Imperial College London

Thermodynamics and phase transitions in magnetic materials

Lecture 2

Karl G. Sandeman
ESM 2013

Imperial College London

Outline of Lecture 2

- More on the theory of tricritical transitions (see blackboard)
- An introduction to magnetic cooling
  (to be continued in Lecture 3)

Imperial College London

Critical exponents: experiment vs theory for *d*=3

Transition type	Material	α	β	γ	ν
		$C \sim \|t\|^{-\alpha}$	$\langle m \rangle \sim \|t\|^{\beta}$	$\chi \sim \|t\|^{-\gamma}$	$\xi \sim \|t\|^{-\nu}$
Ferromag. ($n=3$)	Fe, Ni	-0.1	0.34	1.4	0.7
Superfluid ($n=2$)	He^4	0	0.3	1.3	0.7
Liquid-gas ($n=1$)	CO_2, Xe	0.11	0.32	1.24	0.63
Superconductors		0	1/2	1	1/2
Mean-field		0	1/2	1	1/2

Here "*t*" is proportional to T-T_c

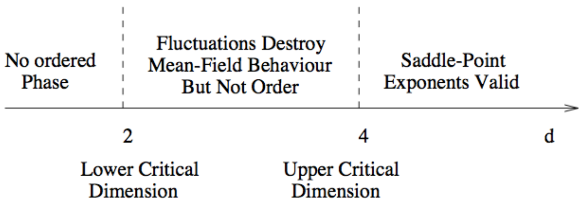
Table from Ben Simons' lectures on Phase Transitions and Collective Phenomena, U. Cambridge.

Imperial College London

More comparisons

	Ising	X-Y	Heisenberg
d=1	No ordering!	No ordering!	No ordering!
d=2	β=1/8; γ=7/4	Special case!	No ordering!
d=3	β=0.32; γ=1	β=0.35; γ=1	β=0.36; γ=1.39
Mean field		β=1/2; γ=1	

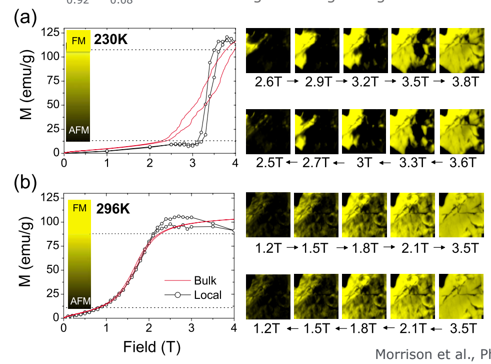
A phase diagram of the Ginzburg-Landau Hamiltonian



This diagram is from Ben Simons' lectures on Phase Transitions and Collective Phenomena, U. Cambridge.

CoMnSi: imaging tricriticality using a Hall probe

$CoMnSi_{0.92}Ge_{0.08}$ Antiferromagnet to high-magnetisation state, induced by field

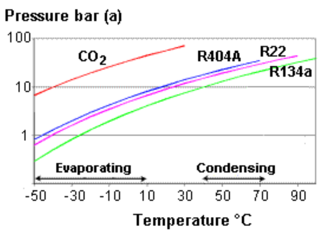


Low T:
- *1st order*
- *Globally "continuous"*
- *Locally sharp, hysteretic*

High T:
- *2nd order*
- *Globally and locally continuous*
- *No hysteresis*

Morrison et al., Phys. Rev. B (2009)

Vapour compression refrigeration



Gas compression refrigeration works in *sub-critical* regime

Refrigerant	Critical temp.	Critical pressure
CO_2	31 °C	7.38 MPa
R22	96.2 °C	4.99 MPa
R134a	101 °C	4.06 MPa

The efficiency of the refrigerant is directly related to the critical temperature.

Tuning the *critical point* and the *pressure-temperature* phase line gradient are very important

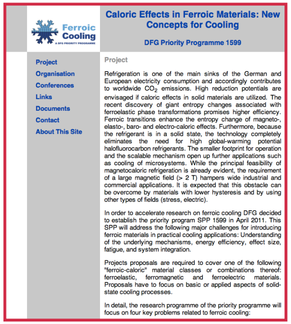
Solid-state cooling at room temperature

Ferroic cooling, including magnetic cooling

Imperial College London

Magnetic refrigeration: a growing area of interest

$$dG = -SdT - MdH_M + \sum_l \sum_{m=-l}^{m=l} K_l^m(H_M)\, d(Y_l^m(\Omega_M)) + Vdp + \ldots$$



Caloric Effects in Ferroic Materials: New Concepts for Cooling

DFG Priority Programme 1599

Project · Organisation · Conferences · Links · Documents · Contact · About This Site

Project

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:

Imperial College London

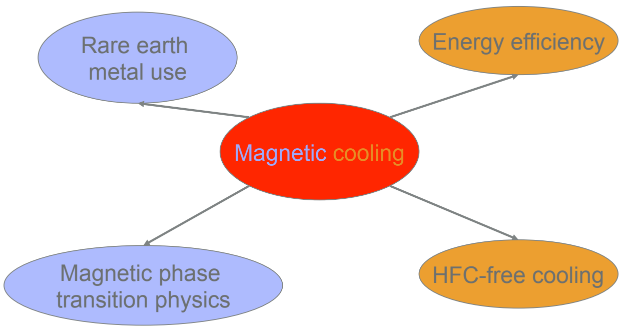
Magnetic cooling: the future

A careful system-wide cost and efficiency analysis revealed the benefit of magnetic cooling at low powers (< 500 Watt).

	Thermodynamic Ideal	Current Solution (Butane)	Magnetic A+++ Solution (no vacuum panels)
Target Cooling Power (W)	30	30	30
External Temperature (˚C)	25	40	35
Internal Temperature (˚C)	5	-15	0
Cooling Engine Power (W)	30	150	30
Technology Efficiency (%)	100%	43%	50%
Running Time (%)	100%	20%	100%
Carnot COP	14	2	4
Relative Efficiency	100%	14%	28%
Energy Consumption (W)	2.2	15	7.5

Imperial College London

A research frontier



Imperial College London

Magnetocaloric principles

Apply magnetic field adiabatically

$S_{total} = S_{magnetic} + S_{lattice} + S_{electronic}$

$S_{magnetic}$	high	$S_{magnetic}$	low
$S_{lattice}$	low	$S_{lattice}$	high

$$\Delta T_{ad}(H,T) = \frac{T\Delta S}{C_p}$$

Can also be described in terms of **isothermal entropy change**, ΔS:

$$\Delta S_{total}(H,T) = \int_0^H \left(\frac{\partial M(T',H')}{\partial T'}\right)_{H'} dH'$$

Maxwell relation for continuous *M(T,H)*

$$\Delta S_{total}(H,T) = -\Delta M \frac{dH_c}{dT}$$

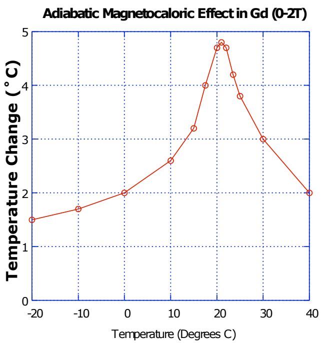
Clausius-Clapeyron eqn. for 1st order transition in *M*

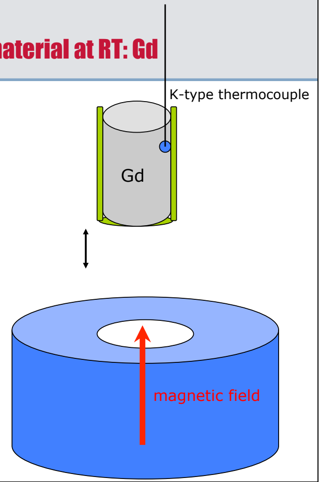
So the material (usually) heats in an applied field ($\Delta T_{ad} > 0$)

The effect is maximal at a (magnetic) phase transition

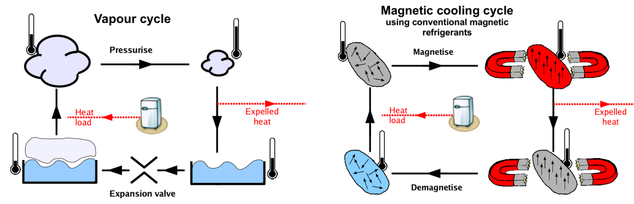
*The sign of (dM/dT) is crucial and yields **two** possibilities for the MCE*

Magnetocaloric benchmark material at RT: Gd



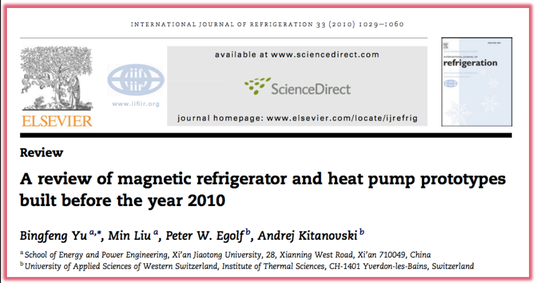


The cycle



K. G. Sandeman, Mag. Tech. Int. 1 30-32 (2011)

State of the art (2010)


INTERNATIONAL JOURNAL OF REFRIGERATION 33 (2010) 1029–1060

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijrefrig

Review

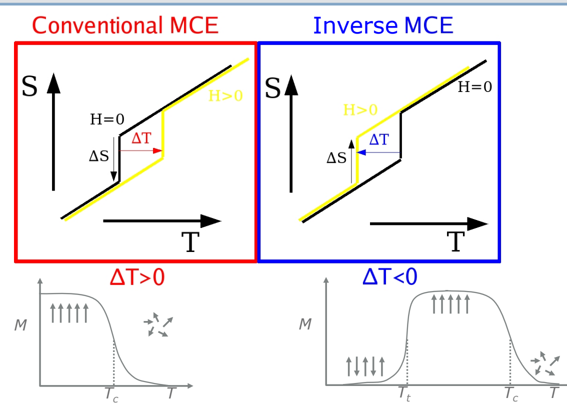
A review of magnetic refrigerator and heat pump prototypes built before the year 2010

Bingfeng Yu [a,*], *Min Liu* [a], *Peter W. Egolf* [b], *Andrej Kitanovski* [b]

[a] School of Energy and Power Engineering, Xi'an Jiaotong University, 28, Xianning West Road, Xi'an 710049, China
[b] University of Applied Sciences of Western Switzerland, Institute of Thermal Sciences, CH-1401 Yverdon-les-Bains, Switzerland

Lists 41 prototypes to 2010.
Most used Gd as refrigerant at that time.
No clear example of end-user integration at that time.
The situation has already changed in the 3 years since…

Magnetocaloric principles



What makes a good magnetic refrigerant?

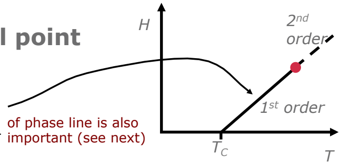
Cheap
d-metal magnetism

MnFe(P,Z)
$La(Fe,Co,Mn,Si)_{13}$

First order transition
because ΔT_{ad} of second order transtion is too low *(if d-metal alloy)*

$$\Delta T_{ad}(H,T) = \frac{T\Delta S}{C_p}$$

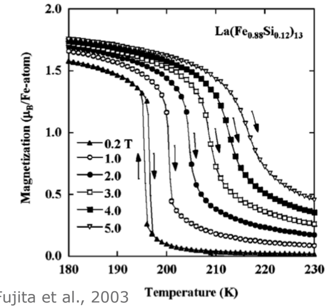
Proximity to (tri)critical point
Minimise energy loss from hysteresis



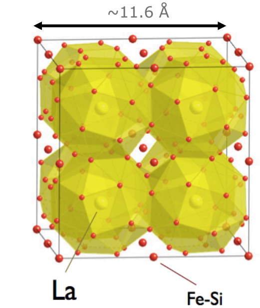
$\frac{\partial H}{\partial T}$ of phase line is also important (see next)

Single phase refrigerants

A candidate magnetic refrigerant at room temperature: $La(Fe,Si)_{13}$



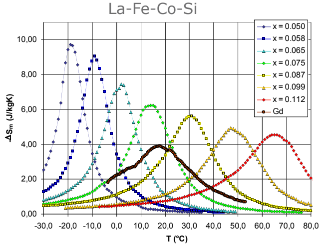
Fujita et al., 2003

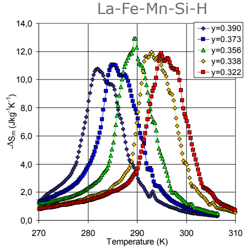


$La(Fe,Si)_{13}$ cubic crystal structure

Tuning transition temperature

VAC VACUUMSCHMELZE





Magnetic entropy change as a function of temperature of: $La(Fe_{0.915}Co_xSi_{0.085})_{13}$ (**left**) and five $LaFe_{11.74-y}Mn_ySi_{1.26}H_{1.53}$ alloys with different *y* (**right**) for a magnetic field change of 1.6 T. The entropy change is higher than that seen in gadolinium (Gd, left plot only).