



Delft Days November 02-03 2015
Science Centre Delft, Mijnbouwstraat 120, Delft
on Magnetocalorics 2015

Temperature hysteresis and latent heat avalanches in $\text{LaFe}_x\text{Mn}_y\text{Si}_z\text{-H}_{1.65}$

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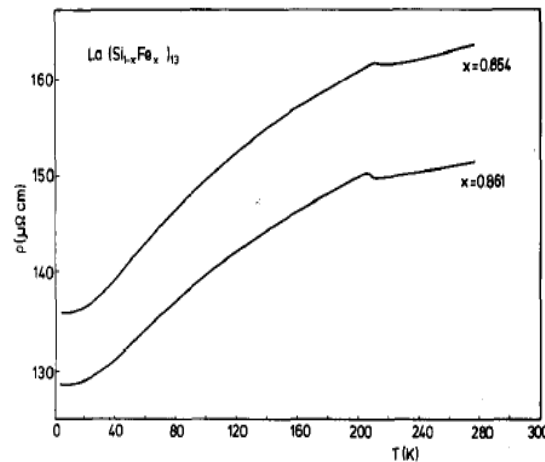
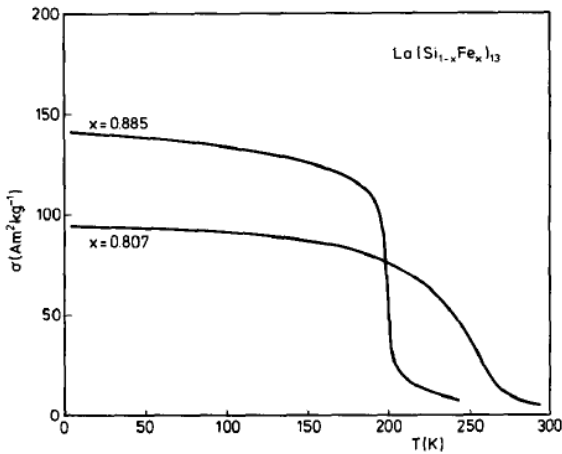
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DRREAM
Drastically Reduced Use of Rare Earths in Applications of Magnetocalorics

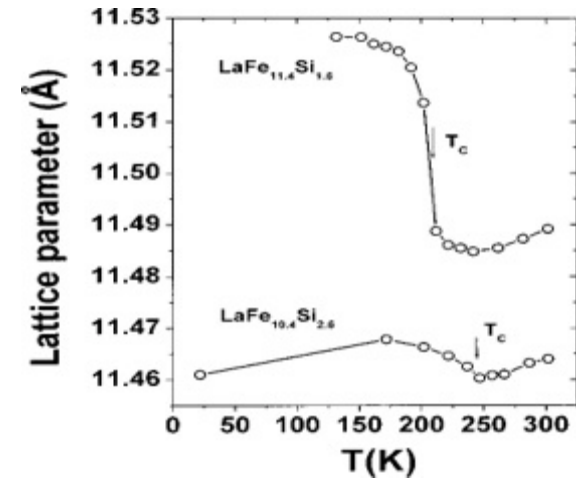
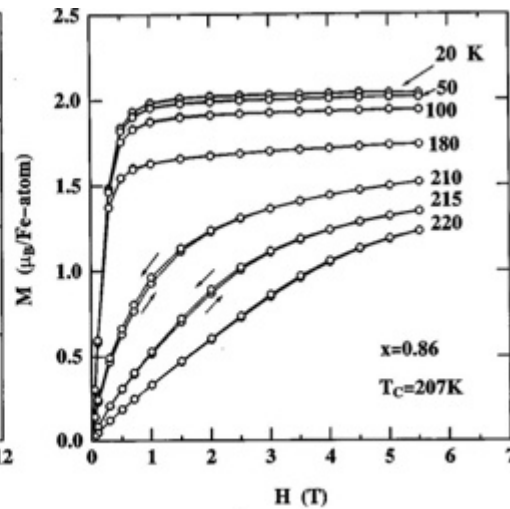
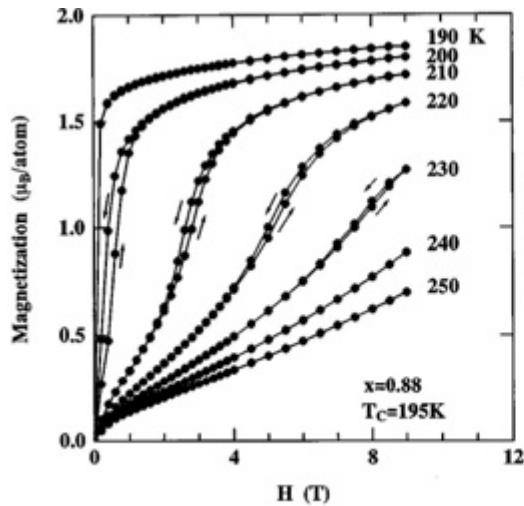
PHASE TRANSITION PROPERTIES IN LaFeSi BASED COMPOUND



“STUDY OF THE CRITICAL BEHAVIOUR OF THE MAGNETIZATION AND ELECTRICAL RESISTIVITY IN CUBIC $\text{La}(\text{Fe},\text{Si})_3$ COMPOUNDS”

Palstra, T. T. M., et al.

Journal of magnetism and magnetic materials 36.3 (1983): 290-296.



FIELD INDUCED PM TO FM TRANSITION:

T_c INCREASES DUE TO THE EFFECT OF APPLIED FIELD

Fujita et al. *Magnetics, IEEE Transactions on* 35.5 (1999): 3796-3798.

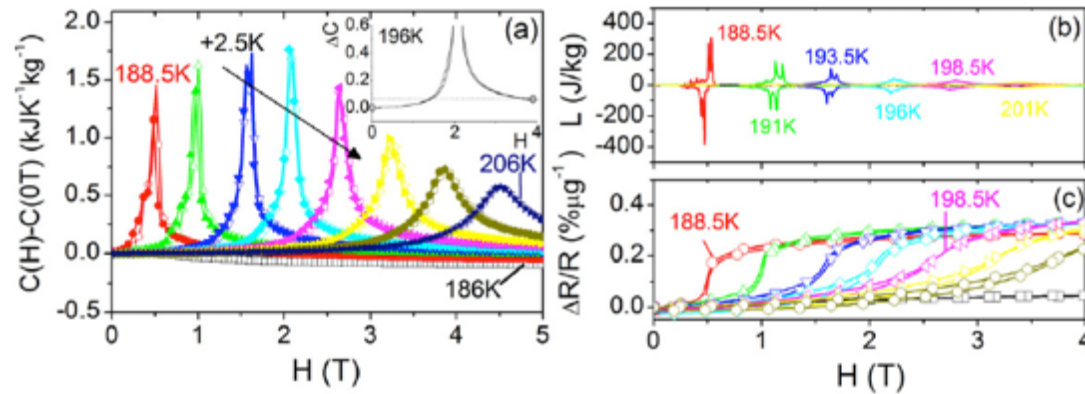
LATTICE CONTRACTION AT PM PHASE

Hu et al. *Appl. Phys. Lett.*, Vol. 78, No. 23, 4 June(2001)

- Large MCE values (ΔS_{ISO} 20 kJ/kg K; ΔT_{AD} 10 K)
- Tunable T_c (Ambient temperature)
- **Small thermal and magnetic hysteresis**

*Candidate
for magneto cooling*

CONTRIBUTIONS TO ΔS_{ISO} IN LaFeSi BASED COMPOUNDS

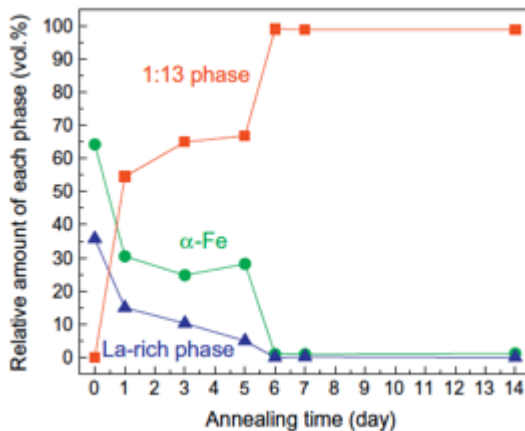


Lowering of latent heat **by magnetic field** and growths of specific heat of transition

Morrison, K., et al.

Journal of Physics D: Applied Physics 43.13 (2010).
Journal of Physics D Applied Physics 45 (2012).

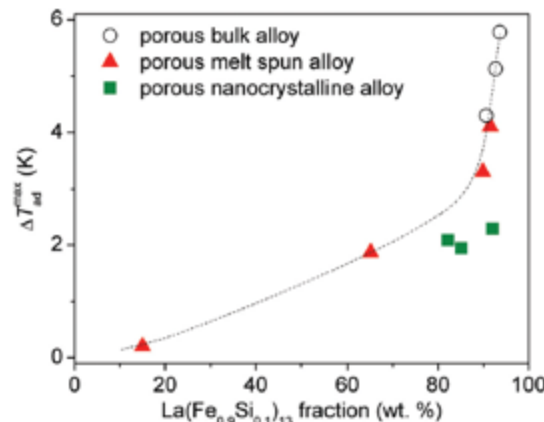
SECONDARY PHASES



Liu, J. et al.

Acta Materialia 59.9 (2011): 3602-3611.

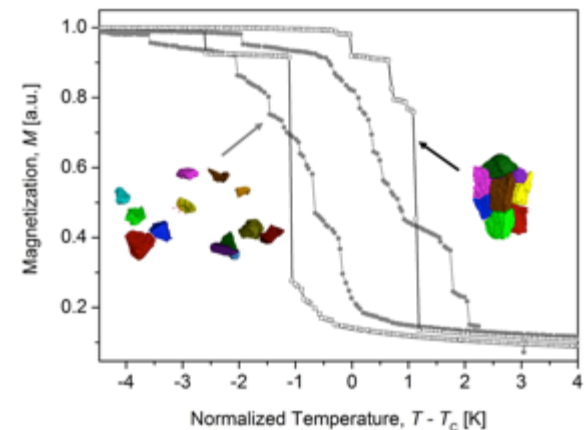
MICROSTRUCTURE



Lyubina, J. et al.

Journal of Applied Physics 109.7 (2011)

SAMPLE SIZE



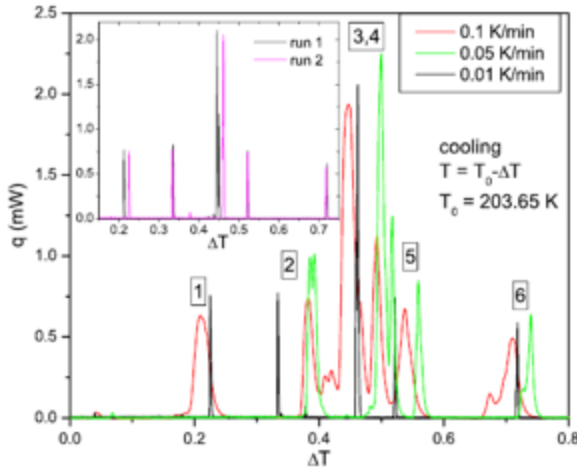
Waske, A., et al.

Phys. Status Solidi RRL 9 (2015).

DYNAMICS OF THE PHASE TRANSITION LaFeSi BASED COMPOUNDS

1st order phase transition in fragment (3 mg) of $\text{La}(\text{Fe}_{0.9}\text{Co}_{0.015}\text{Si}_{0.085})_{13}$ $T_C = 200$ K

DIFFERENTIAL SCANNING CALORIMETRY



Kuepferling, M., et al.

Journal of Applied Physics 115.17 (2014).

Heat flux spikes are related to fast transformations of volumes and reveal as the FAST process is dominated by the pinning of phase boundaries at defects (cracks).

MAGNETO OPTICS IMAGING TECHNIQUE WITH INDICATOR FILM

Laviano F., et al. *Superconductor Science and Technology* 16.1 (2003)

Secondary phases

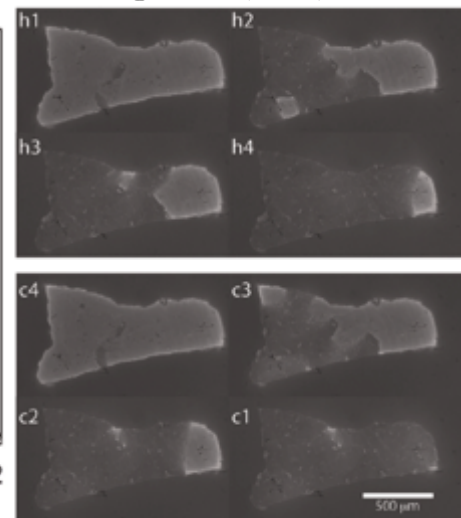
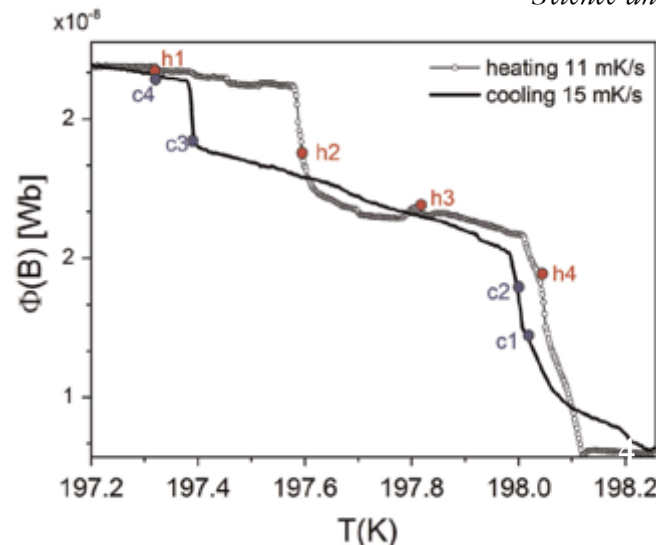
magnetic in homogeneities not always related to strong changes of the path but influence the SLOW dynamics

$H = 70$ mT (small)

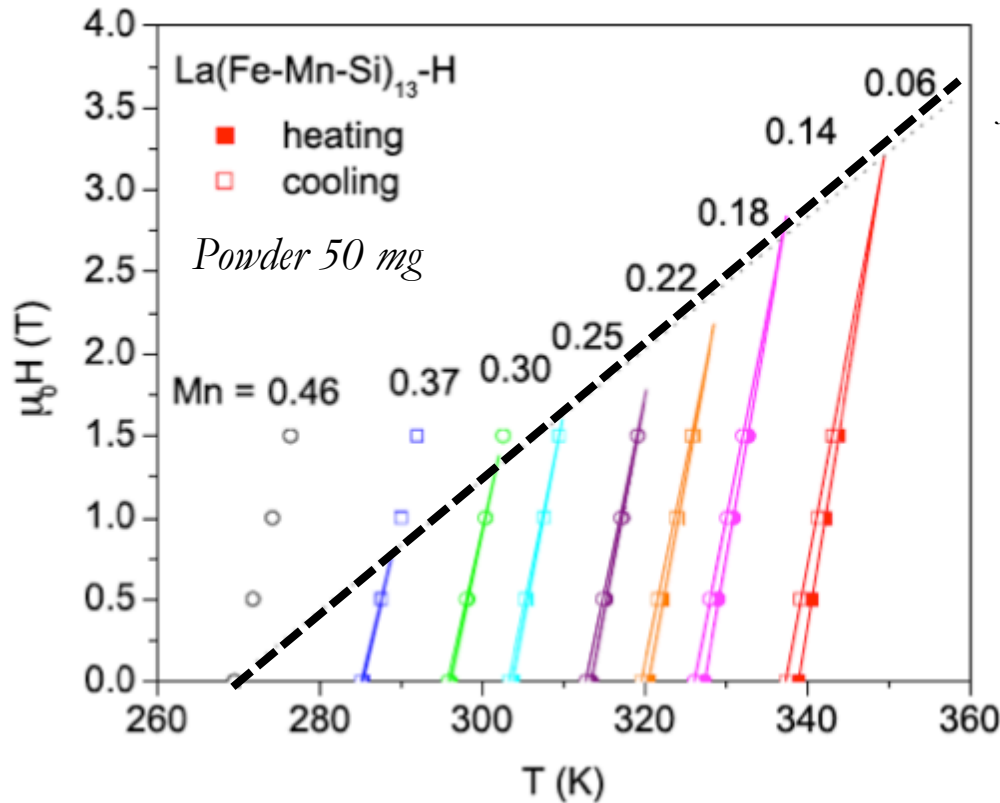
Study of the effect of field is required!

Bennati, C., et al

Journal of Magnetism and Magnetic Materials (2015).



DYNAMICS OF THE PHASE TRANSITION LaFeSi BASED COMPOUNDS



Basso, V., et al.

Journal of Applied Physics 118.5 (2015).

SERIES WITH TUNEABLE CRITICAL POINT
Vacuumschmelze GmbH and CoKG

- Mn (174 K/y(Mn))
- H is saturated (+ 150 K)
- Magnetic Field (+4 K/T)

Cross Over between 1st to 2nd order

SAMPLE DIMENSION:

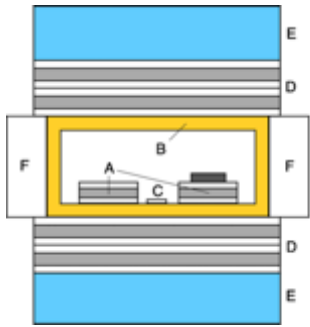
Powder (50 mg) → fragments (< 5 mg)

(avoid extrinsic factor of powder agglomeration)

VAC Code	x (Fe)	y (Mn)	z (Si)	Mass (mg)	Nominal T _c (°C)
MCP 37 (1255)	11.60	0.18	1.22	4.79	49
MCP 34 (1252)	11.41	0.30	1.29	4.53	20
MCP 32 (1250)	11.22	0.46	1.32	2.19	-4

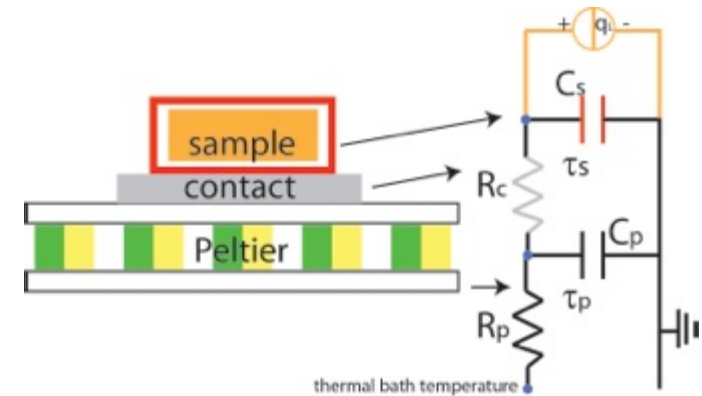
TIME SCALES TO OBSERVE A SINGLE AVALANCHES

PELTIER CELLS DIFFERENTIAL CALORIMETER



Heat diffusion time τ_{EXP}

- PELTIER + CONTACT(MASS)
- dT/dt



Basso, V. *Review of Scientific Instruments* 81.11 (2010)

Kuepferling, M. et al., *EPJ Web of Conferences*. Vol. 40. EDP Sciences, 2013.

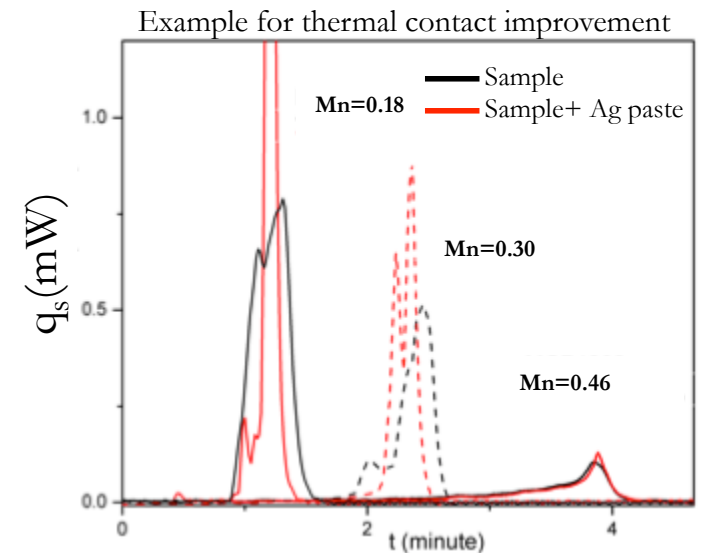
Supposing a characteristic time of the single process (I.E. LATENT HEAT RELEASE) τ

- $\tau \gg \tau_{\text{EXP}}$
- Peltier + Contact large
 - dT/dt large

TEMPERATURE OF THE SAMPLE IS MAINLY
DRIVEN BY RATE (large temperature gradient)

- $\tau \approx \tau_{\text{EXP}}$
- Peltier + Contact small
 - $dT/dt \rightarrow 0$

ABSORPTION/RELEASE OF LATENT HEAT CAN
CHANGE THE TEMPERATURE INSIDE THE
SAMPLE (and be observed).



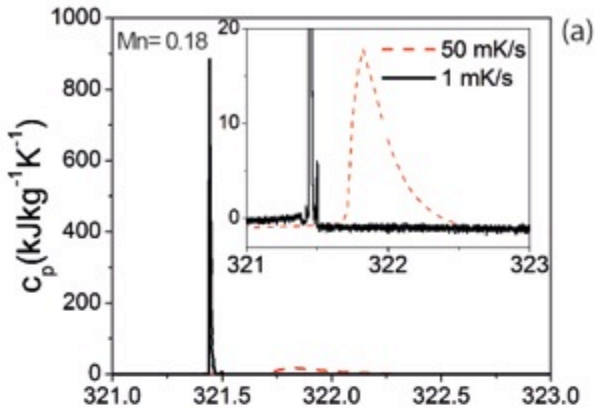
LaFe_xMn_ySi_z-H_{1.65}: EFFECT OF COMPOSITION DISCLOSED BY LOW RATE

H = 0 T and dT/dt → 0

MN = 0.18

- (S)Low rate discloses avalanches
- A single avalanche is present

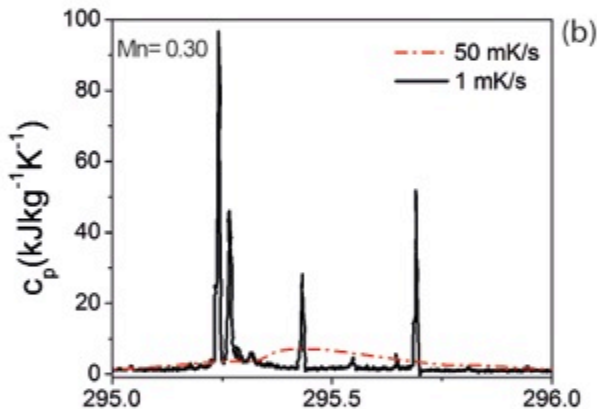
1st order transition



MN = 0.30

- Low rate discloses avalanches
- Mn increases the number of avalanches
- Avalanches are lower
- Higher background

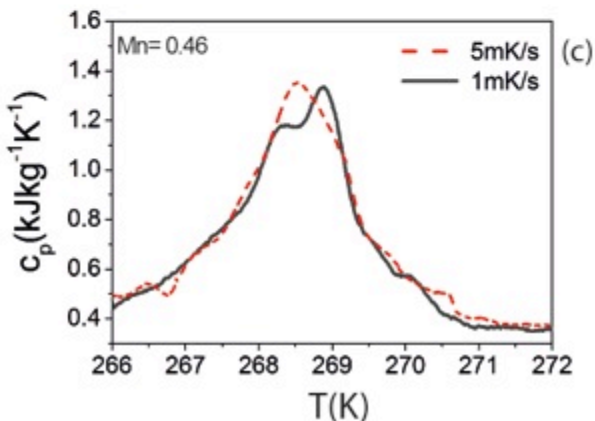
1st order transition



MN = 0.46

- Low rate has no effect
- No avalanches and no hysteresis

2nd order transition

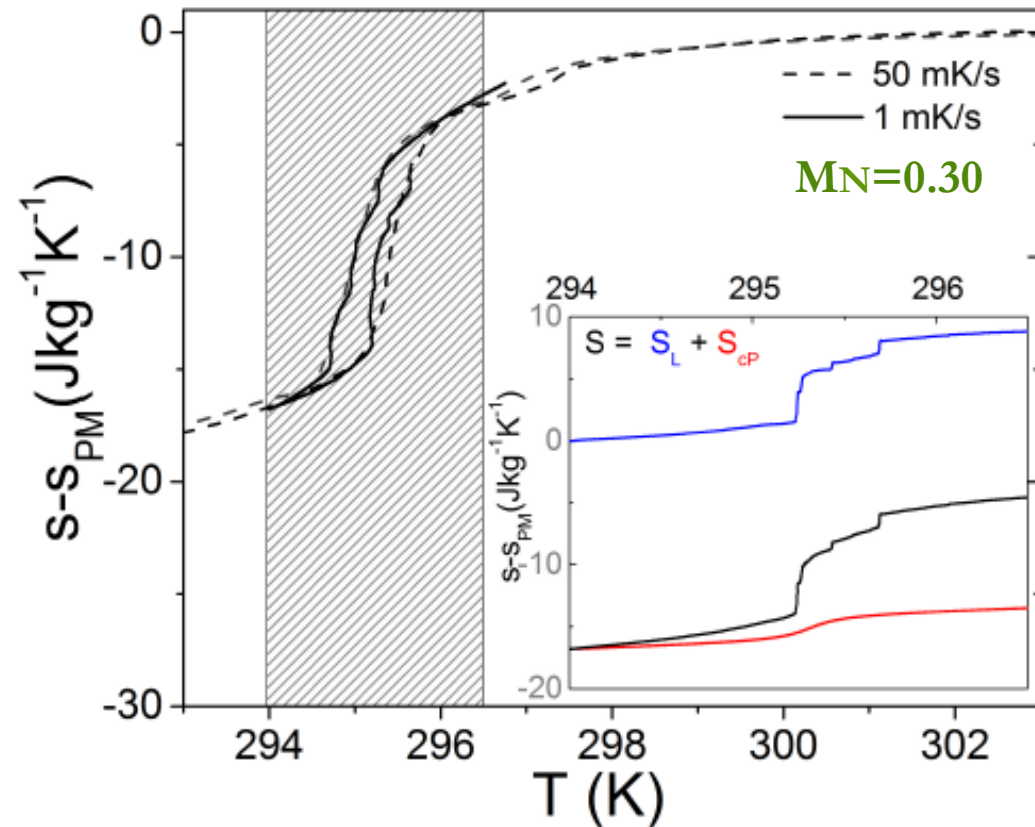
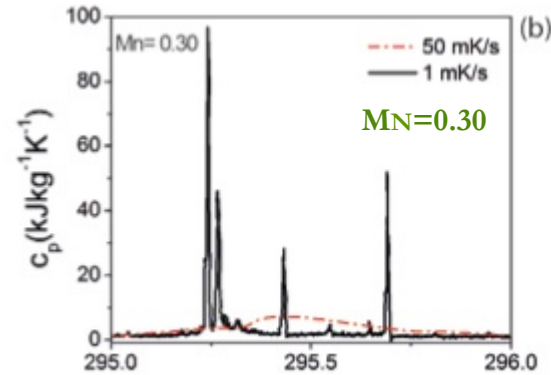


Mn > 0.03 should introduce more secondary phases (defects)

ENTROPY CHANGE WITH AVALANCHES $\tau \approx \tau_{exp}$

Two contributions from specific heat and latent heat, where background and avalanches are clearly distinguished

$$S - S_{PM} = \Delta S_{c_p} + \Delta S_L = \int_{T_i}^{T_f} \frac{c_p(T)}{T} dT + \sum_i \frac{m_i L}{T_i}$$



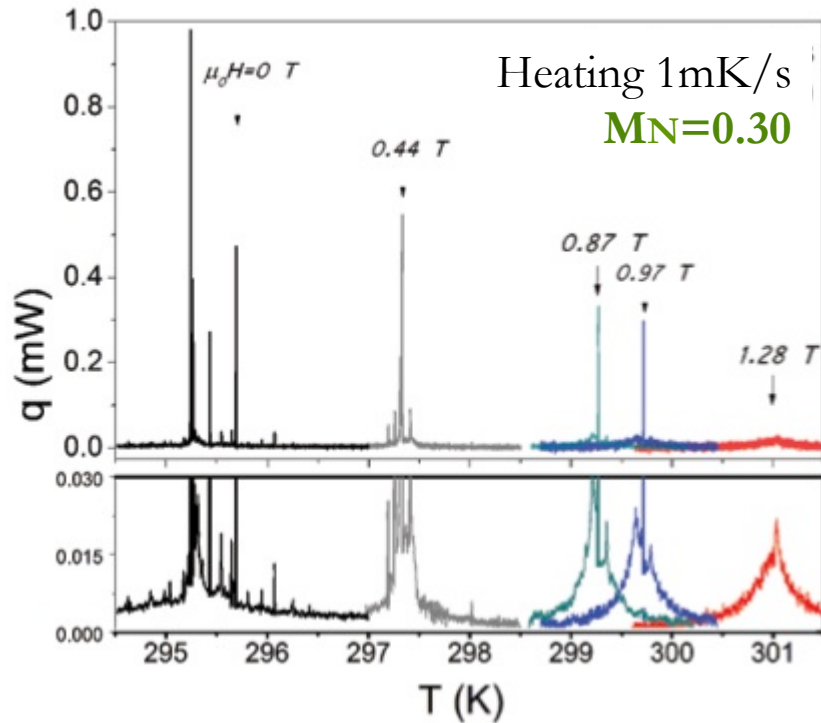
SPECIFIC HEAT OF THE TRANSITION

For a system in thermodynamics equilibrium (slow dynamics)

ISOTHERMAL ENTROPY CHANGES

For irreversible processes which act as a source of energy (fast dynamics)

If no irreversibility is present
 $\Delta S_L = 0 \rightarrow$ as for **MN = 0.46**

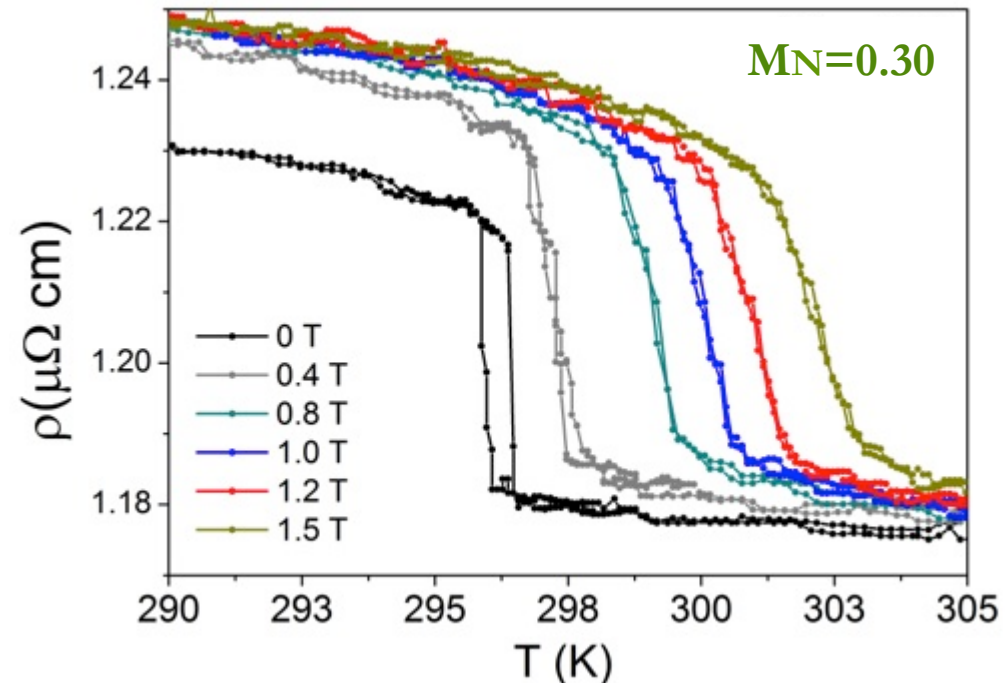
EFFECT OF FIELD ON AVALANCHES: $M_N = 0.30$ 

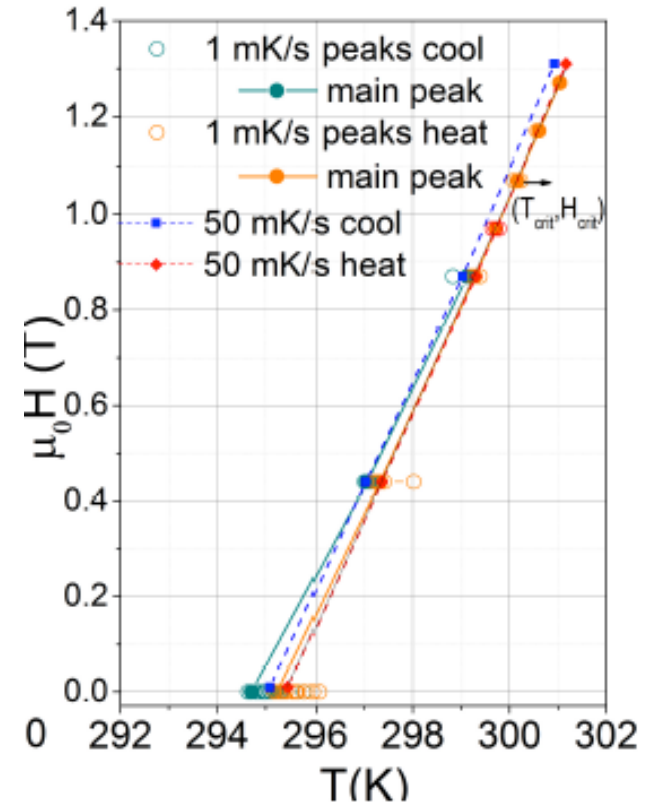
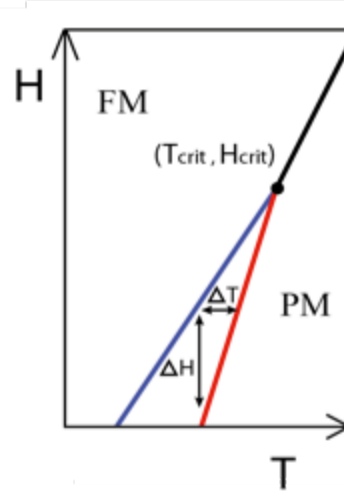
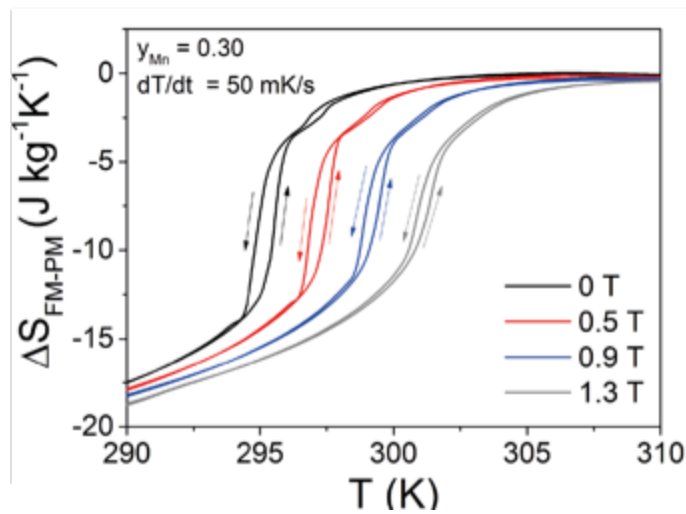
- Magnetic field effect:
MR 3.7 % up to 5% at 0.8 T
i.e. 5% $K_{el}^{th}(H)$ of FM
- Slope with field reflects the volume growth
- Jumps vanish $H > 0.8$ T

AGAIN but with H

- Avalanches change shape and number and vanish at $H > 1.3$ T
- Specific heat background grows

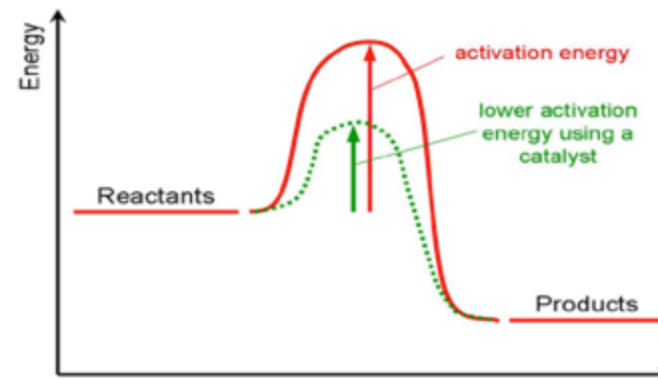
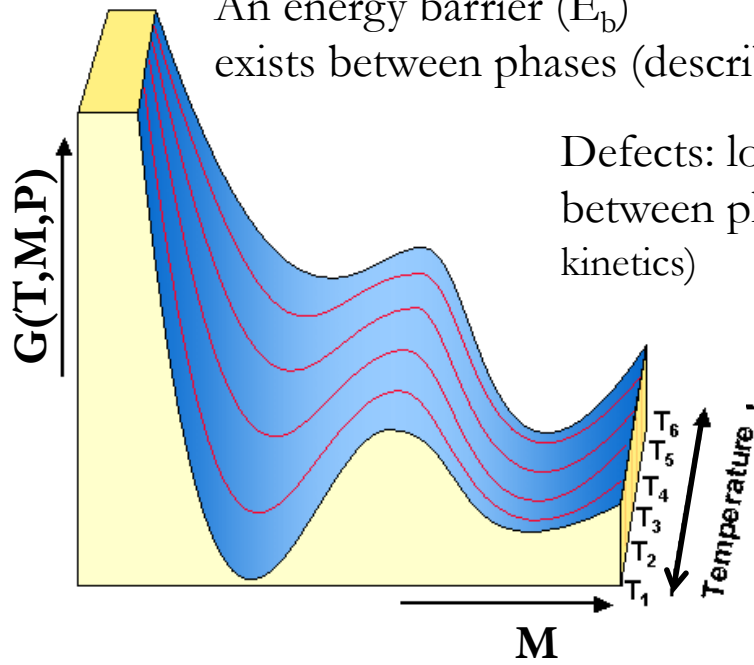
C_p and L compete



EFFECT OF FIELD ON MAGNETIC PHASE DIAGRAM: $M_N = 0.30$ 

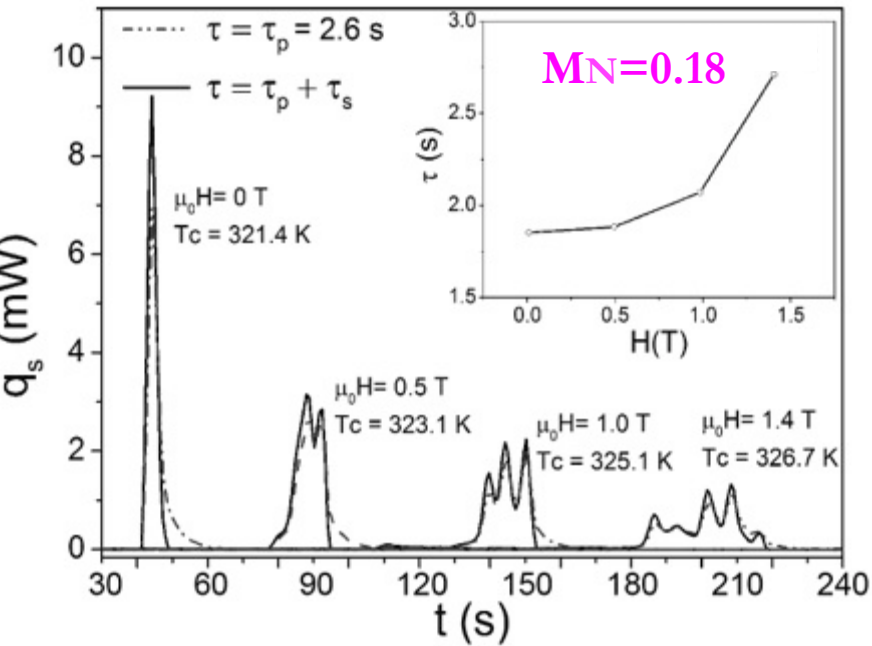
An energy barrier (E_b) exists between phases (described by thermostatics)

Defects: lower the **Effective** E_b between phases (described by kinetics)



E_b decide which **defect** count for the transition
Lower E_b
greater n° of defects

AVALANCHES FAR FROM THE CRITICAL POINT AND SPECIFIC HEAT TOWARD THE CRITICAL POINT

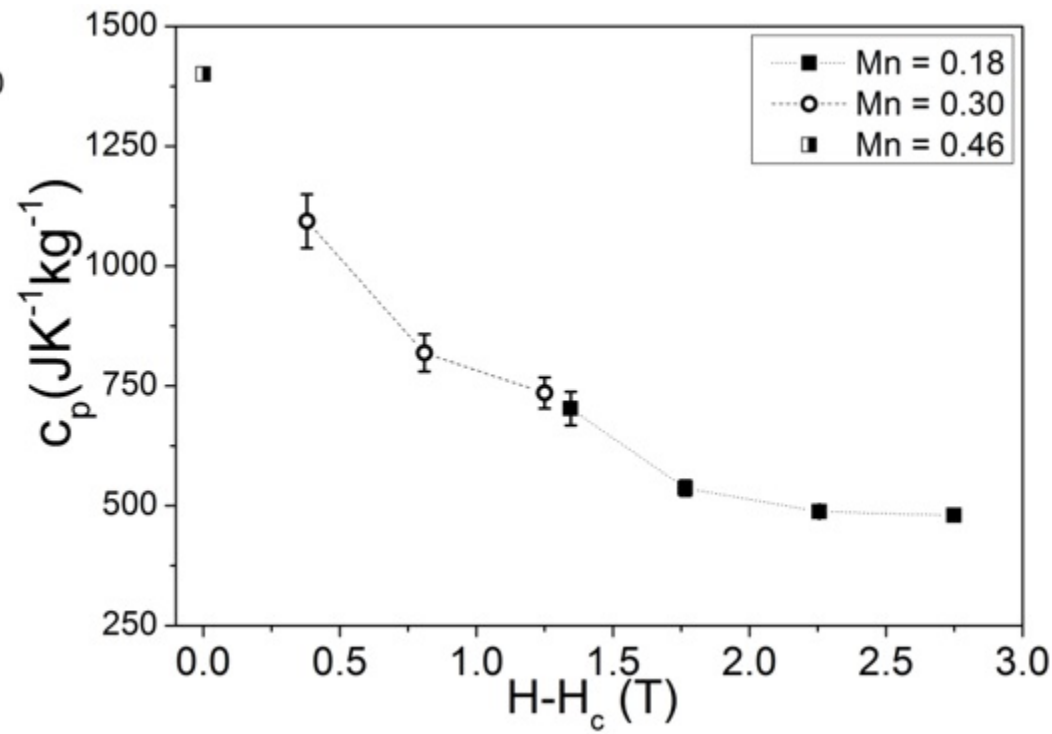
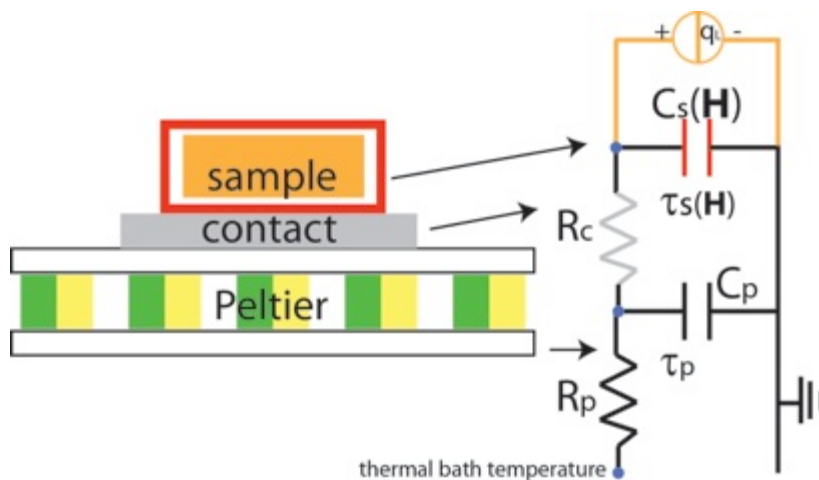


FAR FROM THE CRITICAL POINT $MN = 0.18$

- Increasing \mathbf{H} , the latent heat terms lower
- Unresolved peaks: $\tau_{\text{exp}} \ll \tau$

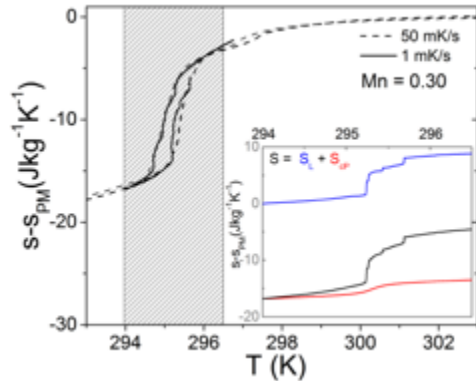
As specific heat may depends on \mathbf{H} : $\tau_s(\mathbf{H})$

$$\Delta C_s^{th}(H) = m \Delta c_p(H) = \frac{1}{R_s^{th}} \cdot \Delta \tau_s(H)$$



CONCLUSION

DSC at low rates is a powerful tool to determine the first/second order character of the transitions

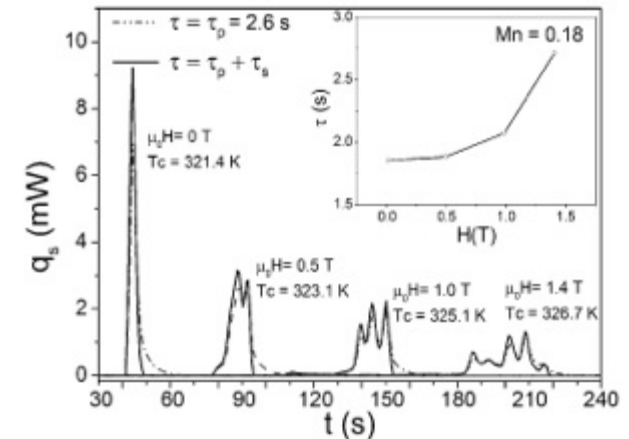
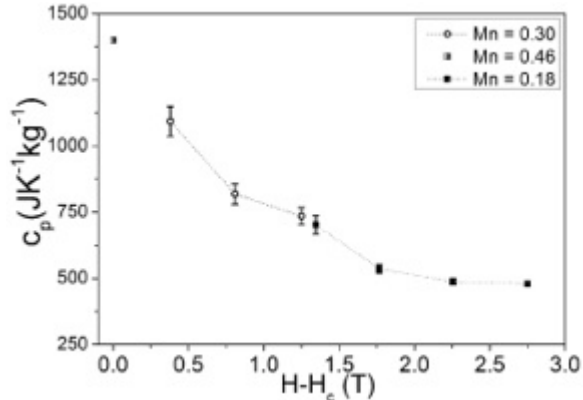


Rate of the experiment 1 mK/s discloses:

- Reversibility \rightarrow Specific heat background
- Irreversibility \rightarrow Avalanches of latent heat
- Best evaluation of the Critical Point and hysteresis

Mn/Field effect on Avalanches :

- Change of Number of nucleation events reveals the lower energy gap between phases



Physical properties revealed by avalanches near the critical point

- Shape \rightarrow Specific heat increases

Thank you for your attention!