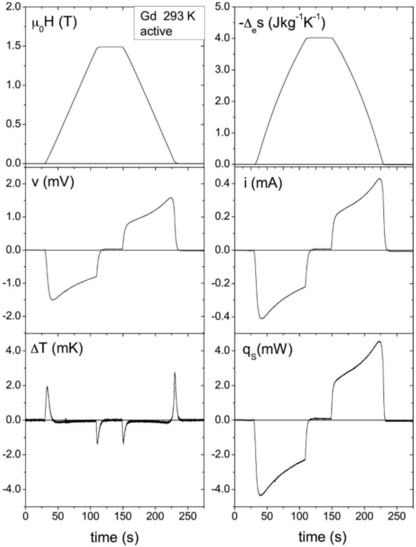
Heat flux measurements

- Determining ΔS_M by means of calorimeter

$$\Delta S = \int_{t_0}^{t_1} \frac{q}{T} dt$$



M. Kuepferling et al., IEEE Trans. Magn. **43** (2007) 2764-2766



M. Kuepferling et al., IEEE Trans. Magn. **43** (2007) 2764-2766

Other methods

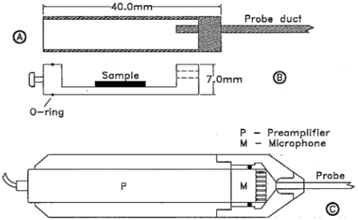
Thermoacustic method

- Thermoacustic waves

$$\delta T = C_{sys} V$$

C_{sys}: calibration constant

V: the voltage from the microphone



B.R. Gopal et al., Rev. Sci. Instrum. **66** (1995) 232?238

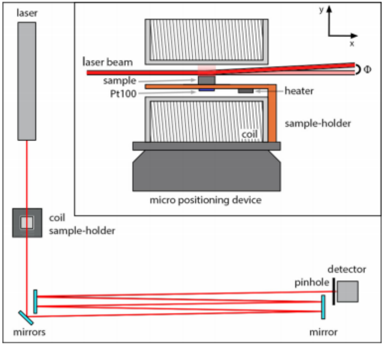
Mirage-based method

- $\Phi(y,t) = \frac{1}{n}\frac{dn}{dT}\frac{\partial T(y,t)}{\partial y} d$

  Φ: deflection angle

  n: refraction index

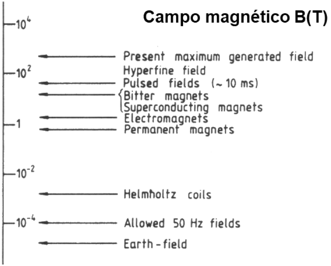
  d: length of the laser path

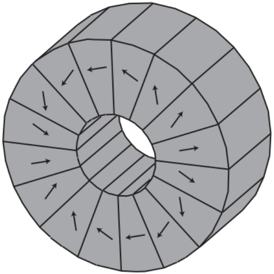


F. Cugini et al., Appl. Phys. Lett. **108** (2016) 012407

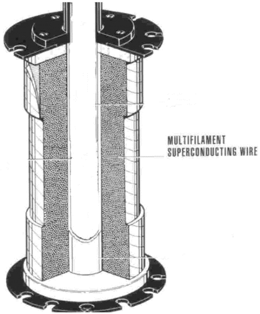
Optimizing the MCE

- High $\mu_0 \Delta H$
- Abrupt variation of the magnetization with temperature
- Null thermal and magnetic hysteresis
- High refrigerant capacity





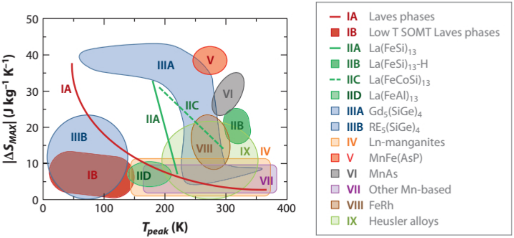
R. Bjørk et al., Int. J. Refrig. **33** (2010) 437-448



First order phase transition materials

Optimizing the MCE

- High $\mu_0 \Delta H$
- Abrupt variation of the magnetization with temperature
- Null thermal and magnetic hysteresis
- High refrigerant capacity

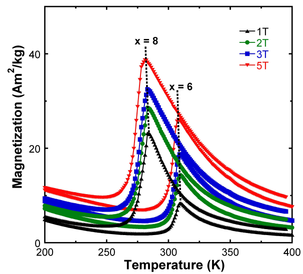


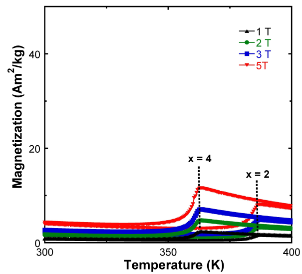
V. Franco et al., Ann. Rev. Mater. Res. **42** (2012) 305-342

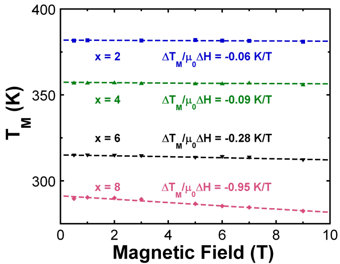
First order phase transition materials

Magnetic measurements

$Ni_{50-x}Fe_xMn_{40}Sn_{10}$ melt-spun ribbons (C.O. Aguilar-Ortiz et al., Acta Mater. **107** (2016) 9-16)



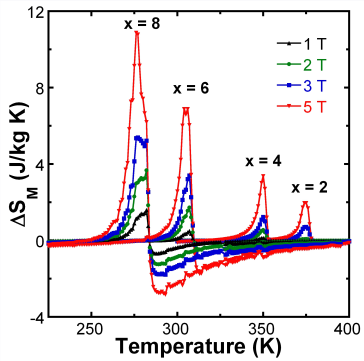




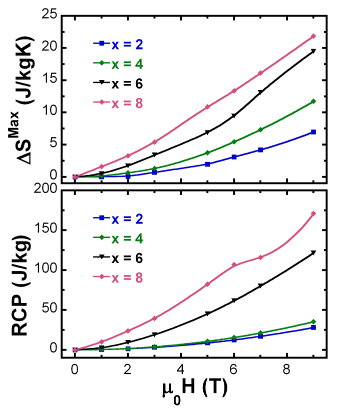
First order phase transition materials

Entropy change

$Ni_{50-x}Fe_xMn_{40}Sn_{10}$ melt-spun ribbons (C.O. Aguilar-Ortiz et al., Acta Mater. **107** (2016) 9-16)



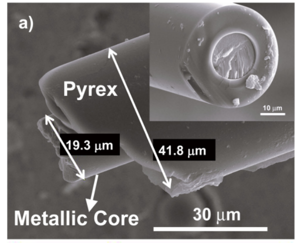
Inverse MCE

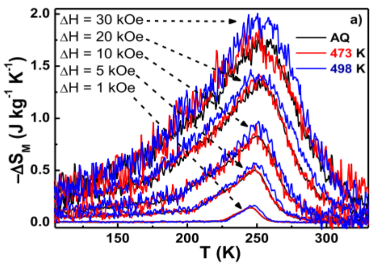


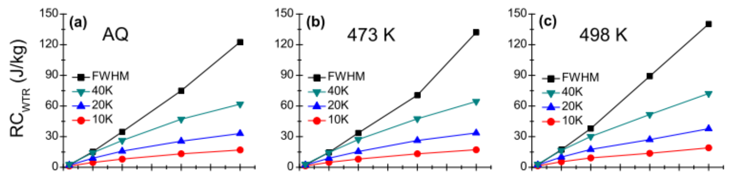
First order phase transition materials

Entropy change in microwires

$Ni_{59}Mn_{24}In_{16}$ (V. Vega et al., J. Appl. Phys. **112** (2012) 033905)





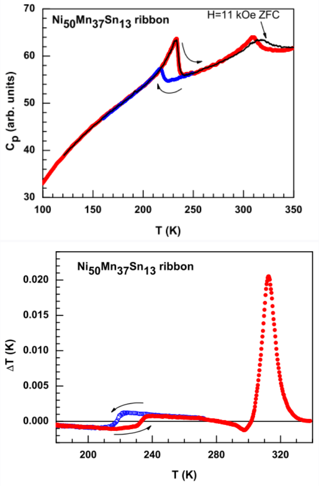


First order phase transition materials

Adiabatic temperature change

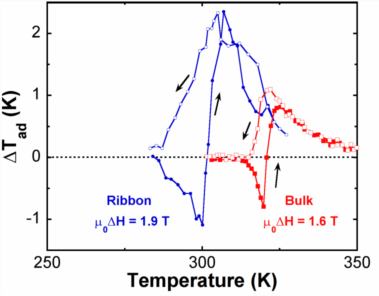
$Ni_{50}Mn_{37}Sn_{13}$ ribbons

(A.M. Aliev et al., Appl. Phys. Lett. **97** (2010) 212505)



Bulk and ribbons $Ni_{50}Mn_{30}In_{15}$

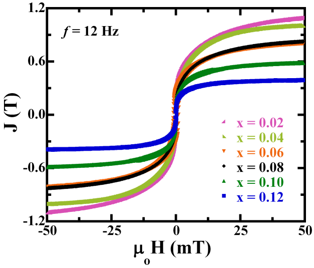
(P. Álvarez-Alonso et al., Appl. Phys. Lett. **109** (2016) 212402)



Second order phase transition materials

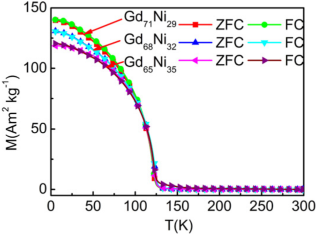
Optimizing the MCE

- High $\mu_0 \Delta H$
- Abrupt variation of the magnetization with temperature
- Null thermal and magnetic hysteresis
- High refrigerant capacity



$(Fe_{1-x}Cr_x)_{80}Si_6B_{14}$

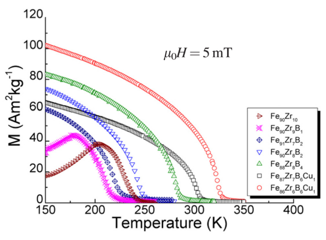
P. Álvarez-Alonso et al., J. Magn. Magn. Mater. **347** (2013) 75-78



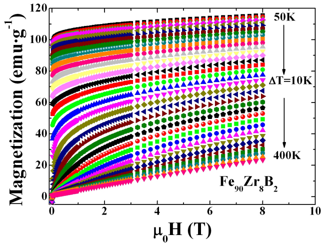
X.C. Zhong et al., J. Alloys Comp. **509** (2011) 6889-6892

Second order phase transition materials

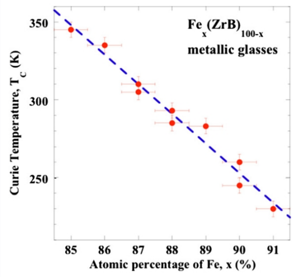
Thermomagnetic curves



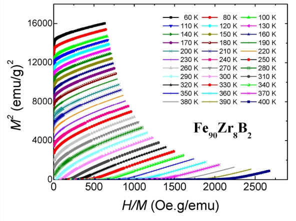
Isothermal magnetization curves



T_C vs Fe-content

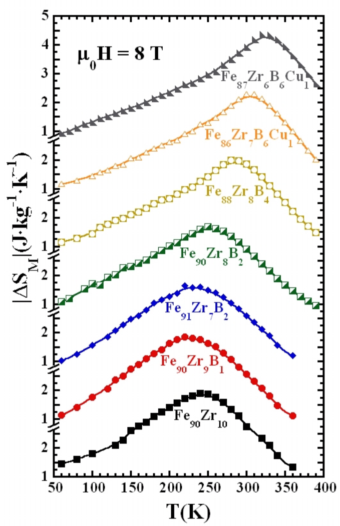


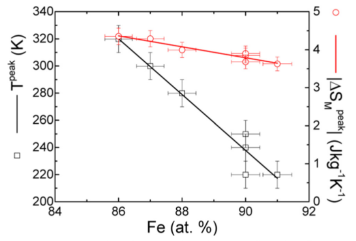
Arrott's Plots

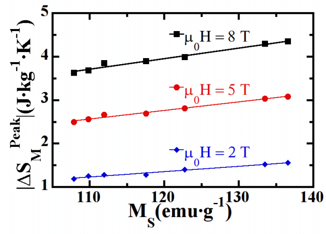


Second order phase transition materials

$\Delta S_M(T)$ in FeZrCuB amorphous ribbons

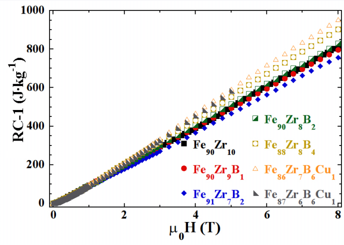




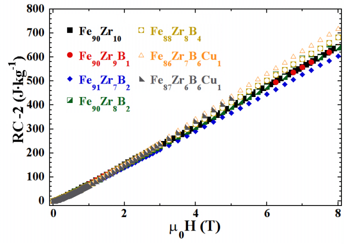


Second order phase transition materials

RC-1



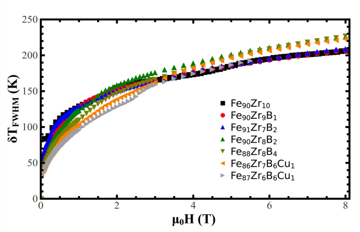
RC-2



Metallic Gd

$$\mathrm{RC1}(\mu_0 H = 5\,\mathrm{T}) = 687\,\mathrm{Jkg}^{-1}$$
$$\mathrm{RC2}(\mu_0 H = 5\,\mathrm{T}) = 503\,\mathrm{Jkg}^{-1}$$

Width of $\Delta S_M(T)$ curves



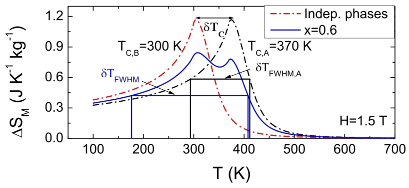
P. Álvarez et al., J. Alloys Compd. **504** (2010) S150-S154
P. Alvarez-Alonso et al., J. Appl. Phys. **117** (2015) 17A710

Composites

Optimizing the MCE

- High $\mu_0 \Delta H$
- Abrupt variation of the magnetization with temperature
- Null thermal and magnetic hysteresis
- High refrigerant capacity

RC improvement

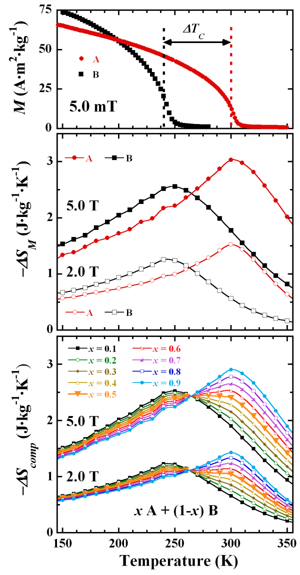


R. Caballero-Flores et al., Appl. Phys. Lett. **98** (2011) 102505

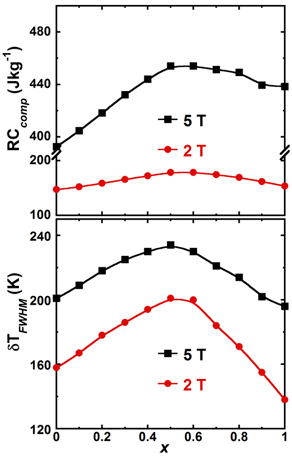
Optimizing the MCE for a two-phases composite

- $\Delta S_M(T)$ shape for each phase
- δT_C
- Relative weight of each phase
- Applied magnetic field

$\Delta S_M(T)$ curves for the composite $Fe_{87}Zr_6B_6Cu_1$ (A) - $Fe_{90}Zr_9B_1$ (B)



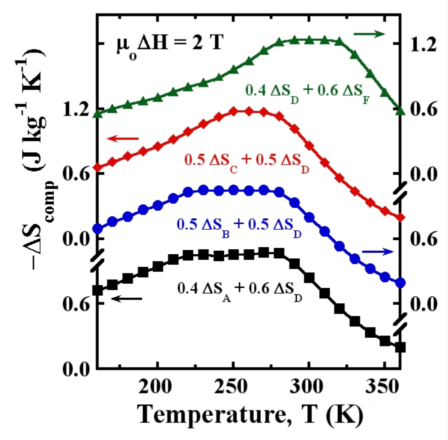
Dependency of δT_{FWHM} and RC constituents ratio



P. Alvarez et al., Appl. Phys. Lett. **41** (2011) 232501

Composites

$\Delta S_M(T)$ for several composites made with FeZrB(Cu) ribbons

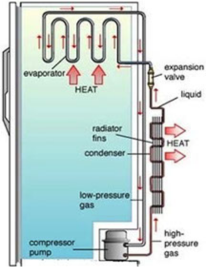


P. Alvarez-Alonso et al., J. Alloys Comp. **568** (2013) 98

A=$Fe_{90}Zr_{10}$
B=$Fe_{91}Zr_7B_2$
C=$Fe_{90}Zr_8B_2$
D=$Fe_{88}Zr_8B_4$
F=$Fe_{86}Zr_7B_6Cu_1$

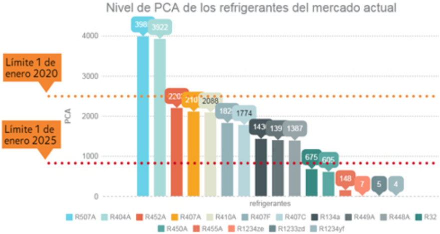
Broadening of $\Delta S_M(T)$ up to 80 K

Magnetic refrigeration



Some data

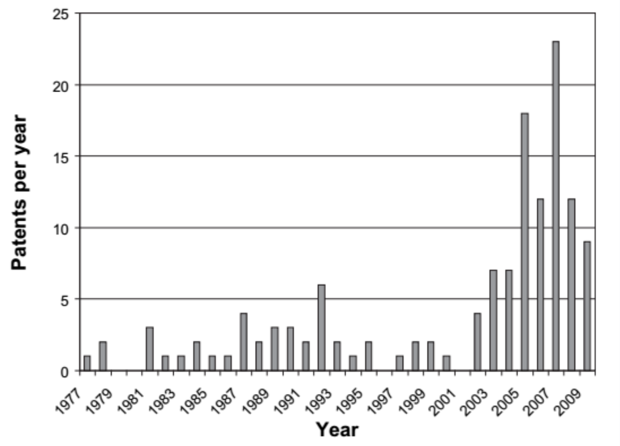
- Domestic energy consumption: 20%
- Efficiency: 15% (Carnot cycle)
- Gasses:
    - CFC, HCFC, HFC: global warming, ozone layer depletion
    - HC: flammables



Ref: www.caloryfrio.com

Magnetic refrigeration

Patent



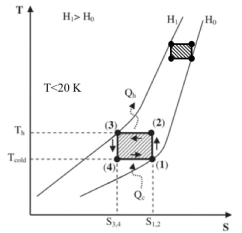
B. Yu et al., Int. J. Refrig. **33** (2010) 1029-1060

Magnetic refrigeration

Parts of a magnetic refrigerator

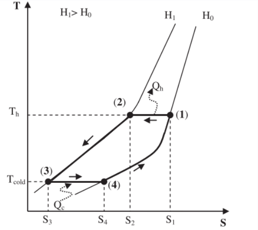
- Magnetic working body
- Magnetization system
- Hot and cold heat exchangers
- Heat transfer fluid
- Regenerator: thermal storage medium serving to transfer heat between different parts of a thermodynamical refrigeration cycle through a working fluid
    - It allows the temperature span of the refrigeration device to increase

Carnot cycle



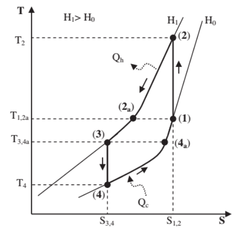
J. Romero Gómez et al., Renew. Sust. Energ. Rev. **17** (2013) 74-82

Ericsson cycle



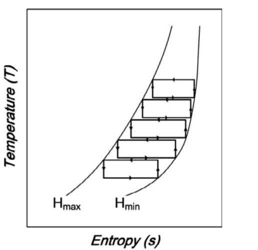
J. Romero Gómez et al., Renew. Sust. Energ. Rev. **17** (2013) 74-82

Braiton cycle



J. Romero Gómez et al., Renew. Sust. Energ. Rev. **17** (2013) 74-82

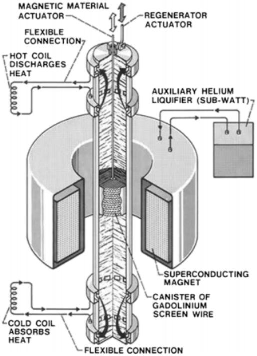
Active Magnetic Regenerator cycle

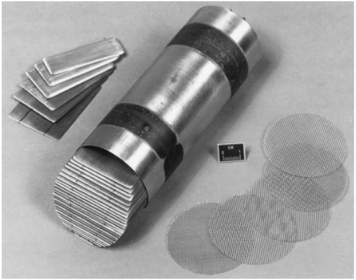


S. Jeong, Cryogenics **62** (2014) 193-201

Magnetic refrigeration

Brown's prototype (Braiton cycle)





Gd Plates 1 mm thick (1 mole)

T_C = 294 K

Regenerator: 80% H_2O -20% C_2H_5OH

ΔH = 70 kOe

50 cycles

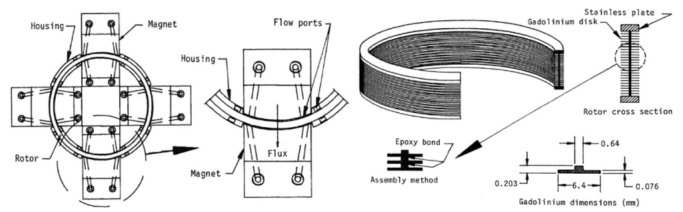
T_{hot} = 319 K
T_{cold} = 272 K $\Big\}$ Δ_T = 47 K

ΔT_{ad} of Gd = 16 K at 294 K (T_C)

K.A. Gschneidner et al., Int. J. Refrig. **31** (2008) 945-961

Magnetic refrigeration

Kirol's prototype (Ericsson cycle)



B. Yu et al., Int. J. Refrig. **33** (2010) 1029-1060

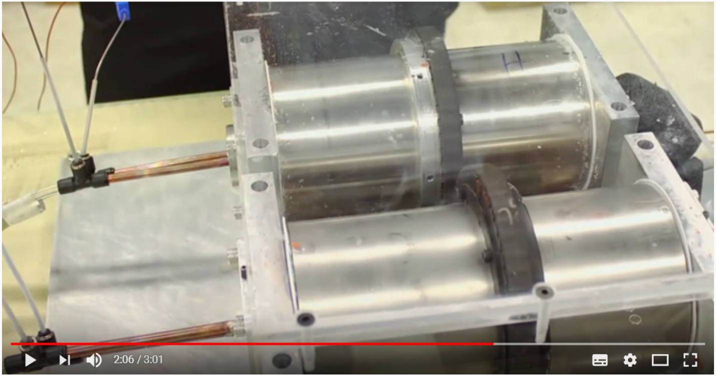
Gd sheets (Width: 0.076 mm) with a space between them 0.127 mm

The rotor consists of 126 discs (total mass: 270 g)

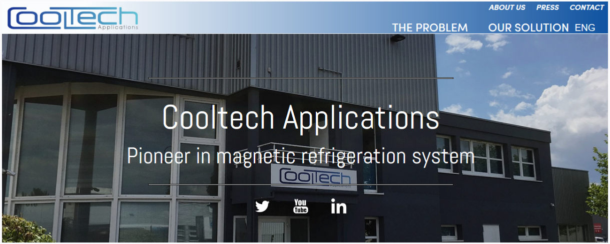
$\Delta T = 11\,\mathrm{K}$ using a permanent magnet $Nd_2Fe_{14}B$ (0.9 T)

Magnetic refrigeration

General Electric prototype (Active Magnetic Regenerator)



Currently



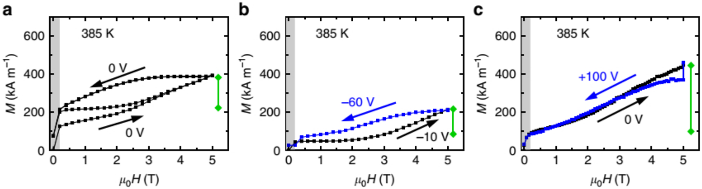
Cooltech Applications

Pioneer in magnetic refrigeration system

Problems

- Higher magnetic fields are required
- Problems with thermal and magnetical hysteresis

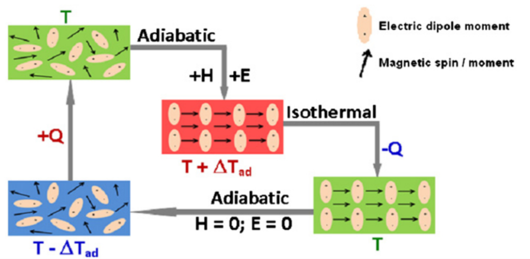
SOLUTION?



Y. Liu et al., Nat. Comm. **7** (2016) 11614

Multicalorics

(Multi)caloric refrigeration



M.M. Vopson, Solid State Comm. **152** (2012) 2067-2070

In summary:

- There exist alternatives (eco) to the conventional refrigeration
- Magnetic cooling is a reality
- It requires materials
    - Hi MCE under low magnetic field application
    - Reduced hysteresis