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Lecture 3: Magnetocaloric materials

Karl G. Sandeman
ESM 2013

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Overview of Lecture 3

1. Examples of tricritical materials
2. What are the limits of magnetocaloric performance?
3. An introduction to several room temperature magnetocaloric materials
4. Some words on measurement
5. An example of material-device integration: the *SSEEC* project
6. Where else to look for caloric effects?
7. Conclusion

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Real tricritical material #1: classic metamagnet $FeCl_2$

MAGNETIC TRICRITICAL BEHAVIOR OF $FeCl_2$

J. A. Griffin* and S. E. Schnatterly
Joseph Henry Laboratories
Princeton University
Princeton, New Jersey 08540

AIP Conf. Proc. **24**, 195 (1975); doi: 10.1063/1.30043

Magnetic Circular Dichroism of $FeCl_2$ vs. Internal Magnetic Field for Different Temperatures

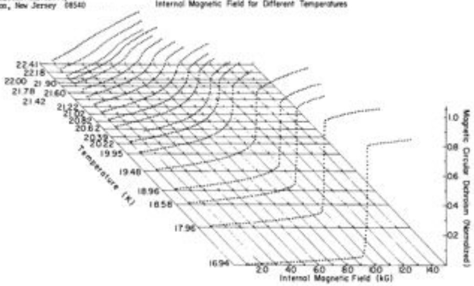

Fig. 3: Normalized magnetic circular dichroism versus internal magnetic field for nineteen isotherms near the tricritical point.

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$FeCl_2$ Continued...

VOLUME 33, NUMBER 18 PHYSICAL REVIEW LETTERS 28 OCTOBER 1974

Tricritical-Point Phase Diagram in $FeCl_2$

R. J. Birgeneau*†
Bell Laboratories, Murray Hill, New Jersey 07974
and
G. Shirane and M. Blume‡
Brookhaven National Laboratory,† Upton, New York 11973
and
W. C. Koehler*†
Oak Ridge National Laboratory,§ Oak Ridge, Tennessee 37830

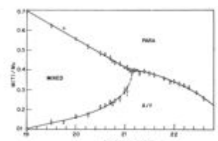

FIG. 1. Reduced magnetization versus temperature in $FeCl_2$ along the first-order phase-separation line and the second-order λ line. The solid (dashed) lines are guides to the eye.

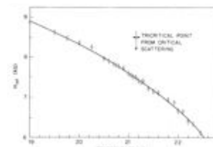

FIG. 2. Internal field versus temperature in $FeCl_2$ along the first-order phase-separation line and the second-order λ line. The solid line is a smooth curve drawn as a guide to the eye.

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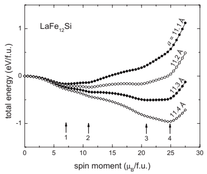
Real tricritical material #2: La-Fe-Si

PHYSICAL REVIEW B **76**, 092401 (2007)

Mechanism of the strong magnetic refrigerant performance of $LaFe_{13-x}Si_x$

Michael D. Kuz'min and Manuel Richter
Leibniz-Institut für Festkörper-und Werkstoffforschung, IFW Dresden, PF 270116, D-01171 Dresden, Germany
(Received 21 June 2007; published 5 September 2007)

Electronic structure calculations reveal the presence of several shallow minima and maxima in the energy-vs-magnetization curves, which otherwise are surprisingly flat. The main implication—a fast magnetization and/or demagnetization process with little hysteresis—is of primary importance for the performance of $LaFe_{13-x}Si_x$ in magnetic cooling devices.



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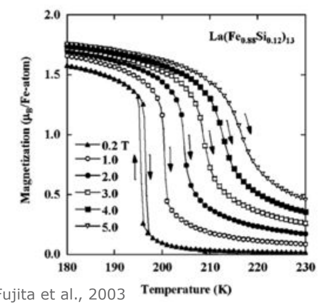
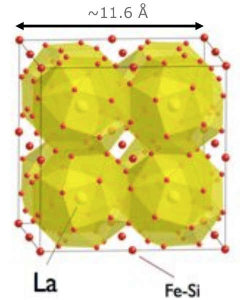
Real tricritical material #2, continued: La-Fe-Si

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



Fujita et al., 2003



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

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Real tricritical material #3: Fe_2P

Similar effects modeled and seen

Phase Transitions, 2002, Vol. 75, No. 1–2, pp. 231–242 Taylor & Francis

FIRST-ORDER TRANSITION OF Fe_2P AND ANTI-METAMAGNETIC TRANSITION

H. YAMADA* and K. TERAO

Faculty of Science, Shinshu University, Matsumoto 390-8621, Japan

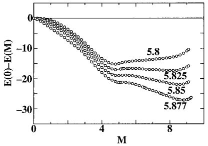
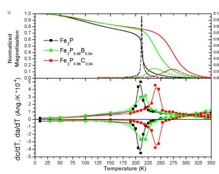


FIGURE 3 Calculated values for $\Delta E(M) = E(0) - E(M)$ in mRy per unit cell as a function of the total moment M (in μ_B/unit cell) for lattice constants $a = 5.8$, 5.825, 5.85 and 5.877 Å.

Experiment:



Gercsi, Sandeman et al., *cond-mat/*

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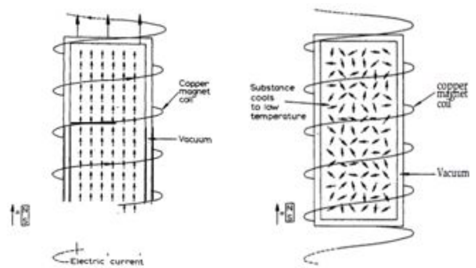
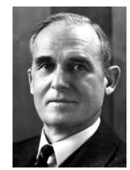
Magnetocaloric principles: not new!

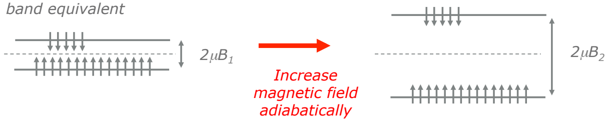




"These are some examples of the type of things that are to be found by those who inquire into the subject of entropy. We consider it a rich field for further investigation."
William Giauque, Nobel Prize Lecture, 1949

Magnetocaloric principles: not new!

e.g. demagnetising a paramagnetic salt - the rubber band equivalent

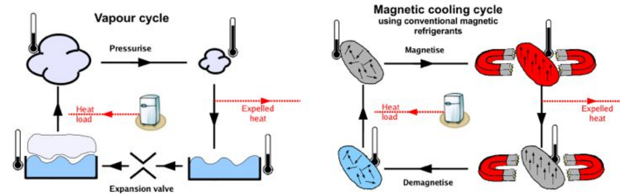


No phase transition here (ie no forced or spontaneous change of state)

Despite bigger energy difference between states, occupation is same (due adiabatic application of field)

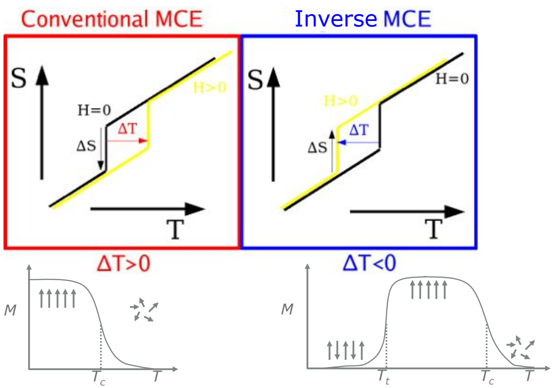
So this new arrangement represents a higher characteristic, thermodynamical temperature

The cycle



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

Magnetocaloric principles



What makes a good magnetic refrigerant?

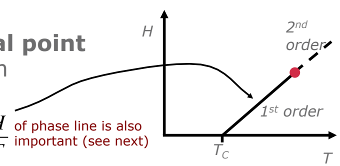
Cheap
d-metal magnetism

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)

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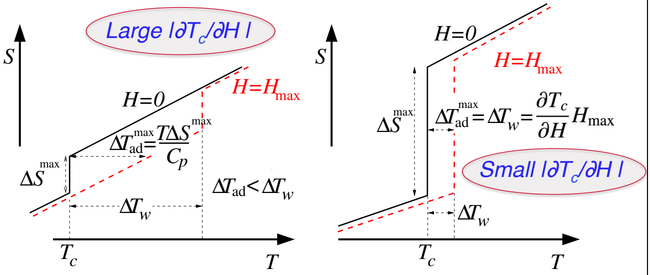
What are the limits?



$$\int_0^\infty \Delta S(T, H_{max})\,dT = M_{sat} H_{max}$$

Refrigerant Sum Rule

K. G. Sandeman, Scripta Materialia **67** 566-571 (2012)

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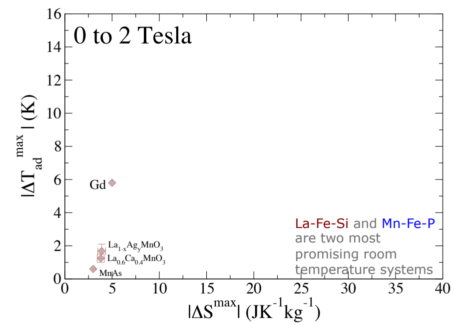
An Ashby plot for magnetic refrigerants



Fe-Rh has AFM-FM transition

Experimental data (diamonds) with error bars indicating compositional variations

K. G. Sandeman, Scripta Materialia **67** 566-571 (2012)

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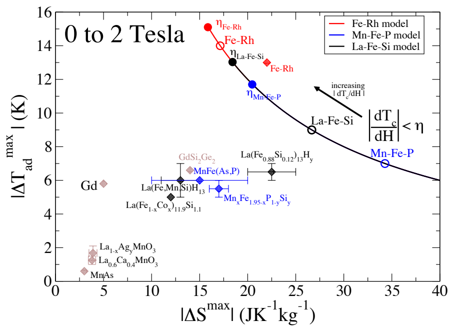
An Ashby plot for magnetic refrigerants



Adding limits:

Open circles: theoretical limits using *experimental* dT_c/dH

Closed circles: theoretical limits using dT_c/dH values that *optimise* ΔT_{ad}

In 2 Tesla, the value of $\mu_0\,|\,\partial T_c/\partial H\,|$ which is optimum is $\mu_0\eta\sim\pm 7$ **KT**$^{-1}$

K. G. Sandeman, Scripta Materialia **67** 566-571 (2012)

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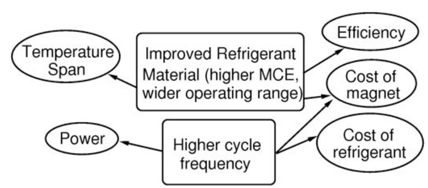
SSEEC

SSEEC Solid State Energy Efficient Cooling

COOPERATION

www.sseec.eu

Scope of the project:



Materials Research Aims:
Identification, synthesis, modelling & production of magnetocaloric materials

Imperial College London, CNRS, SATIE, CMPE, IFW, INRiM, CLIVET, Camfridge, VAC Vacuumschmelze

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Solid State Energy Efficient Cooling

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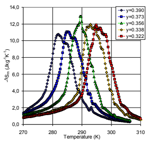
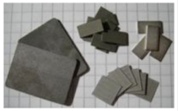
Feedback between the steps in this multidisciplinary research chain is essential





Production (metals) → Fabrication and characterisation (alloys) → Manufacture (plates, particles) → Cooling engine (design integration)

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Strategies for coupling magnetism to the lattice

1) Don't bother! (Gadolinium, second order phase transitions)
2) Push a second order magnetic transition towards a bi/tricritical point ($b \rightarrow 0^+$)
3) Push a first order transition towards a bi/tricritical point ($b \rightarrow 0^-$)

In (2) or (3) we can either:

- Use a magneto-elastic transition (no change of crystal symmetry)
  - $La(Fe,Si)_{13}$, $(Mn,Fe)_2P$, FeRh, CoMnSi, Mn_3GaC
- Use a magneto-structural transition (change in crystal symmetry)
  - Shape memory alloys, Gd_5Ge_4, CoMnGe

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Some examples

Some Examples…

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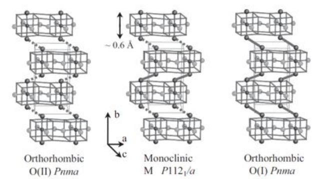
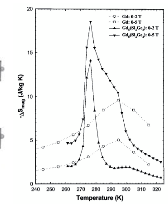
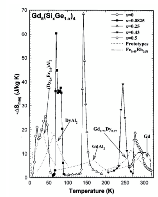
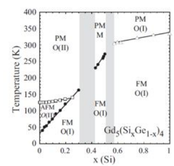
The original giant magnetocaloric: Gd-Si-Ge









V.K. Pecharsky and K.A. Gschneidner Jr., Appl. Phys. Lett. **70**, 3299 (1997)
Phys. Rev. Lett. **78**, 4494 (1997).

Structures differ by number of Si-Ge bonds made or broken

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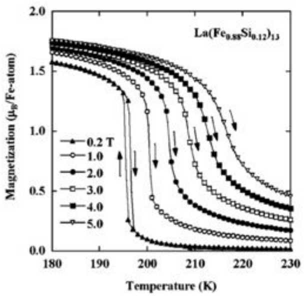
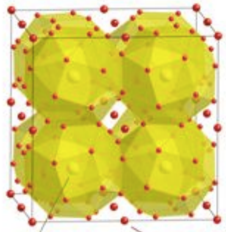
La(Fe,Si)$_3$





Fujita et al., 2003

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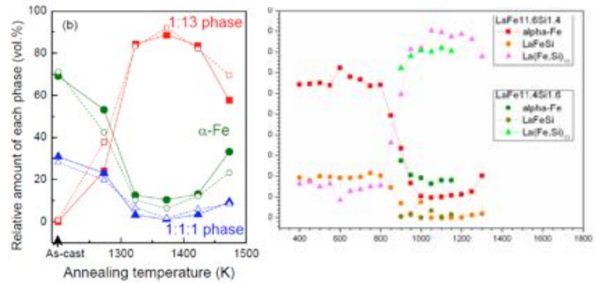
La(Fe,Si)$_{13}$ contd.

Curie temperature ~ 190 K



Left: *Volume fraction of constituent phases as a function of annealing temperature for bulk alloys (closed symbols determined by SEM images, open symbols determined by Rietveld refinement).* ***Right***: *Phase concentration in melt spun ribbons as a function of annealing temperature. Annealing time for all samples was 2 hours.*

Liu et al., *Acta Materialia* (2011)

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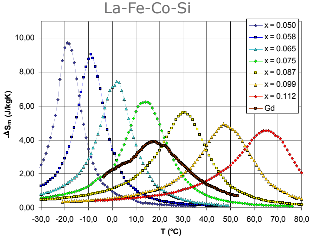
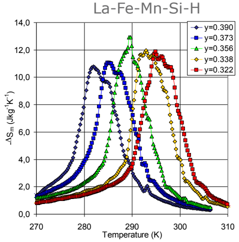
Tuning transition temperature

La-Fe-Co-Si



La-Fe-Mn-Si-H



Magnetic entropy change as a function of temperature of: La(Fe$_{0.915}$Co$_x$Si$_{0.085}$)$_{13}$ (**left**) and five LaFe$_{11.74-y}$Mn$_y$Si$_{1.26}$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).

Katter et al., *private communication*

Barcza et al., *IEEE Trans. Magn.* (2011)

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Hydrogen stability

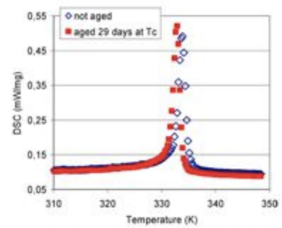

Fig. 1. The aging behavior of fully hydrogenated La$_{1.04}$Fe$_{11.44}$Si$_{1.56}$H$_{1.53}$ produced by rapid solidification. After 29 days at T_C the peak shape is unchanged.

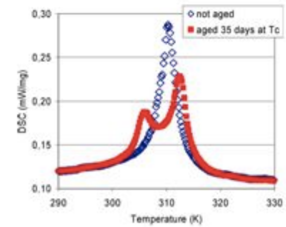

Fig. 2. The aging behavior for partially hydrogenated La$_{1.04}$Fe$_{11.44}$Si$_{1.56}$H$_{1.15}$ produced by arc melting. After 35 days at 309 K the original peak (open symbols) split into two peaks (full symbols).

Barcza et al., *IEEE Trans. Magn.* (2011)

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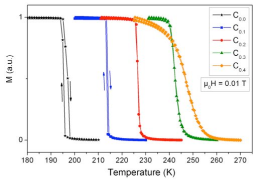
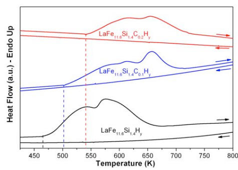
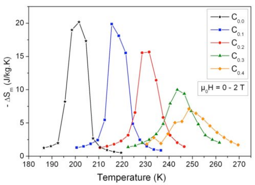
Tuning T_c and controlling H desorption







- With C, desorption temperature is increased to 500 K (x = 0.1) and 540 K (x = 0.2).
- C stabilizes the H in $LaFe_{11.6}Si_{1.4}C_xH_y$ alloys
- Important as the materials should be stable over extended periods of time
- Even small losses in H content translate to large decrease in the working temperature as set by T_c.

C. de Texeira J. Appl. Phys. **111** 07A927 (2012)

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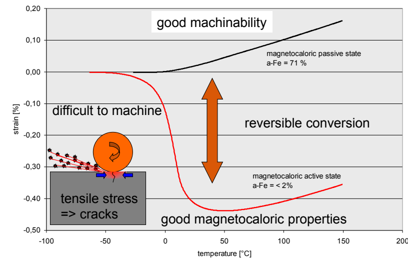
Machinability of La-Fe-Si material



How to avoid cracking during machining

In order to be able to machine parts made of sintered La-Fe-So-Si the materials has to undergo the Thermal Decomposition and Recombination (TDR) process.

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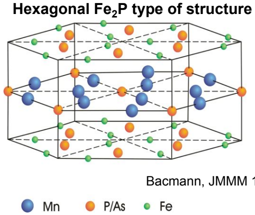
(Mn,Fe)$_2$P-based materials

$MnFeP_{1-x}As_x$

Hexagonal Fe_2P type of structure



Bacmann, JMMM 1994

Mn P/As Fe

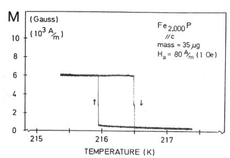
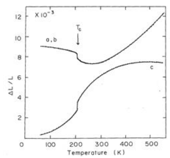


Fig. 10. An M vs T curve for a single crystal of Fe_2P showing the first order ferro- to paramagnetic phase transition.

Lundgren and Nordblad, 1980

Change of c/a ratio across first order phase transition



Fujii et al., 1977

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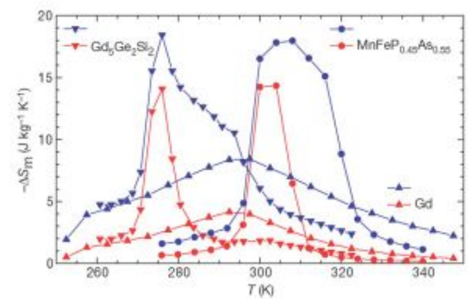
(Mn,Fe)$_2$P-based materials



Tegus et al., Nature (2002)

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$(Mn,Fe)_2P$-based materials

Materials Views — www.MaterialsViews.com — ADVANCED ENERGY MATERIALS — www.advenergymat.de

Mixed Magnetism for Refrigeration and Energy Conversion

*Nguyen H. Dung, Zhi Qiang Ou, Luana Caron, Lian Zhang, Dinh T. Cam Thanh, Gilles A. de Wijs, Rob A. de Groot, K. H. Jürgen Buschow, and Ekkes Brück**

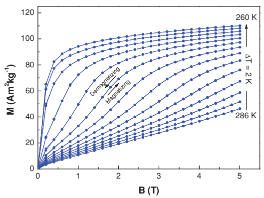
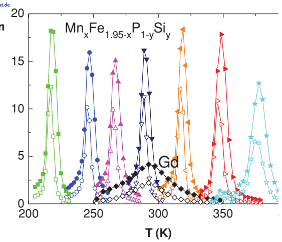


Figure 6. Magnetic isotherms of $Mn_{1.30}Fe_{0.65}P_{0.50}Si_{0.50}$ in the vicinity of the Curie temperature.



re 4. Isothermal magnetic entropy change under a field chan (open curves) and 0-2 T (solid curves) for some typical Mn_xF i_y compounds with from left to right x = 1.34, 1.32, 1.30, 1.28, 0.66 and y = 0.46, 0.48, 0.50, 0.52, 0.54, 0.34, 0.37, respectively of Gd metal under a field change of 0-1 T (open diamond) and d diamond) are included.

Dung et al., Adv. Eng. Mat. (2011)

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Curie temperature and hysteresis dependence

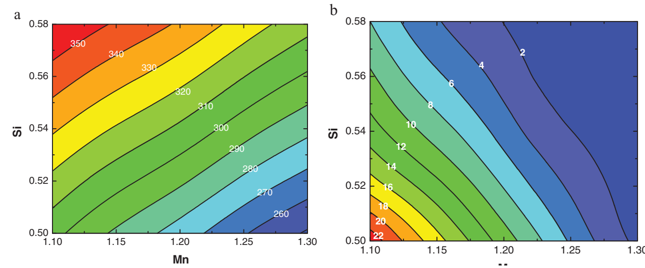

Figure 3. Partial phase diagram of the quaternary (MnFePSi) system (a) illustrating the composition dependence of the magnetic ordering temperature T_C (K) for $Mn_xFe_{2-x}P_{1-y}Si_y$ compounds. (b) Composition dependence of the thermal hysteresis ΔT_{hys} (K) for $Mn_xFe_{2-x}P_{1-y}Si_y$ compounds.

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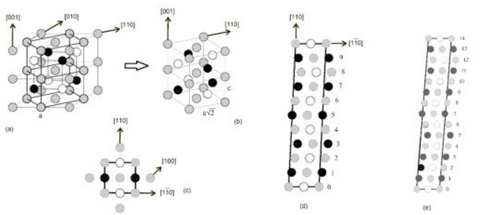
Shape memory alloys



Planes and Mañosa, in *"Magnetic Cooling: from fundamentals to high efficiency refrigeration" Eds. Sandeman and Gutfleisch, (Wiley in press)*

Parent and martensitic structures of Ni-Mn-based Heusler alloys.
a) Parent $L2_1$ structure (Fm3m). Black: 4(a), white: 4(b) and grey: 8(c) positions.
b) The relationship with the tetragonal $L1_0$ unit cell is shown
c) Tetragonal unit cell viewed from top.
d) The 10M structure constructed from nanotwinned variants of the $L1_0$ structure.
e) 14M-modulated structure. "M" refers to monoclinicity which results from the distortion associated with modulation.

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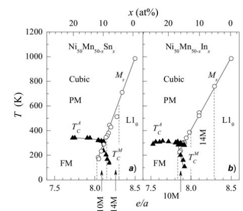
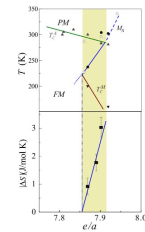
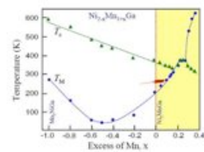
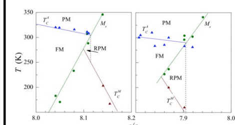
Shape memory ferromagnets: phase diagrams

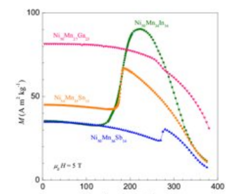








Planes and Mañosa, in *"Magnetic Cooling: from fundamentals to high efficiency refrigeration" Eds. Sandeman and Gutfleisch, (Wiley in press)*



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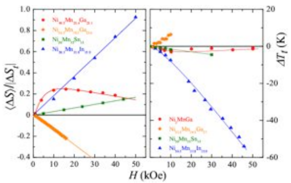
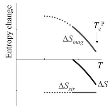
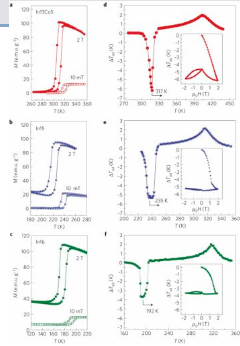
Structural and magnetic entropy, shift of transition temperature





Planes and Mañosa



$$F=\frac{1}{2}a\left(T-T_r\right)\varepsilon^2-\frac{1}{3}b\varepsilon^3+\frac{1}{4}c\varepsilon^4+\frac{1}{2}A\left(T-T_c\right)M^2+\frac{1}{4}BM^4+\kappa\varepsilon M^2$$

Liu et al., Nature Materials (2012)

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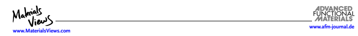
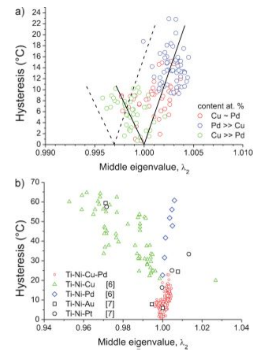
Shape memory alloys: tuning hysteresis


Identification of Quaternary Shape Memory Alloys with Near-Zero Thermal Hysteresis and Unprecedented Functional Stability

By Robert Zarnetta,* Ryota Takahashi, Marcus L. Young, Alan Savan, Yasubumi Furuya, Sigurd Thienhaus, Burkhard Maaß, Mustafa Rahim, Jan Frenzel, Hayo Brunken, Yong S. Chu, Vijay Srivastava, Richard D. James, Ichiro Takeuchi, Gunther Eggeler, and Alfred Ludwig



Hysteresis can potentially be minimised by controlling interfacial strain

Zarnetta et al., Adv. Func. Mat. (2010)

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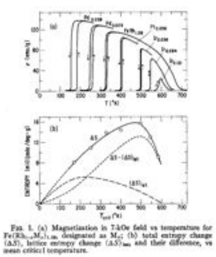
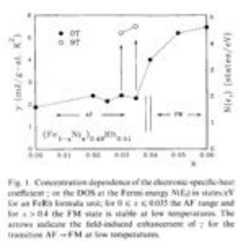
What about antiferromagnets?

Fe-Rh still holds the record for the one-shot ΔT_{ad} per Tesla of applied field.
A ~1μ_B moment develops on the Rh in the FM state!

A large % of ΔS is due to electronic entropy



J.S. Kouvel, J. Appl. Phys. (1966)



K. Kreiner et al., JMMM (1998)

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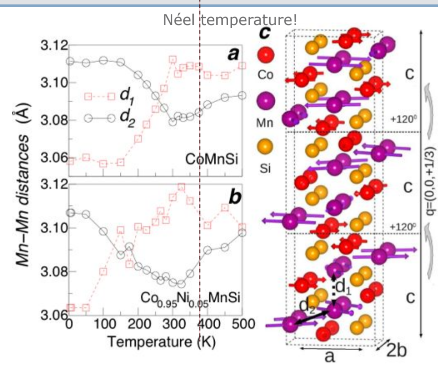
Giant magneto-elastic coupling!



A. Barcza et al., Phys. Rev. Lett. **104** 247202 (2010)

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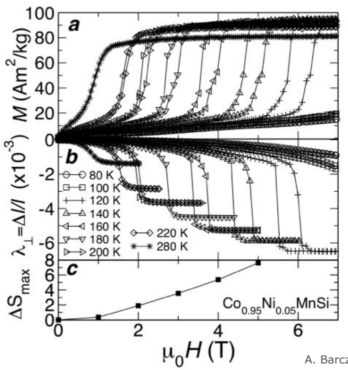
[Co,Ni]MnSi: magnetostriction



Enhanced magnetostriction with onset of first order behaviour

Accompanies enhanced entropy change (magnetocaloric effect)

A. Barcza et al., Phys. Rev. Lett. **104** 247202 (2010)

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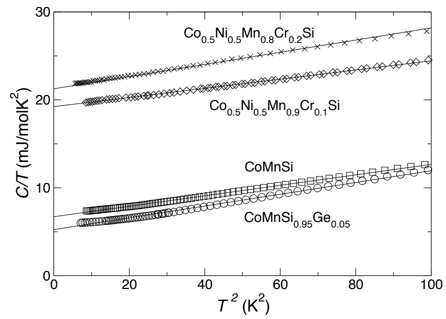
Electronic origin of entropy change



Compositions tuned to high magnetisation (ferromagnetic) ground state

Antiferromagnetic Ground state

A. Barcza et al., Phys. Rev. B **87** 064410 (2013)

Imperial College London

Methods of measurement

Direct

- adiabatic temperature change, ΔT_{ad}
- field-induced latent heat measurement (the first order part of ΔS)

Indirect

- magnetisation vs. temperature and field -> estimated isothermal entropy change
- heat capacity, integrated -> isothermal entropy change and/or adiabatic temperature change

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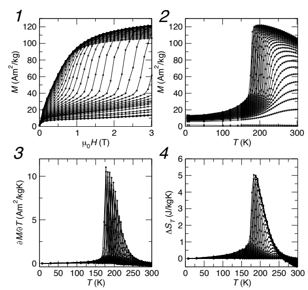
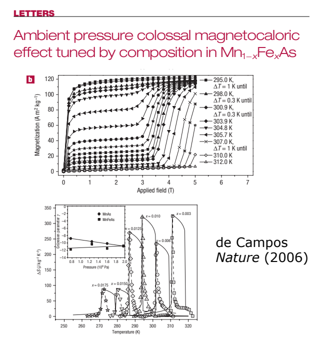
Measurement: estimation of ΔS from magnetisation



A. Barcza, PhD thesis, Cambridge 2009



de Campos *Nature* (2006)

Be careful with magnetisation history

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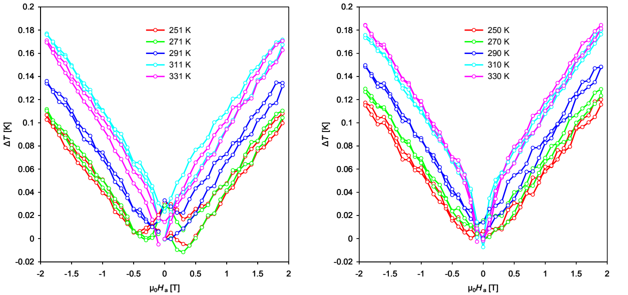
ΔT_{ad}: e.g. in a spin reorientation compound



H parallel to alignment axis

H perpendicular to alignment axis

Pressing equipment (VAC) was used to fabricate magnetically-aligned solid samples of approximately 9 × 9 × 4 mm size.

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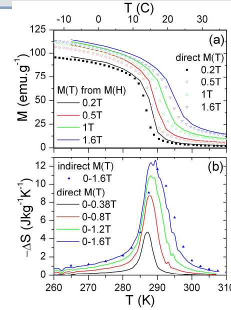
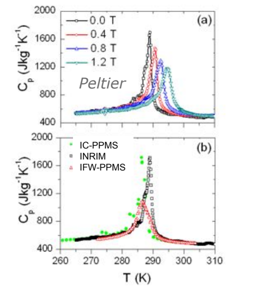
Comparing measurement techniques

Solid State Energy Efficient Cooling

www.sseec.eu



(a) $M(T)$ curves measured directly (VAC) and extracted from $M(H)$ curves (IC/IFW).
(b) Entropy change ΔS calculated from the $M(T)$ curves shown in (a).



(a) INRIM: $C_p(T)$ at different H fields

(b) comparison of 3 different zero-field $C_p(T)$

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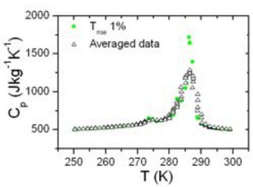
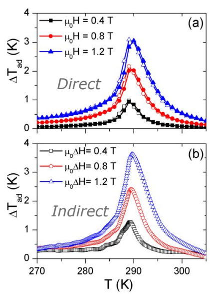
Results of comparison, II

Solid State Energy Efficient Cooling

www.sseec.eu



Result of averaging heat capacity over a large temperature window (~2%T_{bath}) causes the sharp change in heat capacity to instead resemble broad behaviour observed in the pellet.



Good agreement between $\Delta T_{ad}(T)$ curves
~ 10% difference in peak ΔT_{ad}. Could be demag factor or pressing of pellet for upper curve.

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Measurement: phenomenological scaling

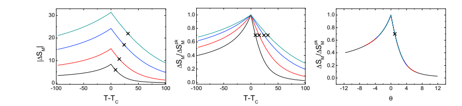
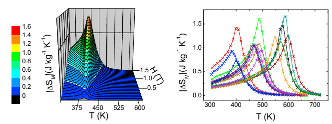


Fig. 2 – The three different steps in the phenomenological construction of the universal curve: identification of the reference temperatures (crosses); normalization; rescaling the temperature axis to place T_r at $\theta=1$.

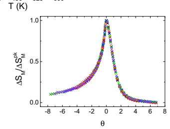


Scaling laws for the magnetocaloric effect in second order phase transitions: From physics to applications for the characterization of materials

V. Franco*, A. Conde

Department of Condensed Matter Physics, ICMSE-CSIC, Sevilla University, P.O. Box 1065, 41080 Sevilla, Spain

INTERNATIONAL JOURNAL OF REFRIGERATION 33 (2010) 465–473



$$\theta = (T - T_C)/(T_r - T_C)$$

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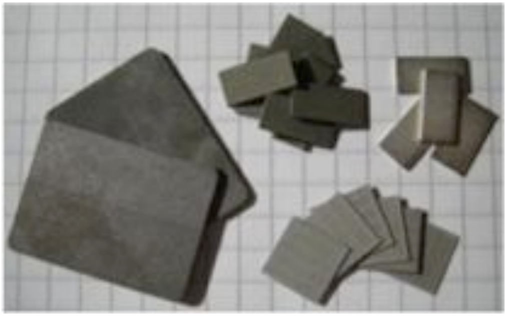
Back to materials...

VAC VACUUMSCHMELZE



Plates of La-Fe-Si material, made by Vacuumschmelze (Germany)

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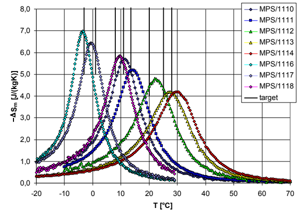
Moving forward 35 years...

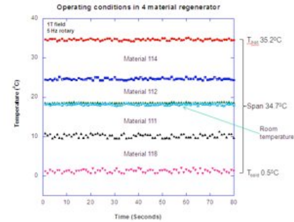
CLIVET The European way to Comfort

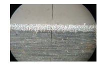
VAC VACUUMSCHMELZE

Camfridge

La-Fe-Co-Si refrigerants







Flat plates machined by EDM

Target for prototype II achieved!

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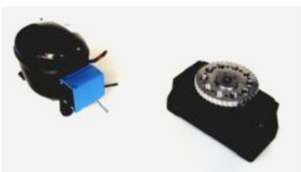
Prototype III

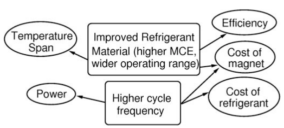
CLIVET The European way to Comfort

VAC VACUUMSCHMELZE

Camfridge

Final device matches weight and size requirements! (Same as gas compressor)





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Where else to look for large changes of entropy?

Elastocalorics

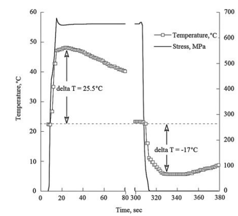
- Strain-driven changes in sample volume
- Large at, e.g. martensitic phase changes
- Hysteresis requires care!

Barocalorics

- Similar, but 3D hydrostatic pressure applied
- MCE materials often yield a "BCE"
  e.g. 0.06 K/MPa in FeRh

Electrocalorics

- Electric field, applied to bulk or to thin film FE/AFE materials



Cui et al., APL (2012)

$$dG = -SdT + \sum_i X_i dY_i$$

$$= -SdT - MdH + Vdp - \varepsilon d\sigma + PdE \ldots$$

Barocaloric *Magnetocaloric* *Elastocaloric* *Electrocaloric*

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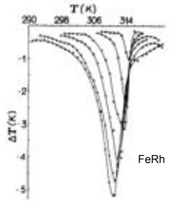

Fig. 3. Temperature dependence of the elastocaloric effect for $Fe_{49}Rh_{51}$ alloy under various tensile stresses: (▲) 56, (□) 151, (▼) 238, (○) 336, (•) 433, (+) 529 MN/m^2.

Nikitin et al., Phys. Lett. A (1992)

$$dG = -SdT + \sum_i X_i dY_i$$

Barocaloric

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Magnetocaloric *Elastocaloric* *Electrocaloric*

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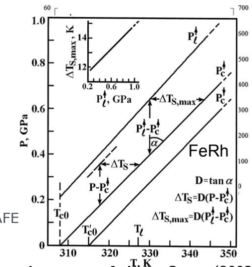

Annaorazov, J. Alloys Comp. (2003)

$$dG = -SdT + \sum_i X_i dY_i$$

Barocaloric

Animated plots
(not preserved in pdf)

$$= -SdT - MdH + Vdp - \varepsilon d\sigma + PdE \ldots$$

Magnetocaloric *Elastocaloric* *Electrocaloric*

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London

Conclusions

EPSRC Engineering and Physical Sciences Research Council
The Newton Trust
COOPERATION
The Leverhulme Trust
THE ROYAL SOCIETY

There's lots of interesting physics, chemistry and materials science in magnetocaloric (MCE) materials!

Structural and calorimetric characterisation is key and can shed light on what triggers the onset of (tri)criticality

[**Theoretical modelling** can help to predict new materials – not shown here

See, e.g. Z. Gercsi et al., Phys. Rev. B **83** 174403 (2011)]

Building a magnetic fridge is an inter-disciplinary challenge that continues to provide challenges in physics, materials science, metallurgy, mechanical engineering, corrosion and other areas.