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Inside the sum

Entropy contributions in conventional magnetocalorics and tricritical metamagnets

Delft Day on Magnetocalorics, Delft, 30th October 2008

Outline

- Introduction to magnetocaloric effect
- The CoMnSi system: a tricritical metamagnet

  Separation I: 1st and 2nd order contributions
  - Co(Mn,Fe)Si
  - CoMn(Si,Ge)

  K. Morrison, J. Moore, Y. Miyoshi and L. Cohen, Imperial College

  Separation II: competing lattice and electronic contributions
  - (Co,Ni)MnSi (see also Alex Barcza's talk this afternoon)
- Adding in harmony: bicriticality in CoMn(Ge,Sn)

  Recombining lattice and magnetic entropies
  - CoMnGe as a second order ferromagnet
  - CoMn(Ge,Sn) as a first order ferromagnet
- Do we even need a magnetic field?
- Conclusions

  How to make a magnetic fridge

The problem

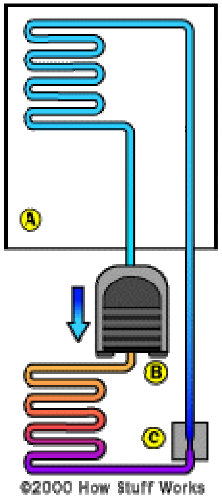
(with gas compression refrigeration)

+

- Cheap to produce
- Established technology
- Works reliably for 1000s of hours

–

- Fairly inefficient and irreversible
- CFC refrigerants damaged the ozone layer
- HFC is a global warming gas
- Noisy and not operational in all orientations ▪ ▪



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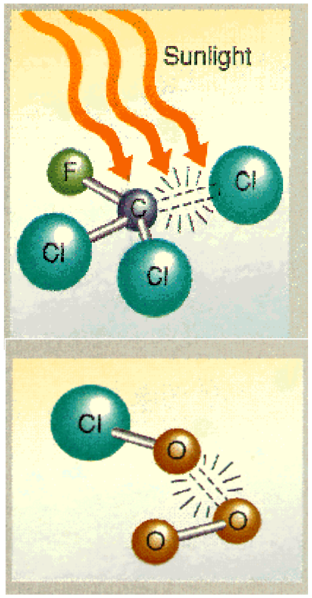
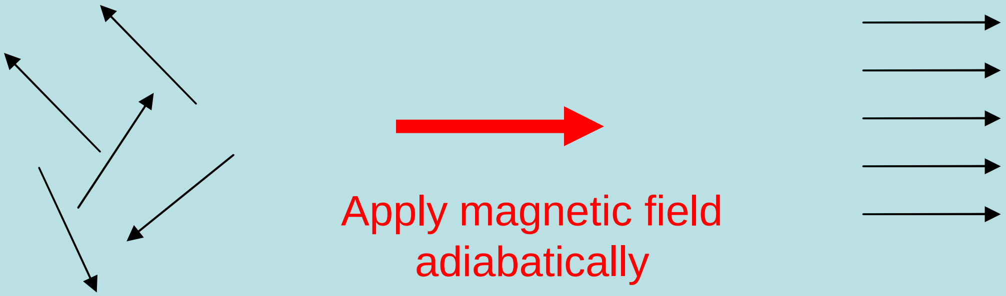


... and a solution?

Technology	Conventional gas compression	Gas absorption	Peltier electric coolers	Thermo-acoustic	Magnetic fridge
Change of state	Liquid↔Gas	Liquid↔Gas	$e^- \leftrightarrow h^+$	High p gas ↔ low p gas	magnetic states
Max. Efficiency (% of Carnot)	45%	30%	<10%	40%	60%
Main uses	Many	Mobile	Small-scale	Early: gas liquefaction	V. early

Conventional magnetocaloric effect (MCE)



Apply magnetic field adiabatically

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

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

Effect is maximal at a (magnetic) phase transition

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

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)*

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

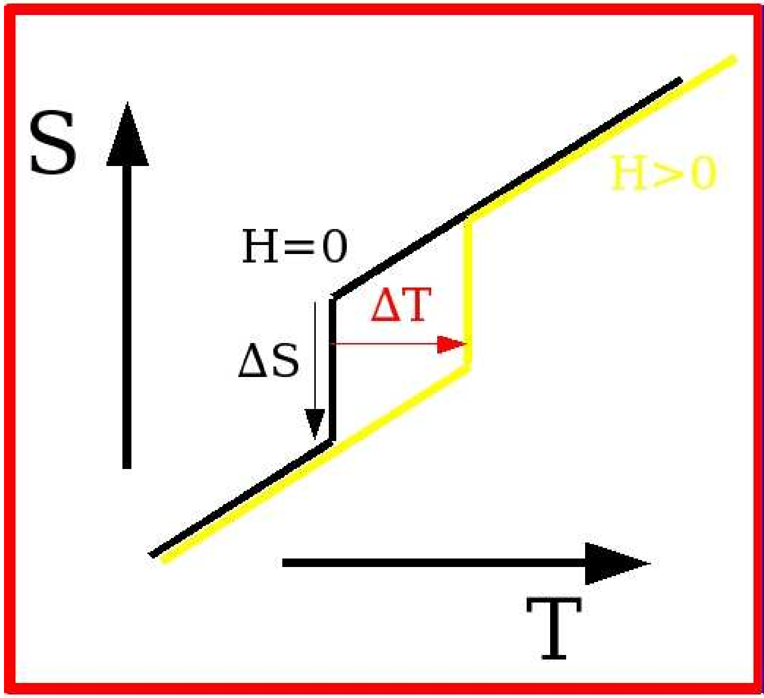
Clausius-Clapeyron eqn. for 1st order transition in *M*

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

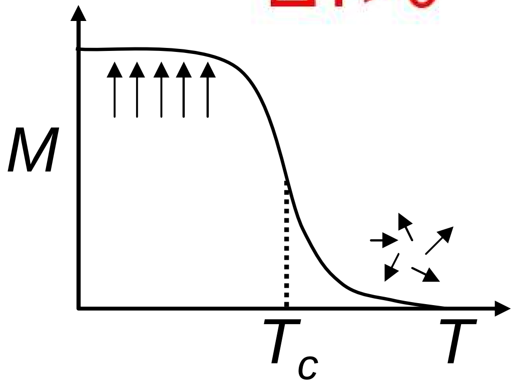
Entropy curves for MCE

shown here for 1st order transitions

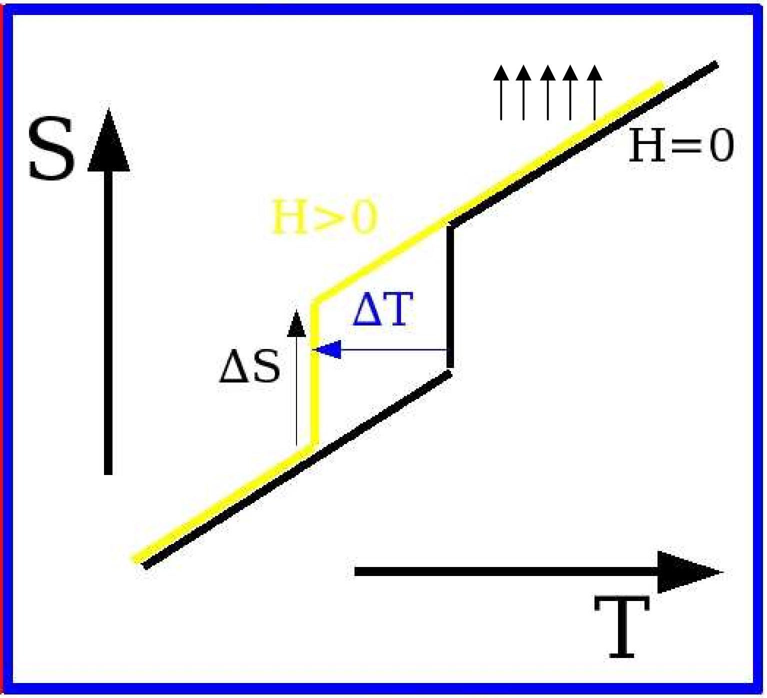
Conventional MCE



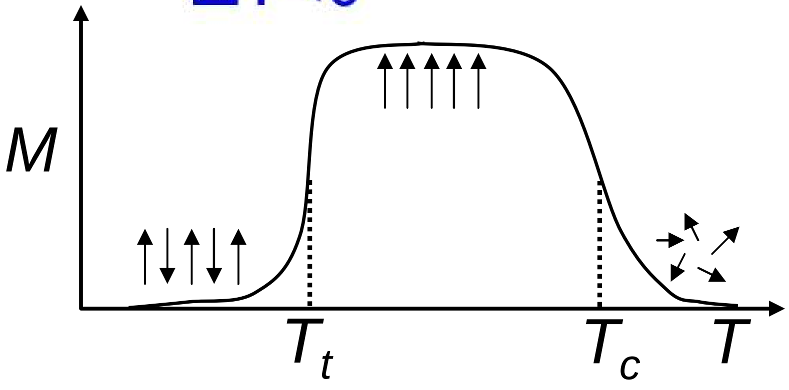
$\Delta T > 0$



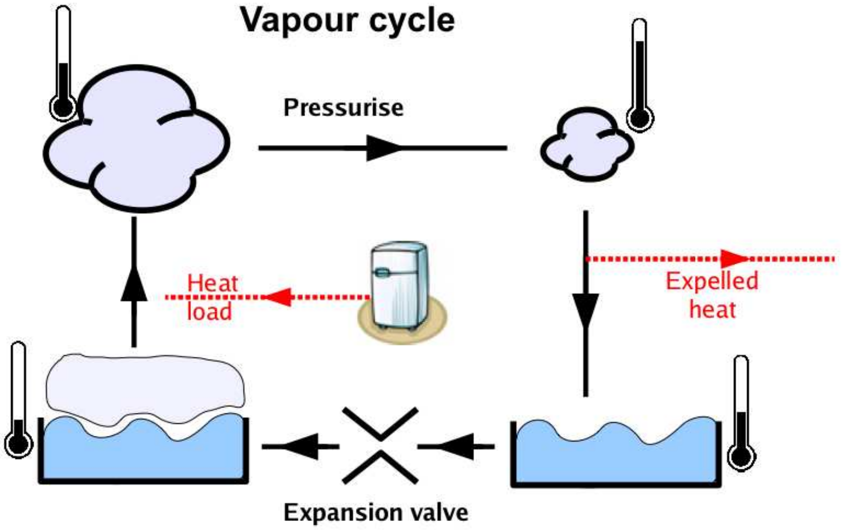
Negative MCE

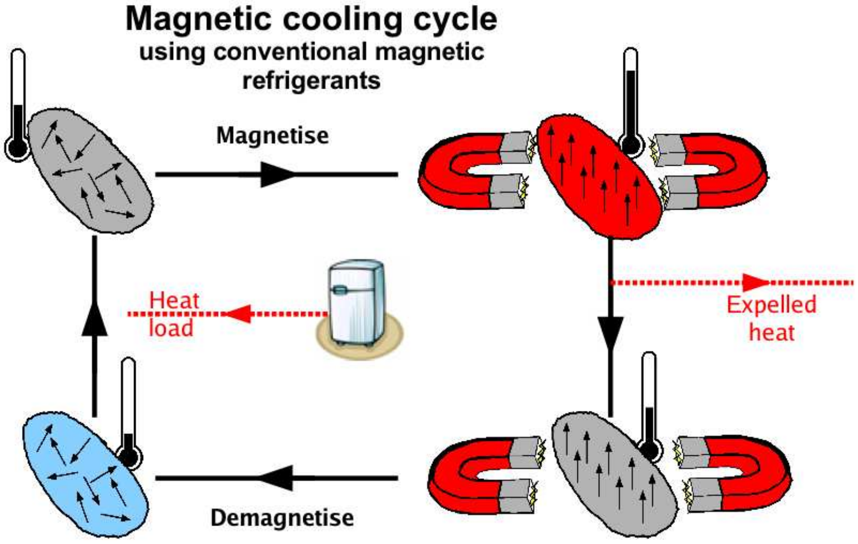


$\Delta T < 0$



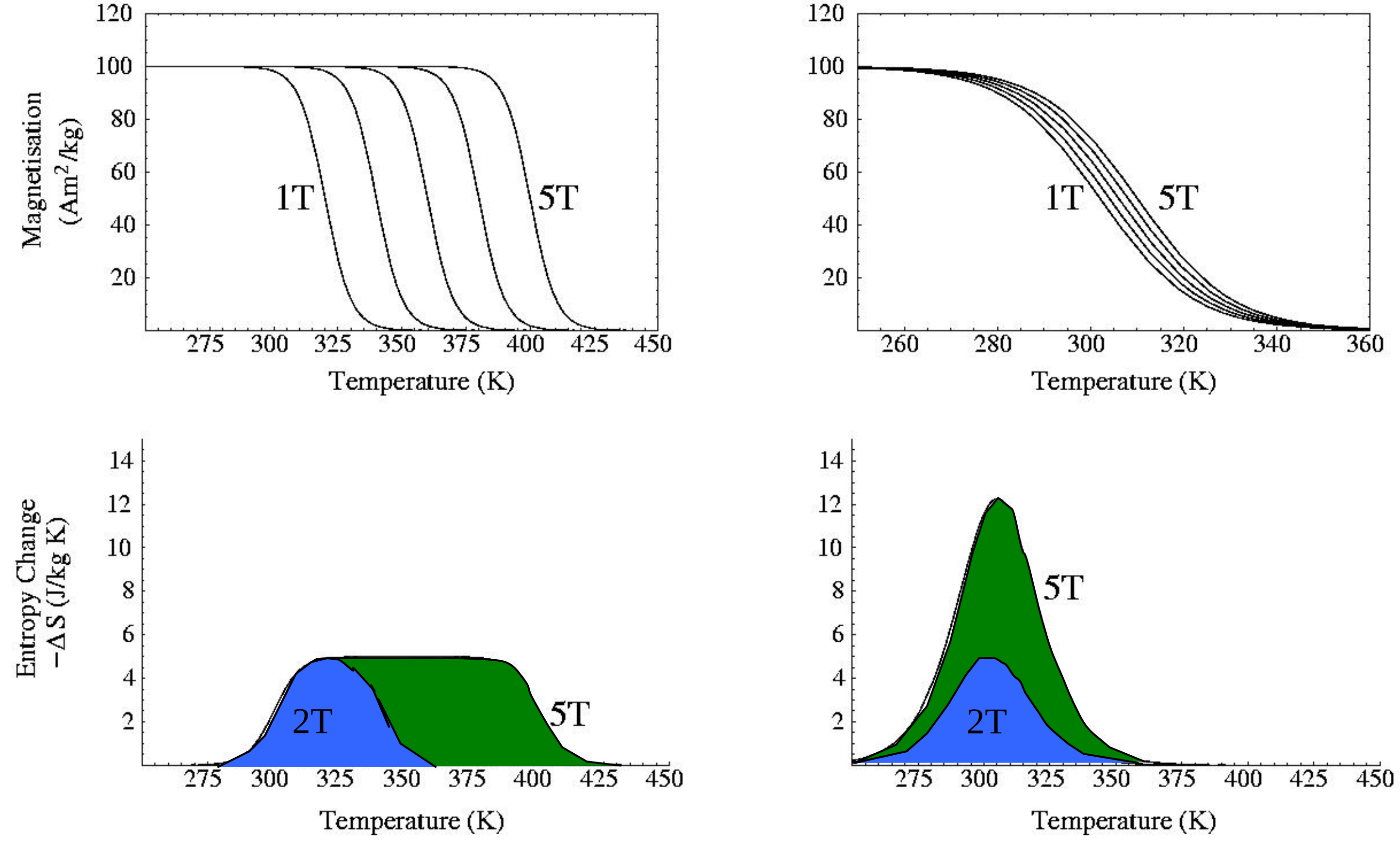
Schematic refrigeration cycle





Phenomenology

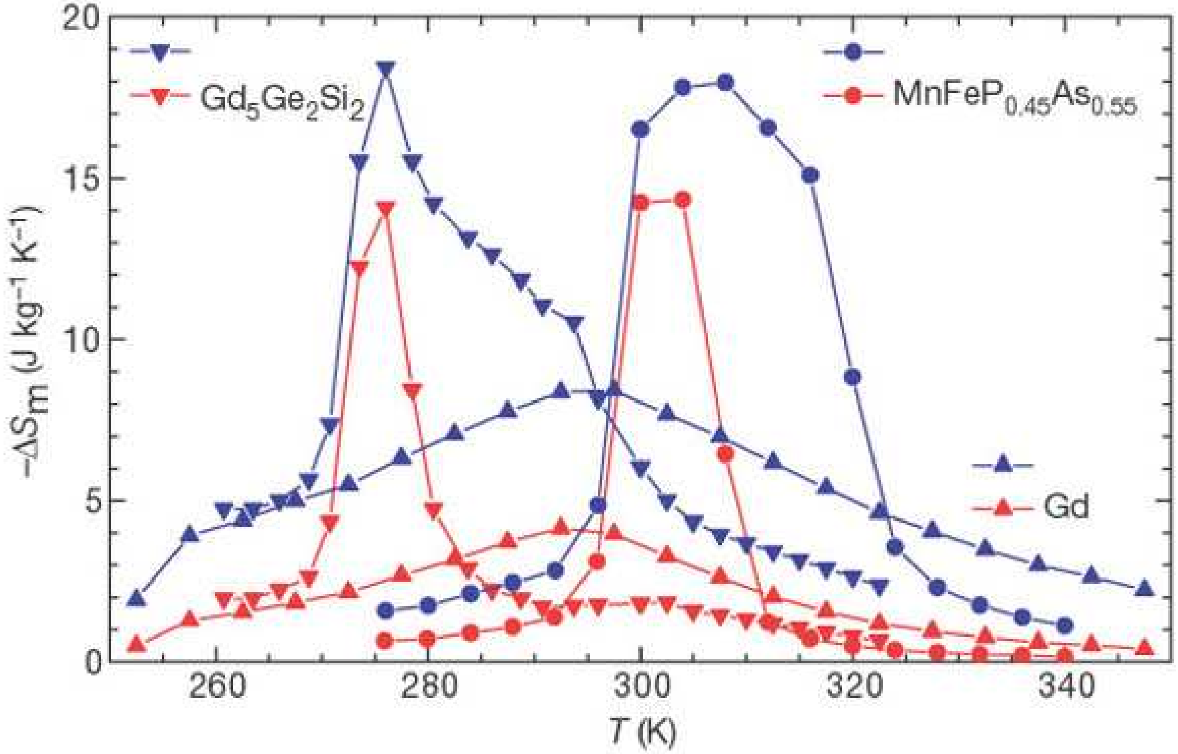
sharp transition with high $\left(\frac{dT_c}{dH}\right)$ gradual transition with lower $\left(\frac{dT_c}{dH}\right)$



$$\Delta S_{total}(H,T) = -\Delta M \frac{dH_c}{dT} = \Delta M \left(\frac{dT_c}{dH}\right)^{-1}$$

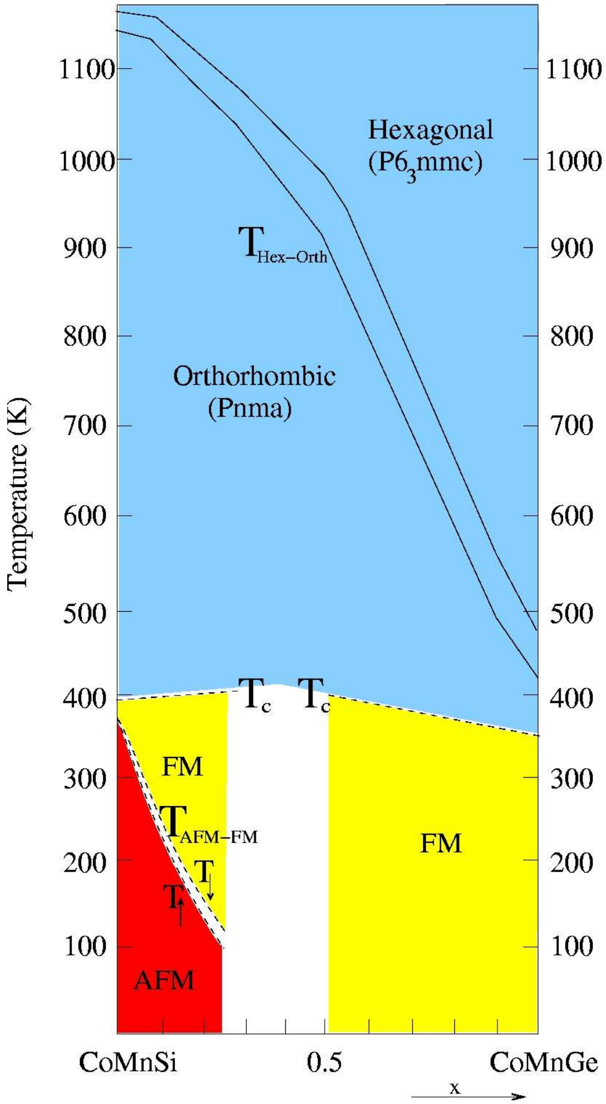
$$\Delta S_{total}(H,T) = \int_0^H \left(\frac{\partial M(T',H')}{\partial T'}\right)_{H'} dH'$$

Some examples of large MCE



Tegus et al., (2002)

Example system: CoMn(Si,Ge,Sn)



Shows many of types of interesting transitions

- AFM/FM (second order and first order, “inverse” MCE),
- FM/PM (second order *and first order*)
- *Martensitic structural transition, can be merged with Tc*
- Not untypical of Mn-based magnetism!

- Samples made by RF melting and subsequent annealing.

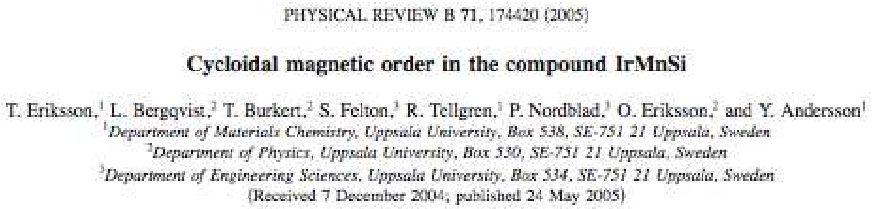
🟦 No long range magnetic order

🟥 Antiferromagnetic

🟨 Ferromagnetic

Niziol et al., (1989)

Cycloidal spin order and crystal structure



PHYSICAL REVIEW B 71, 174420 (2005)

Cycloidal magnetic order in the compound IrMnSi

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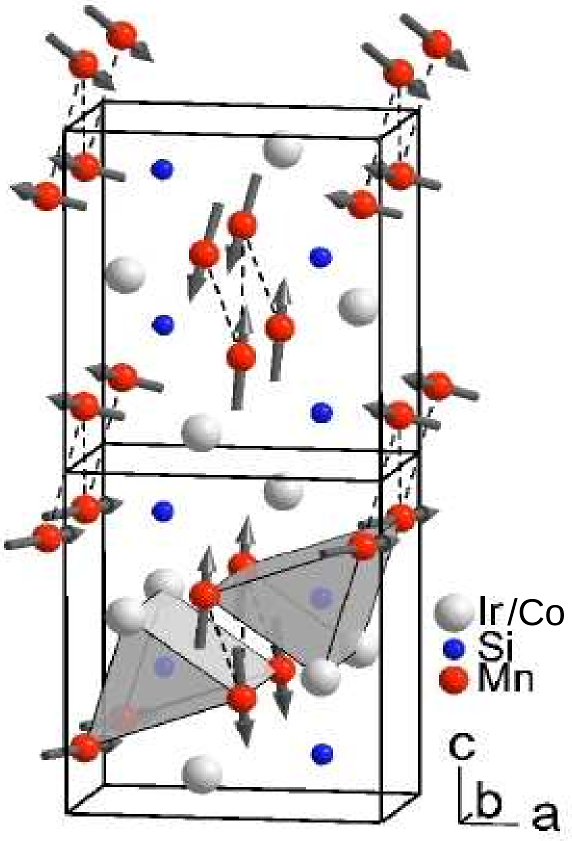
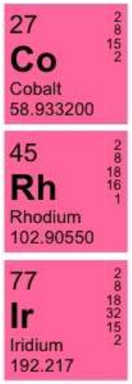
(Received 7 December 2004; published 24 May 2005)

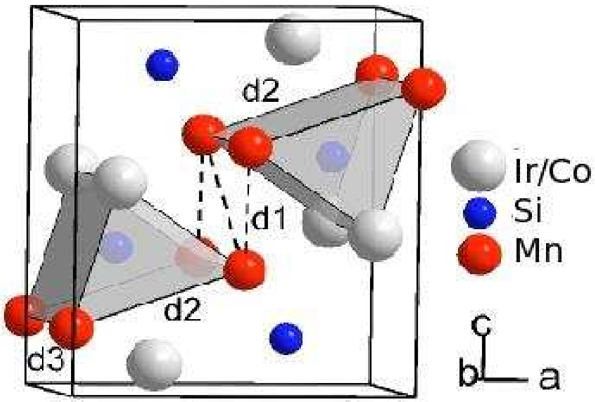
$m_{Mn} \sim 2.2 - 2.6\mu_B$

$m_{Co} \sim 0.2 - 0.4\mu_B$



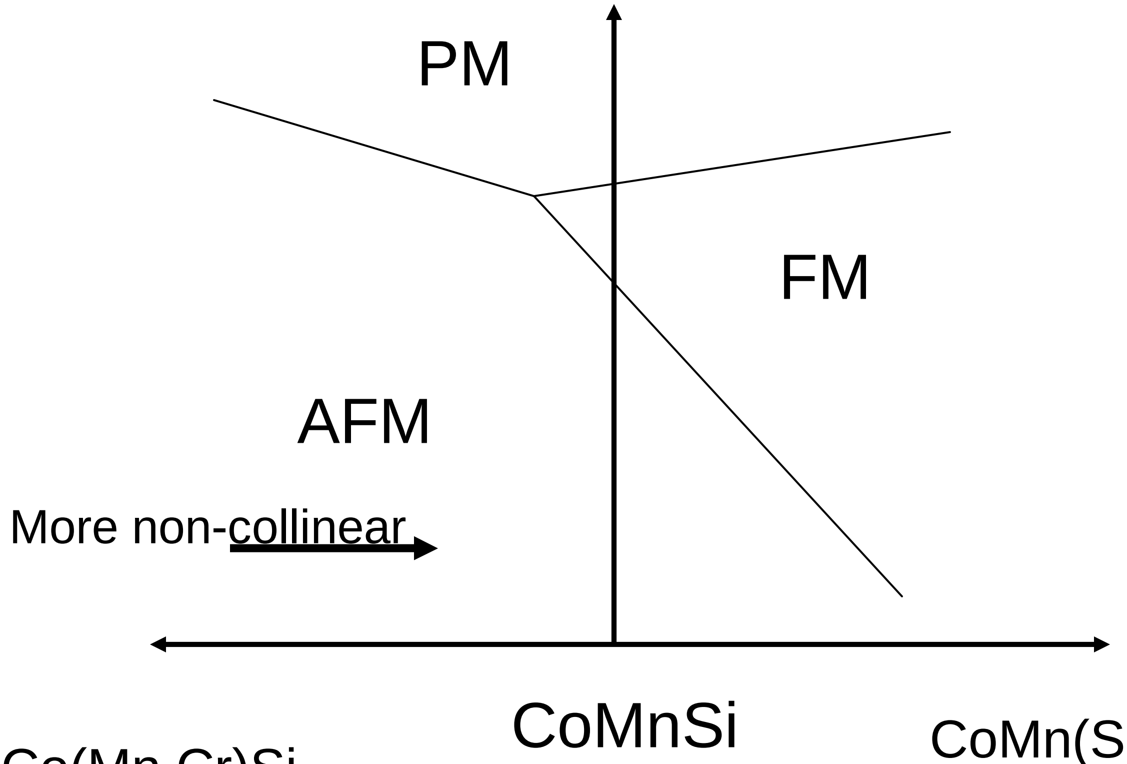


	Vol (Å^3)	T_N or T_t (K)	T_C (K)
CoMnSi	148.2	381	420
IrMnSi	168.0	367	N/A
RhMnSi	173.0	460	N/A



In IrMnSi, Q is close to [0 0 0.45]. For CoMnSi, Q ~ [0 0 0.34]

General phase diagram (close to CoMnSi)



PM

FM

AFM

More non-collinear

CoMnSi

Co(Mn,Cr)Si

RhMnSi

IrMnSi

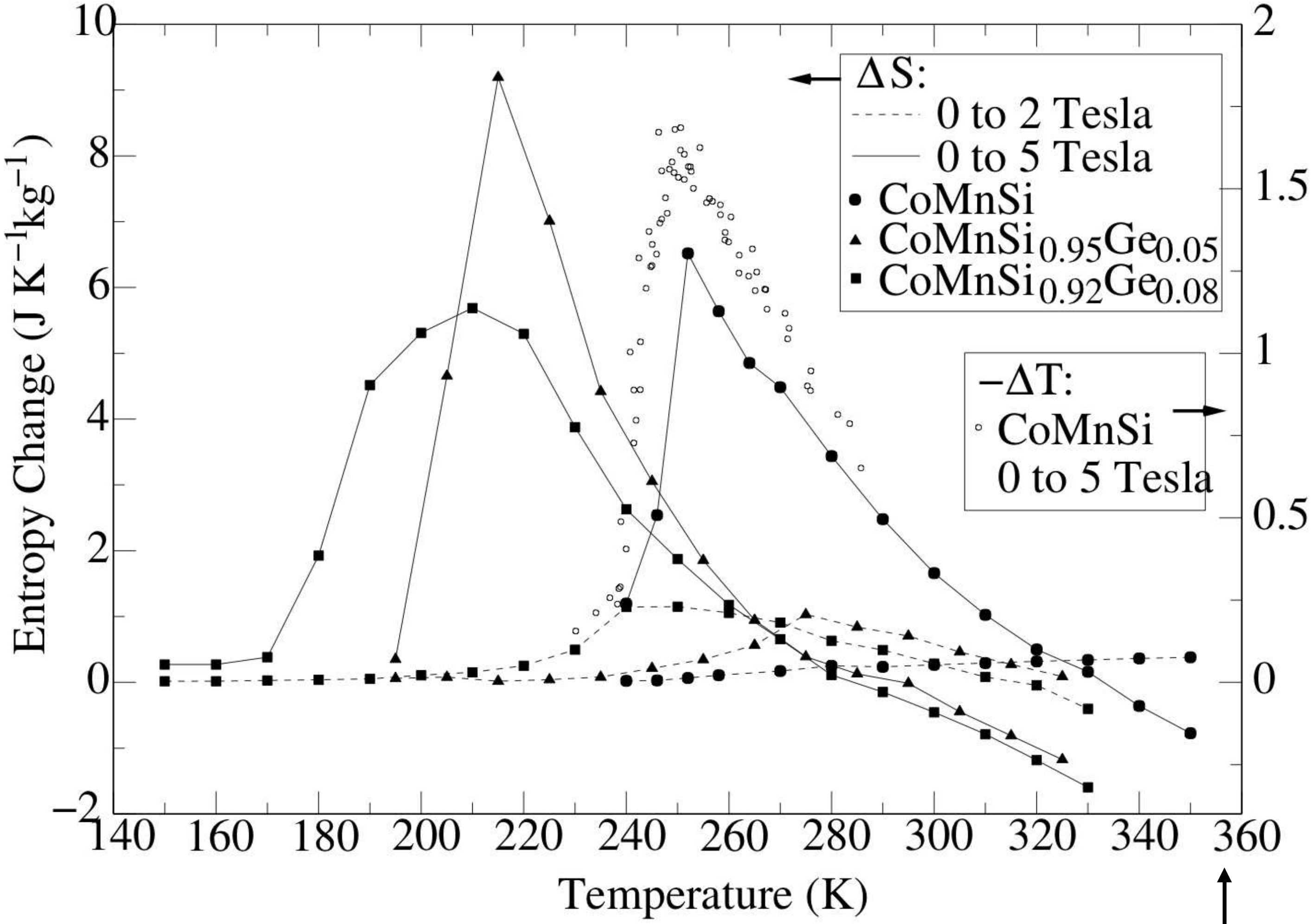
CoMn(Si,Ge)

Co(Mn,Fe)Si

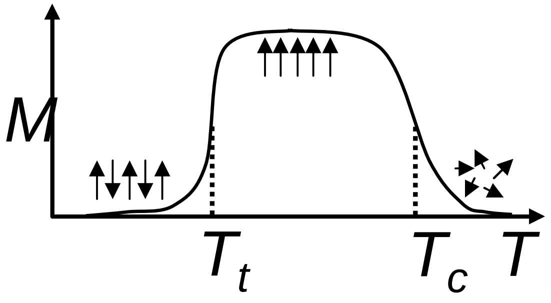
(Co,Ni)MnSi

Co(Mn,Ni)Si

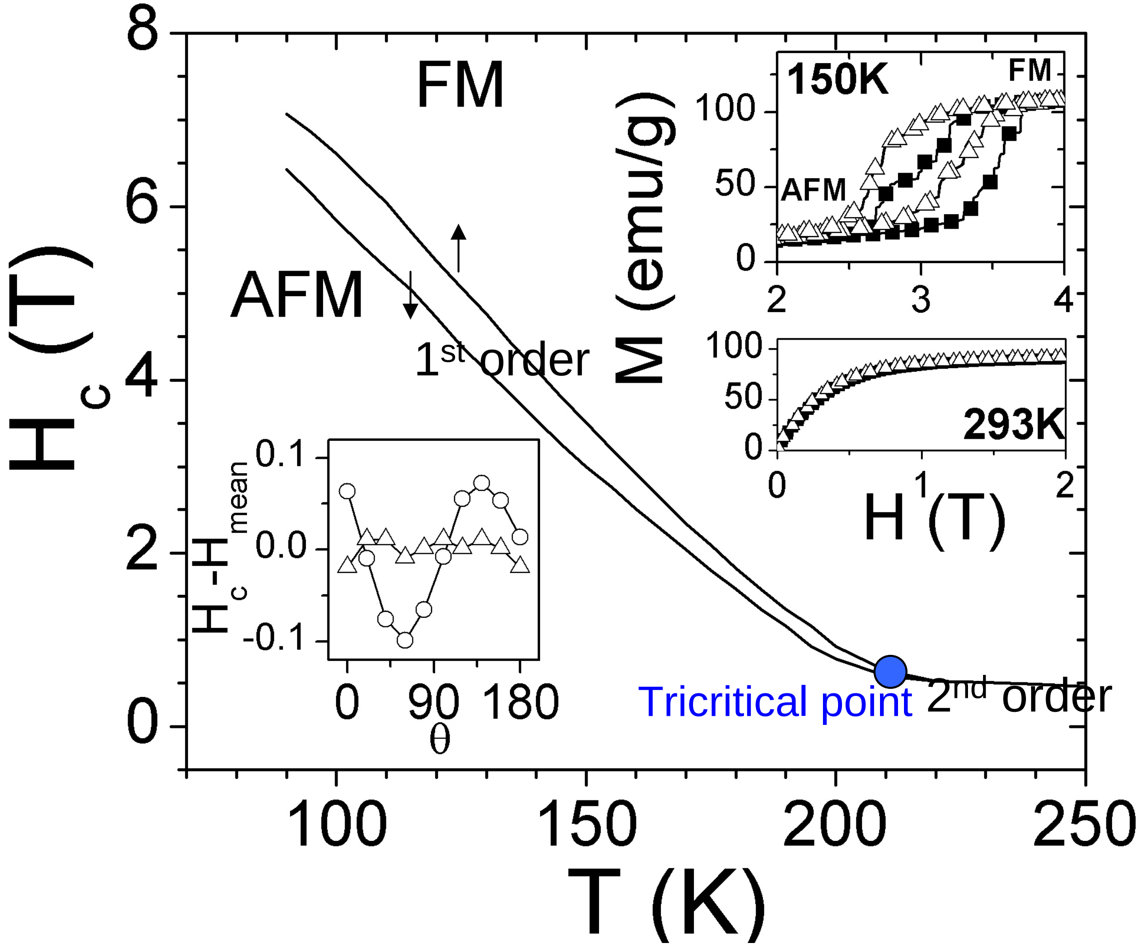
Previous results: CoMn(Si,Ge)

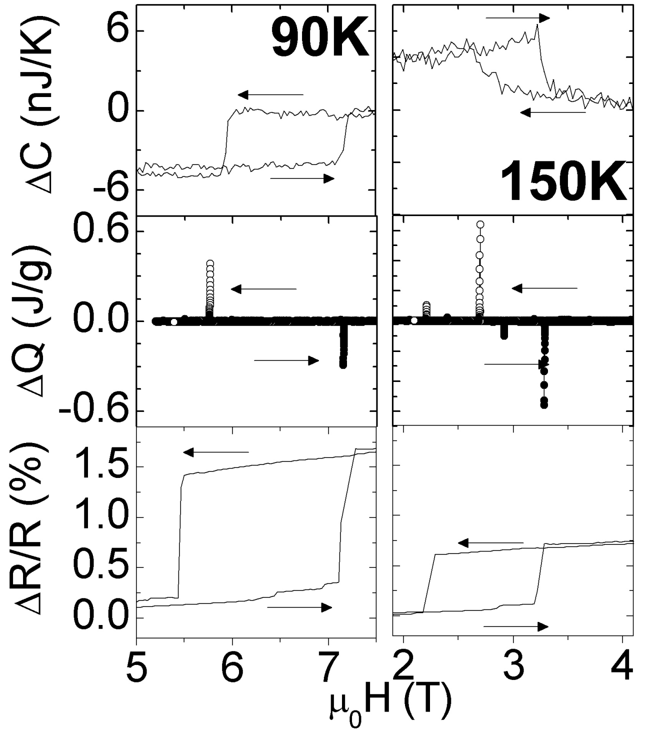


Sandeman et al., Phys. Rev. B (2006)



Tricriticality in $CoMn_{0.95}Fe_{0.05}Si$



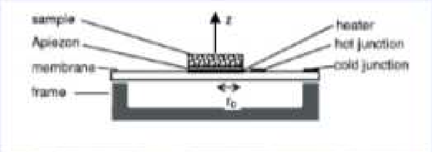


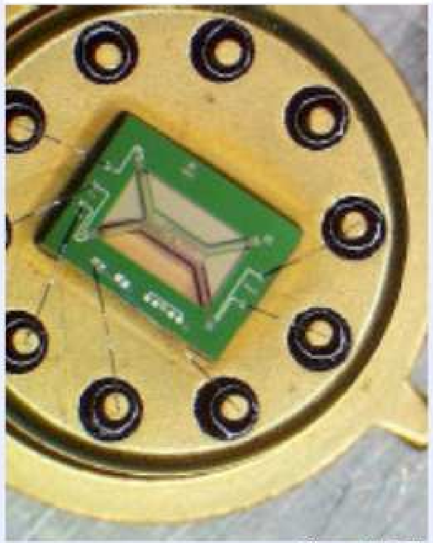
An example of *tricriticality*
We observe this in many
CoMnSi-based metamagnets

Morrison et al., Phys. Rev. B *to appear* (2008)

Measurements of heat capacity and latent heat using a SiN membrane sensor

- Adiabatic set-up
- Measure V_{th} as field is ramped
- Latent heat causes jump in V_{th}
- Use heat capacity data to convert to ΔT and ΔS





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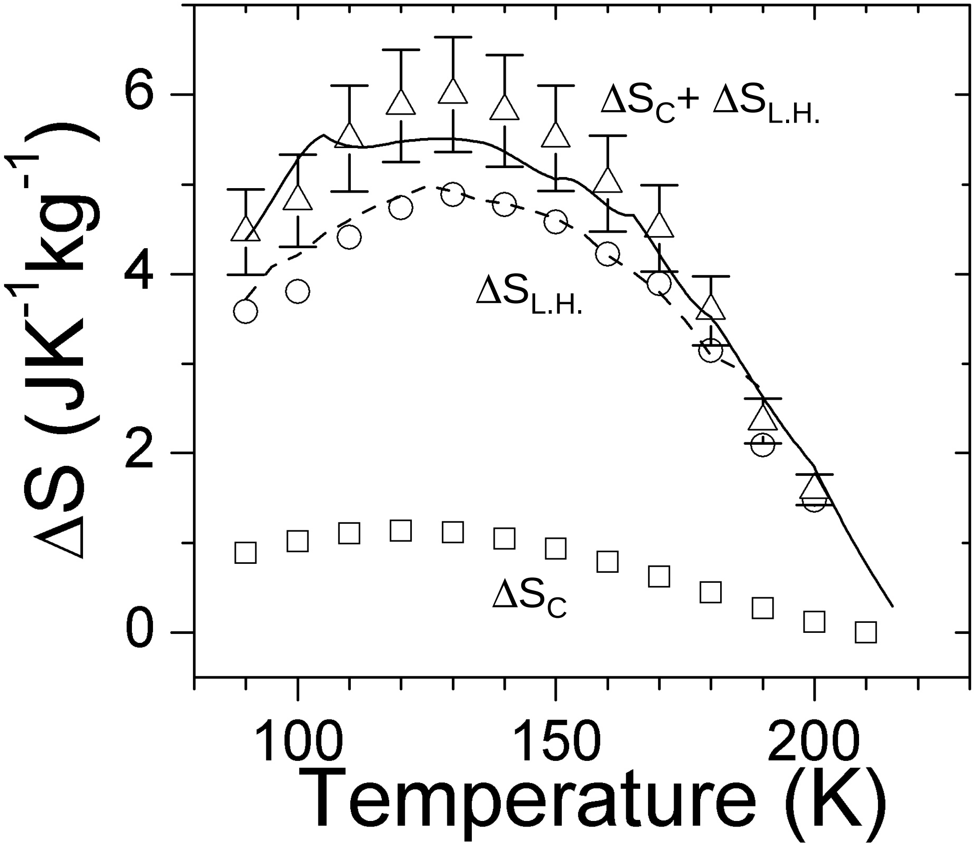
Separation I: First order and second order contributions



-- Clausus-Clapeyron relation
— Maxwell relation

Self-consistent separation and calculation of 1st and 2nd order contributions to the entropy change

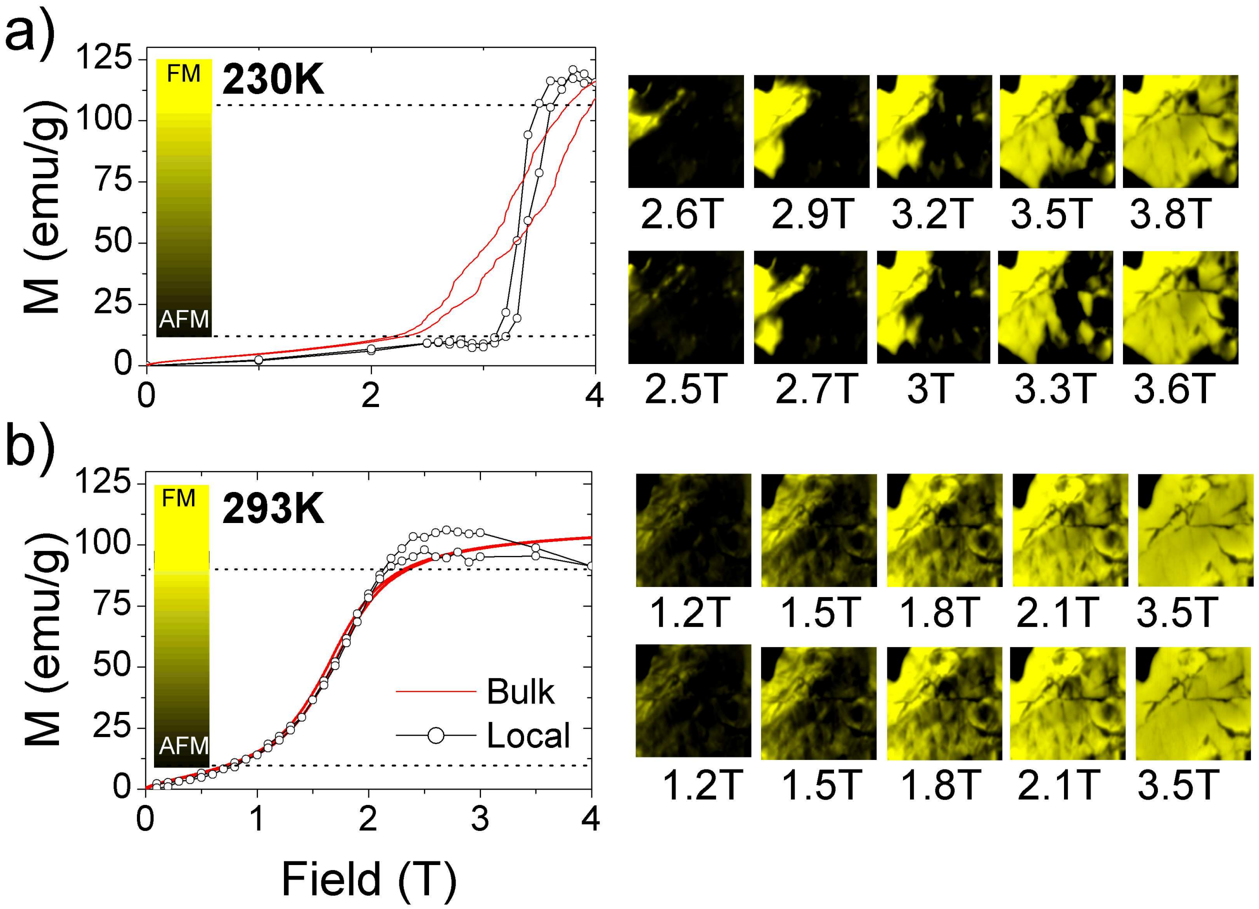
$CoMn_{0.95}Fe_{0.05}Si$

Morrison et al., Phys. Rev. B *to appear* (2008)

Tricriticality, contd.

Imaging of $CoMnSi_{0.92}Ge_{0.08}$
From 1st order to 2nd order

Hall probe imaging
(Imperial College)

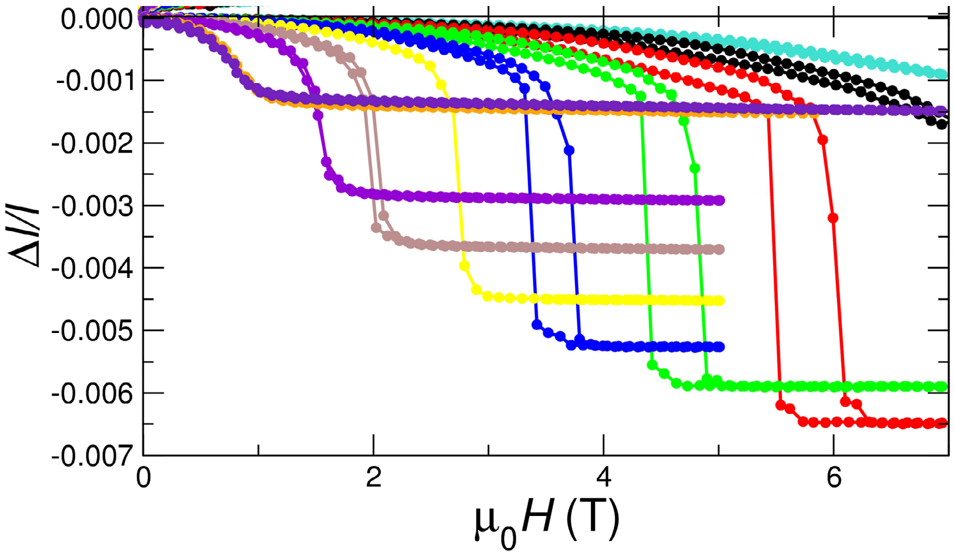


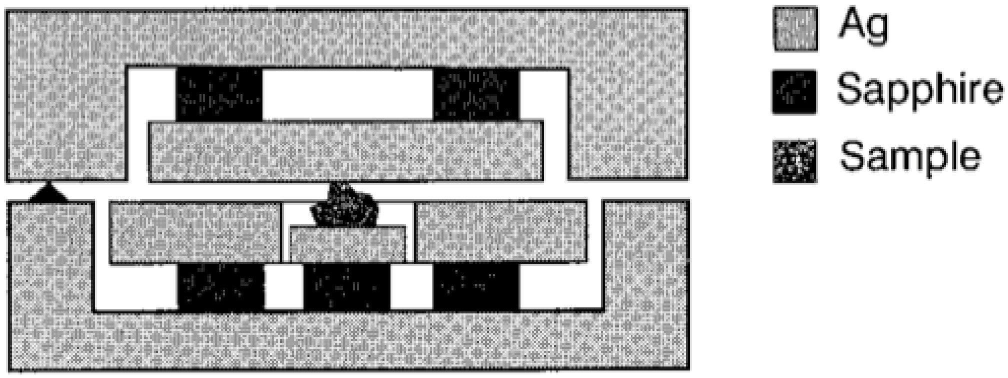
Morrison et al., *in preparation*

Separation II: types of entropy

Magnetostriction (Cambridge)

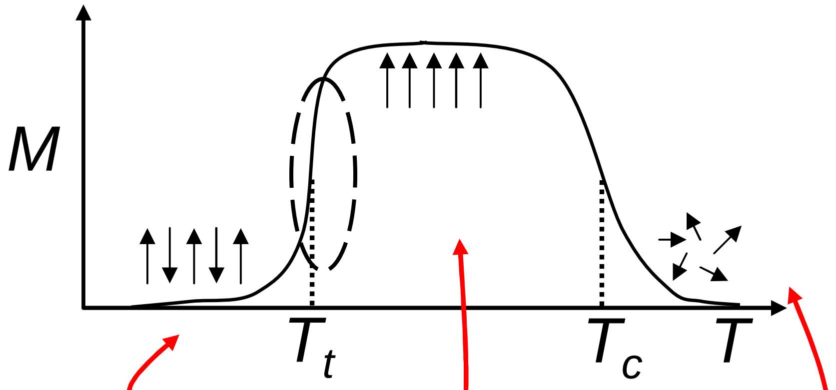
$Co_{0.95}Ni_{0.05}MnSi$





- miniature capacitance dilatometer
- high sensitivity
- look for correlation between *volume change and MCE*

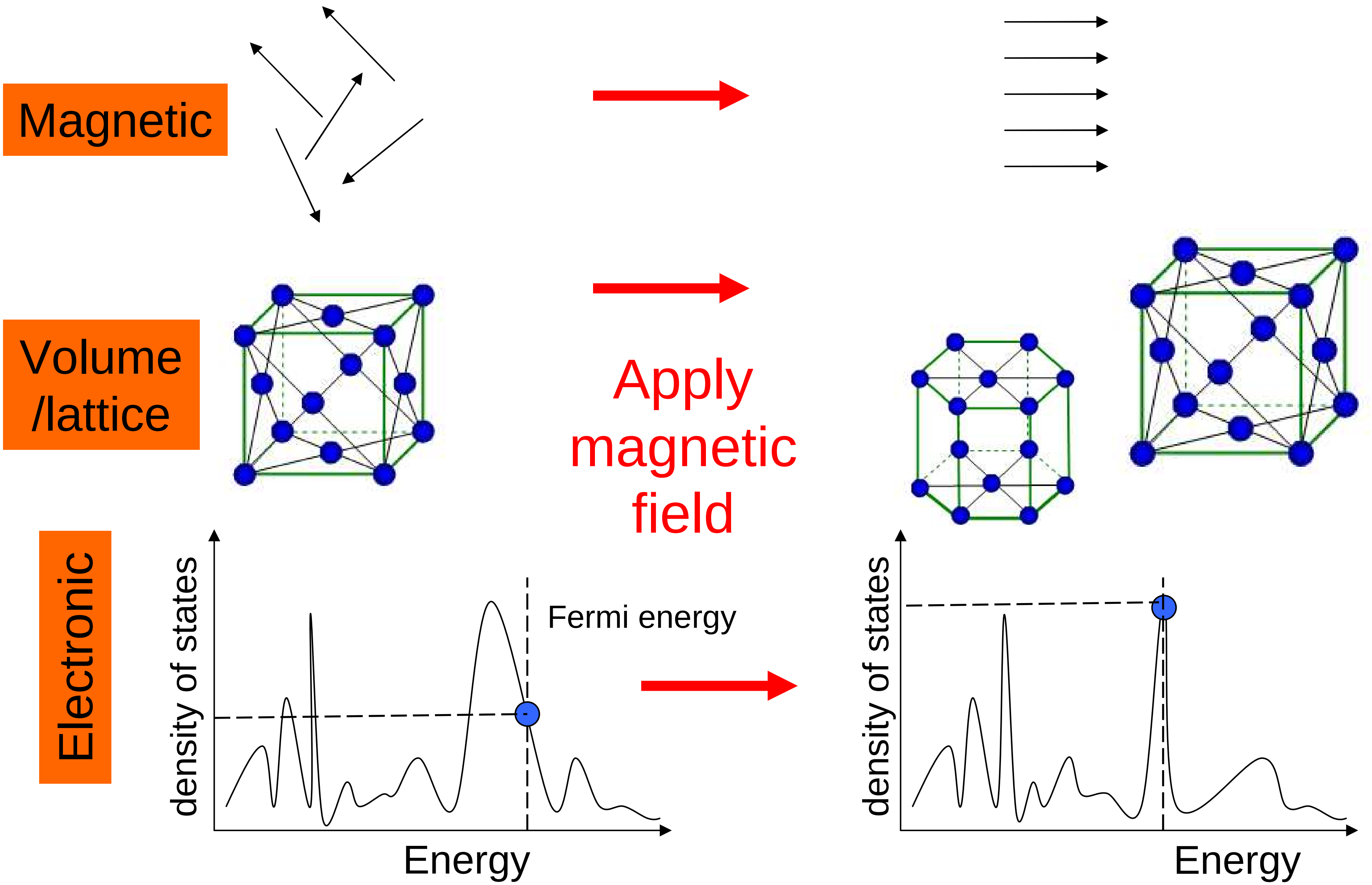
What entropy?



magnetic entropy: low low high

so where does the change in entropy come from?

What entropies are we changing?



Magnetic

Volume /lattice

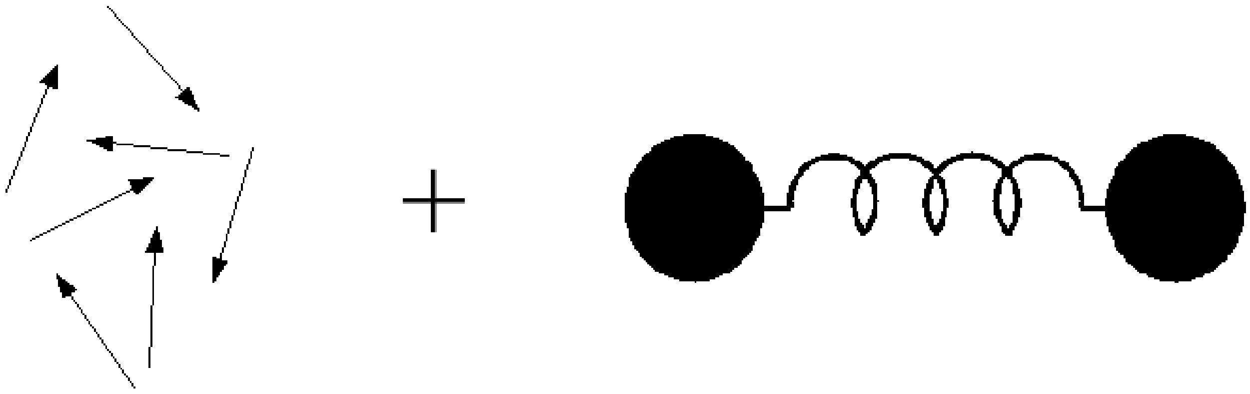
Electronic

Apply magnetic field

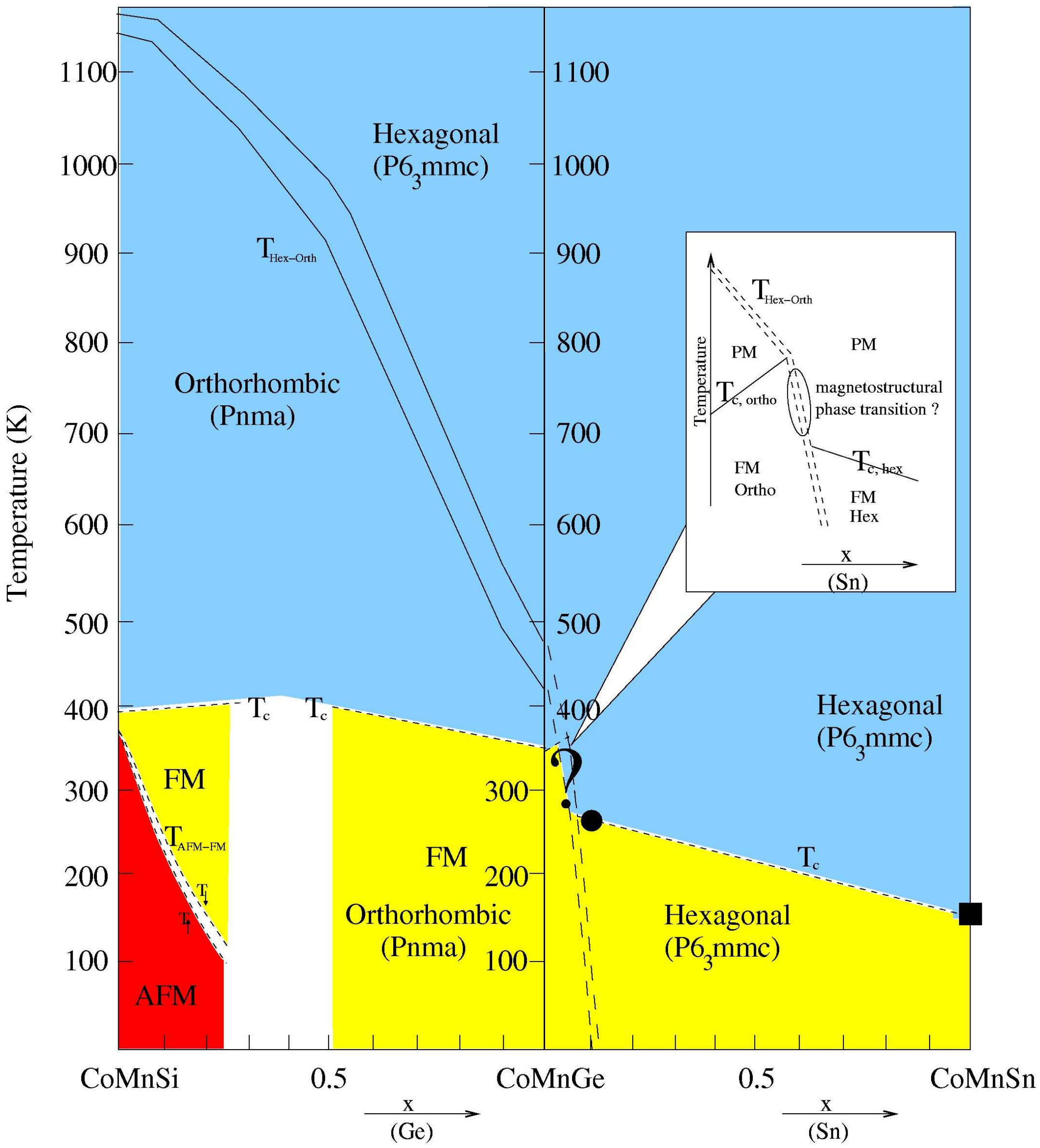
Boosting the entropy change

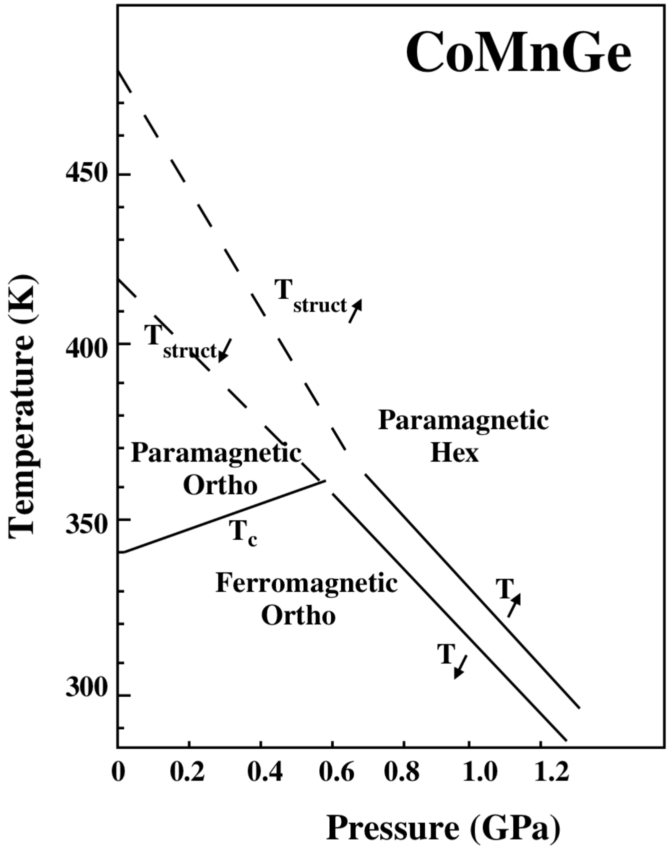
via coupling to the lattice

- The magnetic field changes the total entropy of the material (magnetic, lattice and electronic entropies)
- So we can increase the total entropy change by coupling to the lattice of the material



Lattice + Magnetic entropy: CoMnGe



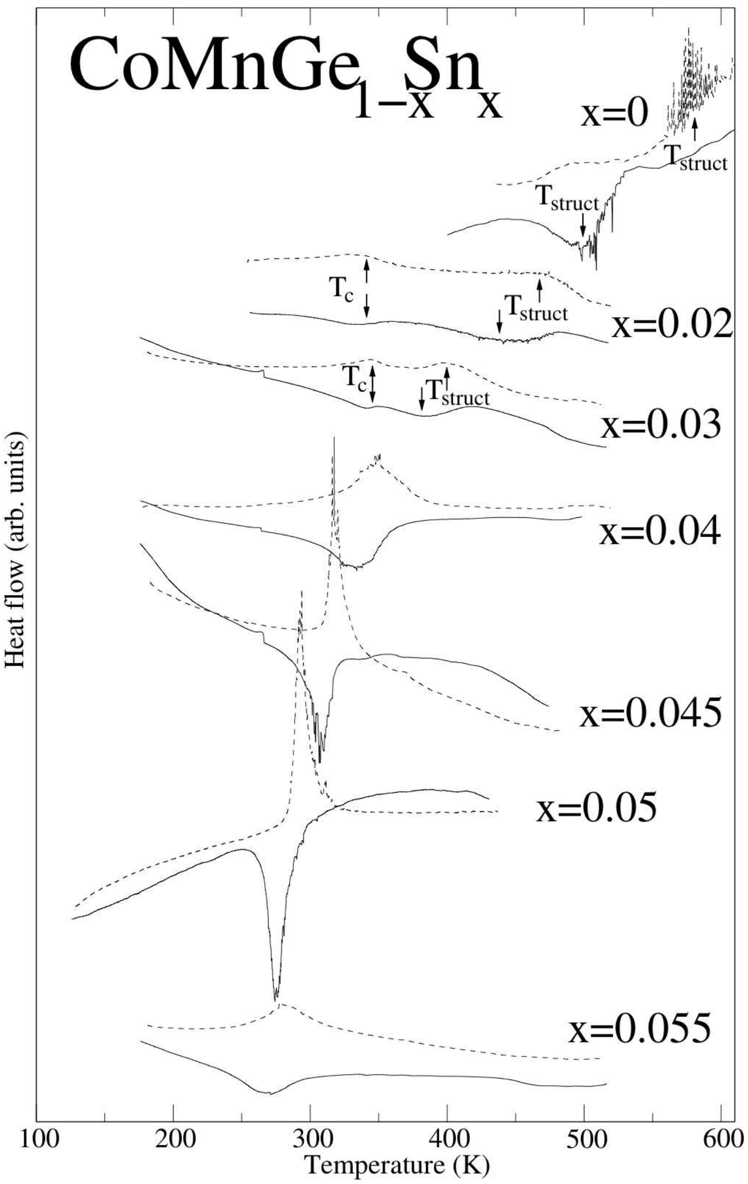


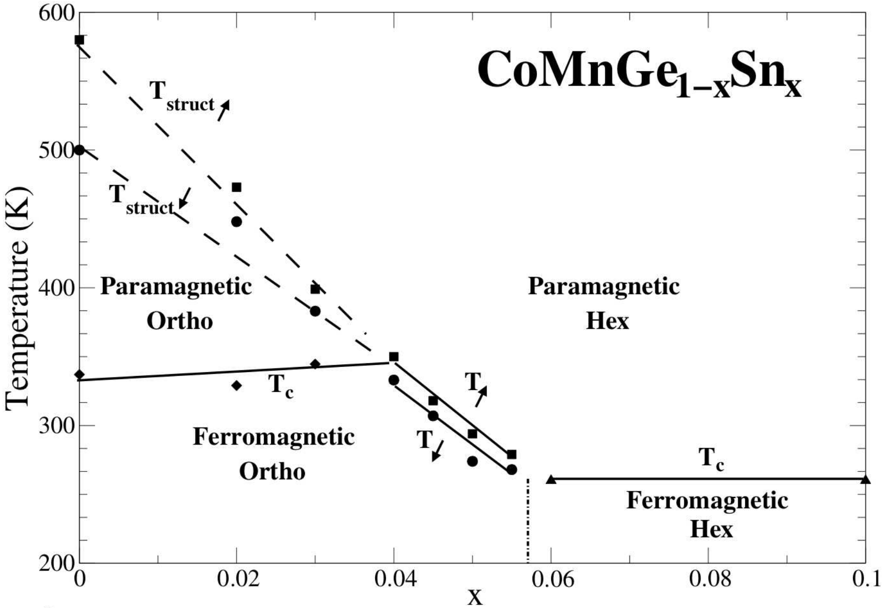
● Sandeman

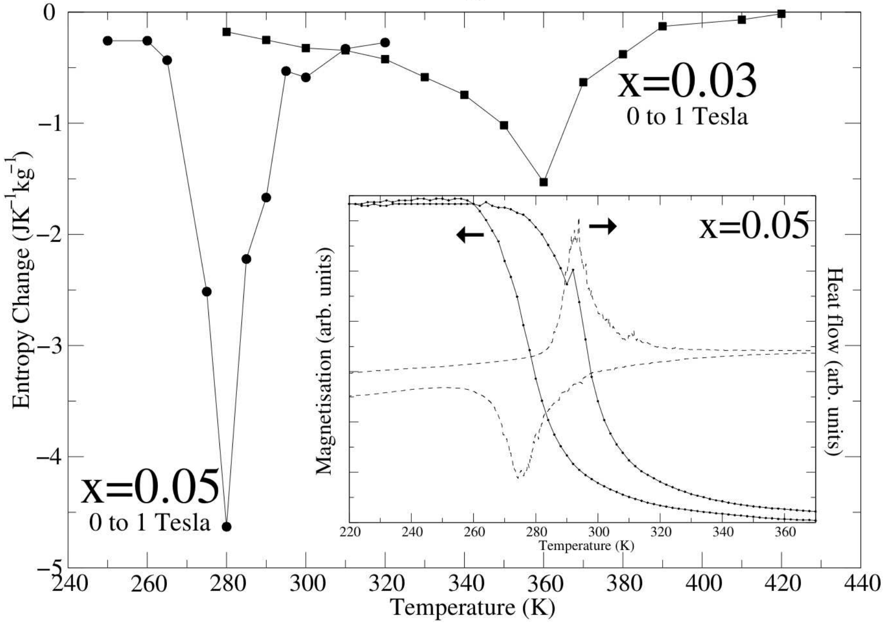
■ Bazela et al.

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

Lattice + Magnetic entropy: CoMnGe (contd.)







Hamer et al., (2008)

Where do we go from here?

Most of the materials described so far have been in the literature for 20-30 years

Why so few new materials/compositions?

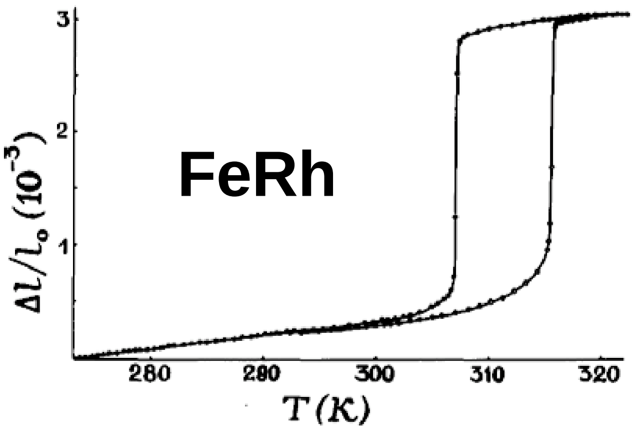
Back to “ideal material” criteria:

- Large angular momentum (high saturation moment)
- Transition temperature in vicinity of working temperature
- Constant, large ΔT_{ad} (>2 K) between T_{hot} and T_{cold}
- Essentially zero magnetic hysteresis
- Small C (high temperature change)
- High $\kappa_{thermal}$ (fast heat exchange)
- Large electrical resistance (avoid eddy current losses)
- Cheap to produce; easy to process

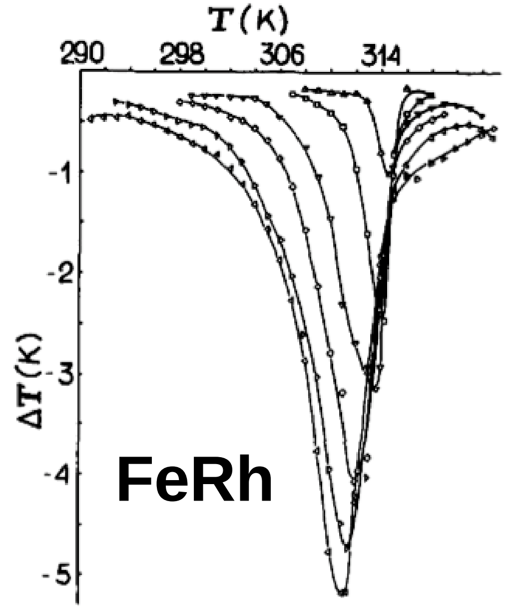
These are tough requirements, especially the last one
Are we limiting ourselves too much?

Do we even need a magnetic field?

- Only need two states of different entropy, with transitions between them driven by a field (pressure, electric field, magnetic field)
- What about the magnetovolume effect?



Nikitin et al. (1992)



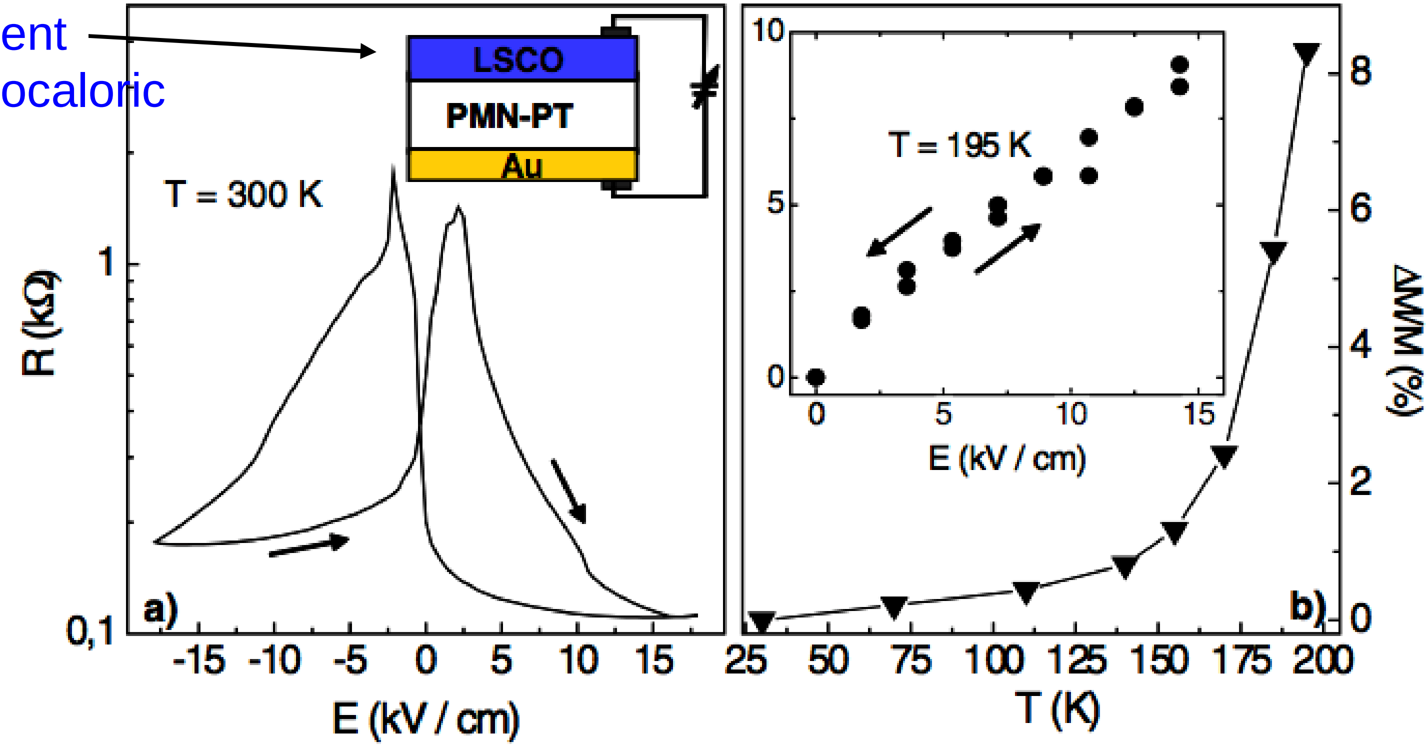
$$dG = -SdT - MdH_M + \sum_{l} \sum_{m=-l}^{m=l} K_l^m(H_M)\, d(Y_l^m(\Omega_M)) + Vdp$$

Extension of thin film work?

e.g. by Rata et al. (2008)

- Could we use an electric field to strain a magnetoelastic magnetocaloric?

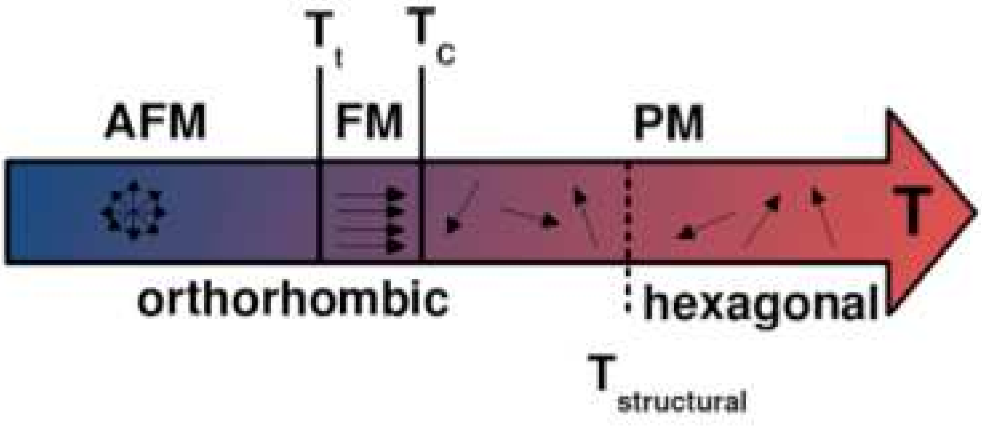
replace with strain-dependent magnetocaloric



Work in progress (Cambridge)

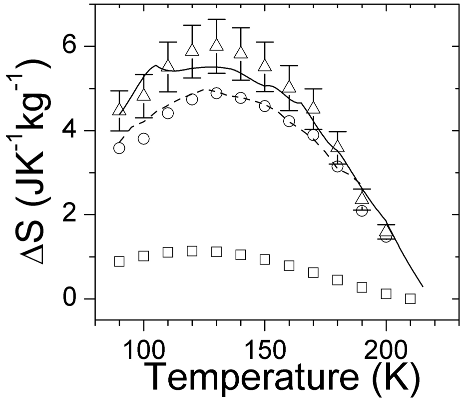
Thin film preparation

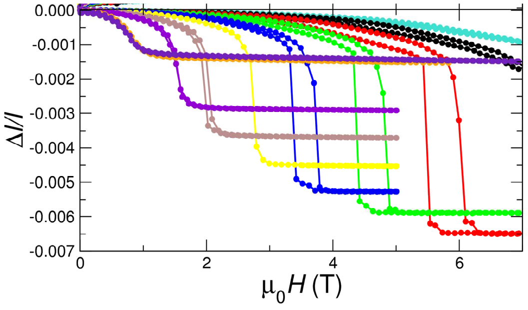
- higher throughput
- Raise T_C while maintaining T_t?
- difference between thin film and bulk properties?



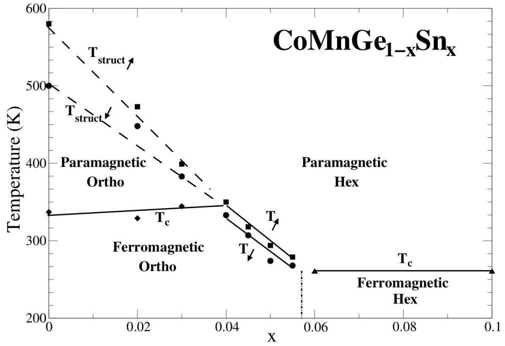
Conclusion

- Tricriticality seen in CoMnS-based metamagnets
- Separate measurement of 1st order and 2nd order contributions shown
- Separate entropic degrees of freedom can have very large and opposite effects
(see Alex Barcza’s talk)





- Bicritical system CoMn(Ge,Sn) demonstrates both the advantages and disadvantages of combining a 1st order structural transition with a 2nd order magnetic transition



Can we get a better control of the separation and combination of degrees of freedom?
And which field or fields are most technologically relevant for coupling to those degrees of freedom?