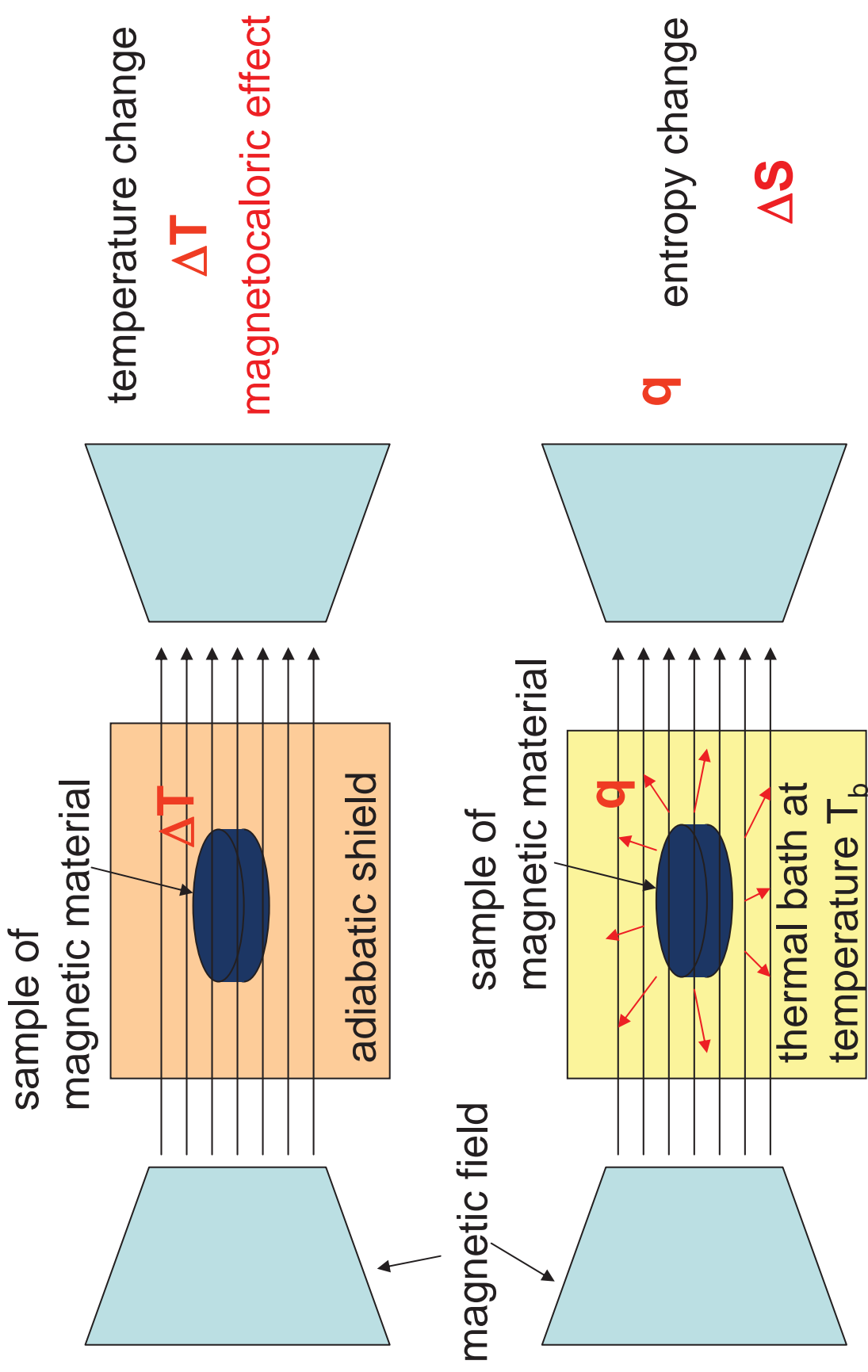


An Isothermal Calorimeter for the direct measurement of magnetocaloric properties

L. Giudici, C.P. Sasso, V. Basso, M. Küpferling, M.Pasquale

INRIM Electromagnetics Division, Torino, Italy

Magnetocaloric Effect



Reversible Process, equilibrium conditions

ΔS isothermal entropy change

ΔT_a adiabatic temperature change

C_p heat capacity in different magnetic fields

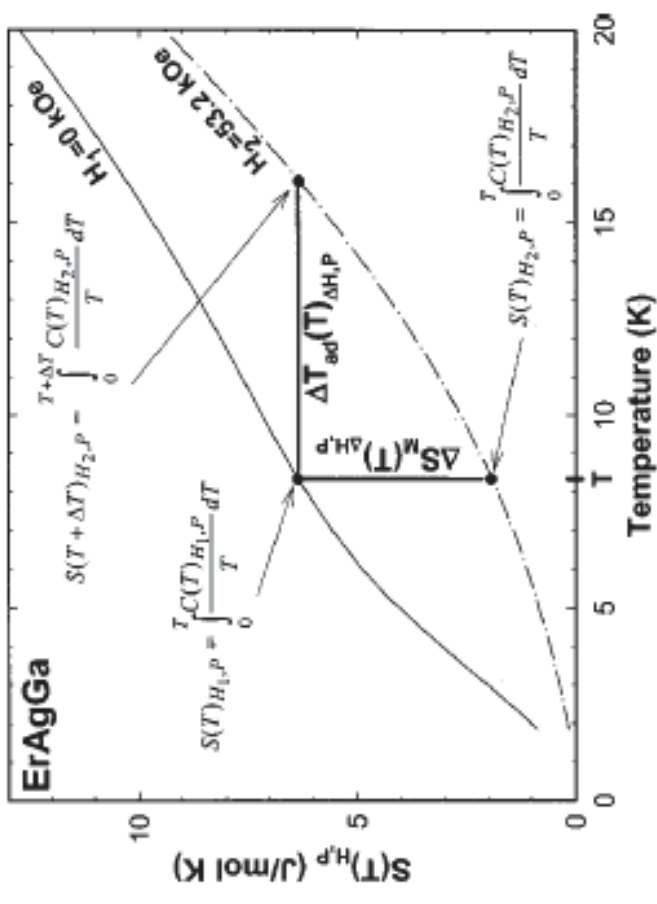
$$\Delta S(T) = [S(T)_{H_2} - S(T)_{H_1}]_{T,P}$$

$$\Delta T_{ad} = [T(S)_{H_2} - T(S)_{H_1}]_{S,P}$$

$$\Delta S(T) = \int_0^T \frac{C(T)_{H_2} - C(T)_{H_1}}{T} dT$$

2° law thermodynamics

Pecharsky et al. PRB 64 (2001)



All quantities are related:

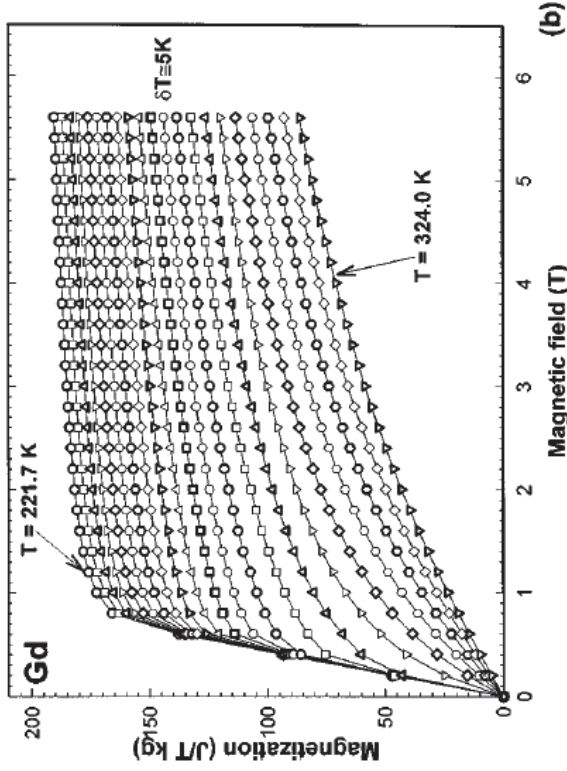
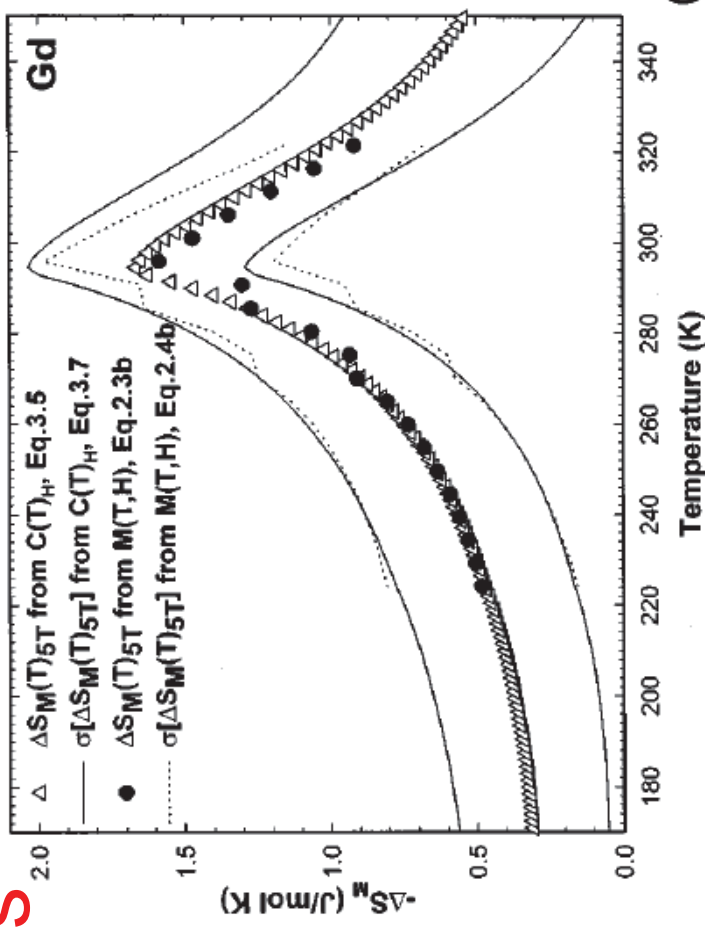
$$dS = \frac{\partial S}{\partial H} dH + \frac{\partial S}{\partial T} dT$$

$$dQ = T dS = T \frac{\partial S}{\partial H} dH + C_p(T, H) dT$$

When the behavior of the total entropy of a magnetic solid is known, the MCE is fully characterized

Maxwell Relationships

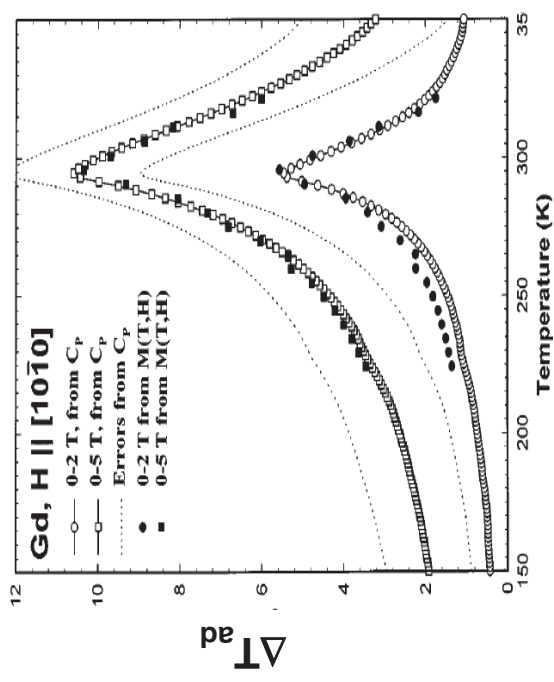
V.K.Pecharsky et al. JAP 86, 1999.



$$\left. \frac{\partial S}{\partial H} \right|_{T=\text{const}} = \left. \frac{\partial m}{\partial T} \right|_{H=\text{const}}$$

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

$$\Delta T_{ad}(T)_{\Delta H} = - \int_{H_1}^{H_2} \frac{T}{C(T, H)} \times \frac{\partial M(T, H)}{\partial T} dH$$



Irreversible process: first order phase transition

Systems with **hysteresis** in Temperature and /or Magnetic field

Not unique function

$$S = S(H, T)$$

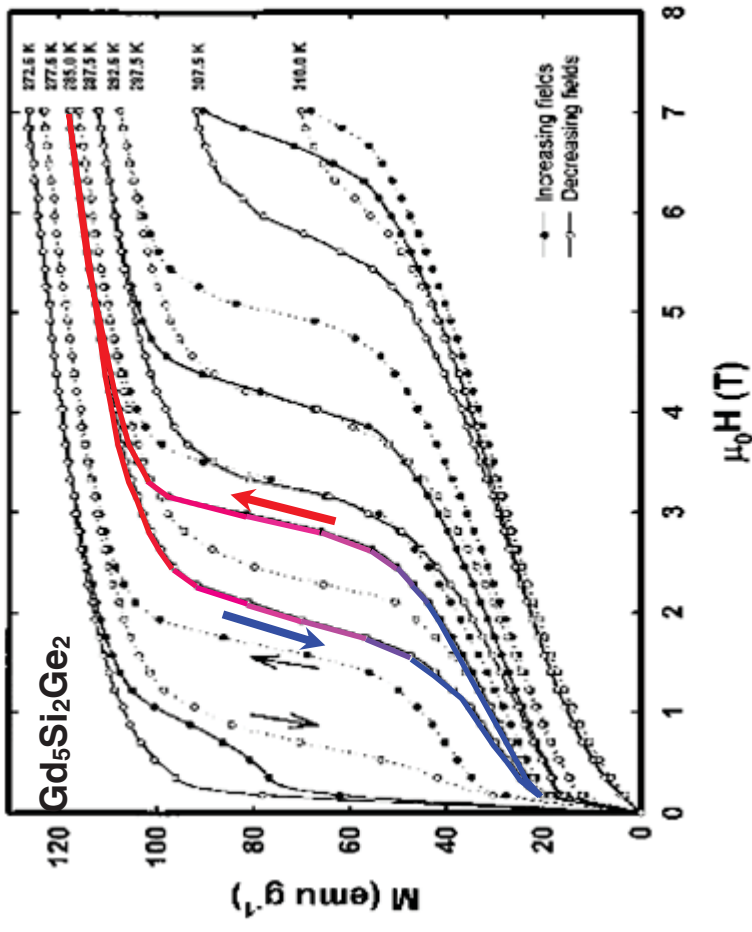
Entropy production

$$dS = d_e S + d_i S \quad dS \geq \frac{dQ}{T}$$

$$dQ = T d_e S = T dS - T d_i S$$

What is the entropy generated along the hysteresis loop?

1° order transition: equilibrium thermodynamics can be applied ?



data from A. Giguere et al. PRL 83, 1999

phase 1 -> FM, orthorhombic
phase 0 -> PM, monoclinic

Irreversible processes :Measurements

Comparison of results of different measurements

- ΔS isothermal entropy change
- ΔT adiabatic temperature change
- C_p heat capacity in magnetic fields

C_p measurements and magnetization measurements, using Maxwell's relations, deliver to different results!

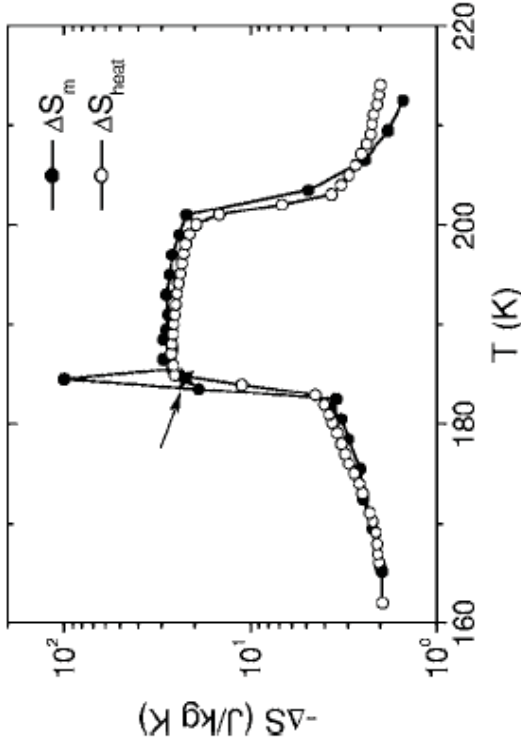
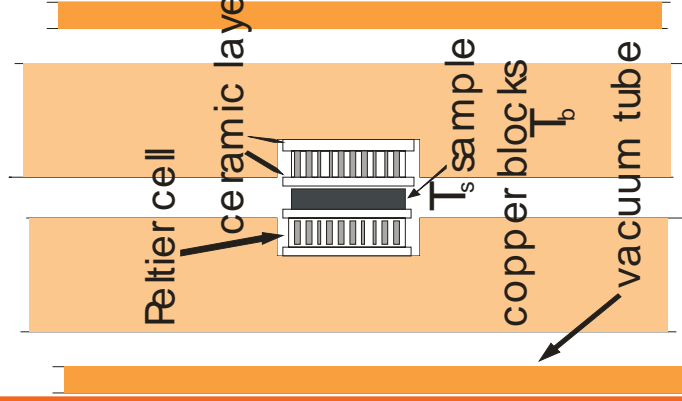


FIG. 2. Temperature-dependent entropy changes of $\text{La}_{0.7}\text{Pr}_{0.3}\text{Fe}_{11.5}\text{Si}_{1.5}$ calculated from magnetic data (solid circles) and heat capacity (open circles). The peak value drops from ~ 99 to ~ 22 J/kg K if only the contributions from the metamagnetic transition are considered (marked by an arrow). Δ has been set ~ 1.5 J/kg K. Solid lines are guides for the eyes.

G.J.Liu et al, APL 90 (2001)

How to determine
correctly the cooling power of a MC
material in a refrigeration cycle?

Direct measurements of isothermal entropy change

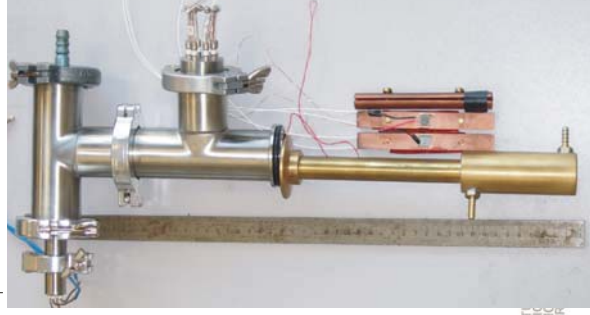


- **Peltier cells** are used as heat flux **sensors** and **actuators** for heating/cooling the sample simultaneously

Peltier as **sensors**: high sensitivity

little affected by the magnetic field
small time constants

Seebeck effect



Peltier as **actuators**: strict isothermal conditions even in higher field rates

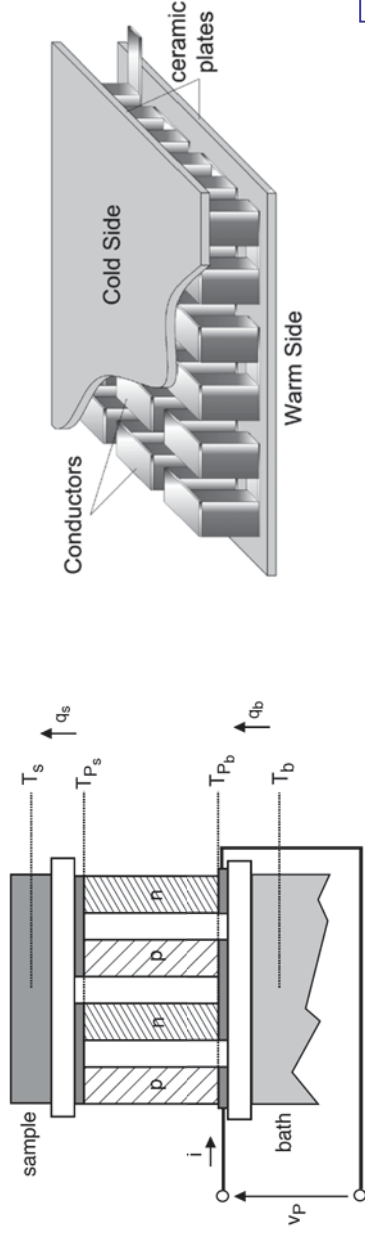
Peltier effect

allows to measure $\Delta S(H)_T$ curve
and not only initial and final states.



- the temperature of the thermal bath can be changed between -30°C and 100°C by using liquid nitrogen and electric heaters
- setup in vacuum (0.5 Pa, rotary pump) in order to avoid heat loss by convection of air and change of temperature
- magnetic field produced by electromagnet up to 2T

Peltier cell equations



time independent relations between current, voltage and heat flux of a thermo-electric material:

$$v_P = \epsilon (T_{P_s} - T_{P_b}) + R i \quad (1) \quad \text{Seebeck effect}$$

$$q_s = \Pi i + \frac{1}{2} R i^2 - K (T_{P_s} - T_{P_b}) \quad (2) \quad \text{Peltier effect}$$

during measurement time dependence plays a role due to finite heat capacity of the cell and the sample

Assumption:

for small variations of the quantities in time (small T difference, slowly time varying magnetic field), the equations 1 and 2 can be applied, introducing cell dependent parameters

- $\epsilon =$ total seebeck coefficient
- $R =$ total electric resistance
- $\Pi = T \epsilon$ Peltier coefficient
- $K =$ thermal conductance of the columns
- $T =$ absolute temperature

Peltier cell equations

$$T_s - T_b = \frac{1}{\epsilon_P} (v_P - R_{PI}i)$$

$$q_s = \Pi_P i - \frac{1}{S_P} (v_P - R_{PI}i) + \frac{1}{2} R i^2$$

$$v_P = \epsilon_P (T_s - T_b) + R_{PI} i$$

$$q_s = \Pi_P i + \frac{1}{2} R i^2 - K_P (T_s - T_b)$$

Peltier effect **Seebeck effect** **Joule heat (negligible!)**

for a simplified case the cell parameters can be determined:

Ceramic layers: negligible thermal capacity, finite thermal conductivity
temperatures of bath and sample: homogeneous (check sample case by case)

Effective cell coefficient:

$$S_P = \epsilon_P / K_P \quad \Pi_P = \Pi \frac{K_P}{K} \quad \epsilon_P = \epsilon \frac{K_P}{K} \quad R_P = R + \left(1 - \frac{K_P}{K}\right) \frac{\epsilon \Pi}{K} \quad K_P = \frac{K K_l}{K + K_l}$$

Parameters include effects of finite heat conductivity (inclusively of contact resistances)

Equations appropriate to describe cells with fast response: transient state are not described!

In order to pass from v and i to ΔT and q_s , the effective parameters must be calibrated!

Calibration

Based on the equations 3 and 4, a calibration at constant temperature of the thermal bath is performed in three independent experiments:

- calibration of S_P

$$q_s = q_0; i = 0; \Delta T \neq 0$$

$$q_s = -\frac{1}{S_P} v_P$$

passive configuration = Peltier cell used as heat sensor

- calibration of R_P

both sides of cell in contact with thermal bath

$$q_s \neq 0; i = i_0; \Delta T = 0$$

$$R_P = \frac{v_P}{i}$$

- calibration of Π_P

with sample in measurement configuration

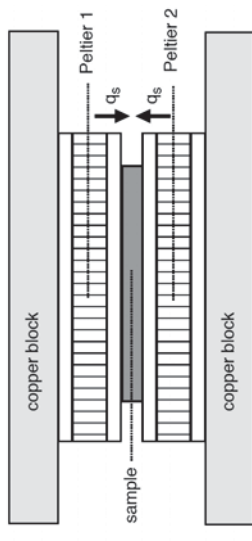
$$q_s = 0; i = i_0; \Delta T \neq 0$$

$$\Pi_P = \frac{1}{S_P} \left(\frac{v_P}{i} - R_P \right) - \frac{1}{2} R i$$

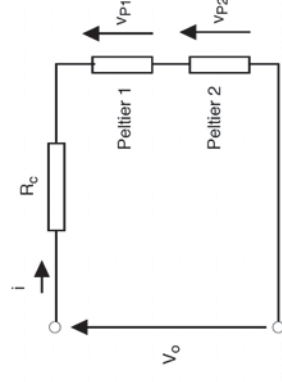
$$T_s - T_b = \frac{1}{\epsilon_P} (v_P - R_P i) \quad (3)$$

$$q_s = \Pi_P i - \frac{1}{S_P} (v_P - R_P i) + \frac{1}{2} R i^2 \quad (4)$$

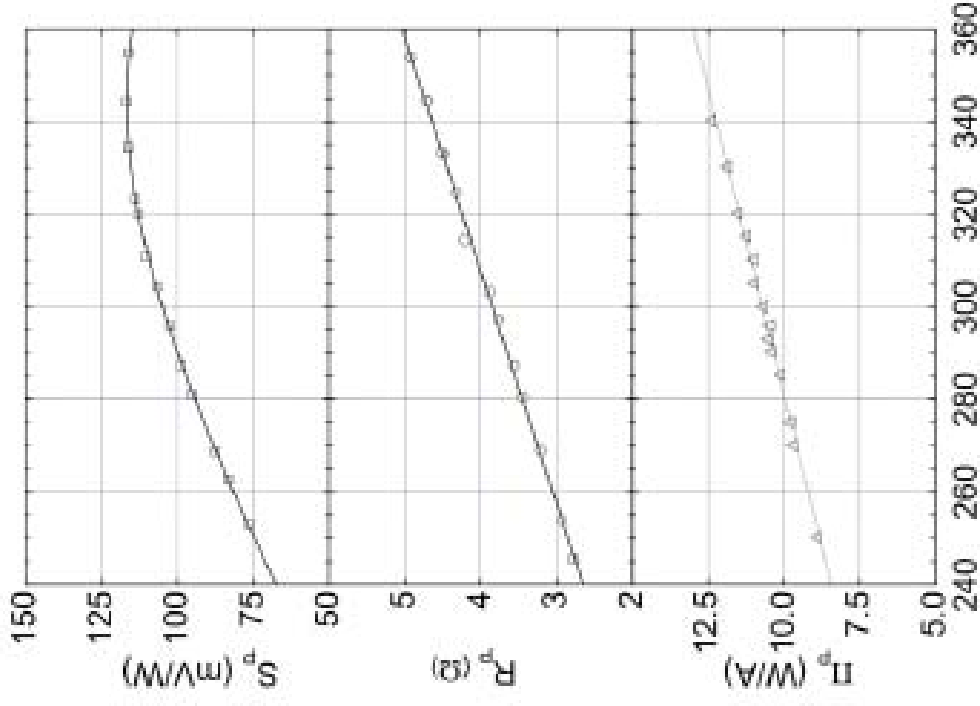
a. thermal



b. electric



Coefficients as a function of the temperature



Sensitivity as heat flux sensor:

Room Temperature:

$$S_p = 0,103 \text{ V/W}$$

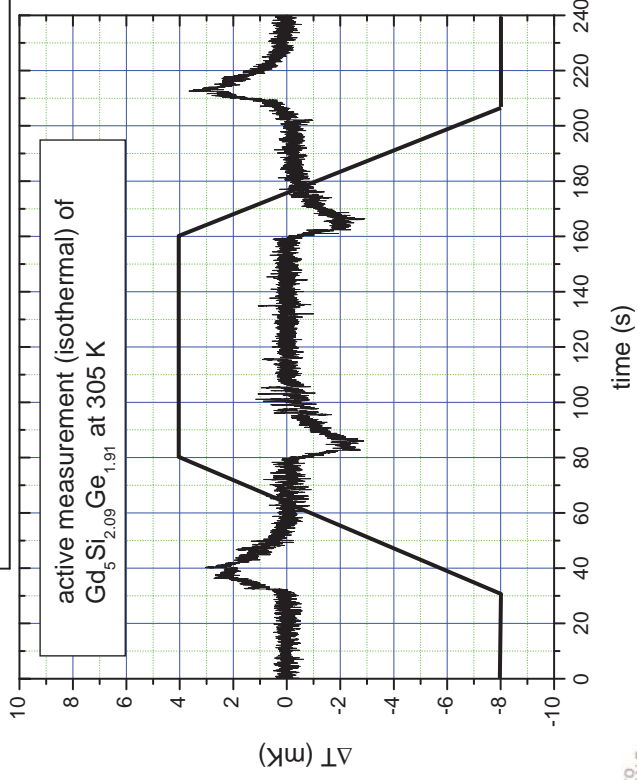
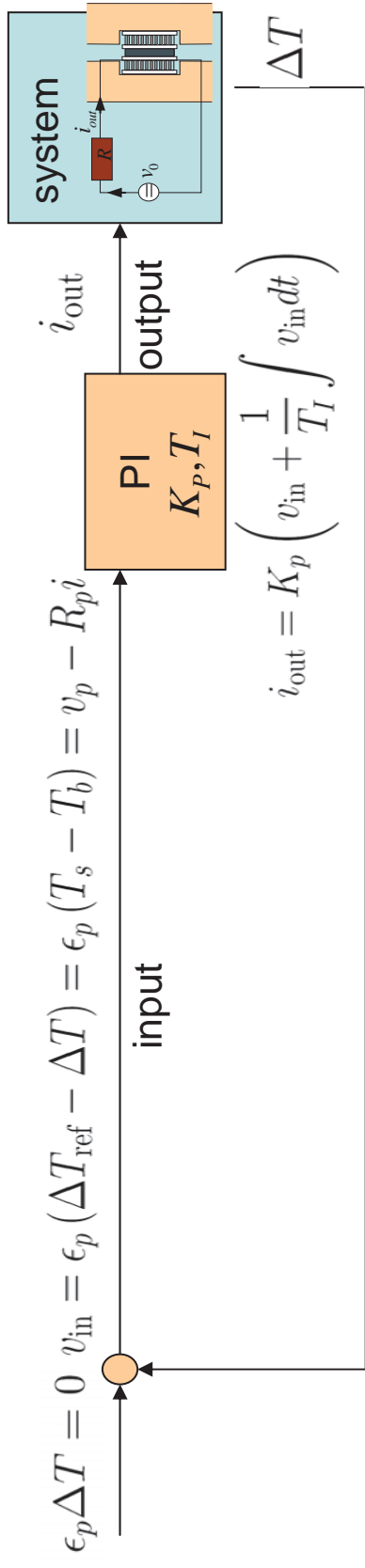
Resolution on $q=1 \mu\text{W}$

(Using a nanovoltmeter)

V.Basso et al. Rev.Sci.Instrum. 79, 063907, (2008)

Digital control for isothermal conditions

The PI control changes the Peltier cell current in order to minimize the temperature difference between sample and bath:



isothermal within 5mK

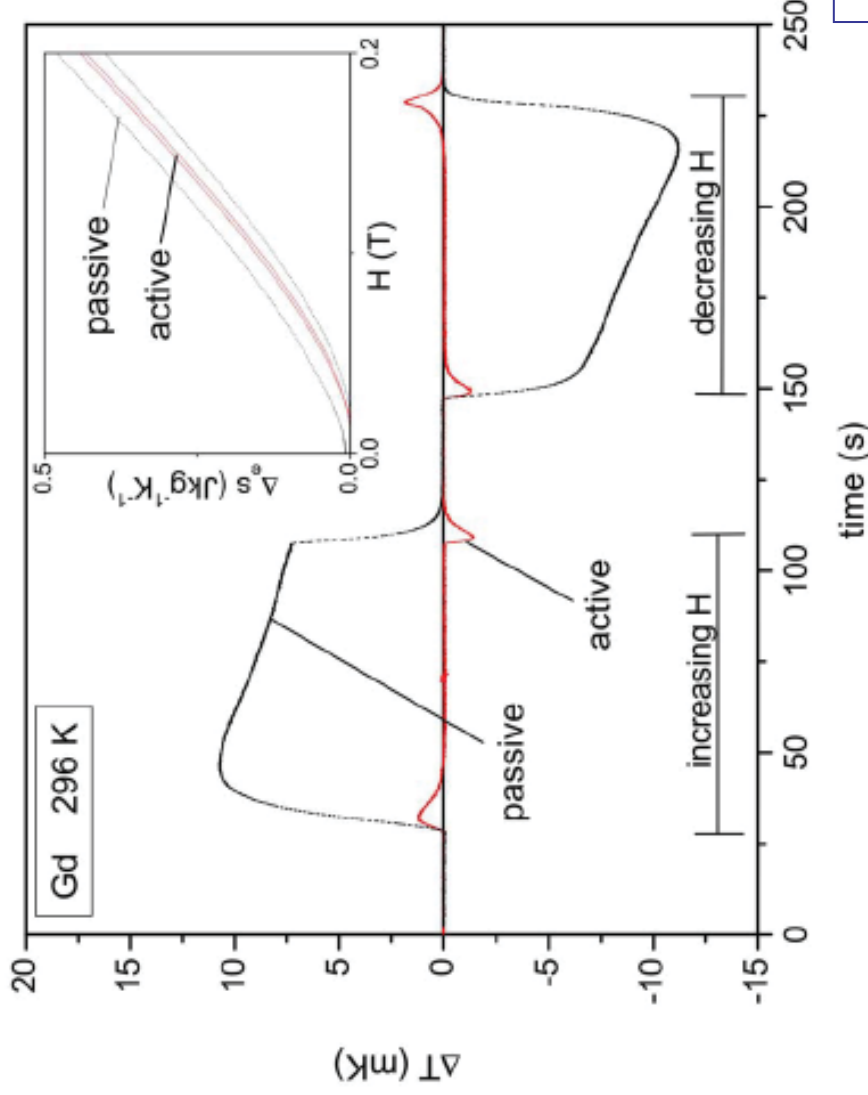
peaks at field change points

limit: noise

future: nanovoltmeter

Comparison of passive and active measurements

Gd $T = 296 \text{ K}$ ($T_c = 293 \text{ K}$)



Negligible entropy production is expected

$$\Delta s = \Delta_e s$$

Single valued curve with no hysteresis

$$\Delta_e s = \frac{1}{mT} \int_0^t q_s(t') dt'$$

Passive: ΔT proportional to heat flux

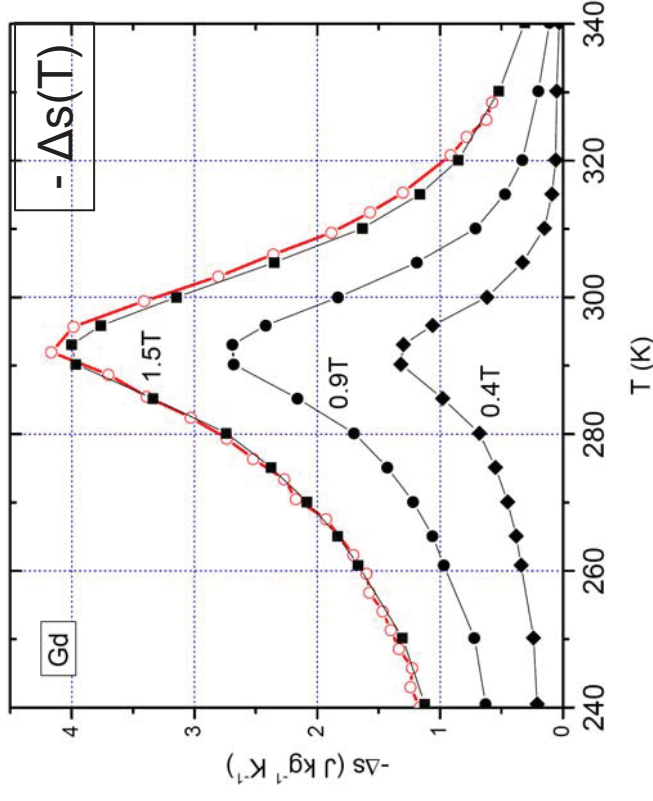
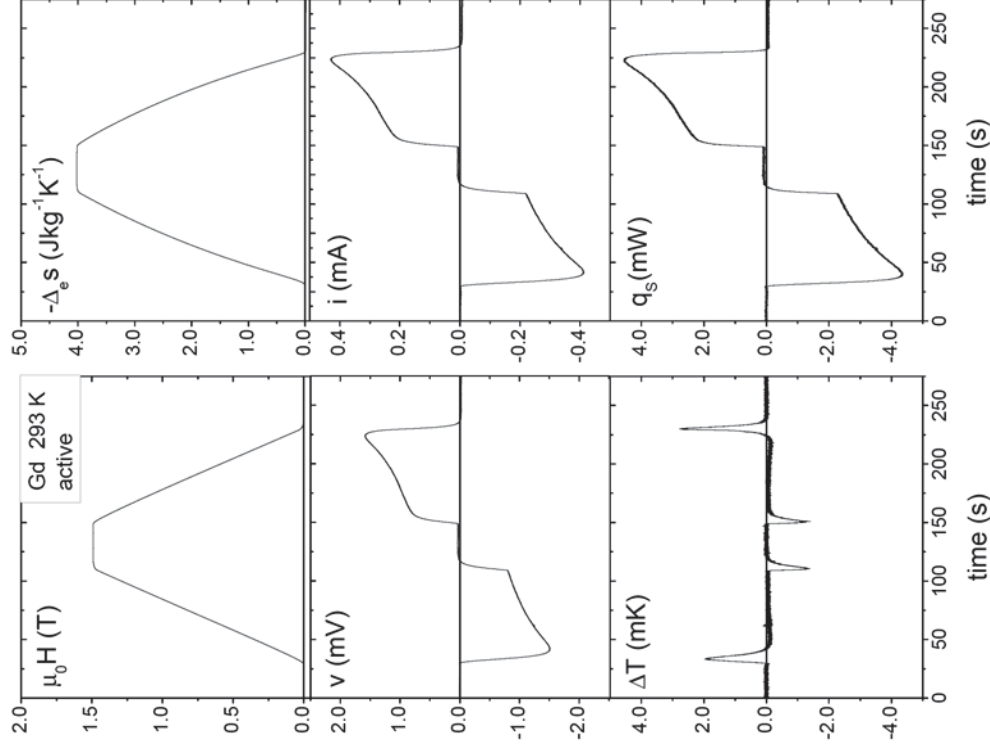
Active: ΔT close to zero

(peaks when q in changing in time)

Hysteresis effect due to time delay
Introduced by the fact that sample is changing T

Single value curve with no hysteresis

Gd sample (sheet of 5x5x1mm):
 maximum field 1.5T, rate 20mT/s
 293K



Open points: measurements performed at University of Zaragoza

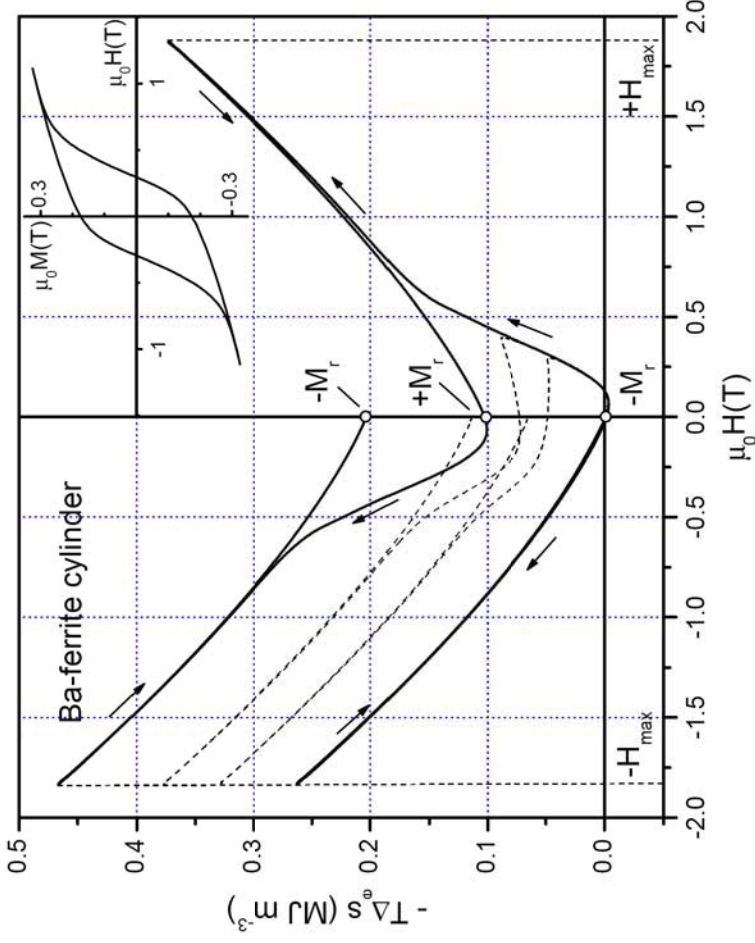
$$\Delta S = S(0) - S(H) = \frac{1}{T} \int_{t_0}^t q dt'$$

q_s mainly due to Peltier effect

V. Basso et al., Rev.Sci.Instrum, 79, 063907, (2008)

$q_s > 0$ heat absorbed (decreasing field)
 $q_s < 0$ heat released (increasing field)

Barium ferrite BaFe₁₂O₁₉



Dissipated energy in a closed hysteresis loop:

$$T\Delta_i s = \oint T d_i s = -\oint T d_e s = 0.205 \text{ MJ m}^{-3}$$

Area of magnetic saturation hysteresis loop:

$$\mu_0 \oint H dM = 0.209 \text{ MJ m}^{-3}$$

Reversible MCE



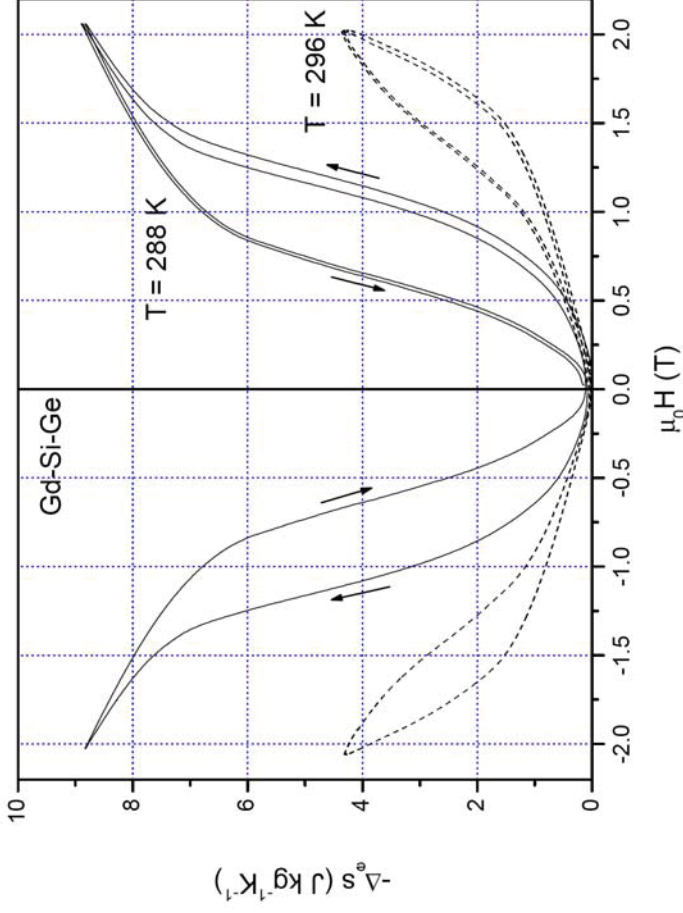
Entropy Production:
Upper shift of the curve:
dissipation of energy

Active measurements

T=288K



Coupled magnetostructural transition:
FM orthorhombic to PM monoclinic structure



Entropy change associated to latent heat of the first order phase transition:
hysteresis

$-\Delta s_e$ as function of magnetic field

$$\mu_0 H_{\max} = 2 \text{ T}$$

Small entropy production

Small positive shift of $\Delta_e s$ curve

Only **1%** of the maximum entropy change

Effects of hysteresis in NiMnGa and NiMnSn

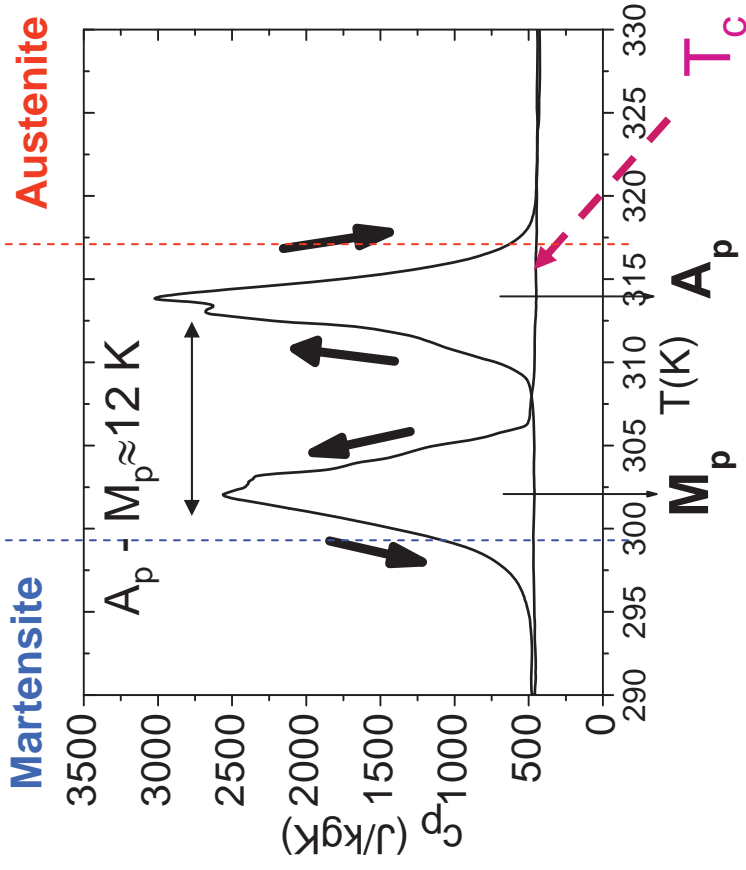
GMCE: first order and second order transition superimposed

High enthalpy of transformation: promising materials

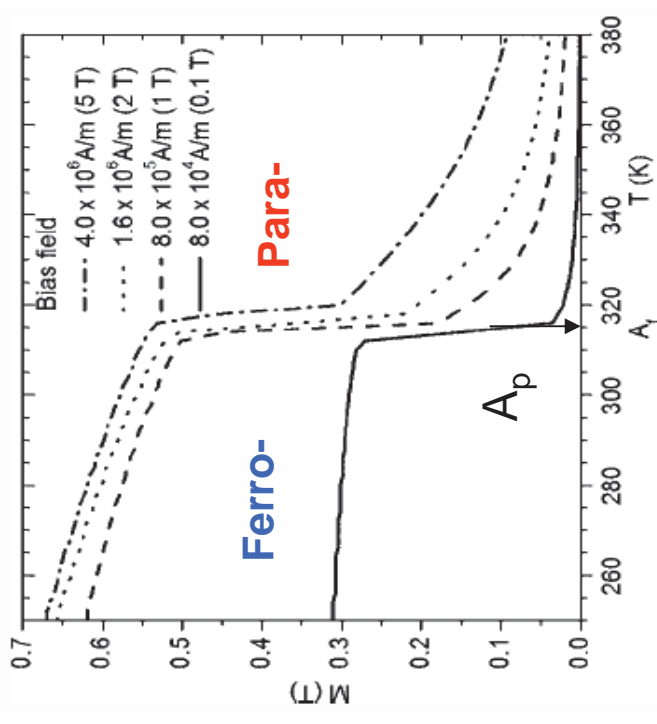
History dependence of $\Delta S(\Delta H; T)$: direct measurements

Experimental measurements $\text{Ni}_{55}\text{Mn}_{20}\text{Ga}_{25}$ single crystal

DSC measurements



Magnetization measurements



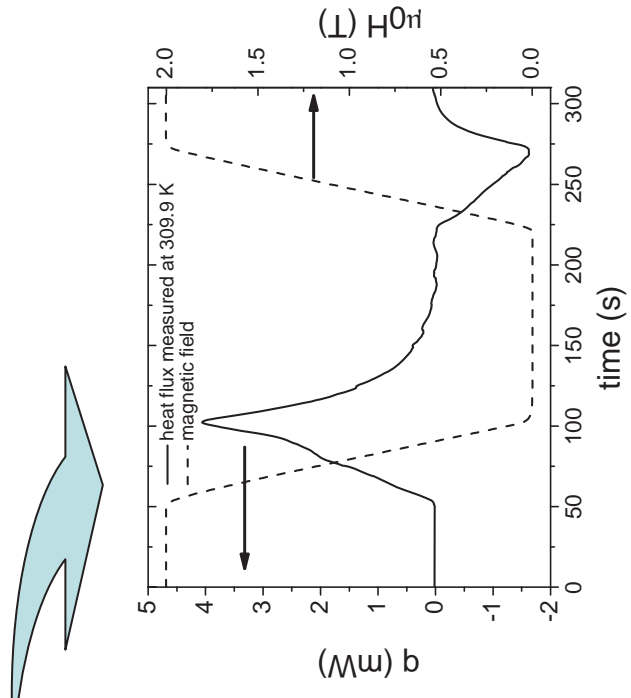
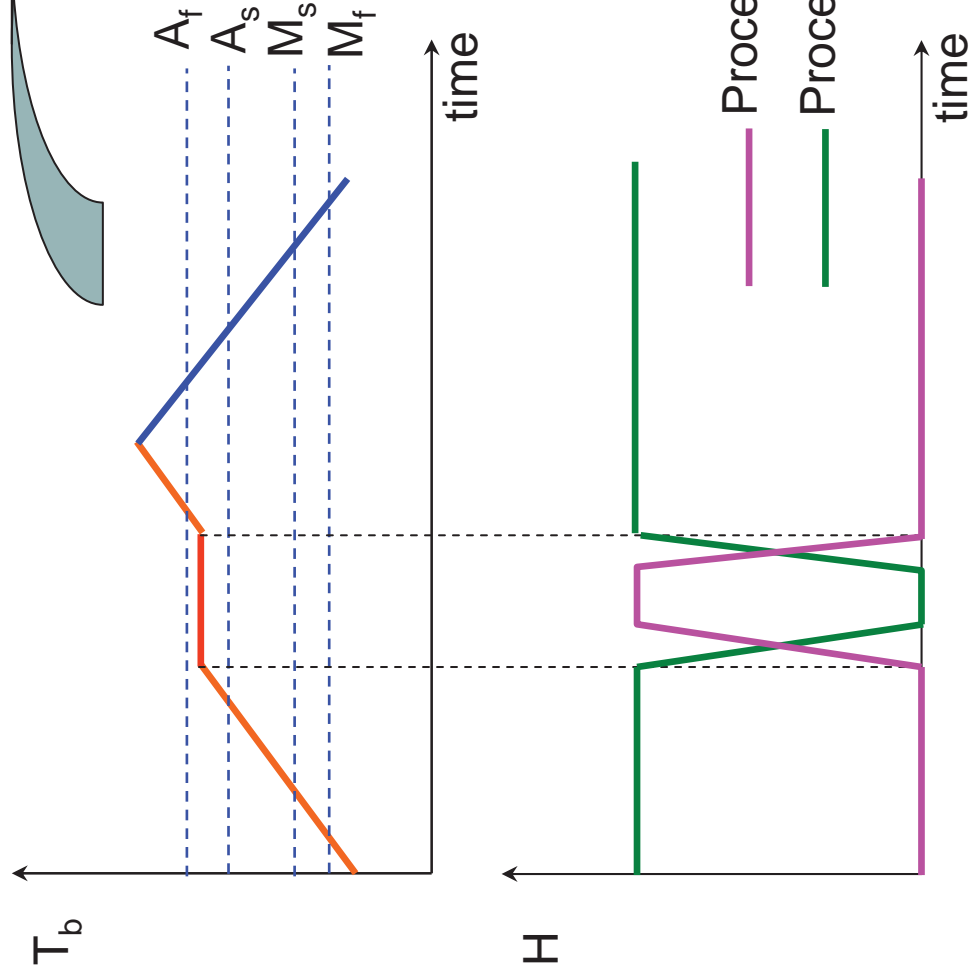
$T_c = 312.6$ K $A_p = 314$ K $M_p = 302$ K

First order endothermic transition peak superimposed to T_c during heating

Hysteresis in first order transition T

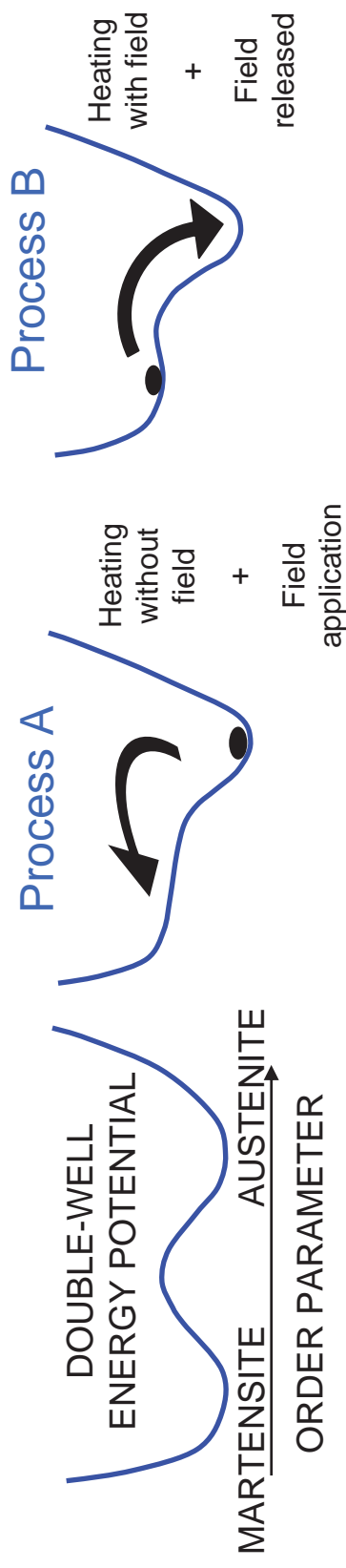
C.P.Sasso et al., JAP 103 (2008)

History dependence of $\Delta S(\Delta H; T)$



Qualitative explanation of hysteresis effects

Energy potential can be distorted by temperature and magnetic field
When one minimum becomes unstable the transition occurs



Direct MCE: A) H stabilizes martensite, M-A transition unfavorable
B) H removed: M-A transition favorable

Direct measurements of exchanged Entropy

Different preparation histories

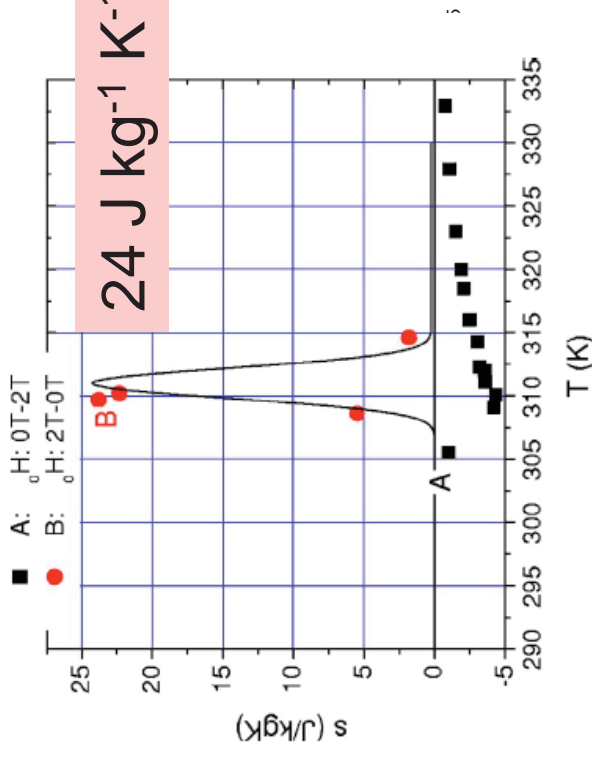
A: Starting from $T < M_f$
 T is increased with $H=0$ up to T_1
 Then $\mu_0 H=2T$ is applied
 and $\Delta S(H_1, T_1)$ is measured

B: Starting from $T < M_f$
 T is increased with $\mu_0 H=2T$ up to
 T_1 then field is decreased to 0
 and $\Delta S(H_1, T_1)$ is measured

Different results !

A) Hysteresis of Phase Transition
 H promotes martensite
 S is decreasing
 $\Delta S_{Amax} = -4.4 \text{ J kg}^{-1} \text{ K}^{-1}$

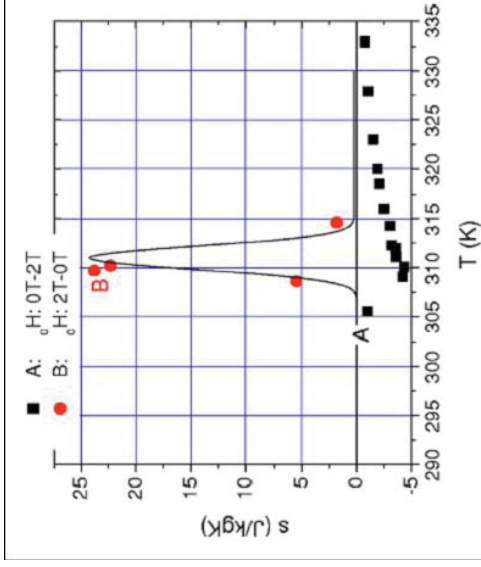
B): H stabilizes martensite
 Removing H and increasing T
 Total entropy change associated
 to magnetostructural transition
 $\Delta S_{Bmax} = 24 \text{ J kg}^{-1} \text{ K}^{-1}$



C.P.Sasso et al., JAP 103 (2008)

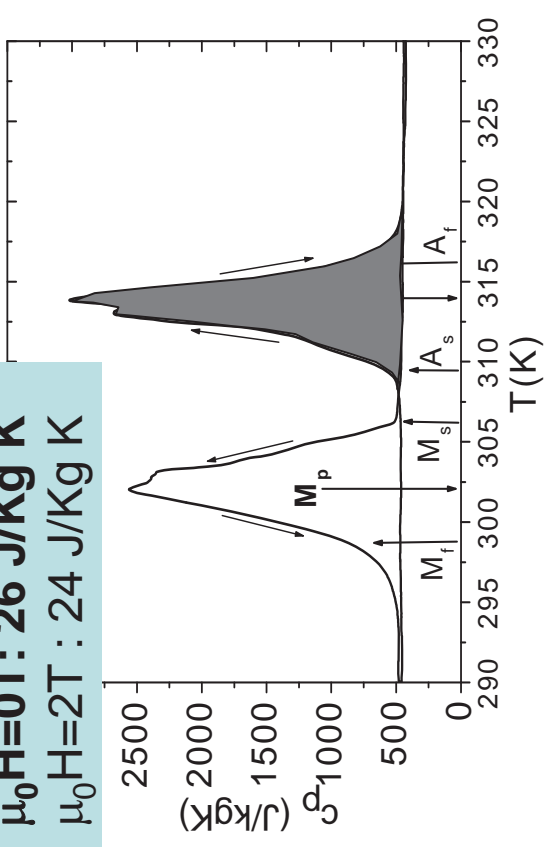
Direct measurements of exchanged Entropy

Isothermal ΔS : 24 J/kg K

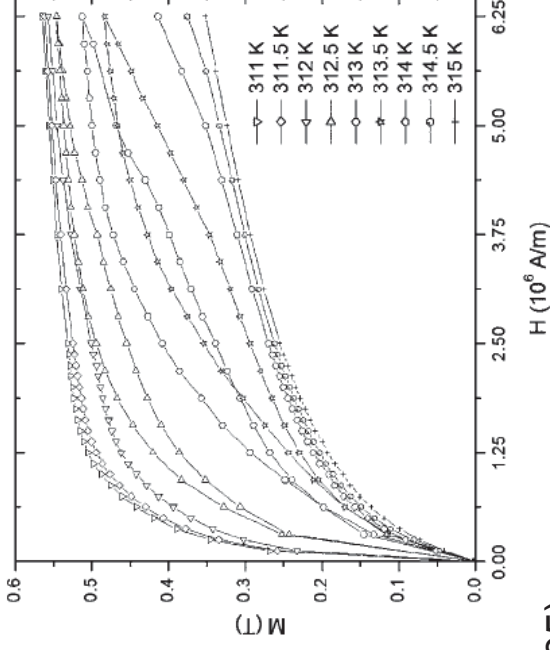
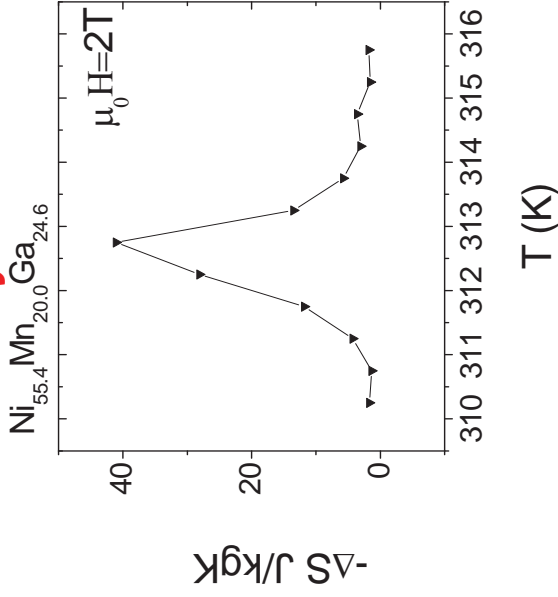


ΔS evaluated by DSC measurements

$\mu_0 H=0T$: 26 J/Kg K
 $\mu_0 H=2T$: 24 J/Kg K



ΔS evaluated by Maxwell relations

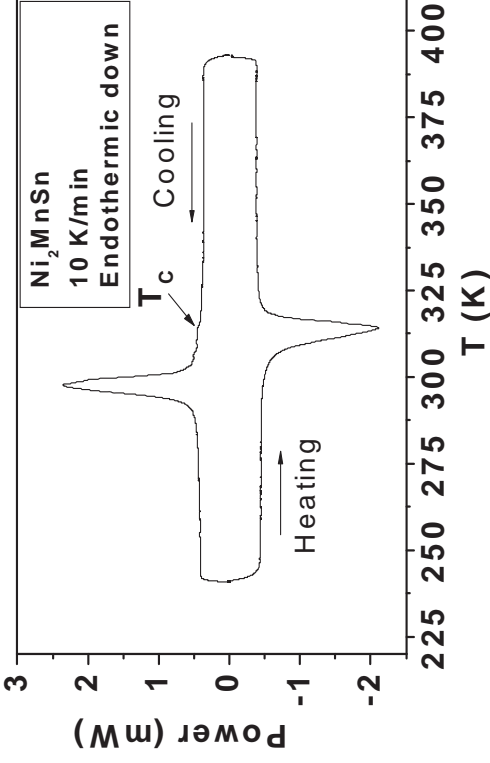


Maxwell
 Relations:
 $\Delta S= 40 \text{ J/kg K}$
 $\mu_0 H=2T$

Ni₅₀Mn₃₇Sn₁₃ polycrystalline sample

Ames Laboratory (T.Lograsso, D.Schlagel)
 Annealed at 900°C for 72 hours

DSC curve



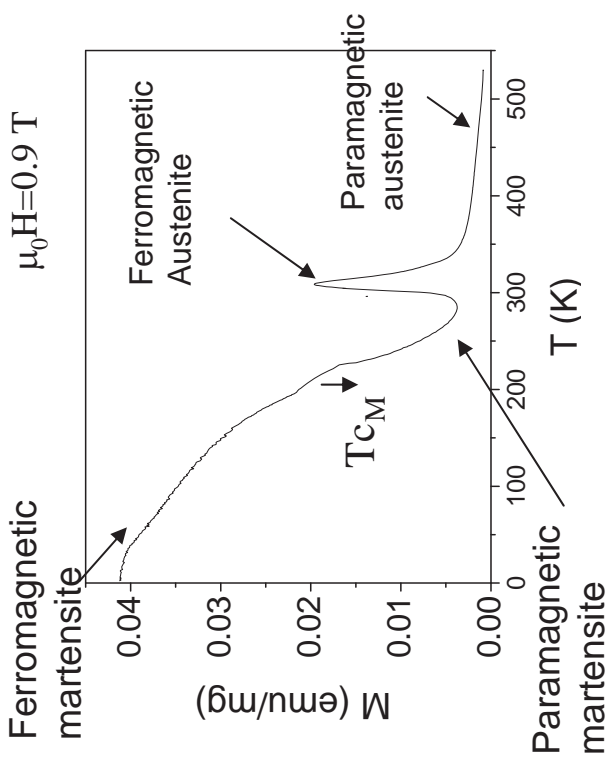
Hysteresis of 15 K in 1st order transition T

Heat Capacity $C_p = 430 \text{ J/kg K}$

$|\Delta S| = |\Delta H/T| = 35 \text{ J/Kg K}$

M.Pasquale et al. APL 91 (2007)

Magnetization measurements (heating)



Magneto-Structural phase transition
 at room temperature:

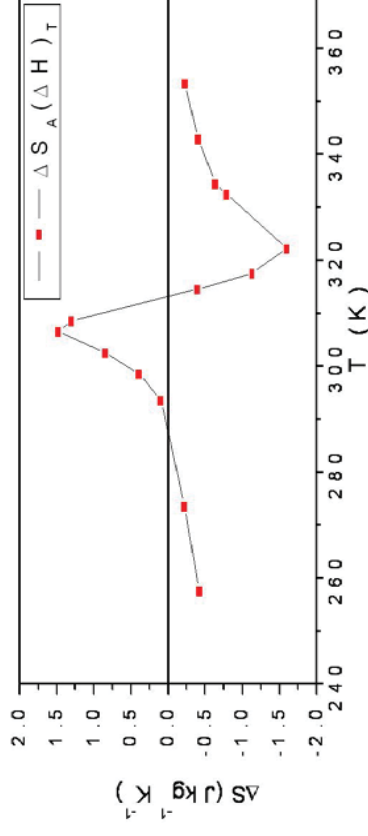
From a martensite (M) phase with
 lower magnetization
 to an austenite (A) phase with
 higher magnetization.

Inverse MCE:

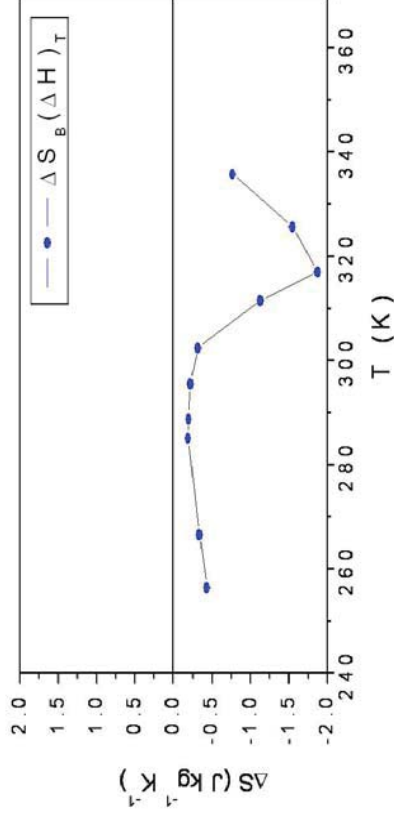
$$\left. \frac{\partial S}{\partial H} \right|_T = \left. \frac{\partial M}{\partial T} \right|_H > 0$$

Direct measurements of exchanged Entropy, $\mu_0 H = 2T$

$\Delta S_A(H)_T$: sample T was increased up to a target value, then H was applied; each $\Delta S_A(H)_T$ point measured after zero field cooling in order to have the same initial conditions.



$\Delta S_B(H)_T$: H was applied at low T, the sample was heated, once the target T was reached H was removed.



- A) both positive and negative $\Delta S_A(H)_T$ are measured associated to the magnetic and structural transition
- B) only negative $\Delta S_B(H)_T$ is measured, close to T_c , associated to the magnetic transition

A) Heating without field M-A transition is occurring

Field application promotes the growth of ferromagnetic austenite phase, (M-A transition)

$\Delta S_A(H)T > 0$ INVERSE Magnetocaloric Effect

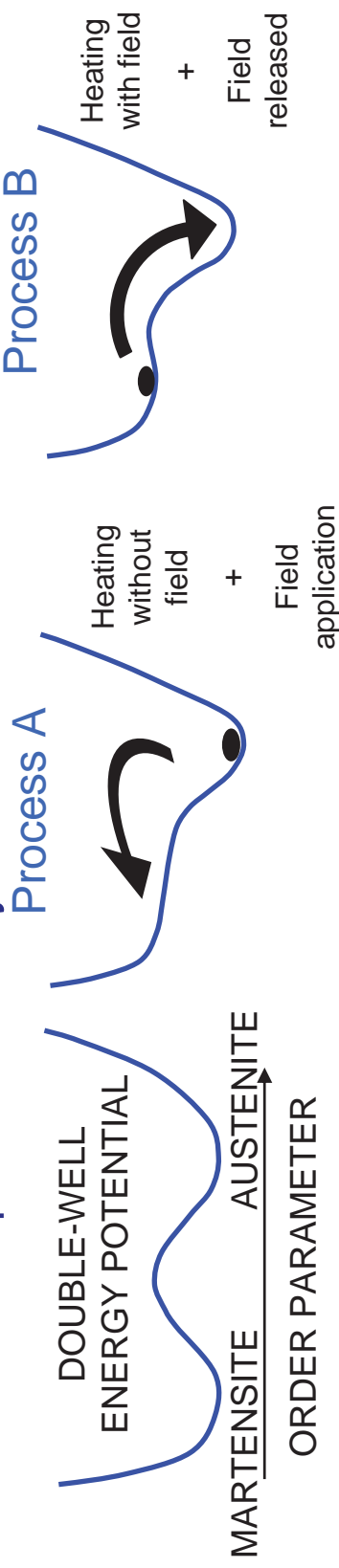
B) Heating with field

M-A transition is occurring

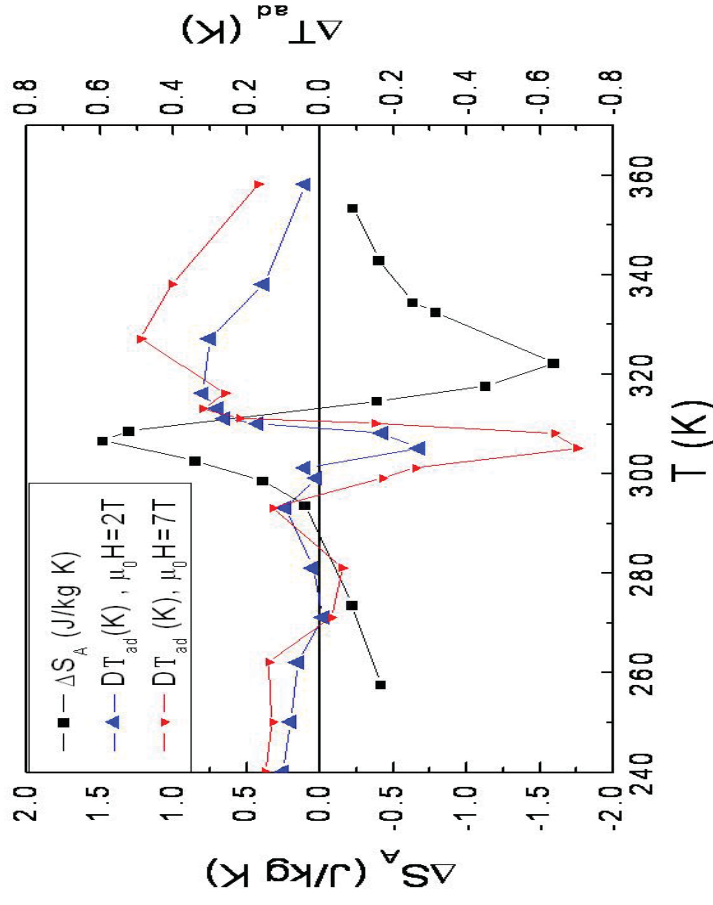
Field removal should promote the paramagnetic martensite phase, with lower entropy, (A-M transition), leading to $\Delta S_B(H)T > 0$ but the thermal hysteresis in the phase transition hinders the reverse austenite to martensite phase transition.

NO Inverse Magnetocaloric effect is measured

Qualitative explanation of hysteresis effects



Direct ΔS and ΔT_{ad} measurements



Adiabatic Temperature Change:

$$\Delta T_{ad} = -0.9 \text{ K} \quad \mu_0 H = 7T \quad T = 305 \text{ K}$$

$$\Delta T_{ad} = -0.3 \text{ K} \quad \mu_0 H = 2T \quad T = 305 \text{ K}$$

Isothermal entropy change:

$$\Delta S_A = 1.5 \text{ J kg}^{-1} \text{ K}^{-1} \quad \mu_0 H = 2T \quad T = 306 \text{ K}$$

DSC measurements:

$$|\Delta S| = \left| -\frac{\Delta H}{T} \right| = 35 \text{ J/Kg K}$$

$$\mu_0 H = 0T$$

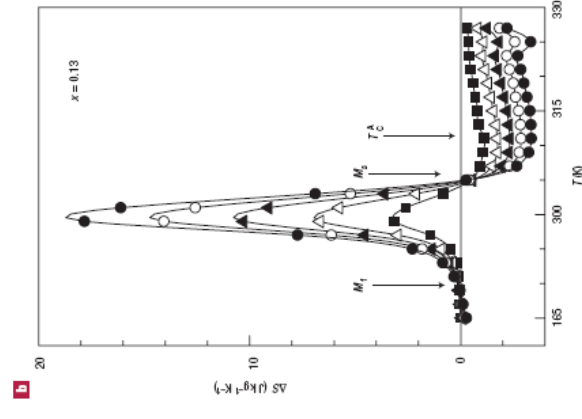
$$\frac{\partial A_p}{\partial \mu_0 H} \cong 0.14 \text{ K / T}$$

Maxwell Relations:

$$\Delta S = 7 \text{ J/kg K}$$

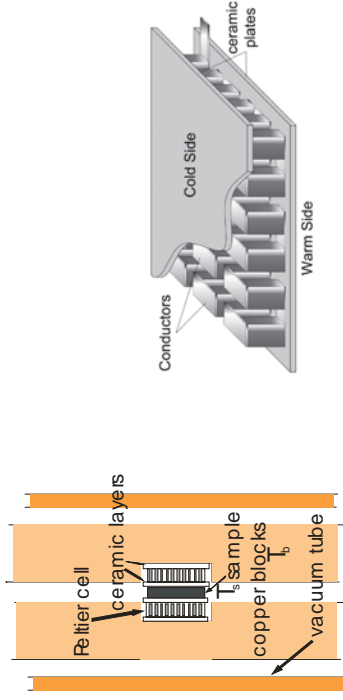
$$\mu_0 H = 2T$$

Unknown heat treatment



Conclusion

Peltier Cells Calorimeter



simple setup

Peltier cells

direct measurement of entropy change

measurements of magnetocaloric materials and magnetic materials with hysteresis

actuator and sensor

test measurement of Gd showed good results

NiMnGa NiMnSn

Hysteresis is important for the cooling performances of giant magnetocaloric materials.

Time history of H and T must be carefully controlled in order to compare magnetocaloric properties of the materials.

Further developments

fields up to 7T, cryostat

Delft days on Magnetocalorics

Peltier Effective coefficients

$$T_s - T_b = \frac{1}{\epsilon_P} (v_P - R_P i) \quad (3)$$

$$q_s = \Pi_P i - \frac{1}{S_p} (v_P - R_P i) + \frac{1}{2} R i^2 \quad (4)$$

$$\Pi_P = \Pi \frac{K_P}{K} \quad \epsilon_P = \epsilon \frac{K_P}{K}$$

$$R_P = R + \left(1 - \frac{K_P}{K}\right) \frac{\epsilon \Pi}{K} \quad K_P = \frac{K K_l}{K + K_l}$$

ϵ = total seebeck coefficient

R = total electric resistance

$\Pi = T \epsilon$ Peltier coefficient

K = thermal conductance of the columns

T = absolute temperature

K_p = total thermal conductance
 K = thermal conductance of the columns
 K_l = thermal conductance of the 2 layers
 R_p = effective resistance
 Π_p = effective Peltier coefficient
 E_p = effective seebeck coefficient

V. Basso et al. Rev. Sci. Instrum. 79, 063907, (2008)