Magnetocaloric Effect: From Energy Efficient Refrigeration to Fundamental Studies of Phase Transitions

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2019 IEEE Magnetics Society Distinguished Lecture

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Cathedral and Giralda

World records

Largest Gothic Cathedral

3rd largest church

UNESCO World Heritage


Plaza de España
Tourists from all over the World…
and beyond

Royal Tobacco Factory

- Stone-built in the XVIII century
- First tobacco factory stablished in Europe
  - The most important one (produced 75% of the cigarettes consumed in Europe)
- Bizet’s opera Carmen was set here

Universidad de Sevilla

Founded in 1505

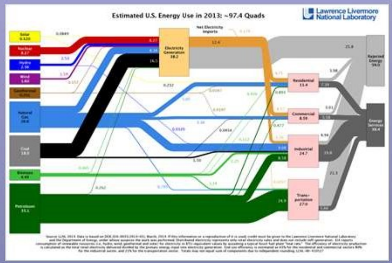
~ 74,000 students; 4,500 academic staff

2nd largest in Spain in number of students

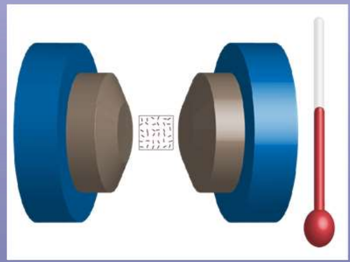
8th in Spain in scientific production

1st in Spain in international patents

MCE: Materials research & phase transitions

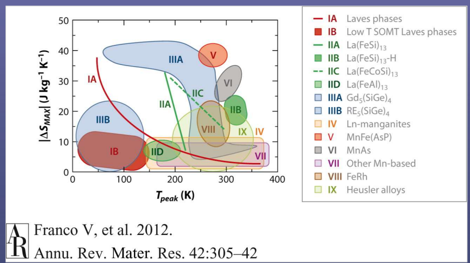


Energy



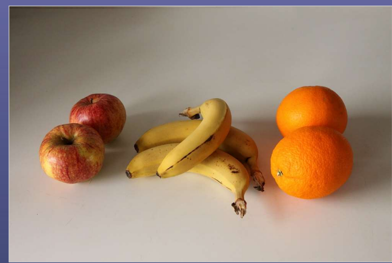
What is MCE?

Magnitudes



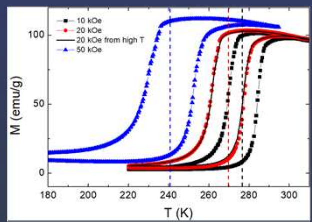
Types of materials

How to measure?

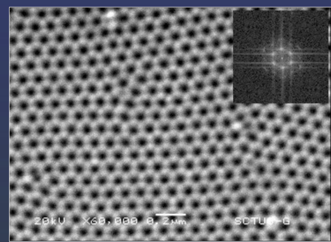


How to compare?

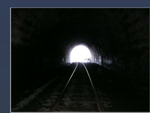
Phase transitions



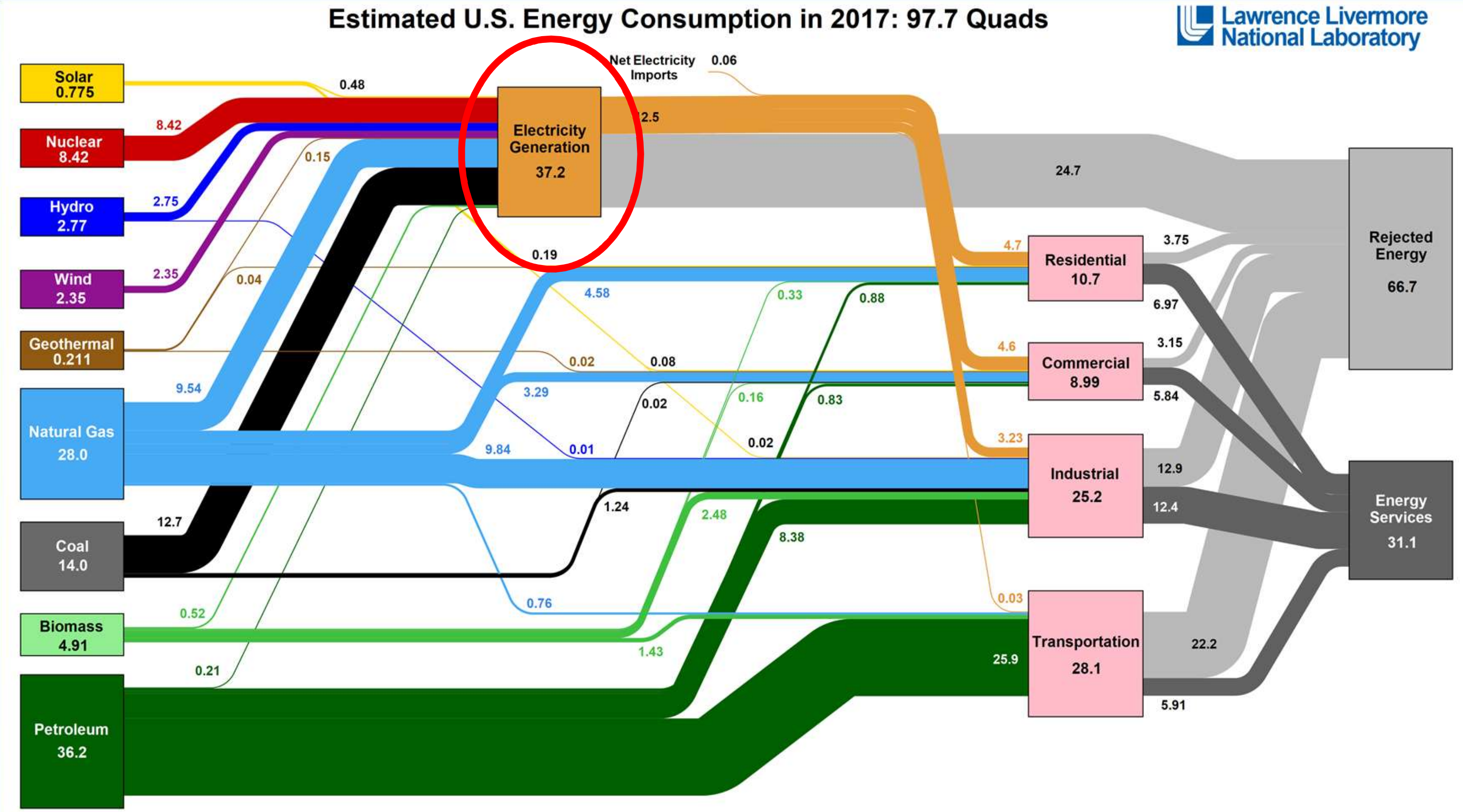
Hysteresis



Nanomaterials



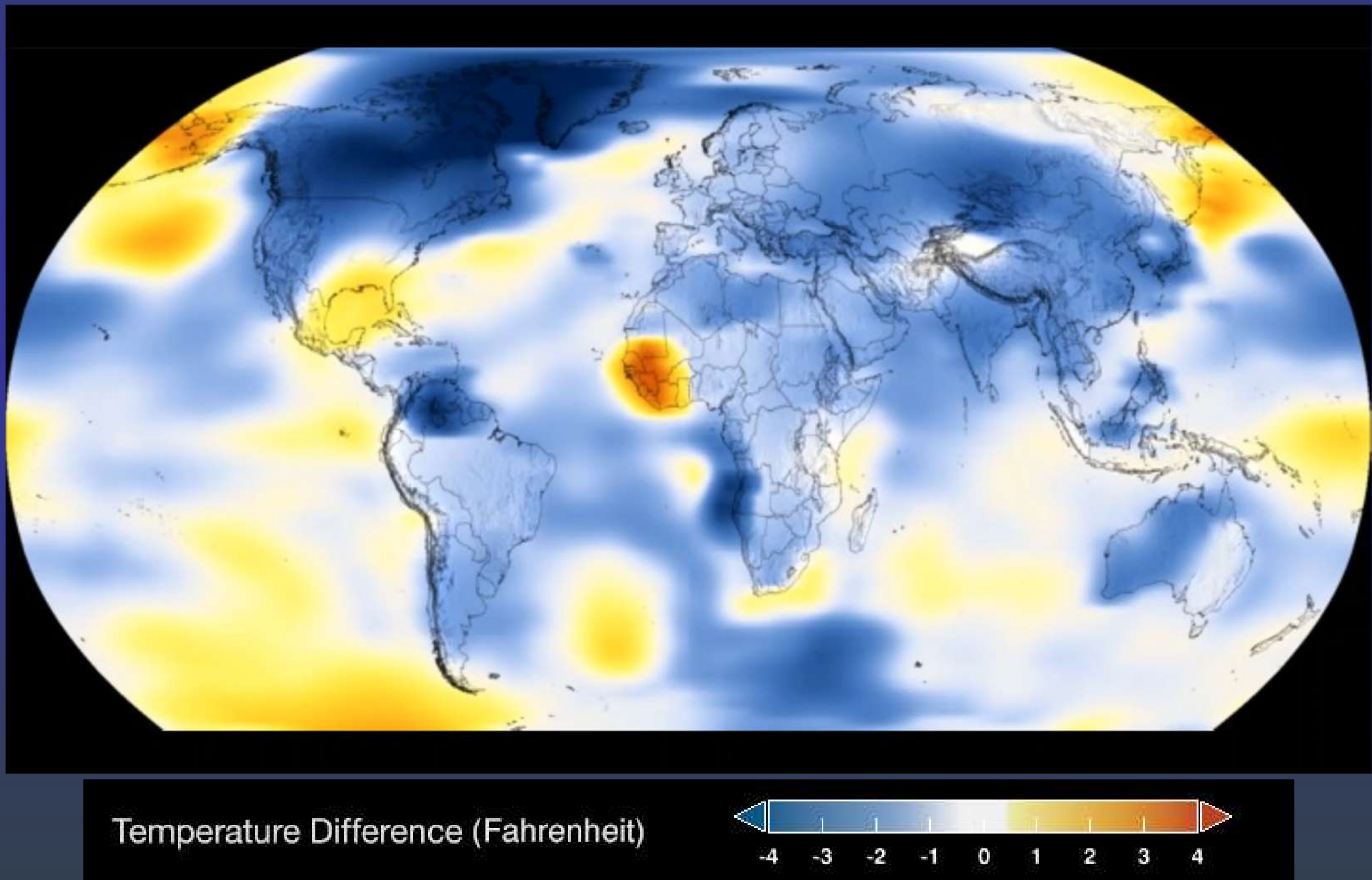
Magnetic materials for energy applications



- Using non-renewable energy sources is a problem
- Non-efficient conversion is even worse

GLOBAL CLIMATE CHANGE
Vital Signs of the Planet

Influence on Earth? 1884-2018



MAGNETIC REFRIGERATION:

towards an increased energy efficiency

Residential and Commercial sectors account for ~42% of the total energy consumption

More than 50% for HVAC

Larger energetic efficiency

60% vs. 40 % of the theoretical limit

Environmental benefits

No green house or ozone depletion gas

Vibration and noise

Special applications

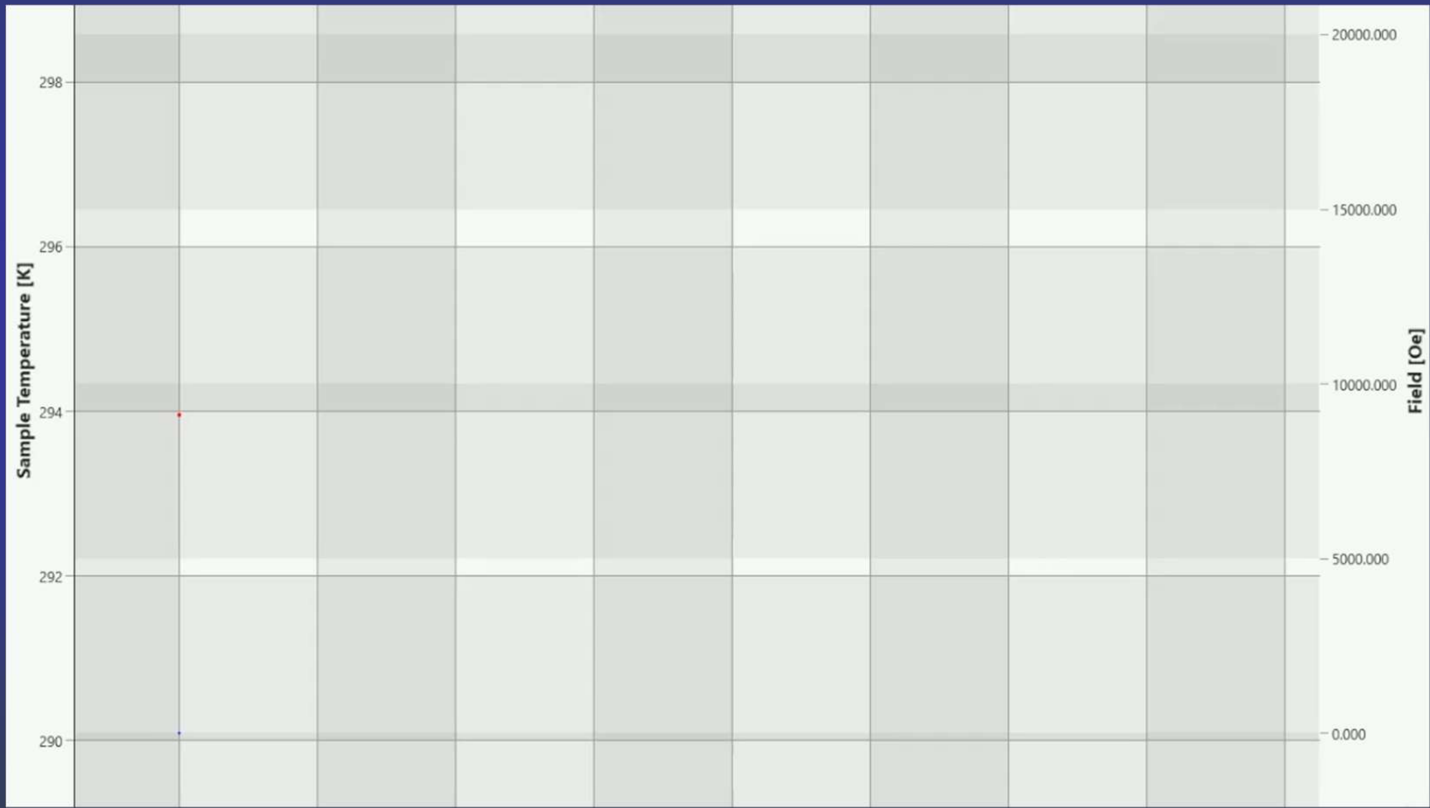
Room temperature magnetic refrigeration → phase transitions

V.Franco, J.S.Blázquez, J.J.Ipus, J.Y.Law, L.M.Moreno-Ramírez, A.Conde, Progress in Materials Science, 93 (2018) 112

What is magnetocaloric effect?

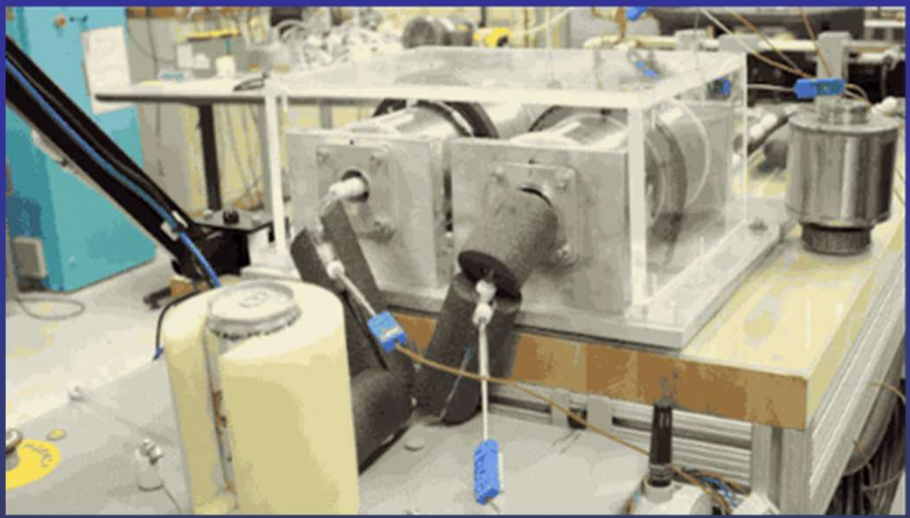
- Link to offline video

Real experiment



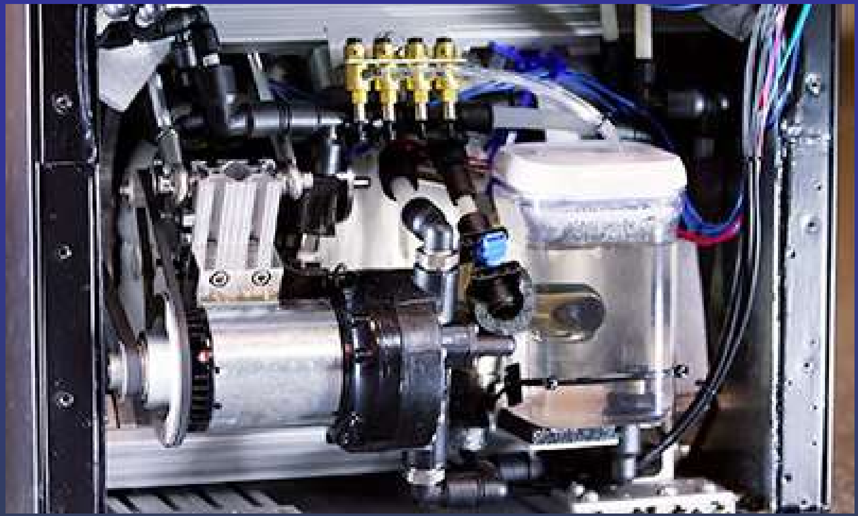
Real life applications

GE prototype 2014

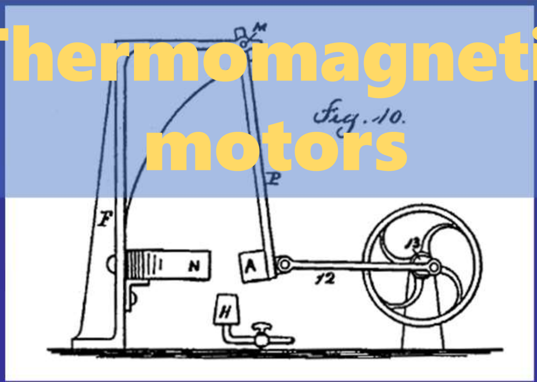


Real life applications

Haier + Astronautics Corporation of America + BASF @ CES Las Vegas 2015



Not only fridges



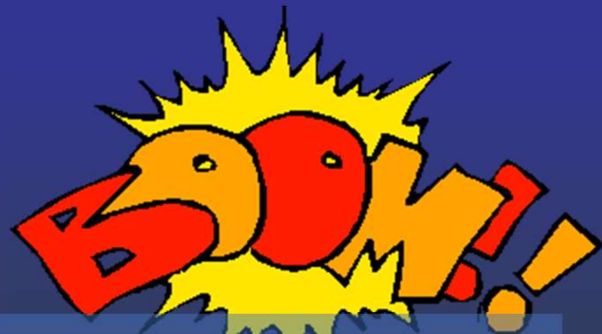
Thermomagnetic motors

Cooling data centers

E-mobility

MRI switchable contrast

Controlled drug delivery



Transient cooling

Characteristic parameters

Magnetic entropy change

$$\Delta S_M = \mu_0 \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T} \right)_H dH$$

Adiabatic temperature change

$$\Delta T_{ad} = -\mu_0 \int_0^{H_{\max}} \frac{T}{C_{p,H}} \left(\frac{\partial M}{\partial T} \right)_{p,H} dH$$

Characteristic parameters

Magnetic entropy change

$$\Delta S_M = \mu_0 \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T} \right)_H dH$$

Adiabatic temperature change

$$\Delta T_{ad} \approx -\frac{T \Delta S_M}{C_{p,H}}$$

Refrigerant capacity

$$RC(\Delta H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M (T, \Delta H)\, dT$$

Amount of heat that can be transferred between reservoirs
Dangerous to use for shallow peaks

Coef. of Refrigerant Performance

$$CRP(H_{\max}) = \frac{\Delta S_M \Delta T_{rev}}{\mu_0 \int_0^{H_{\max}} M\, dH}$$

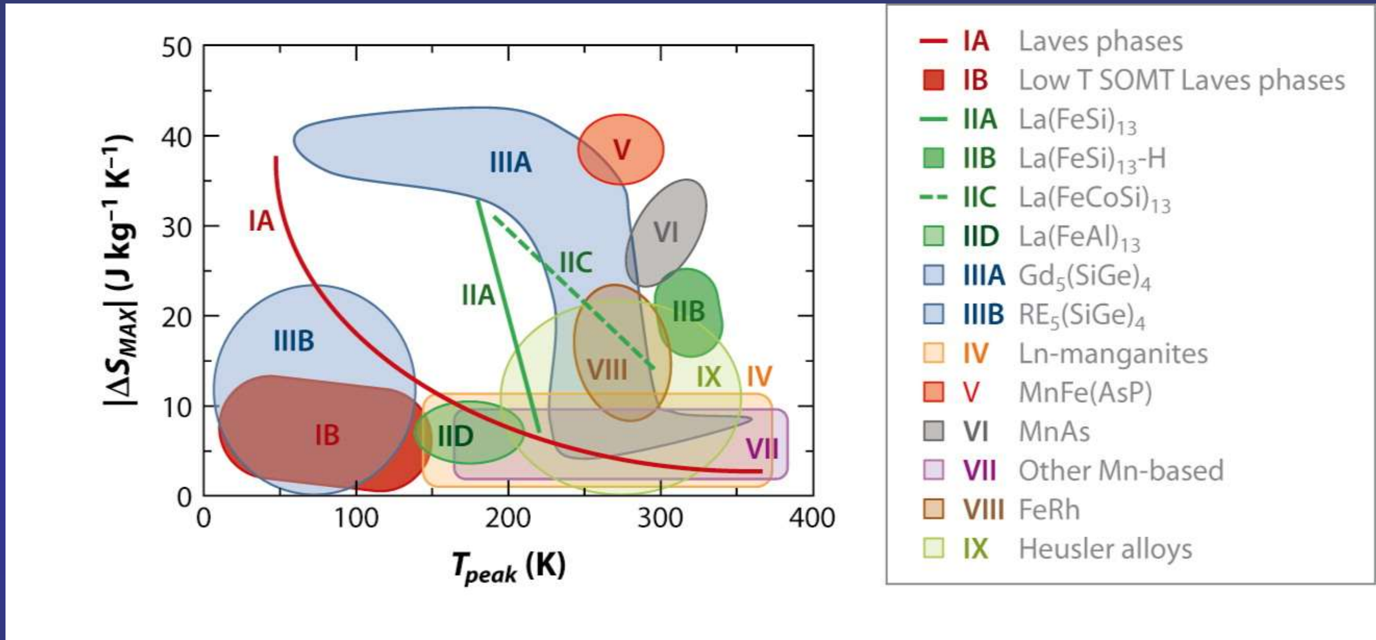
E. Bruck et al. Philos. Trans. R. Soc. A-Math. Phys. Eng. Sci. 374 (2016) 20150303

Temperature averaged Entropy Change

$$TEC(\Delta T_{lift}) = \frac{1}{\Delta T_{lift}} \max_{T_{mid}} \left\{ \int_{T_{mid} - \frac{\Delta T_{lift}}{2}}^{T_{mid} + \frac{\Delta T_{lift}}{2}} \Delta S_M (T)\, dT \right\}$$

L.D. Griffith et al. J. Appl. Phys. 123 (2018) 034902

TYPES OF MCE MATERIALS



Franco V, et al. 2012.
Annu. Rev. Mater. Res. 42:305–42

TYPES OF MCE MATERIALS

SOPT

- Moderate MCE peak
- Broad temperature span
- No hysteresis
- Examples: Gd, amorphous alloys…

Ideal MCE material for magnetic refrigeration

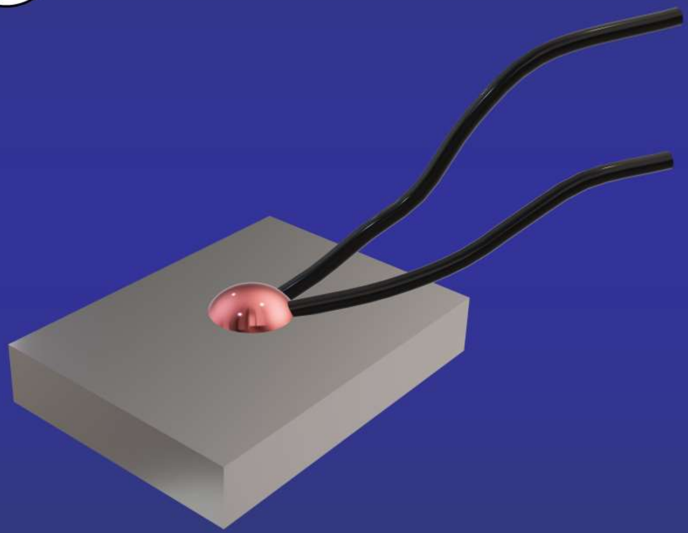
between FOPT and SOPT

FOPT

- Large MCE peak
- Reduced temperature span
- **Hysteresis**
- Magnetostructural transitions require large field
- Examples: $Gd_5Si_2Ge_2$, $La(FeSi)_{13}$, MnFePAs, Heusler alloys

Measurement techniques

Direct



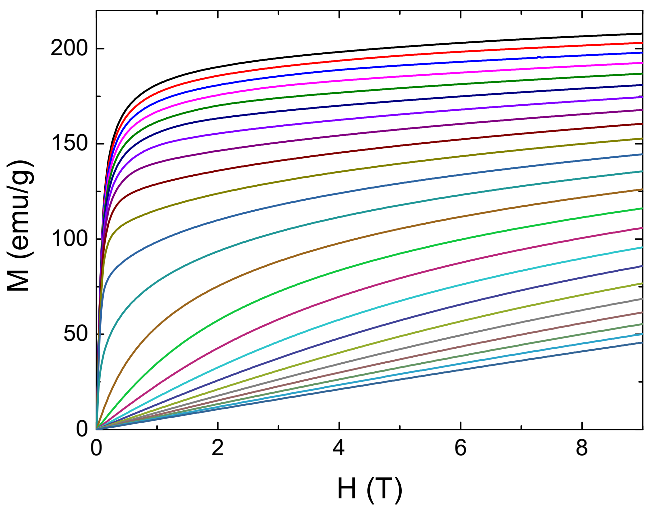
- Temperature sensor in contact with the sample
  - Thermal mass of the sensor has to be much lower than that of the sample
  - Not broadly available as commercial systems
  - Low signal for low field
- Possible options
  - AC techniques
  - Mirage effect
  - Pulsed fields
  - Recalibration of sensor measurements

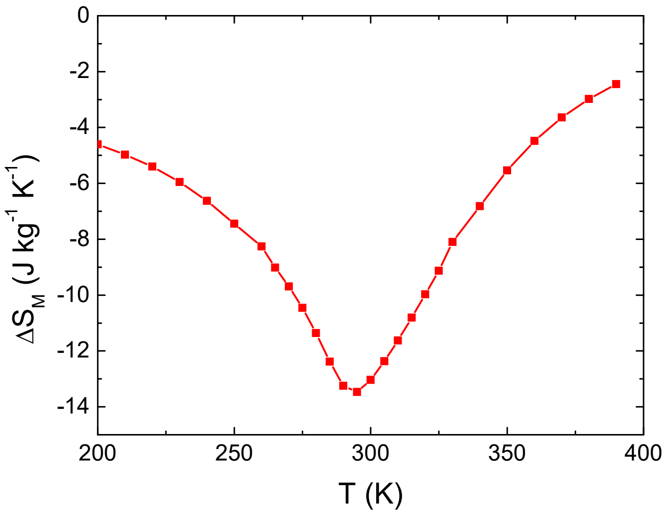
Measurement techniques

- Direct
- Indirect → *Magnetic*

- Magnetometer with variable temperature option

$$\Delta S_M = \mu_0 \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T} \right)_H dH$$





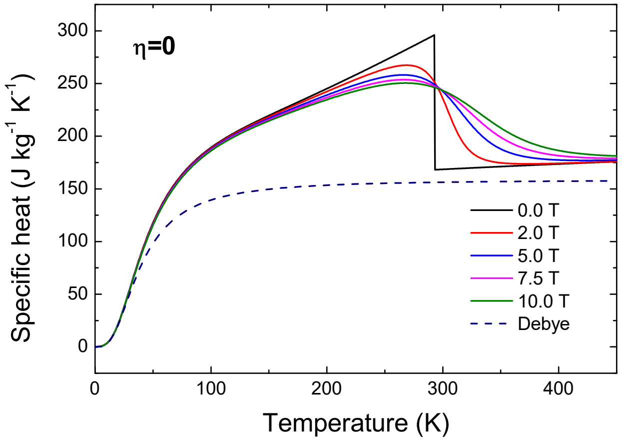
Measurement techniques

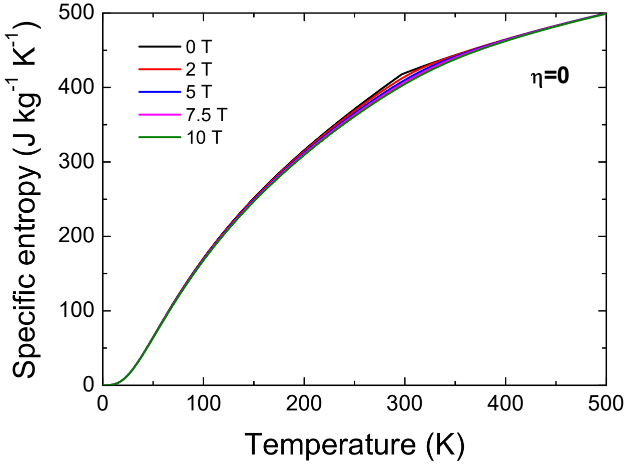
- **Direct**
- **Indirect**

Magnetic

Calorimetric

- Calorimeter with applied magnetic field





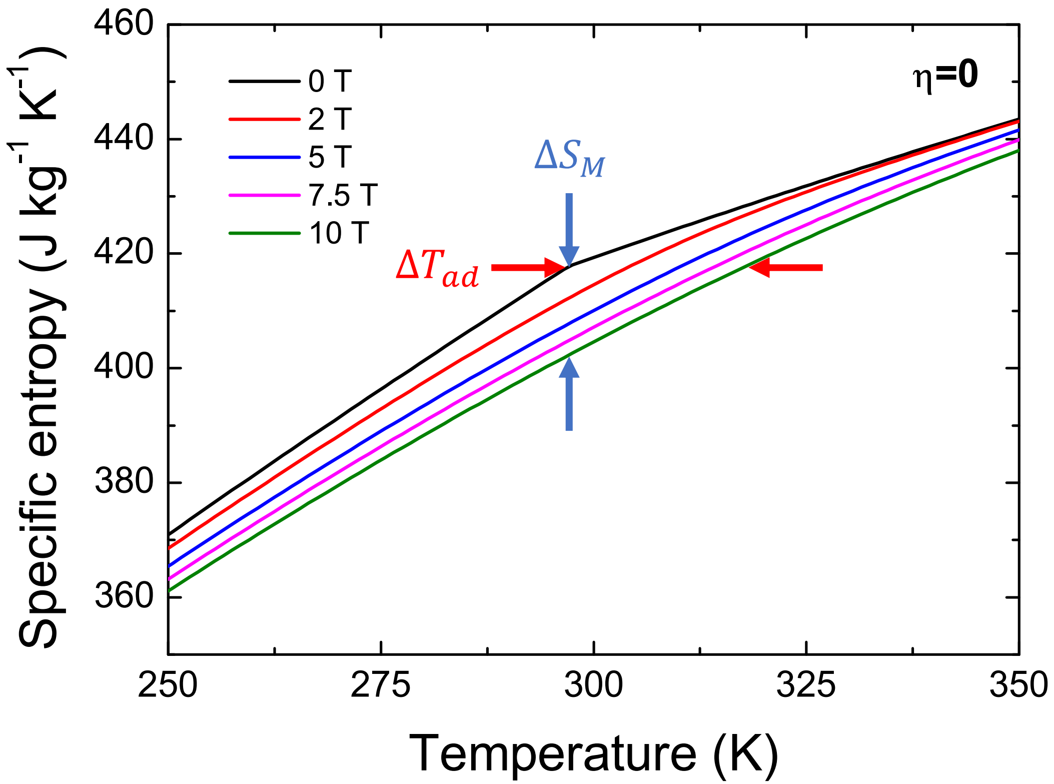
$$S_H(T) = S_{0,H} + \int_{0\,\mathrm{K}}^{T} \frac{C_H(T)}{T}\,\mathrm{d}T$$

Cannot reach 0 K

$$S_H^{ap}(T) \approx \frac{1}{2} C_H(T_{ini}) + \int_{T_{ini}}^{T} \frac{C_H(T)}{T}\,\mathrm{d}T$$

Measurement techniques

- Direct
- Indirect → *Magnetic* / *Calorimetric*

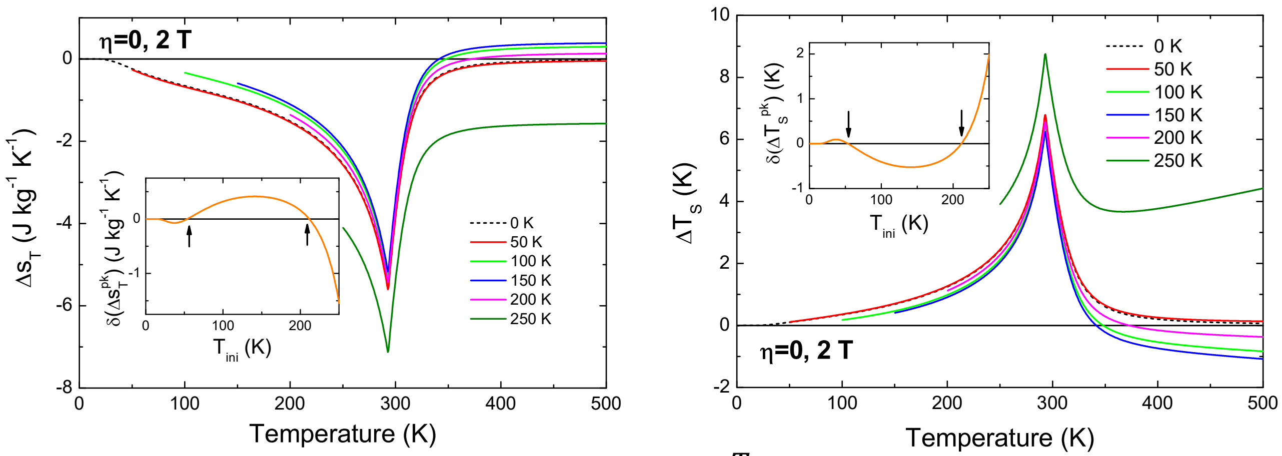


Measurement techniques

- Direct
- Indirect

Magnetic

Calorimetric



$$S_H^{ap}(T) \approx \frac{1}{2} C_H(T_{ini}) + \int_{T_{ini}}^{T} \frac{C_H(T)}{T} \mathrm{d}T$$

T_{ini} plays a very important role

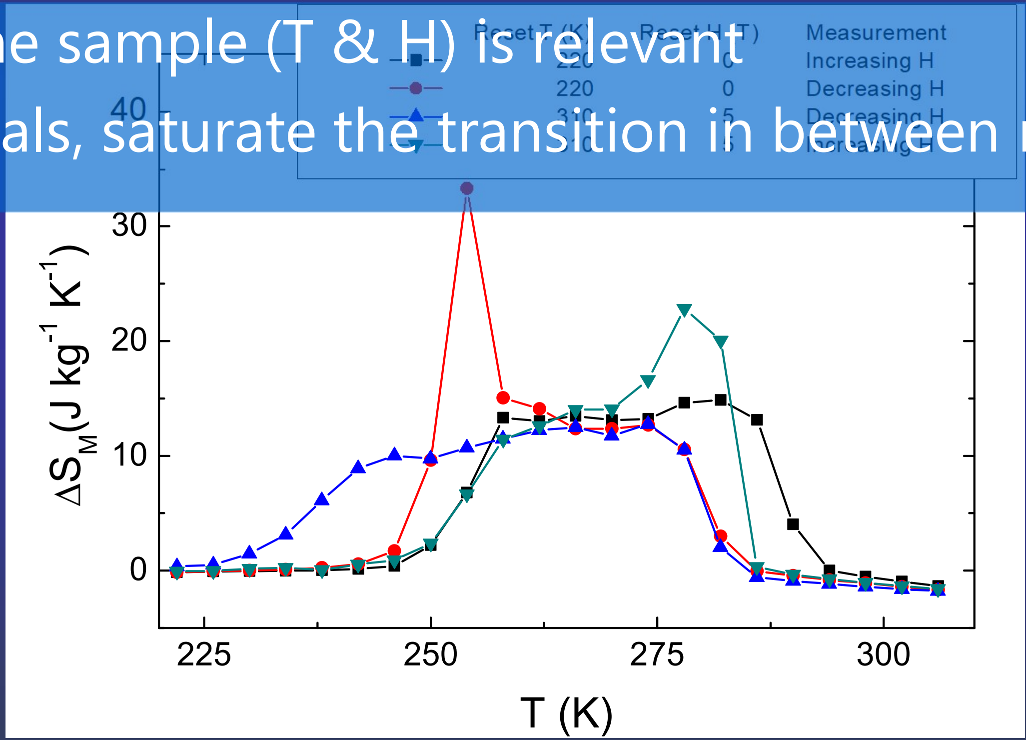
There is an optimal value for which we do not have to reach 0 K and prevents errors

J. Phys., D, Appl. Phys **49** (2016) 495001

Beware of the measurement protocol!!!

The history of the sample (T & H) is relevant

For FOPT materials, saturate the transition in between measurements



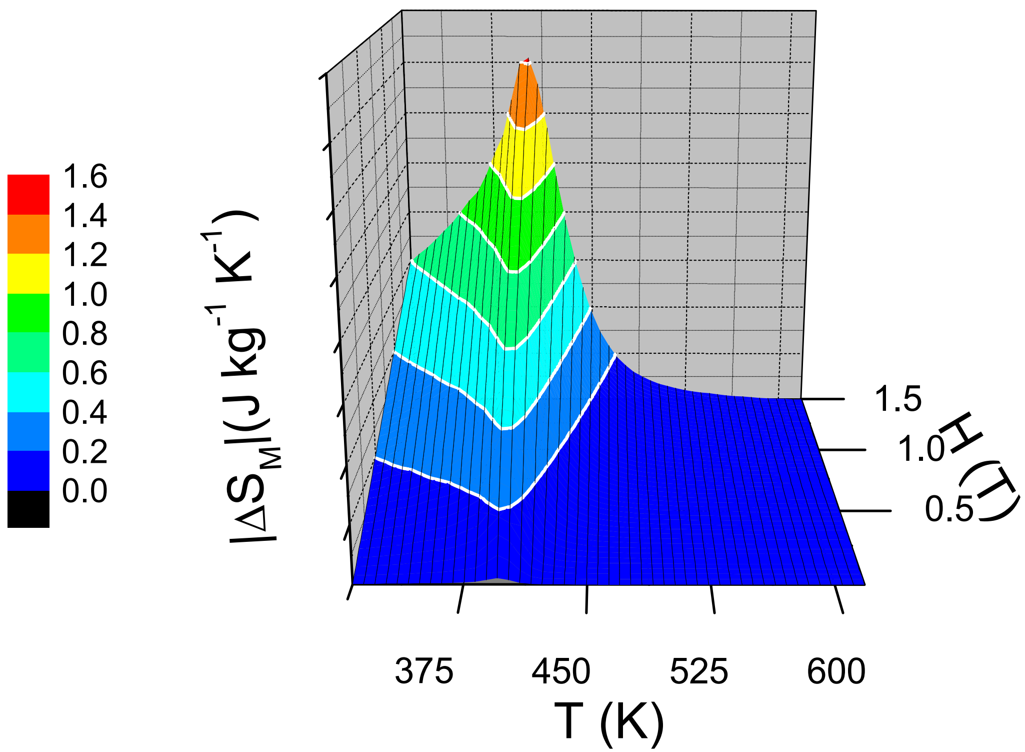
More info about protocol at:

-B. Kaeswurm, V. Franco, K. P. Skokov, and O. Gutfleisch, J. Magn. Magn. Mater. 406(2016) 259

-Lake Shore application note

Field dependence of $\Delta S_M(H)$

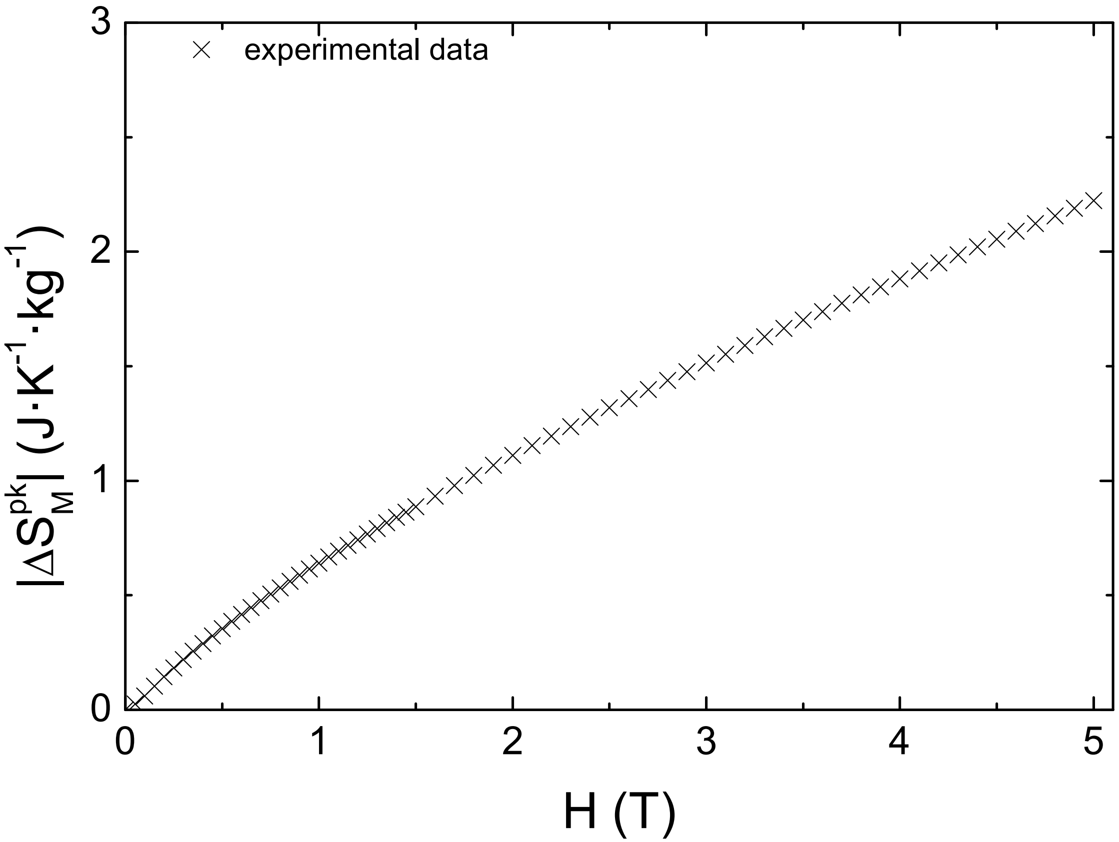
(AKA: how to compare with data from the literature)



- Data evolve differently with field for different T
- Usual assumption: linear behavior

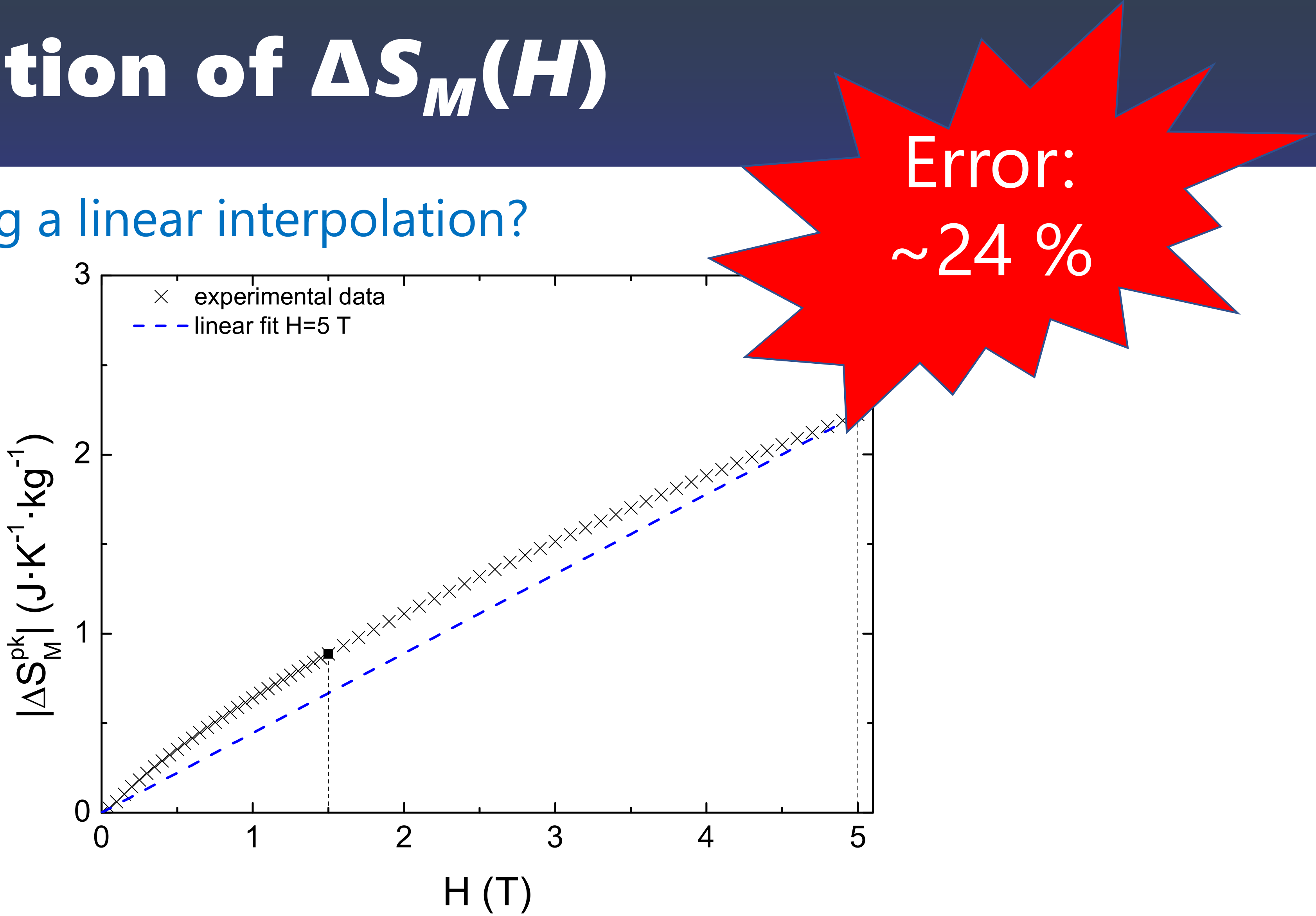
Description of $\Delta S_M(H)$

Why not using a linear approach for the value of the peak?



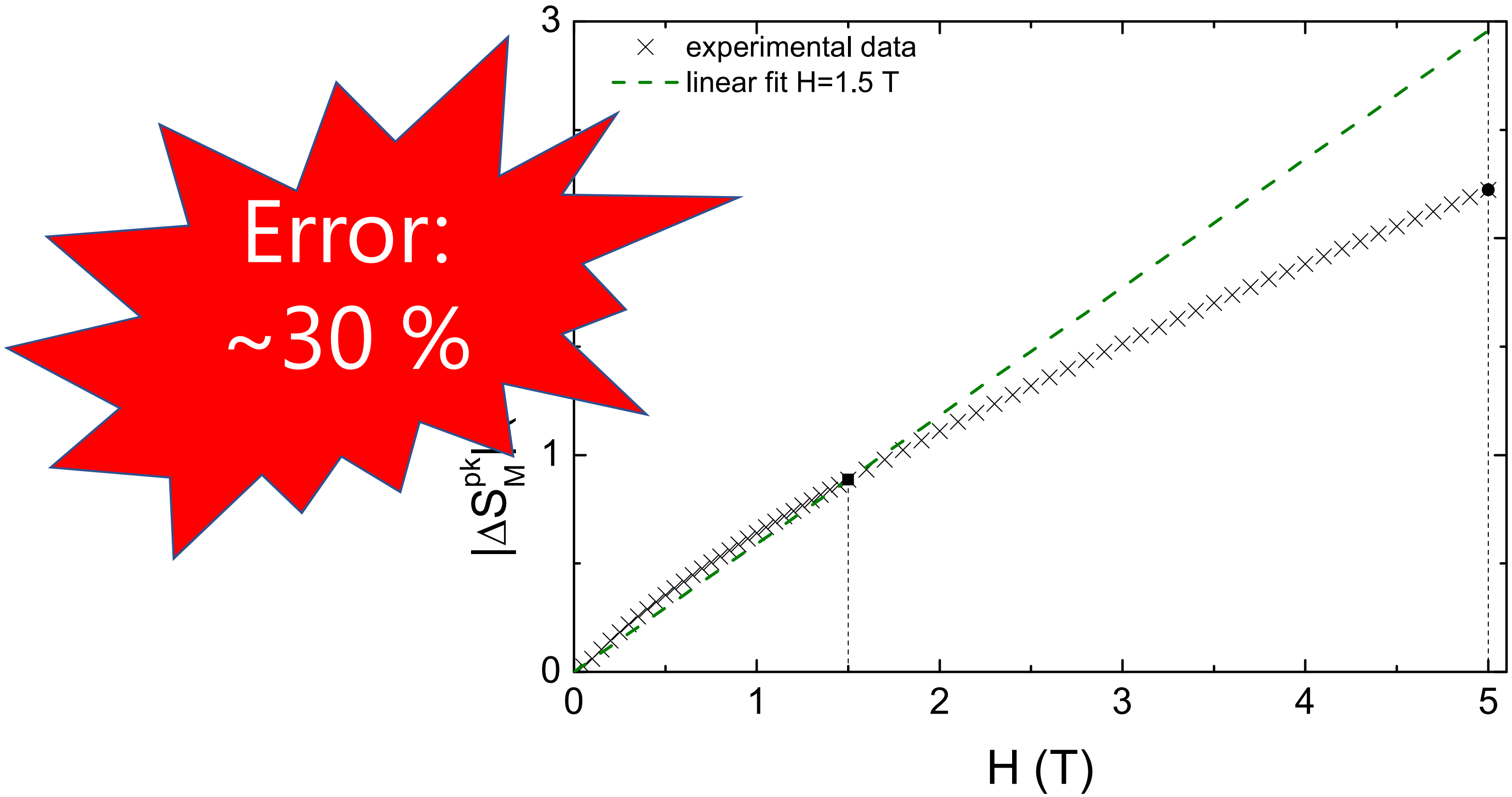
Description of $\Delta S_M(H)$

Why not using a linear interpolation?



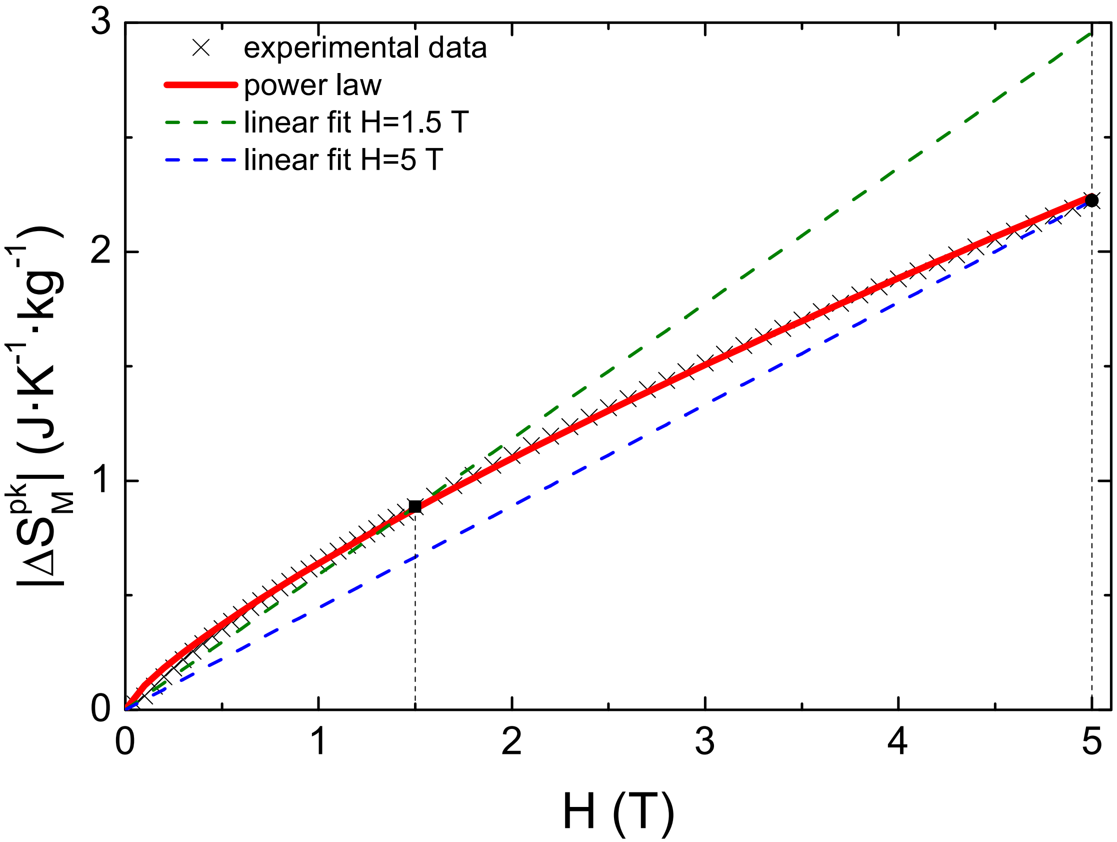
Description of $\Delta S_M(H)$

Why not using a linear extrapolation?



Description of $\Delta S_M(H)$

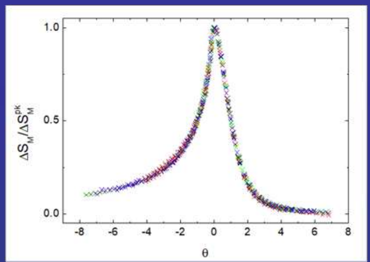
A power law represents properly the data



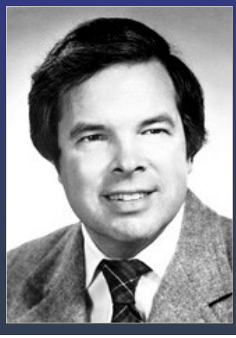
TYPES OF MCE MATERIALS

SOPT

- Universal scaling

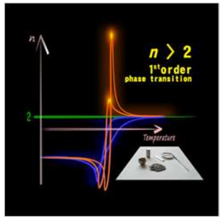


- Critical exponents

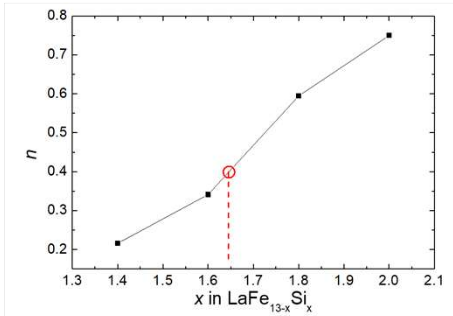


FOPT

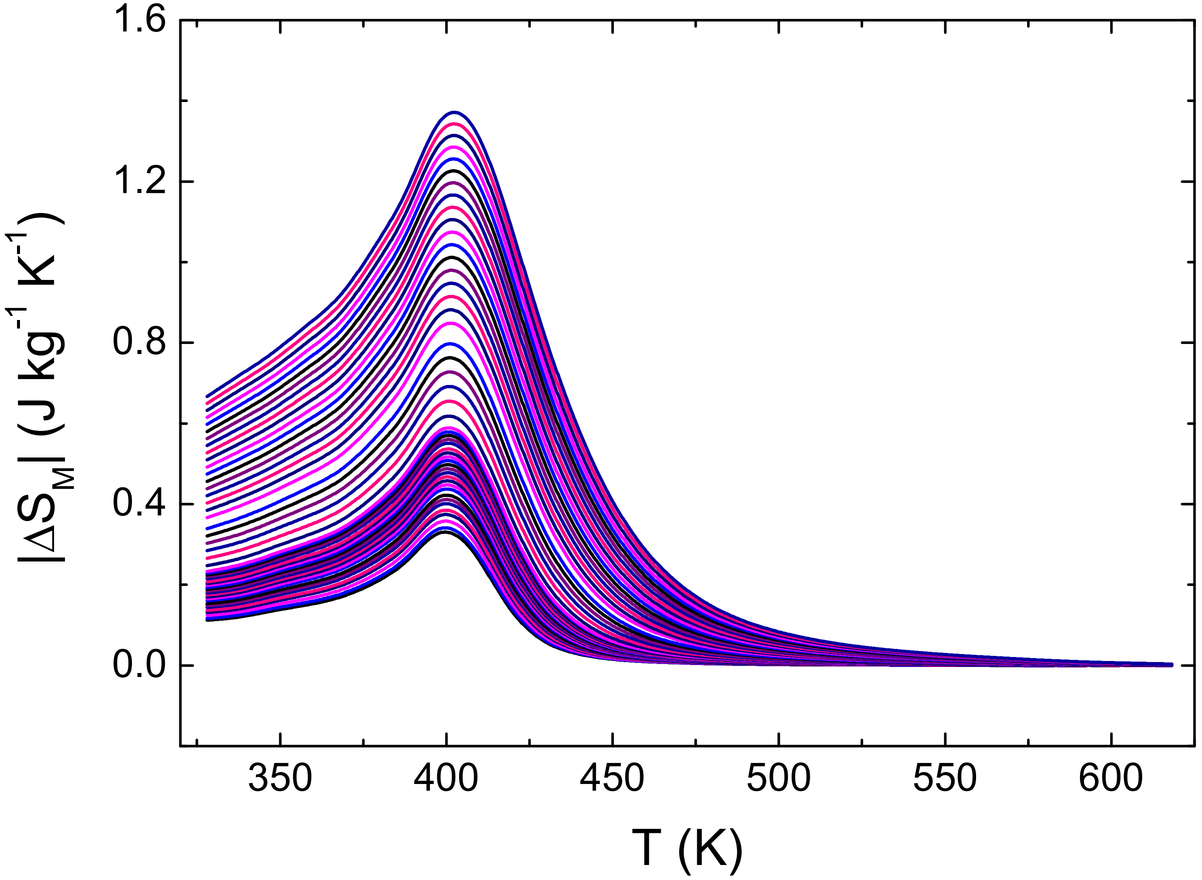
- How to know if it is FOPT?



- Critical point of the SOPT



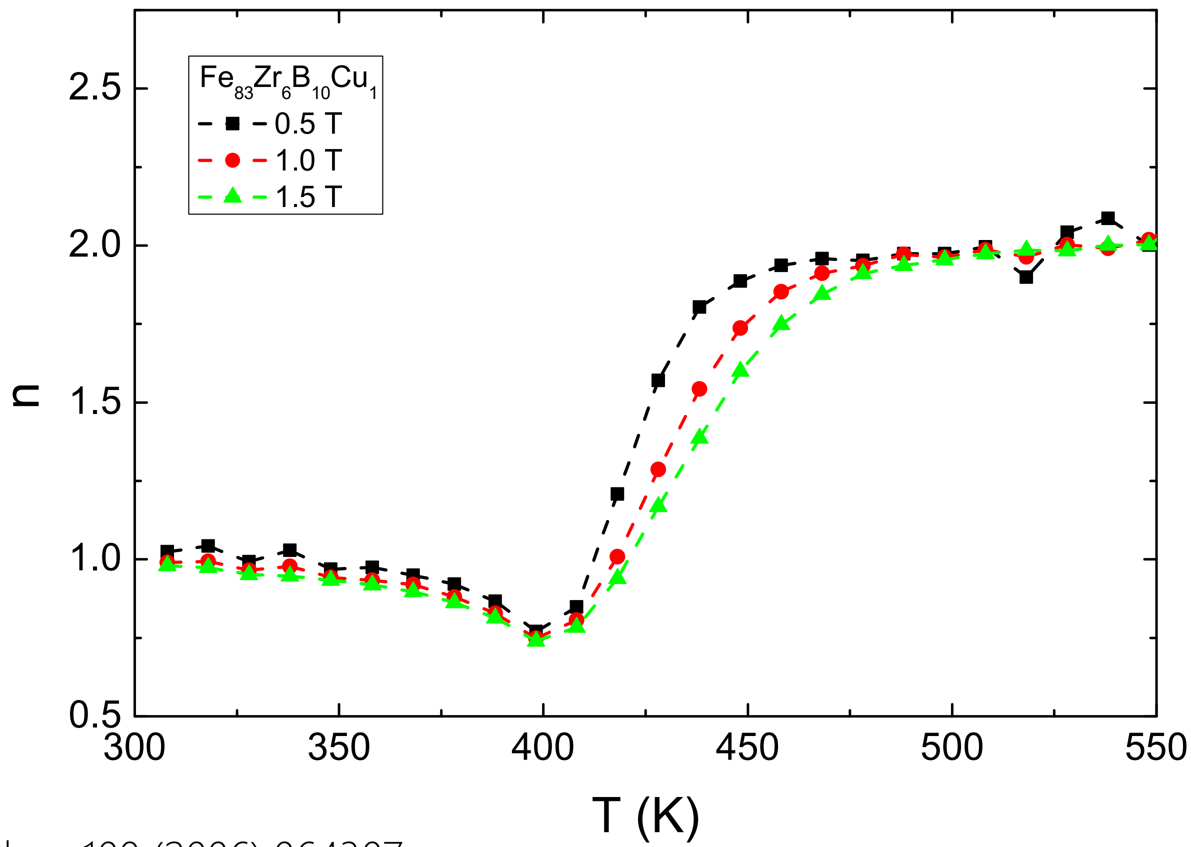
Data reduction



Field dependence of $\Delta S_M(H)$

$$\Delta S_M \propto H^n \qquad n = \frac{d \ln|\Delta S_M|}{d \ln H}$$

- T<<T$_C$: n=1
- T>>T$_C$: n=2
- T=T$_C$: $n = 1 + \frac{1}{\delta}\left(1 - \frac{1}{\beta}\right)$



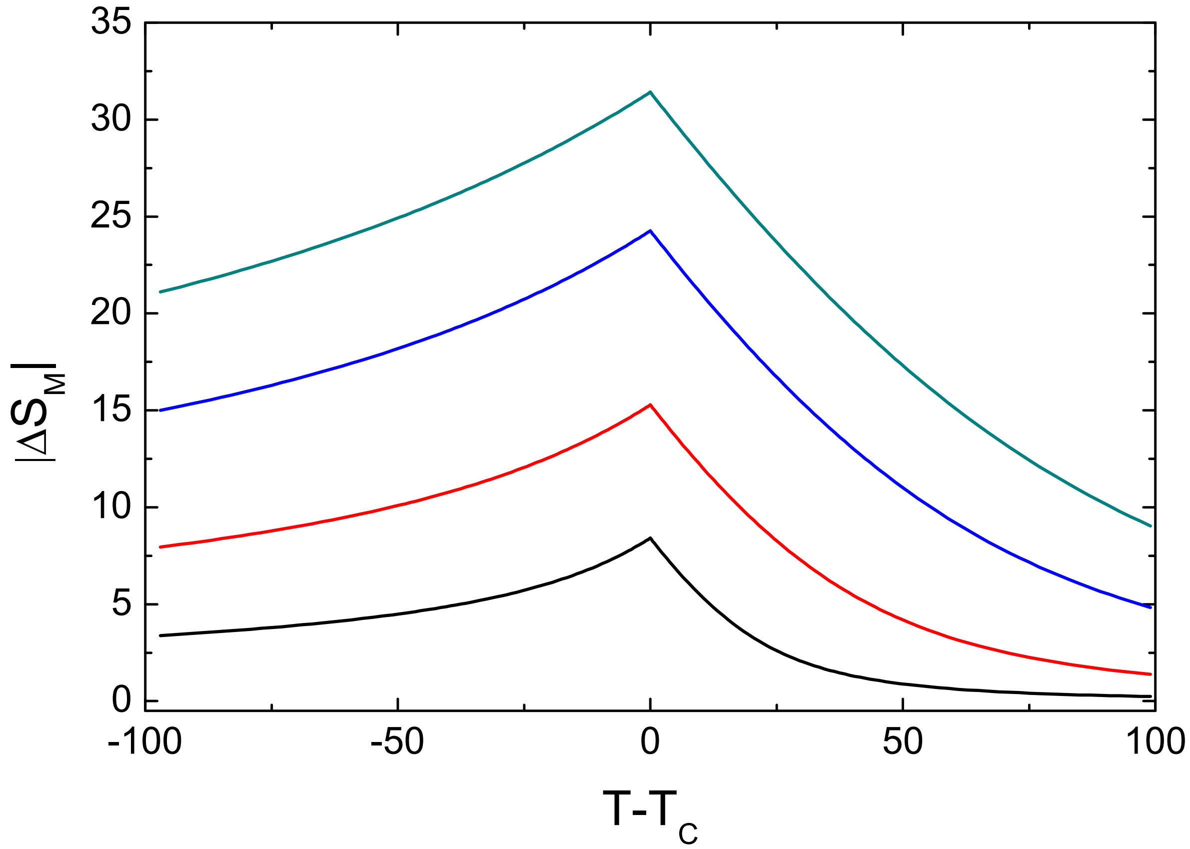
V. Franco, J.S. Blázquez, and A. Conde, J. Appl. Phys. 100 (2006) 064307

Universal curve for the field dependence ?

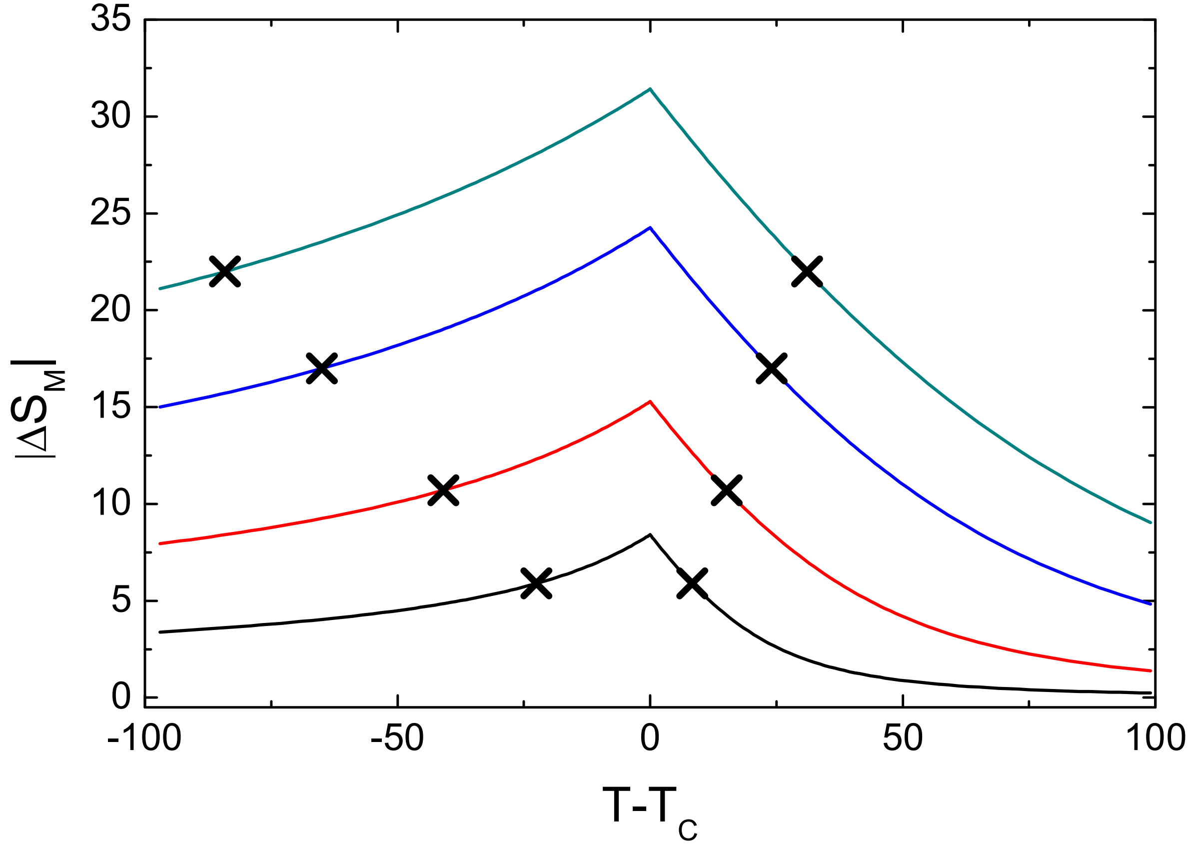
- Different characteristic regions of *n*
- The temperature dependence of ΔS_M also changes above and below T_C
- Phenomenological universal curve:
  - Normalization of ΔS_M
  - Rescaled temperature using 2 reference points

$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C); & T \le T_C \\ (T - T_C)/(T_{r2} - T_C); & T > T_C \end{cases}$$

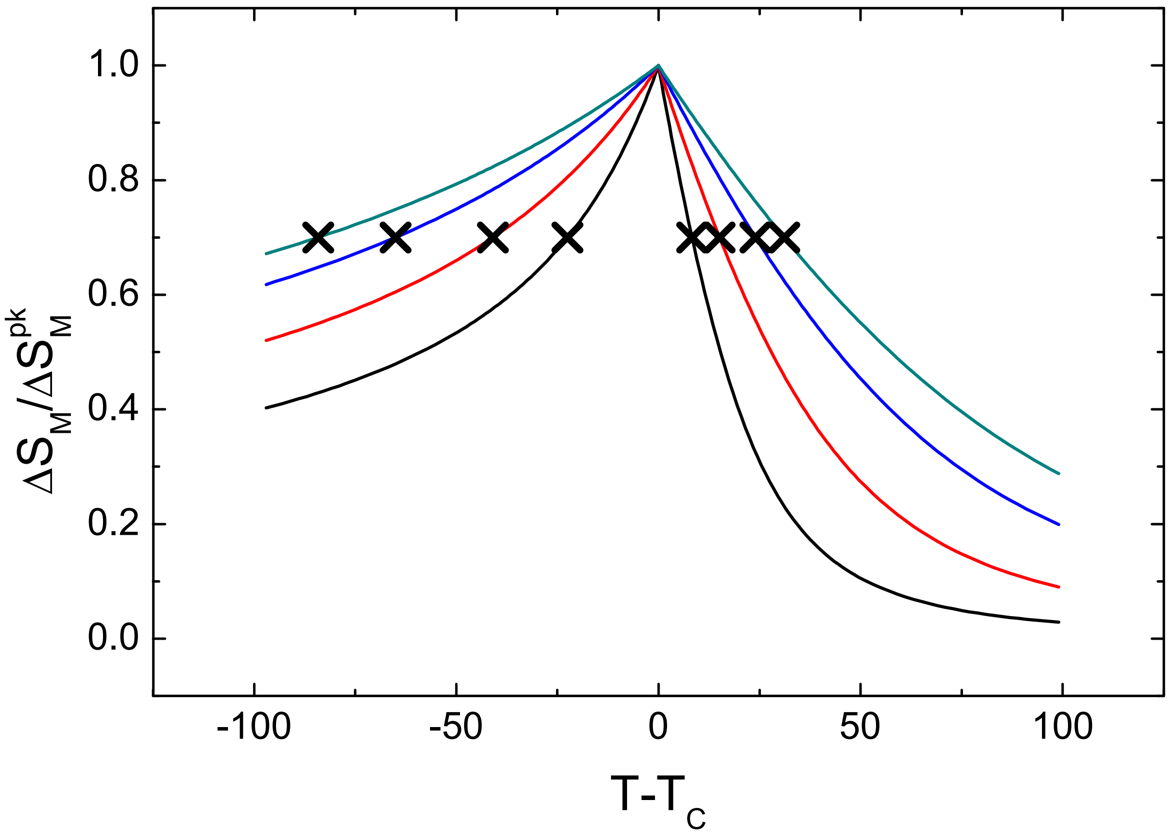
“Measurements”
for different applied fields



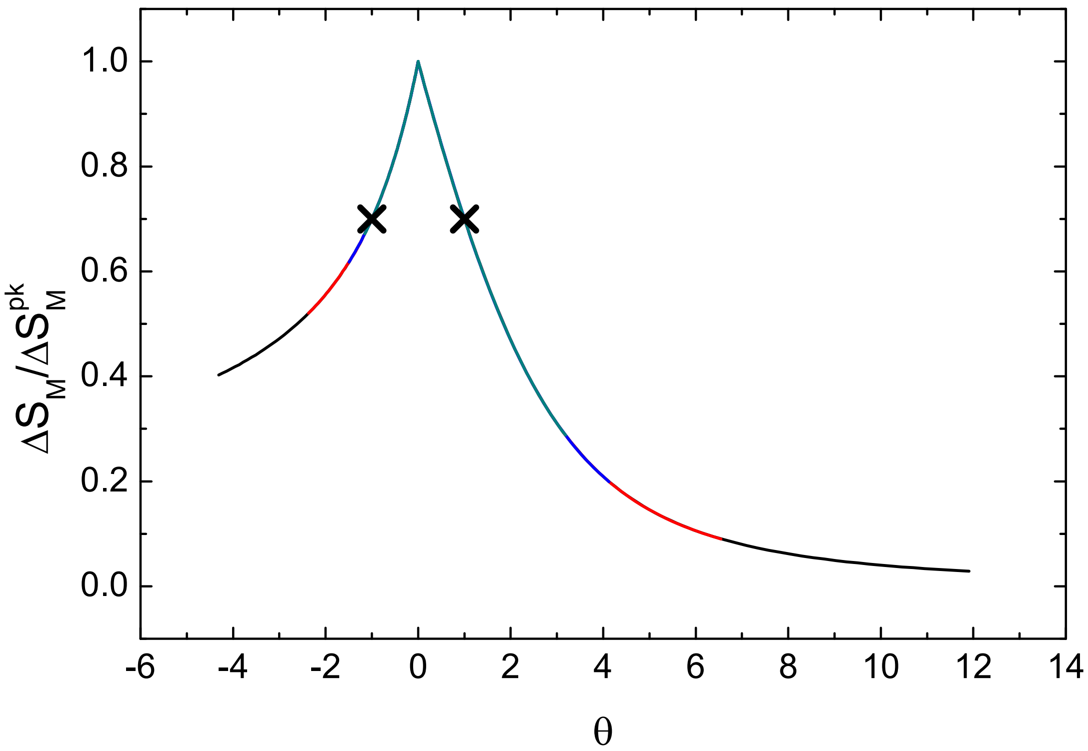
Selection of equivalent points
(with respect to the peak)



Rescale (normalize) the vertical axis



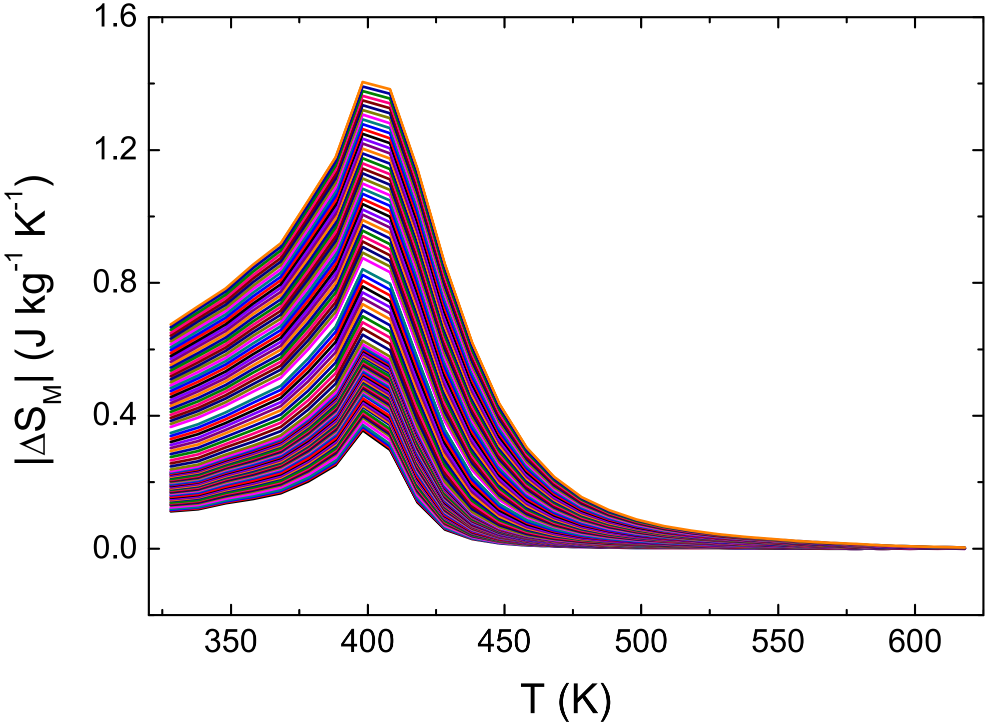
Rescale the temperature axis

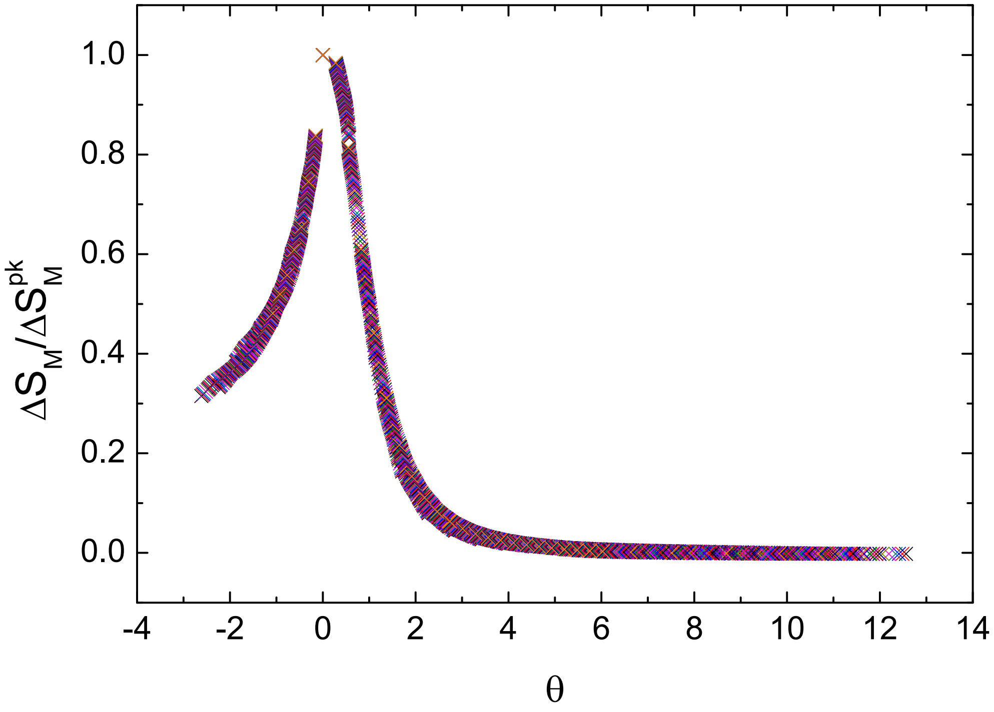


$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C); & T \le T_C \\ (T - T_C)/(T_{r2} - T_C); & T > T_C \end{cases}$$

Experimental results

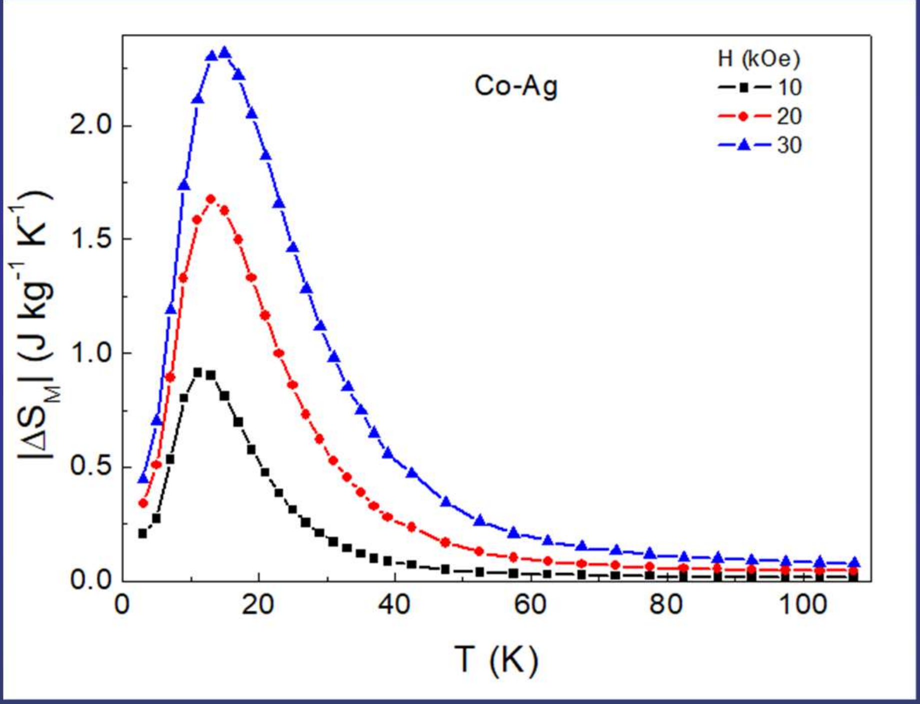
96 curves; 0.25 – 1.5 T

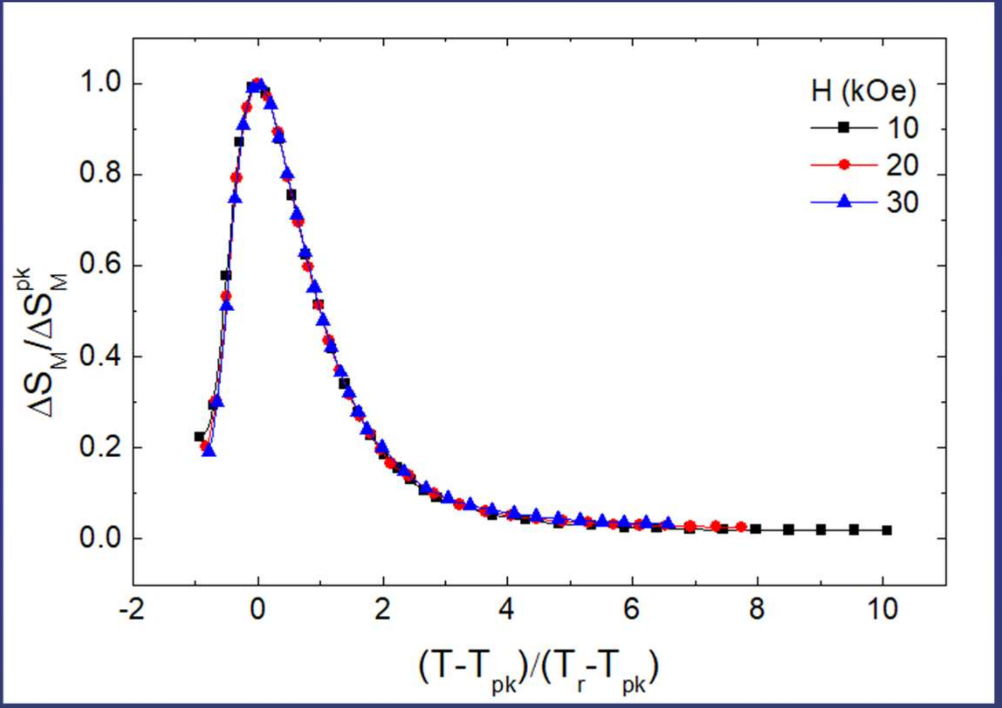




V. Franco, J.S. Blázquez, and A. Conde, Appl. Phys. Lett. 89 (2006) 222512

Spin freezing transition
in core-shell nanoparticles: field dependence

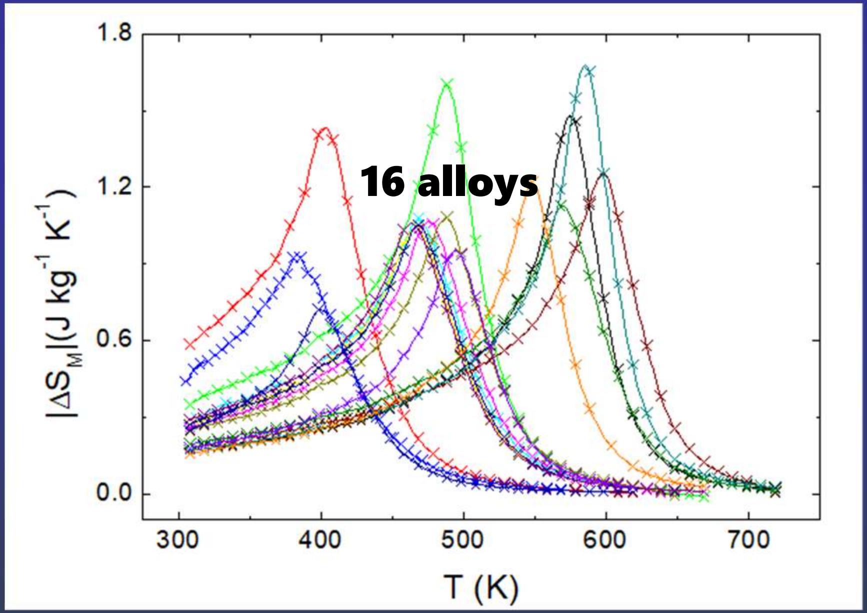


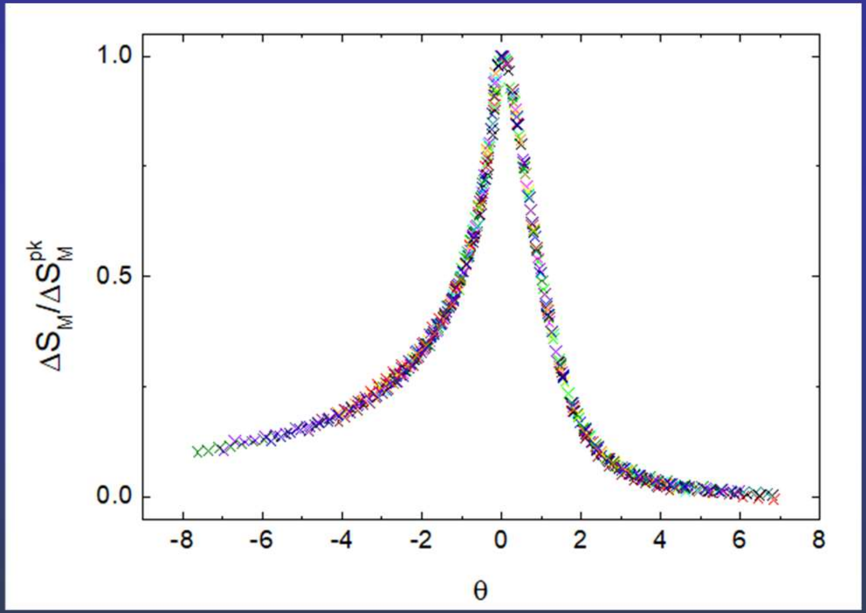


V. Franco, A. Conde, D. Sidhaye, B.L.V. Prasad, P. Poddar, S. Srinath, M.H. Phan, H. Srikanth,
J. Appl. Phys. 107 (2010) 09A902

MCE of different alloy series

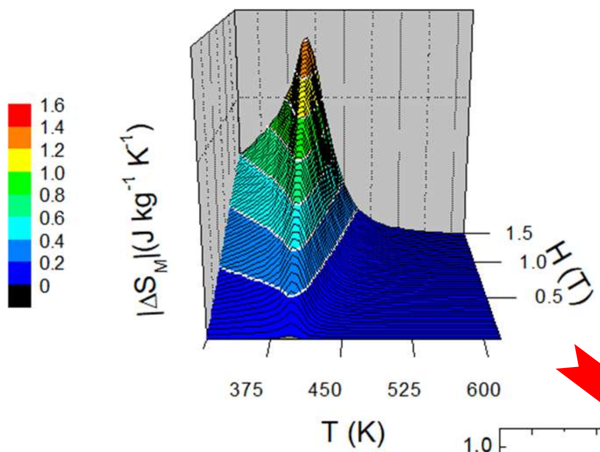
Field dependence is eliminated
Temperature dependence is related to the critical exponents
Similar values of the critical exponents

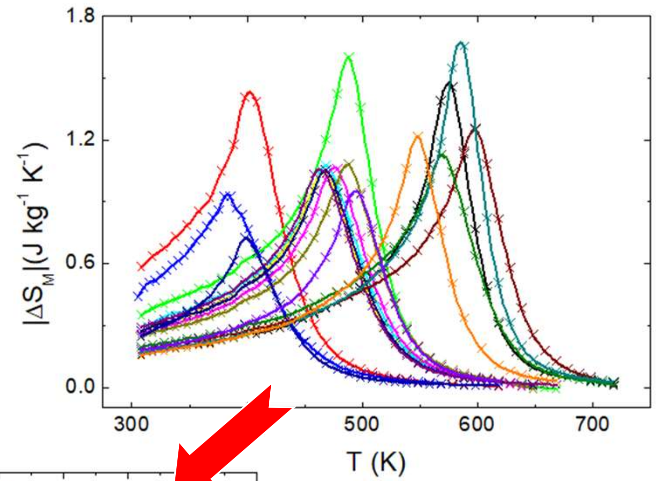


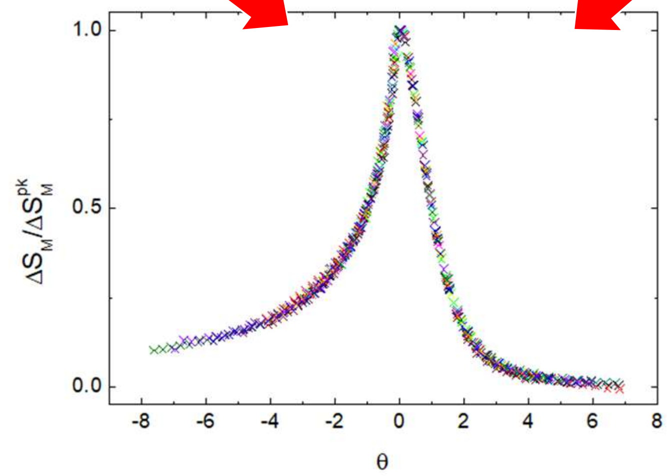


V. Franco, J.S. Blázquez, M. Millán, J.M. Borrego, C.F. Conde, A. Conde, J. Appl. Phys. 101 (2007) 9C503

Universal curve for ΔS_M







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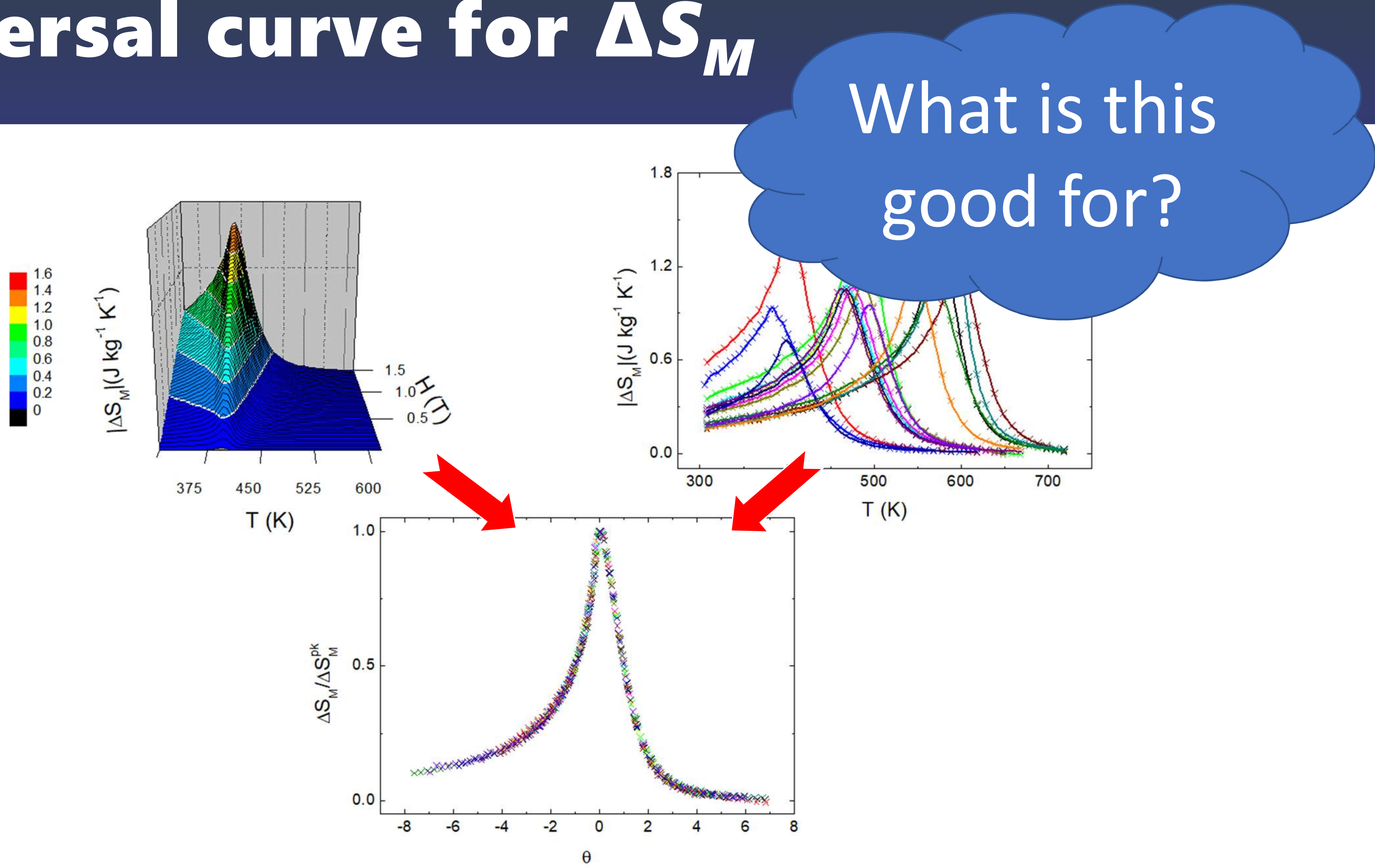
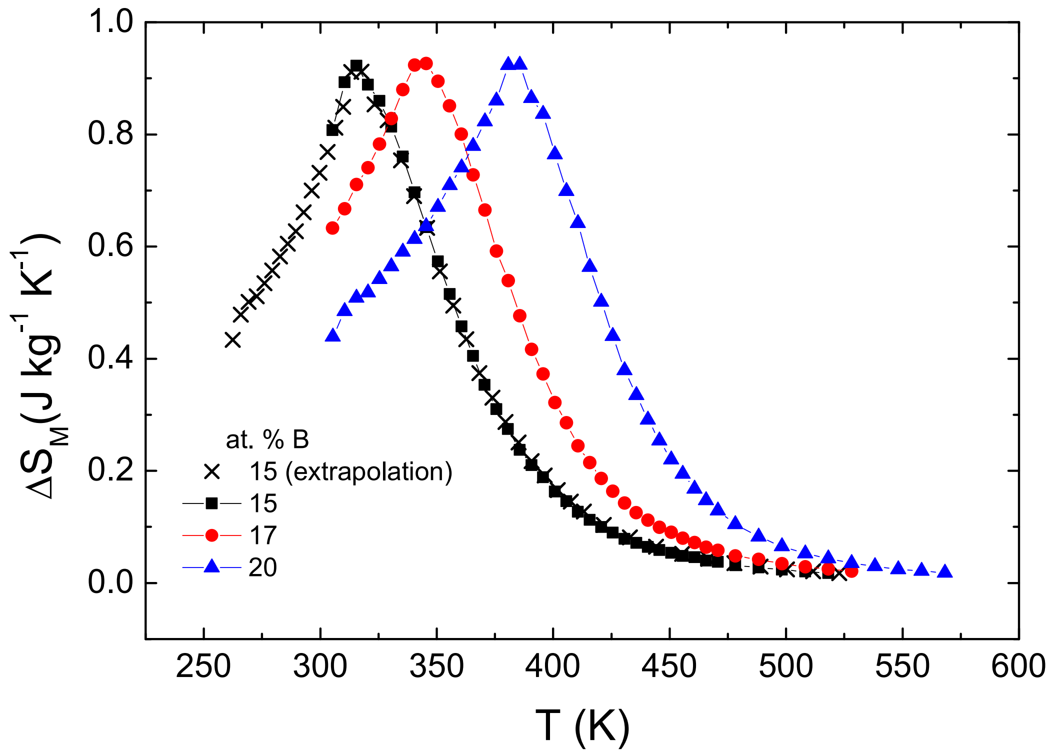


Extrapolation using the universal curve

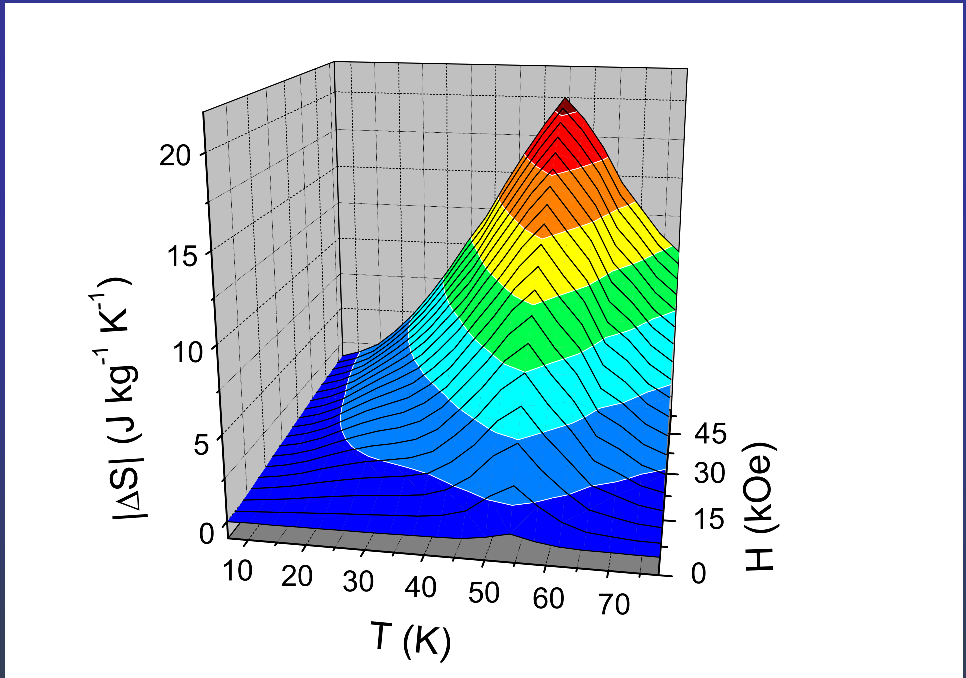
$Fe_{91-x}Mo_8Cu_1B_x$ (x=15, 17, 20)

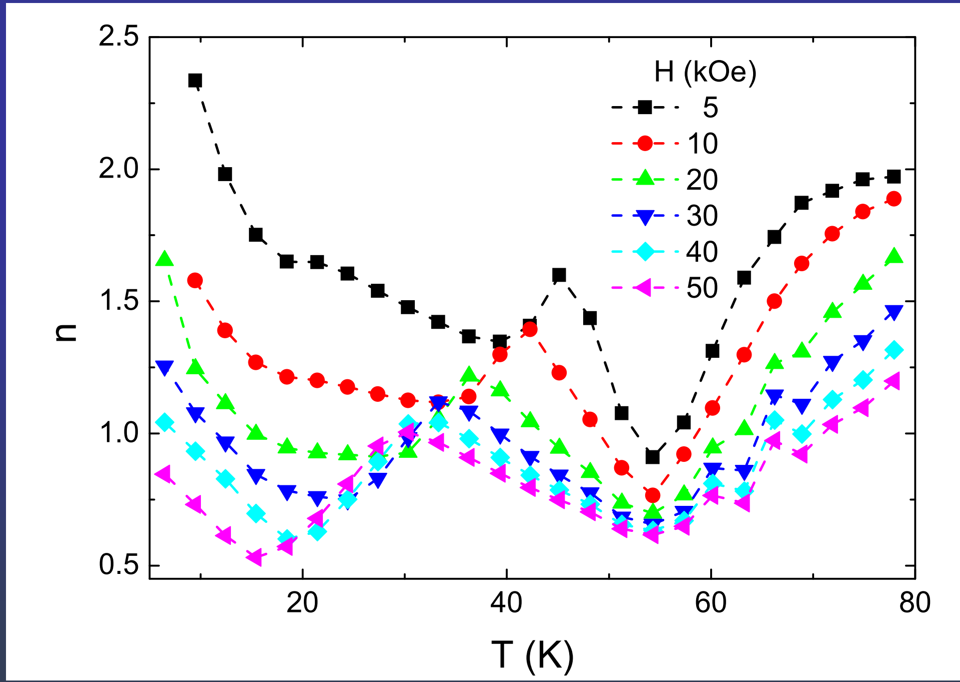


V. Franco, C.F. Conde, J.S. Blázquez, A. Conde, P. Švec, D. Janičkovič, L.F. Kiss, J. Appl. Phys. 101 (2007) 093903

Overlapping magnetic phenomena: the use of n

$Er_{0.15}Dy_{0.85}Al_2$

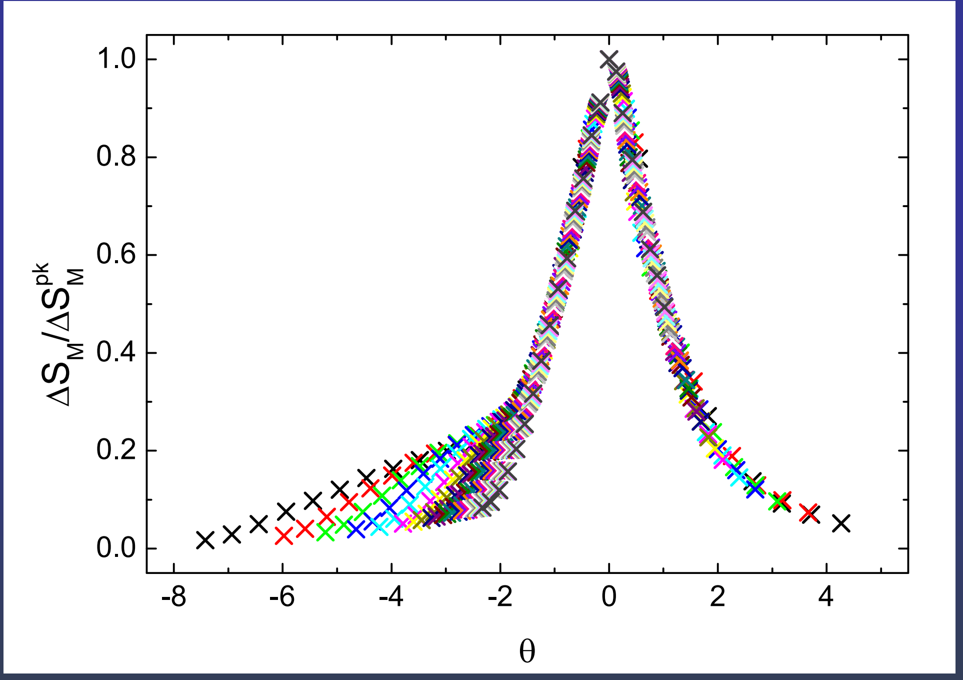




V. Franco, A. Conde, V.K. Pecharsky, K.A. Gschneidner, Jr., Europhys. Lett. 79 (2007) 47009

Overlapping magnetic phenomena: universal curve

$Er_{0.15}Dy_{0.85}Al_2$



V. Franco, A. Conde, V.K. Pecharsky, K.A. Gschneidner, Jr., Europhys. Lett. 79 (2007) 47009

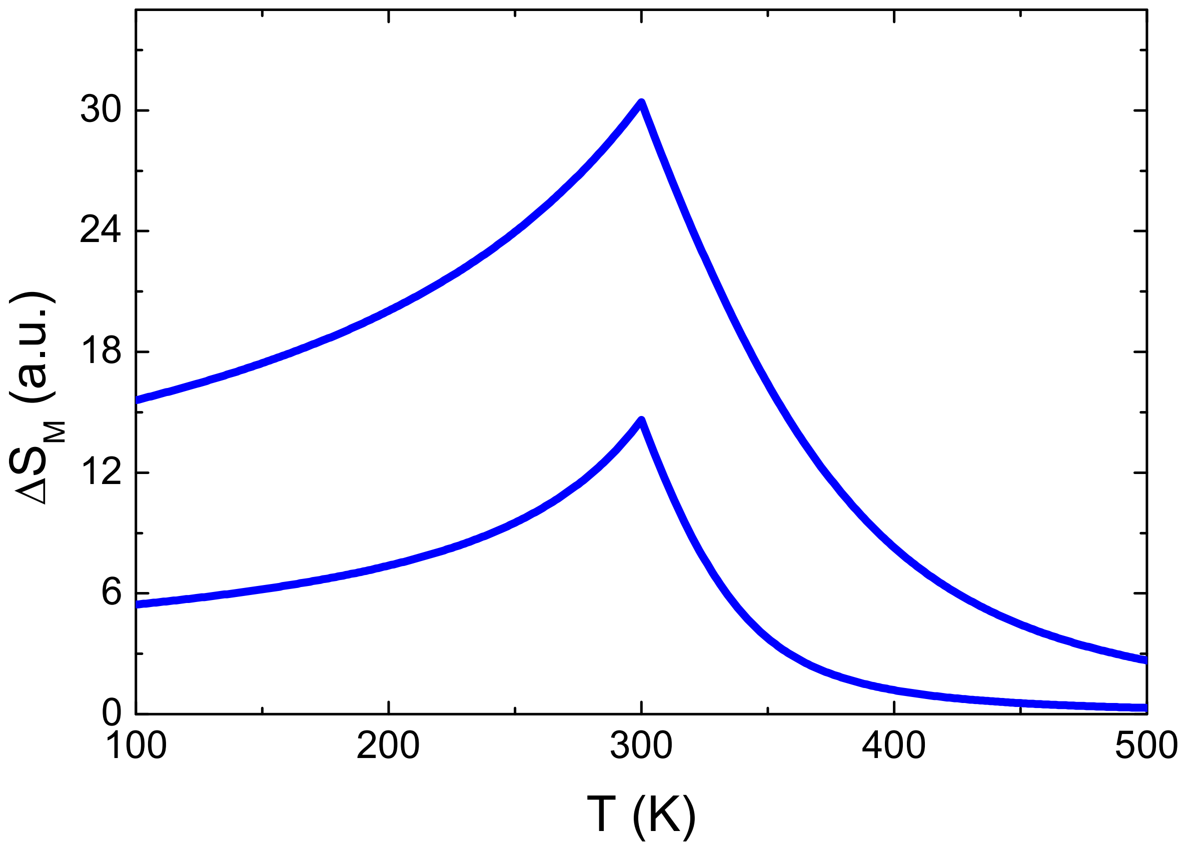
Noise reduction

Problem:

- Experimental data might be noisy
  - Derivatives
- Smoothing would alter the shape of the peak

Solution:

- Universal scaling?



Noise reduction

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Solution:

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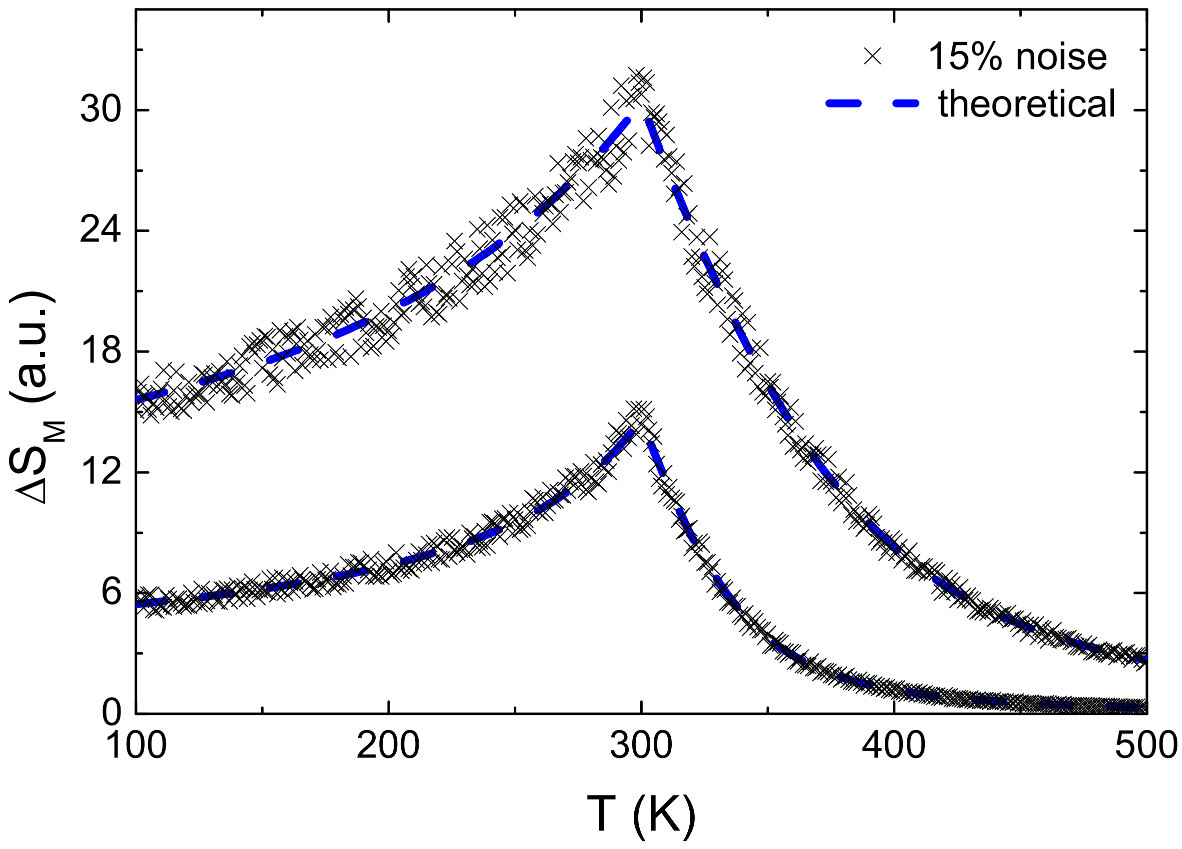


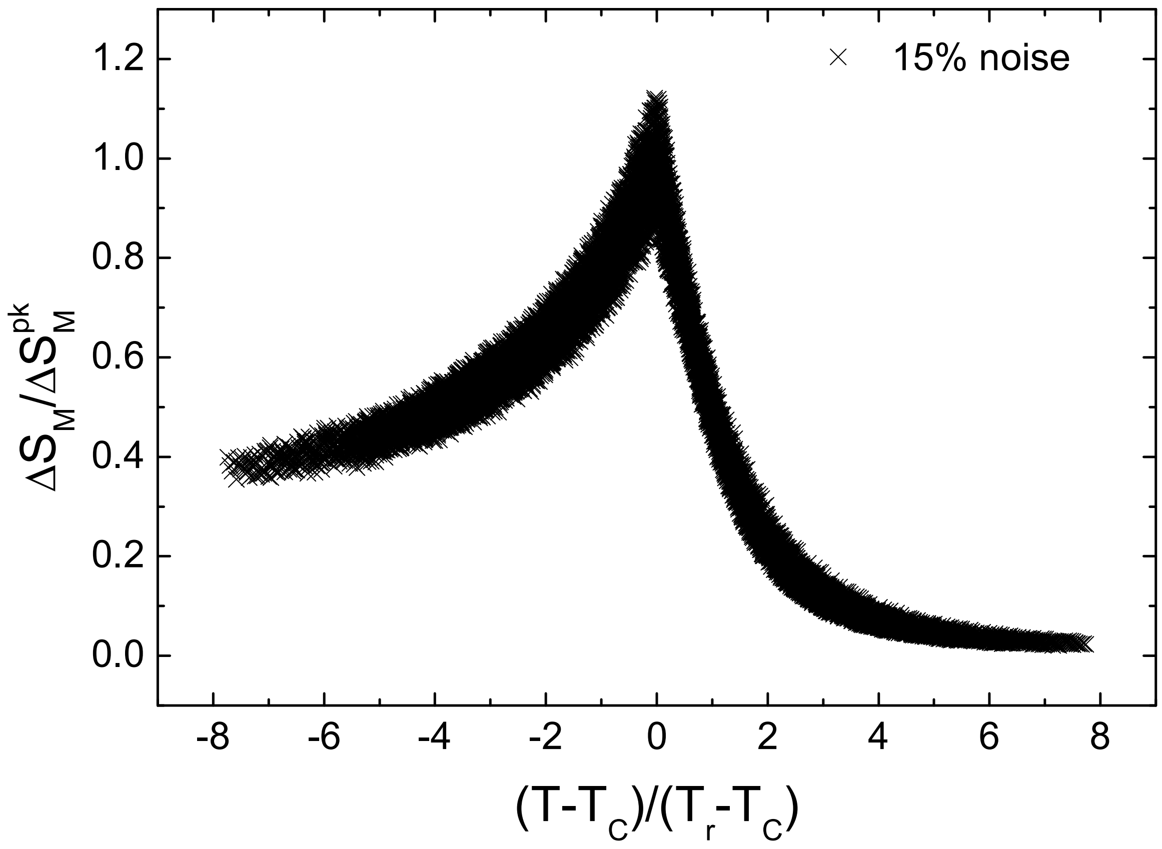
Noise reduction

Problem:

- Experimental data might be noisy
  - Derivatives
- Smoothing would alter the shape of the peak

Solution:

- Universal scaling?



Noise reduction

Problem:

- Experimental data might be noisy
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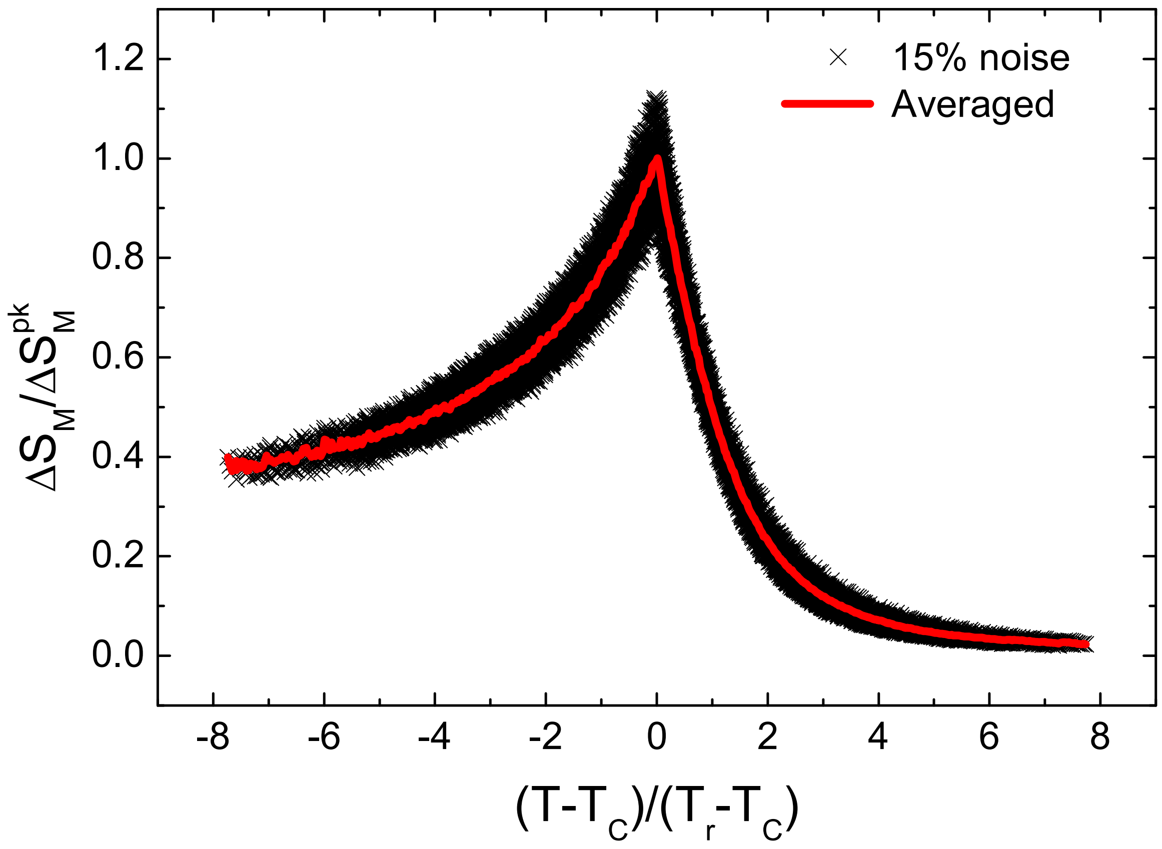
- Smoothing would alter the shape of the peak

Solution:

- Universal scaling?



Noise reduction

Problem:

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- Smoothing would alter the shape of the peak

Solution:

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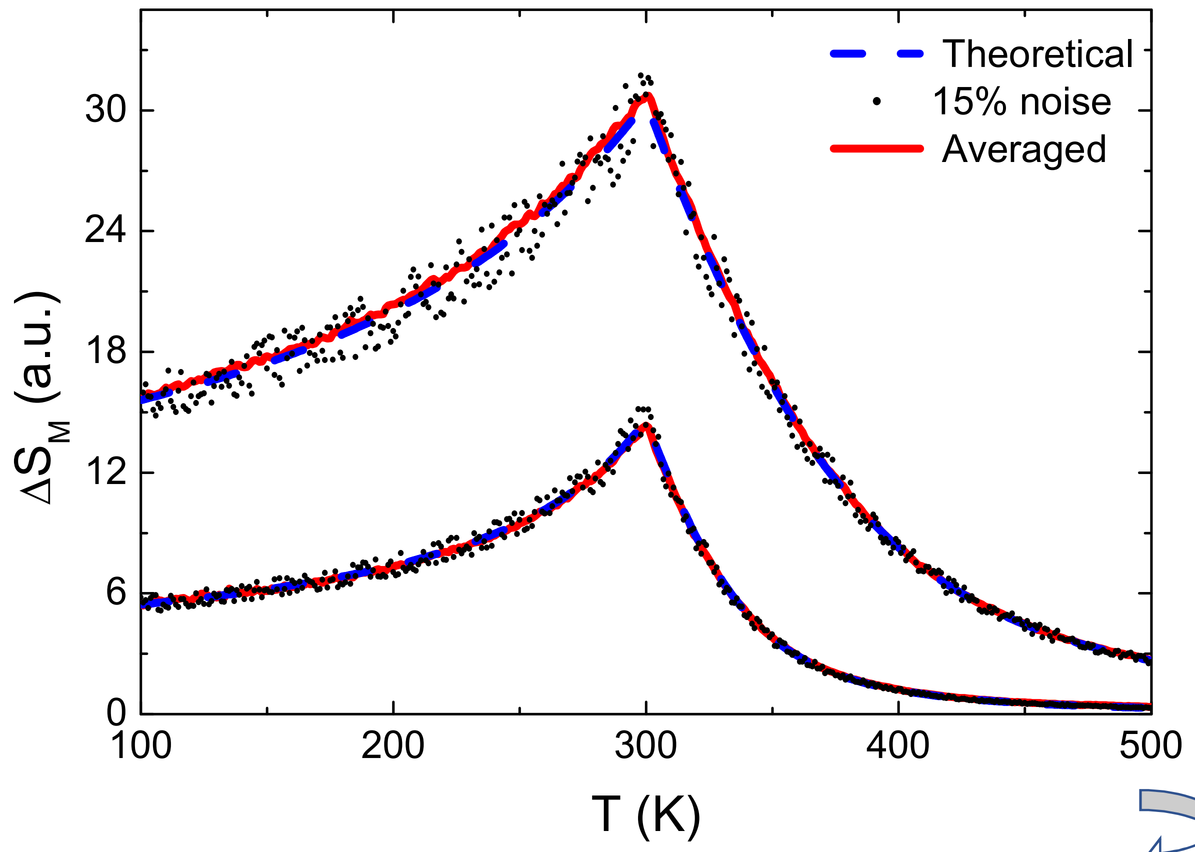


The physics behind the universal curve: Scaling

- 2nd order phase transitions scale:
  - For a given universality class, all magnetization curves collapse
  - MCE should collapse
- Theoretician's point of view: *if EOS and critical exponents are known, the universal curve can be calculated*
- Our point of view: *the universal curve can be found without knowing <u>neither EOS</u>, <u>nor the critical exponents</u>*

Features which are EOS-independent

- Scaling EOS

$$\frac{M}{|t|^{\beta}} = m_{\pm}\left(\frac{H}{|t|^{\Delta}}\right)$$

- Magnetic entropy change and temperature axis scale with field

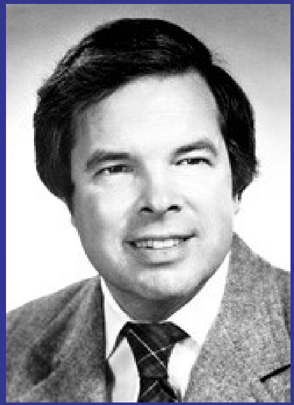
$$\Delta S_M / a_M = H^{\frac{1-\alpha}{\Delta}} s(t / H^{1/\Delta})$$

- By using the reference temperatures there is no need to know the critical exponents or the EOS to use this scaling

V. Franco, A. Conde, J.M. Romero-Enrique, J. S. Blázquez, J. Phys. Condens. Matter 20 (2008) 285207

Critical Exponents

- Describe the behavior of physical quantities **near** continuous phase transitions.
- They are universal
  - do not depend on the details of the physical system,
  - depend only on some of its general features, e.g.
    - dimensionality of the system
    - range of the interactions



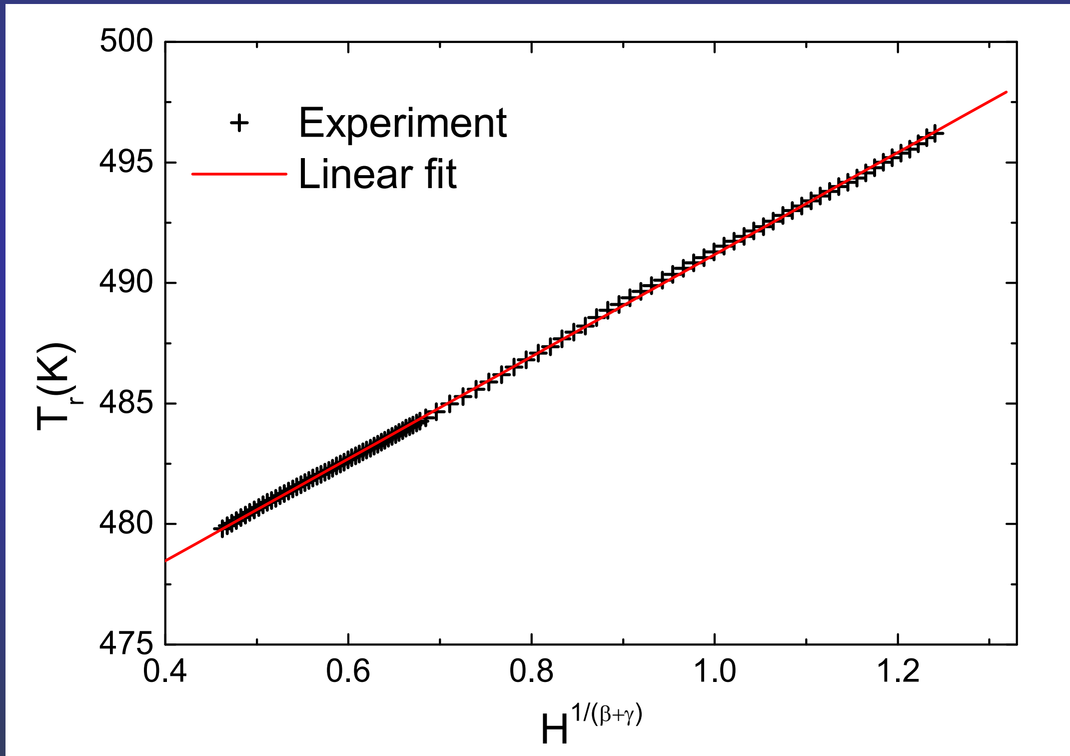
- Kenneth G. Wilson, Nobel Prize in Physics 1982 “for his theory for critical phenomena in connection with phase transitions”

Magnitude	Exponent
ΔT_{ad}^{pk}	$1/\Delta$
T_r	$1/\Delta$
$T_{pk} - T_C$ **(not mean field)**	$1/\Delta$
$T_{pk} - T_C$ **(mean field)**	0
$\Delta S_M \left(T = T_c\right)$	$1 + 1/\delta\left(1 - 1/\beta\right) = \left(1 - \alpha\right)/\Delta$
ΔS_M^{pk}	$1 + 1/\delta\left(1 - 1/\beta\right) = \left(1 - \alpha\right)/\Delta$
$\boldsymbol{RC}_{\mathbf{Area}}$ **or** $\boldsymbol{RC}_{\mathbf{FWHM}}$	$1 + 1/\delta$

In the mean field case, $\alpha=0$ → ΔT_{ad} and ΔS_M would have the same field dependence

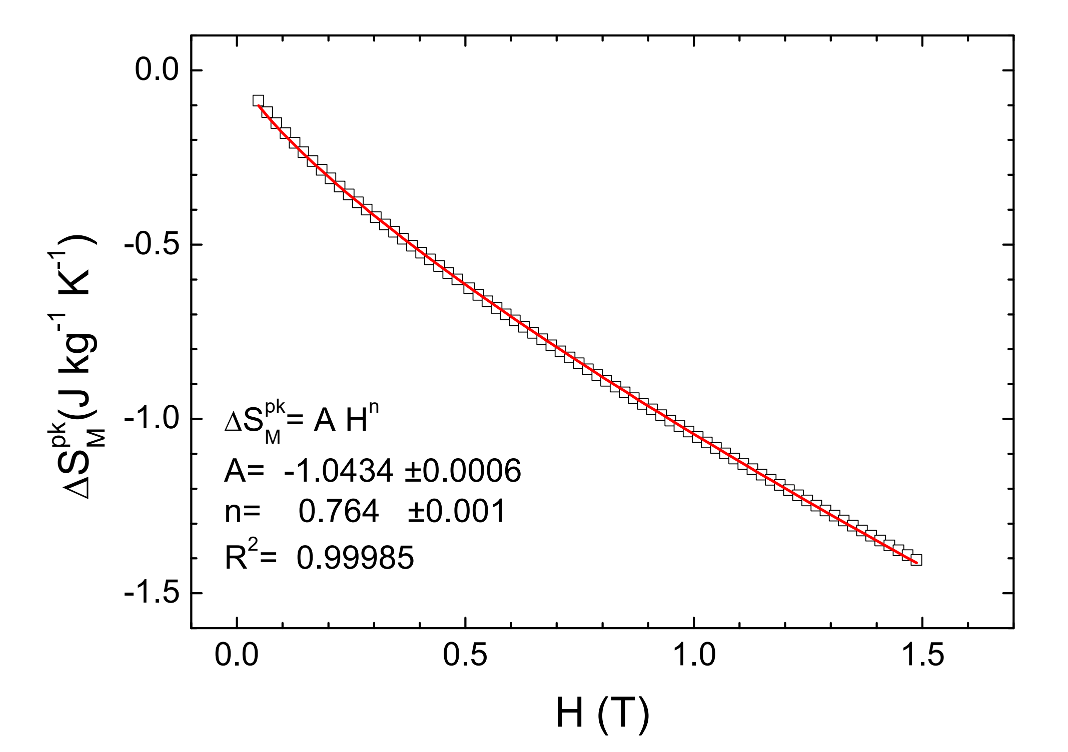
V. Franco, A. Conde, Int. J. Refrig. 33 (2010) 465

Field dependence of the reference temperature

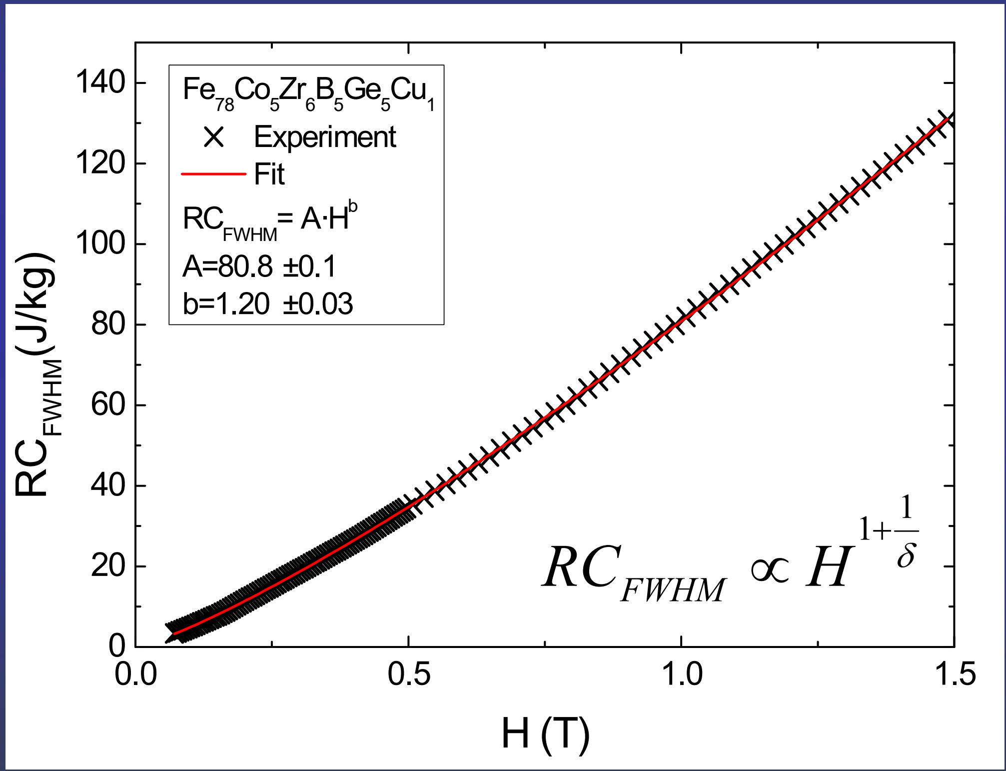


$Fe_{78}Co_5Zr_6B_5Ge_5Cu_1$

Field dependence of the peak entropy change



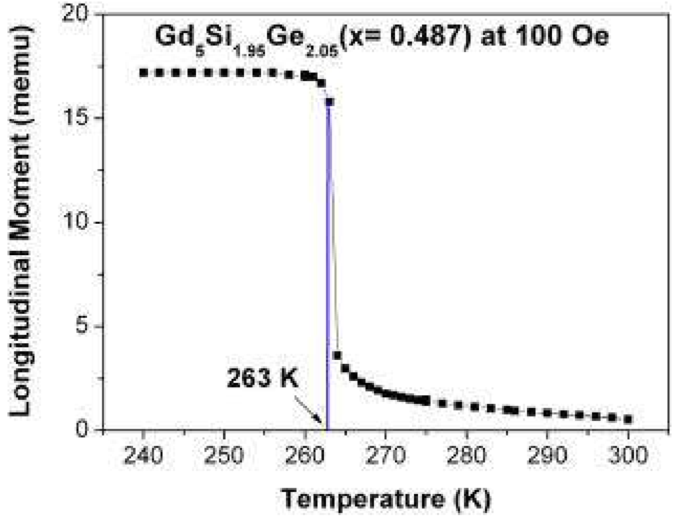
Field dependence of the refrigerant capacity

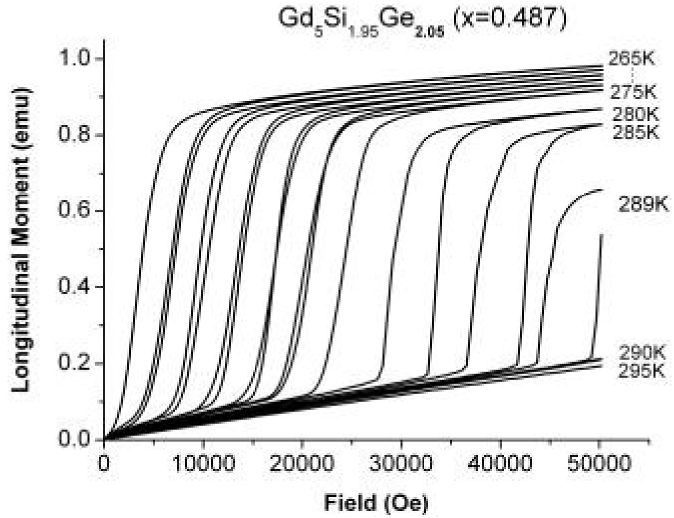


V. Franco, J. S. Blázquez, and A. Conde, J. Appl. Phys. 103, 07B316 (2008)

The problem

- $Gd_5Si_2Ge_2$ has a structural phase transition:
  - The low temperature phase disappears before it reaches its Curie temperature.
- How to determine T_c?

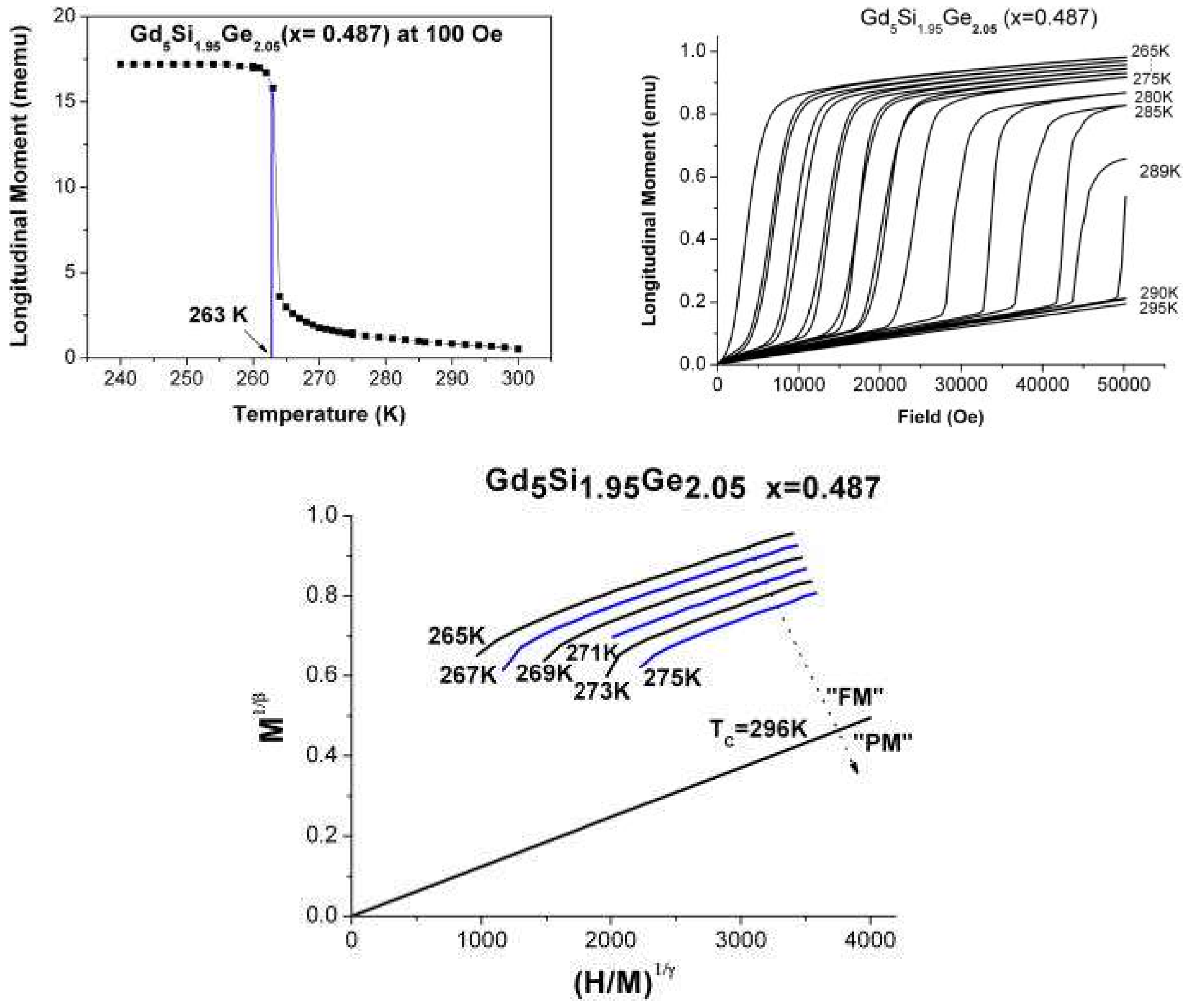




Solution?

- Use Arrott plot only on one side
- Extrapolate to higher temperatures

- Anomalous values of the critical exponents (β=2.2; γ=0.9)
- Reason: A-N plots are approximately linear, even for large variations of the critical exponents



R. L. Hadimani, Y. Melikhov, J. E. Snyder, and D. C. Jiles, J. Appl. Phys. **103**, 033906 (2008)

Alternative solution

- **Suppress the magneto-structural transition** by proper doping, as was done for the case of the $Gd_5Si_2Ge_2$ compound

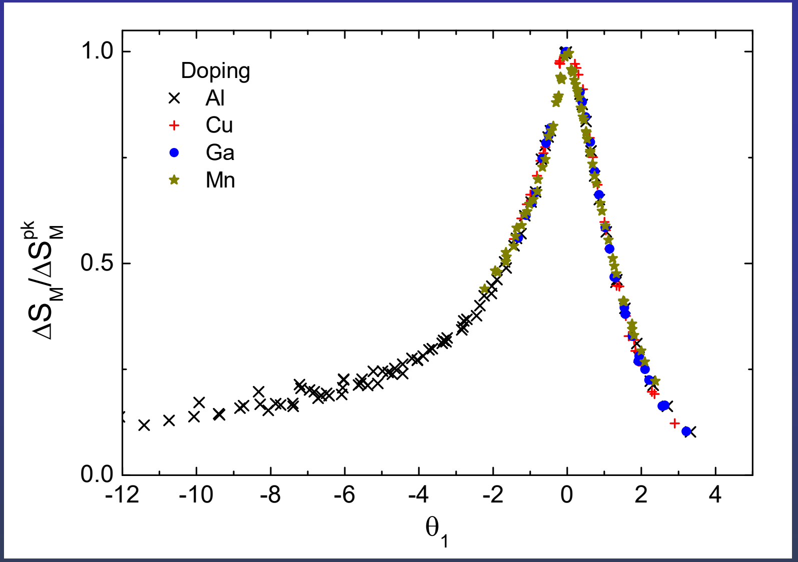
- In the undoped compound, the low temperature phase is orthorhombic and it transforms to a monoclinic phase at temperatures above 270 K.

- In the $Gd_5Si_2Ge_{1.9}X_{0.1}$ doped alloy (with X= Al, Cu, Ga, Mn, Fe, Co) the **monoclinic phase is entirely suppressed** in the case of the first four of these metal additives, and is **mostly suppressed in the cases of the latter two of these additives**.

V. Franco, A. Conde, V. Provenzano, R.D. Shull, JMMM 322 (2010) 218

Universal curve

- Evidence of a second order phase transition



V. Franco, A. Conde, V. Provenzano, R.D. Shull, JMMM 322 (2010) 218

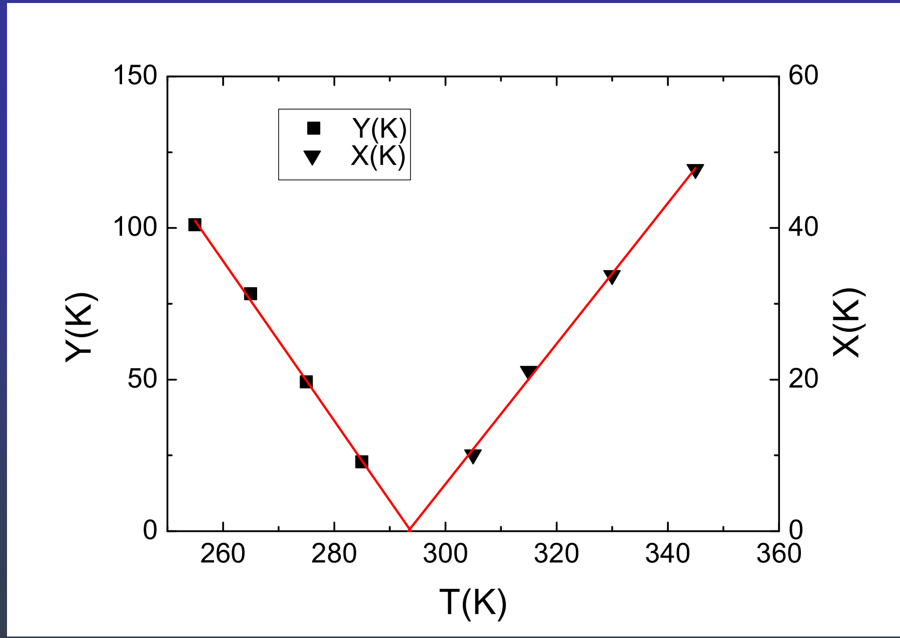
Kouvel-Fisher method

- Iterative process:
  - Arrott-Noakes plot ($M^{1/\beta}$ vs $(H/M)^{1/\gamma}$)
  - M_0 and χ_0 via extrapolation (intersection with axes)
  - Define

$$X(T) = \chi_0^{-1}\left(d\chi_0^{-1}/dT\right)^{-1} = \left(T - T_C\right)/\gamma$$

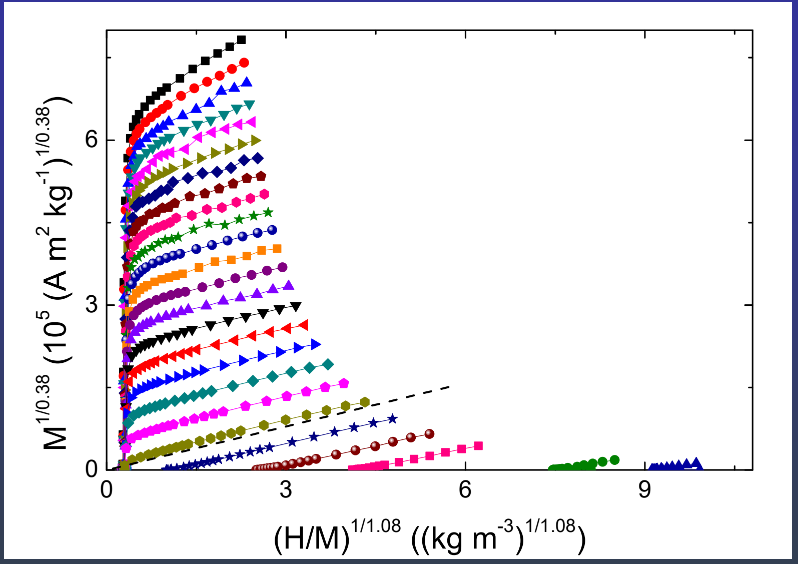
$$Y(T) = M_0\left(dM_0/dT\right)^{-1} = \left(T - T_C\right)/\beta$$

  - Extract exponents and T_c
  - Iterate until convergence

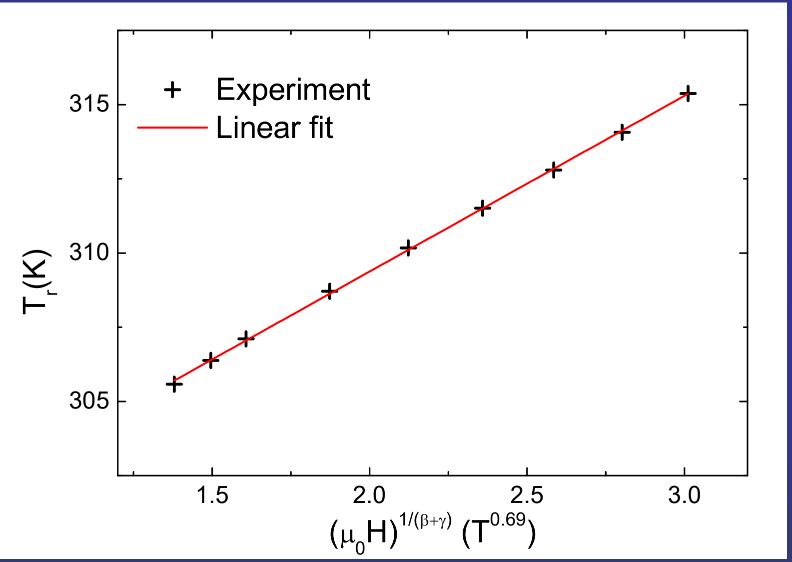


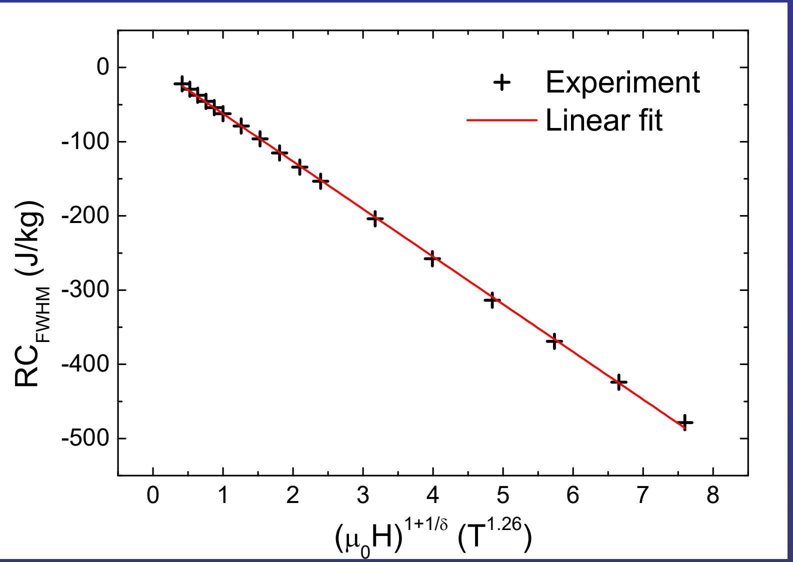
A fully second order case

Arrott-Noakes plot for the Al doped $Gd_5Ge_2Si_2$ alloy using the exponents extracted from the Kouvel-Fisher analysis

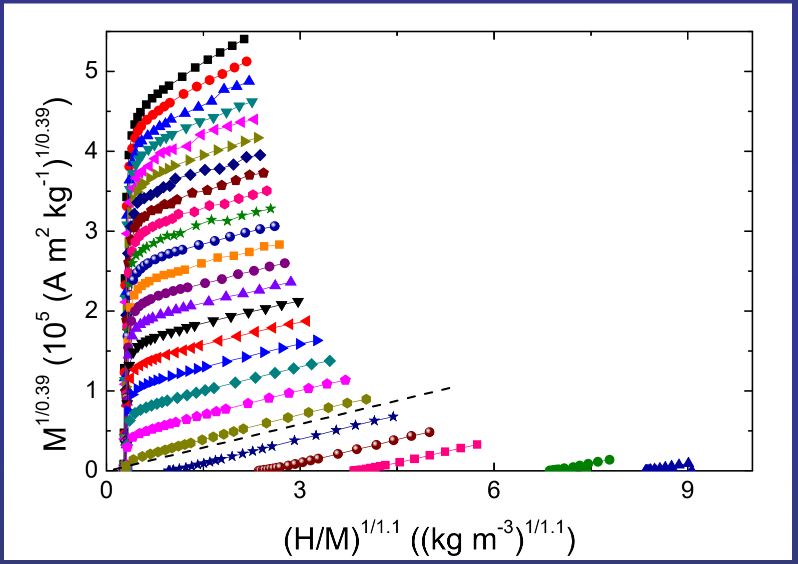


Scaling of MCE using K-F exponents



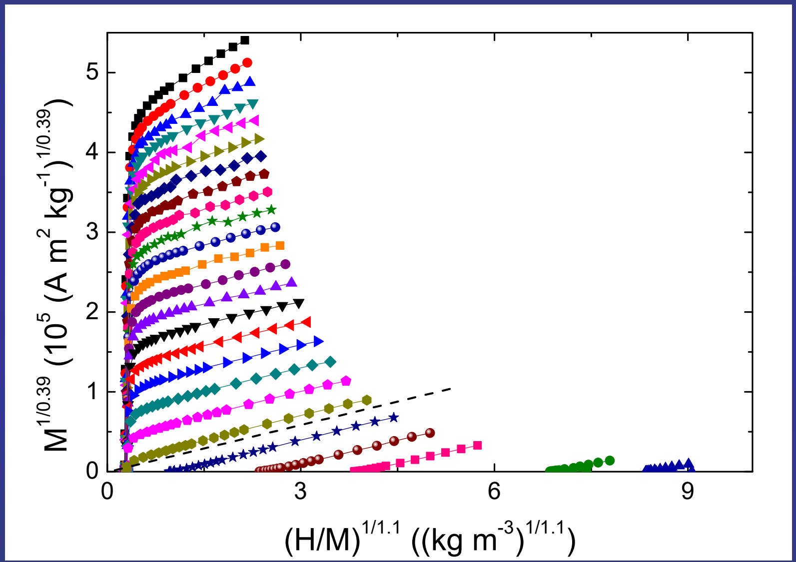


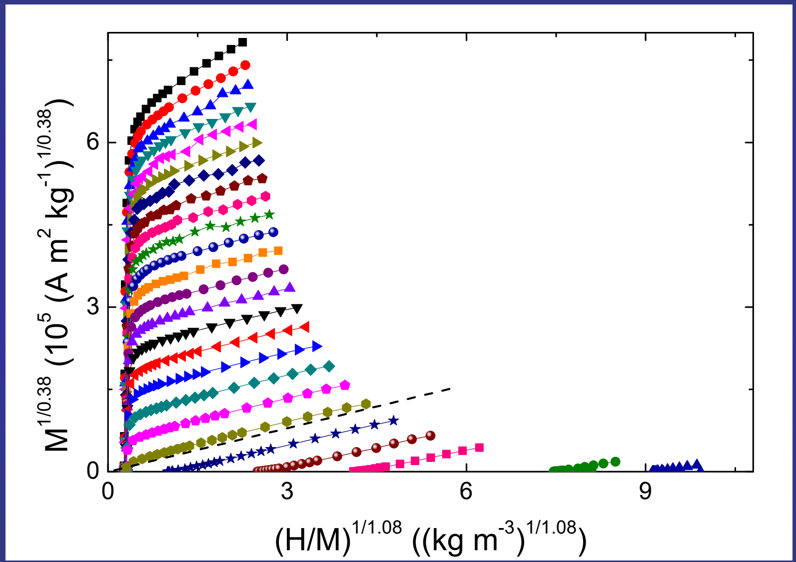
Arrott plot using exponents obtained from MCE



Exponents were extracted from the scaling of the magnetic entropy change

No qualitative difference

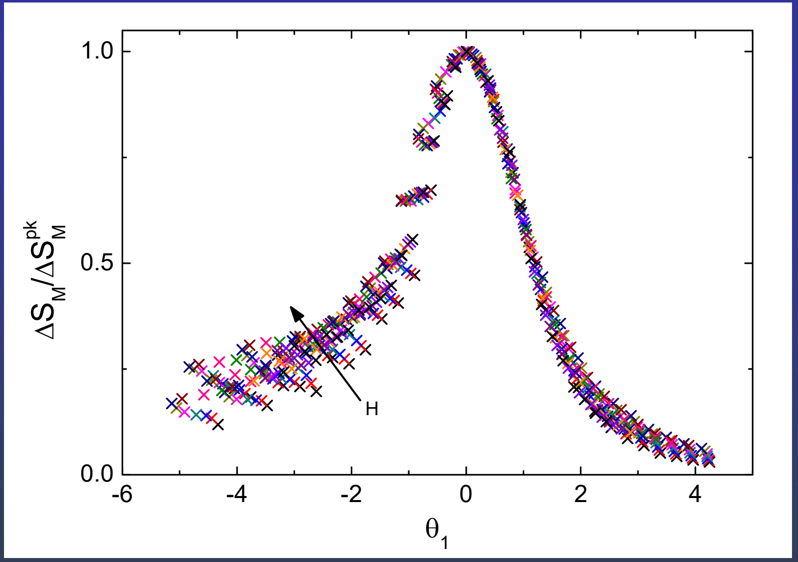




- Differences between critical exponents obtained in both ways are within error margin

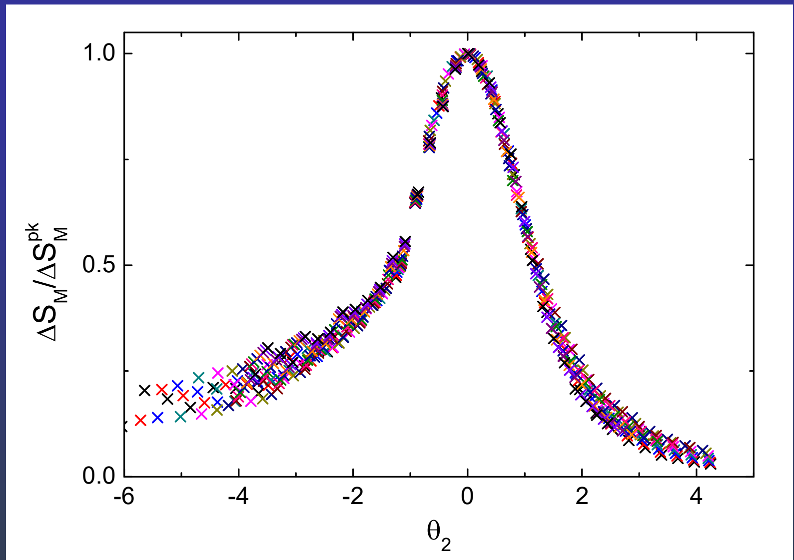
Fe doped $Gd_5Ge_2Si_2$

Scaling with a single reference temperature does not fully hold

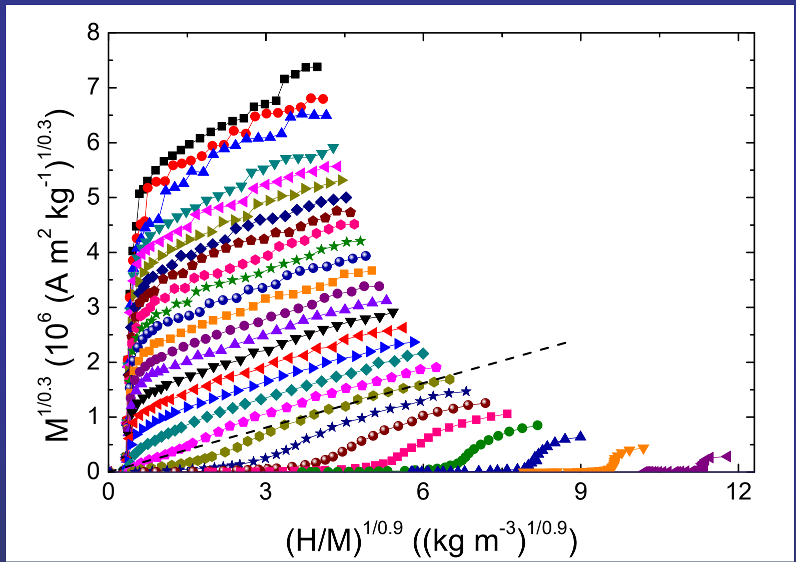


Fe doped $Gd_5Ge_2Si_2$

Using two reference temperatures allows the collapse → mostly second order transition

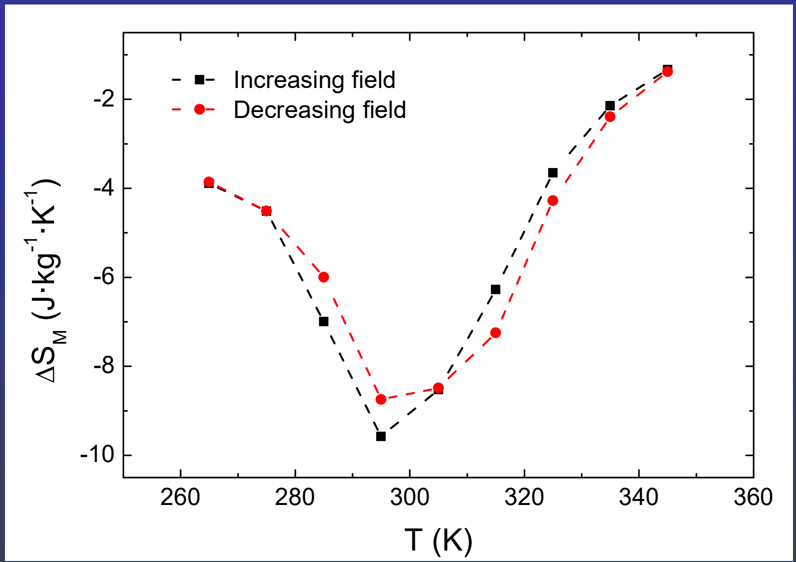


Arrott plot using exponents obtained from MCE



- K-F method could not be used due to the remaining structural transition

Reduced thermal hysteresis (mostly second order)



Doped GdSiGe: critical exponents determination

	T_c (K)	β	γ	δ
Pure Gd (literature)	293.3	0.381	From 1.196 to 1.24	Measured 3.615 Calculated* from 4.139 to 4.25
Cu-doping	295.5	0.38 [0.4]	1.15 [1.1*]	4.03* [3.5]
Mn-doping	295.6	0.41 [0.40]	1.05 [1.2*]	3.56* [4.1]
Ga-doping	289.5	0.34 [0.42]	1.17 [1.3*]	4.44* [4.1]
Al-doping	293.5	0.38 [0.39]	1.08 [1.1*]	3.84* [3.8]
Fe-doping	292	[0.3]	[0.9*]	[4]

[] MCE; others, Kouvel-Kisher

V. Franco, A. Conde, V. Provenzano, R.D. Shull, JMMM 322 (2010) 218

Hysteresis… who cares?

Magnetic refrigeration

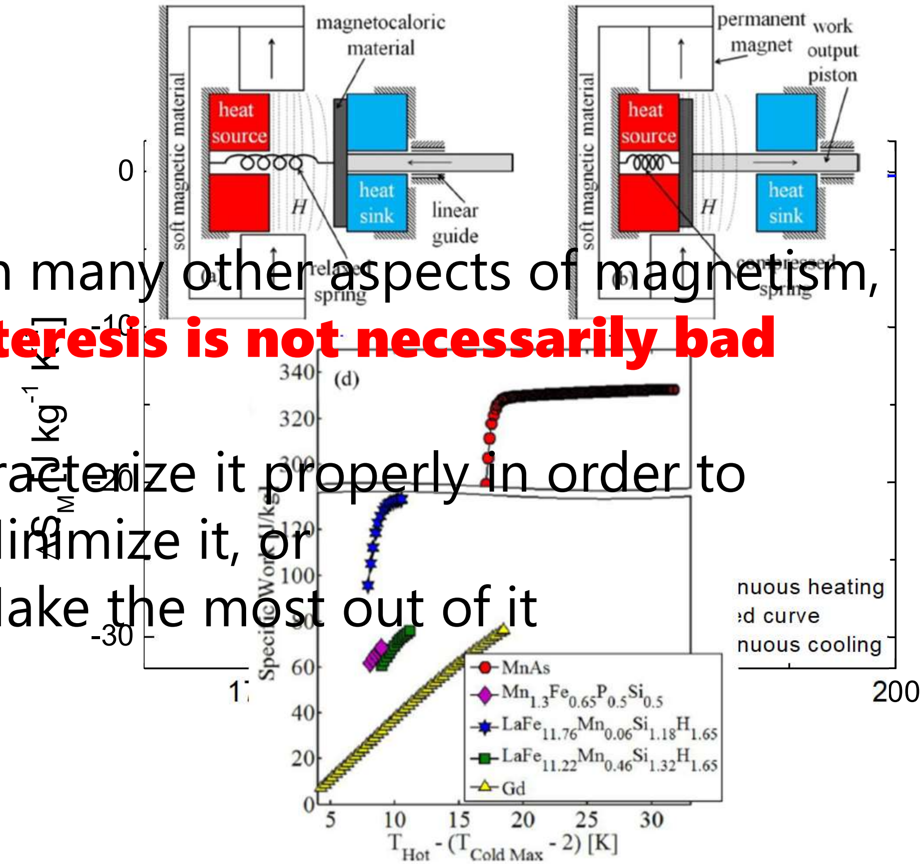
- Requires cyclic operation (T and H)
- Thermal hysteresis reduces the cyclic response
- Rate dependent phenomena limits the speed of operation

Thermomagnetic motor

- Cyclic operation
- Simulations indicate that performance is enhanced with hysteresis

Single shot operation

- Hysteresis might prevent undesirable triggers



As in many other aspects of magnetism,
hysteresis is not necessarily bad

Characterize it properly in order to

- Minimize it, or
- Make the most out of it

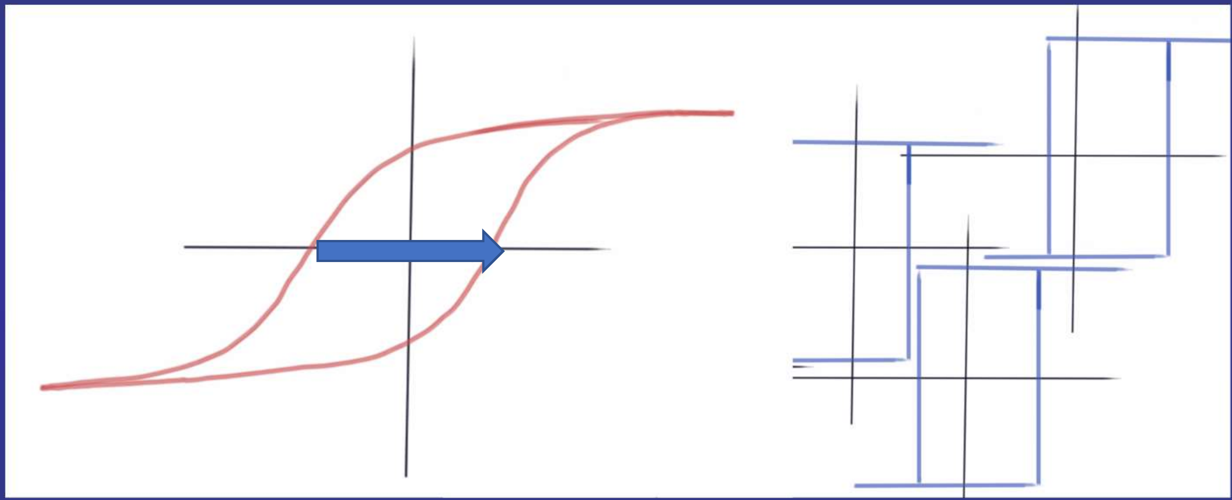
B. Kaeswurm, V. Franco, K.P. Skokov, O. Gutfleisch, J. Magn. Magn. Mater. 406 (2016) 259

C. V. X. Bessa, L. D. R. Ferreira, O. Horikawa, J. C. B. Monteiro, F. G. Gandra, and S. Gama, J. Appl. Phys. 122 (2017) 244502

How to characterize hysteresis? FORC

- FORC = First Order Reversal Curves
- Initially proposed as a method to identify the Preisach model parameters
- Later extended as a model-independent technique to characterize the irreversibility in magnetic materials magnetization reversal.

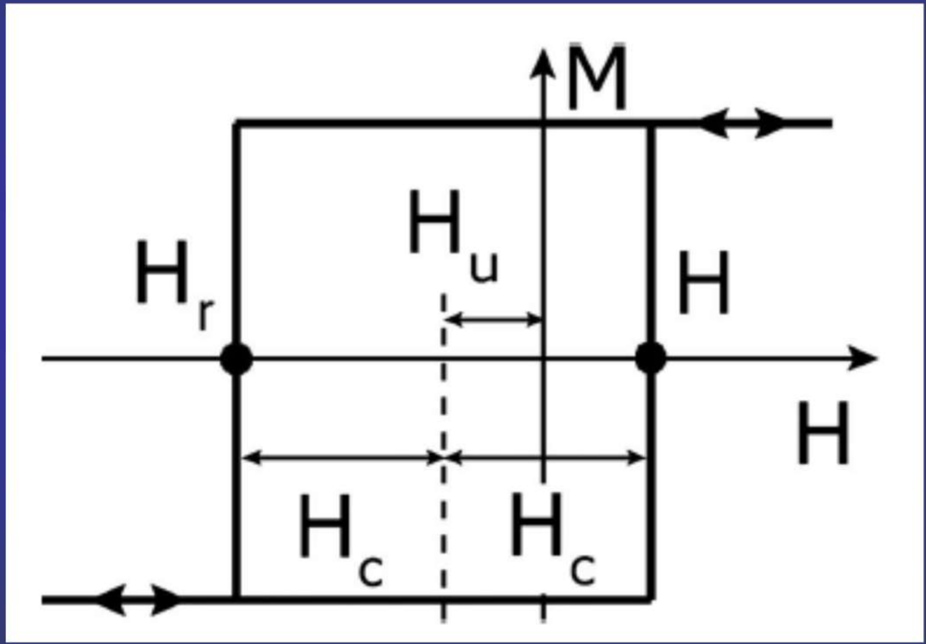
Distribution of hysteresis operators



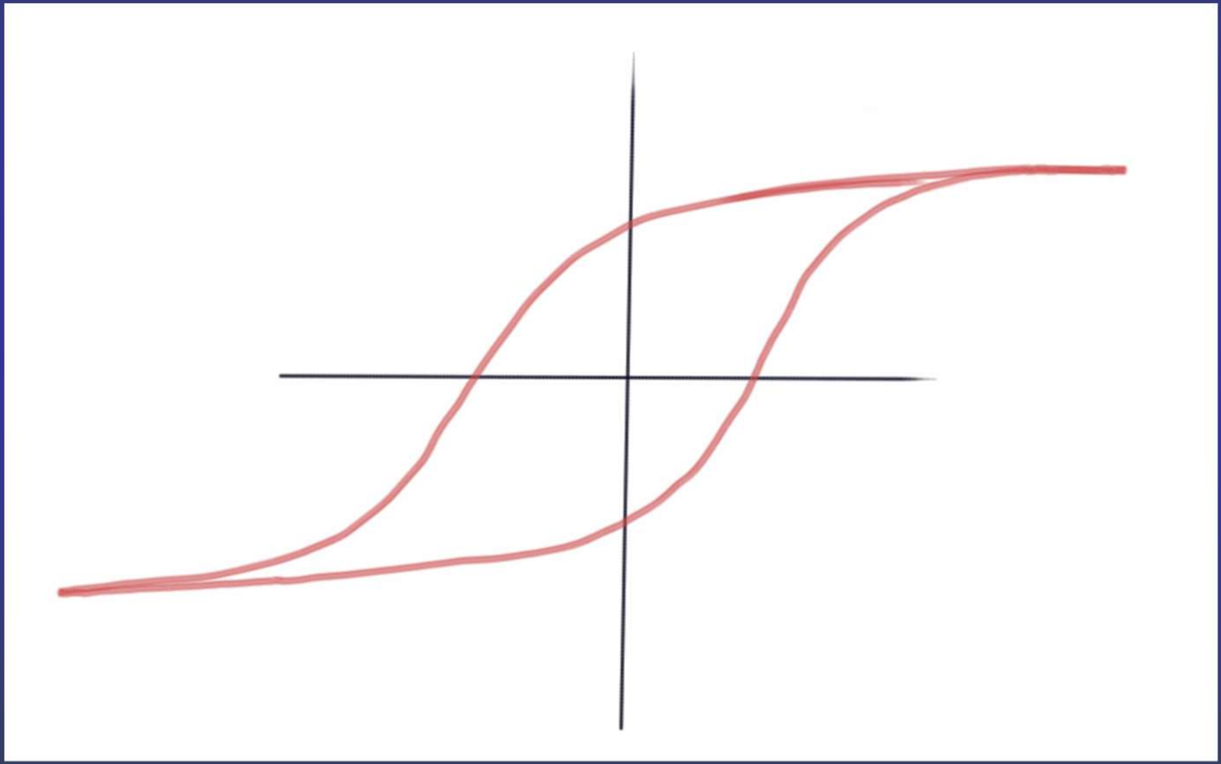
Spectral decomposition of the loop using hysterons

Characteristics of a hysteron

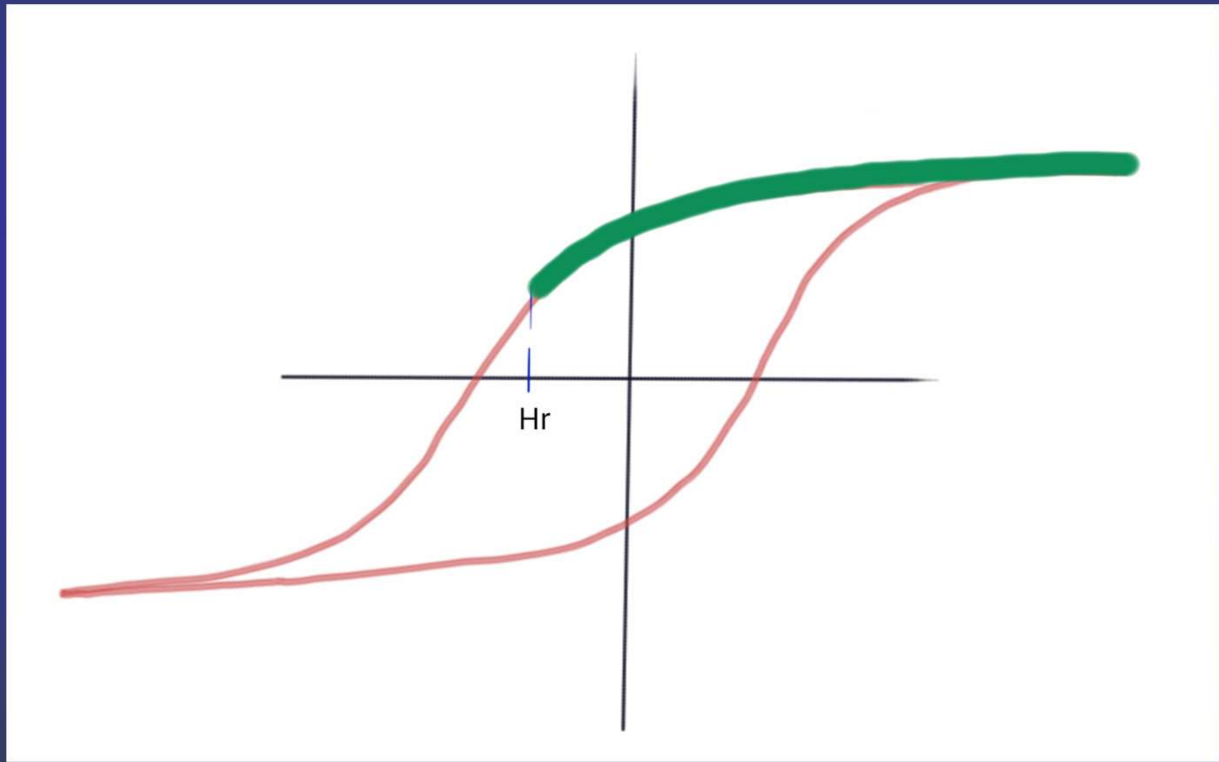
- Rectangular loops
- Coercivity
  H_c
- Interaction field
  H_u
- Reversing at
  $-(H_c+H_u)$ and (H_c-H_u)



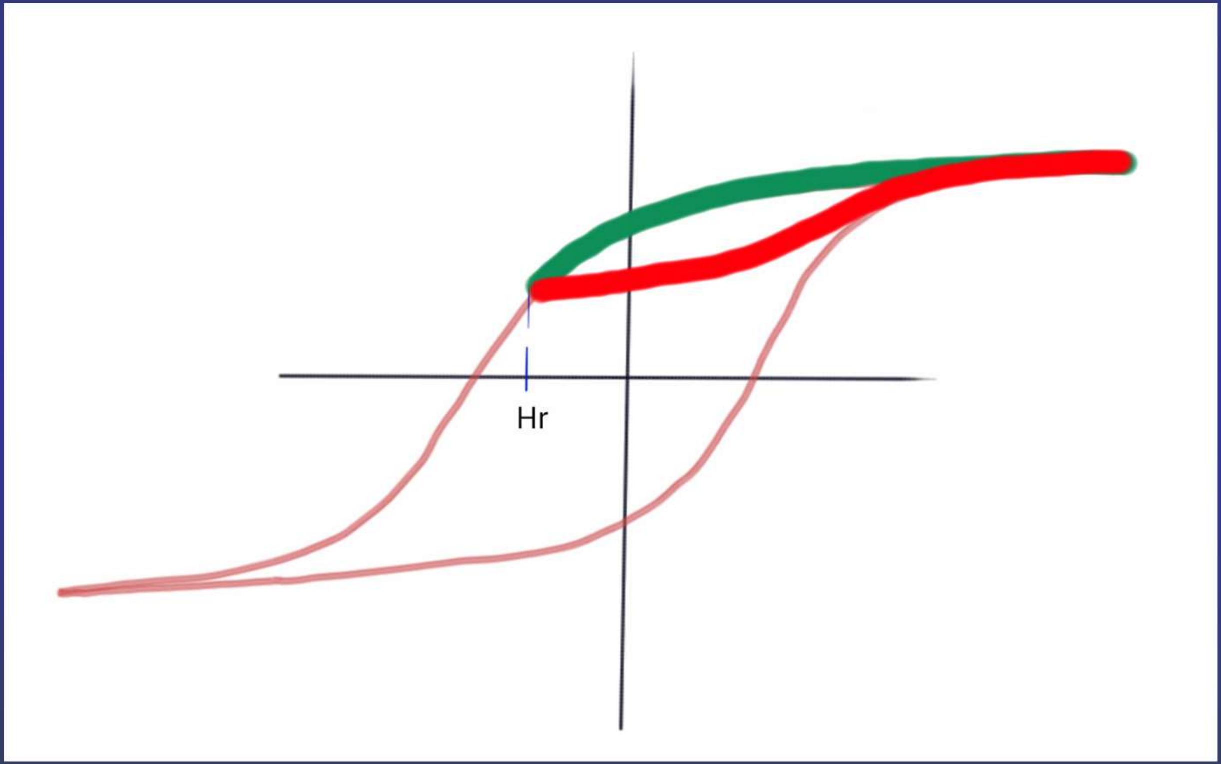
Determination of the FORC distribution



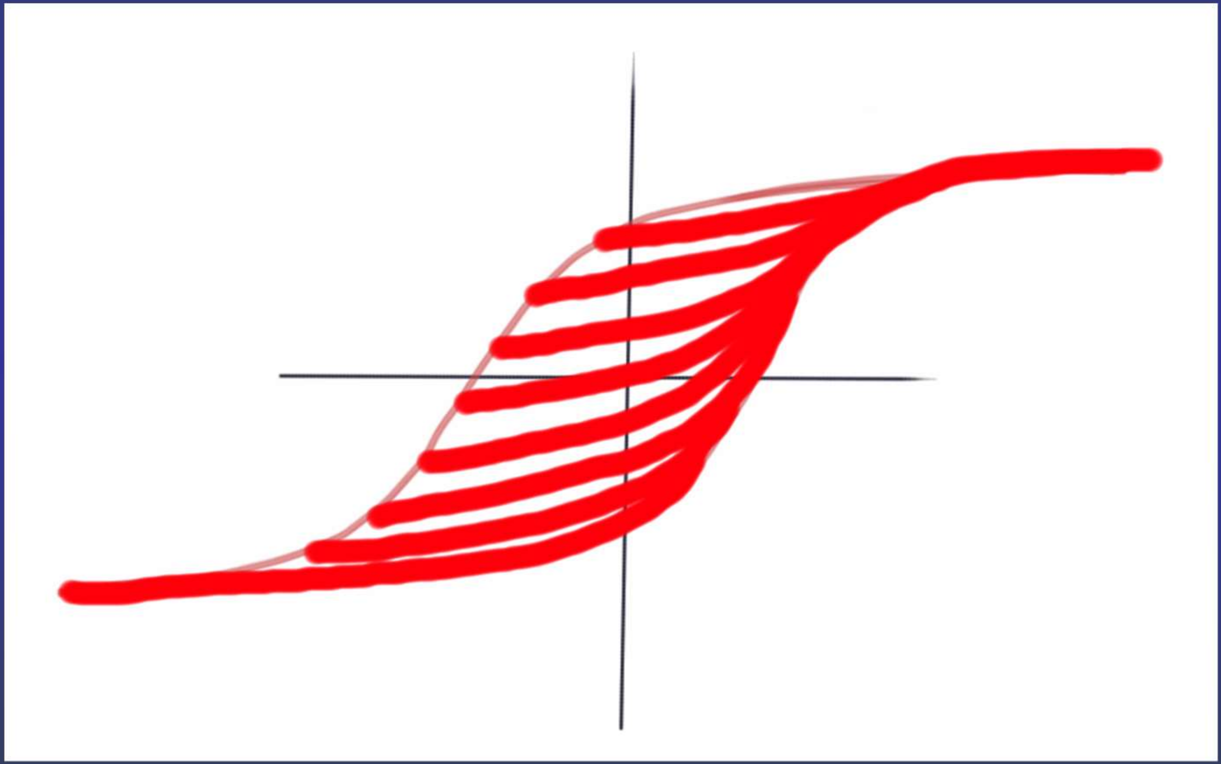
Determination of the FORC distribution



Determination of the FORC distribution



Determination of the FORC distribution



$$\rho(H, H_r) = -\frac{1}{2}\frac{\partial^2 M(H, H_r)}{\partial H_r \partial H} \quad (H \geq H_r)$$

H vs T FORC

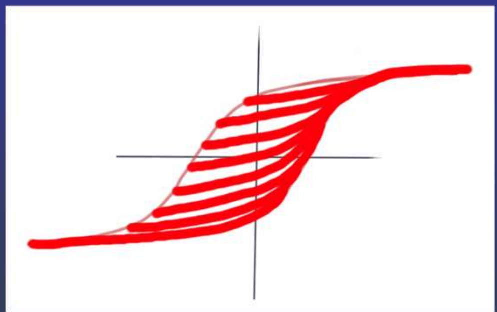
H FORC

H, H_r plane

$$\rho(H,H_r) = -\frac{1}{2}\frac{\partial^2 M(H,H_r)}{\partial H_r \partial H} \quad (H \geq H_r)$$

H_c and H_u

Field sweep



T FORC

T, T_r plane

$$\rho(T,T_r) = -\frac{1}{2}\frac{\partial^2 M(H,H_r)}{\partial T_r \partial T} \quad (T \geq T_r)$$

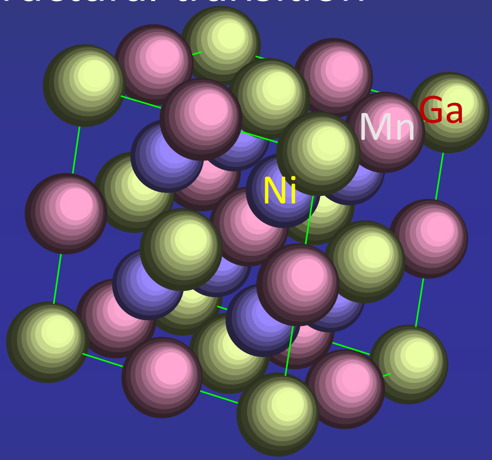
T_h and T_u

Temperature sweep

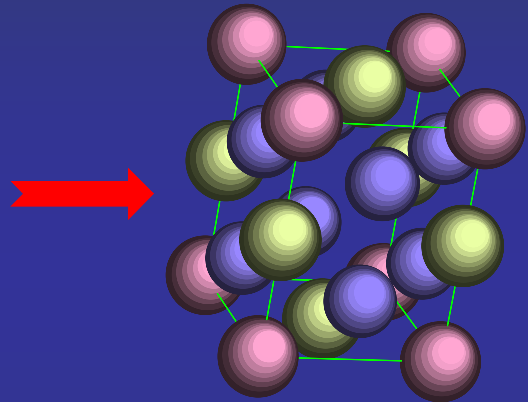
Time consuming

Heusler alloys

- Structural transition



Austenite (Fm3m)
High temperature phase



Martensite (P4/mmm)
Low temperature phase

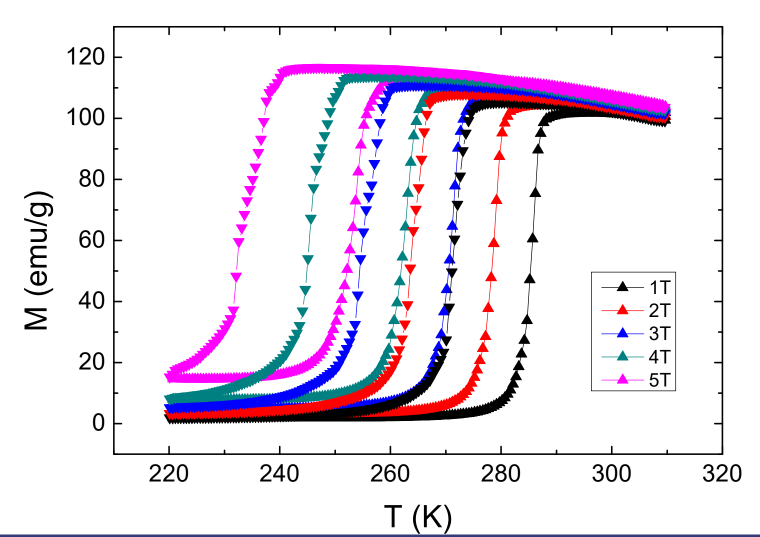
- Our sample composition

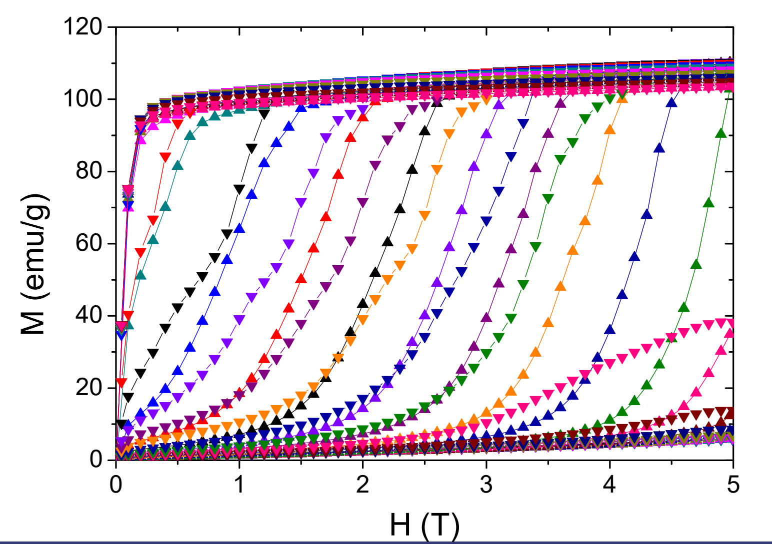
  $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$

- Non-magnetic phase at low T → ferromagnetic phase at high T

$Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$

First measurement increasing field
(precooling before each measurement)



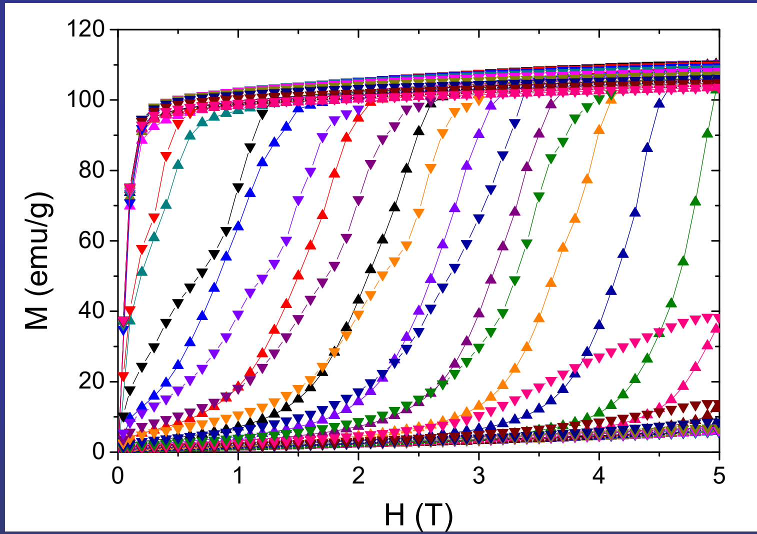


The transition can be induced by field and temperature

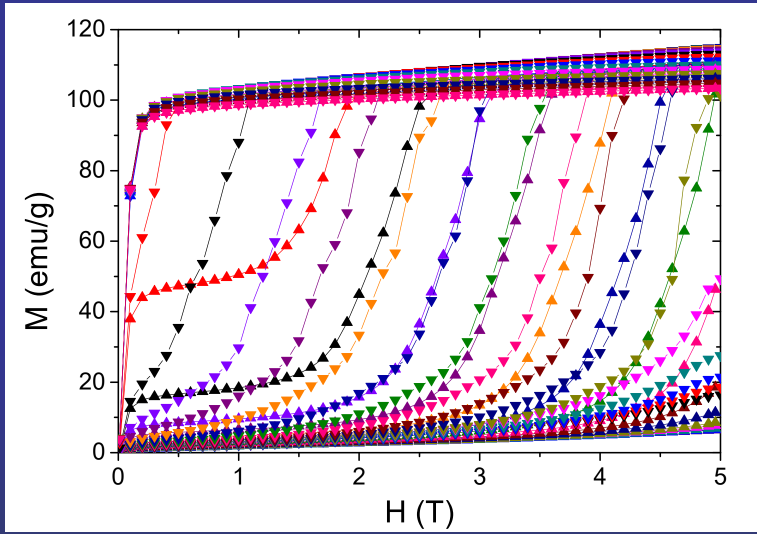
V. Franco, T. Gottschall, K. Skokov, O. Gutfleisch, IEEE Magnetics Letters 7 (2016) 6602904

$Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$

First measurement increasing field
(precooling before each measurement)

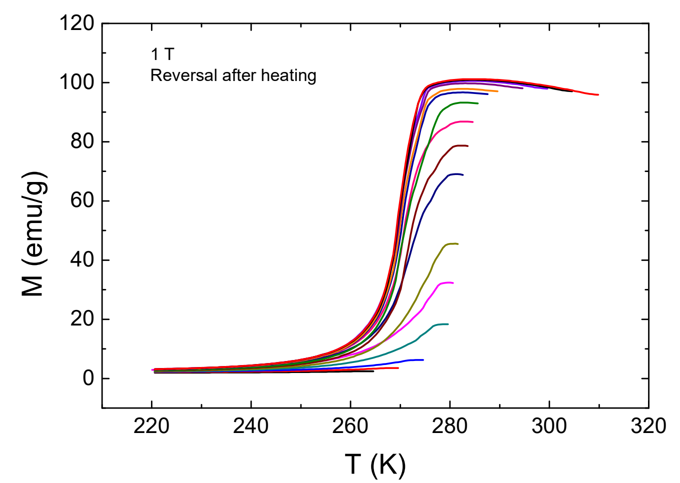


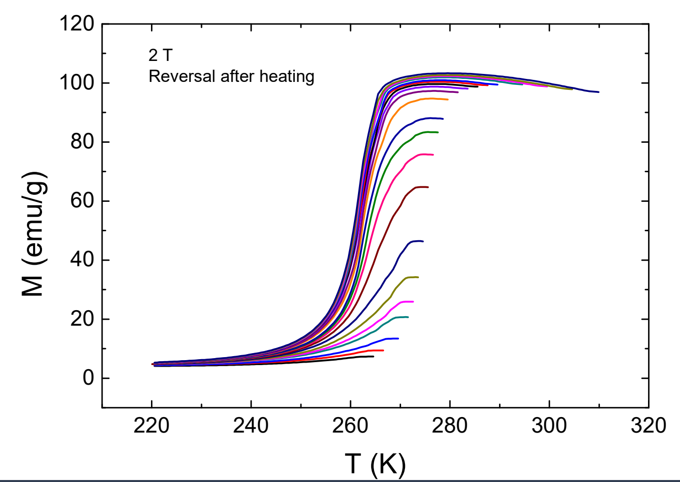
First measurement decreasing field
(preheating before each measurement)

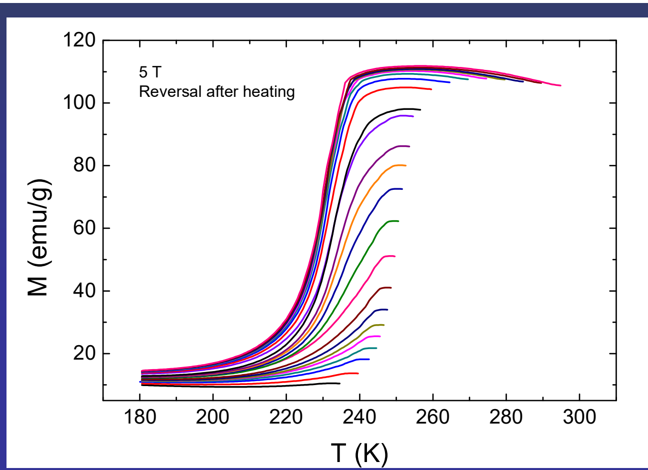


M(H) curves depend on the field and temperature history
→ USE THE APPROPRIATE MEASUREMENT PROTOCOL

Temperature FORC





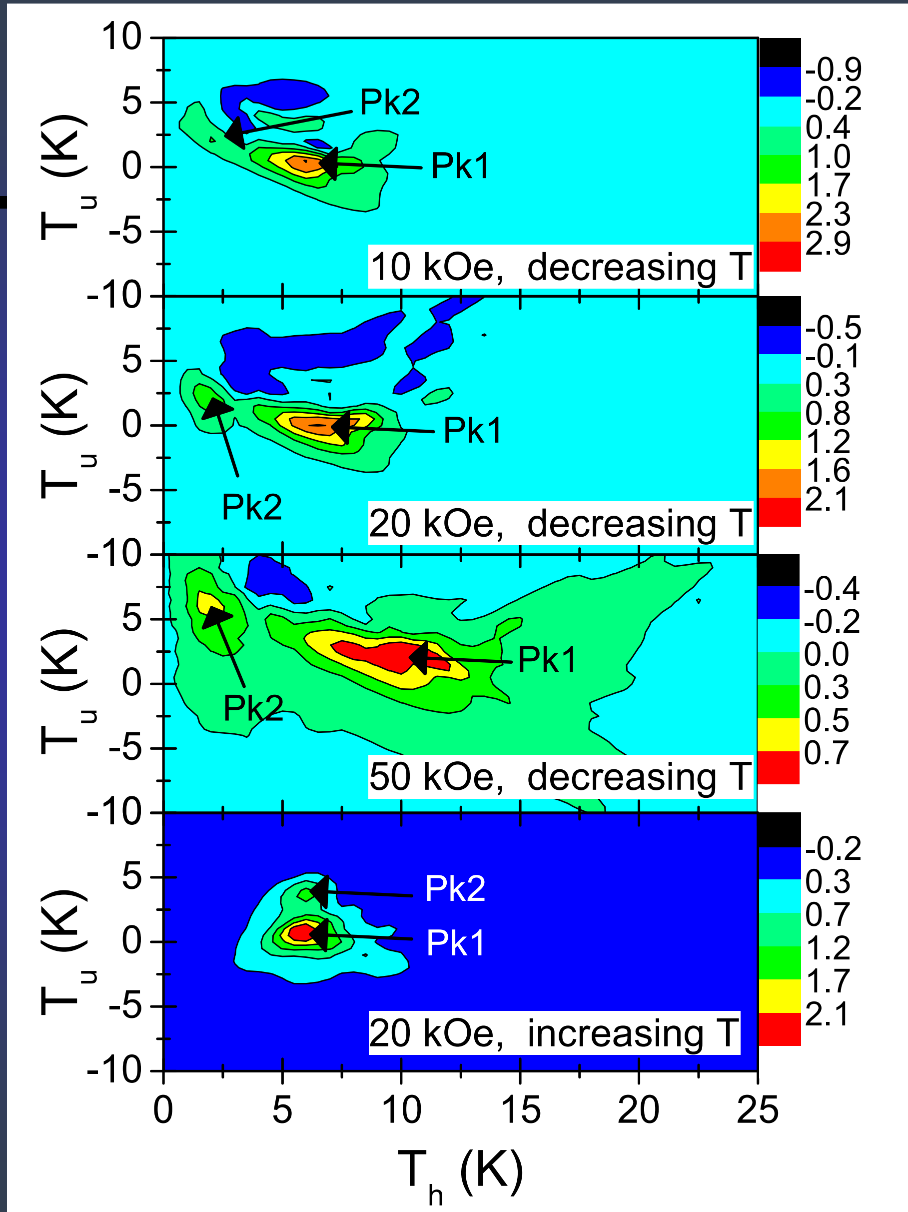


The transition gets displaced for different fields

FORC curves also do

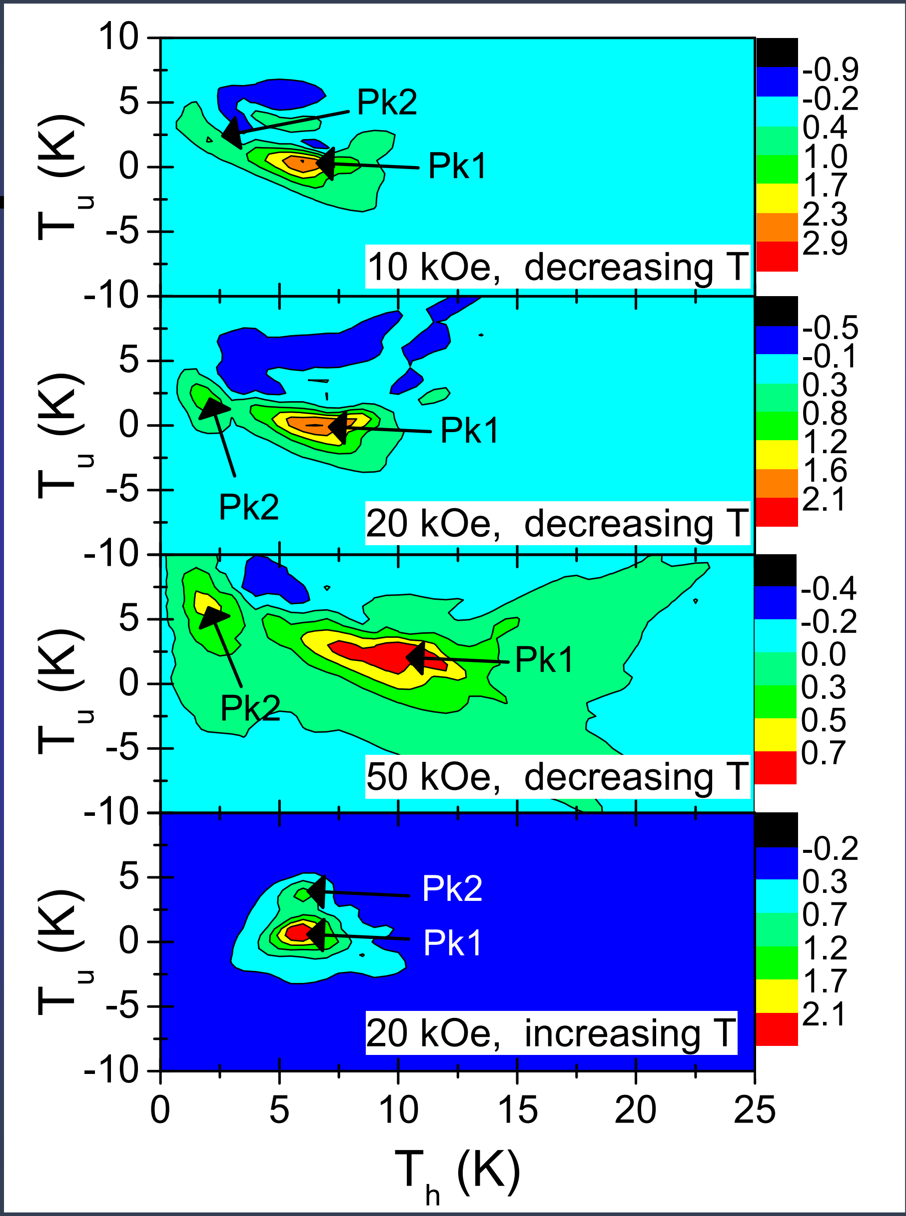
FORC distribution

- Obtaining the distribution requires smoothing
- While there can be many T values, T_r is more limited
  - Different smoothing factor along the different axes
- Procedure:
  - Modified Pike's algorithm: fitting to a polynomial surface
    - linear in T_r
    - quadratic in T
    - using a matrix of 3 data points along the T_r axis and 5 along the T axis.



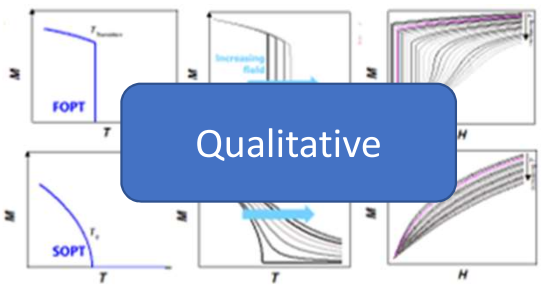
FORC distribution

- Qualitatively similar behavior
- T_u axis is referred to the center of the loop
- Cooling or heating does not play a remarkable role (asymmetry of the transition)



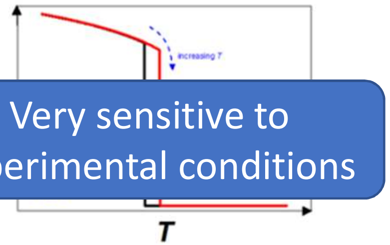
Existing methods to determine the order of MCE phase transitions

Shape of Magnetization curve



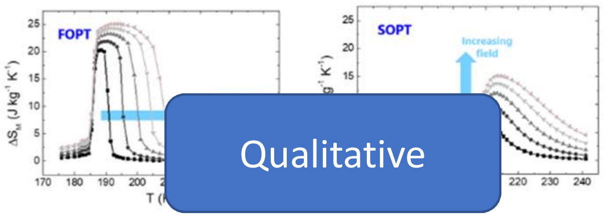
Qualitative

Hysteresis



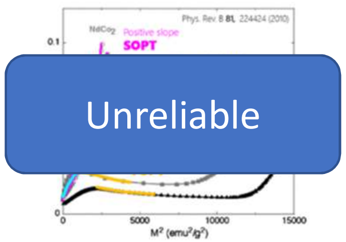
Very sensitive to experimental conditions

Shape of MCE curve



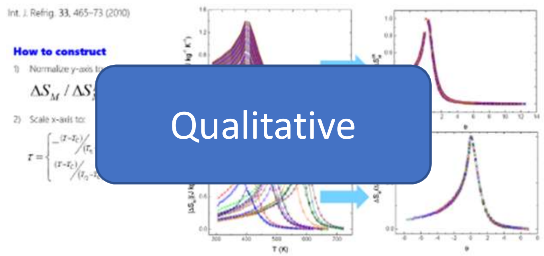
Qualitative

Arrott plots



Unreliable

Universal Curve



Qualitative

Banerjee criterion

- Landau expansion of free energy leads to

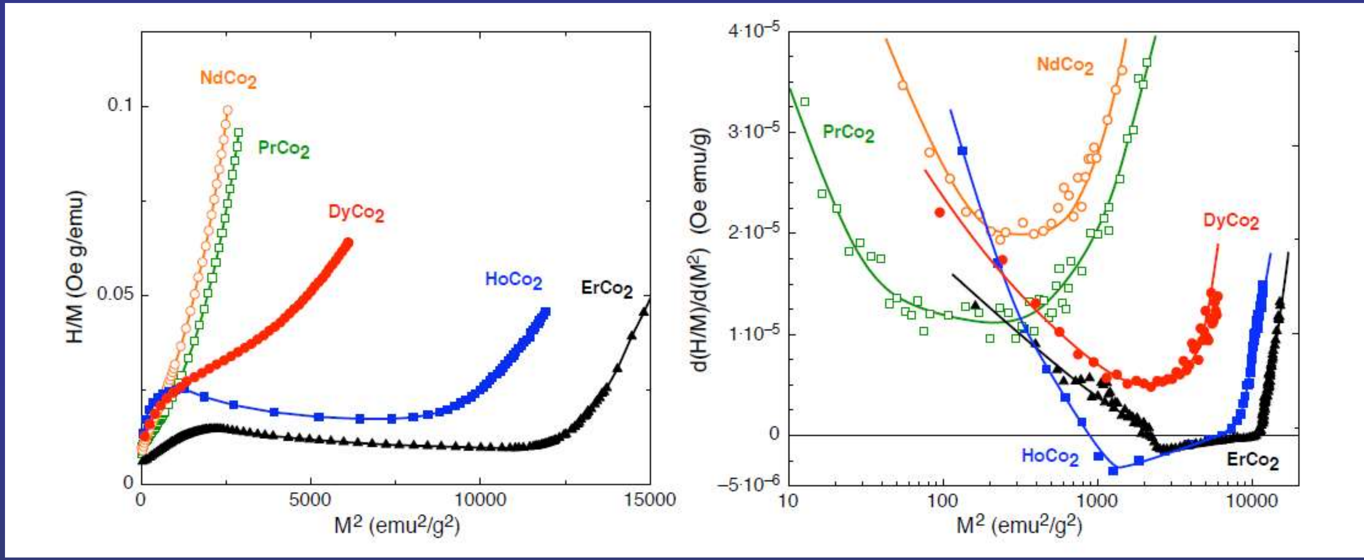
$$H = aM + bM^3 = a'(T - T_C)M + bM^3$$

- Second order phase transitions have a positive b
- At the Curie temperature $a = 0$
- The order of the phase transition can be determined from the slope of H/M vs M^2

S. K. Banerjee, Phys. Lett. 12, 16 (1964).

Application to RCo_2

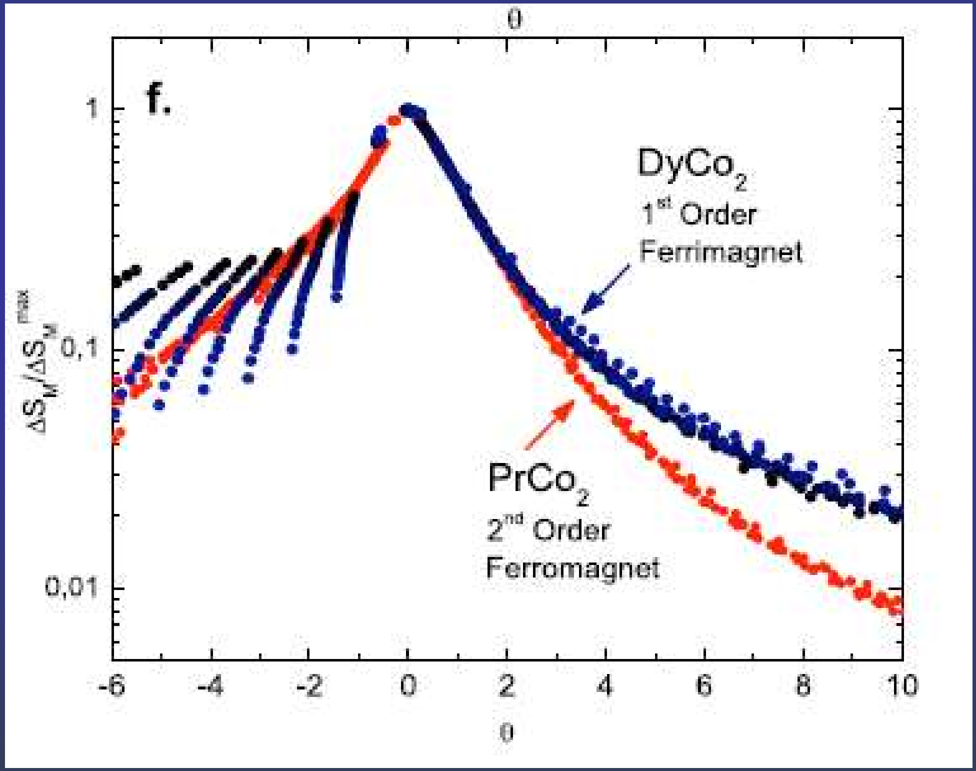
- Banerjee criterion: $DyCo_2$?



- Calorimetric measurements indicate that $DyCo_2$ is first order

C.M. Bonilla, J. Herrero-Albillos, F. Bartolomé, L.M. García, M. Parra-Borderías, V. Franco, Phys. Rev. B 81 (2010) 224424

Universal scaling



C.M. Bonilla, J. Herrero-Albillos, F. Bartolomé, L.M. García, M. Parra-Borderías, V. Franco, Phys. Rev. B 81 (2010) 224424

Why does this work?

- Banerjee criterion was based on a particular equation of state (Landau expansion)
- Universal scaling does not impose any restriction to the formulation of the equation of state
  - We only asume that second order phase transitions scale
  - The universal curve is a more general approach to determine the order of the phase transition
  - Unfortunately, it relies on qualitative features→subjective

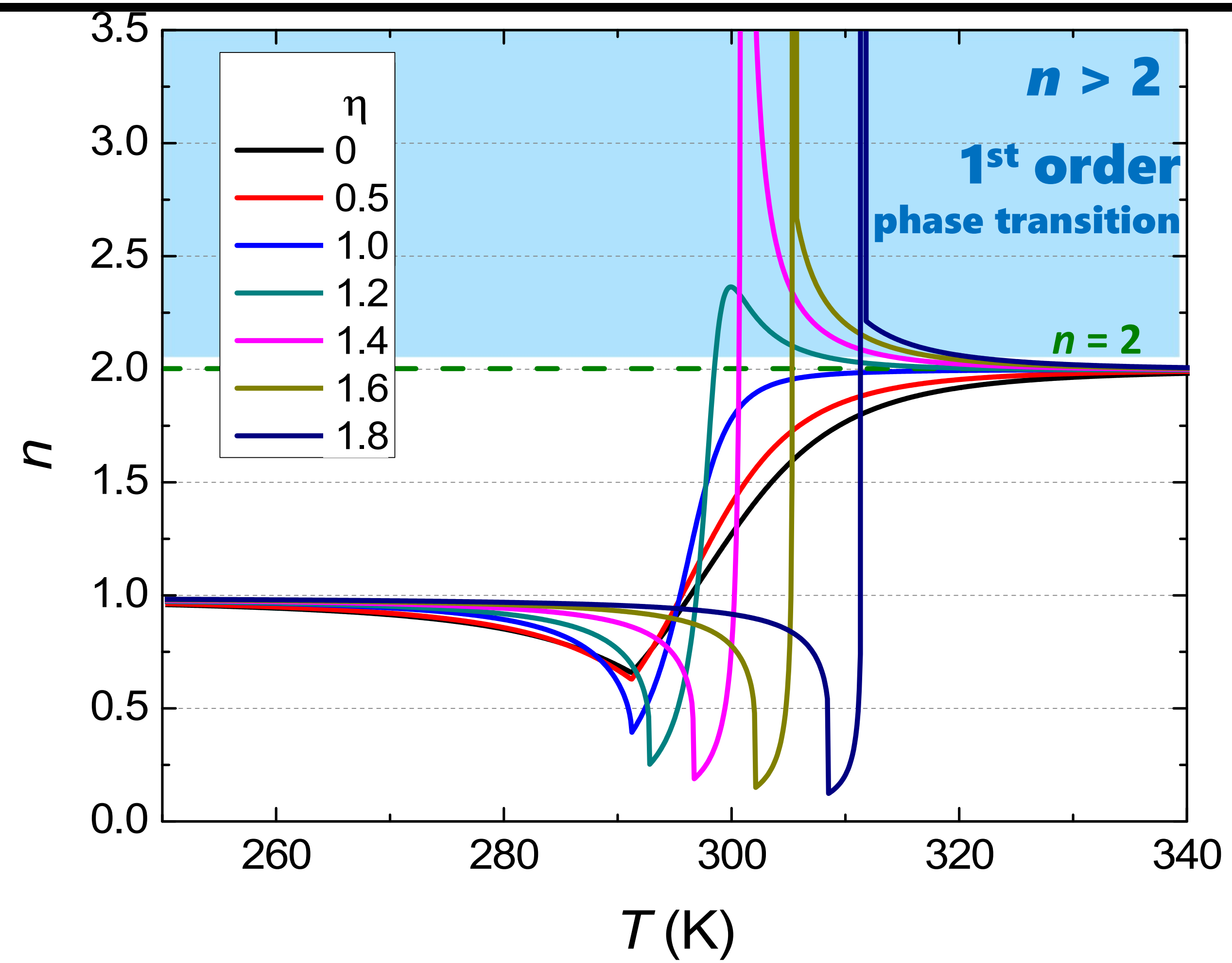
New method for Fingerprinting the order of the phase transition

Bean-Rodbell model

$\Delta S_M \propto H^n$

- ✓ **SOPT**
- ✓ **FOPT**

OVERSHOOT



J.Y. Law et al. Nature Communications 9, 2680 (2018)

New method for Fingerprinting the order of the phase transition

$$\Delta S_M \propto H^n$$

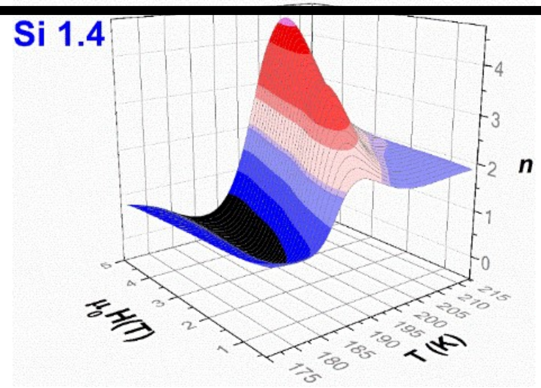
- **SOPT**
- **FOPT**

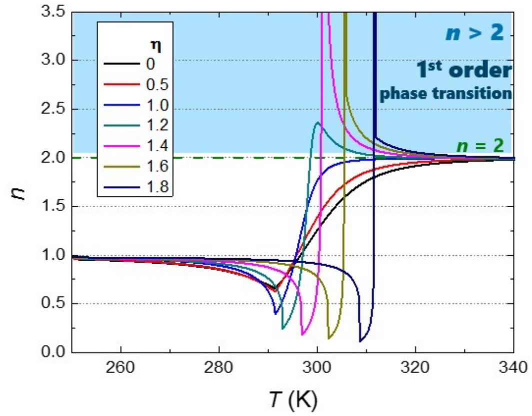
  OVERSHOOT

- **Applicable to diverse types of materials**

J.Y. Law et al. Nature Communications 9, 2680 (2018)

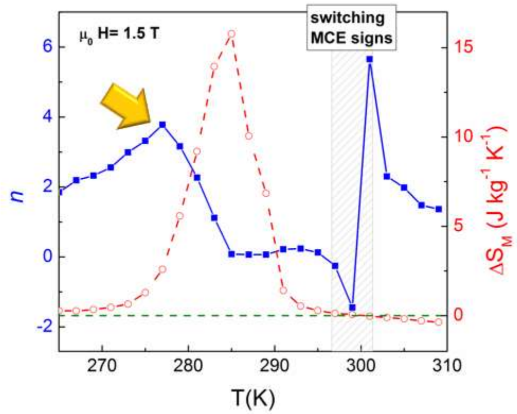
La(FeSi)$_{13}$





Simulations

Heusler

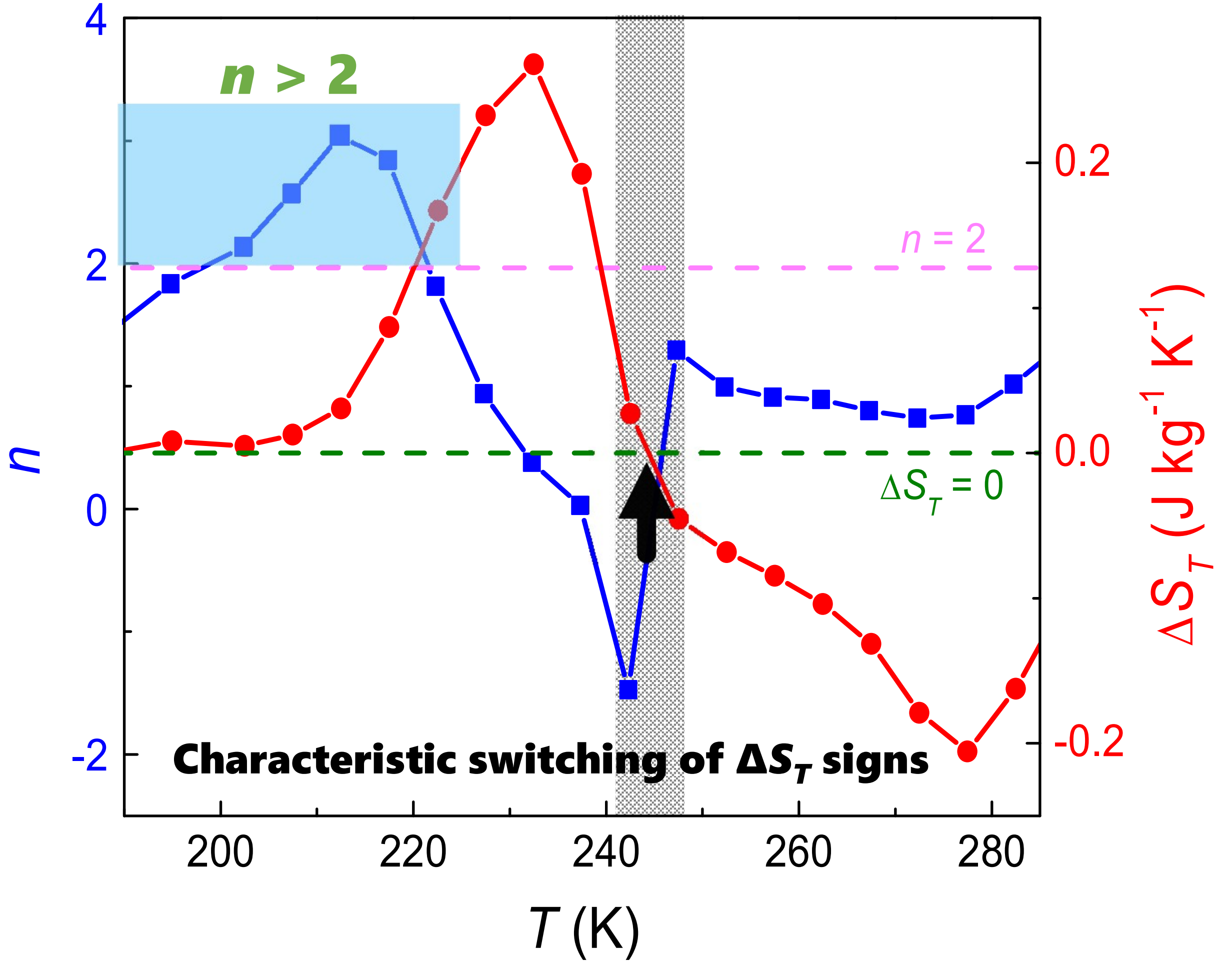


A peculiar case

- **$GdBaCo_2O_{6-\delta}$**
- perovskite cobaltite

- Low T: AFM-FM
- High T: FM-PM

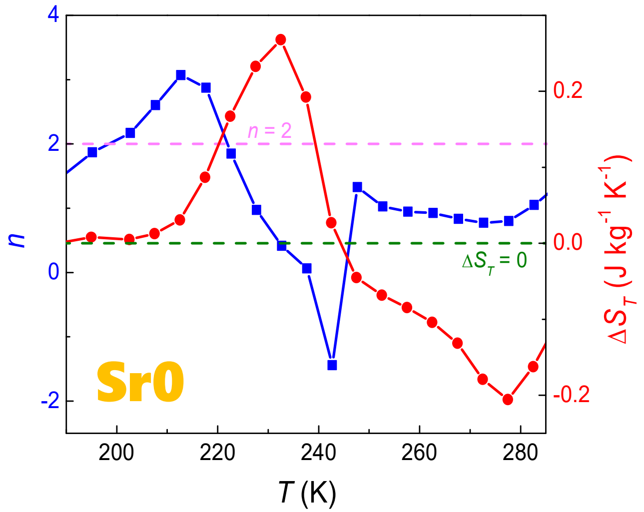
J Alloys Compds. 777, 1080 (2019).

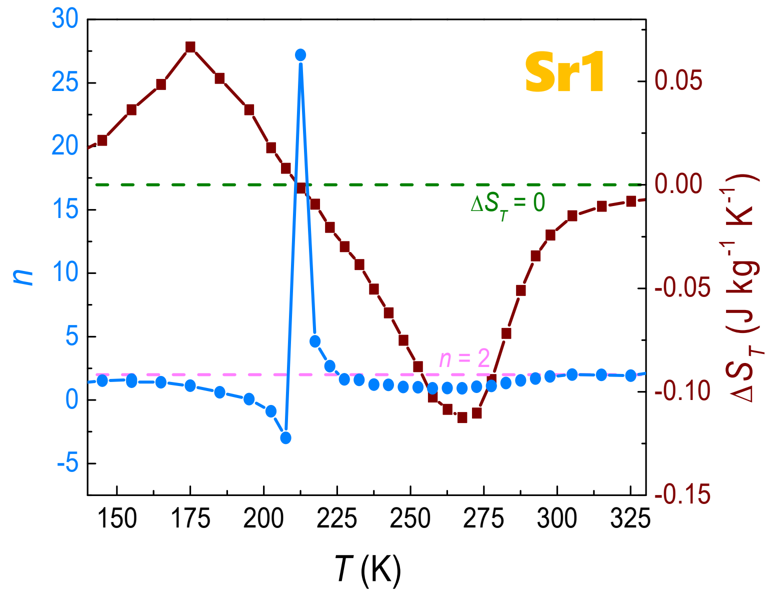


A peculiar case

- **$GdBa_{1-x}Sr_xCo_2O_{6-\delta}$**
- Same crystal symmetry for x=0 & 1

- Unlike x=0, x=1 becomes SOPT





J Alloys Compds. 777, 1080 (2019).

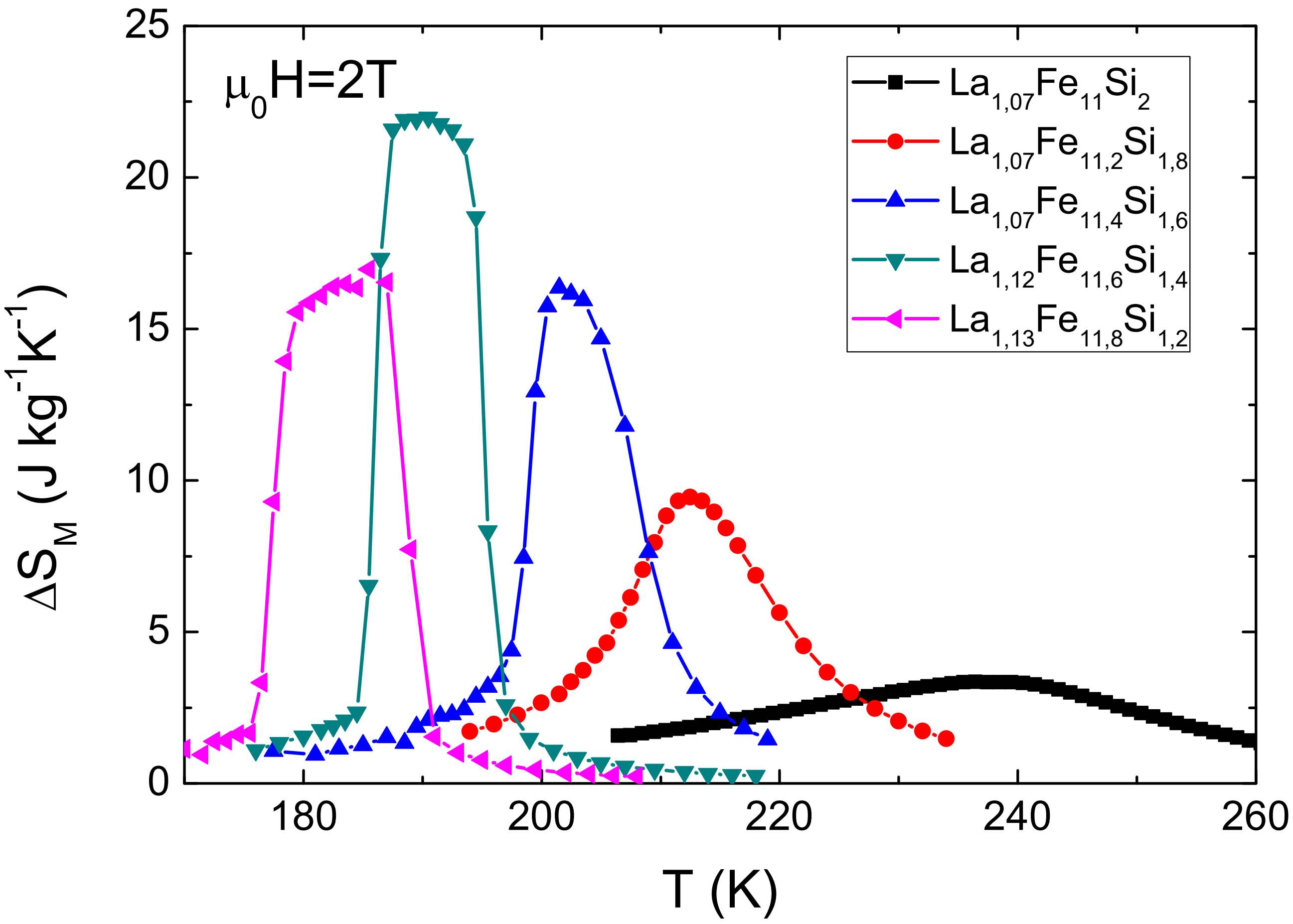
How to find the critical point?

Experimental

- $LaFe_{13-x}Si_x$ samples prepared by suction casting
  - Annealed at 1373 K for 12 h
- Microstructural characterization by XRD and SEM
- M(H,T) measured in a VSM using two different protocols:
  - Temperature sweeping at different fields
  - Discontinuous isothermal protocol:
    - Heat the sample in zero field above the transition
    - Cool down to measurement temperature in zero field
    - Measure increasing field (also decreasing for control)
- Magnetic entropy change calculated from magnetization measurements
- Adiabatic temperature change measured in a custom made set-up

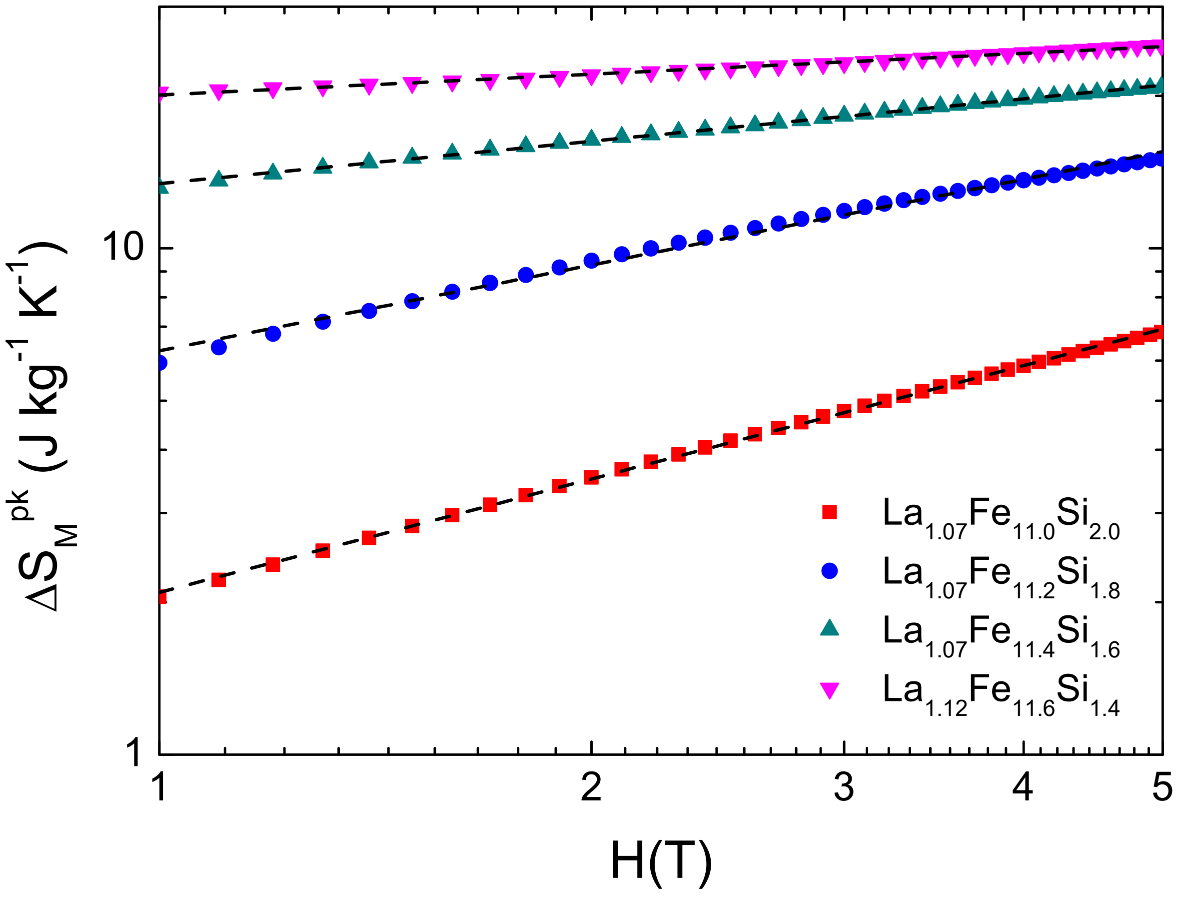
How to find the critical point?

- ✓ **Experimental**
- **MCE response**



How to find the critical point?

- Experimental ✓
- MCE response ✓
- Field dependence of MCE



How to find the tricritical point?

- **Experimental** ✓
- **MCE response** ✓
- **Field dependence of MCE**

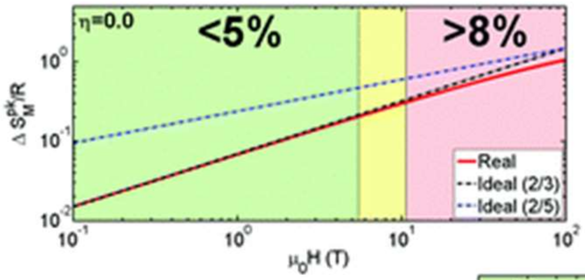
Bean-Rodbell model

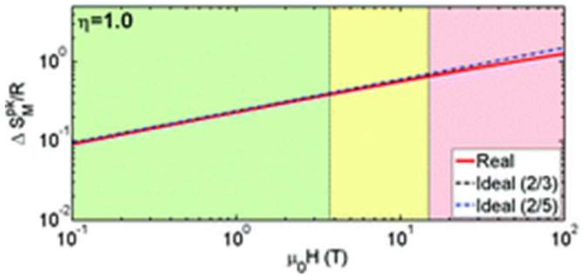
$\Delta S_M \propto H^n$

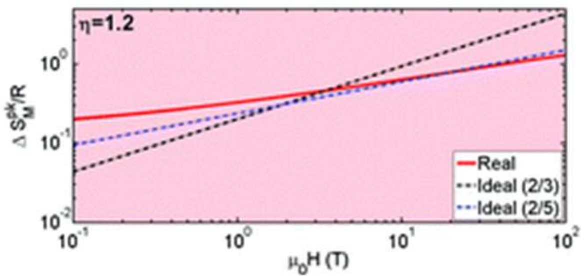
Scaling holds for

SOPT

Tricritical





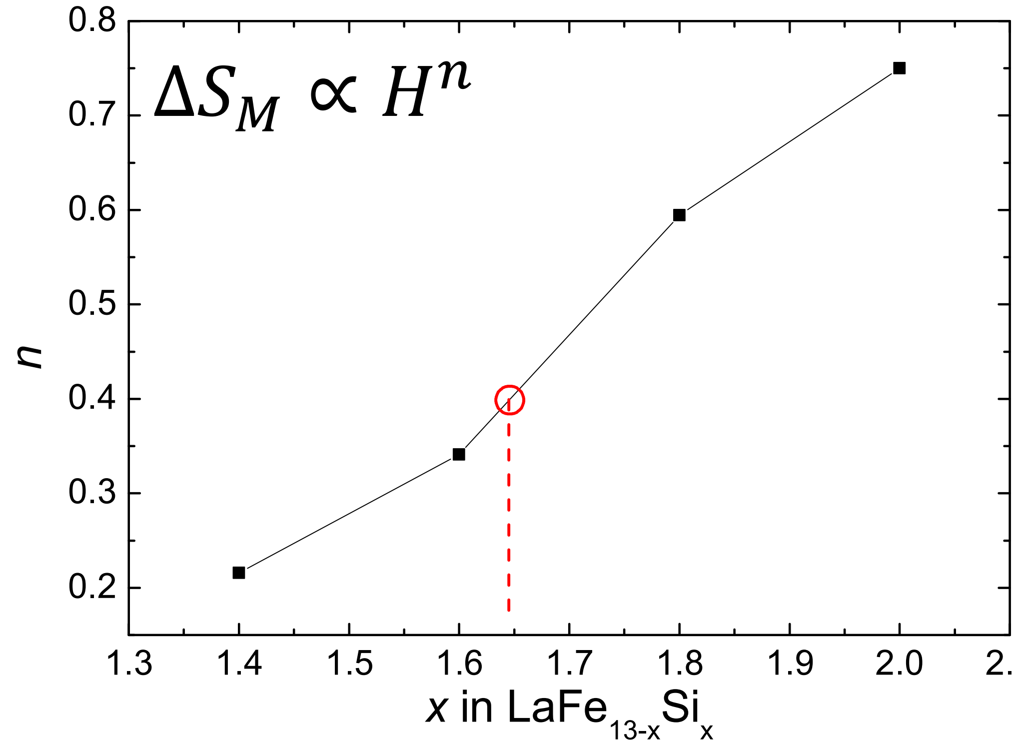


C. Romero-Muñiz, V. Franco, A. Conde, Phys.Chem.Chem.Phys. 19 (2017) 3582

How to find the critical point?

- **Experimental** ✓
- **MCE response** ✓
- **Field dependence of MCE**

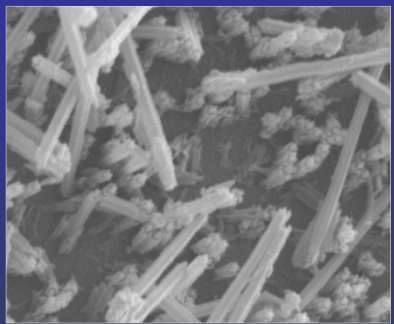
High field slope: n=2/5 (tricritical) for x=1.65



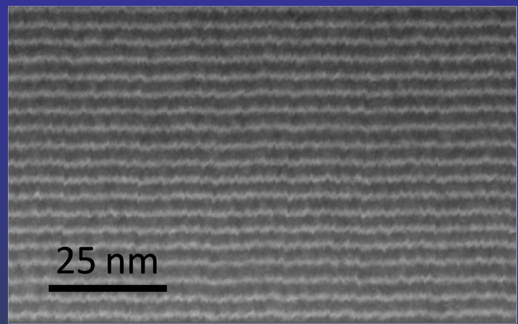
V. Franco, J.Y. Law, A. Conde, V. Bravander, D. Y. Karpenkov, I. Radulov, K. Skokov, and O. Gutfleisch, J. Phys D: Appl. Phys. 50 (2017) 414004.

MCE in Nanomaterials:

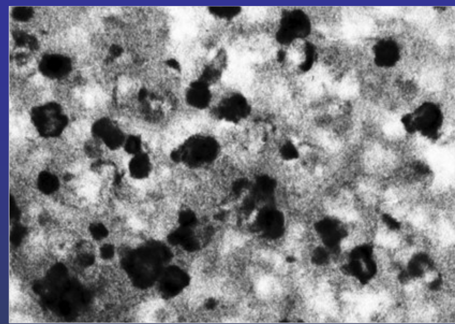
a qualitatively different behavior



1D

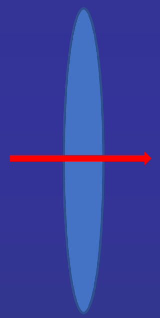


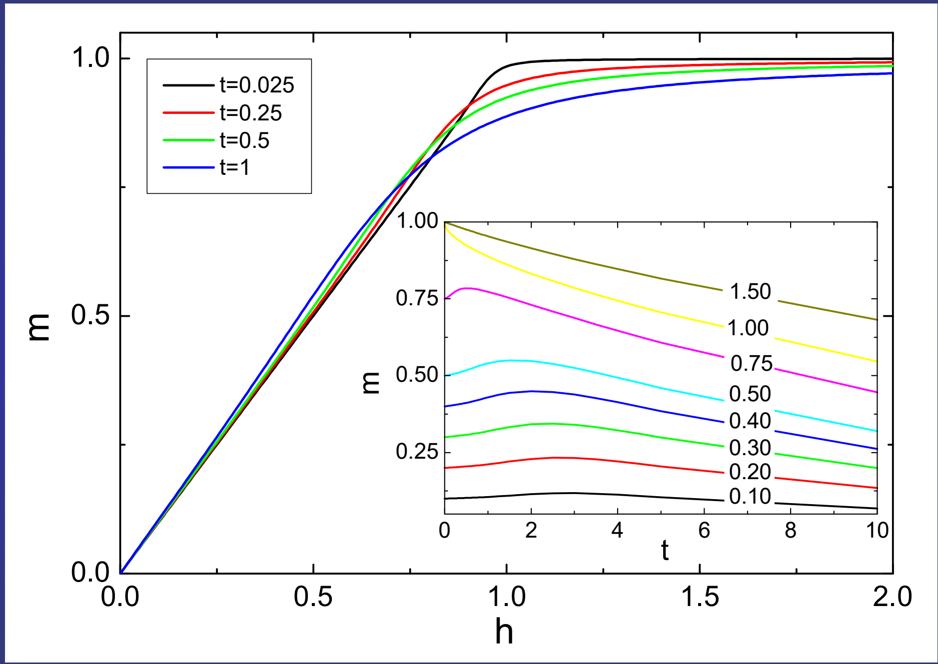
2D



3D

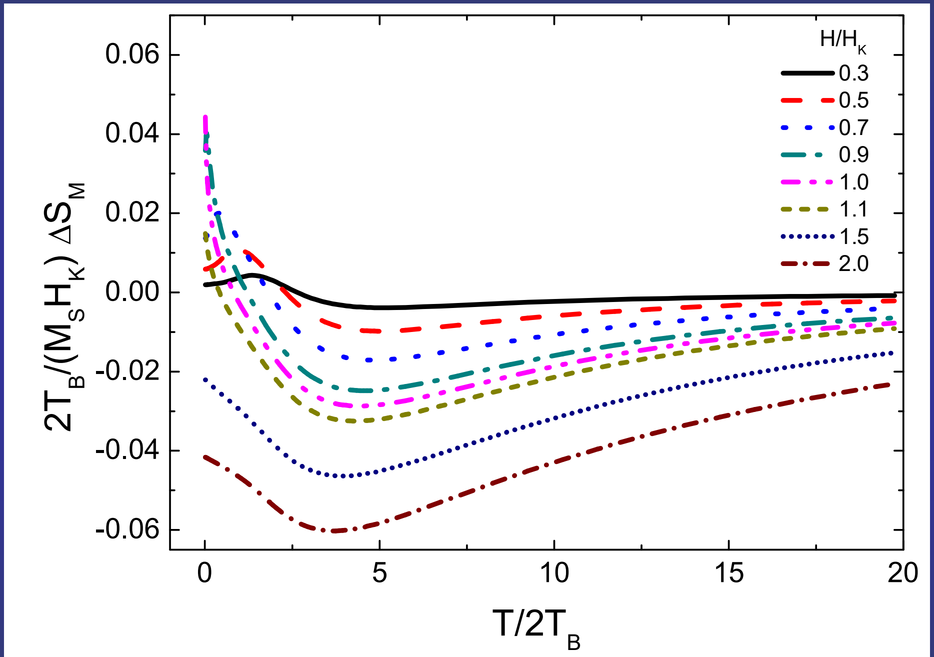
An ensemble of single domain nanoparticles

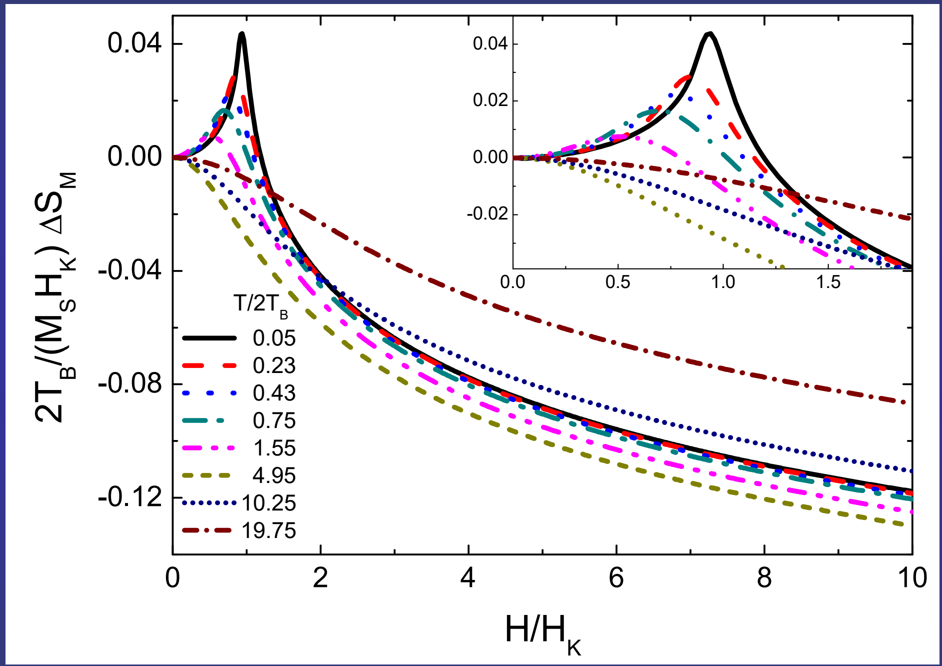




$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH$$

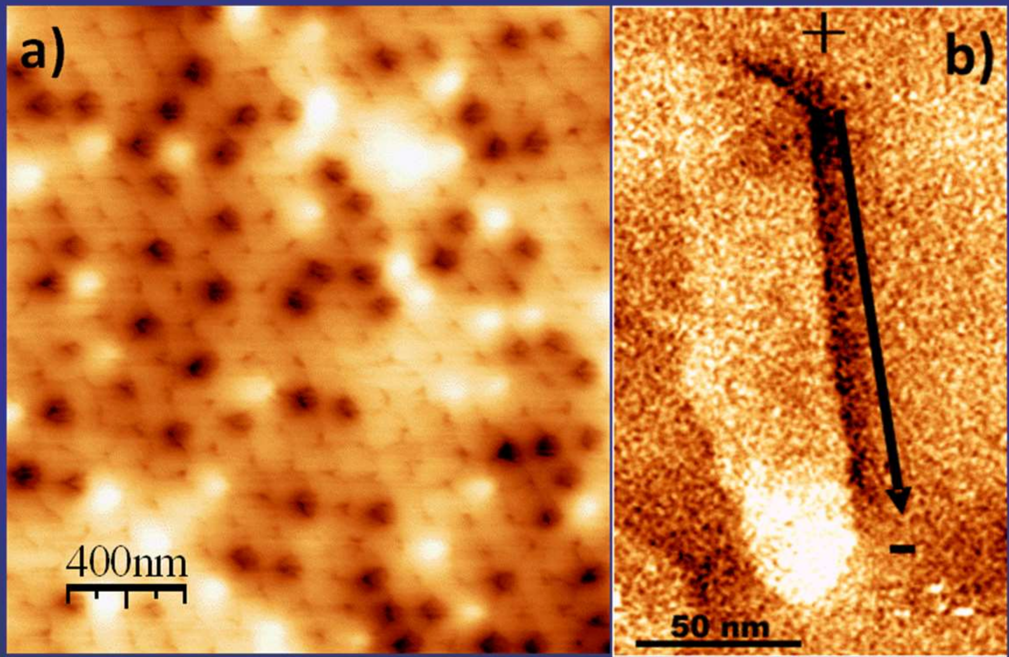
Combined direct and inverse MCE

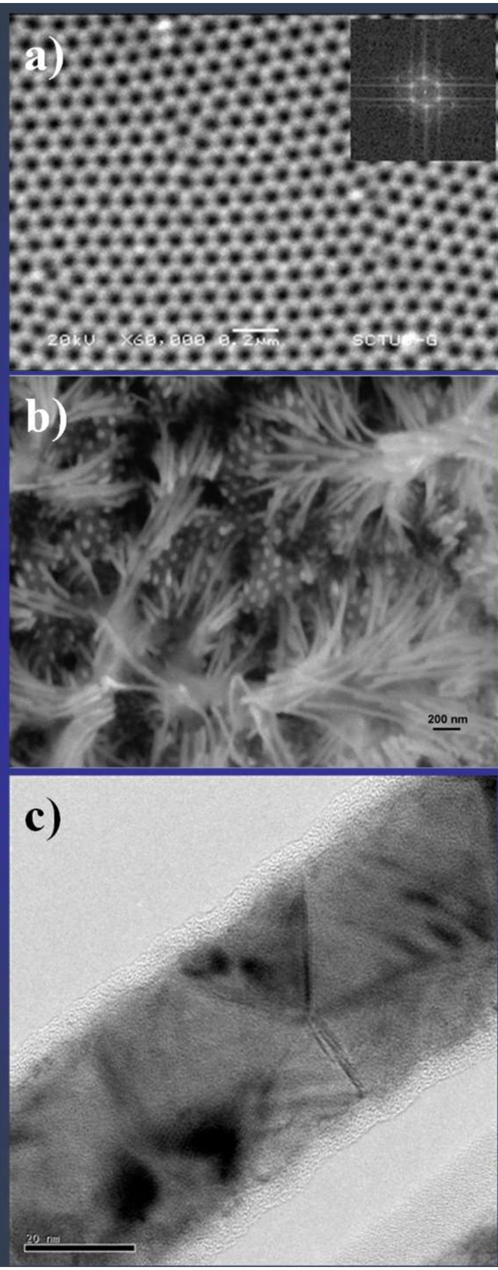




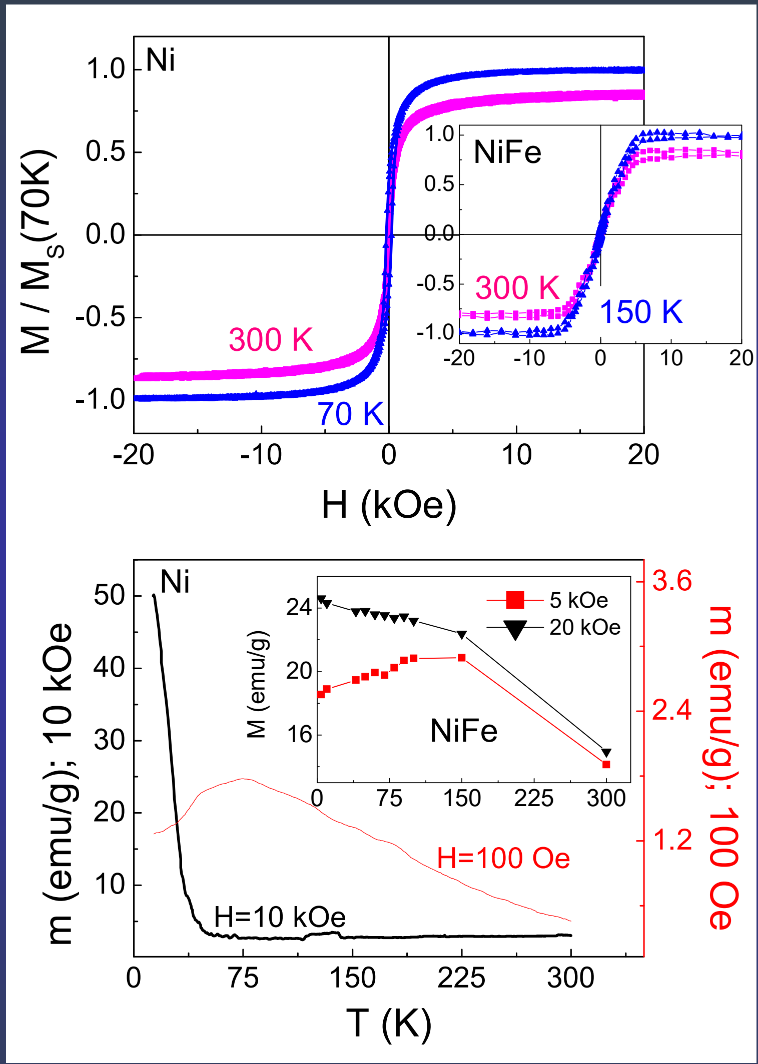
V. Franco, K.R. Pirota, V.M. Prida, A.M.J.C. Neto, A. Conde, M. Knobel, B. Hernando, M. Vazquez, Phys. Rev. B 77 (2008) 104434

Self assembled array of nanowires





V. Franco, K.R. Pirota, V.M. Prida, A.M.J.C. Neto, A. Conde, M. Knobel, B. Hernando, M. Vazquez, Phys. Rev. B 77 (2008) 104434

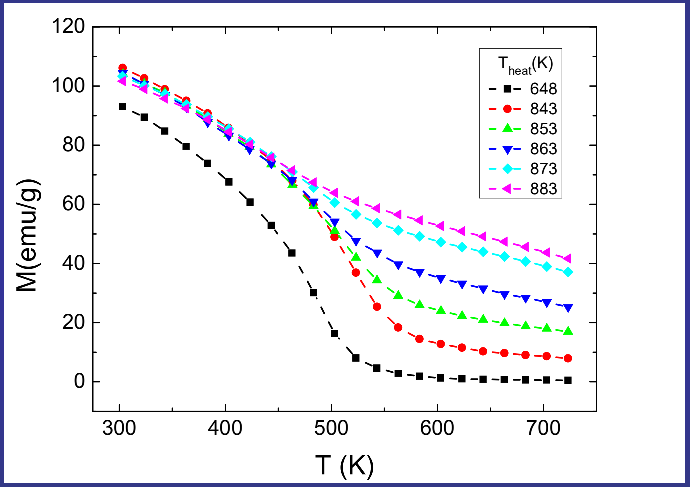


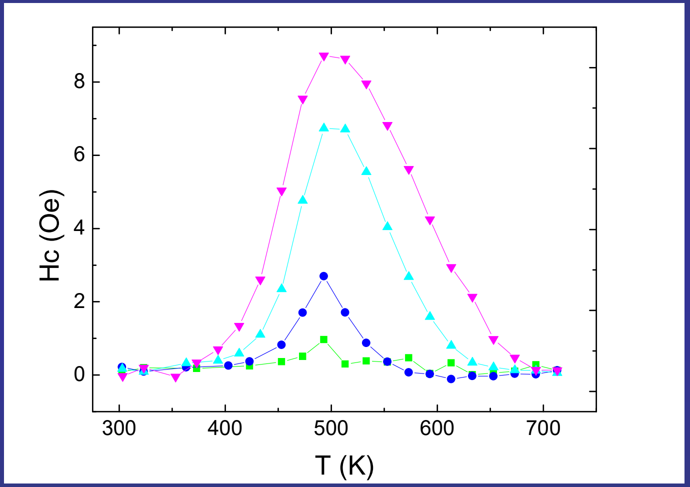
V. Franco, K.R. Pirota, V.M. Prida, A.M.J.C. Neto, A. Conde, M. Knobel, B. Hernando, M. Vazquez, Phys. Rev. B 77 (2008) 104434

MCE in Nanocrystalline alloys:

Not as good as initially expected

Nanocrystallization of Mo-Finemet

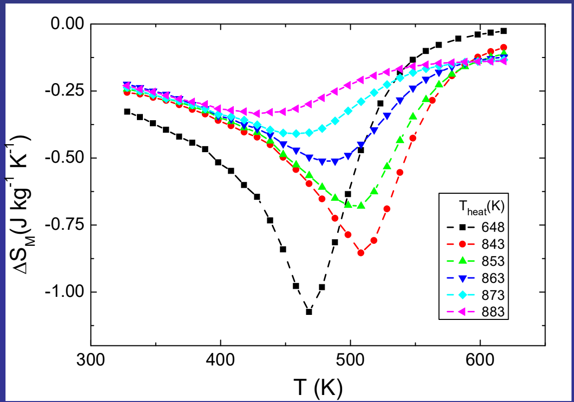


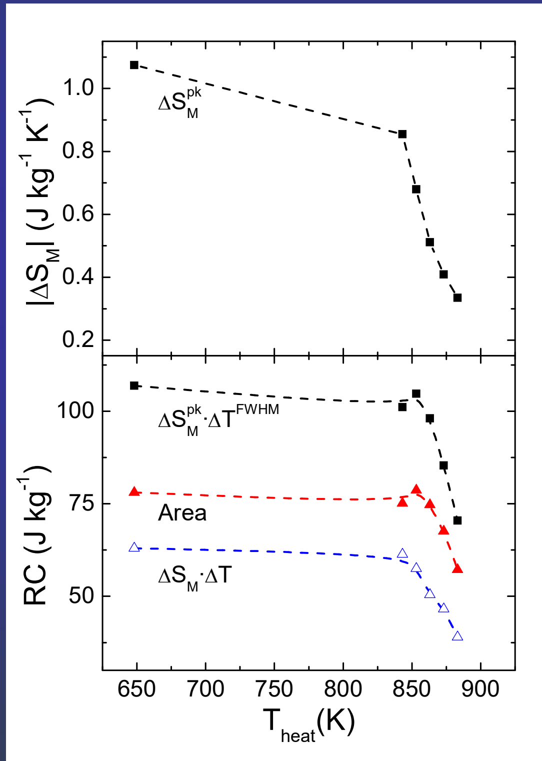


Smaller values of the coercivity peak → More reduced dipolar interactions

V. Franco, J.S. Blázquez, C.F. Conde, A. Conde, Appl. Phys. Lett. 88 (2006) 042505

MCE of nanocrystalline Mo-Finemet





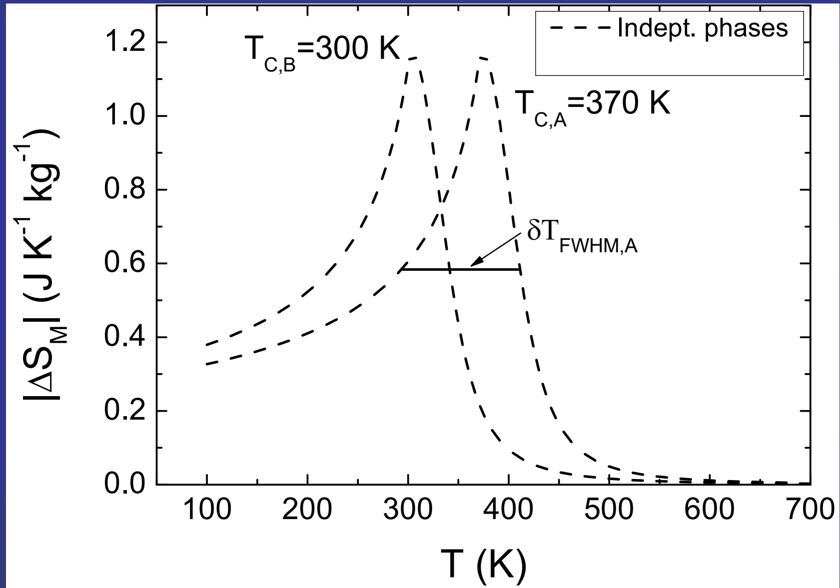
- SPM better than paramagnets
- The peak is broadened due to different T_C (sum rule)
- RC does not increase

V. Franco, J.S. Blázquez, C.F. Conde, A. Conde, Appl. Phys. Lett. 88 (2006) 042505

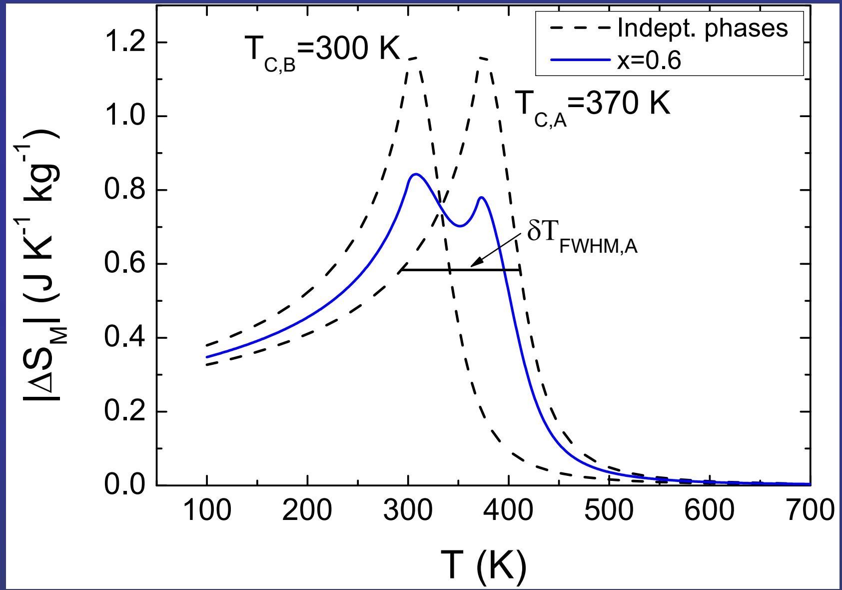
MCE in Multiphase materials:

is there a way of increasing RC?

Non-interacting composite (calculations)

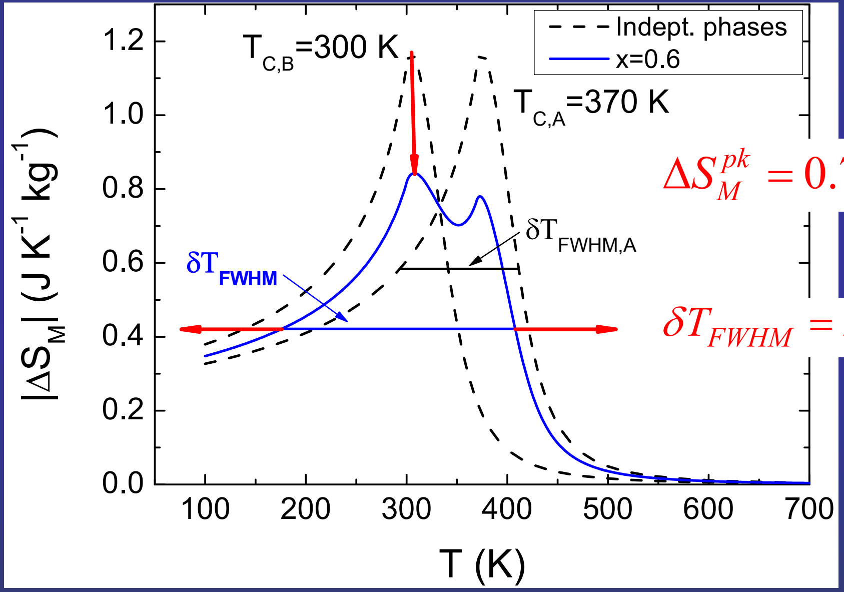


Non-interacting composite (calculations)



$$\Delta S_M(x,T,H_{max}) = x\ \Delta S_{M,A} + (1-x)\ \Delta S_{M,B}$$

Non-interacting composite (calculations)

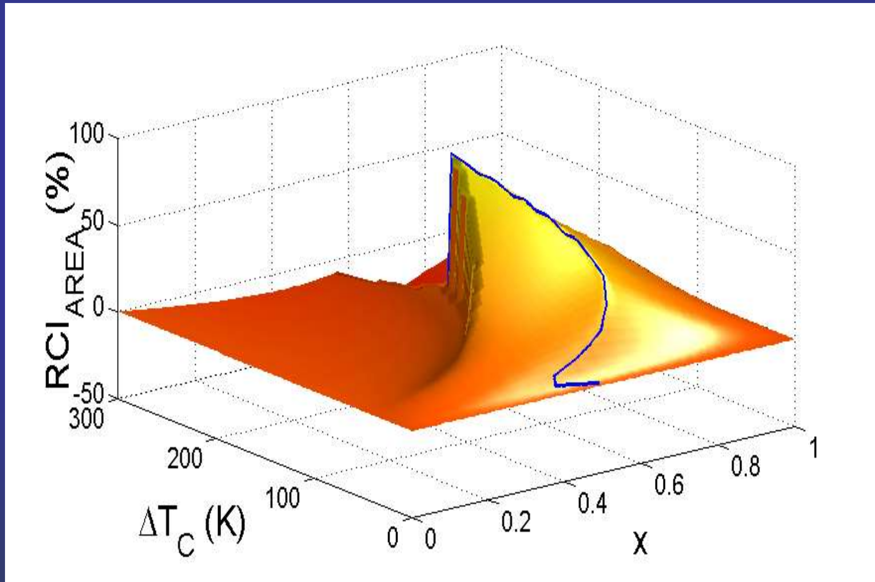


$$\Delta S_M^{pk} = 0.72\ \Delta S_{M,A}^{pk}$$

$$\delta T_{FWHM} = 2\ \delta T_{FWHM,A}$$

$$\Delta S_M(x,T,H_{max}) = x\ \Delta S_{M,A} + (1-x)\ \Delta S_{M,B}$$

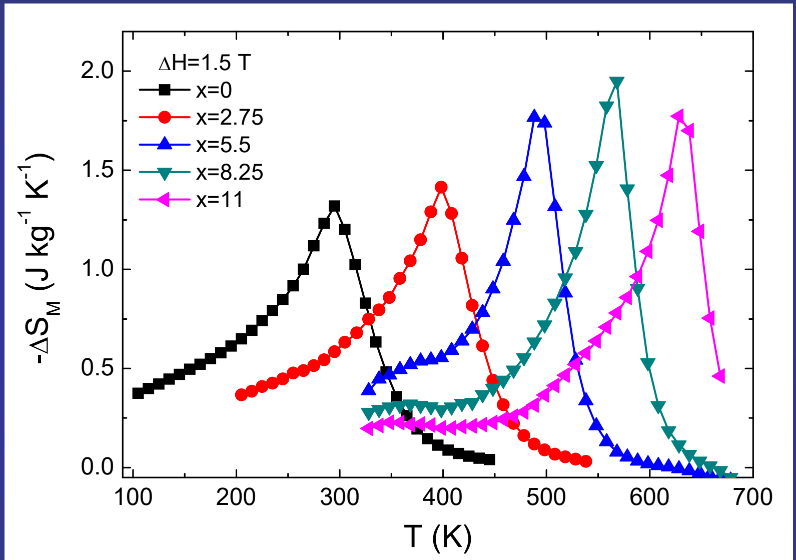
Improvement of RC



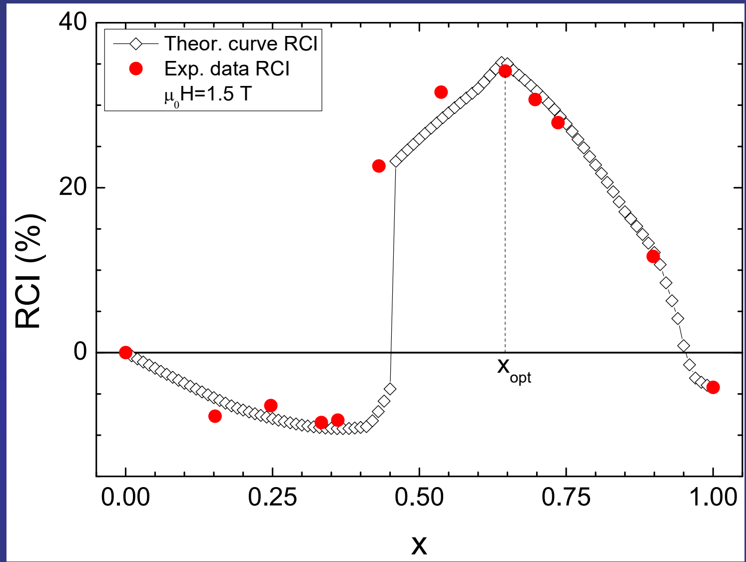
R. Caballero-Flores, V. Franco, A. Conde, K. E. Knipling, and M. A. Willard. Appl. Phys. Lett. 98 (2011) 102505

- If phases have very distant T_C, RC diminishes
  - There exists $\Delta T_{C,opt}$
- The majority phase should have the largest T_C (x_{opt}>0.5)
- Improvements of RC as large as 83% can be obtained
- Optimal values are dependent on H_{max}

RC of composite: Comparison with experiments



$Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$



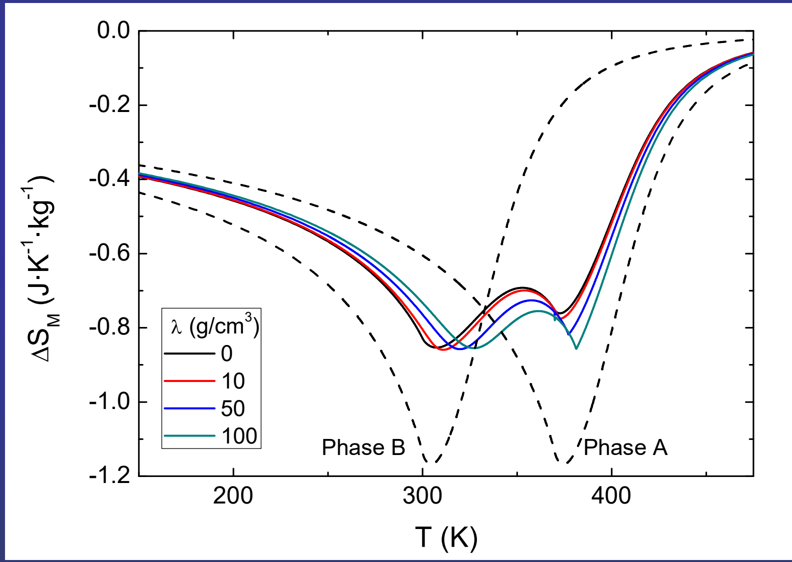
- Is there a shift in the data?
- Do interactions between phases play a role?

S.C. Paticopoulos, R. Caballero-Flores, V. Franco, J. S. Blázquez, A. Conde, K. E. Knipling, M. A. Willard. Solid State Comm. 152 (2012) 1590

Model material

- Each phase $$H^{\frac{1}{\gamma}} = a_i(T - T_{Ci})M^{\frac{1}{\gamma}} + b_i M^{\frac{1}{\beta}+\frac{1}{\gamma}}$$
- Composite $$M = xM_A + (1-x)M_B$$
- Interactions (mean field) $$H_{eff} = H + \lambda M$$
- ΔS_M calculated from Maxwell relation

Influence of interactions



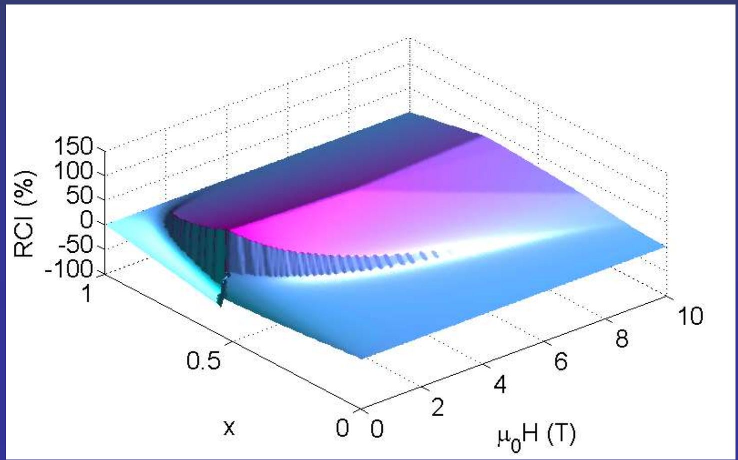
- Peak temperatures are shifted with increasing interaction strength

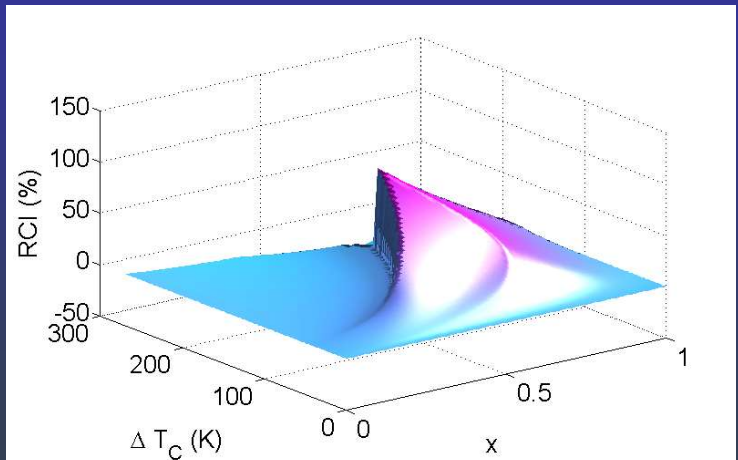
- Table-like character is enhanced

C. Romero-Muñiz, V. Franco, A. Conde. Appl. Phys. Lett. 102 (2013) 082402

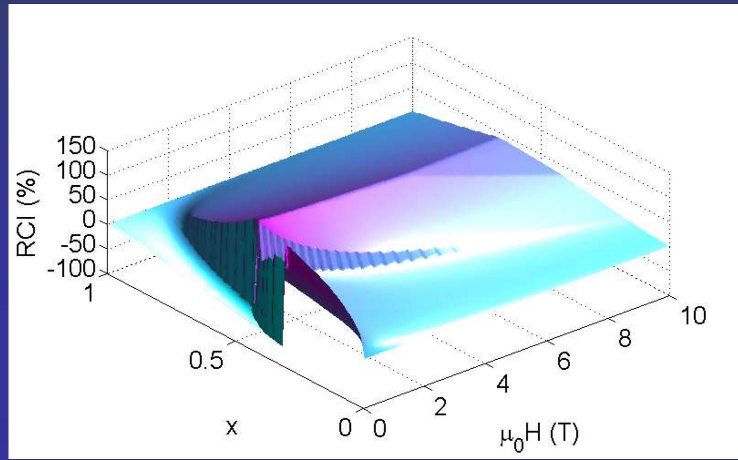
RCI

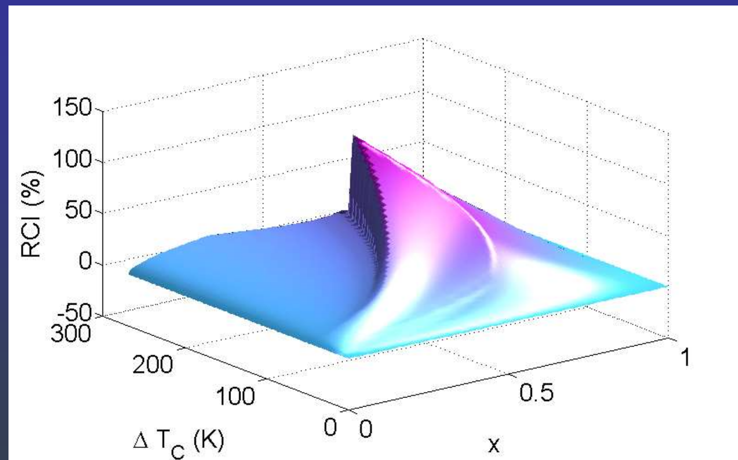
λ = 0 g/cm^3





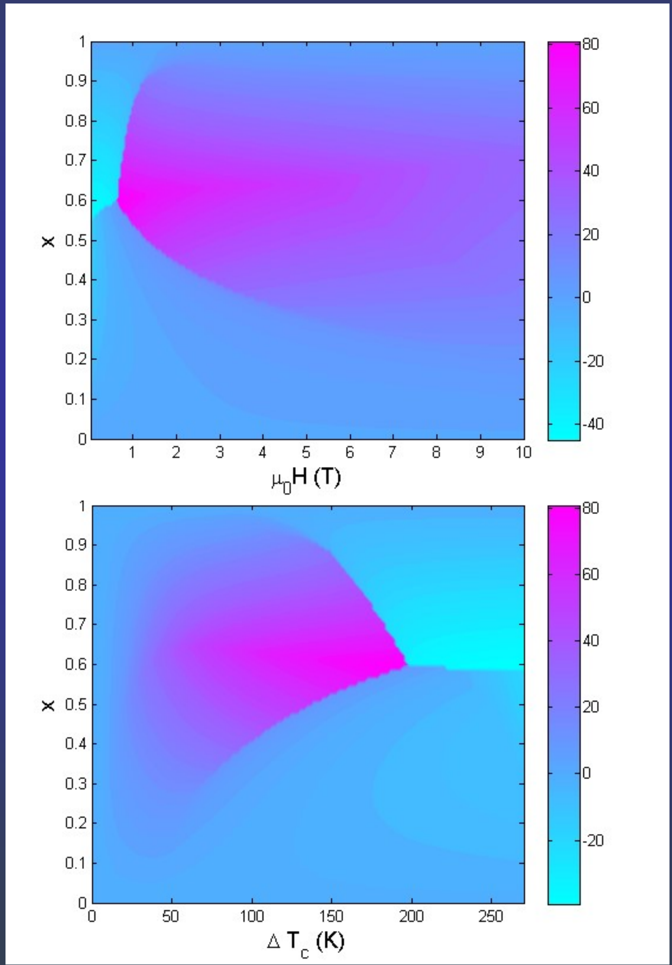
λ = 100 g/cm^3



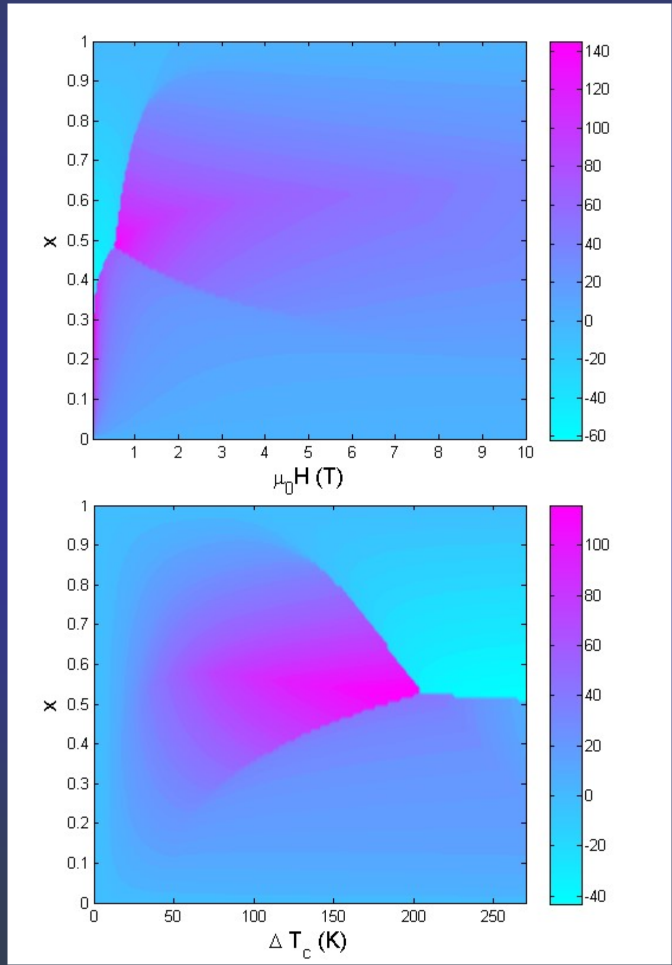


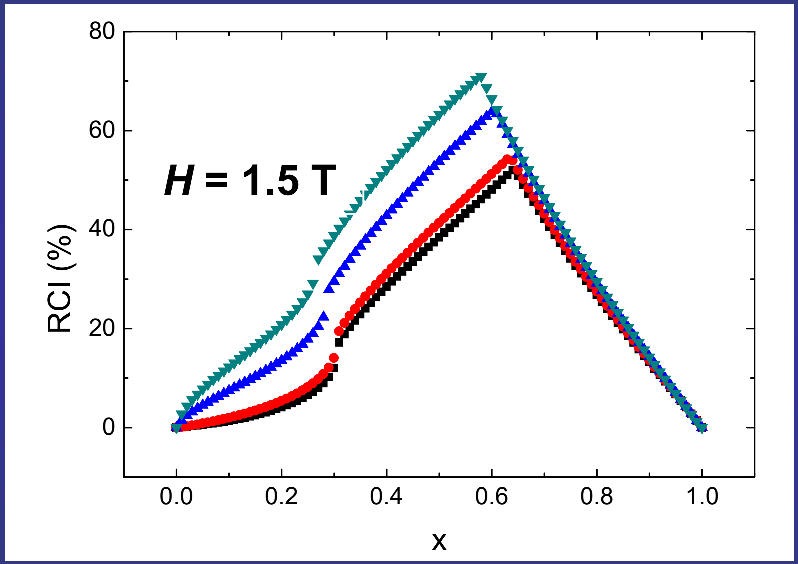
RCI

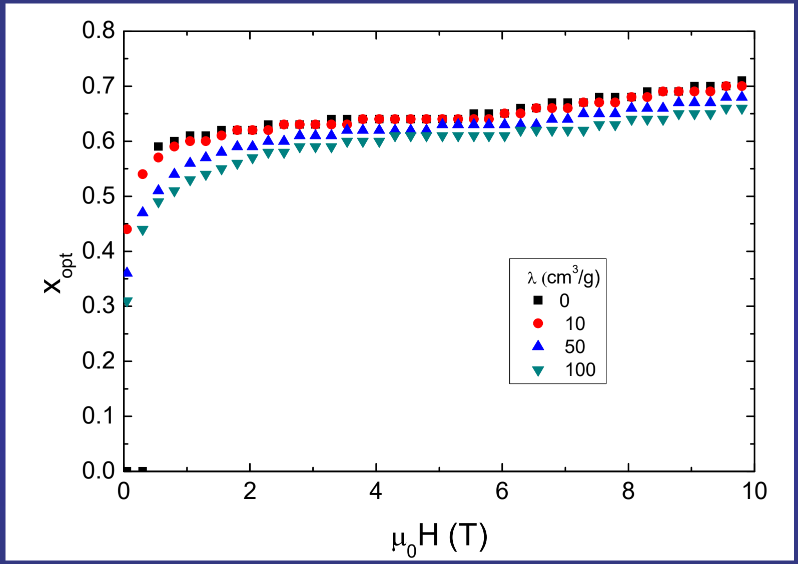
λ = 0 g/cm^3



λ = 100 g/cm^3

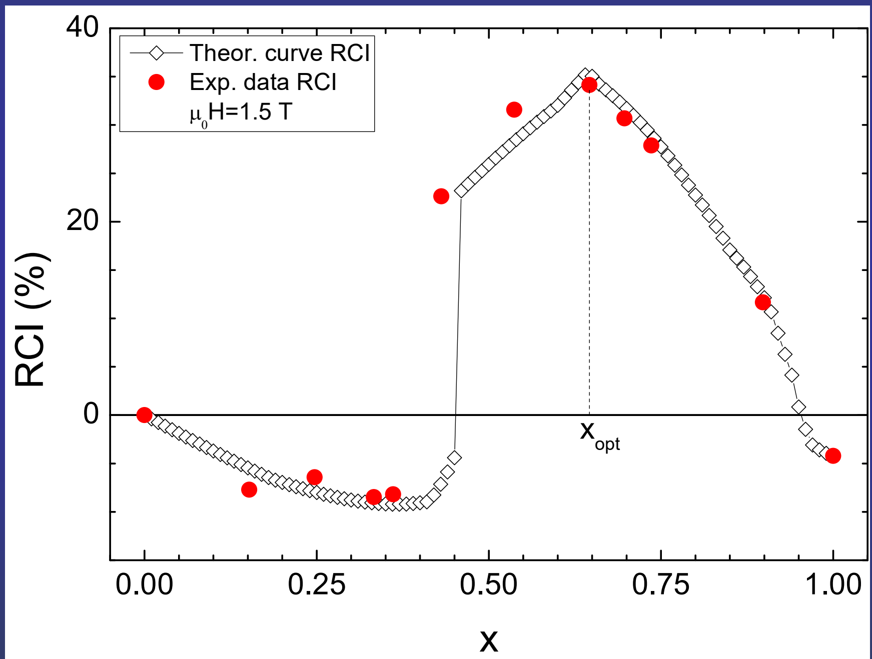






- There is no qualitative change of the curves due to interactions
- There is a shift of x_{opt} to lower values

Comparison with experiments



- The shift found experimentally can be ascribed to interactions between phases
- $\lambda \approx 50$ g/cm^3
- Equivalent to fields between 0.4 T and 0.1 T between T_c's

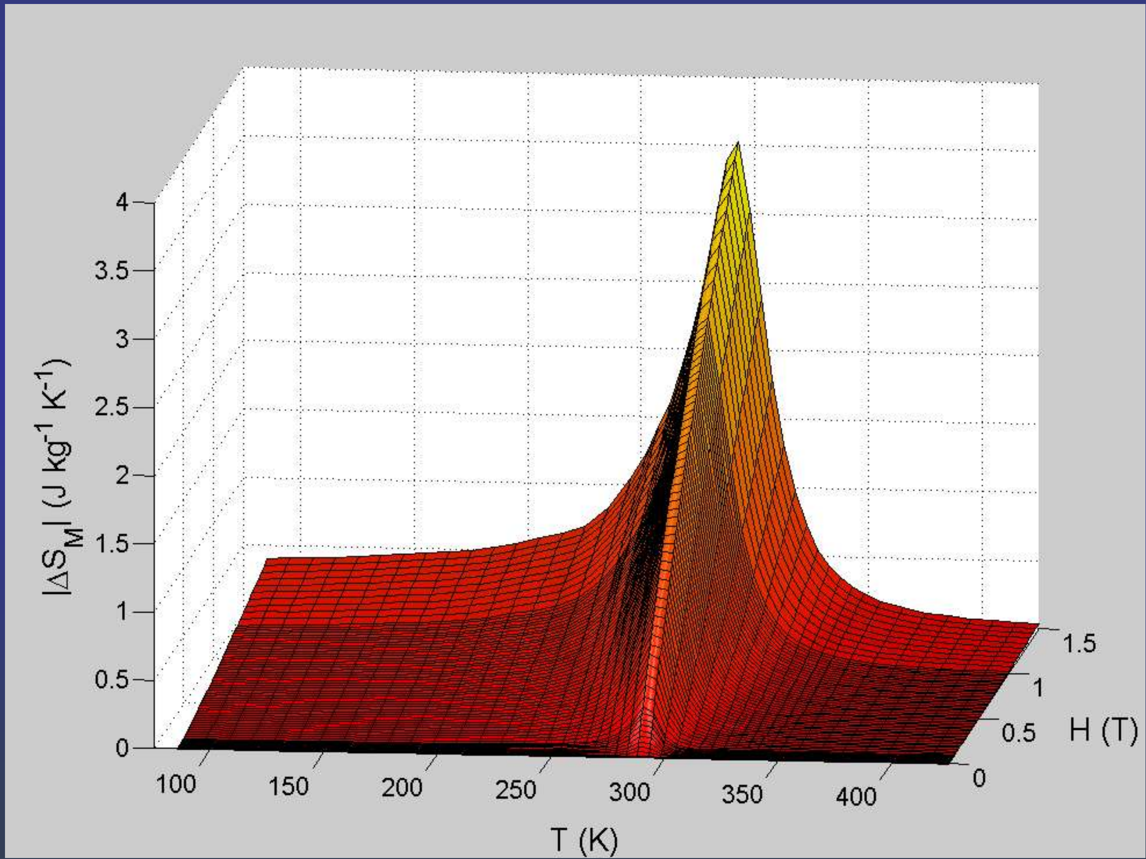
C. Romero-Muñiz, V. Franco, A. Conde. Appl. Phys. Lett. 102 (2013) 082402

Multilayered structures

A way to control the field dependence of MCE

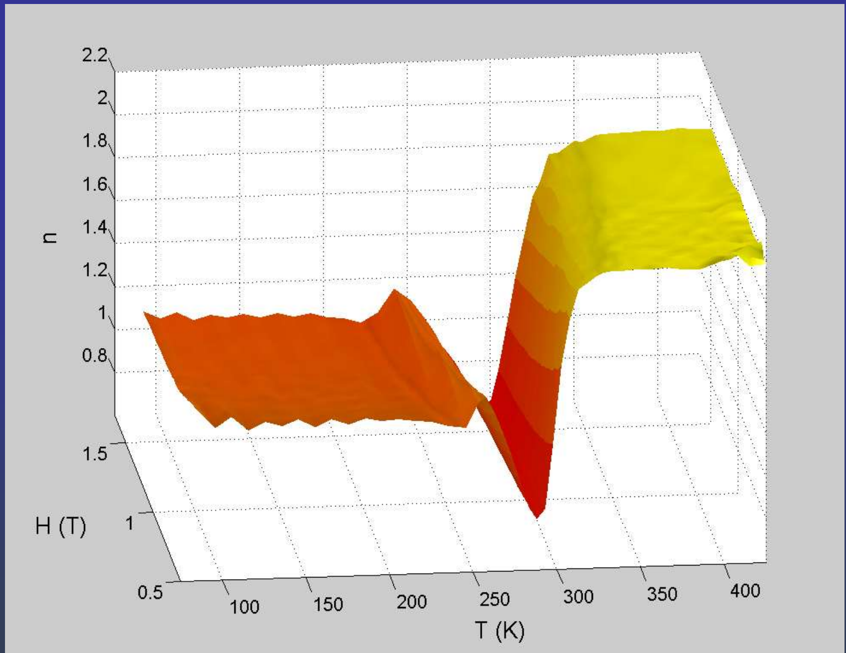
our reference:
Single phase materials

Bulk Gd sample

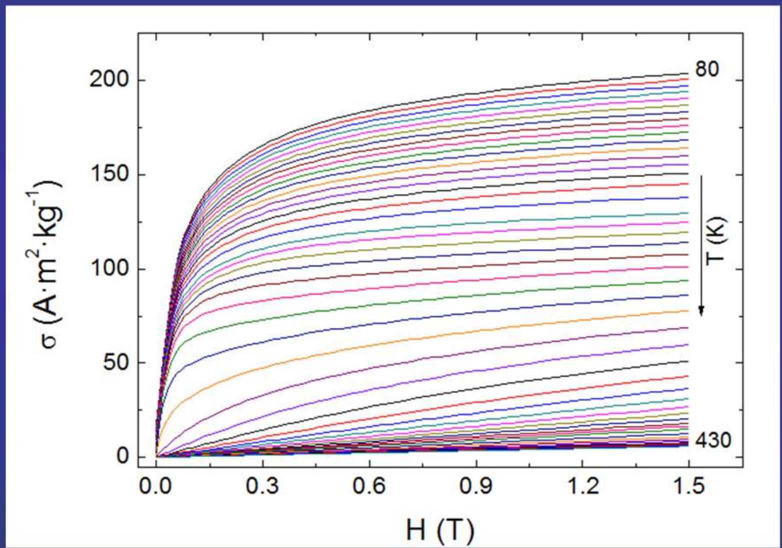


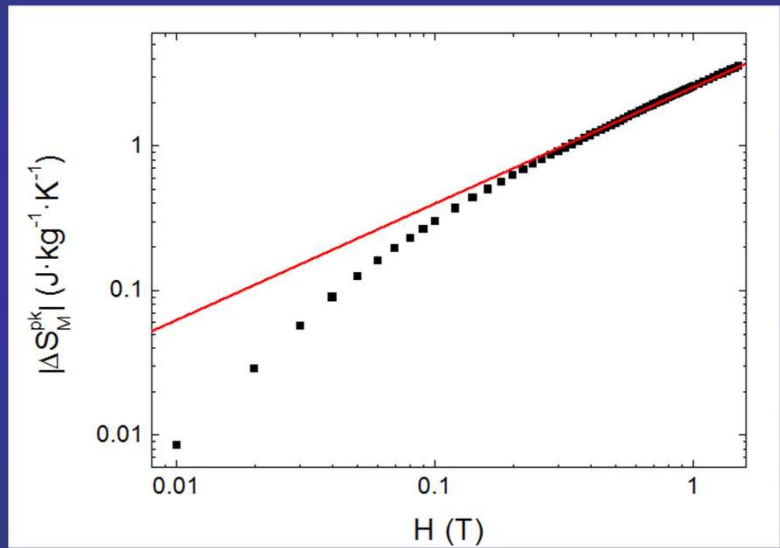
Field dependence of ΔS_M

$$\Delta S_M \propto H^n \qquad n = \frac{d \ln|\Delta S_M|}{d \ln H}$$



- T<<T$_C$: n=1
- T>>T$_C$: n=2
- T=T$_C$: $$n = 1 + \frac{1}{\delta}\left(1 - \frac{1}{\beta}\right)$$
- The field dependence is the lowest when the MCE signal is the largest



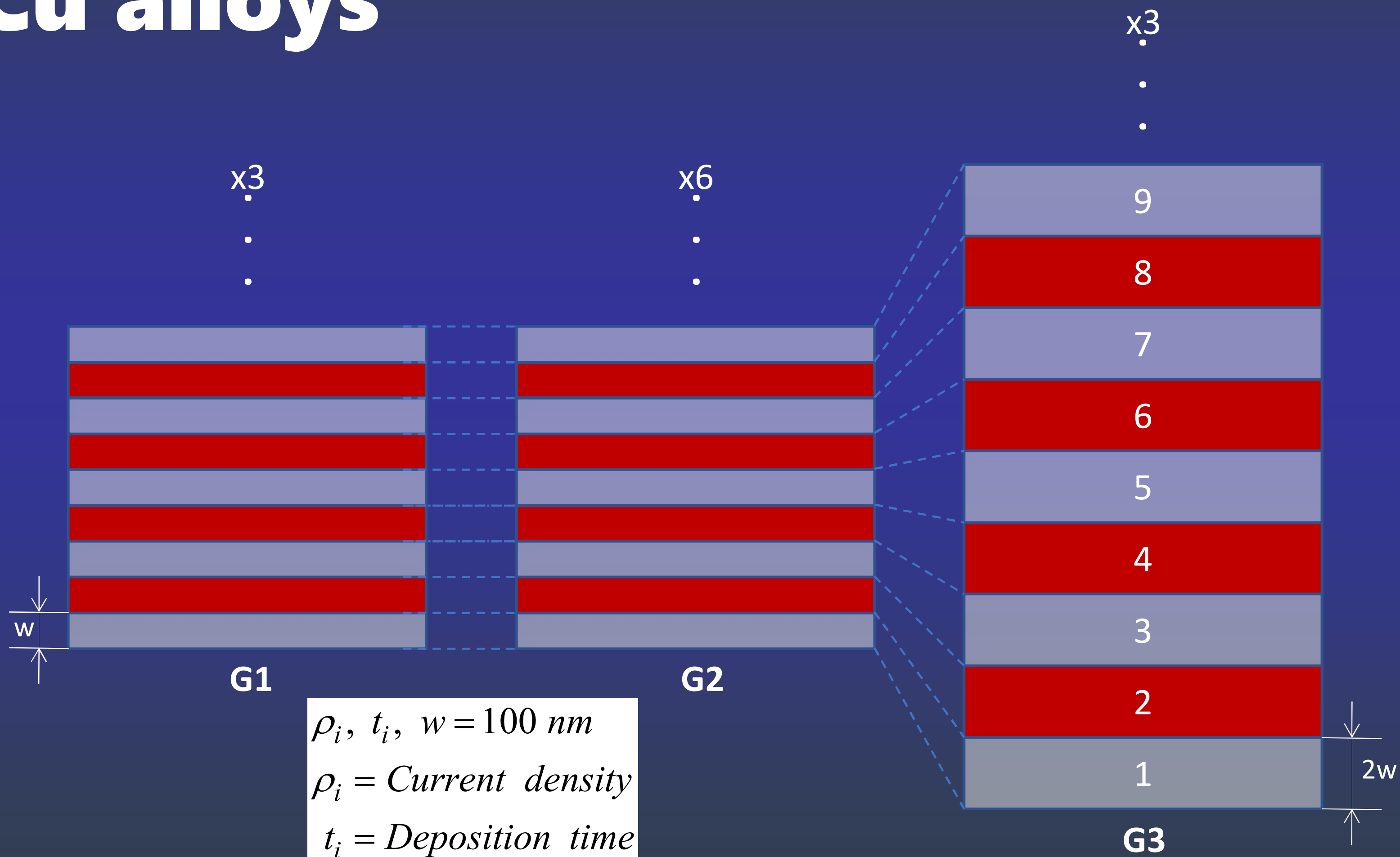


- Deviations from the power law at low fields due to non-saturation

our Goal:
To increase the field dependence at the peak

VIa nanostructuring?

Electrodeposited samples. NiCu alloys



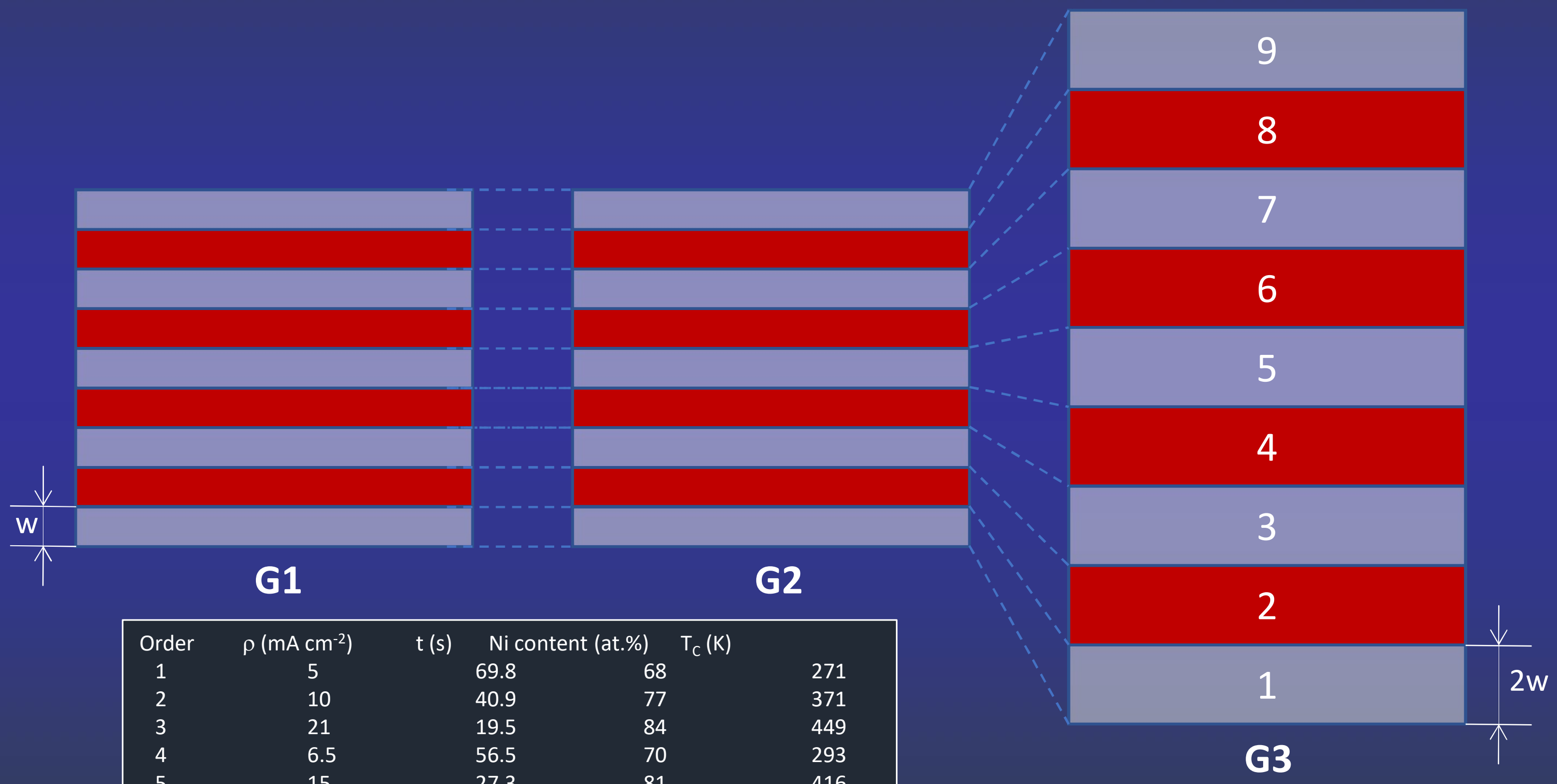
$\rho_i,\ t_i,\ w = 100\ nm$

$\rho_i = Current\ \ density$

$t_i = Deposition\ \ time$

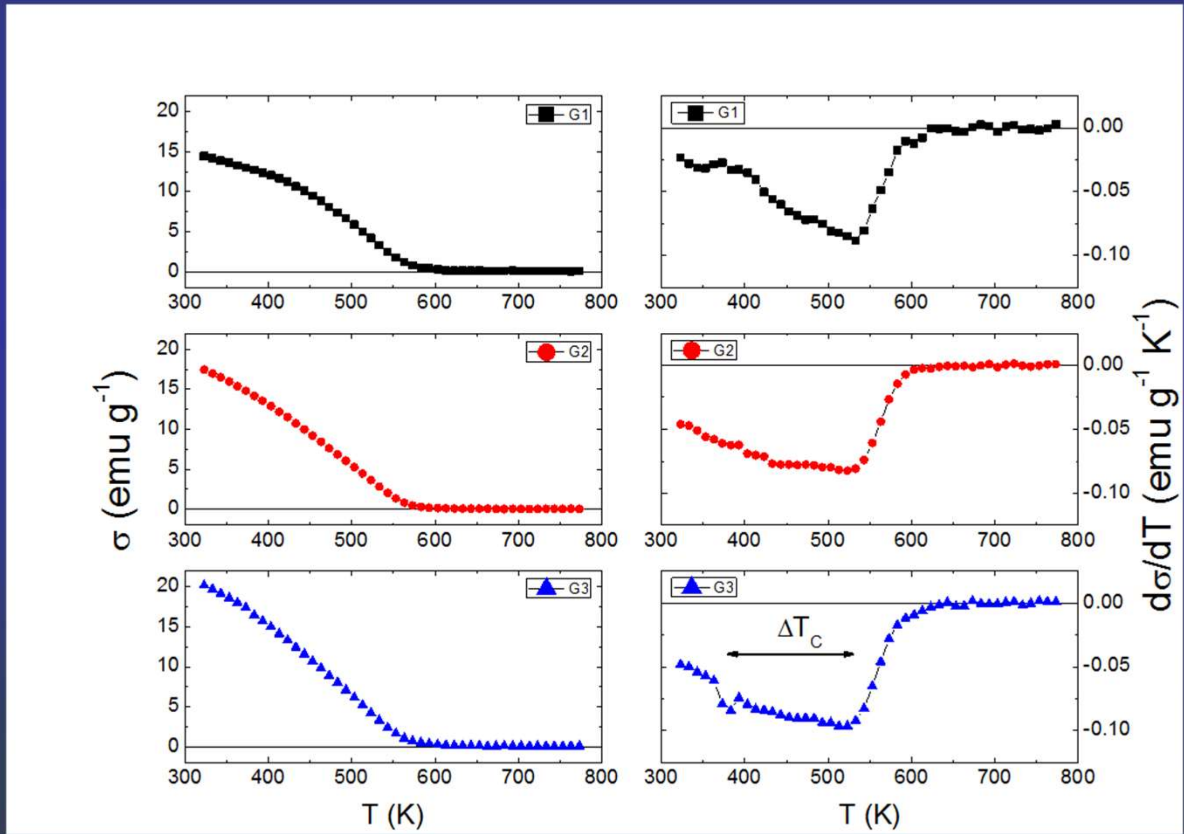
$\rho_i,\ 2t_i,\ 2w = 200\ nm$

Fabrication parameters

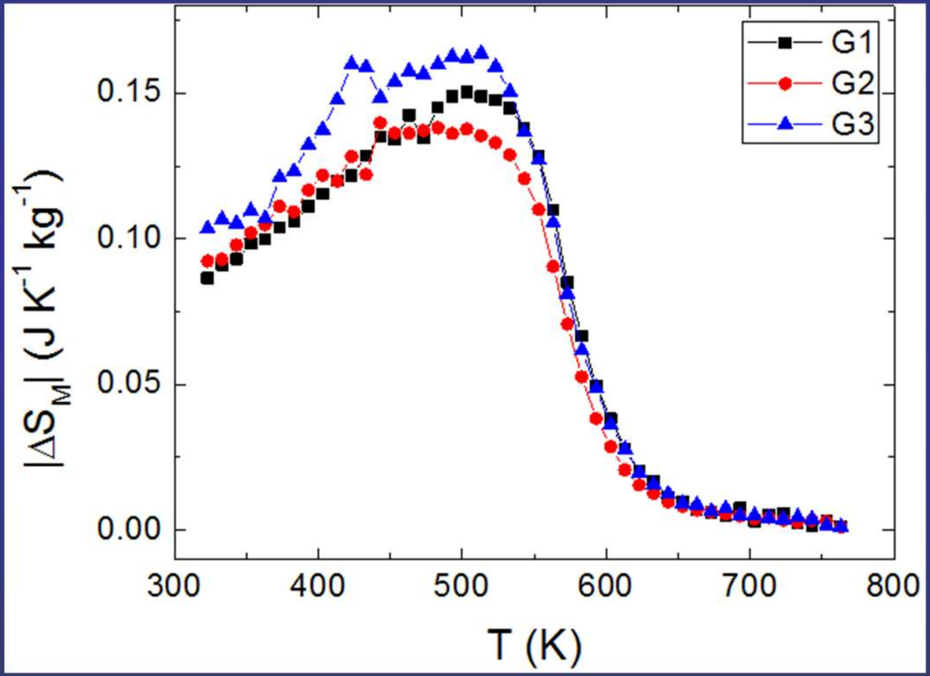


Order	ρ (mA cm^{-2})	t (s)	Ni content (at.%)	T_C (K)
1	5	69.8	68	271
2	10	40.9	77	371
3	21	19.5	84	449
4	6.5	56.5	70	293
5	15	27.3	81	416
6	4	84.2	66	248
7	2.6	122.3	61	193
8	8	48.4	73	326
9	3	108.4	64	226

Thermomagnetic curves



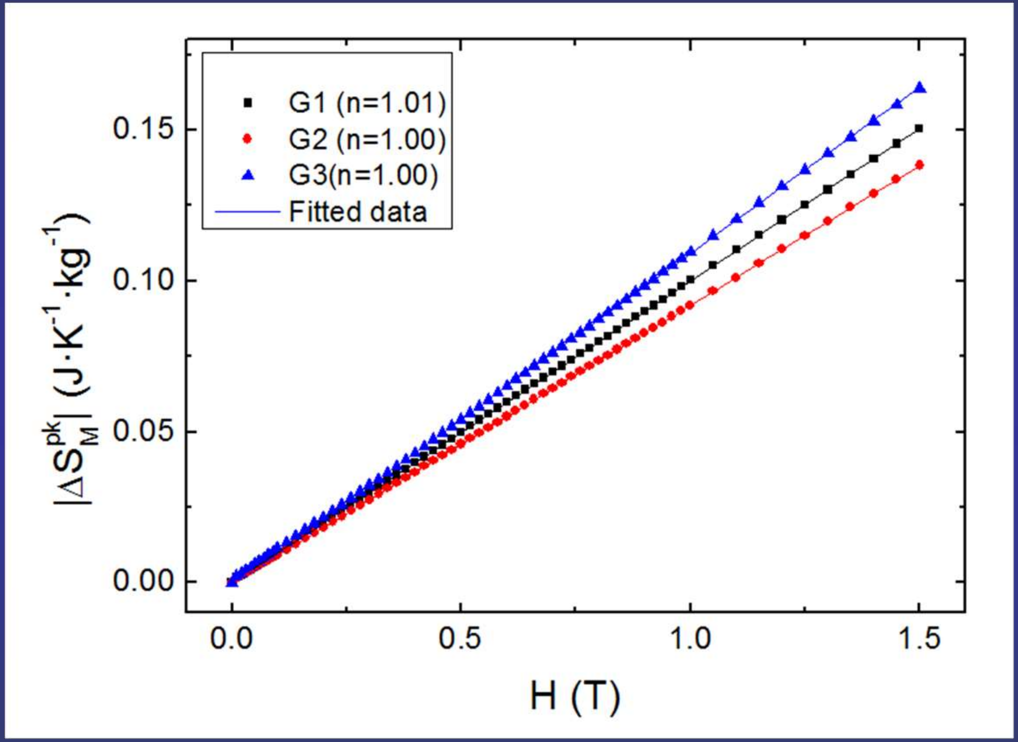
Magnetic entropy change



- Peaks are broadened due to the distribution of T_c's
- Longer deposition times enhances this effect
- Overlapping of the different peaks from the different phases

R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
Journal of Nanoscience and Nanotechnology 12 (2012) 7432

Field dependece at the peak



A linear field dependence of the peak is achieved

R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
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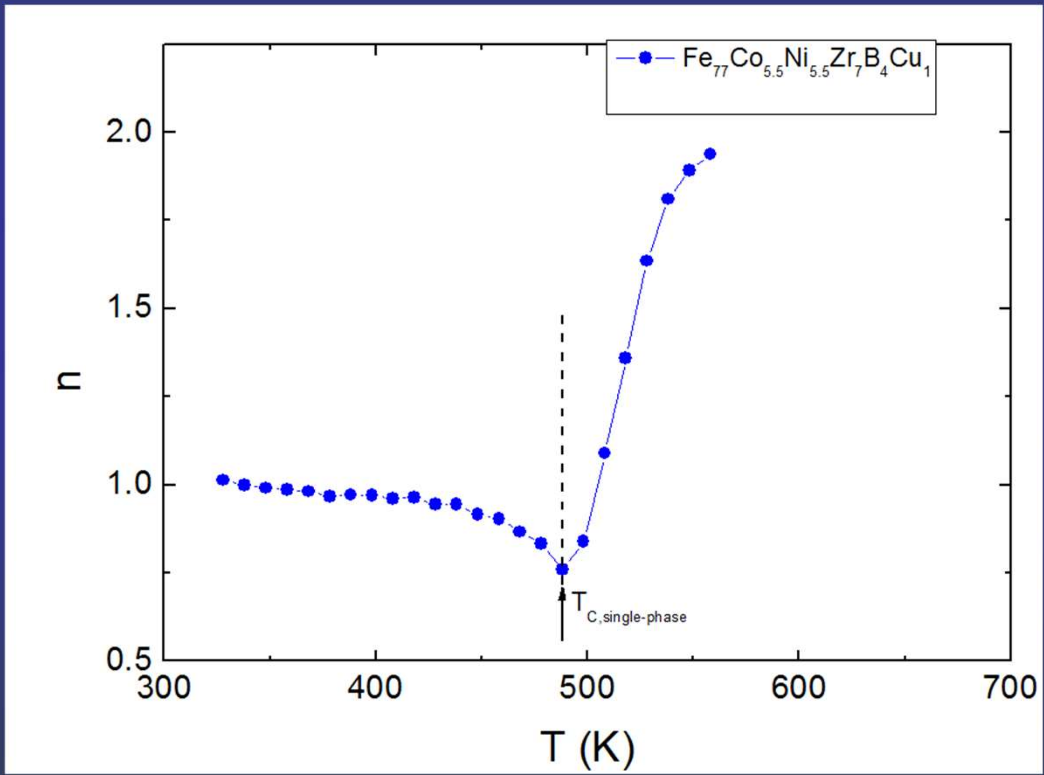
Field dependence in an extended T range



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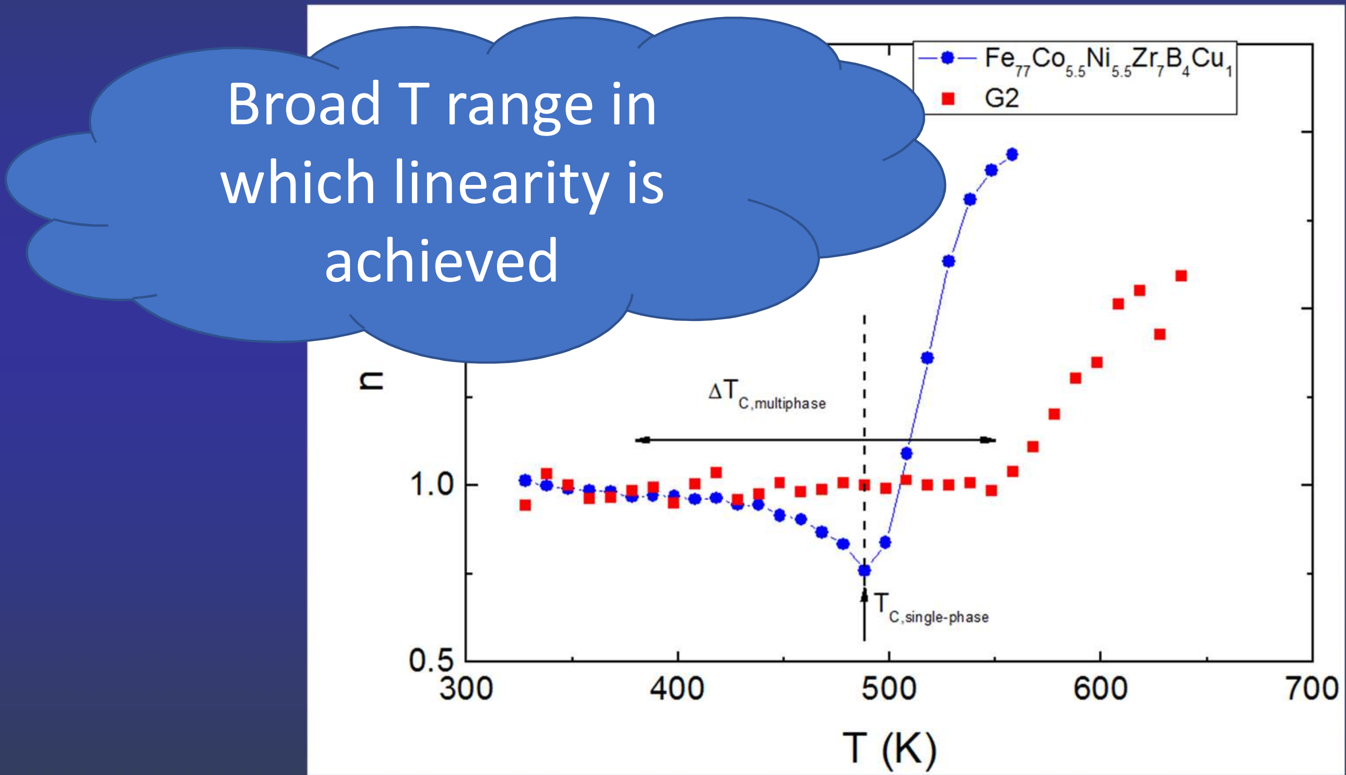
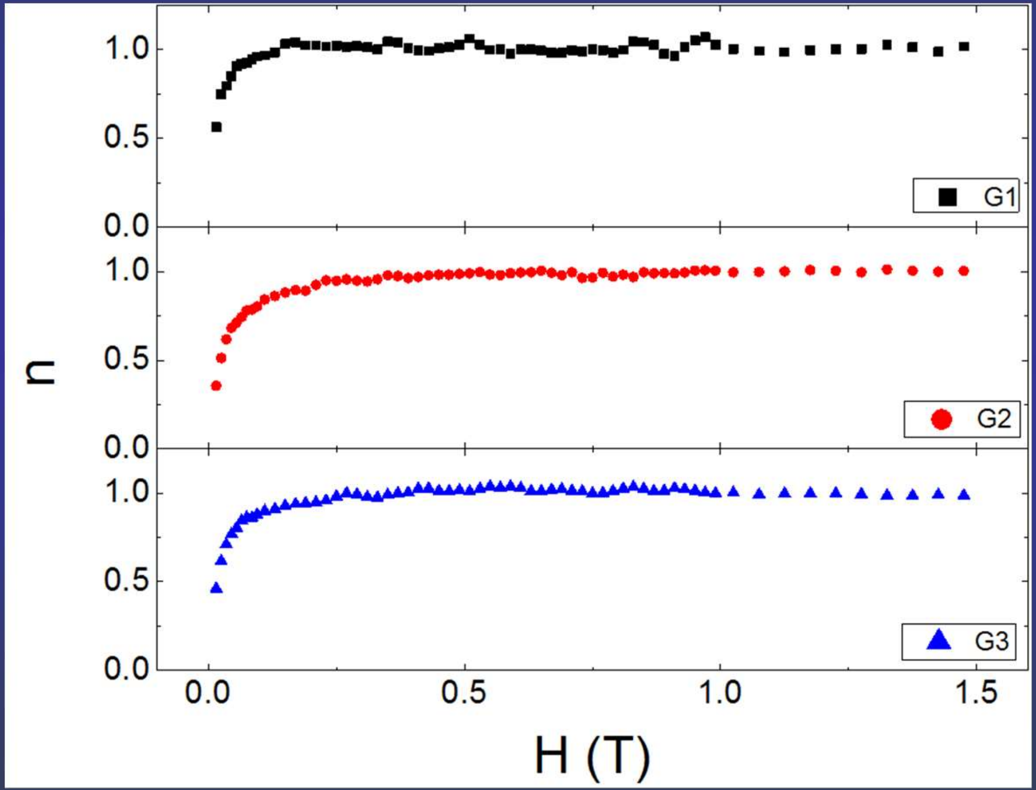
Field dependence in an extended T range



R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
Journal of Nanoscience and Nanotechnology 12 (2012) 7432

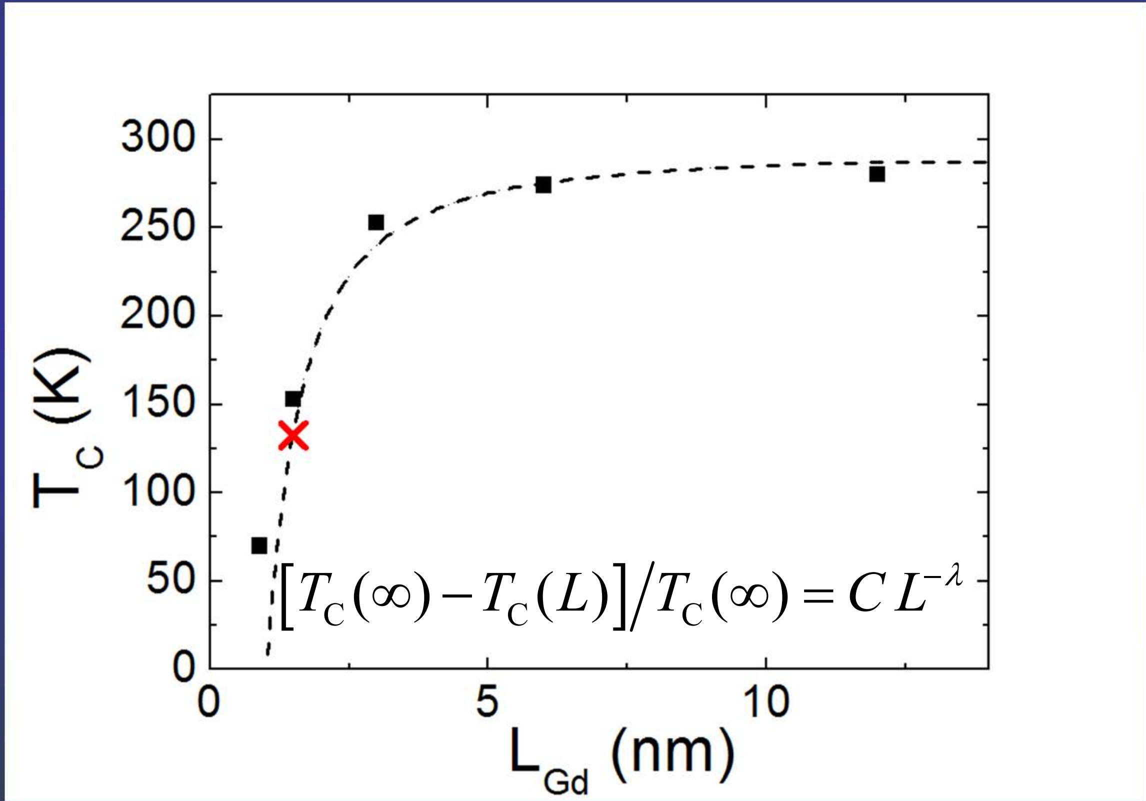
Field dependence of n



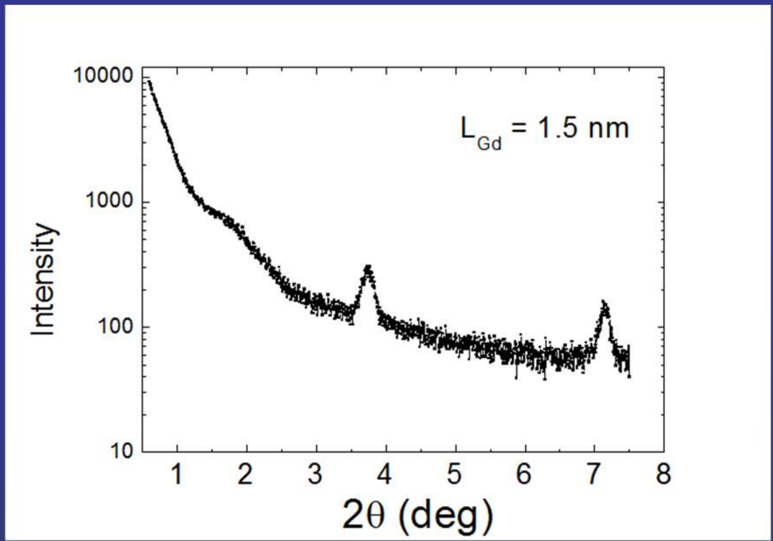
Difference with bulk composites (H independent)

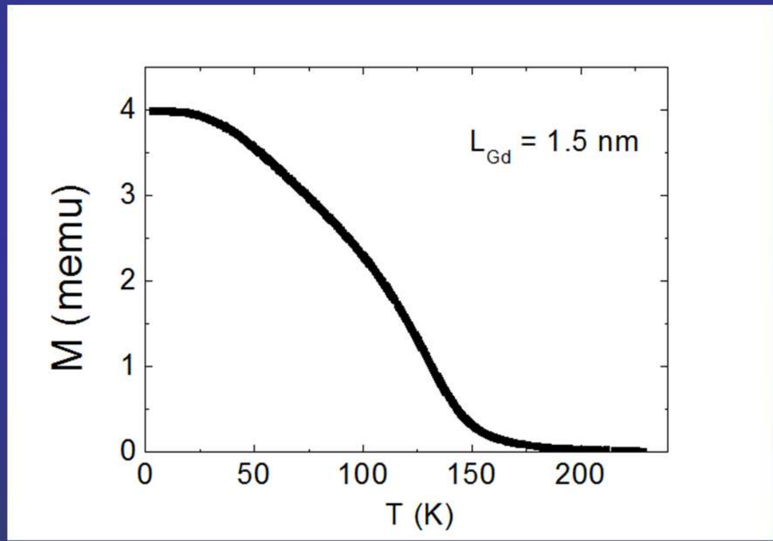
Can we achieve something similar without compositional gradients?

Sputtered Gd/Ti multilayers: Finite size scaling

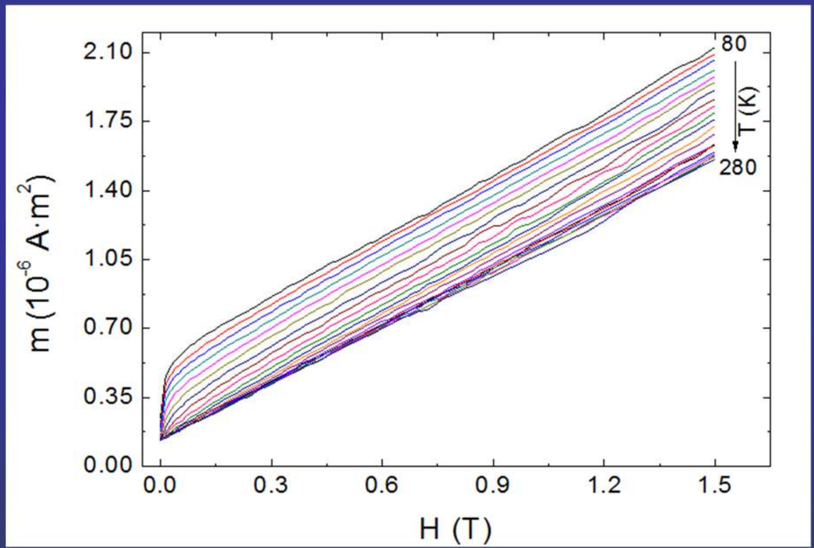


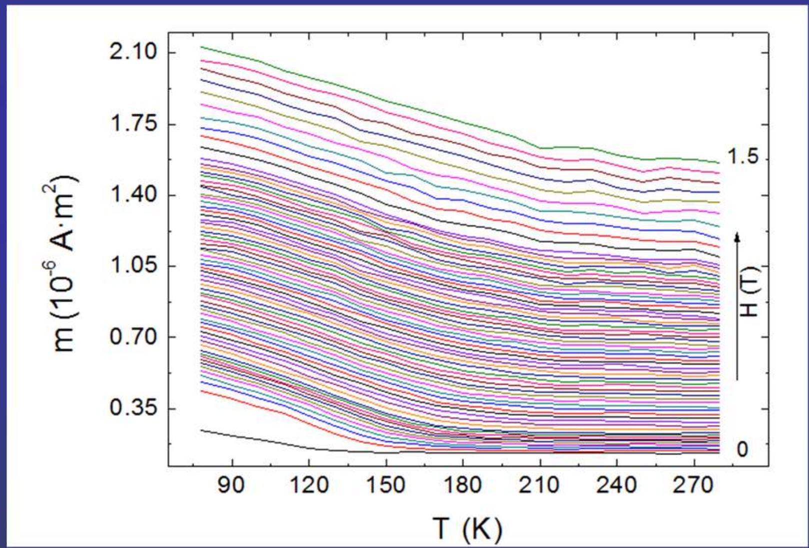
A.V. Svalov et al., Solid State Phenomena 168-169 (2011) 281



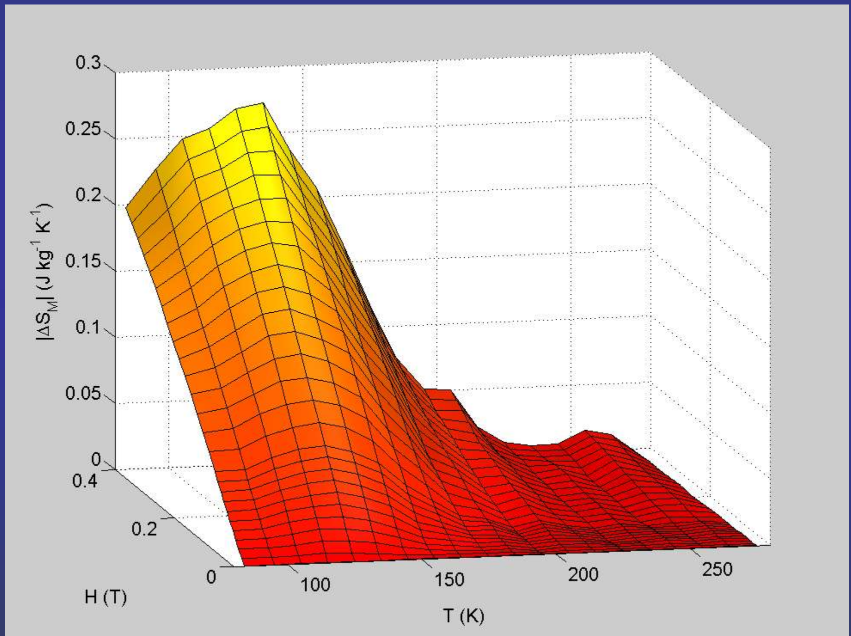


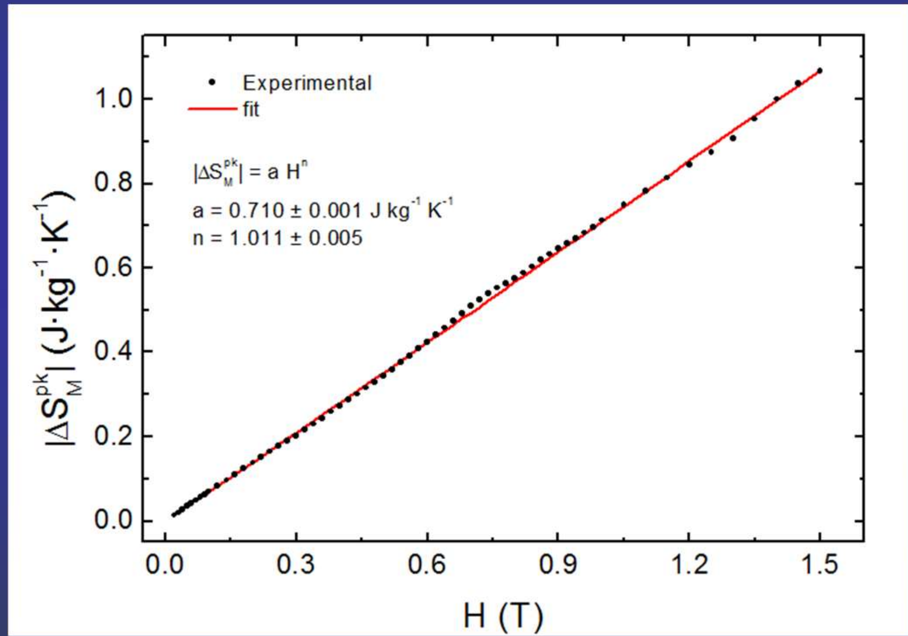
D. Doblas, V. Franco, A. Conde, A.V. Svalov, G.V. Kurlyandskaya, Materials and Desing 114 (2017) 214





D. Doblas, V. Franco, A. Conde, A.V. Svalov, G.V. Kurlyandskaya, Materials and Desing 114 (2017) 214





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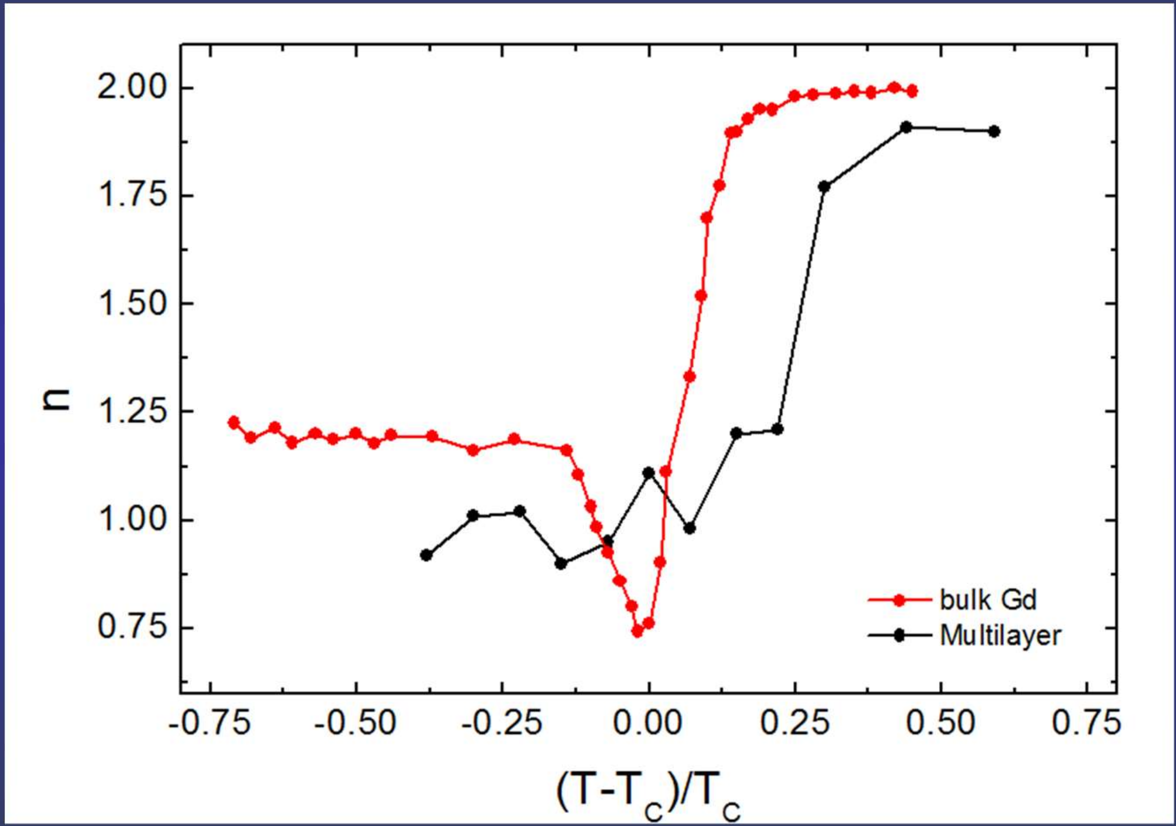

D. Doblas, V. Franco, A. Conde, A.V. Svalov, G.V. Kurlyandskaya, Materials and Desing 114 (2017) 214

Conclusions

- MCE is a promising alterative for energy efficient refrigeration
- It can be used to characterize phase transitions
- For SOPT materials, there is an universal curve for MCE
- The order of the phase transition can be determined quantitatively
- T-FORC gives valuable information about FOPT materials
- There are alternative applications of MCE
- Nanomaterials for MCE are less studied than bulk → interesting science

Acknowledgements

Sevilla University

IEEE Magnetics Society

Non-Crystalline Solids group

Numerous collaborators worldwide (cited)

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Advice for the young out there

- Do not trust black boxes (experimental devices/programs)
- Apply techniques from other fields to your own research
- Attend as many talks as possible, even outside your field
- Discuss topics with colleagues from other areas
- Network with researchers, use mentoring possibilities…