

Methods and problems in the characterization of magnetocaloric materials

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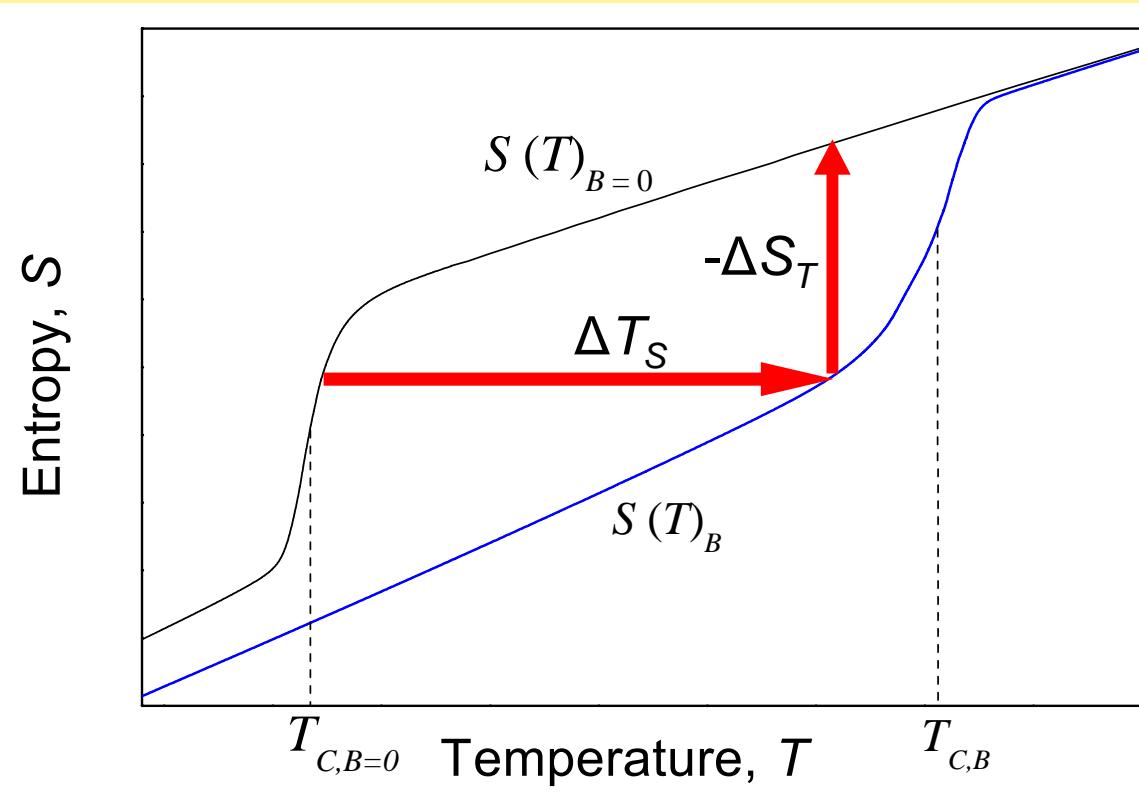
We need reliable values for the magnetocaloric parameters

- How reliable and how useful are the reported values for ΔT_S , ΔS_T , RC
- How valid are for hysteretic transitions
- Results from $C_B(T)$: Good, but depends on the T range
- Direct measurements
- Results obtained from $M(B)$, $M(T)$
- Considerations in hysteretic compounds:
Mixed phase, irreversibility

Magnetocaloric parameters

Effect of a magnetic field change on T and S

- Adiabatic temperature change, ΔT_S
- Isothermal entropy change, ΔS_T



Determination of ΔT_S and ΔS_T

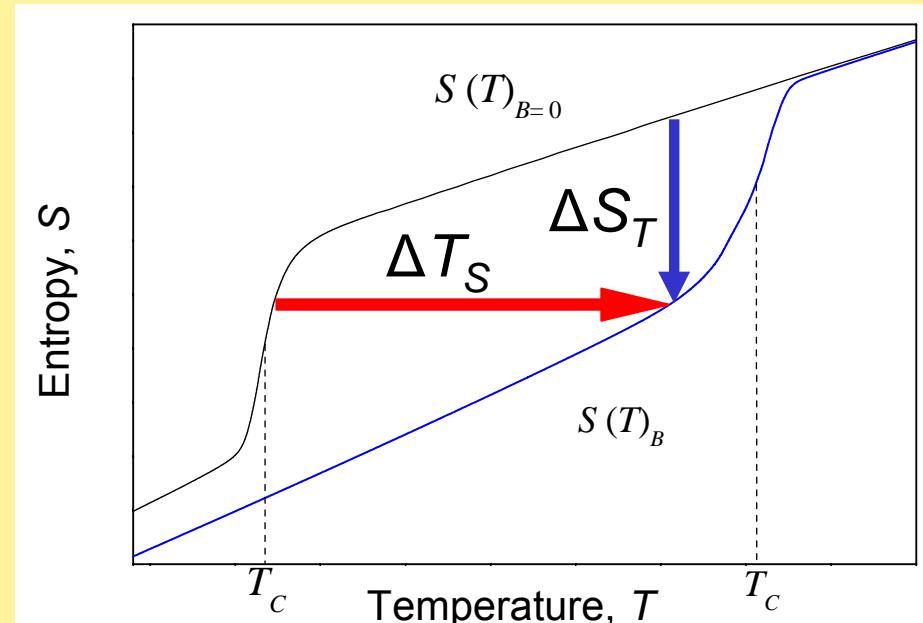
◆ Calorimetric methods

➤ Specific heat

$$S(T)_B = \int_0^T \frac{C(T)}{T} dT$$

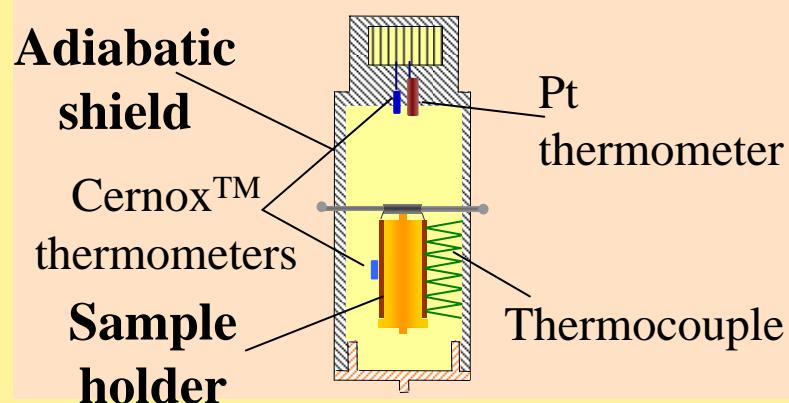
$$\boxed{\Delta T_S} = T(S)_{B_2} - T(S)_{B_1}$$

$$\boxed{\Delta S_T} = S(T)_{B_2} - S(T)_{B_1} = \int_0^T \frac{C(T)_{B_2} - C(T)_{B_1}}{T} dT$$



Adiabatic installation

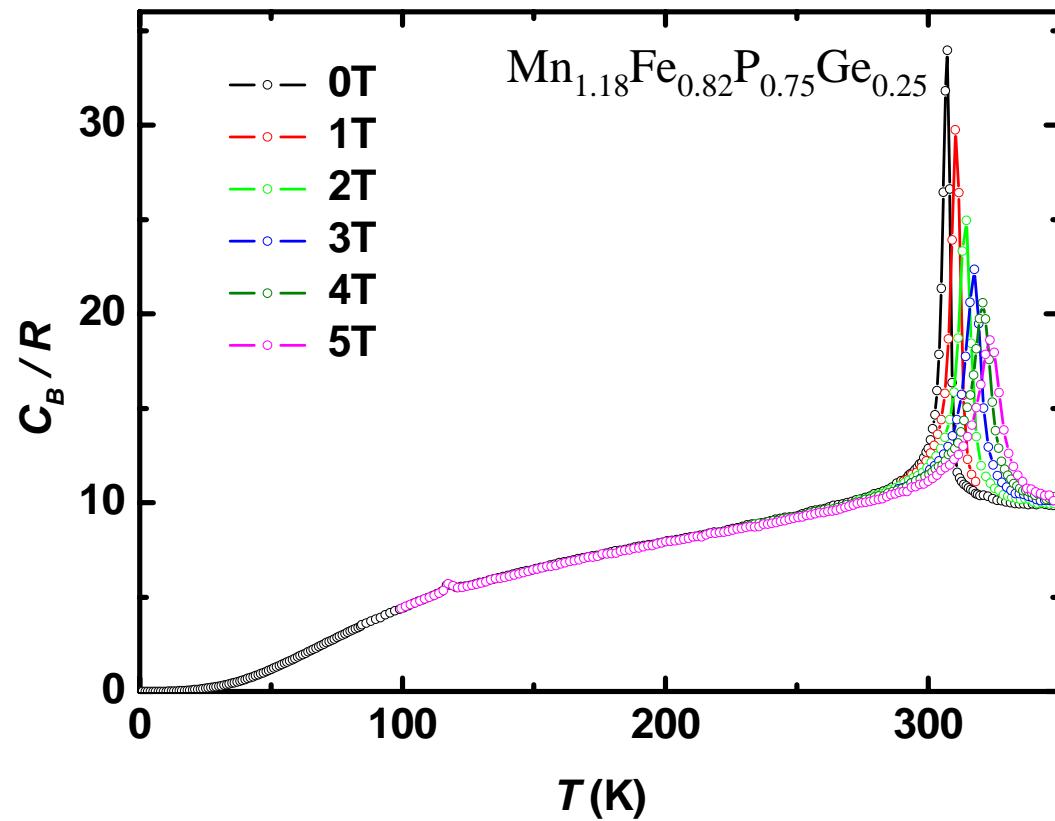
- ✓ 4.2 K – 350 K
- ✓ Magnetic Field up to 9 T



- Heat capacity:
 - Heat pulse method.
 - Continuous cooling and heating thermograms.
- Transition enthalpy.
- Direct measurement of the MCE parameters.
- Adiabatic field cycles.

Experimental techniques for ΔS_T and ΔT_S

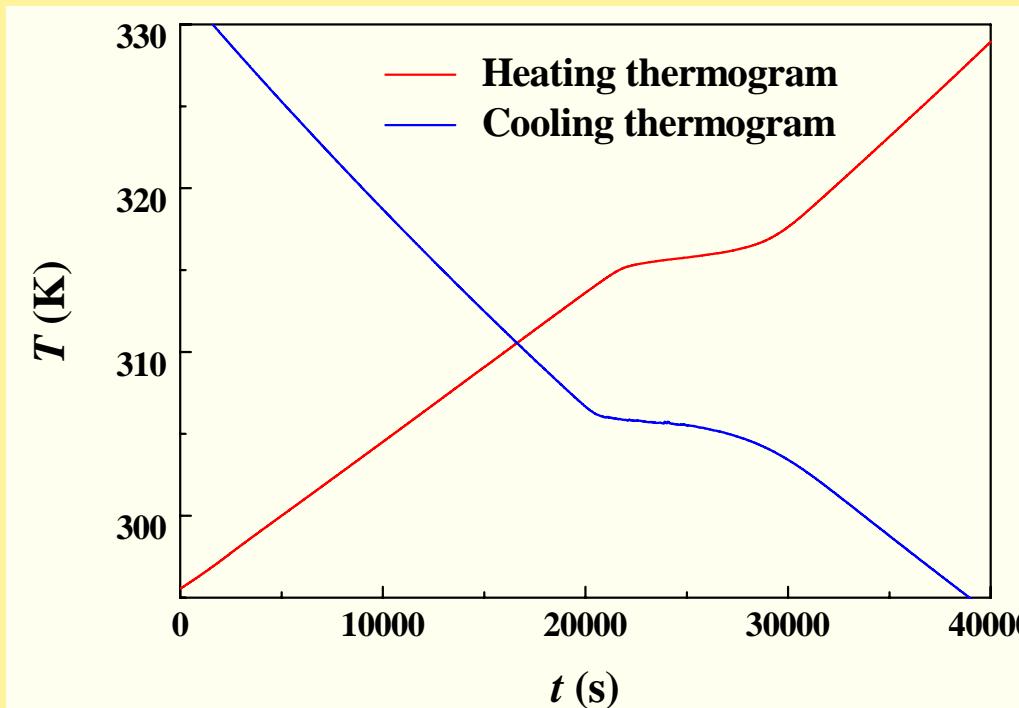
- **Heat pulse:** Quasi-static heat, $C(T)_B = Q/(T_2 - T_1)$



Adiabatic calorimetry
Fields $B = 1, 2, 3, 4, 5$ T
First-order transition
Ferro \longrightarrow Para

➤ Thermograms

- Map the heat capacity of sharp transitions
- Cooling and heating thermograms: Thermal hysteresis



Experimental method

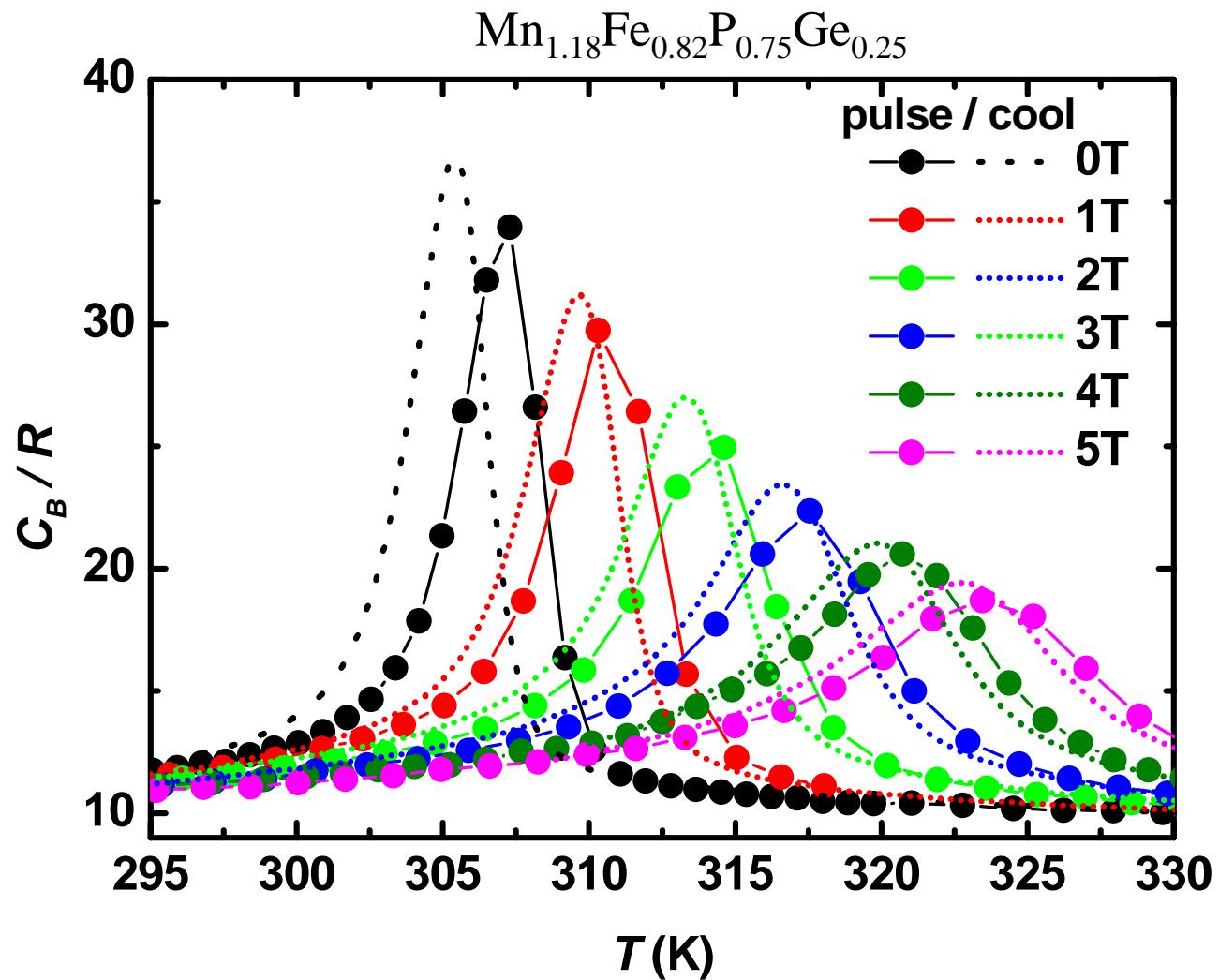
$$\delta T = T_{\text{sample}} - T_{\text{adiabatic shield}}$$

$$\frac{dQ}{dt} = \frac{dQ}{dT} \frac{dT}{dt} = C_B \frac{dT}{dt}$$

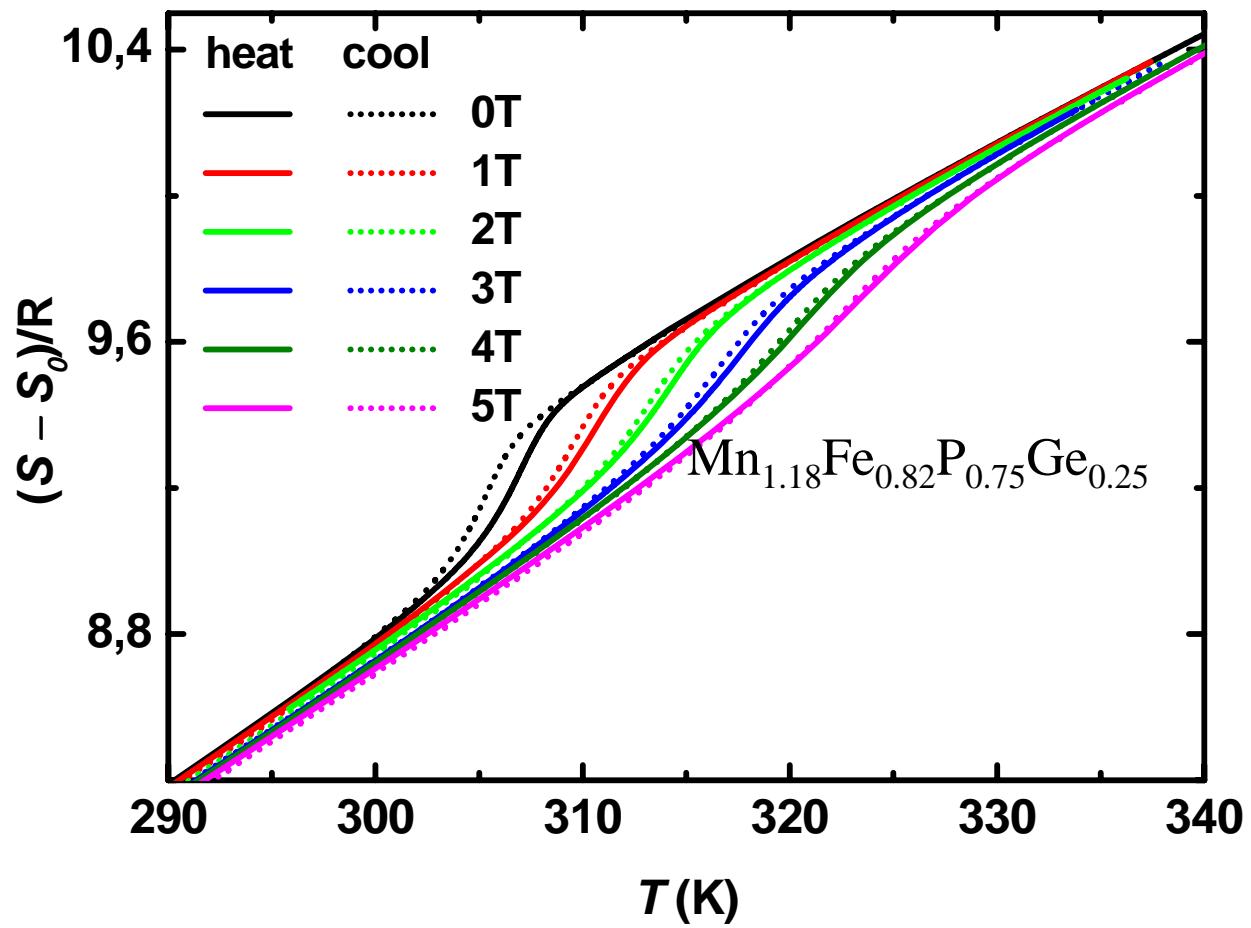
$$\frac{dQ}{dt} = \alpha \delta T + \sigma' [(T + \delta T)^4 - T^4]$$

$$\Rightarrow C_B \approx \frac{(\alpha + \sigma T^3) \delta T}{dT/dt}$$

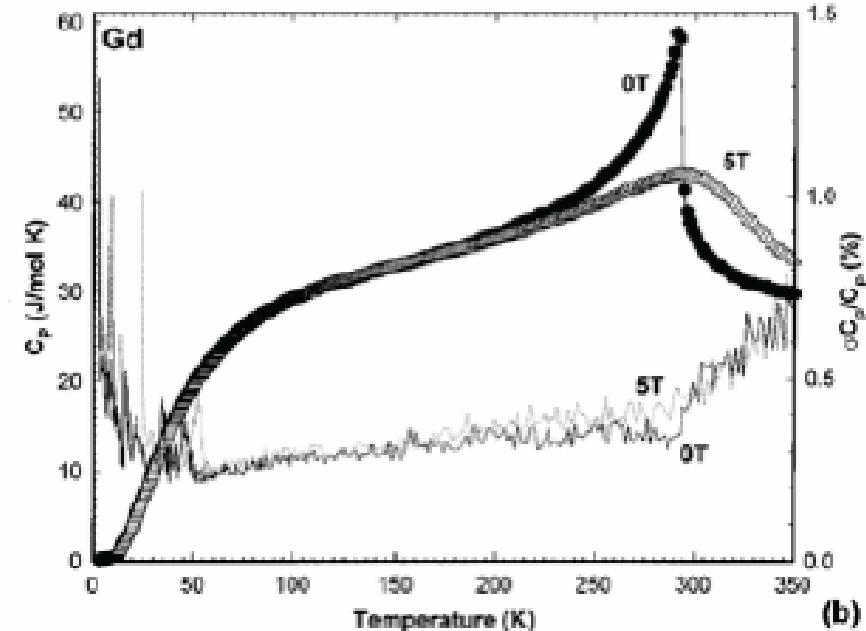
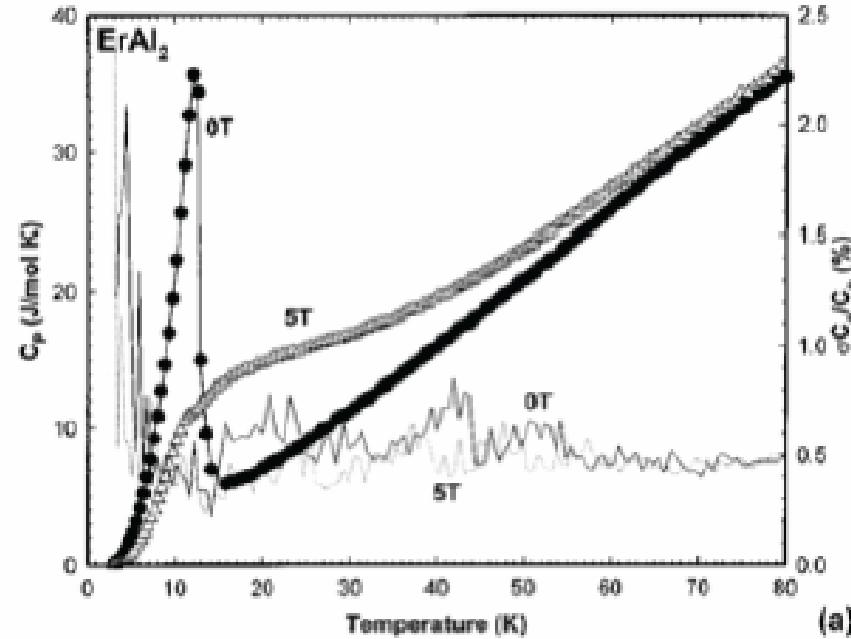
Tocado et al, J. Therm. Anal. Calorim. 84, 213 (2006)



$$S(T)_B = \int_0^T (C_B/T) dT$$



Problems from *specific heat* determinations of S



Pecharsky and Gschneidner, J. Appl. Phys. 86, 565 (1999)

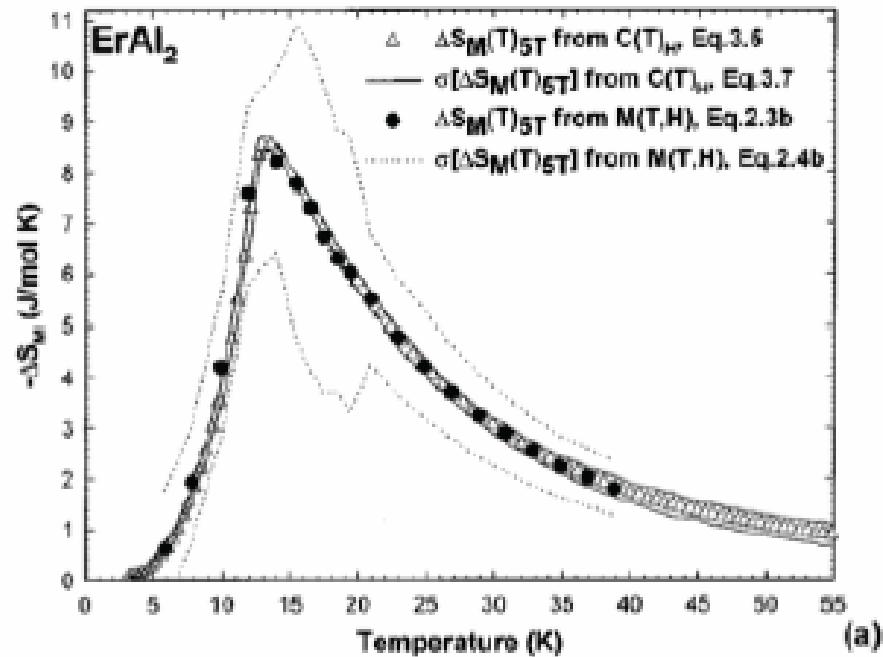
- Good at low T
- Low precision at high T

$$S(T)_{B=0} \gg S(T)_{B=5}$$

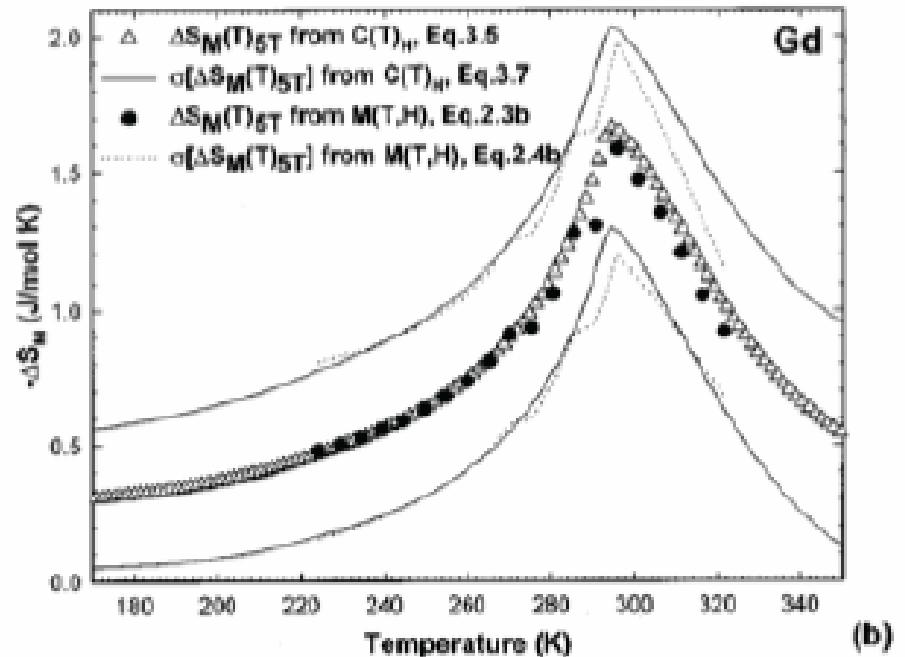
Precision of ΔS_T and S_T are similar

$$\Delta S_T < 5\% \text{ of } S_T$$

Error in $\Delta S_T > 20$ times the error in S_T



(a)



(b)

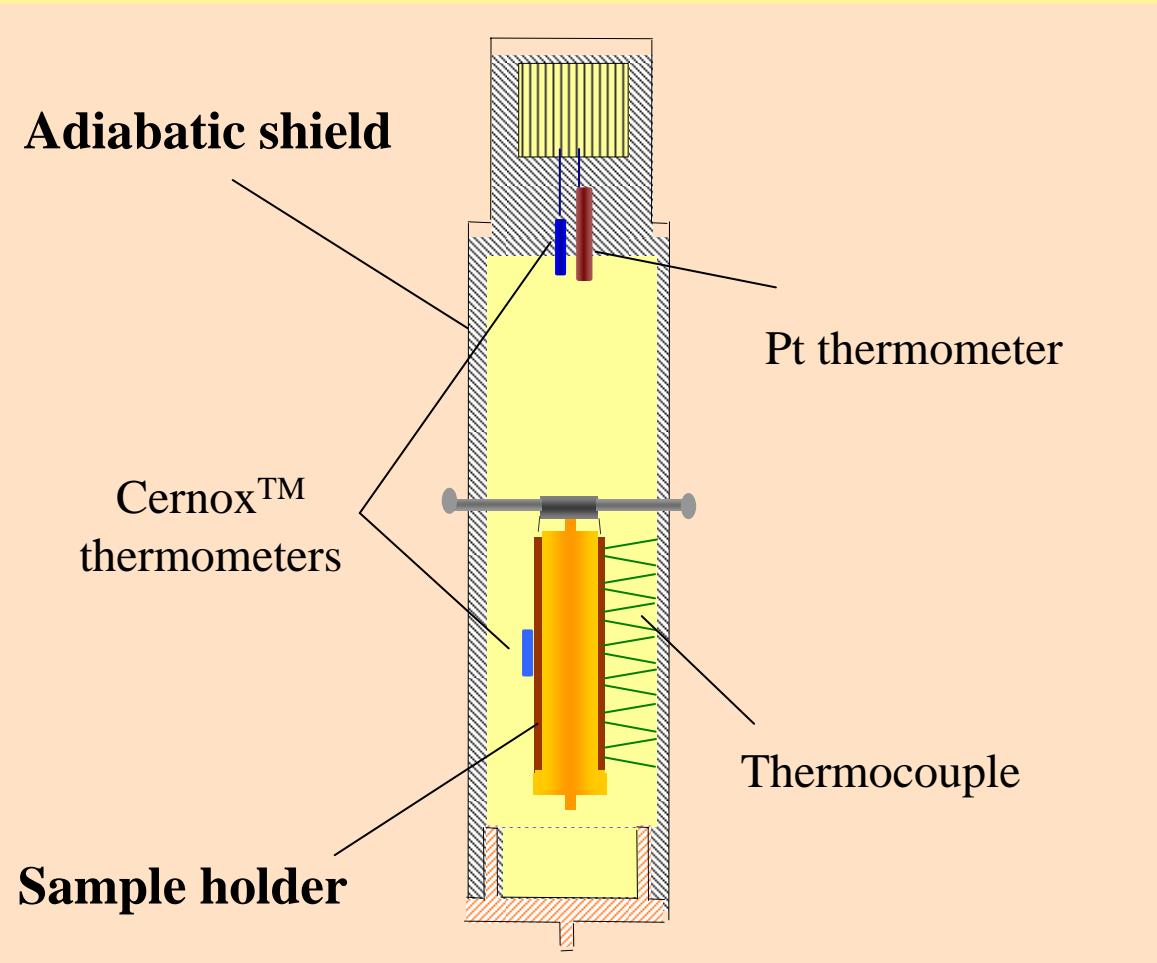
Pecharsky, Gschneidner, J. Appl. Phys. 86, 565 (1999)

- Improvement combining C_B with direct measurements
 - Avoids the need of C_B at low temperatures
 - Without increased error at high T

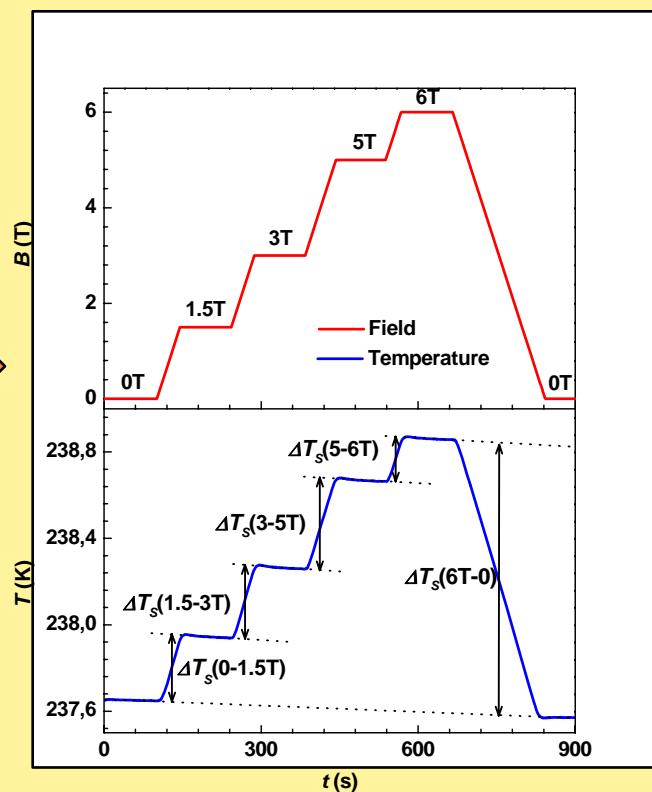
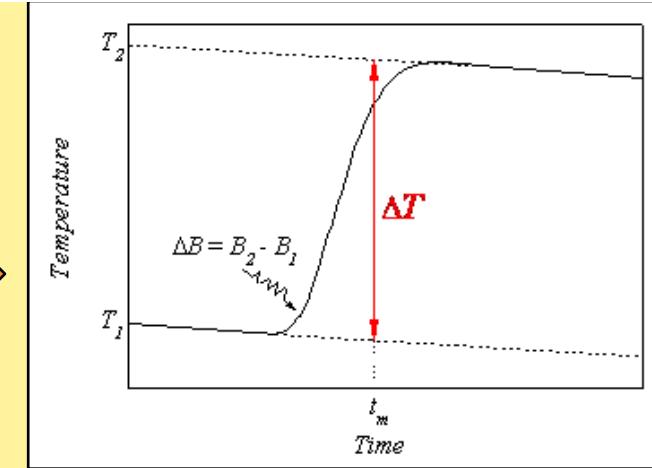
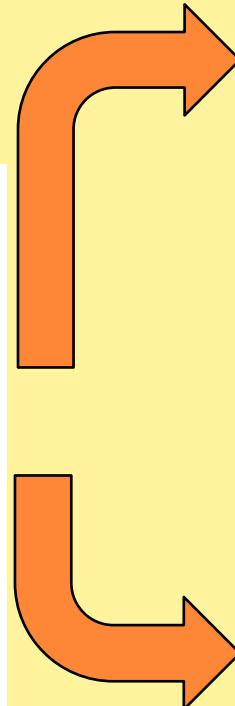
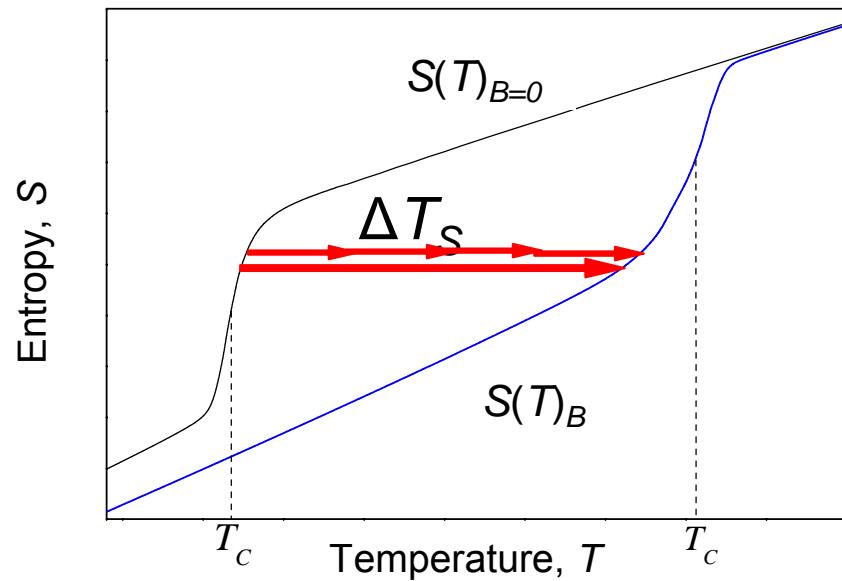
➤ Direct measurements

Adiabatic system

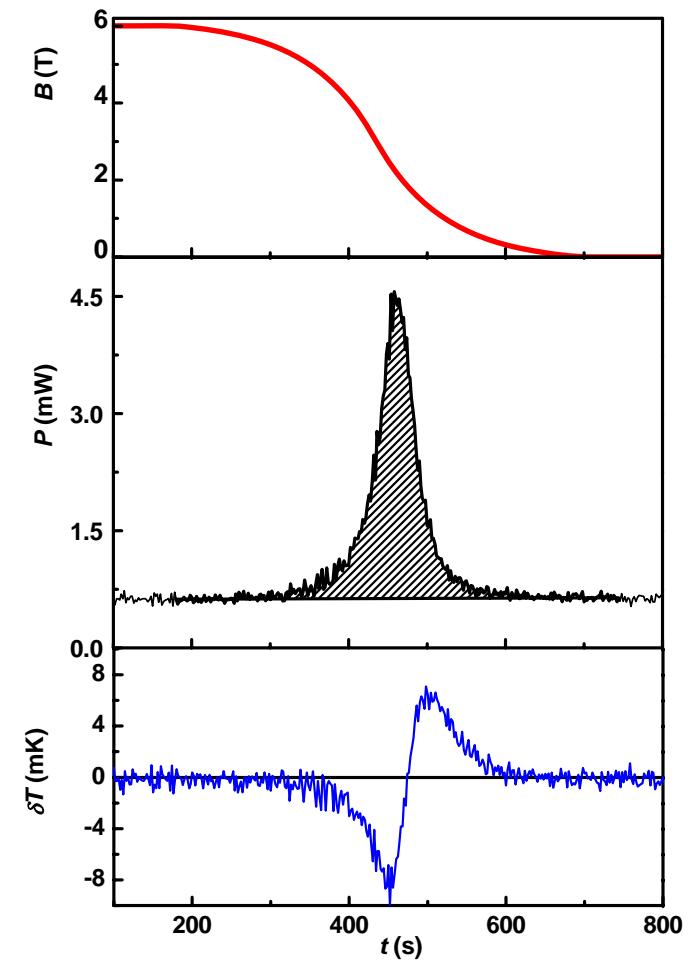
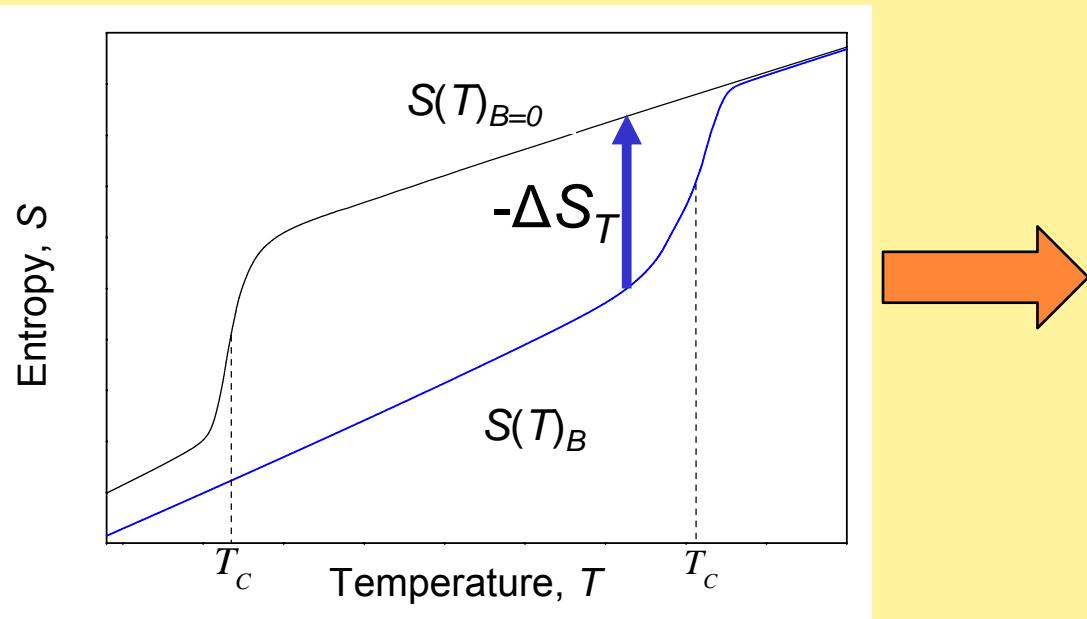
Control of T , Q and B
in the sample and in
the surrounding shield



$$\Delta T_S = [T_S(B_2) - T_S(B_1)]$$

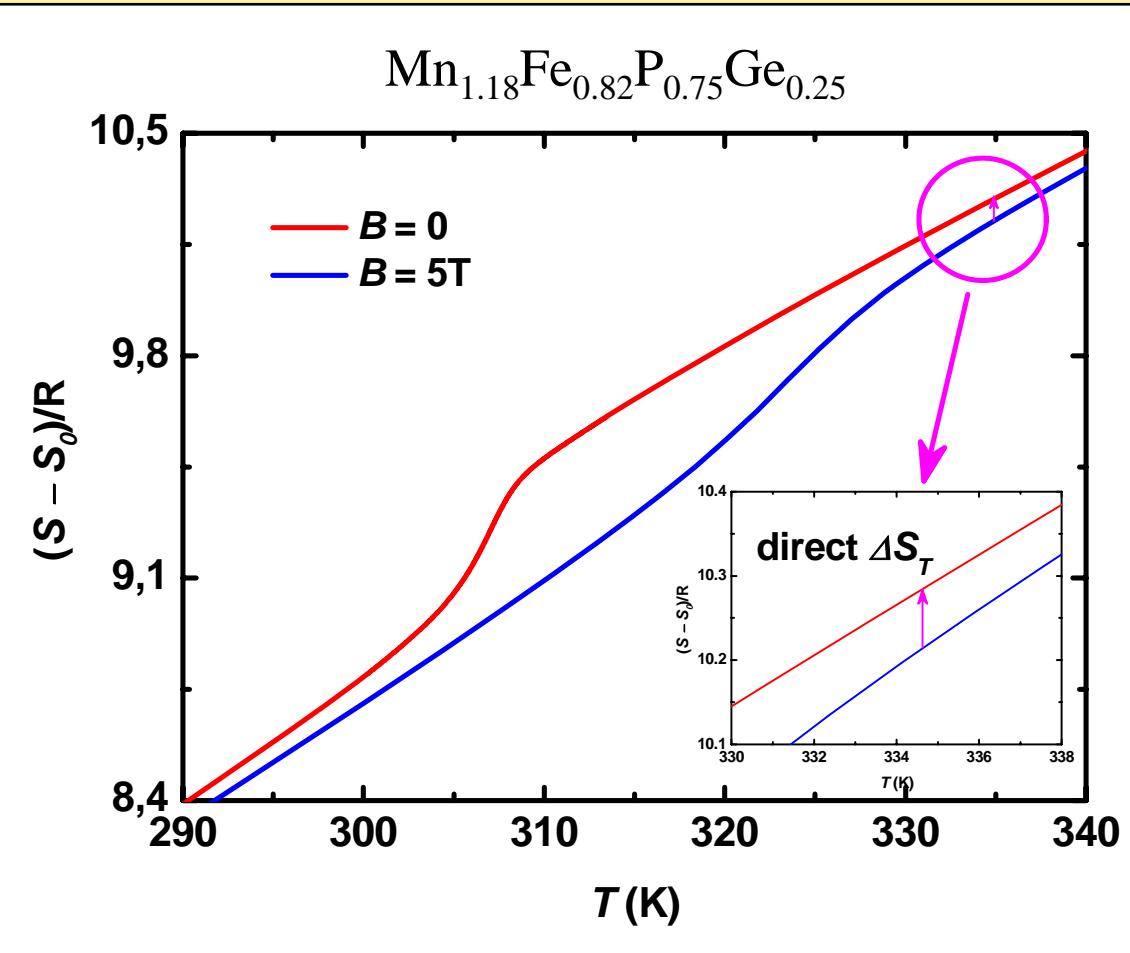


$$\Delta S_T = Q/T = [S_T(B_2) - S_T(B_1)]$$



Other methods: Peltier cell

Basso et al, Rev. Sci. Instrum. 79, 63907 (2008)



Solution to S calculation
from $C_B(T)$

Combined $C_B(T)$
and direct ΔS_T

Entropy curves from

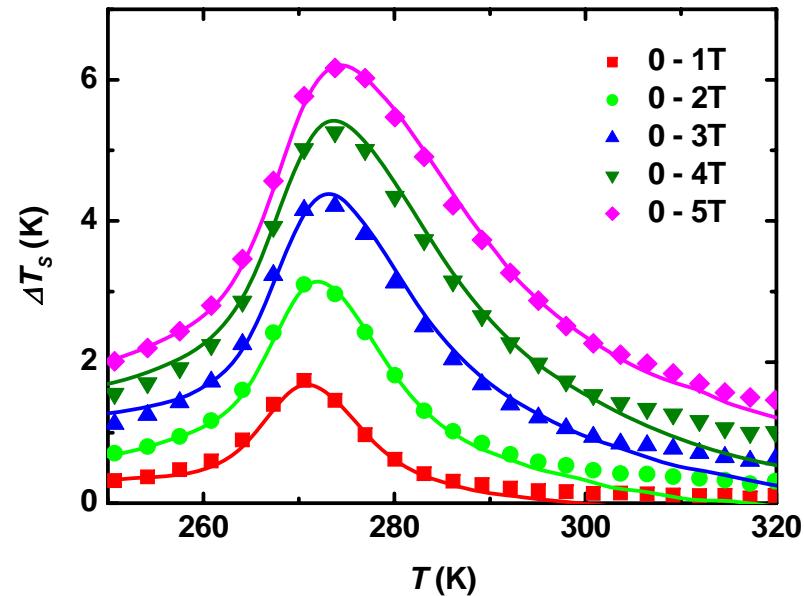
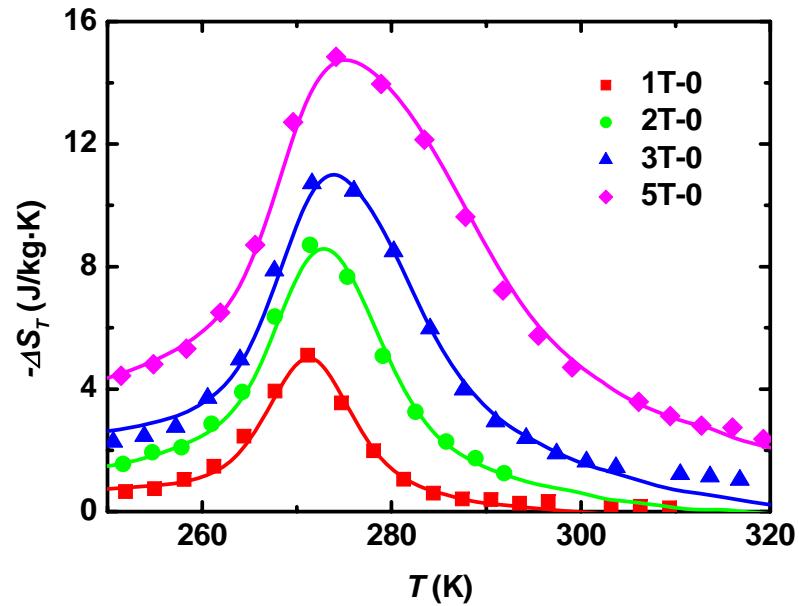
- C_B , unknown S_0
- Direct ΔS_T , common S_0

Measured

$$S(T)_B = S(T_0)_B + \int_{T_0}^T \frac{C(T)_B}{T} dT$$

$$S(T_0)_B = S(T_0)_{B=0} + \Delta S_T(T_0)$$

$\text{Mn}_{1.26}\text{Fe}_{0.74}\text{P}_{0.75}\text{Ge}_{0.25}$



Full symbols: Results from direct measurements

Continuous lines: From C_B

Magnetocaloric parameters from magnetic measurements

Gibbs free energy

$$G = U - TS - BM$$

$$dG = -S\,dT - MdB$$

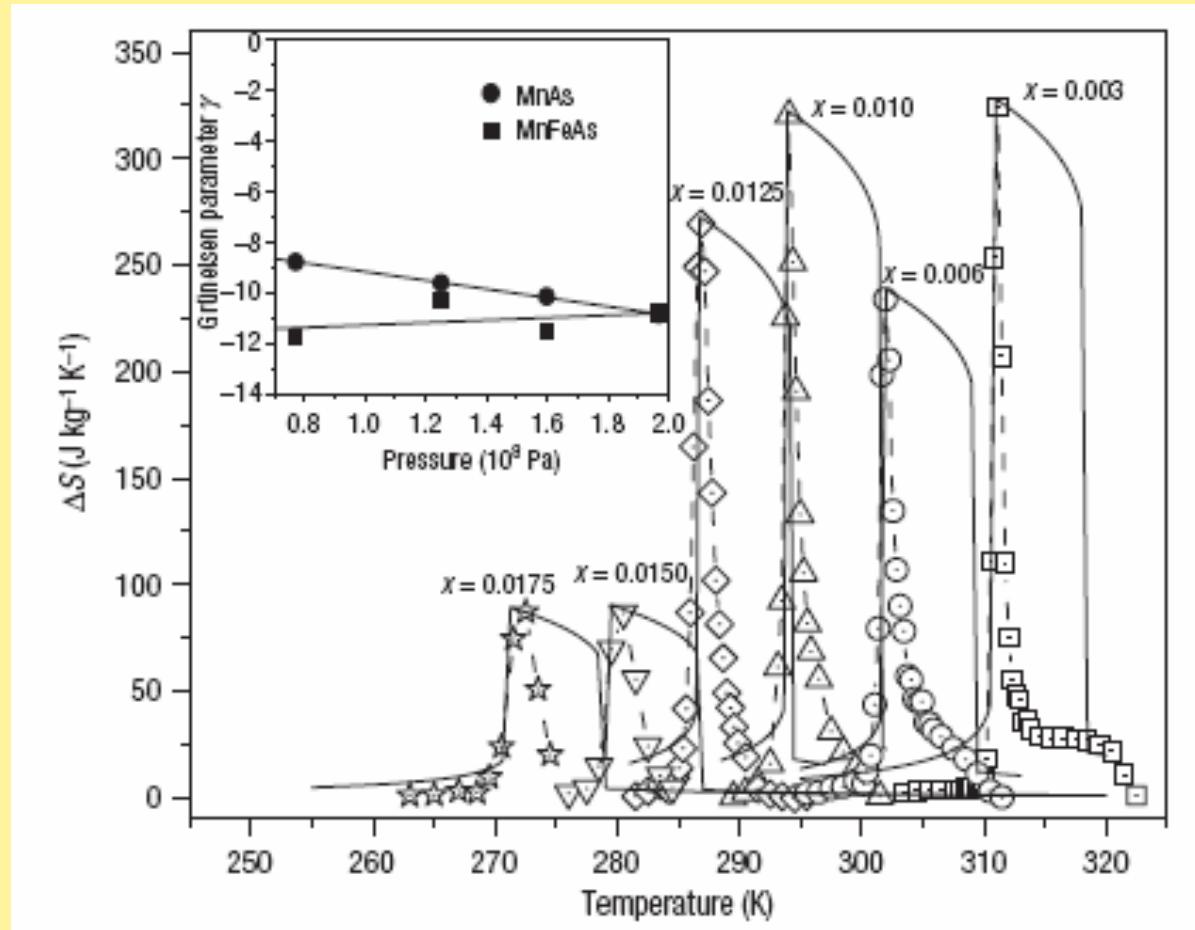
Maxwell relation

$$\left(\frac{\partial^2 G}{\partial B \partial T} \right) = \left(\frac{\partial^2 G}{\partial T \partial B} \right) \quad \longrightarrow \quad \left(\frac{\partial S}{\partial B} \right)_T = \left(\frac{\partial M}{\partial T} \right)_B$$

$$\boxed{\Delta S_T} = \int_0^B \left(\frac{\partial M(T, B)}{\partial T} \right)_B dB$$

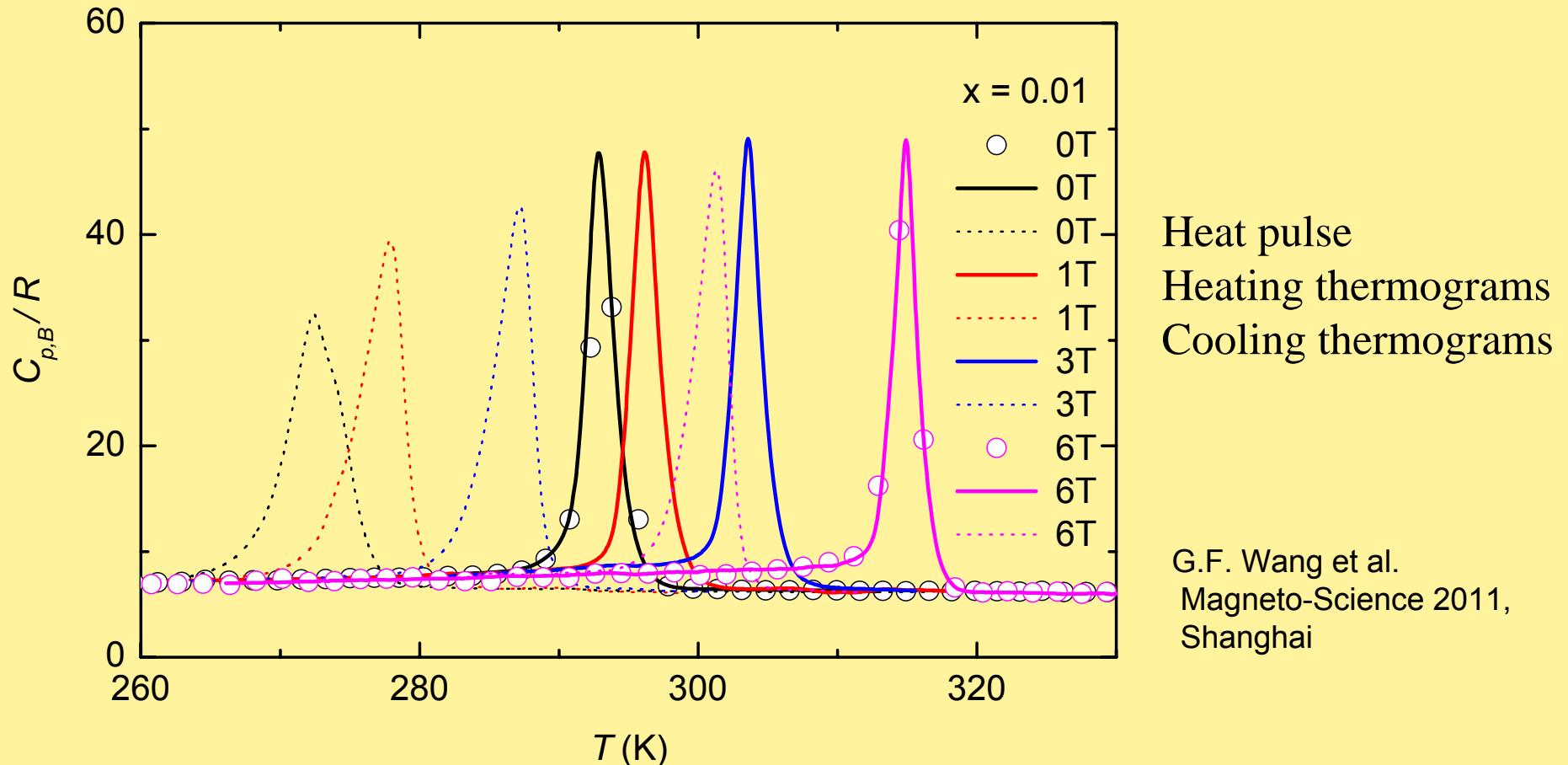
$$\boxed{\Delta S_T} = \int_0^B \left(\frac{\partial M(T, B)}{\partial T} \right)_B dB = \frac{1}{T_2 - T_1} \int_0^B [M(T_2) - M(T_1)]_B dB$$

Problem with derived “spikes” from Maxwell relation

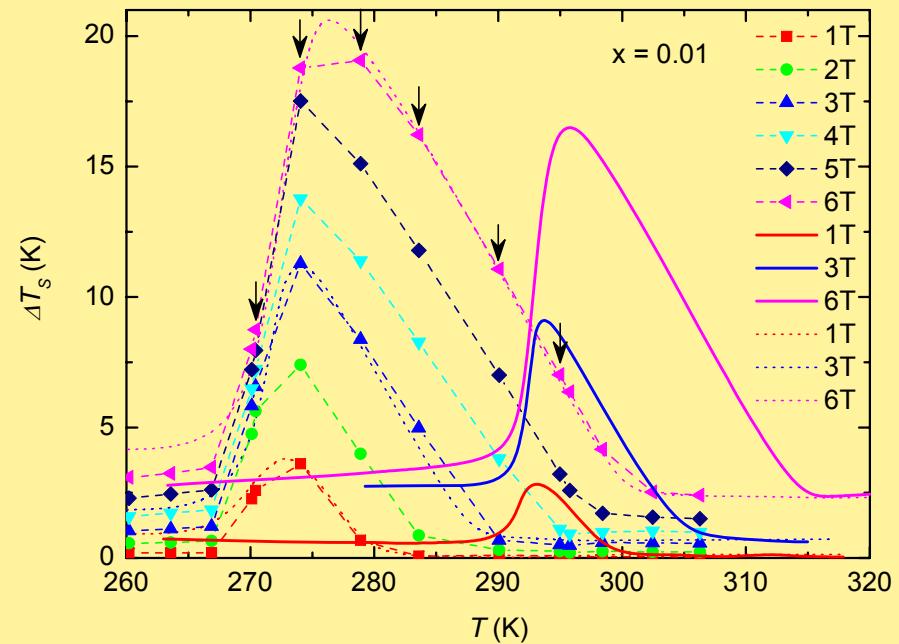
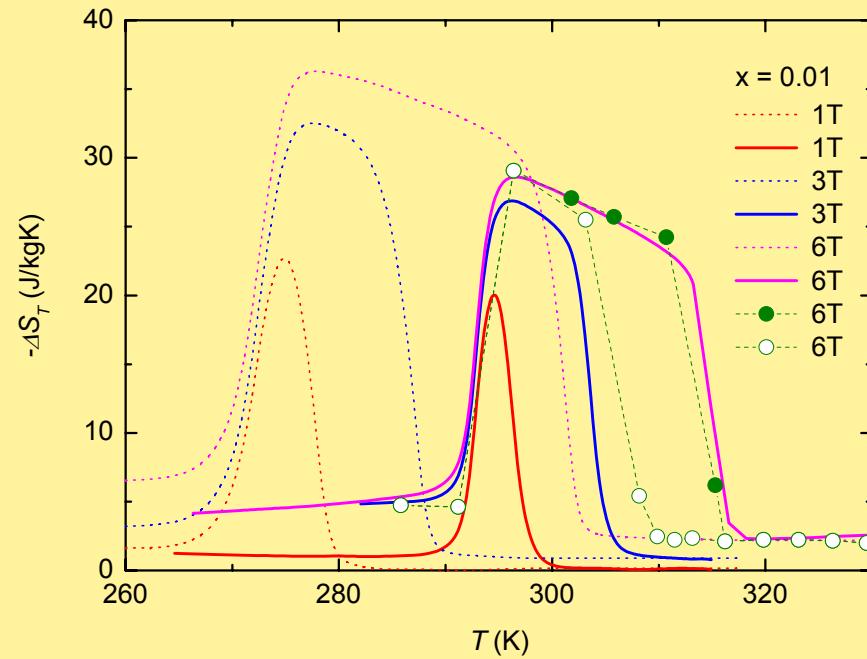


The colossal effect for $\text{Mn}_{1-x}\text{Fe}_x\text{As}$
Nature Materials **5**, 804 (2006)

$\text{Mn}_{1-x}\text{Fe}_x\text{As}$ ($x=0.01$)



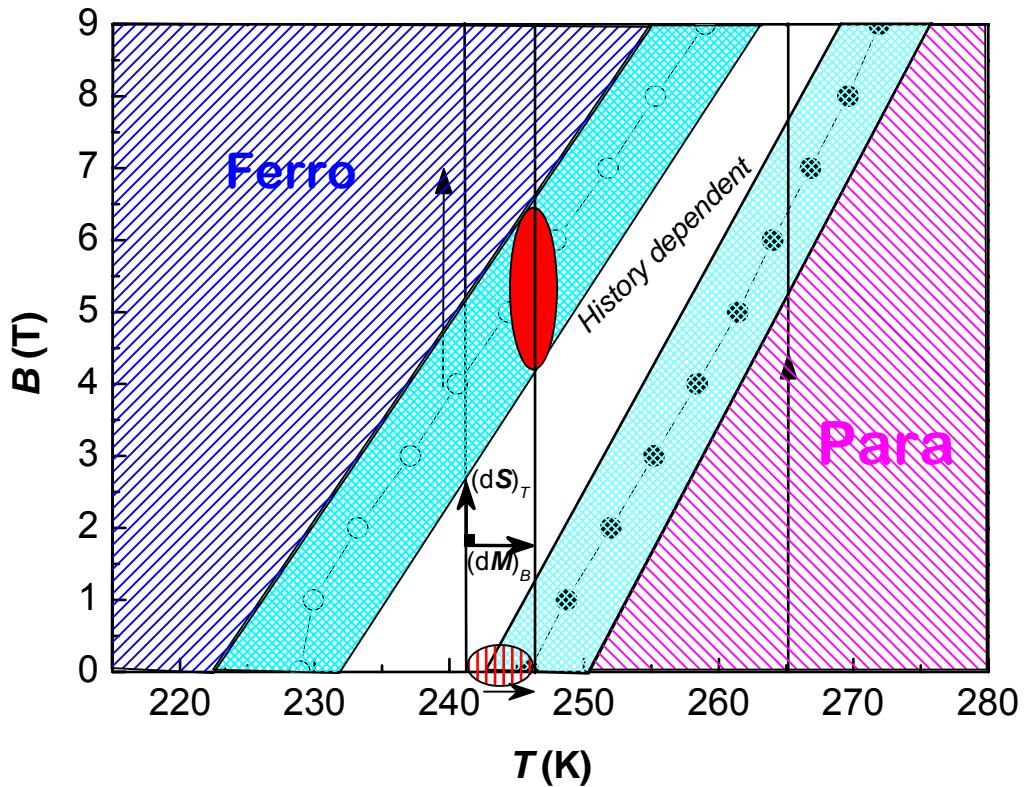
$Mn_{1-x}Fe_xAs$ ($x=0.01$)



Symbols: from direct measurements.
 Dotted and solid lines: from heat capacity
 on cooling and heating
 Giant MCE but not colossal

G.F. Wang et al.
 Magneto-Science 2011, Shanghai

Hysteretic compounds



Tocado et al, *J. Appl. Phys.* **105**, 093918 (2009)

Mixed phase:

$$M = x \cdot M_P + (1-x) \cdot M_F$$

Calculation from $\mathbf{M}(B)_T$

$$\Delta S_T = \Delta S + \Delta S_{ex}$$

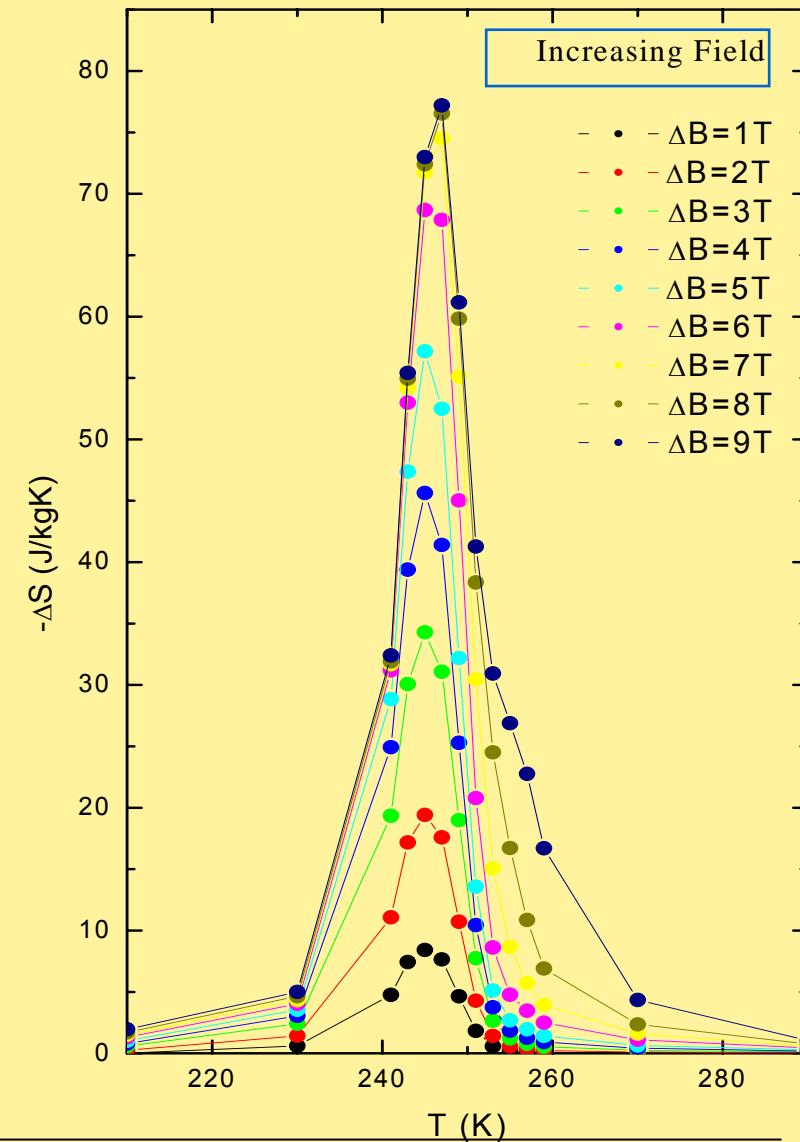
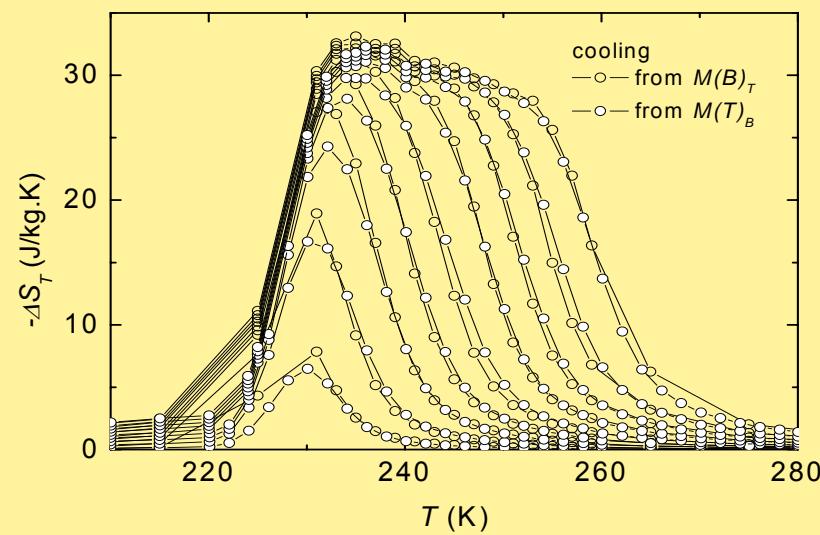
$$\Delta S_{ex} = \int_0^{B_t} (M_F - M_P) \left(\frac{\partial x}{\partial T} \right)_B dB$$

$$\Delta S_{ex} = \int_0^{B_t} (M_F - M_P) \frac{C_{an}(T)_{B=0}}{(\Delta H)_{B=0}} dB$$

Results for ΔS_T from $M(T)_B$, $M(B)_T$, and $M(B)_T$ with cycling in T (same scale)

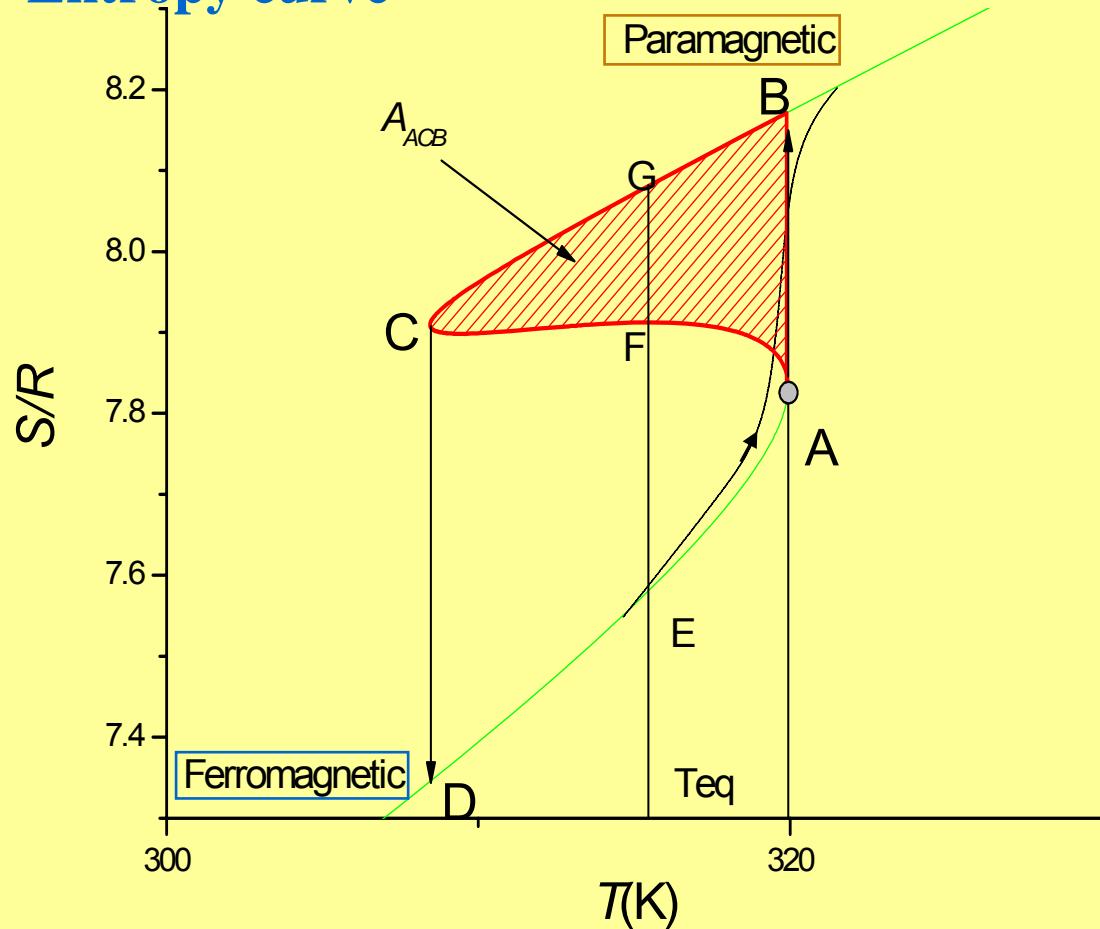
Same results for ΔS_T from:

- Field dependent magnetization $M(B)_T$ with complete phase conversion
- Temperature dependent magnetization $M(T)_B$
- And also from $C_{p,B}(T)$ and direct values



Irreversibility: Entropy $dS \geq dQ/T$

Entropy curve



Heating process:

- $D \rightarrow A$, Stable phase Ferro-
- $A \rightarrow B$, Transition to Para-

Cooling process:

- $B \rightarrow C$, Stable phase Para-
- $C \rightarrow D$, Transition to Ferro-

A to C, unstable $\partial S/\partial T < 0$

Phase equilibrium at T_{eq}

$$G_E = G_G$$

Estimation of the real entropy jump

Heating

$$G_A - G_B = \int_A^B SdT = A_{ACB}$$

$$= H_A - T_A S_A - H_B + T_B S_B = \\ -\Delta H + T_A \Delta S > 0 \Leftrightarrow$$

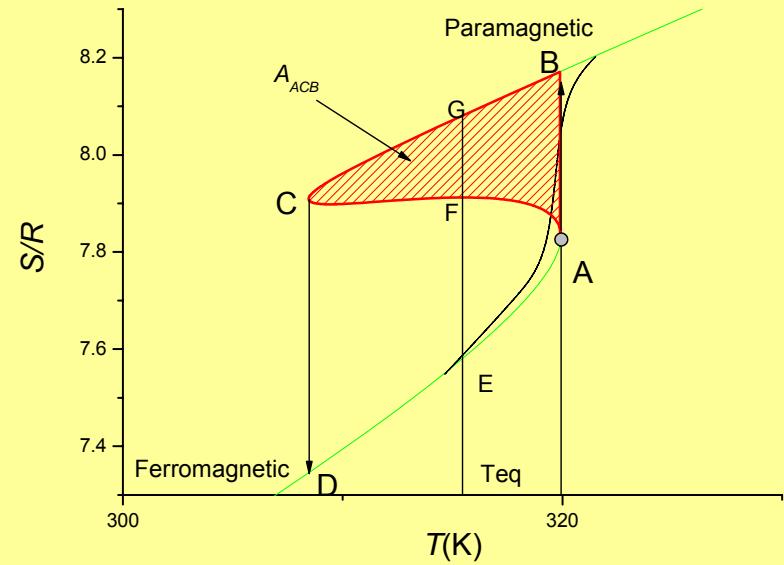
$$T_A \Delta S = \Delta H + A_{ACB} > \Delta H = \int C_{p,B}(T) dT$$

$$\Rightarrow \Delta S > \frac{\Delta H}{T_A}$$

Estimation of the area A_{ACB} (as a triangle): $A_{ACB} \cong \frac{1}{2}(S_B - S_A)(T_A - T_C) = \frac{1}{2}\Delta S(T_A - T_C)$

$$\Delta S_{heat} \cong \Delta S'_{heat} \frac{2T_A}{T_A + T_C}$$

where the pseudo-entropy $\Delta S' = \frac{\Delta H}{T_A}$



Estimation of the real entropy jump

Similarly, on cooling

$$G_C - G_D = A_{CAD}$$

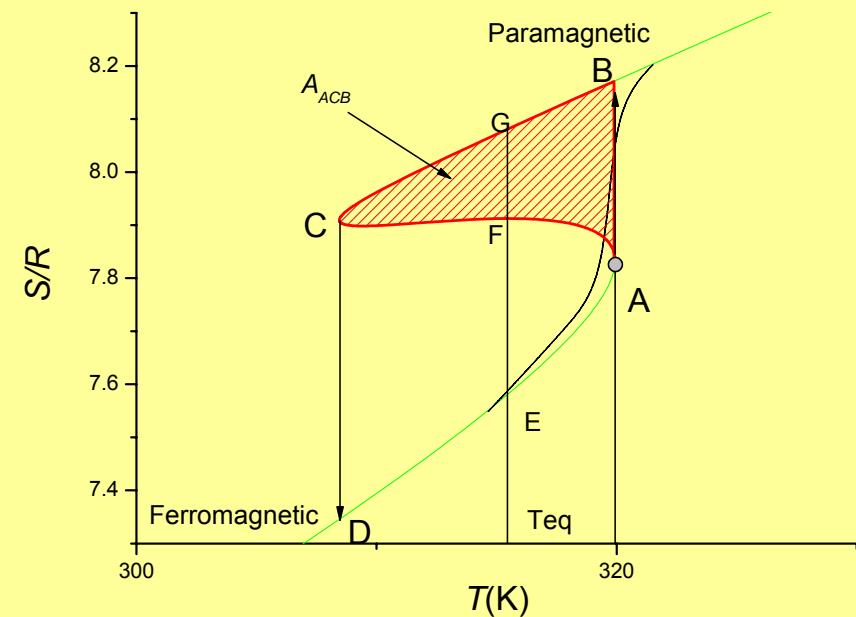
$$\Rightarrow |\Delta S| < \frac{|\Delta H|}{T_A}$$

$$|\Delta S_{cool}| \cong |\Delta S'_{cool}| \frac{2T_C}{T_A + T_C}$$

Heating-cooling cycle DABCD

$$0 = \oint dS = S_D - S_C + S_C - S_B + S_B - S_A + S_A - S_D \cong$$

$$\int_D^A \frac{C_{p,B,heat}(T)dT}{T} - \int_C^B \frac{C_{p,B,cool}(T)dT}{T} + \Delta S'_{heat} - |\Delta S'_{cool}| + \left(\Delta S'_{heat} + |\Delta S'_{cool}| \right) \frac{T_A - T_C}{T_A + T_C}$$



Error in the measurement of the entropy cycle

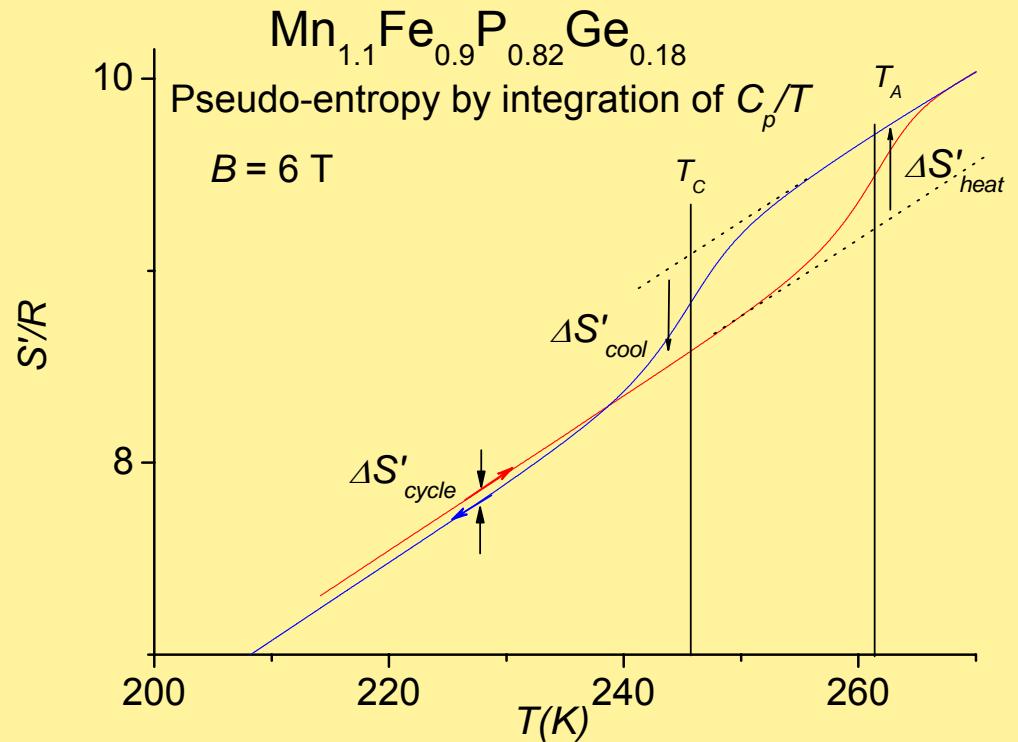
$$\frac{\Delta S'_{cycle}}{\langle \Delta S' \rangle} \cong -\frac{\Delta T_{hys}}{\langle T_{crit} \rangle}$$

$$\Delta S' = \frac{\Delta H}{T_{crit}}$$

$$\Delta T_{hys} = T_{heat} - T_{cool}$$

$$\langle T_{crit} \rangle = 1/2(T_{heat} + T_{cool})$$

It coincides with the experimental value: 6%



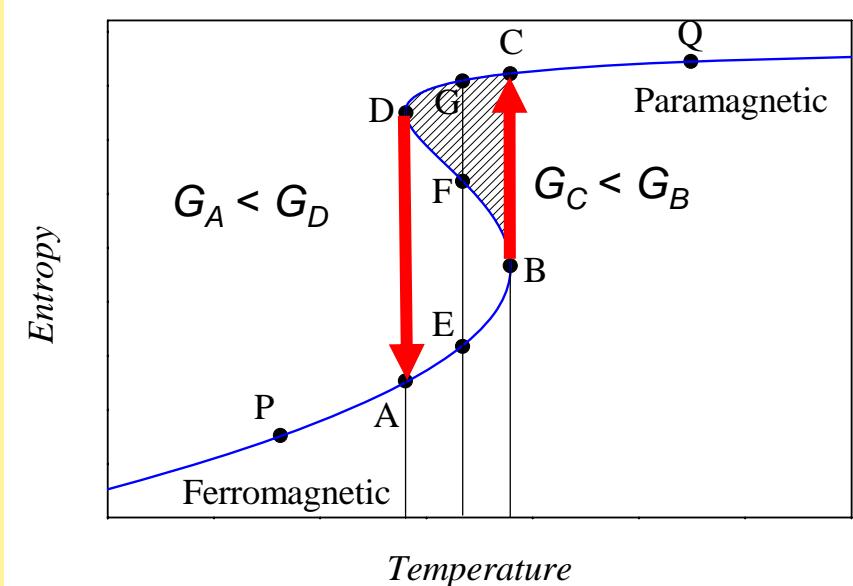
Effects of hysteresis and irreversibility

- Hysteresis: possible mixed phase
 - Wrong application of the Maxwell relation in $M(B)_T$ measurements
 - Unphysical “colossal” effect ΔS_{ex}

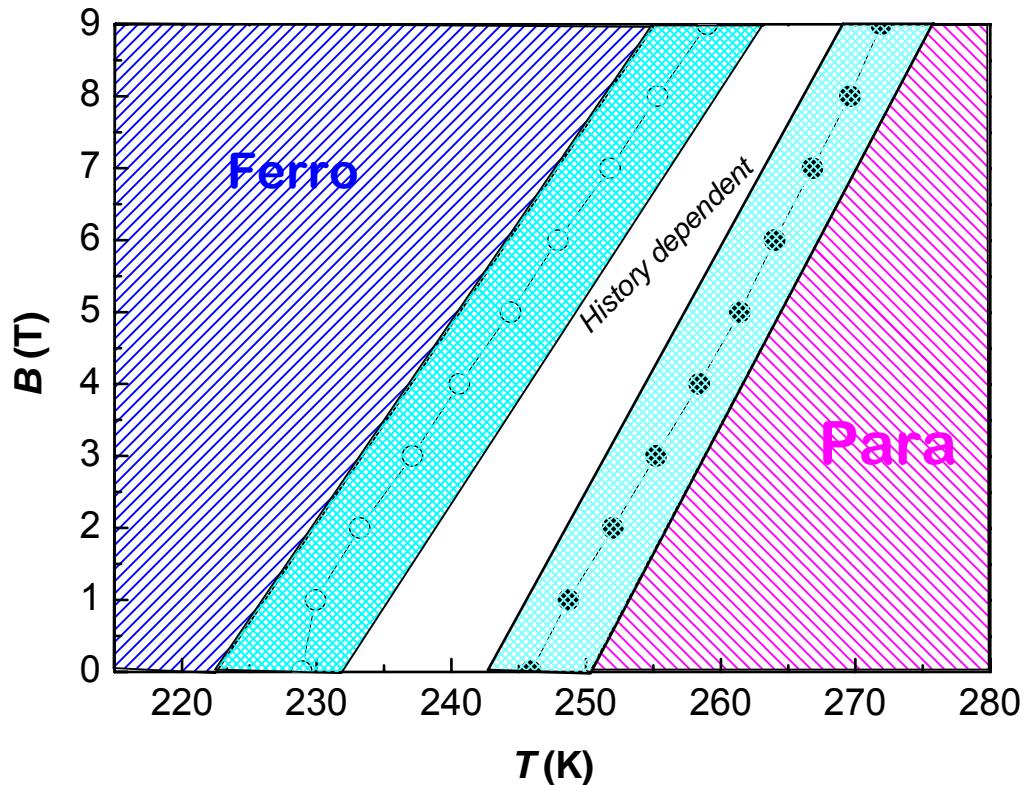
$$\Delta S_{ex} = \int_0^{B_t} (M_F - M_P) \frac{C_{p,anom}(T)_{B=0}}{(\Delta H)_{B=0}} dB$$

- Irreversibility: Entropy $dS \geq dQ/T$
 - Cycle of pseudo-entropy from calorimetric measurements

$$\frac{\Delta S'_{cycle}}{\langle \Delta S' \rangle} \approx - \frac{\Delta T_{hys}}{\langle T_{crit} \rangle}$$



Hysteretic compounds



Reduction of the efficient T region in practical cycles

Reduced effective parameters and cooling efficiency

Phase diagram

- Ferro - para
- First order
- Hysteresis

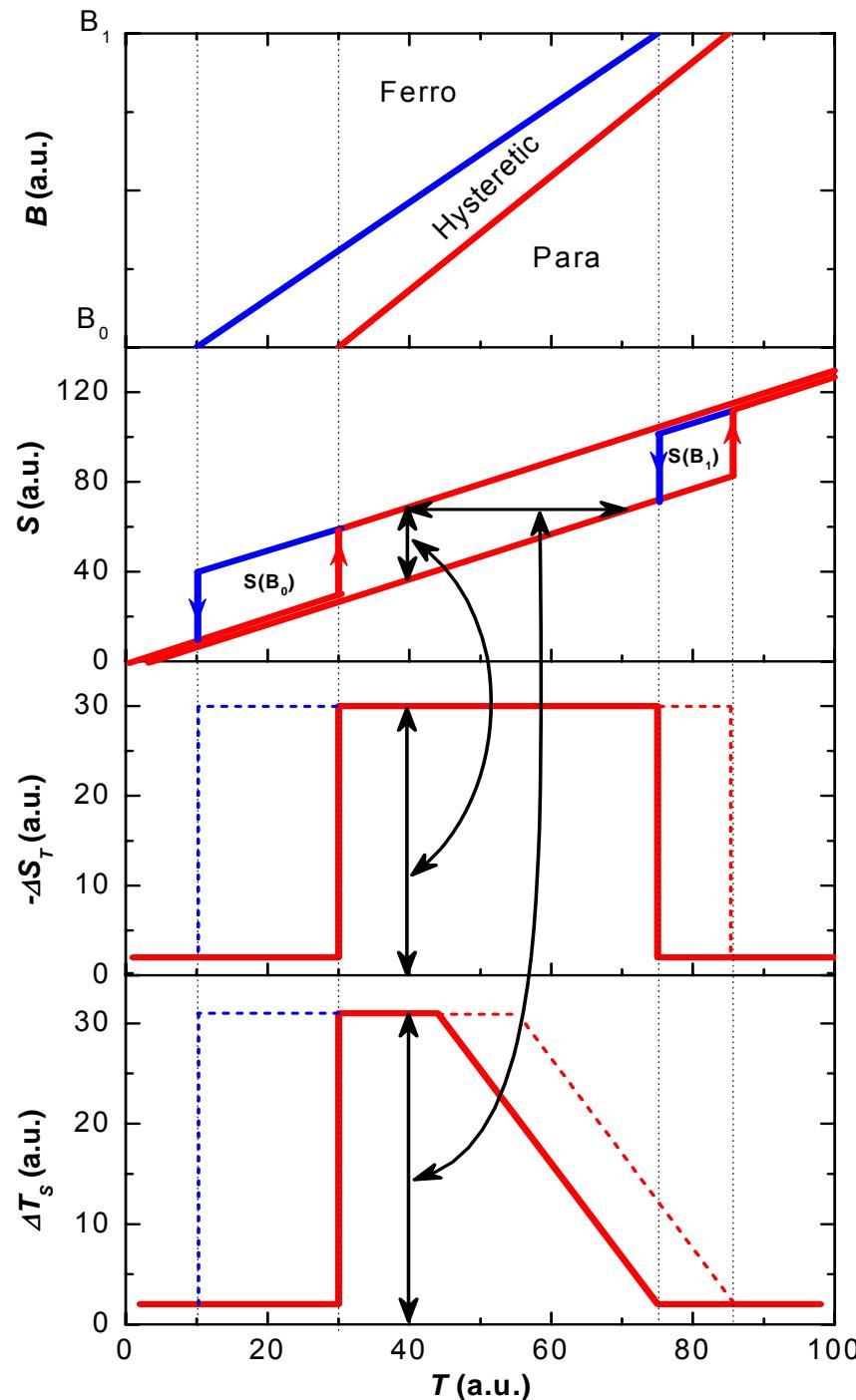
Entropy curves

at fields B_0 and B_1 ,
heating and cooling

Derived entropy
change ΔS_T

Derived temperature
change ΔT_s

DDMC 2011



Conclusions

- Precise determination of the MCE parameters.
- Measurement and control of: Q , T , and $B \longrightarrow \Delta T_S$ and ΔS_T
- Determinations from C_B , good at low T , no precision at high T .
 - Solved with C_B around T_c plus one direct measurement of ΔS_T .
- Hysteretic compounds. Spike problem from $M(B)_T$
- Irreversible entropy. Small correction.
- Hysteresis: reduces the effeteive ΔT_S , ΔS_T and RC

Contributors to this work at the Institute of Materials Science of Aragon (ICMA)

- **Ramon Burriel**
- **Elias Palacios**
- **Leticia Tocado**
- **Gaofeng Wang**