Magnetic Materials for Energy: Magnetocalorics

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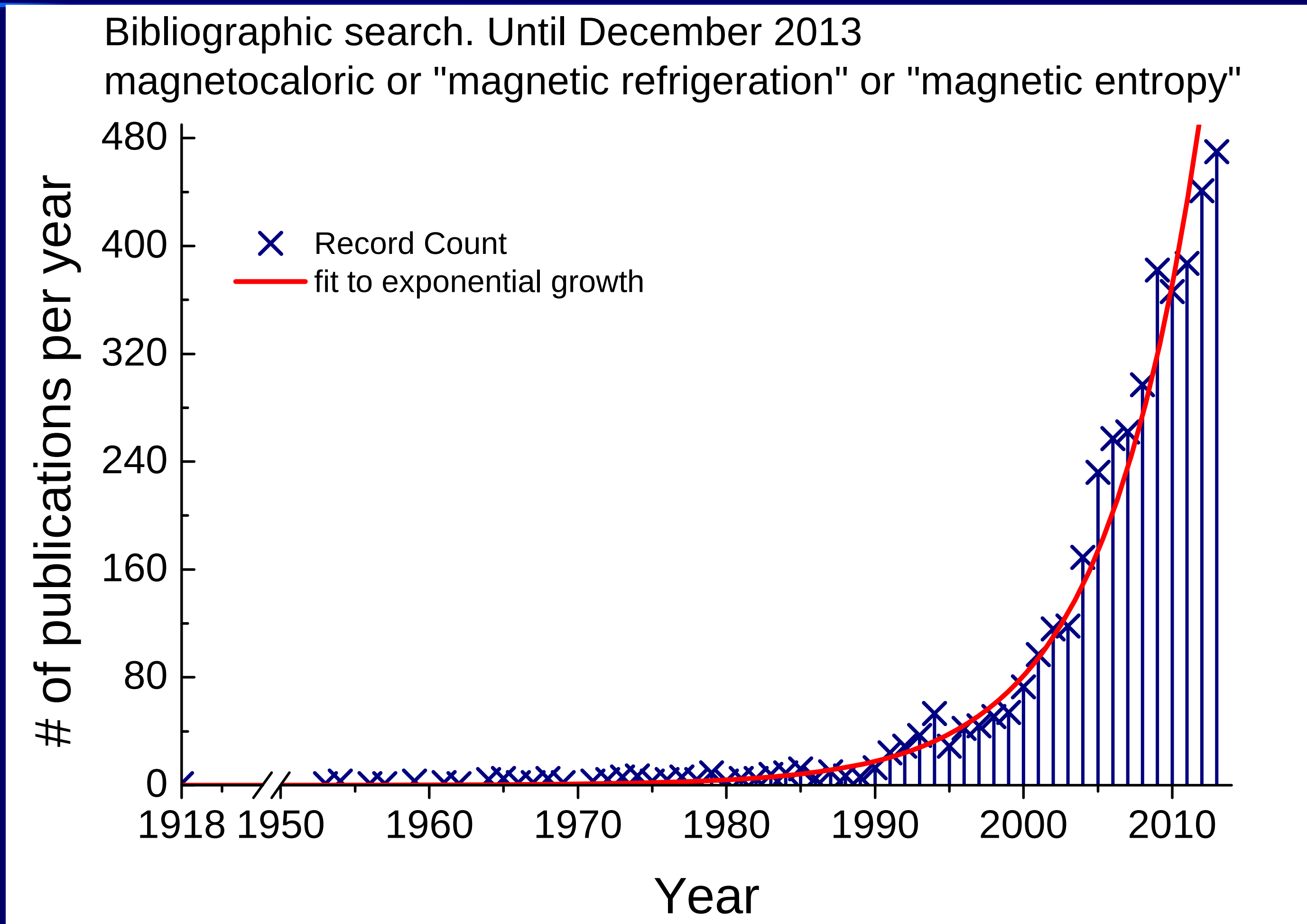
Structure of this talk

- MCE in a nutshell (what, when, which, where and why)
- How to compare experimental results (aka Field dependence of ΔS_M)
- MCE for those not working in magnetocaloric materials (phase transitions and critical phenomena)
- MCE in nanostructured materials: qualitatively different behavior
- Alternative ways of improving MCE: Composites
- Conclusions

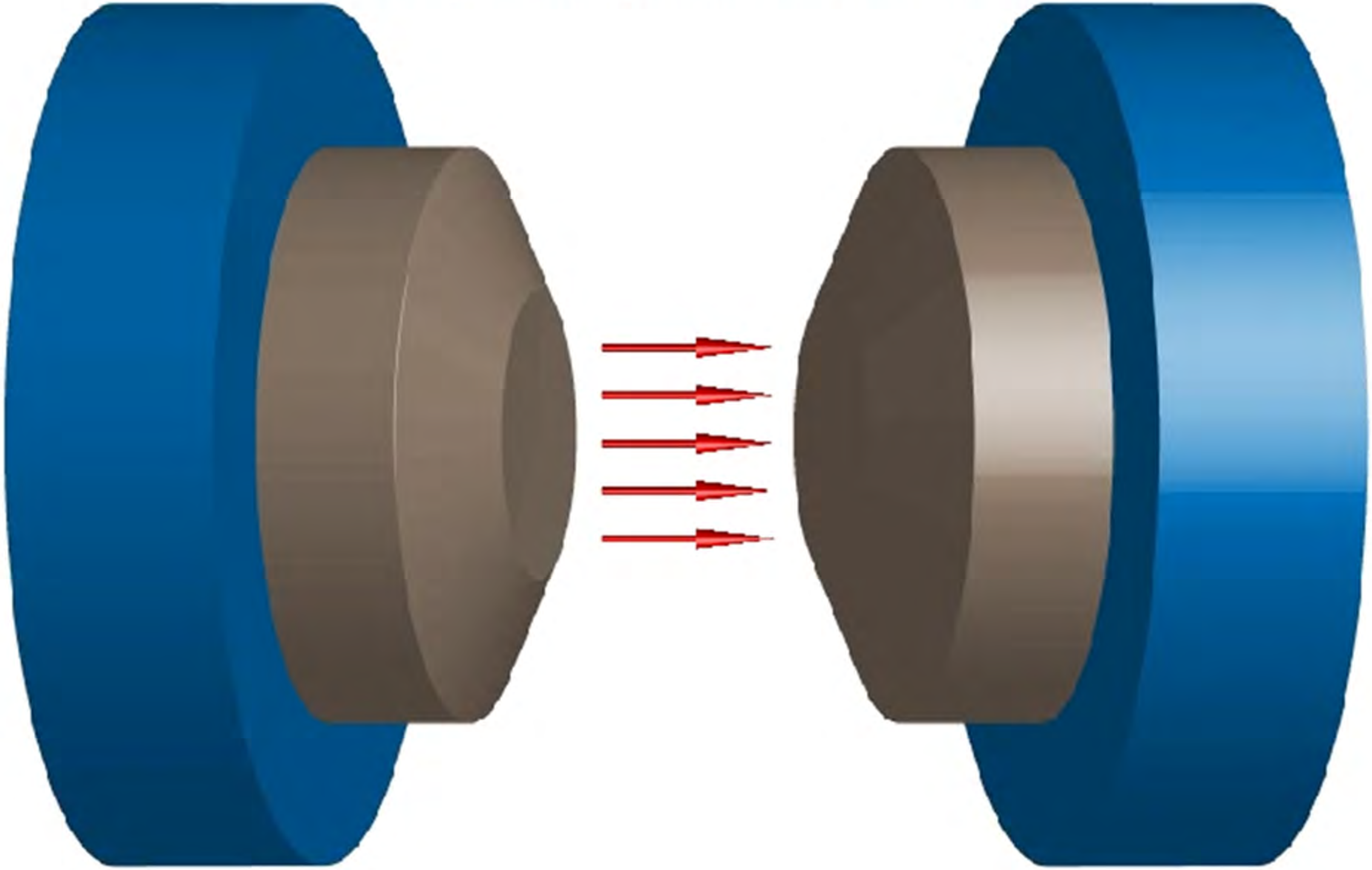
MCE:
a current research topic



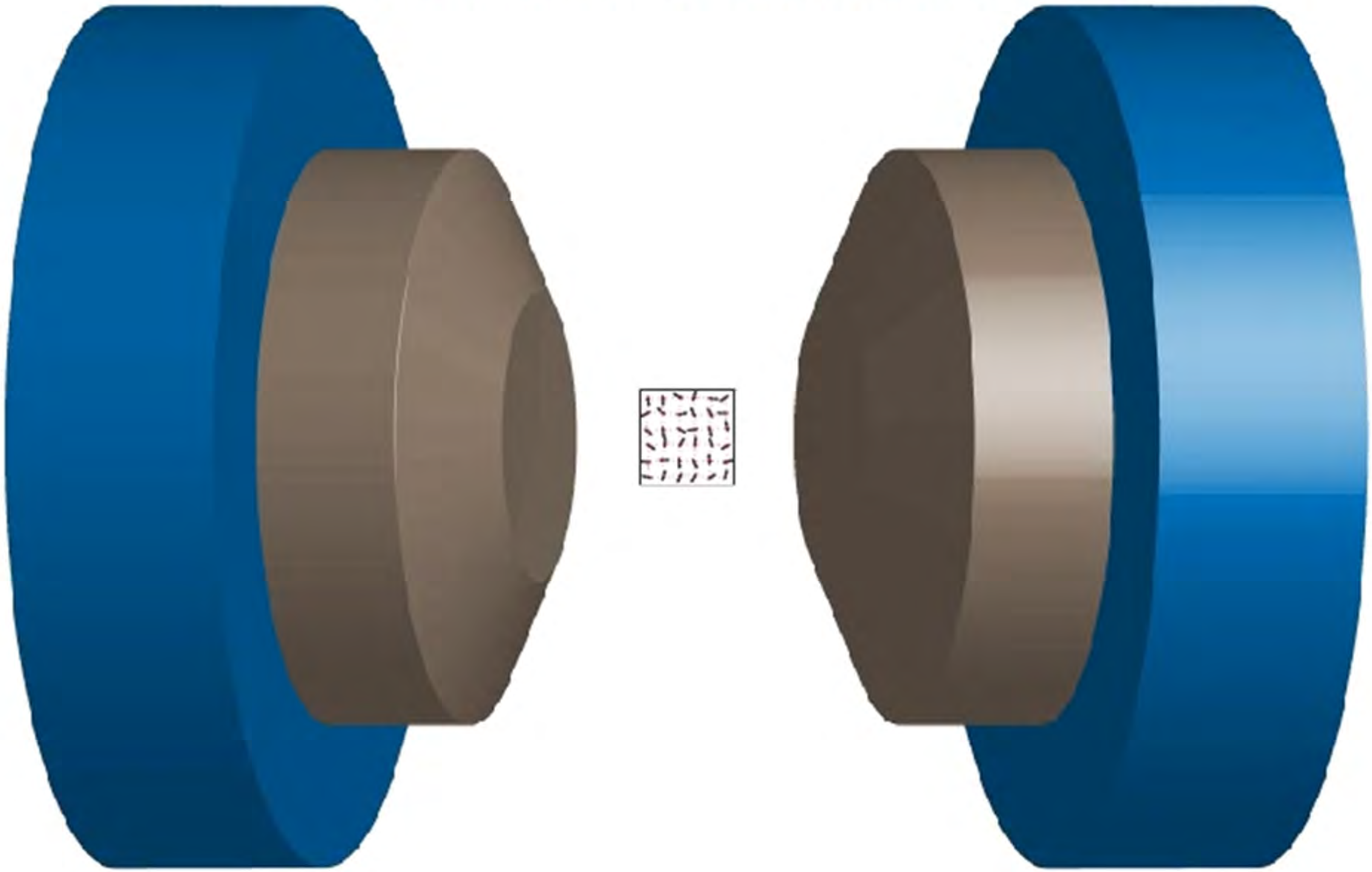
V. Franco, J.S. Blázquez, B.D. Ingale, A. Conde
Annual Review of Materials Research 42 (2012) 305

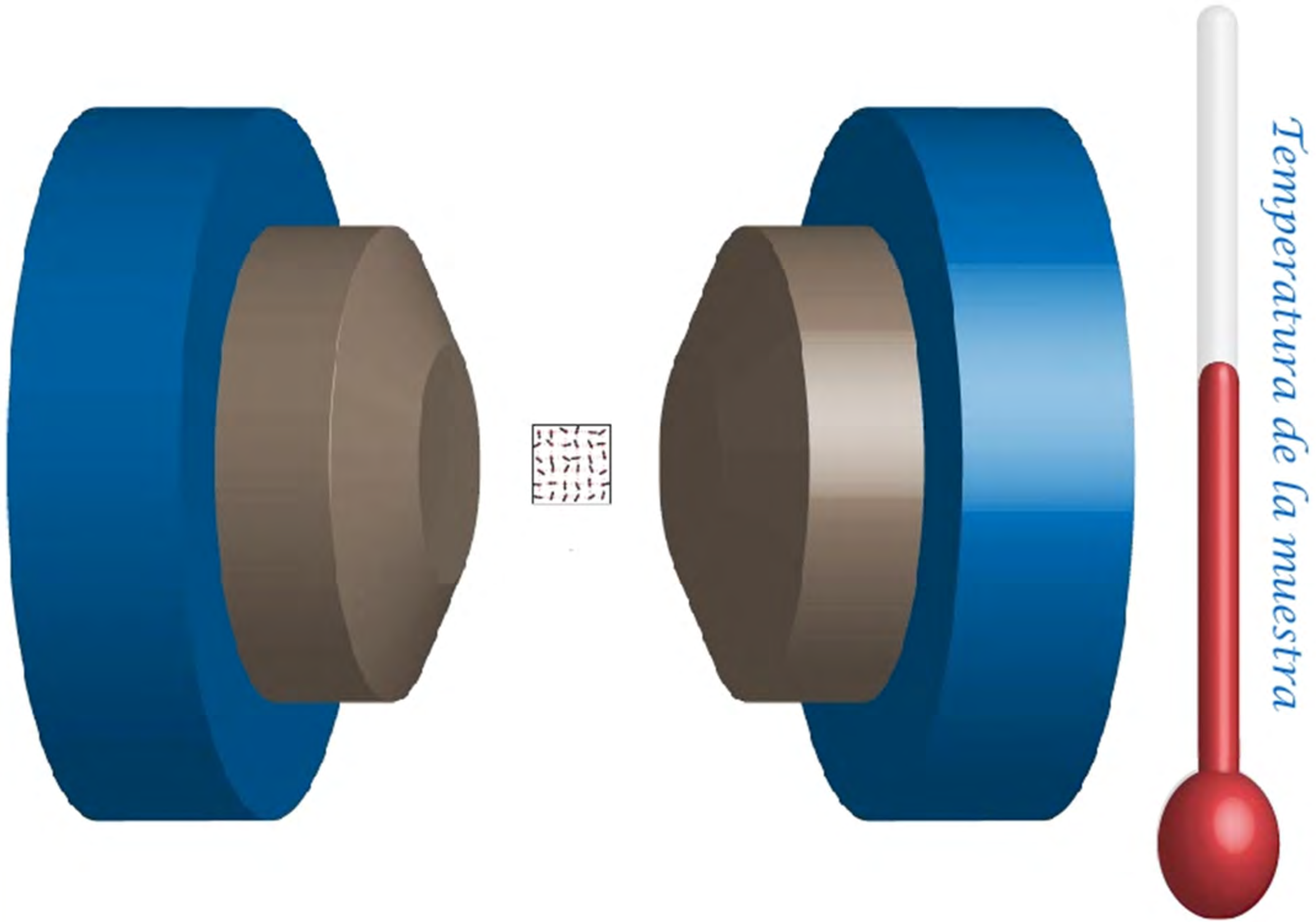
ELECTROIMÁN

campo magnético variable

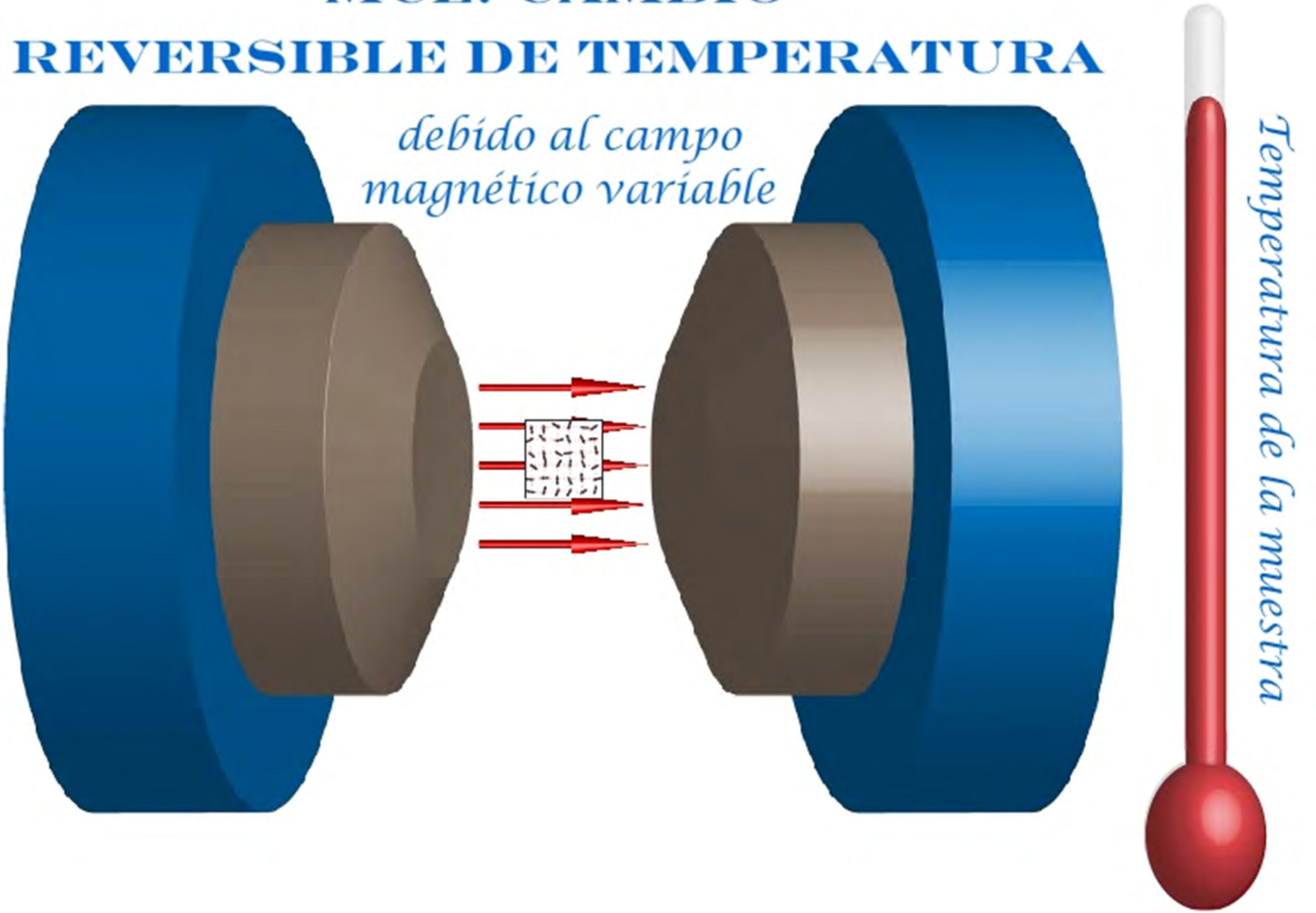


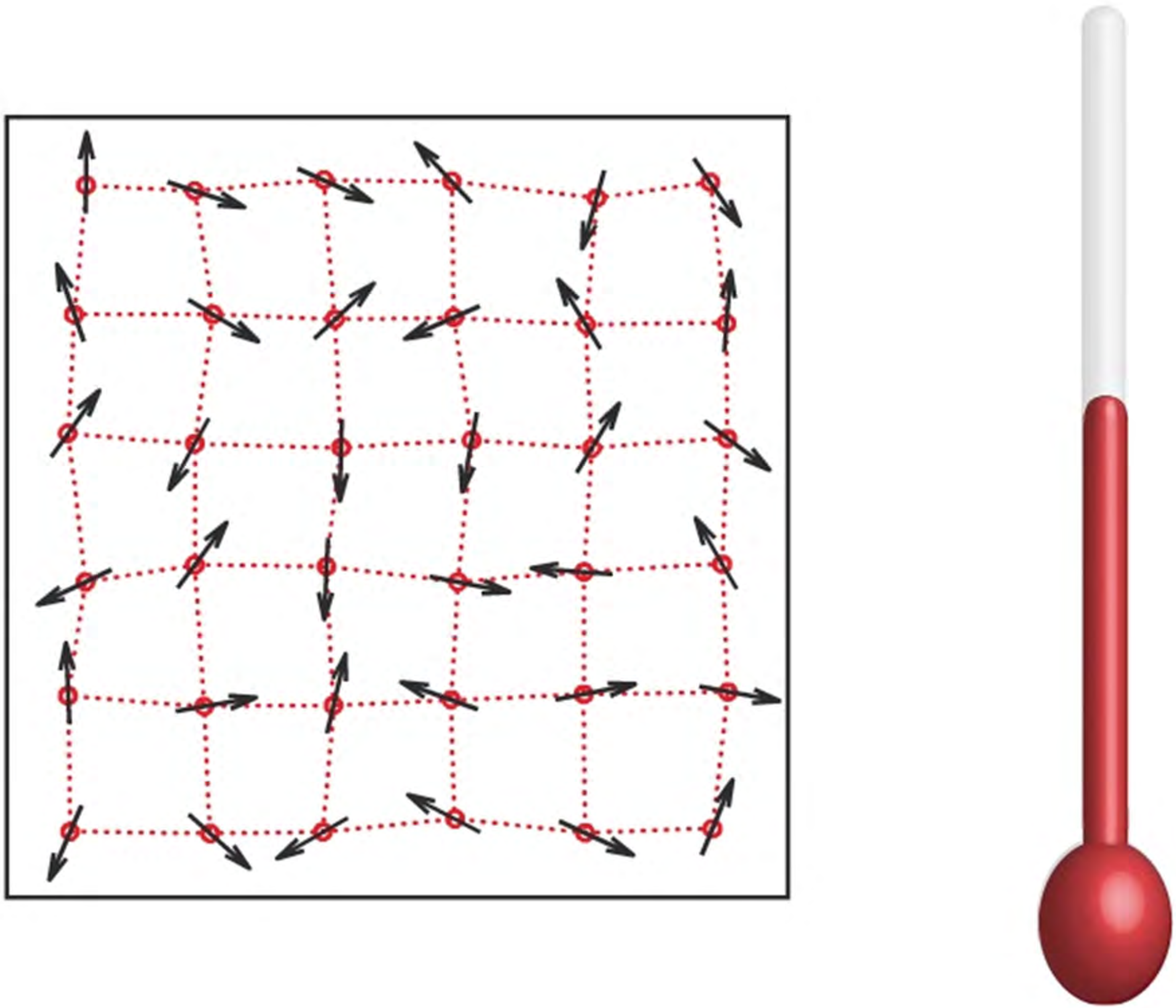
MATERIAL MAGNETOCALÓRICO



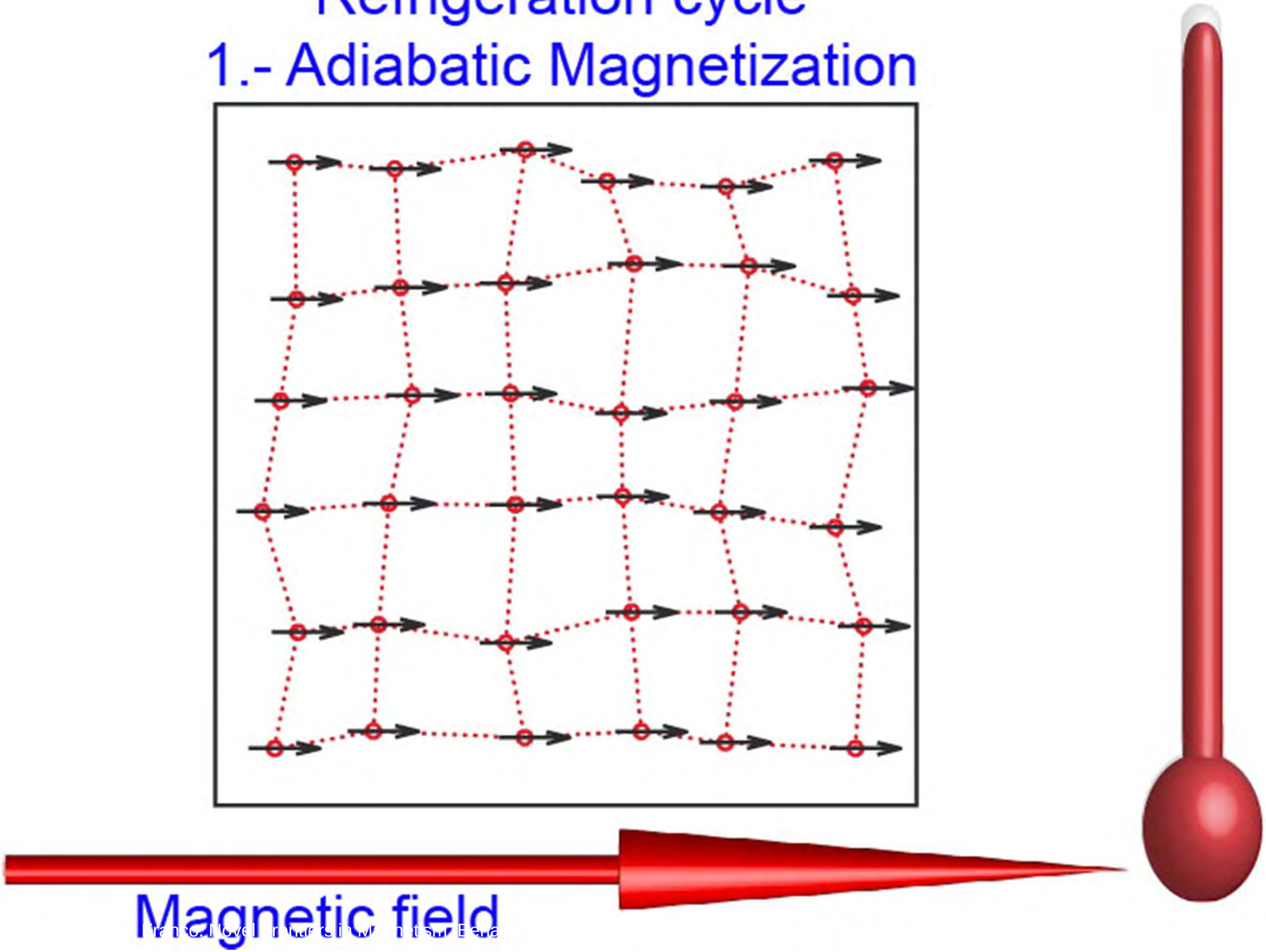

Temperatura de la muestra

MCE: CAMBIO REVERSIBLE DE TEMPERATURA

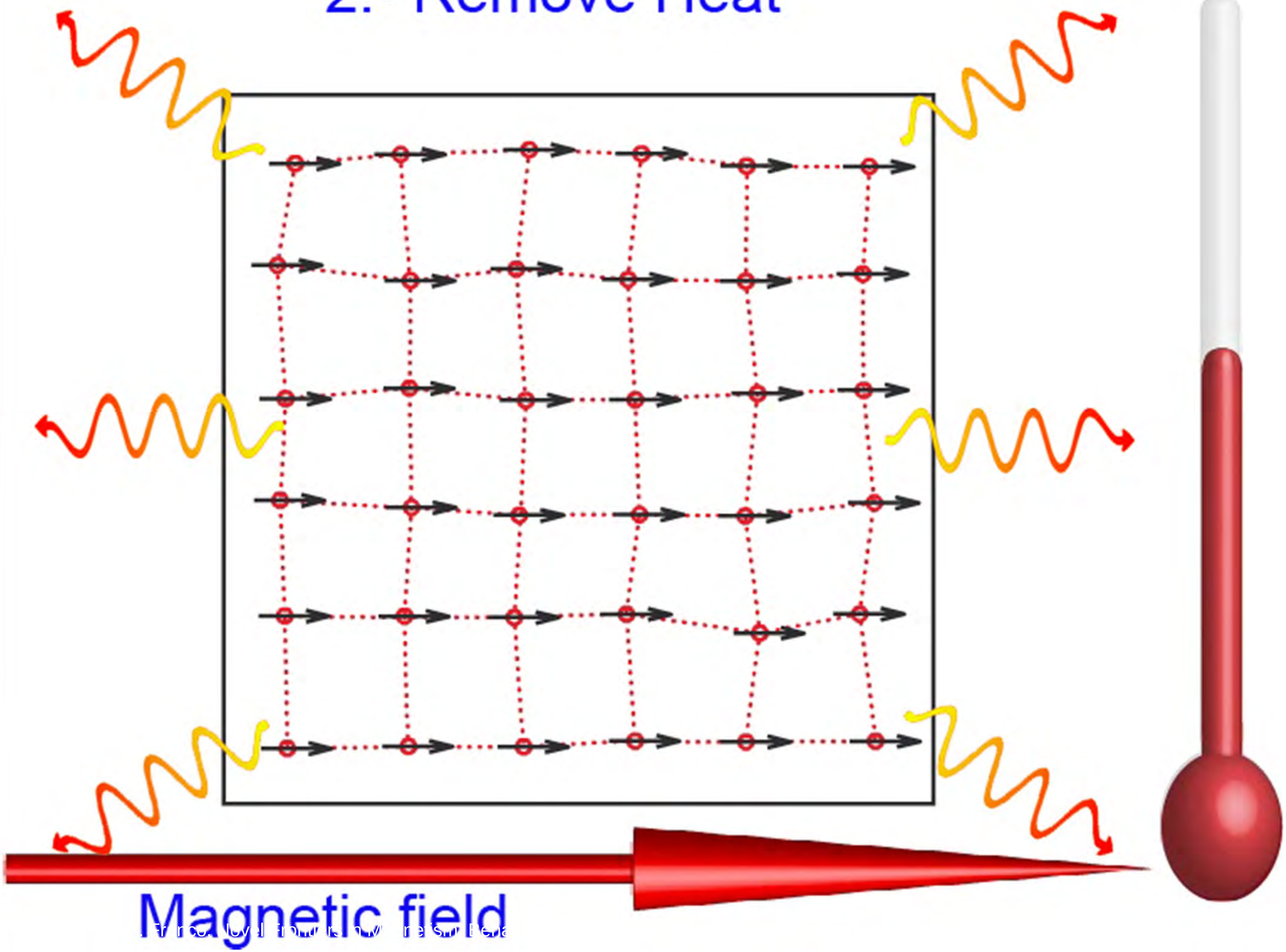




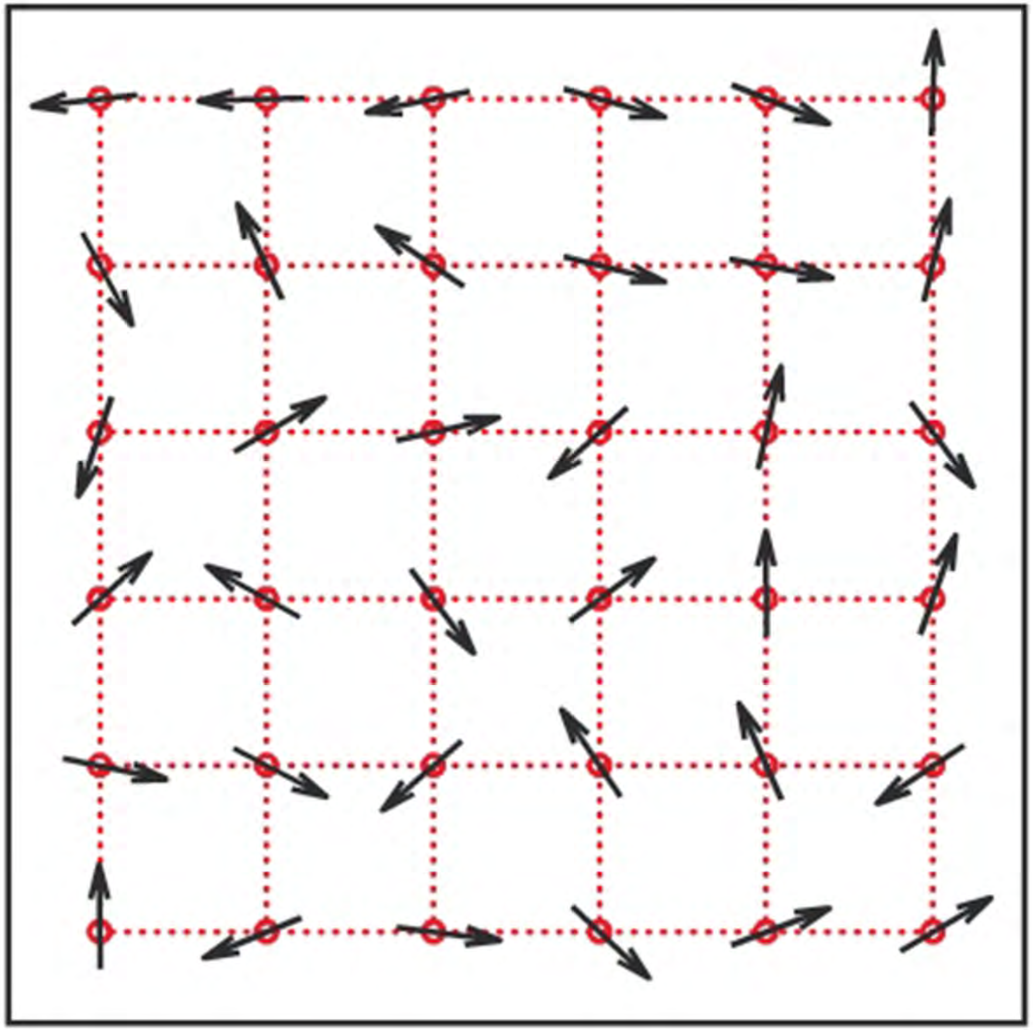
Refrigeration cycle
1.- Adiabatic Magnetization



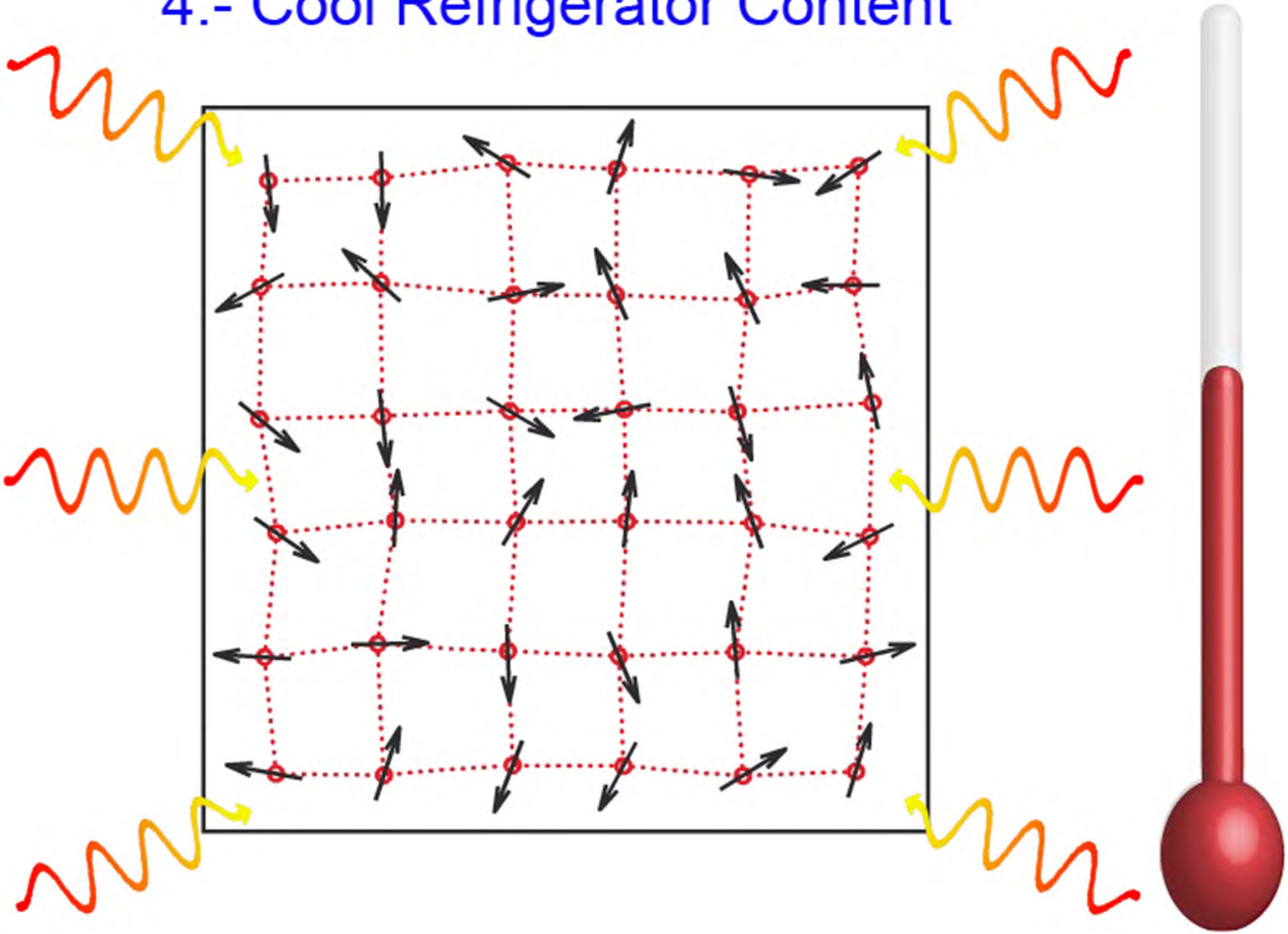
2.- Remove Heat



3.- Adiabatic Demagnetization



4.- Cool Refrigerator Content



Magnetic refrigeration: towards an increased energy efficiency

- Residential and Commercial sectors account for ~42% of the total energy consumption
  - Out of it, ~50% at homes and ~57% at commercial buildings is used for HVAC and cooling
- Larger energetic efficiency
  - 60% vs. 40 % of the theoretical limit
- Environmental benefits
- Reduction of vibration and noise
- Applied to low temperature refrigeration long time ago
- Room temperature:
  - Phase transition

Characteristic parameters

- Magnetic entropy change

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

- Adiabatic temperature change

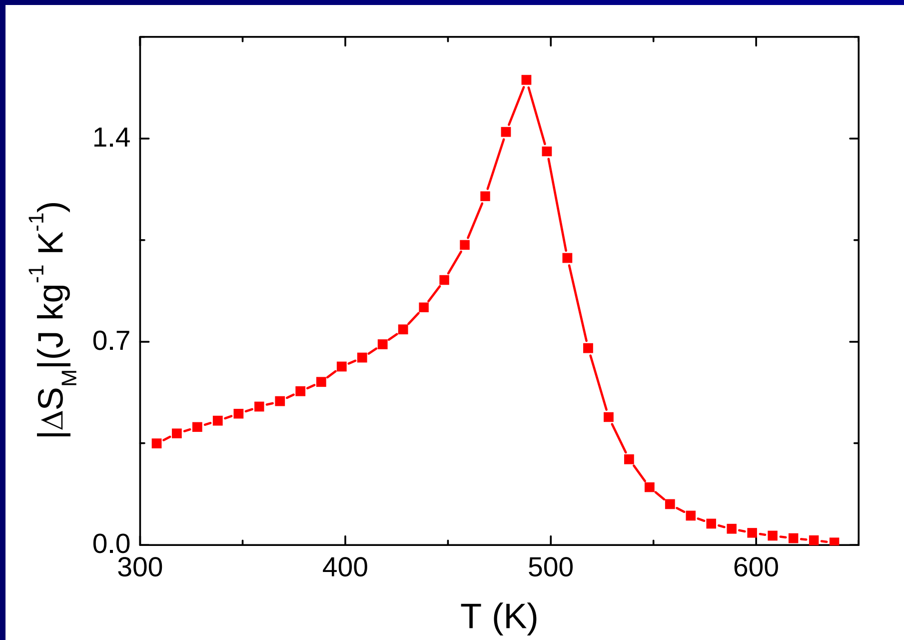
$$\Delta T_{ad} = \int_0^{H_{\max}} \frac{T}{c_p} \left(\frac{\partial M}{\partial T} \right)_H dH$$

- Refrigerant capacity RC
  - Measure of the amount of heat that can be transferred between the hot and cold reservoirs

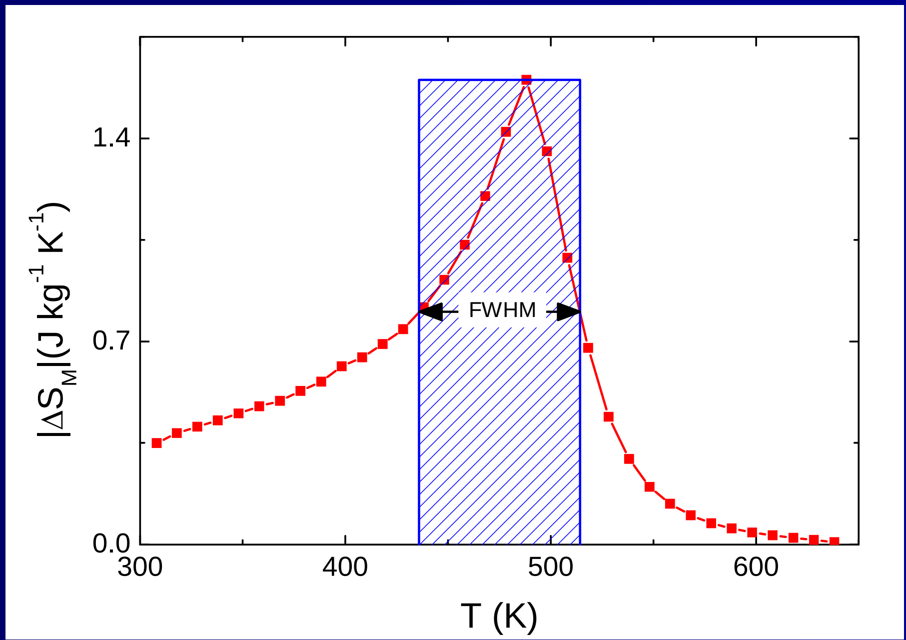
$$RC(\Delta H) = \int_{T_{cold}}^{T_{hot}} \Delta S_M (T, \Delta H)\, dT$$

  - Different definitions depending on how the integral is calculated

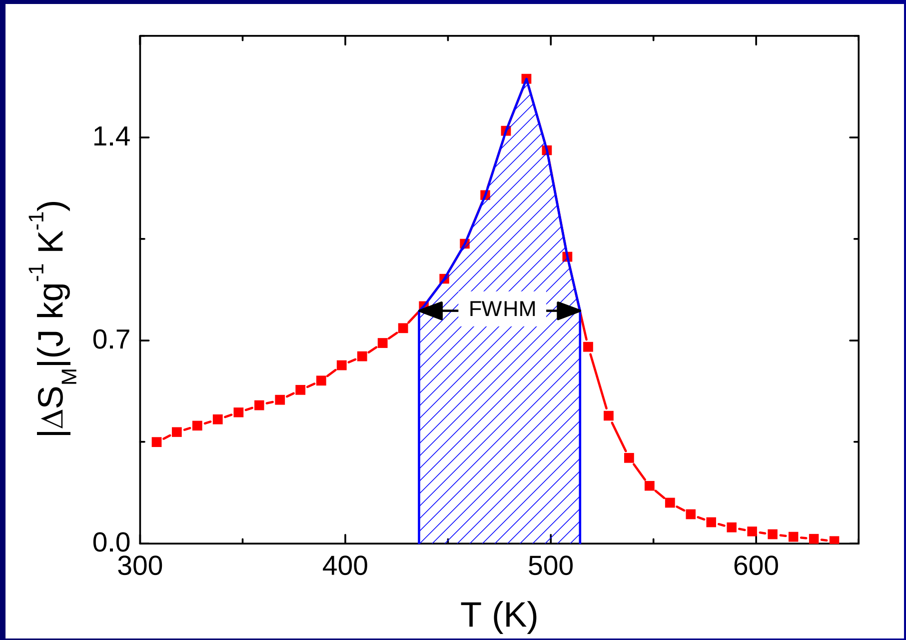
RC definitions



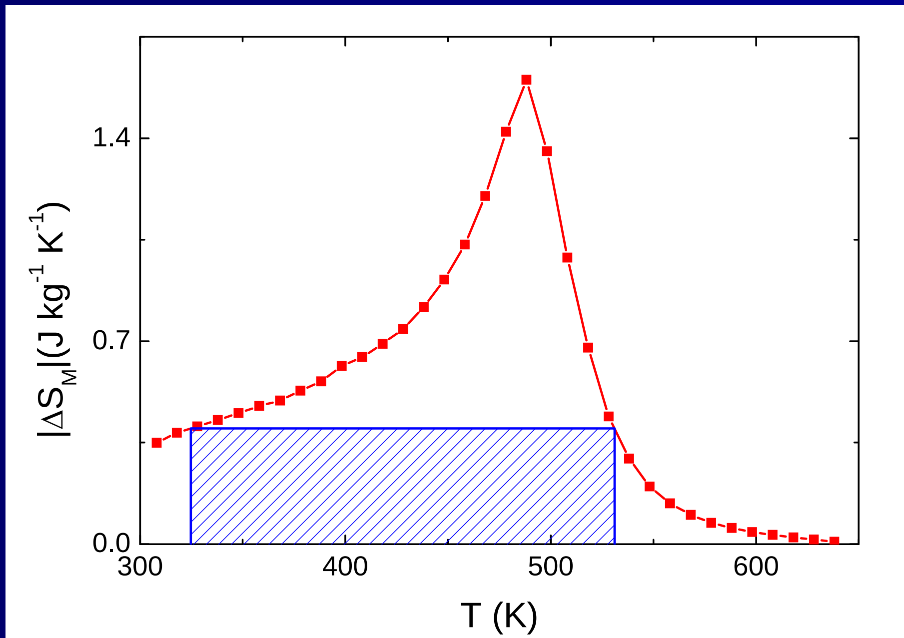
RC definitions: RC_{FWHM}



RC definitions: RC_{Area}



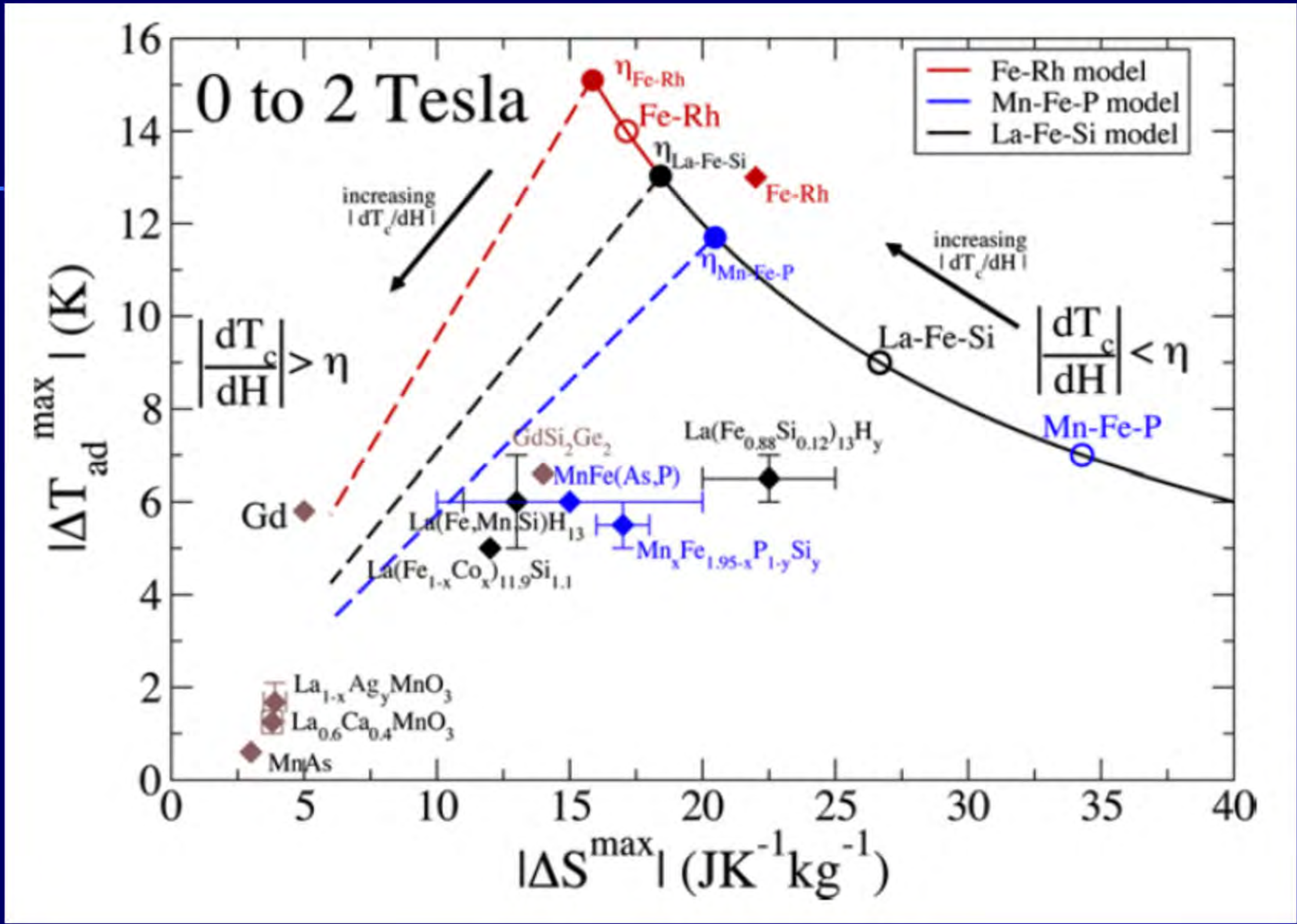
RC definitions: RC_{WP}



Magnetocaloric materials

- 1st order phase transition
  - Large peak
  - Reduced temperature span
  - Hysteretic
  - Magnetostructural transitions require large field
- 2nd order phase transition
  - Moderate peak
  - Large RC
  - Non hysteretic

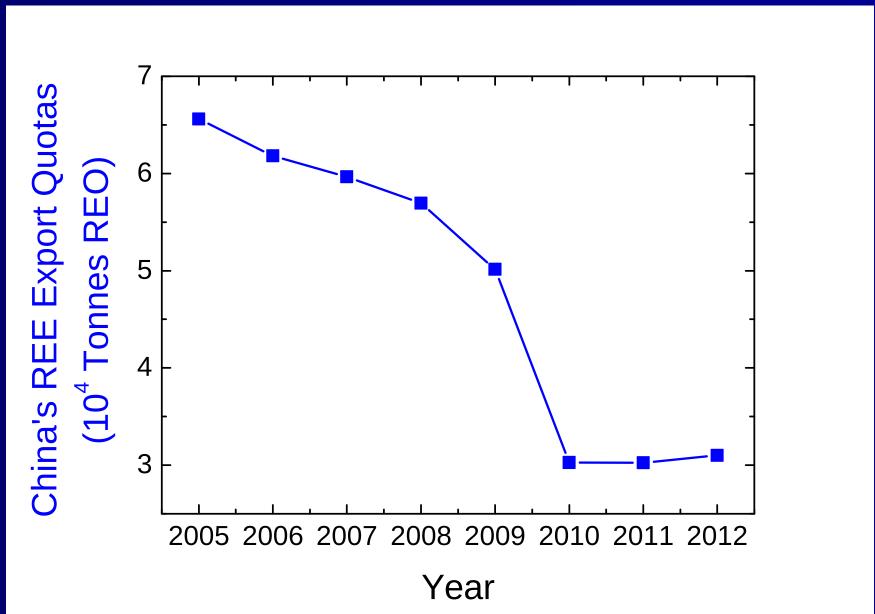
Objective:
Maximization of both ΔS_M^{pk} and *RC*



K. G. Sandeman, Scripta Materialia **67,** 566 **(2012)**

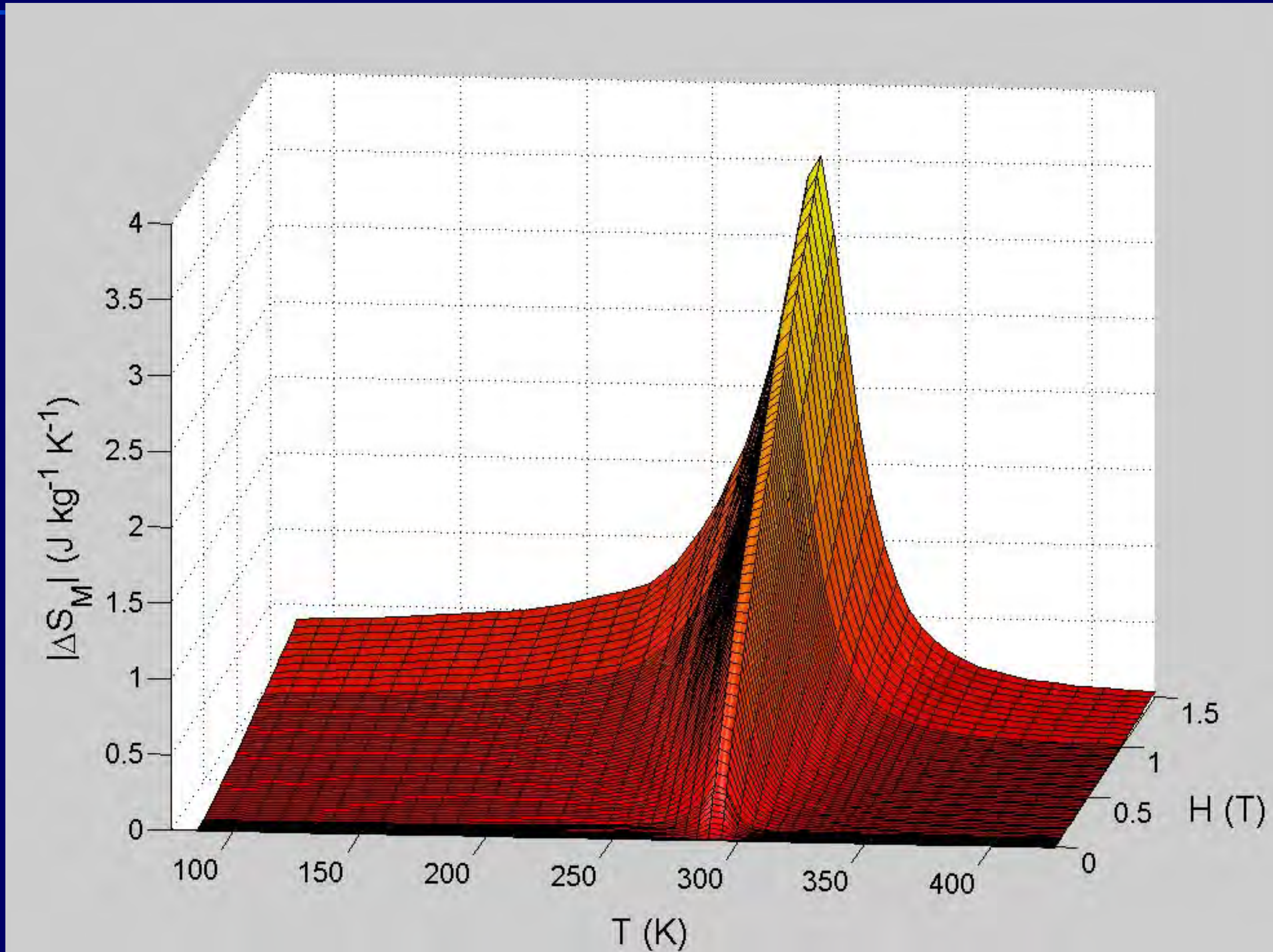
MCE materials : Should we avoid rare earths?

- China is the largest RE producer (95%)
- and has the largest reserves of RE (36%)



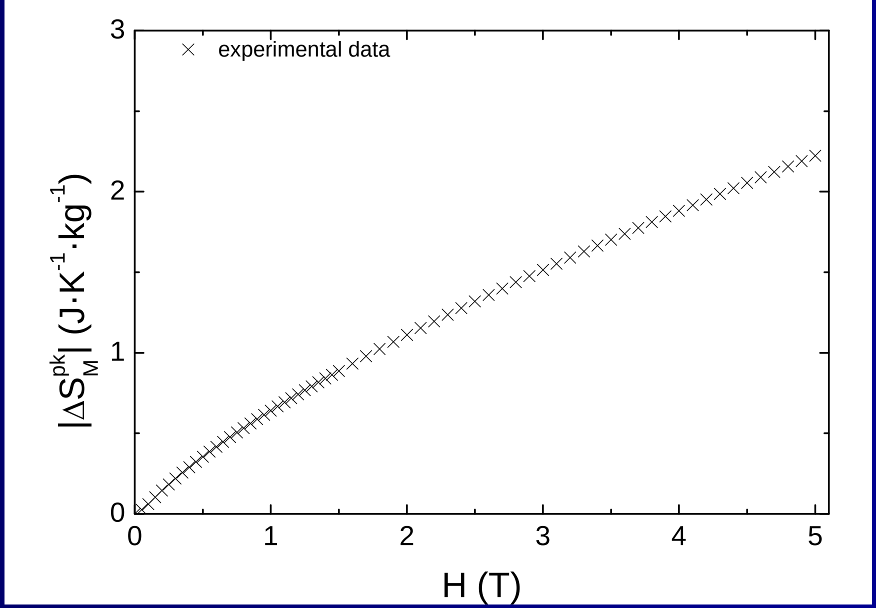
FIELD DEPENDENCE OF THE MAGNETOCALORIC EFFECT

Field dependence of ΔS_M



Description of $\Delta S_M(H)$

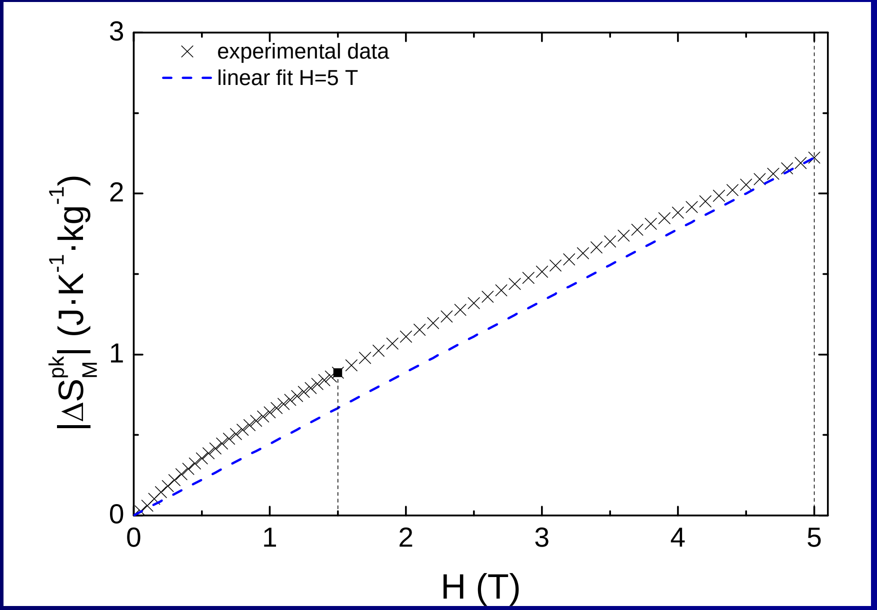
Why not using a linear extrapolation for the value of the peak?



Description of $\Delta S_M(H)$

Why not using a linear extrapolation?

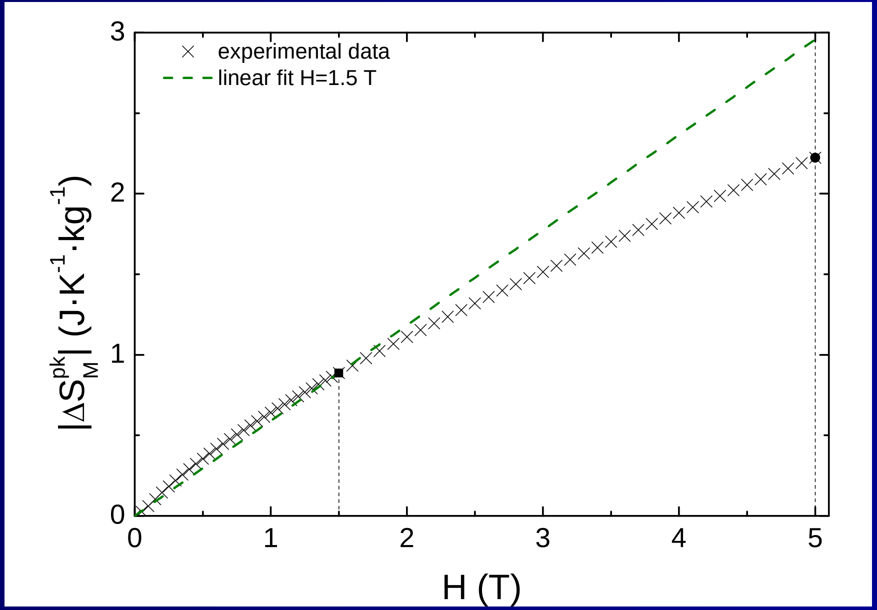
Error: ~24 %



Description of $\Delta S_M(H)$

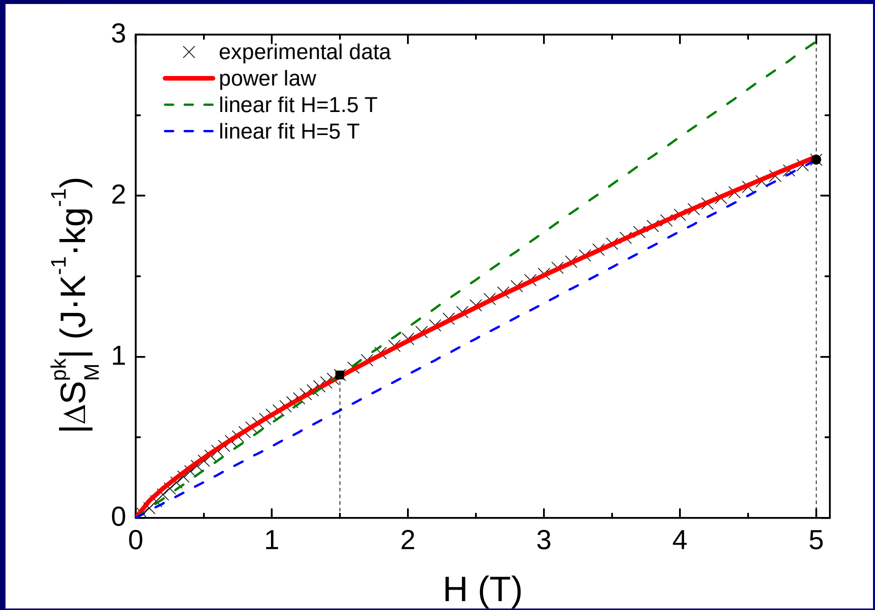
Why not using a linear extrapolation?

Error: ~30 %



Description of $\Delta S_M(H)$

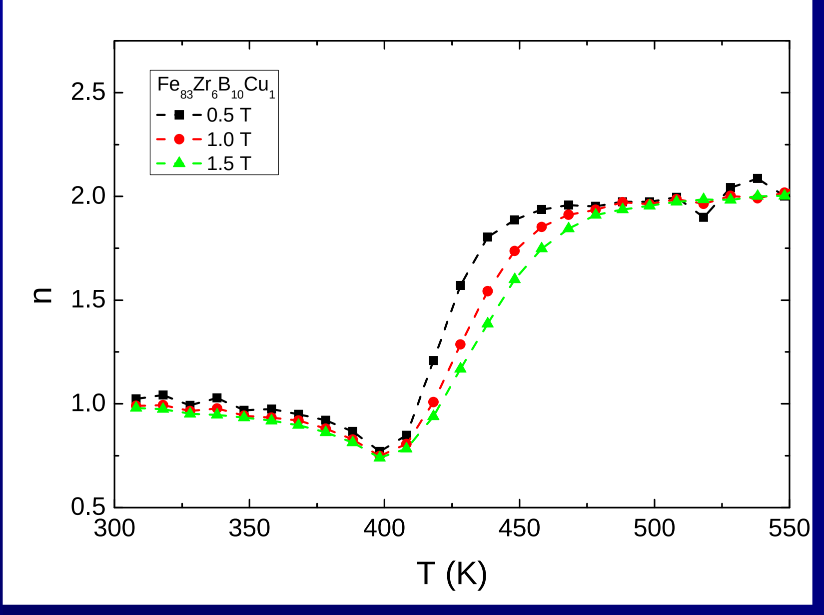
A power law represents properly the data



Field dependence of ΔS_M

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

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



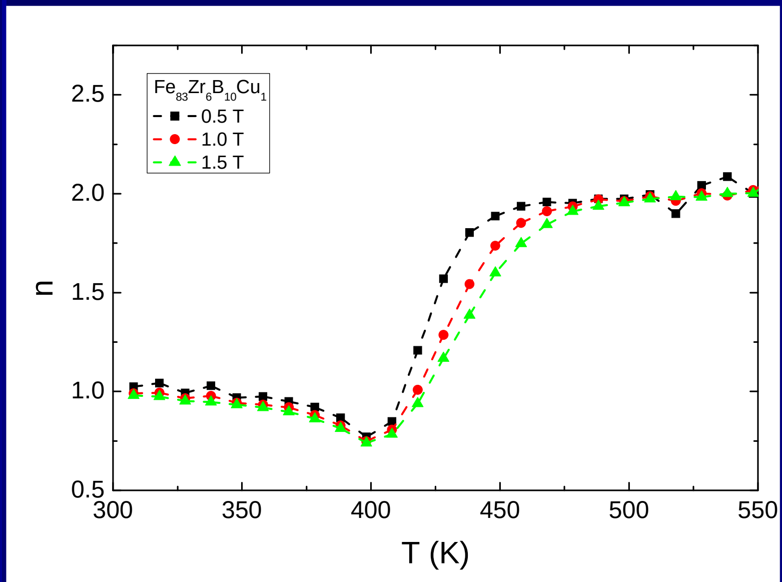
- T<<T$_C$: n=1
- T>>T$_C$: n=2
- T=T$_C$: $n = 1 + \frac{1}{\delta}\left(1 - \frac{1}{\beta}\right)$
- MCE can be used to determine critical exponents

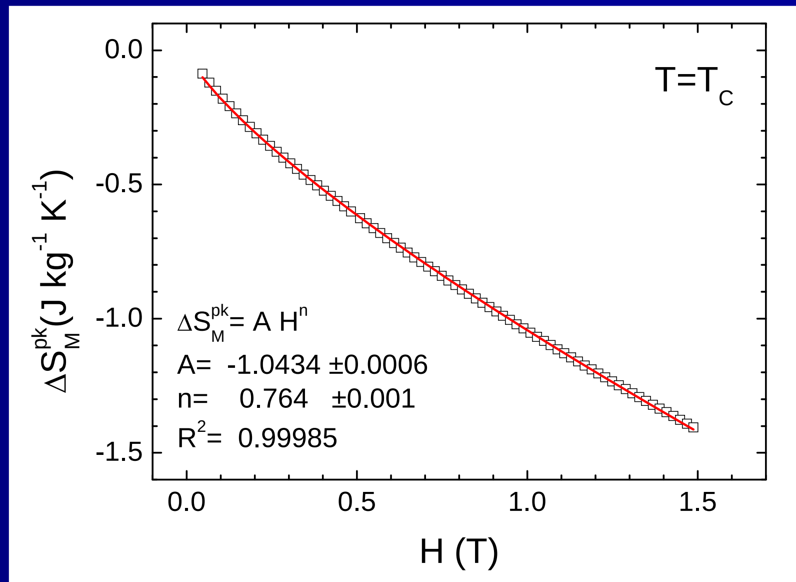
V. Franco, J.S. Blázquez, and A. Conde, J. Appl. Phys. 100 (2006) 064307
V. Franco, A. Conde, Int. J. Refrig. 33 (2010) 465

n from two methods

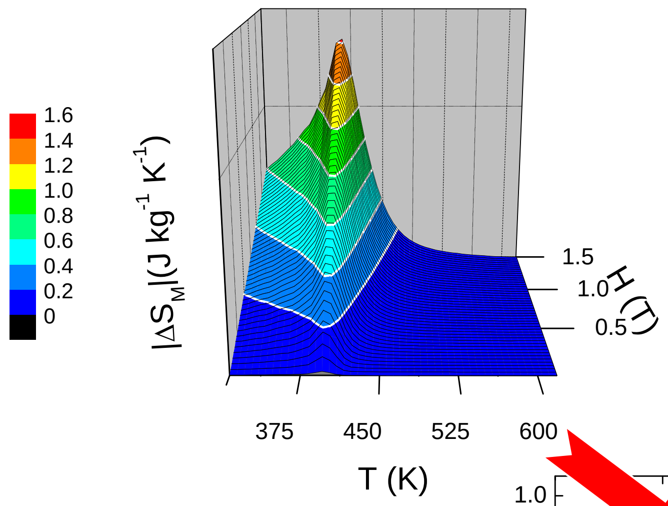
$$\Delta S_M \propto H^n$$

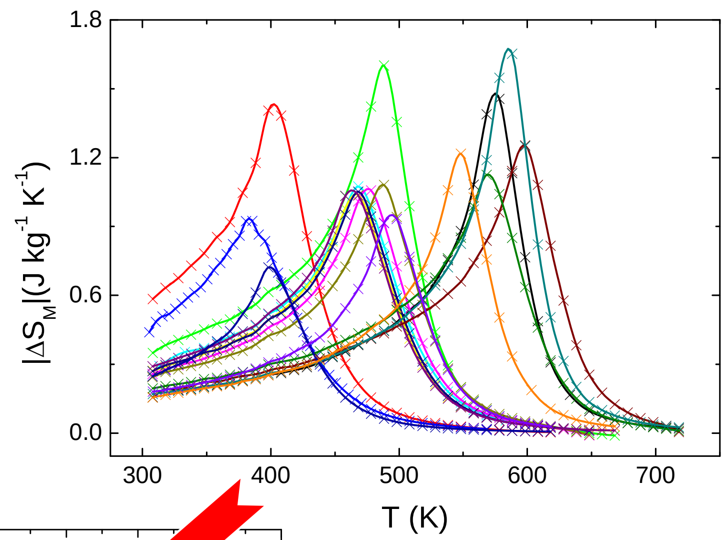
$$n = \frac{d \ln|\Delta S_M|}{d \ln H}$$

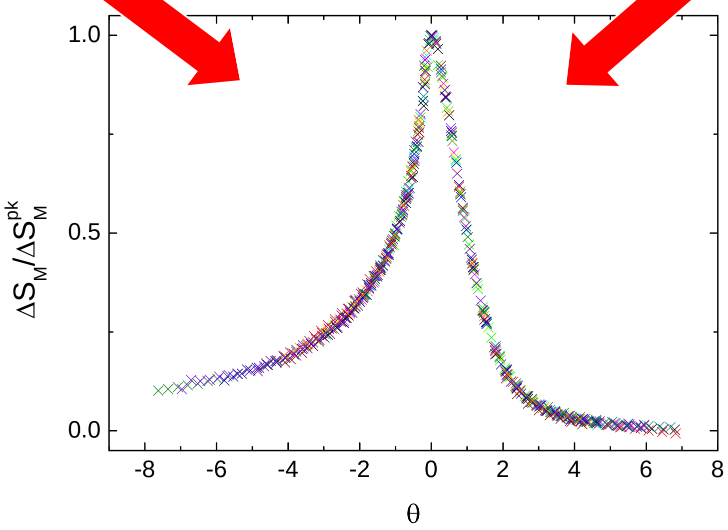




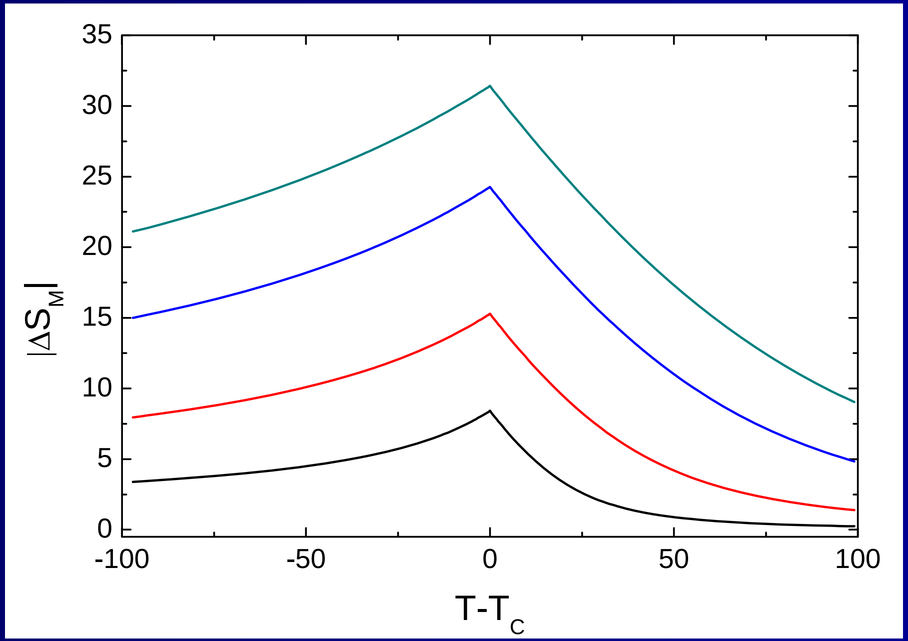
Universal curve for ΔS_M



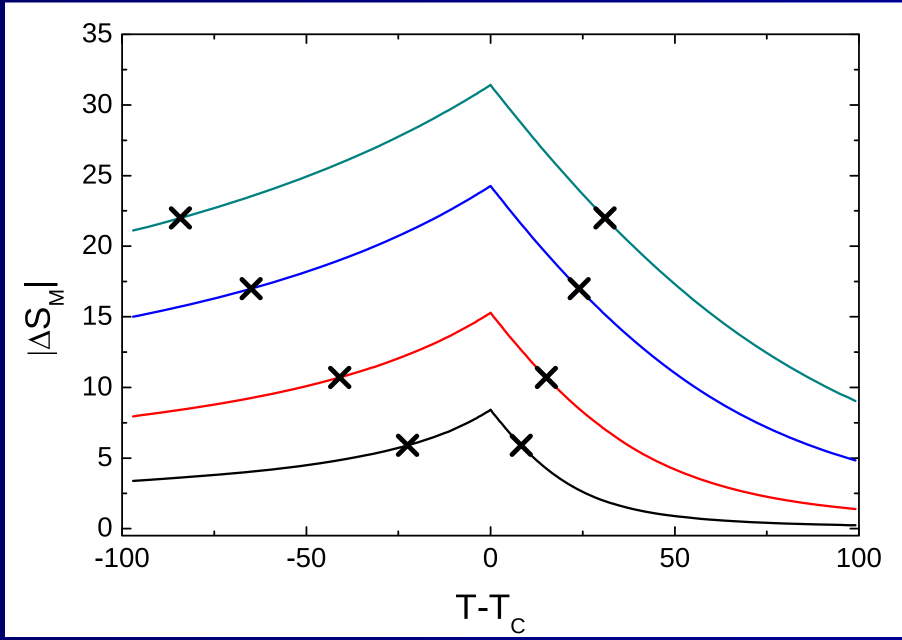




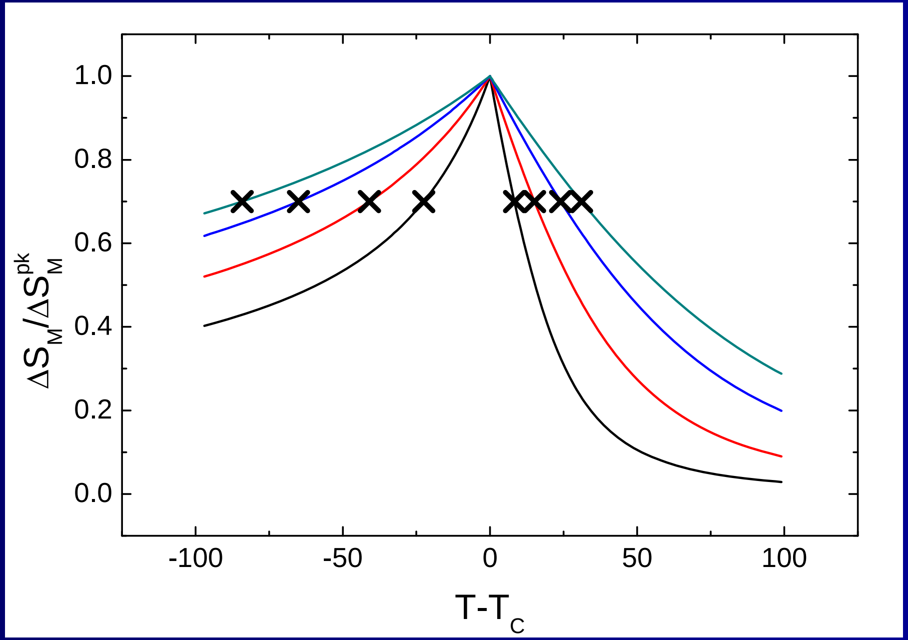
“Measurements” for different applied fields



Selection of equivalent points (with respect to the peak)

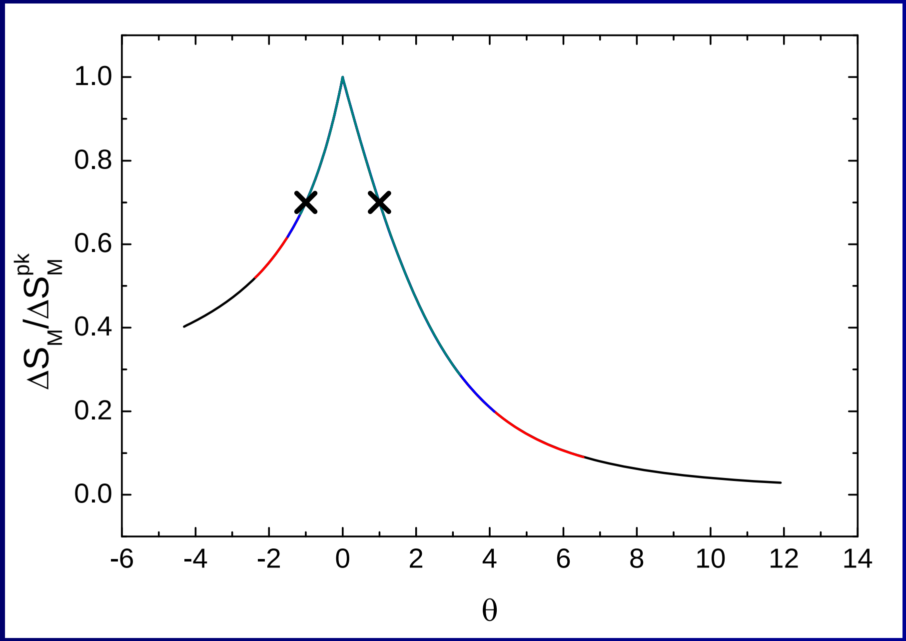


Rescale (normalize) the vertical axis



Rescale the temperature axis

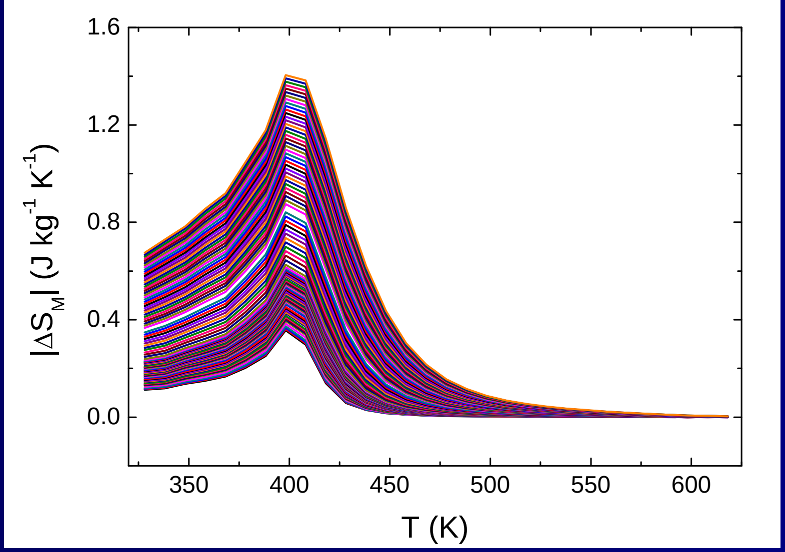
The use of a single reference temperature is also posible... most of the times

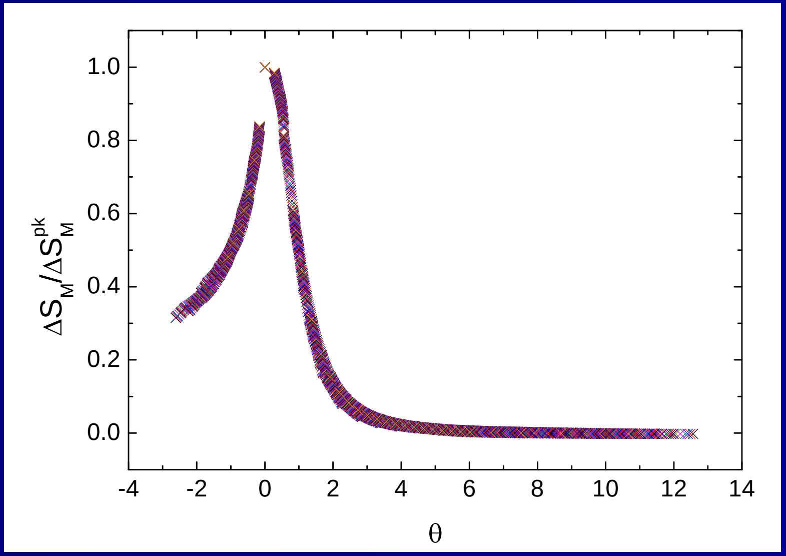


$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C); & T \le T_C \\ (T - T_C)/(T_{r2} - T_C); & T > T_C \end{cases}$$

Universal curve for the field dependence of ΔS_M

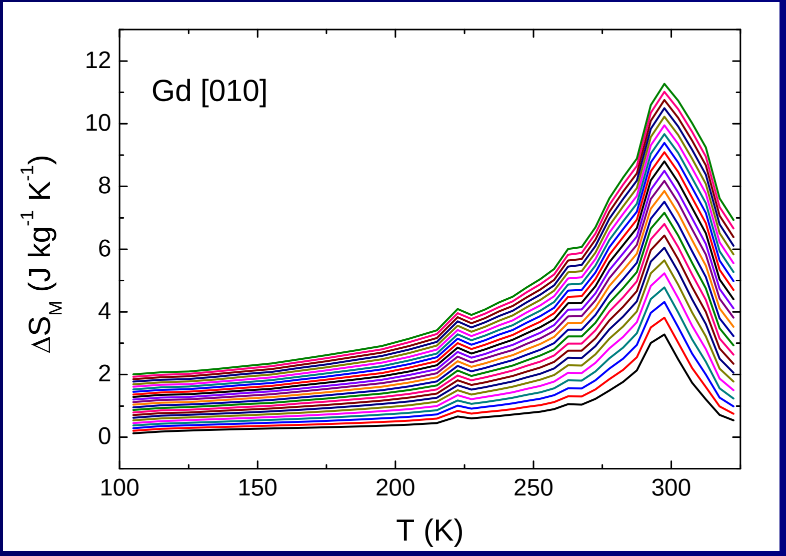
96 curves; 0.25 – 1.5 T

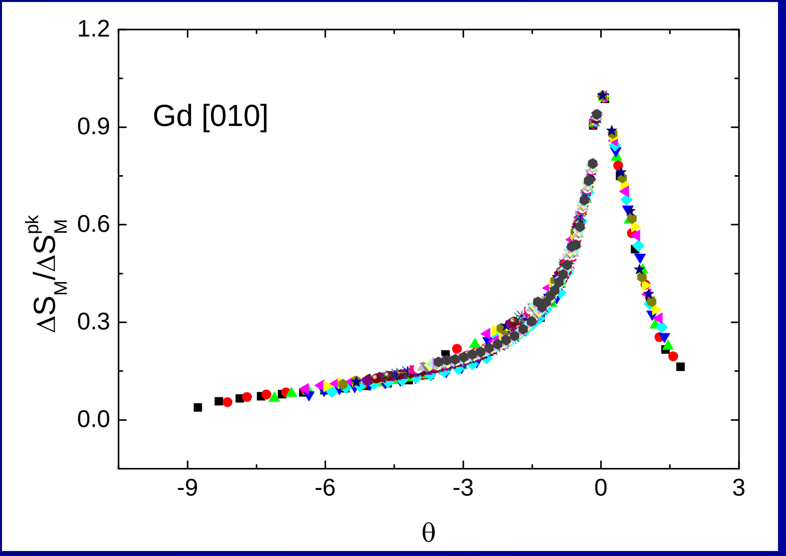




V. Franco, J.S. Blázquez, and A. Conde, Appl. Phys. Lett. 89 (2006) 222512

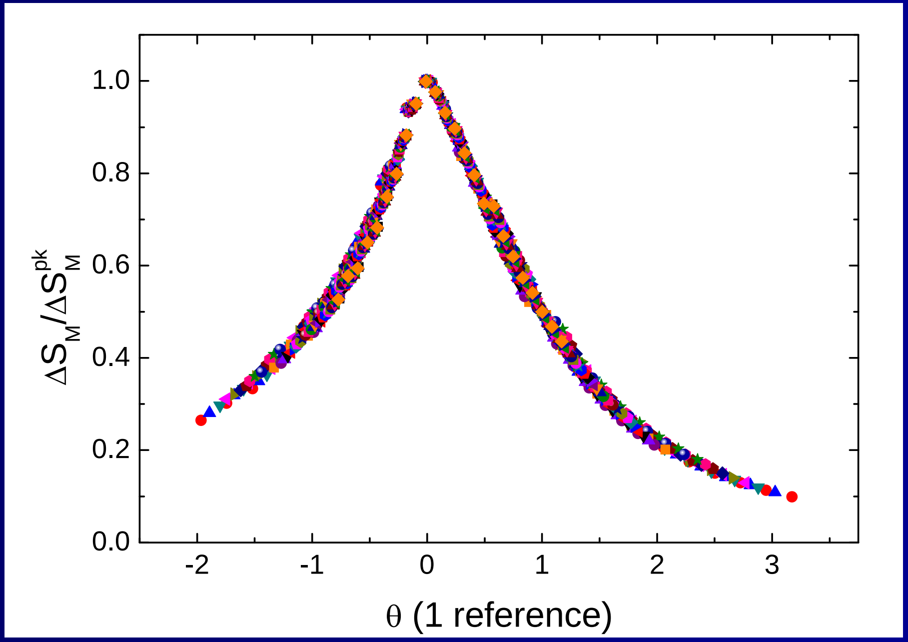
Gd (single crystal)





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

$TbCo_2$

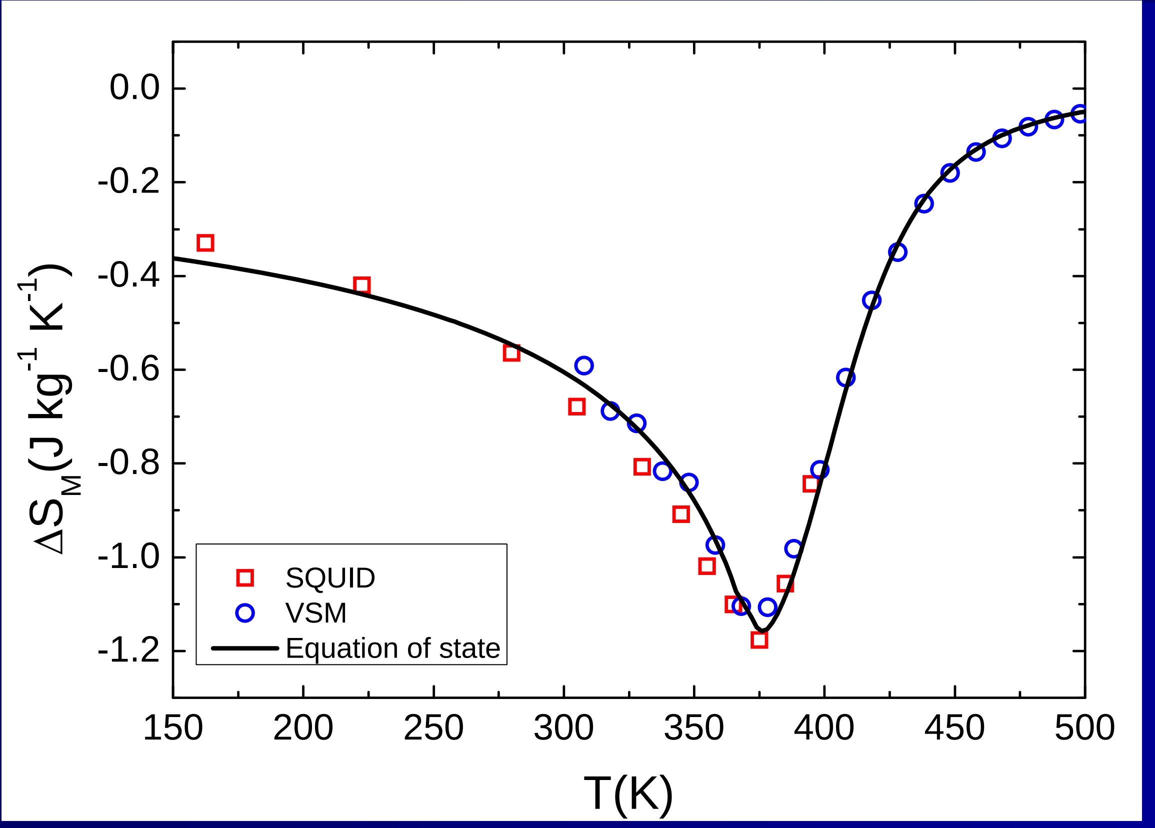


Q. Y. Dong, H. W. Zhang, J. R. Sun, B. G. Shen, and V. Franco, J. Appl. Phys. 103 (2008) 116101

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 neither EOS, nor the critical exponents*

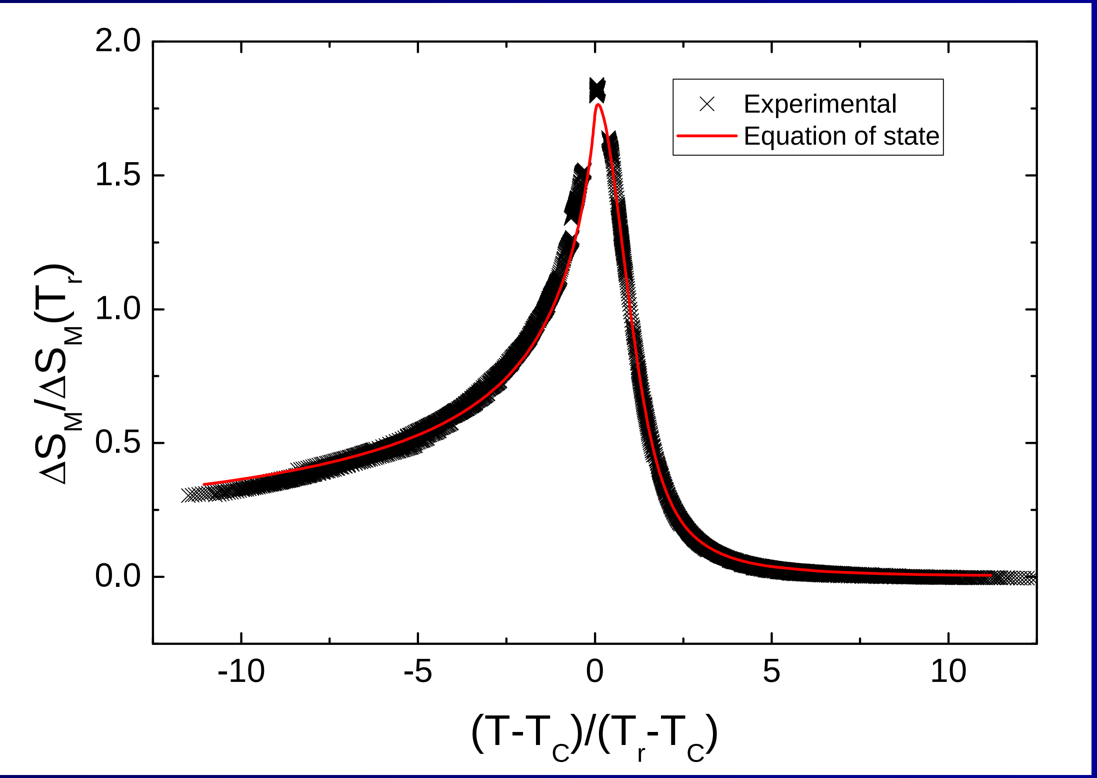
EOS-predictions



V. Franco, A. Conde, L.F. Kiss, J. Appl. Phys. 104 (2008) 033903

Comparison with theory

$Fe_{78}Co_5Zr_6B_5Ge_5Cu_1$



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

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

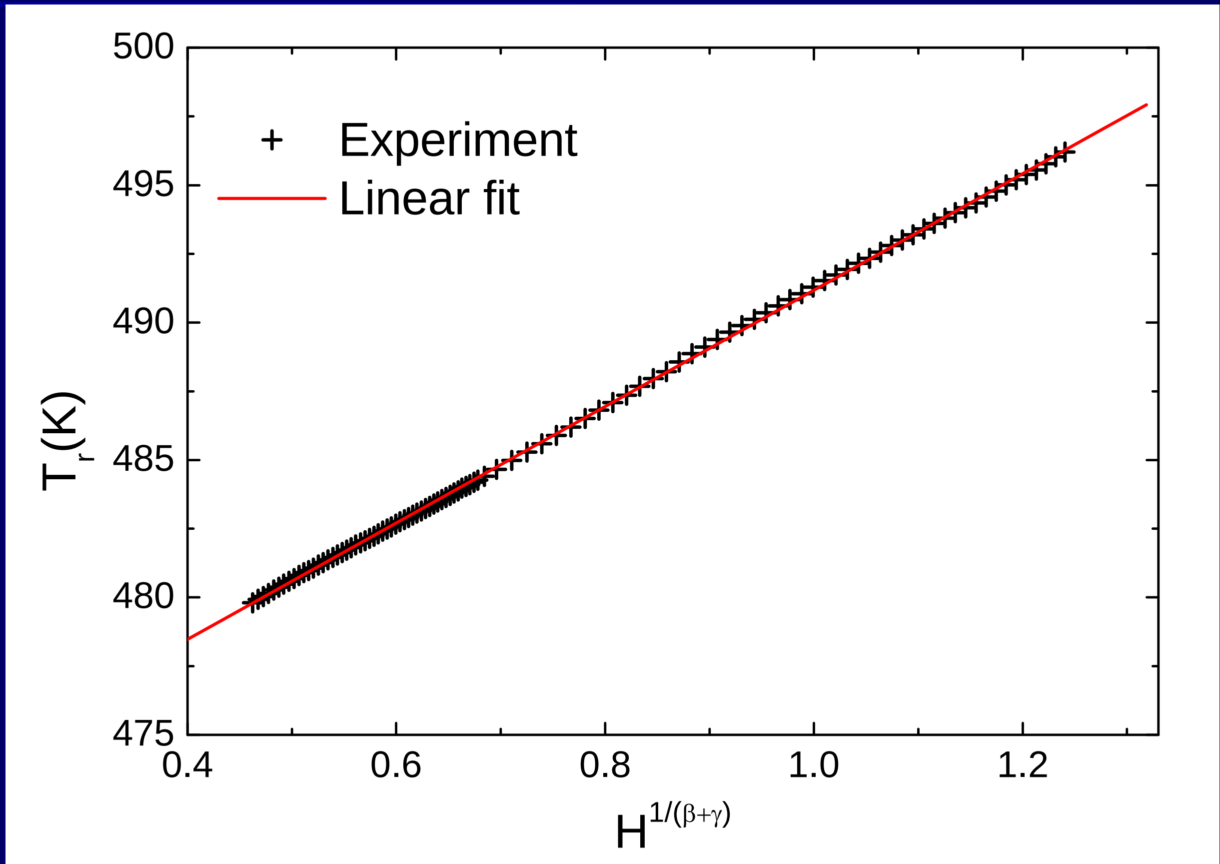
V. Franco, A. Conde, J.M. Romero-Enrique, J. S. Blázquez, J. Phys. Condens. Matter 20 (2008) 285207

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}	$1 + 1/\delta\left(1 - 1/\beta\right) = \left(1 - \alpha\right)/\Delta$
RC_{Area} **or** RC_{FWHM}	$1 + 1/\delta$

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

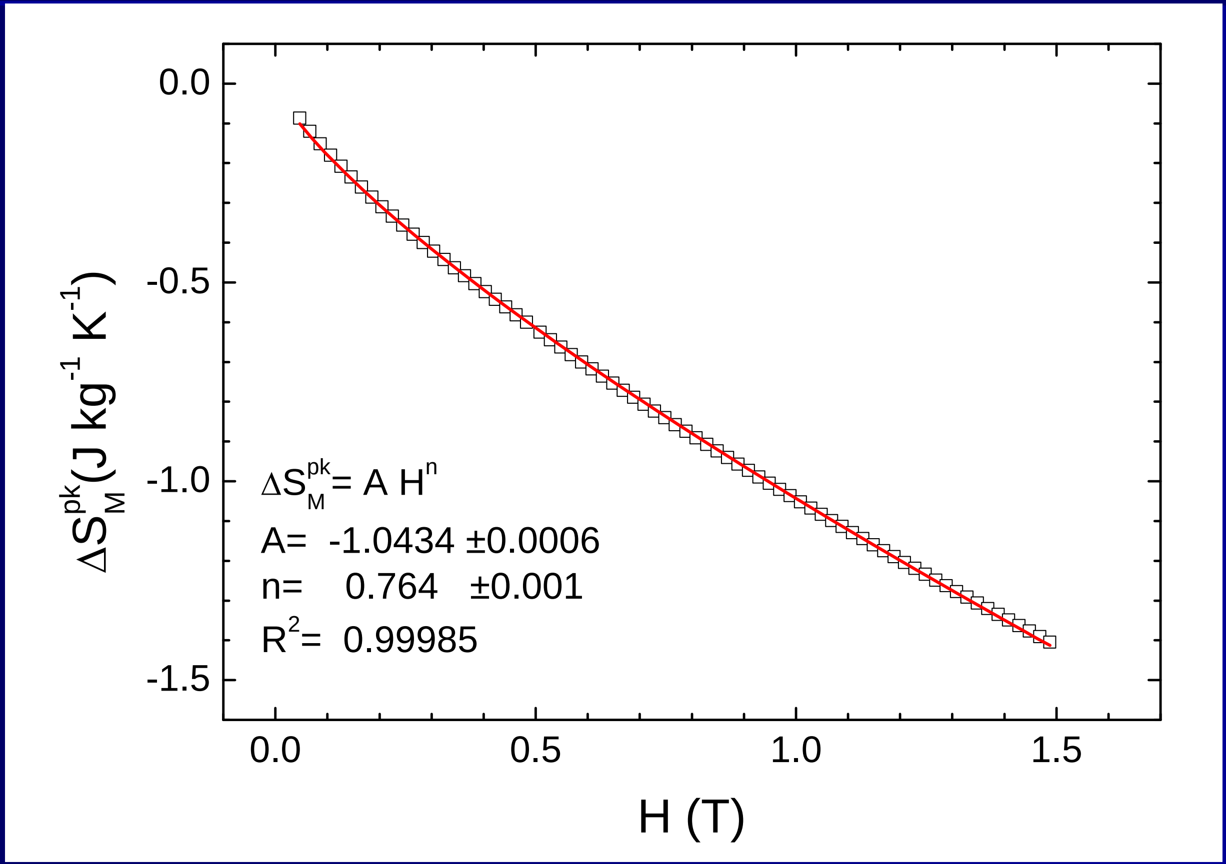
V. Franco, A. Conde, Int. J. Refrig. 33 (2010) 465

Field dependence of the reference temperature

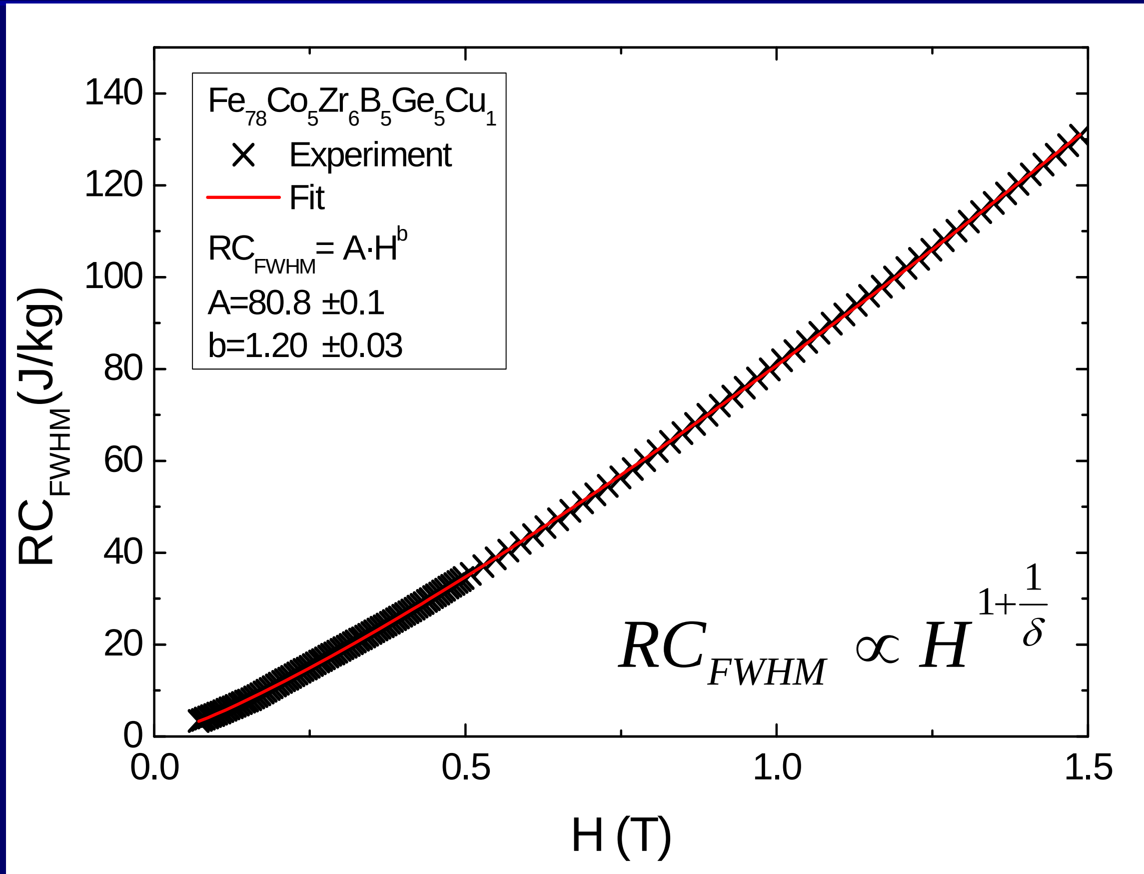


$Fe_{78}Co_5Zr_6B_5Ge_5Cu_1$

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)

ANALYZING THE ORDER OF A PHASE TRANSITION

Alternative to other purely magnetic procedures

Banerjee criterion

- Landau expansion of free energy leads to

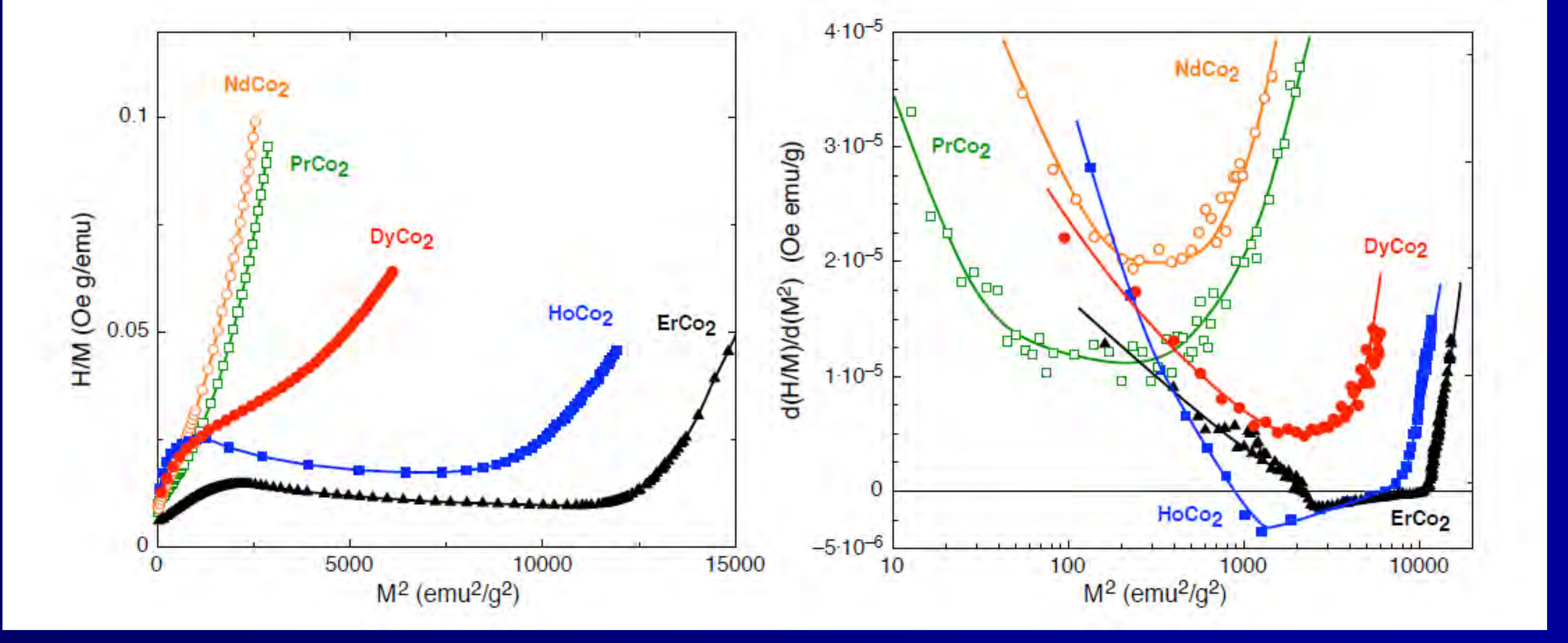
$$H = aM + bM^3 = a'(T - T_C)M + bM^3$$

- 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

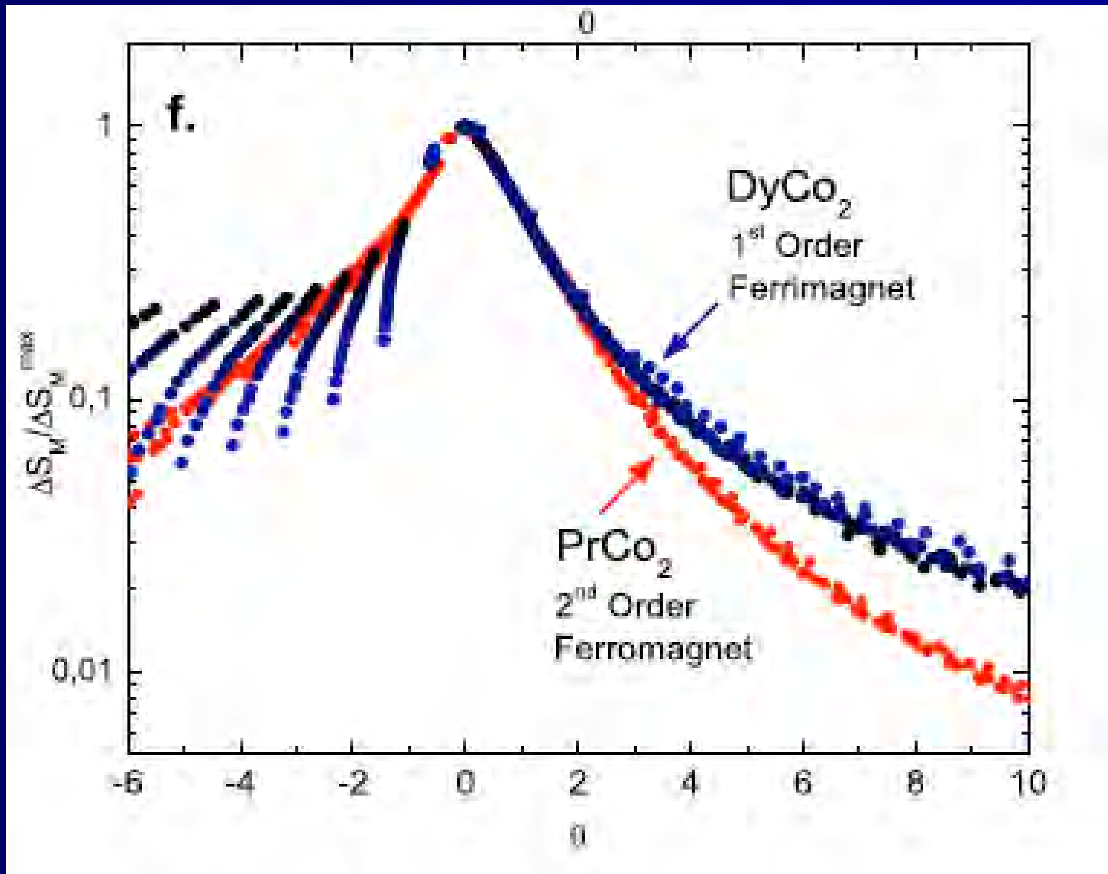
- Banerjee criterion: $DyCo_2$?



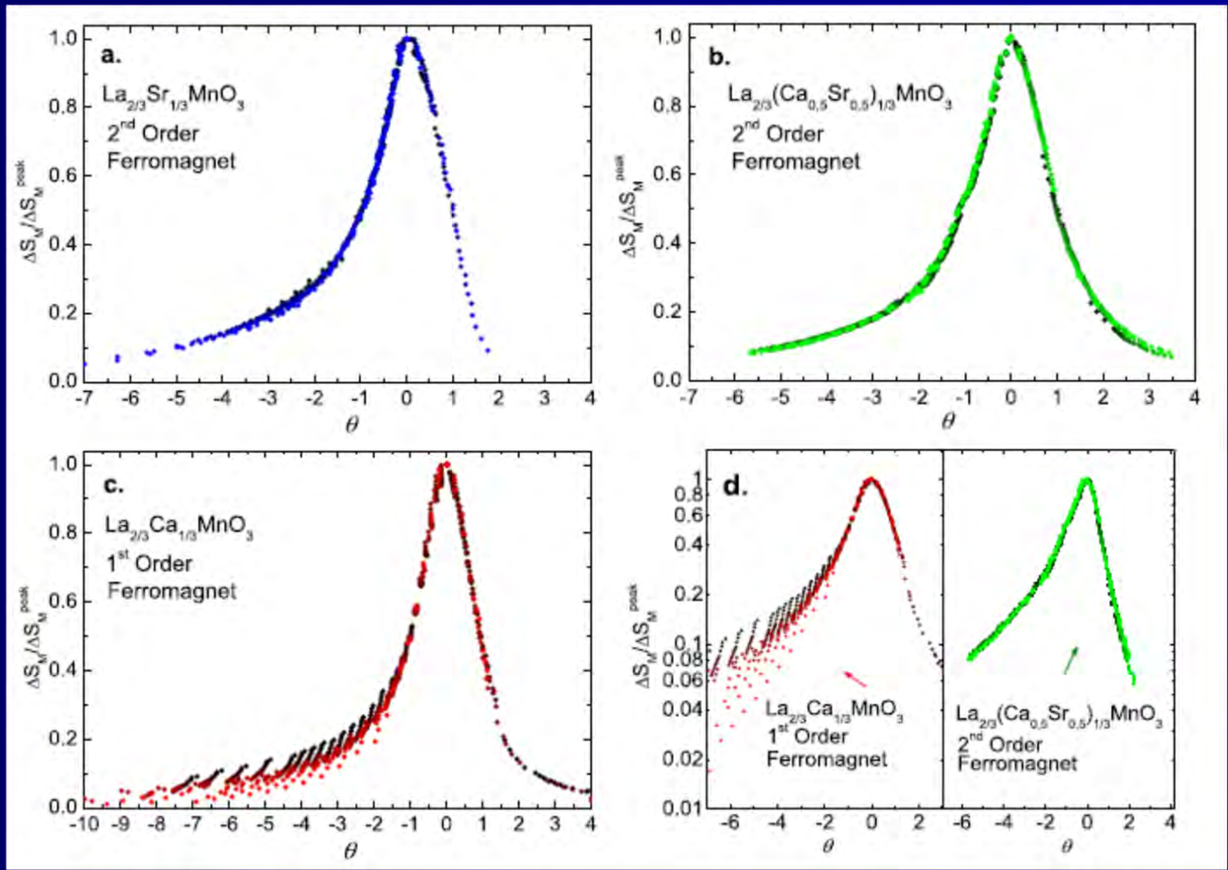
- Calorimetric measurements indicate that $DyCo_2$ is first order

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

The universal curve: a new criterion for determining the order of phase transitions



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



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?

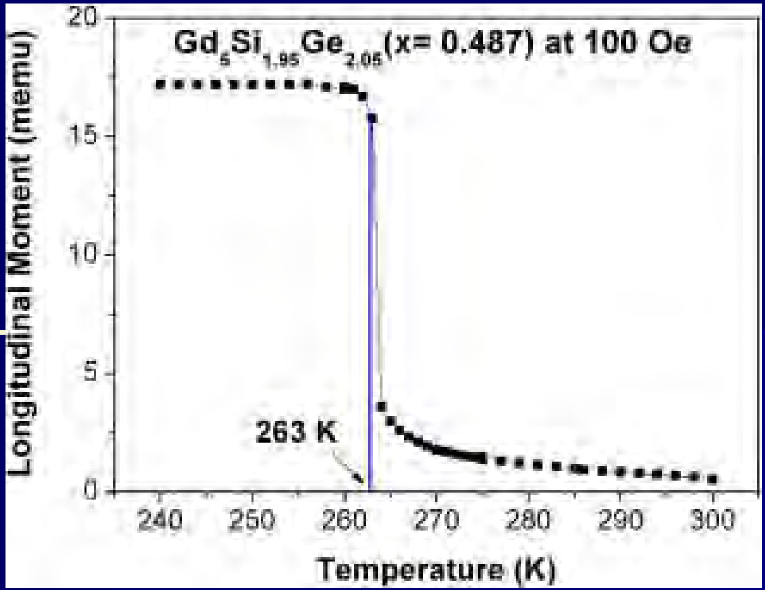
- Banerjee criterion was based on a particular equation of state (Landau expansion)
- We are not imposing any restriction to the shape of the equation of state
  - We only asume that second order phase transitions scale
  - The universal curve is a more general approach to determine the order of the phase transition

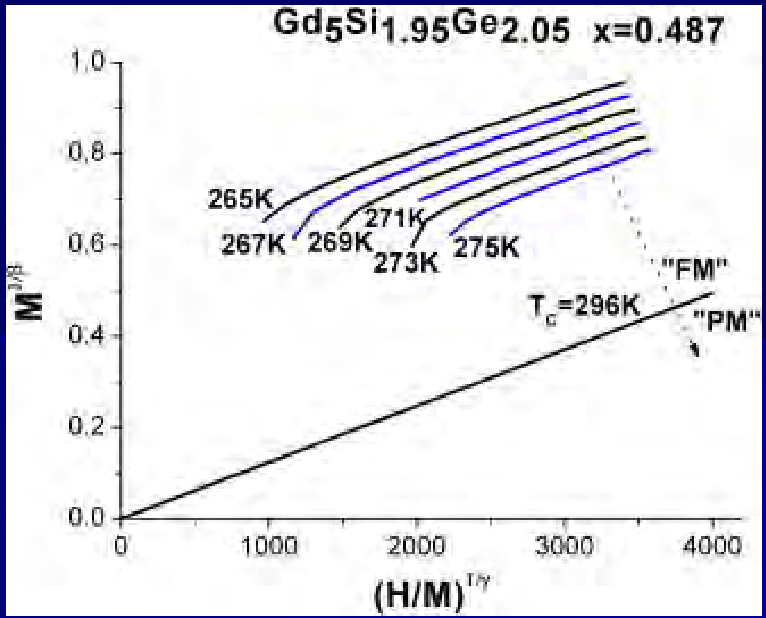
DETERMINATION OF CRITICAL EXPONENTS

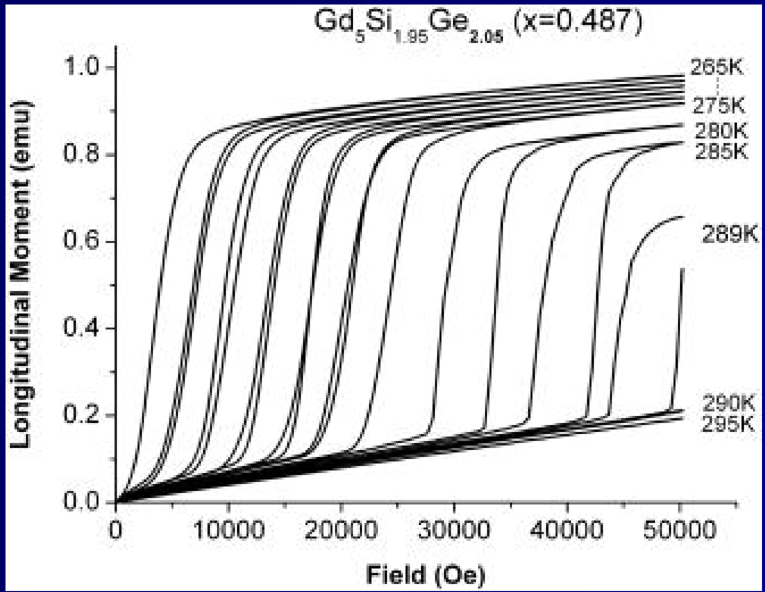
When other procedures fail

The problem

- $Gd_5Si_2Ge_2$ has a structural phase transition:
  - The low temperature phase disappears before it reaches its Curie temperature.
- Tentative solution for determining T_c:
  - 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

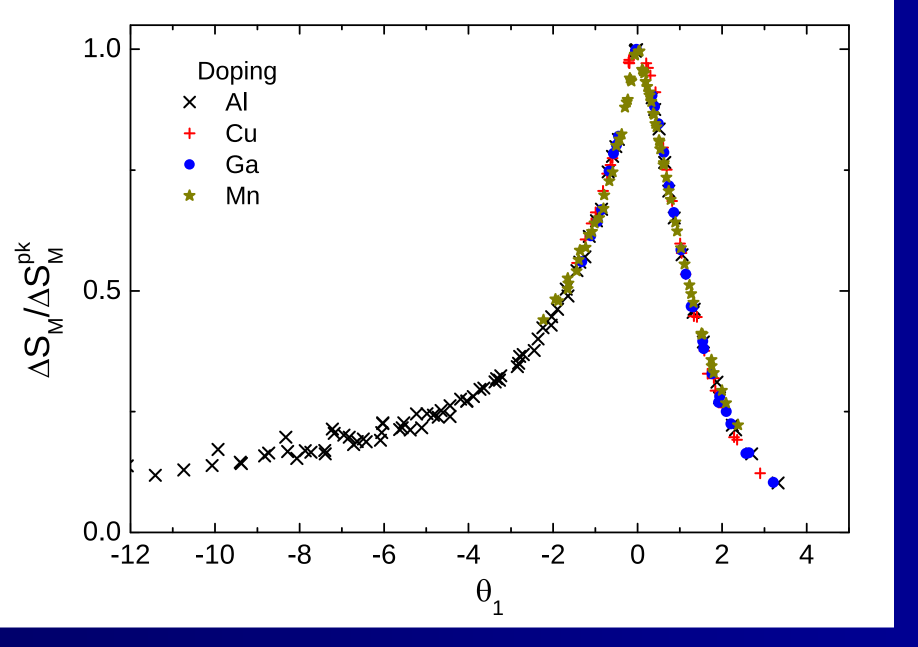
- In the undoped compound, the low temperature phase is orthorhombic and it transforms to a monoclinic phase at temperatures above 270 K.

- 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



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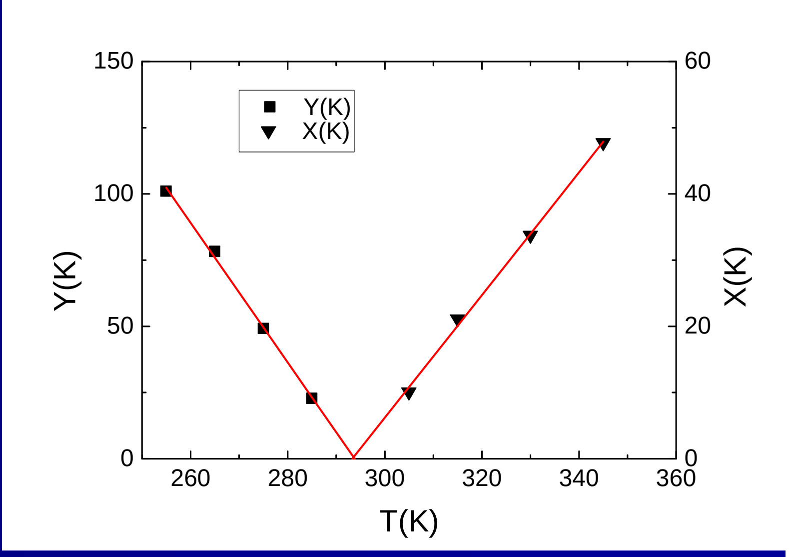
Kouvel-Fisher method

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

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

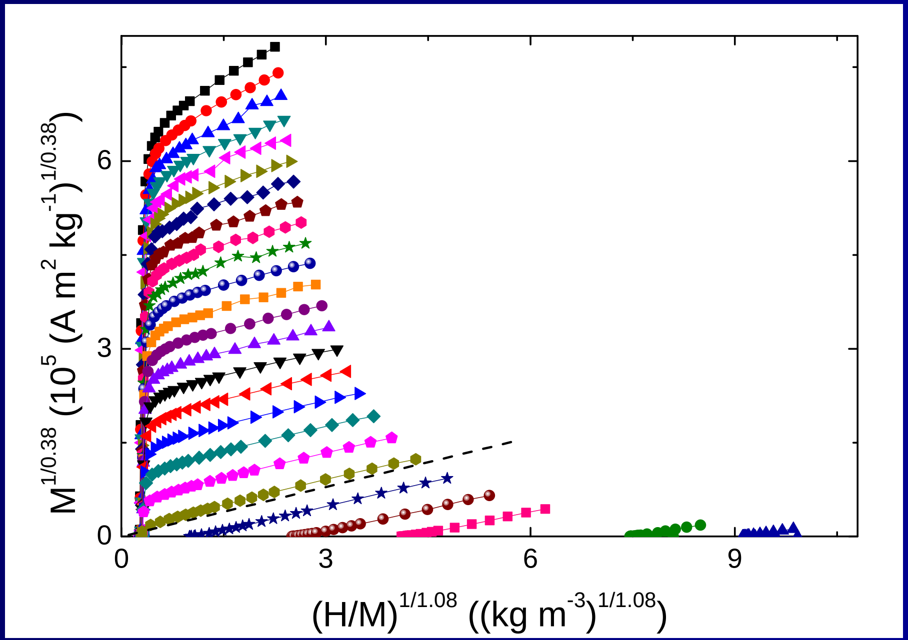
$$Y(T) = M_0\left(dM_0/dT\right)^{-1} = \left(T - T_C\right)/\beta$$

  - Extract exponents and T_c
  - Iterate until convergence

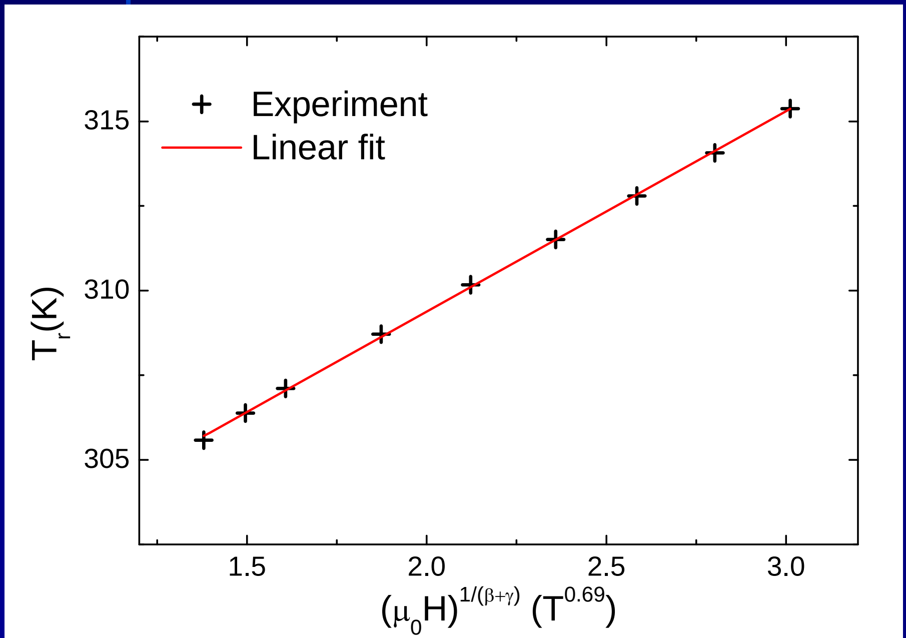


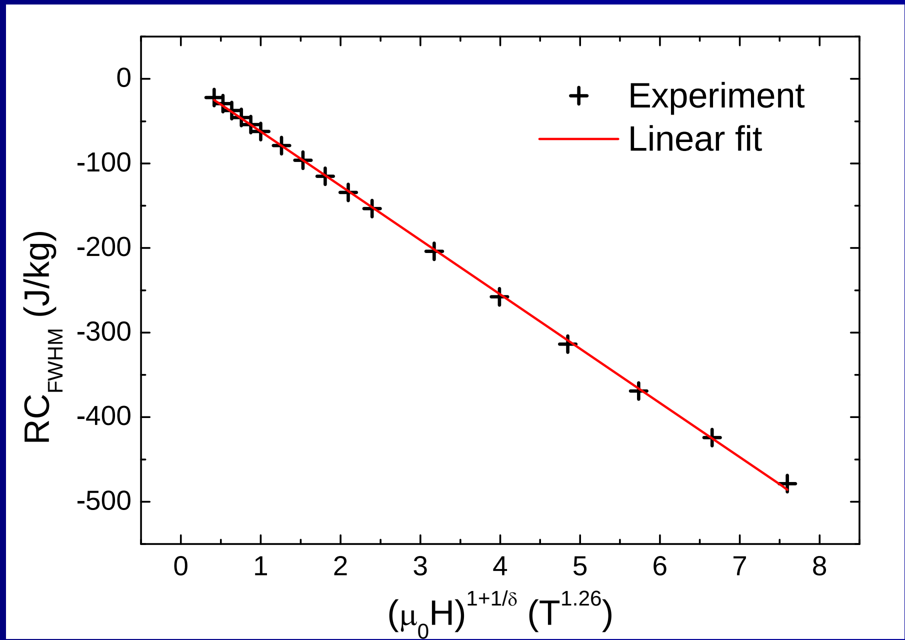
A fully second order case

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

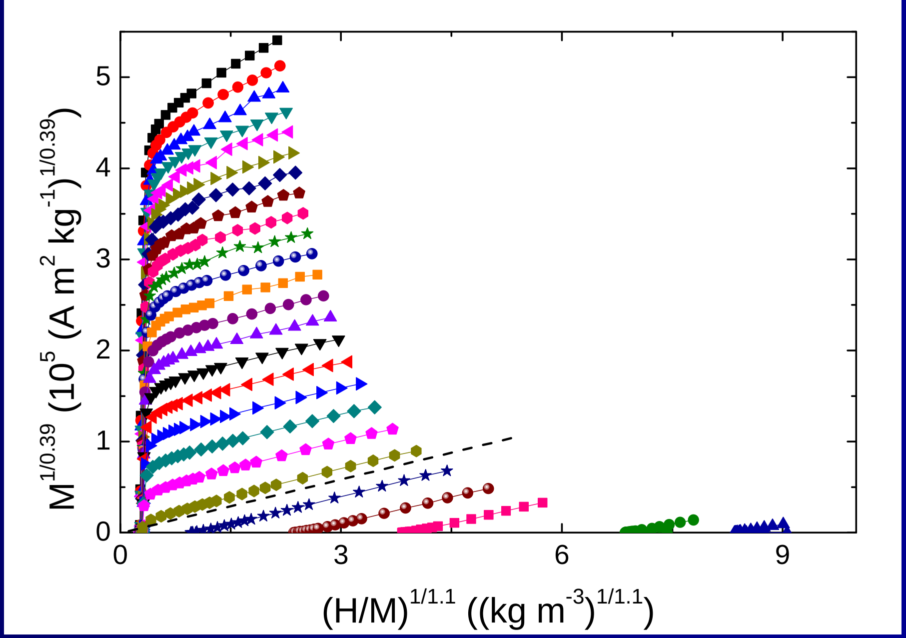


Scaling of MCE using K-F exponents



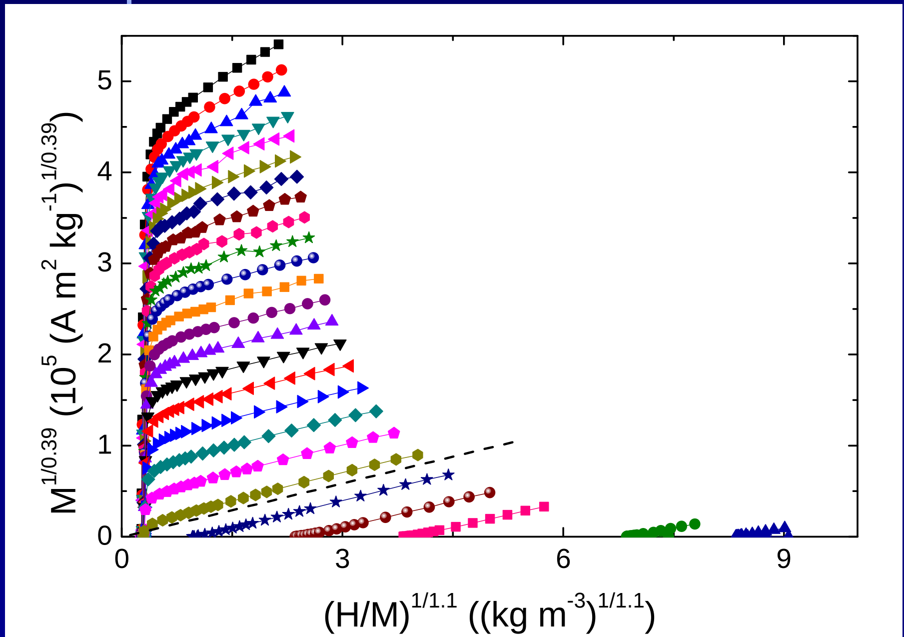


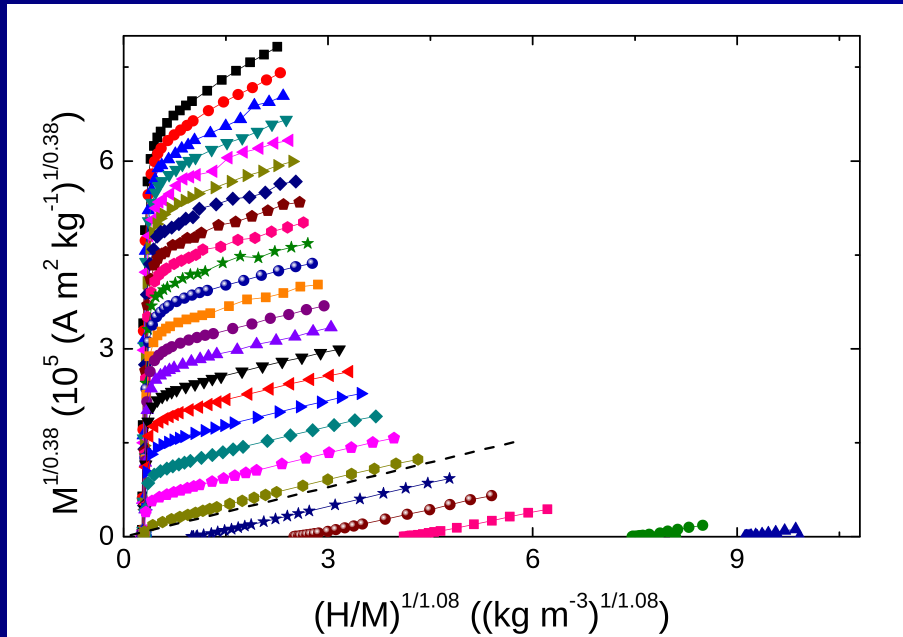
Arrott plot using exponents obtained from MCE



Exponents were extracted from the scaling of the magnetic entropy change

No qualitative difference

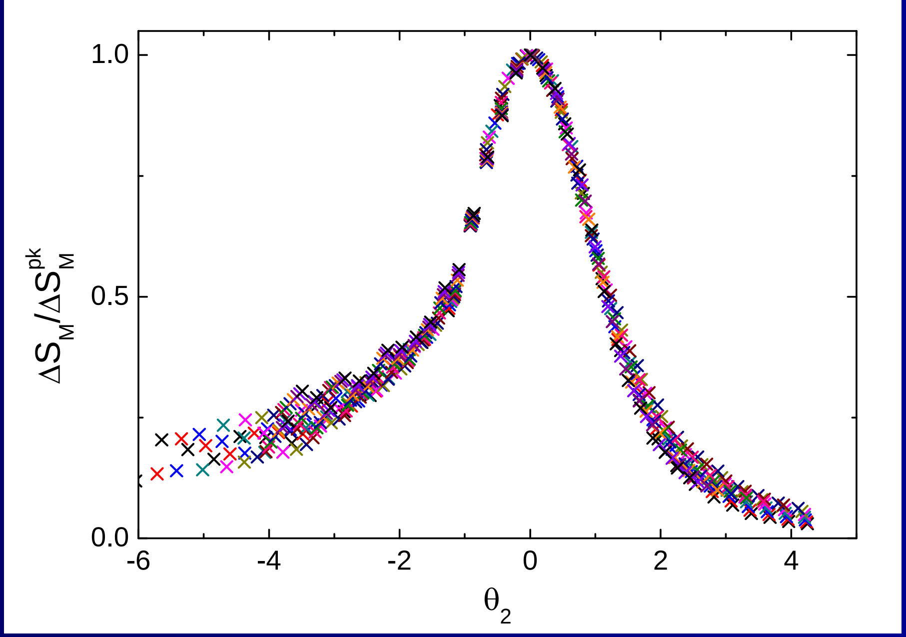




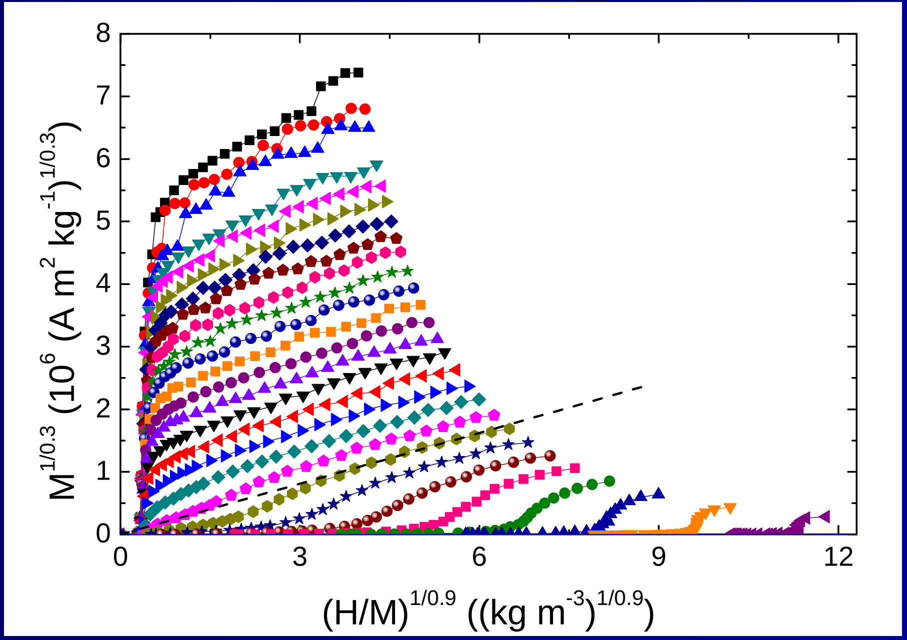
- Differences between critical exponents obtained in both ways are within error margin

Fe doped $Gd_5Ge_2Si_2$

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

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

BUT… IS IT REALLY USEFUL?

IOP PUBLISHING JOURNAL OF PHYSICS D: APPLIED PHYSICS
J. Phys. D: Appl. Phys. 46 (2013) 295001 (6pp) doi:10.1088/0022-3727/46/29/295001

Analysis of the first-order phase transition of $(Mn,Fe)_2(P,Si,Ge)$ using entropy change scaling

G F Wang[1], Z R Zhao[1,2], X F Zhang[1] L Song[3] and O Tegus[3]

[1] Key Laboratory of Integrated Exploitation of Bayan Obo Multi-Metal Resources, Inner Mongolia University of Science and Technology, 014010, Baotou, People's Republic of China
[2] School of Mathematics, Physics and Biological Engineering, Inner Mongolia University of Science and Technology, 014010, Baotou, People's Republic of China
[3] Key Laboratory for Physics and Chemistry of Functional Materials, Inner Mongolia Normal University, 010022, Hohhot, People's Republic of China

E-mail: gaofengwang1982@gmail.com

Received 19 December 2012, in final form 18 March 2013
Published 27 June 2013
Online at stacks.iop.org/JPhysD/46/295001

"The results suggest that the entropy change scaling method is more appropriate for determining the nature of transition in such materials with small magnitude of sharp change in magnetization at the transition"

PHYSICAL REVIEW B 87, 195102 (2013)

Critical behavior of the ferromagnetic perovskites $RTiO_3$ (R = Dy, Ho, Er, Tm, Yb) by magnetocaloric measurements

Yantao Su,[1] Yu Sui,[1,*] J.-G. Cheng,[2,3] J.-S. Zhou,[2] Xianjie Wang,[1] Yang Wang,[1] and J. B. Goodenough[2]
[1]*Department of Physics, Harbin Institute of Technology, Harbin 150001, China*
[2]*Texas Materials Institute, University of Texas at Austin, Austin, Texas 78712, USA*
[3]*Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China*
(Received 6 November 2012; published 2 May 2013)

Ferromagnetism in perovskites $RTiO_3$ can be induced by a steric effect. The way in which the subtle local structural change can induce three-dimensional (3D) ferromagnetic coupling through Ti-O-Ti superexchange interactions remains controversial. A critical behavior study for the ferromagnetic phase has been made so far only on $YTiO_3$ because the magnetization measurements are plagued by the contribution from the magnetic rare earth. Here we report critical exponents for most ferromagnetic members in the $RTiO_3$ family by measuring the magnetocaloric effect and applying the corresponding scaling laws. Our results indicate that the ferromagnetic coupling in the $RTiO_3$ can be well described by the 3D Heisenberg model.

DOI: 10.1103/PhysRevB.87.195102 PACS number(s): 75.40.Cx, 75.30.Sg, 75.47.Lx

"In summary, we have determined that the critical behavior in RTiO3 single crystals belongs to the 3D Heisenberg universality class by using the MCE scaling laws, which also agree with the specific-heat measurement. This approach not only eliminates the influence of other paramagnetic contributions in the critical region, it also avoids the drawback of the iteration procedure in the conventional Arrott-plot method. Therefore, the MCE scaling laws can be applied to complex magnetic systems involving different magnetization processes in the critical region."

Journal of Alloys and Compounds 530 (2012) 1-5

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Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Effect of Ti-substitution on magnetic and magnetocaloric properties of $La_{0.57}Nd_{0.1}Pb_{0.33}MnO_3$

A. Dhahri[a,*], J. Dhahri[a], E.K. Hlil[b], E. Dhahri[c]

[a] Unité de Recherche de Physique des Solides, Département de Physique, Faculté des Sciences de Monastir, 5019, Tunisia
[b] Institut Néel, CNRS-Université J. Fourier, Bp 166, 38042 Grenoble, France
[c] Laboratoire de Physique Appliqué, Département de Physique, Faculté des Sciences de Sfax, 3018, Tunisia

JOURNAL OF APPLIED PHYSICS **108**, 113913 (2010)

Magnetic field dependence of magnetic entropy change in nanocrystalline and polycrystalline manganites $La_{1-x}M_xMnO_3$ (M=Ca,Sr)

Marek Pękała[a)]
Department of Chemistry, University of Warsaw, Al. Zwirki i Wigury 101, PL-02-089 Warsaw, Poland

(Received 23 June 2010; accepted 24 October 2010; published online 8 December 2010)

Experimental results of magnetocaloric effect for several polycrystalline and nanocrystalline manganites $La_{1-x}M_{0.x}MnO_3$ (M=Ca and Sr) are analyzed. Influence of magnetic field is accounted for by the exponent N. The relatively deep N(T) minimum located close to the Curie temperature is found in the polycrystalline manganites. Temperature dependence of N(T) exponent is comparable with those of the soft magnetic and rare earth containing alloys. The slightly higher sensitivity of magnetocaloric effect in nanocrystalline manganites to magnetic fields is revealed by the N exponent. © *2010 American Institute of Physics*. [doi:10.1063/1.3517831]

JOURNAL OF APPLIED PHYSICS **113**, 093902 (2013)

CrossMark

Investigation of the critical behavior in $Mn_{0.94}Nb_{0.06}CoGe$ alloy by using the field dependence of magnetic entropy change

J. C. Debnath,[1,a)] P. Shamba,[2] A. M. Strydom,[1] J. L. Wang,[2,3] and S. X. Dou[2]

[1]*Department of Physics, University of Johannesburg, P.O. Box 524, Auckland Park 2006, South Africa*

[2]*Institute for Superconducting and Electronic Materials, University of Wollongong, Squaire Way, North Wollongong, Wollongong, NSW 2500, Australia*

[3]*Bragg Institute, Australian Nuclear Science and Technology Organization, Lucas Heights, NSW 2234, Australia.*

(Received 1 February 2013; accepted 19 February 2013; published online 1 March 2013)

The critical behaviour of $Mn_{0.94}Nb_{0.06}CoGe$ alloy around the paramagnetic-ferromagnetic phase transition was studied based on the field dependence on magnetic entropy change. By using the obtained exponents, the modified Arrott plot is consistent with that by using conventional method. These critical exponents are confirmed by the Widom scaling relation. Based on these critical exponents, the magnetization, field and temperature data around Tc collapse into two curves obeying the single scaling equation $M(H, \varepsilon) = \varepsilon^{\beta} f \pm (H/\varepsilon^{\beta+\gamma})$. The calculated critical exponents not only obey the scaling theory but also anastomose the deduced results from the Kouvel-Fisher method [J. S. Kouvel and M. E. Fisher, Phys. Rev. **136**, A1626 (1964)]. The values deduced for the critical exponents in the $Mn_{0.94}Nb_{0.06}CoGe$ alloy are close to the theoretical prediction of the mean-field model, indicating that the magnetic interactions are long range. This method eliminates the drawback due to utilization of multistep nonlinear fitting in a conventional manner. So it provides an alternative method to investigate the critical behaviour. [http://dx.doi.org/10.1063/1.4794100]

"This method eliminates the drawback due to utilization of multistep nonlinear fitting in a conventional manner. So it provides an alternative method to investigate the critical behaviour."

Eur. Phys. J. Appl. Phys. (2013) 62: 30601
DOI: 10.1051/epjap/2013120256

THE EUROPEAN PHYSICAL JOURNAL
APPLIED PHYSICS

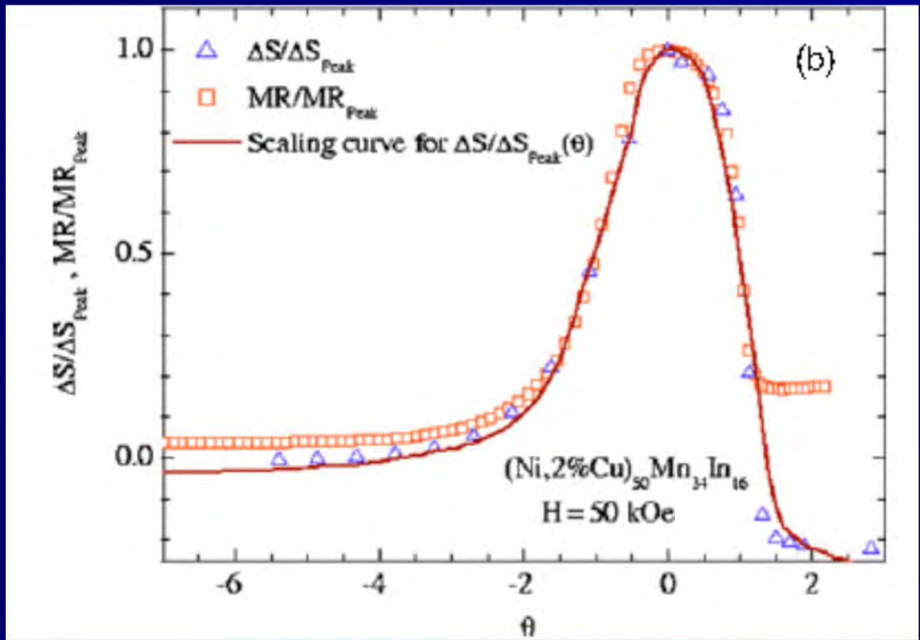
Regular Article

Scaling of the isothermal entropy change and magnetoresistance in Ni-Mn-In based off-stoichiometric Heusler alloys

V.K. Sharma[a], M.K. Chattopadhyay, L.S. Sharath Chandra, Ashish Khandelwal, R.K. Meena, and S.B. Roy

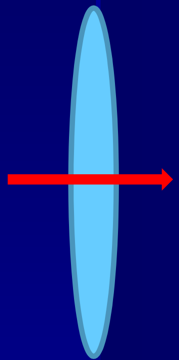
Magnetic and Superconducting Materials Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India

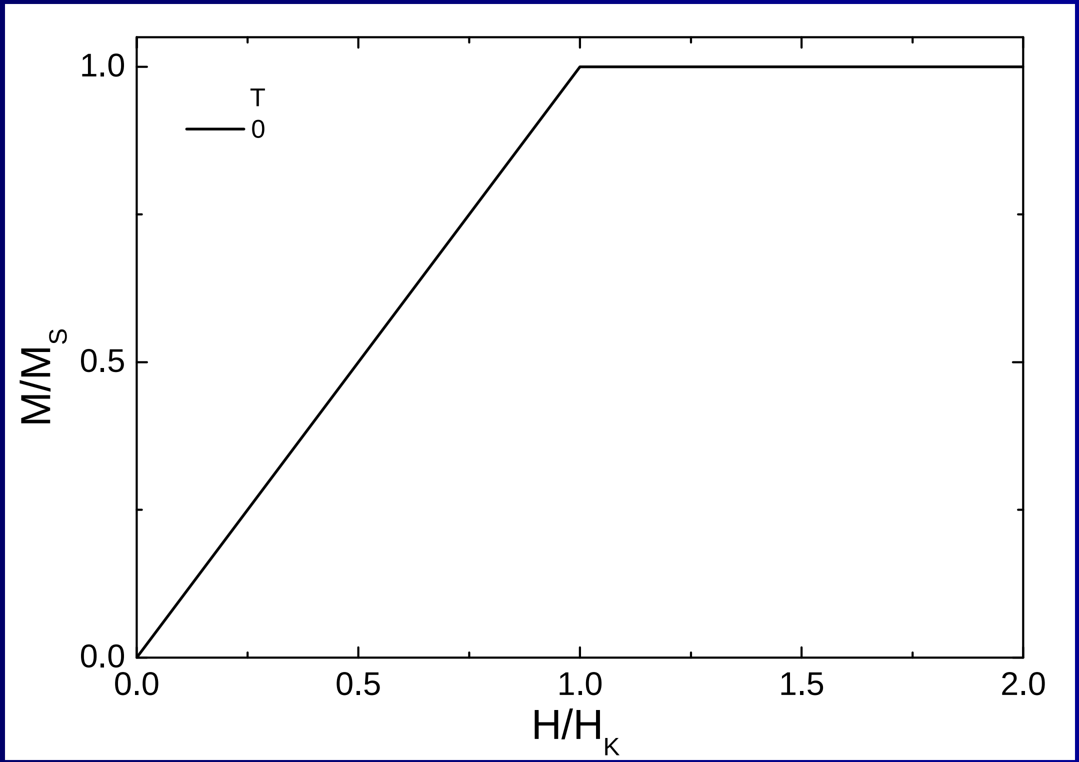
Received: 27 June 2012 / Received in final form: 6 November 2012 / Accepted: 25 January 2013
Published online: 11 June 2013 – © EDP Sciences 2013



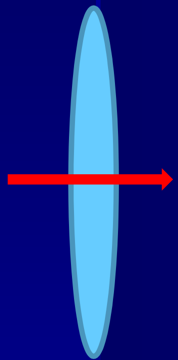
MCE IN NANOMATERIALS:
A QUALITATIVELY DIFFERENT BEHAVIOR

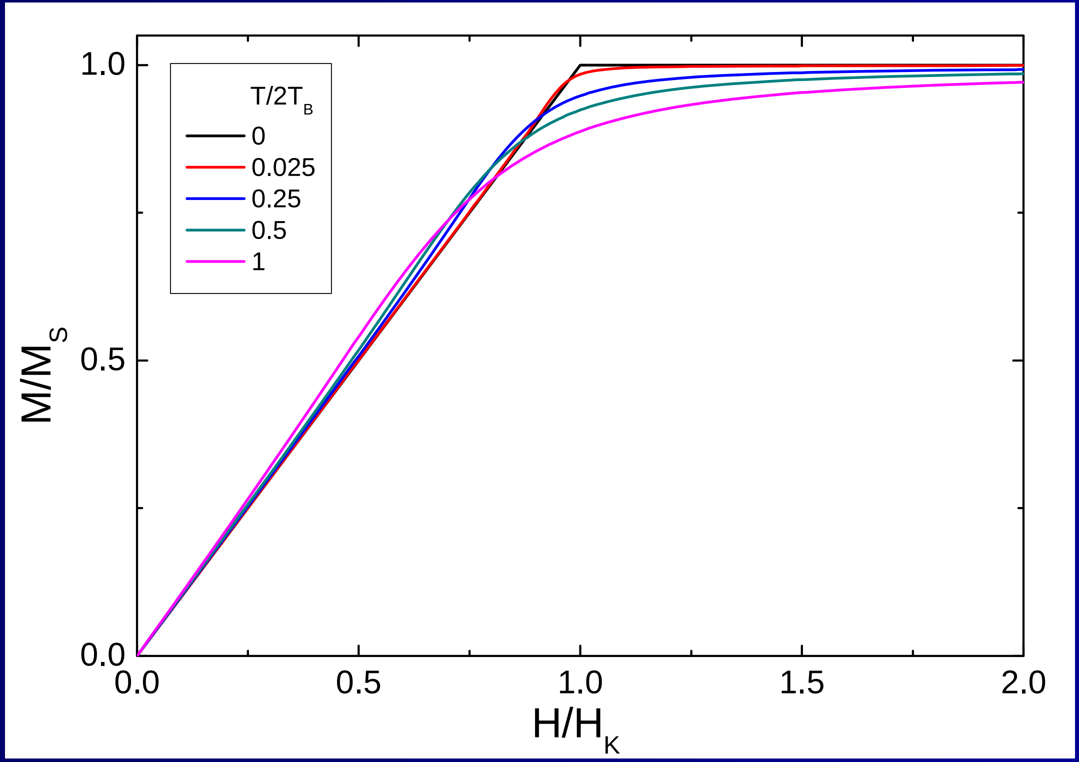
An ensemble of single domain nanoparticles





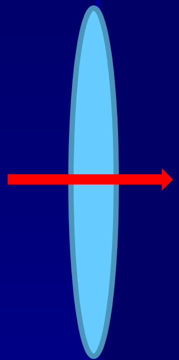
An ensemble of single domain nanoparticles

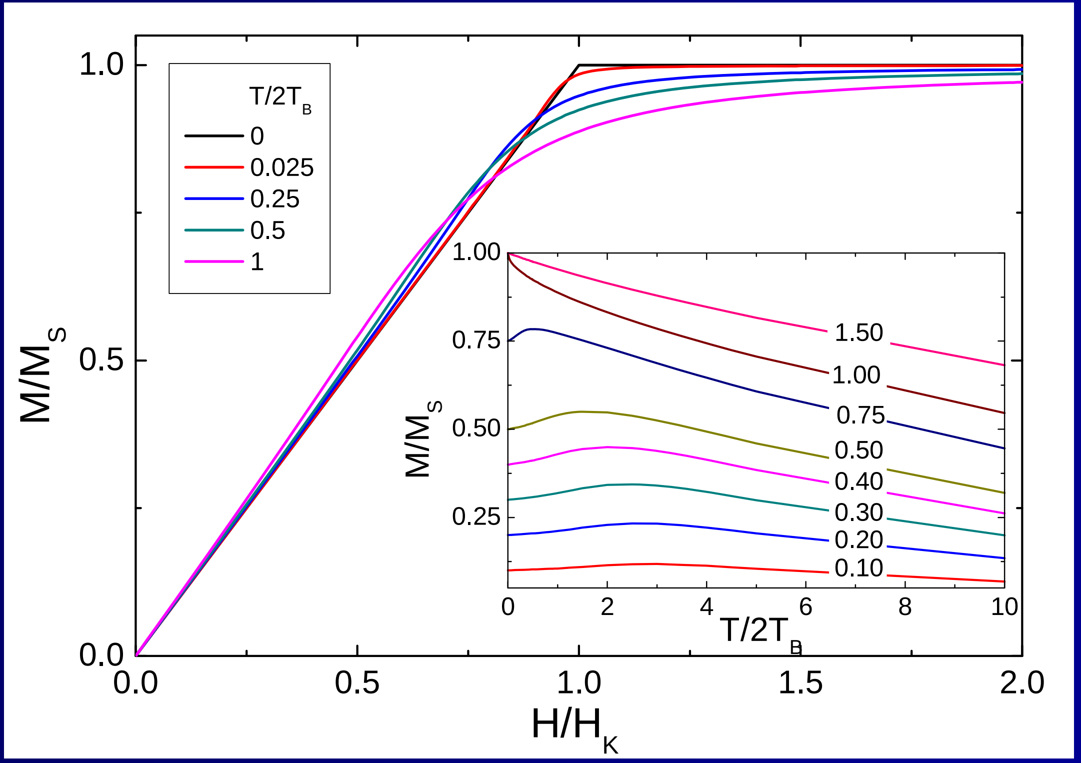




V. Franco, A. Conde, J. Magn. Magn. Mater. 278 (2004) 28

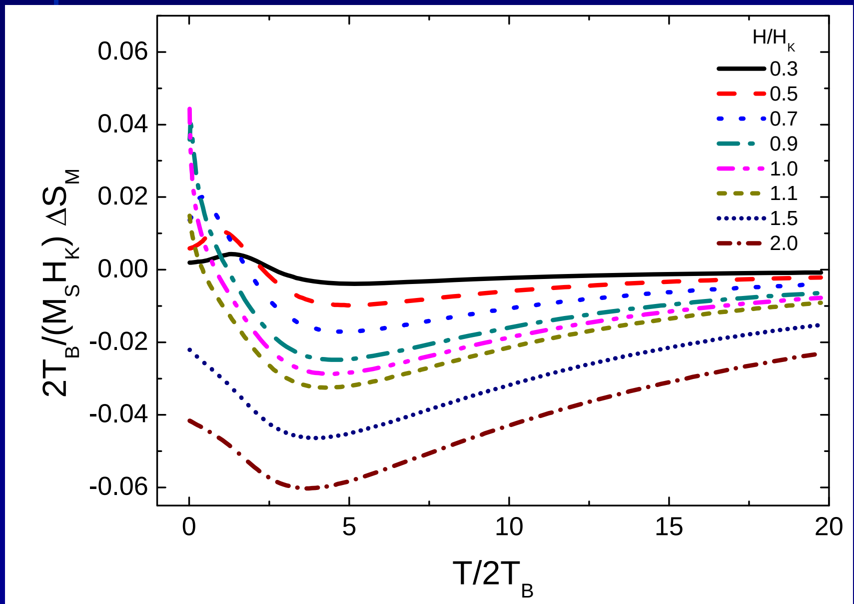
An ensemble of single domain nanoparticles

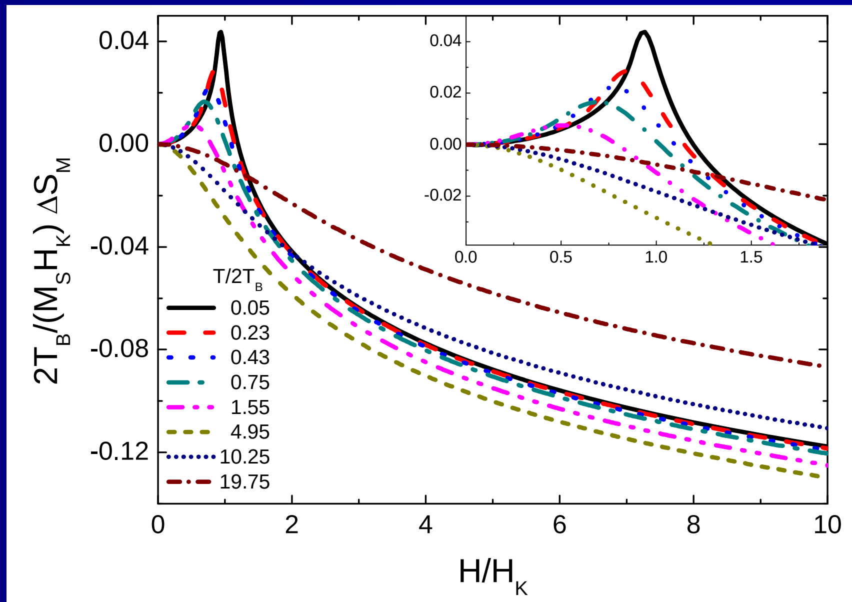




$$\Delta S_M = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH$$

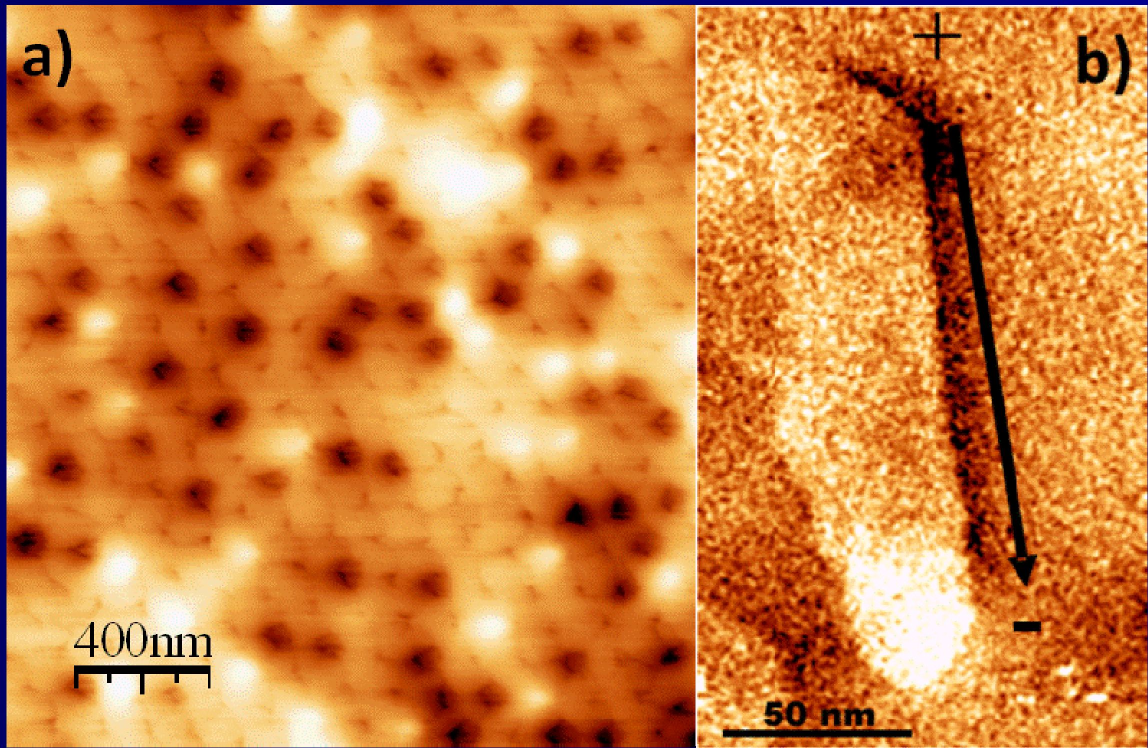
Combined direct and inverse MCE

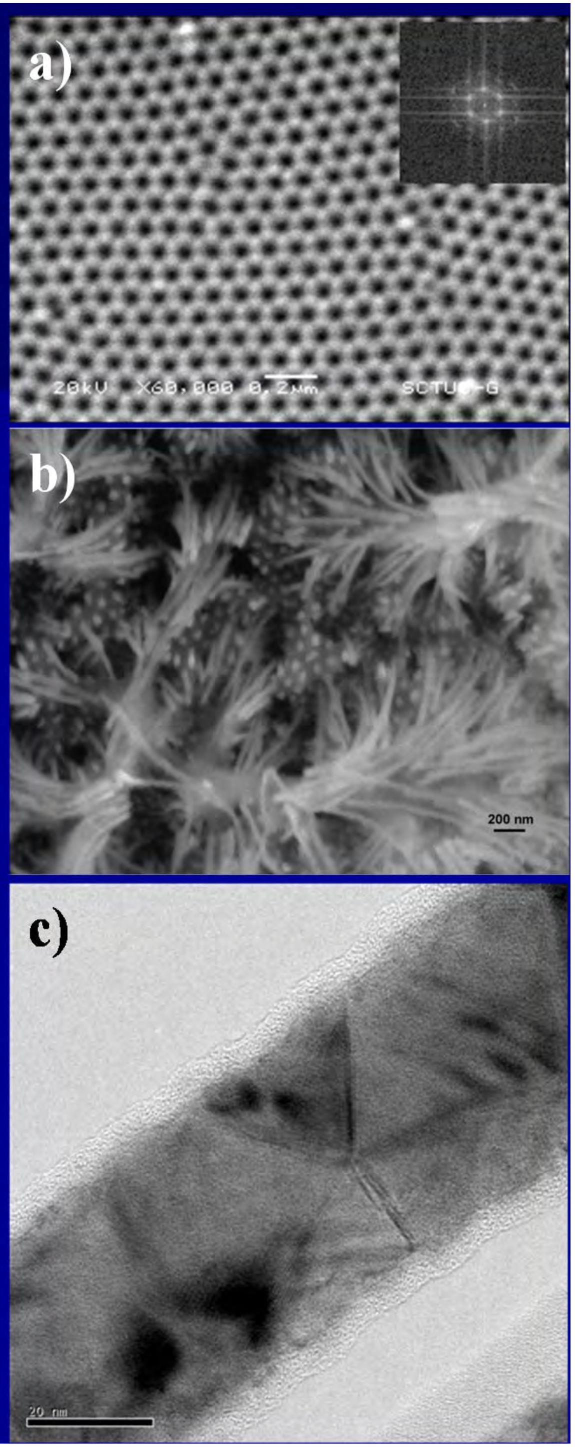




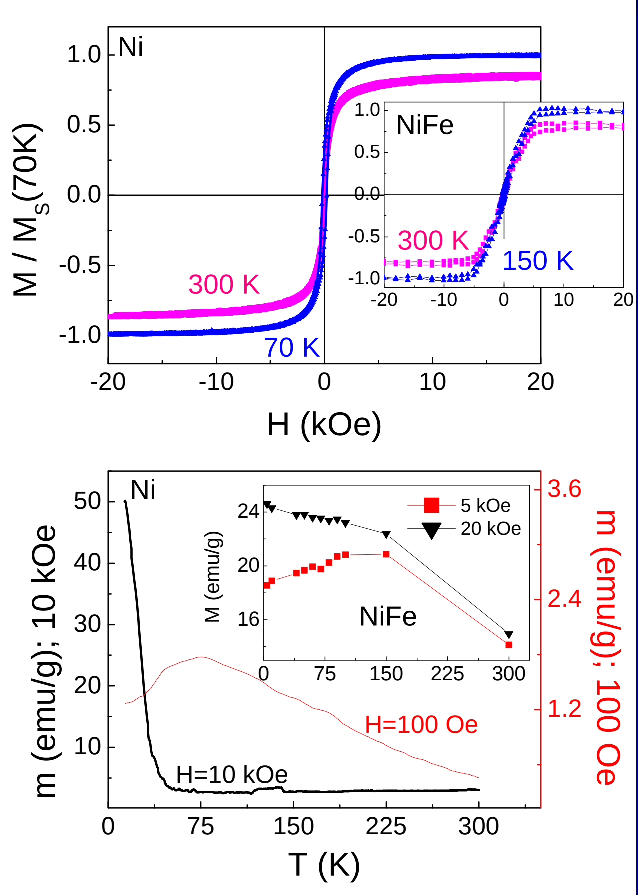
V. Franco, K.R. Pirota, V.M. Prida, A.M.J.C. Neto, A. Conde, M. Knobel, B. Hernando, M. Vazquez, Phys. Rev. B 77 (2008) 104434

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

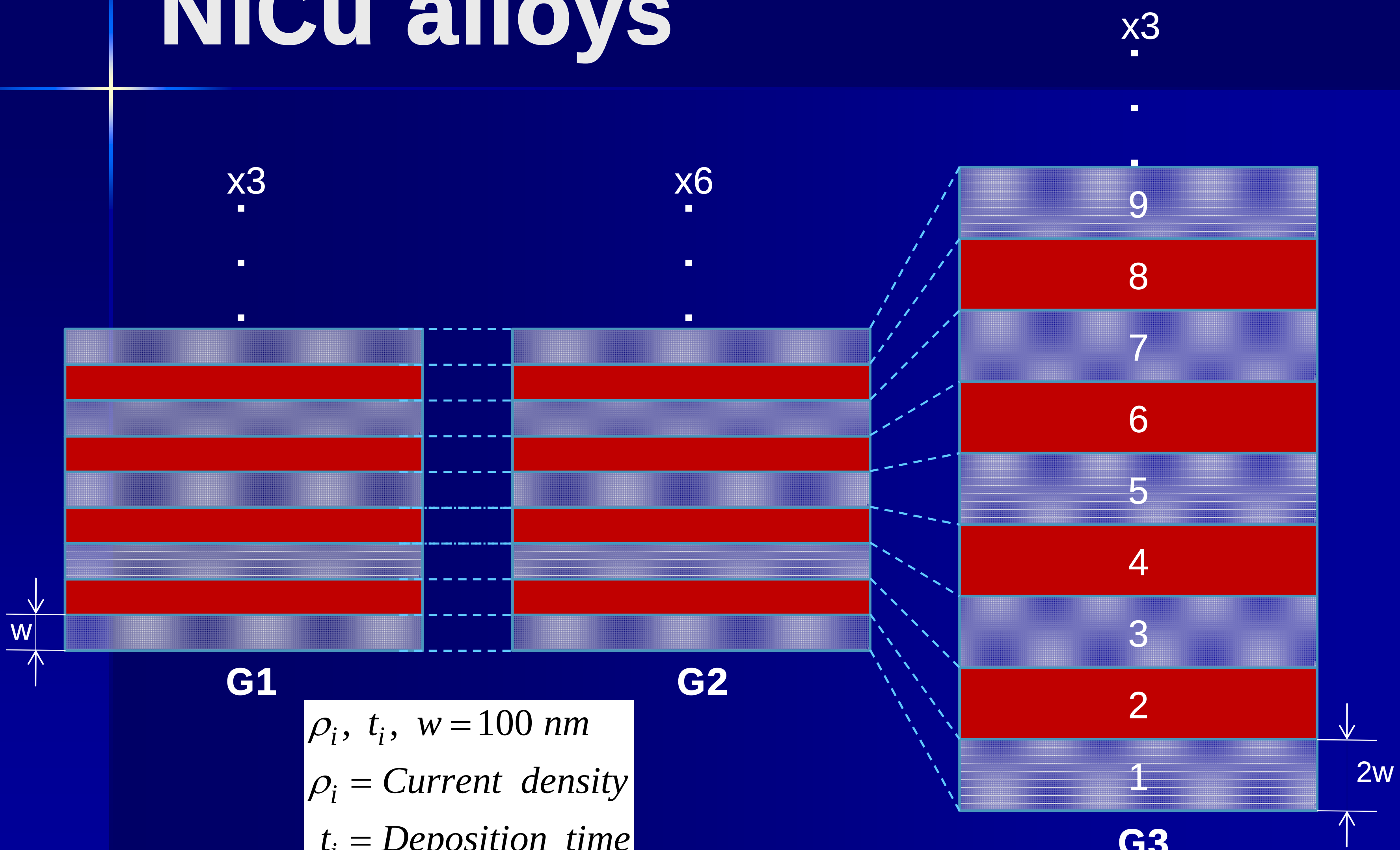


V. Franco, K.R. Pirota, V.M. Prida, A.M.J.C. Neto, A. Conde, M. Knobel, B. Hernando, M. Vazquez, Phys. Rev. B 77 (2008) 104434

MULTILAYERED STRUCTURES

A way to control the field dependence of MCE

Electrodeposited samples. NiCu alloys



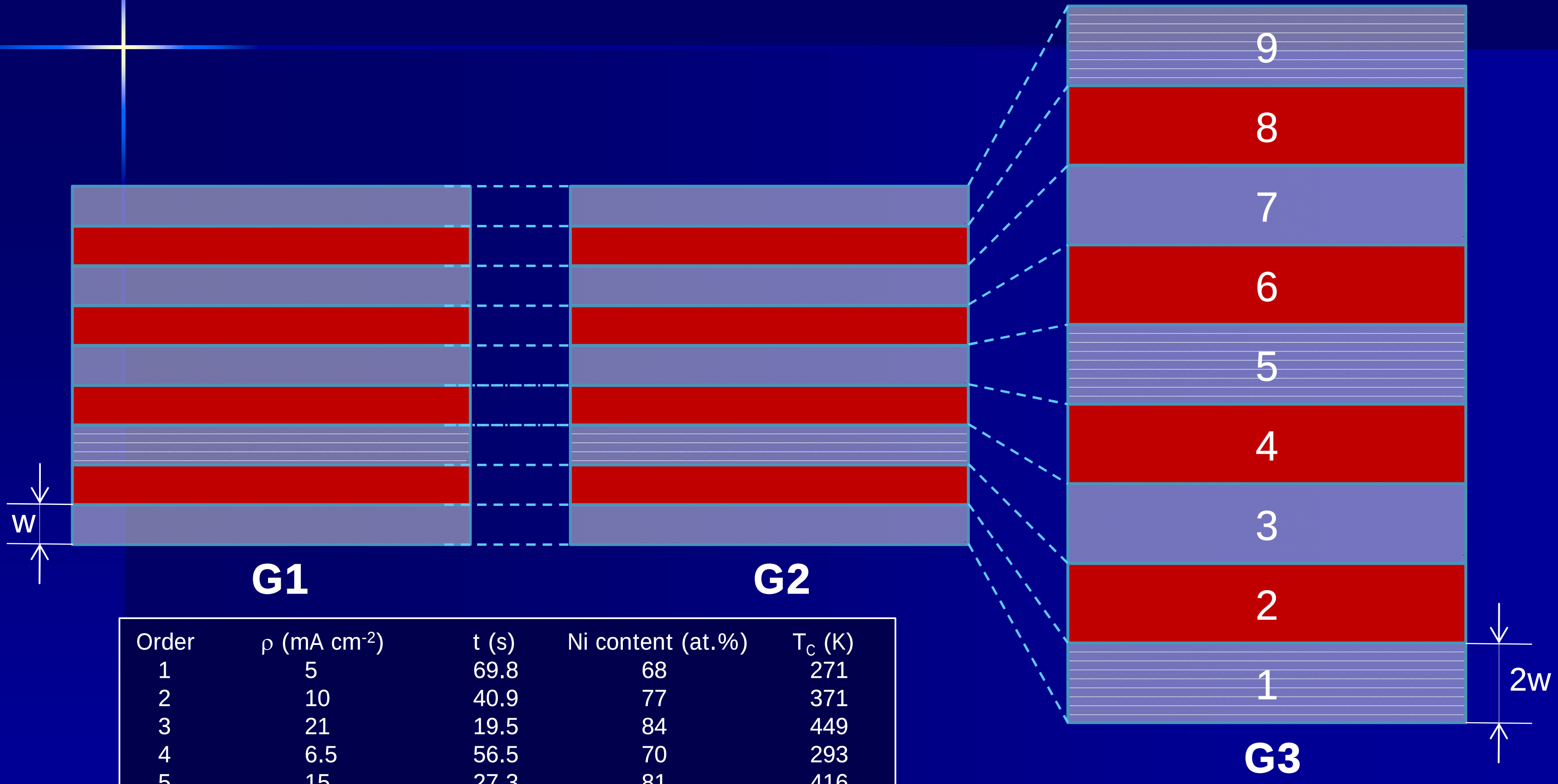
$\rho_i,\ t_i,\ w = 100\ nm$

$\rho_i = Current\ \ density$

$t_i = Deposition\ \ time$

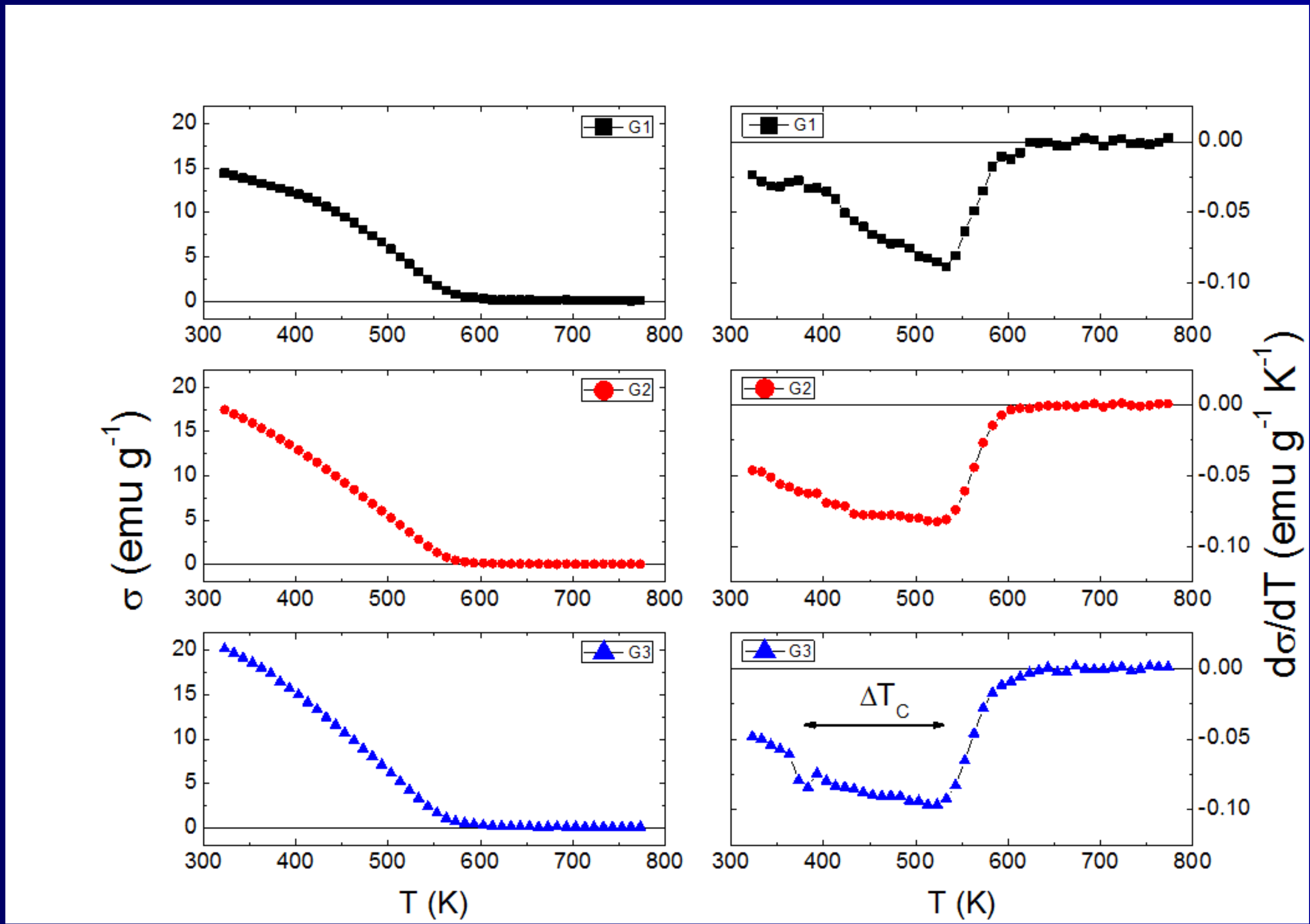
$\rho_i,\ 2t_i,\ 2w = 200\ nm$

Fabrication parameters

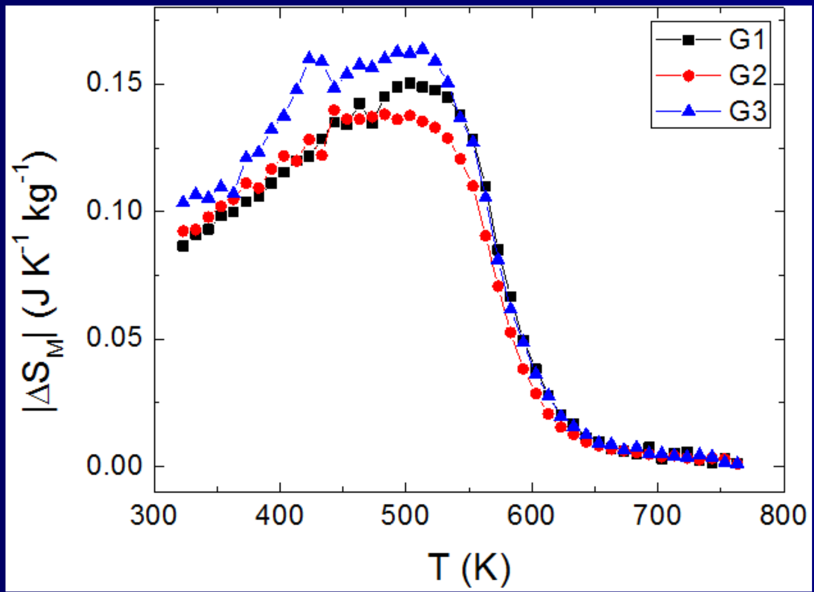


Order	ρ (mA cm^{-2})	t (s)	Ni content (at.%)	T_C (K)
1	5	69.8	68	271
2	10	40.9	77	371
3	21	19.5	84	449
4	6.5	56.5	70	293
5	15	27.3	81	416
6	4	84.2	66	248
7	2.6	122.3	61	193
8	8	48.4	73	326
9	3	108.4	64	226

Thermomagnetic curves



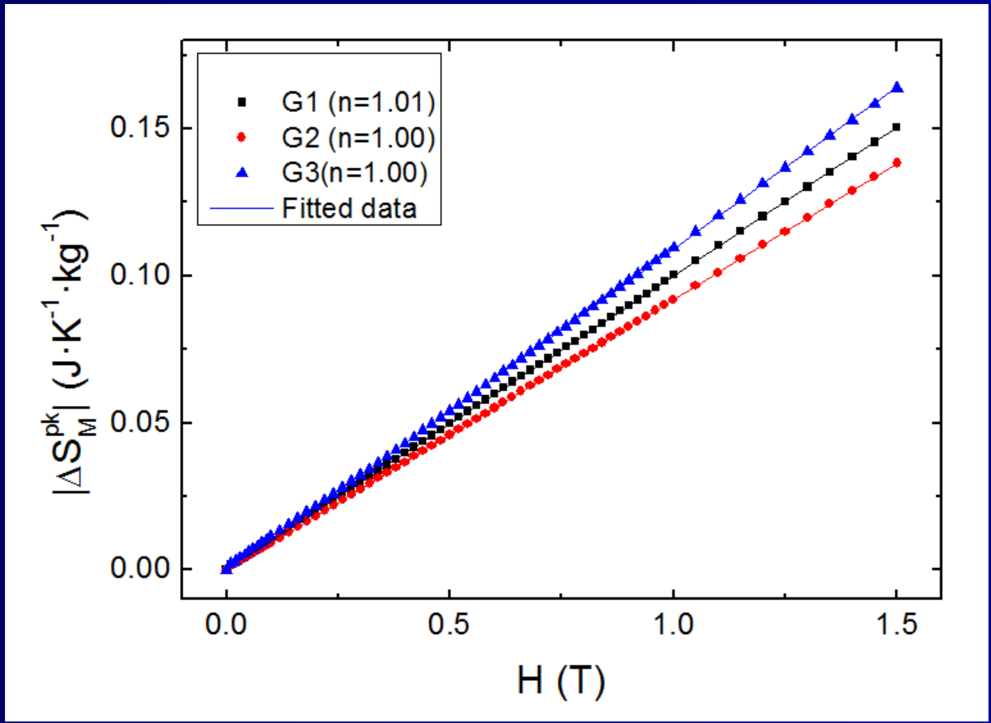
Magnetic entropy change



- 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

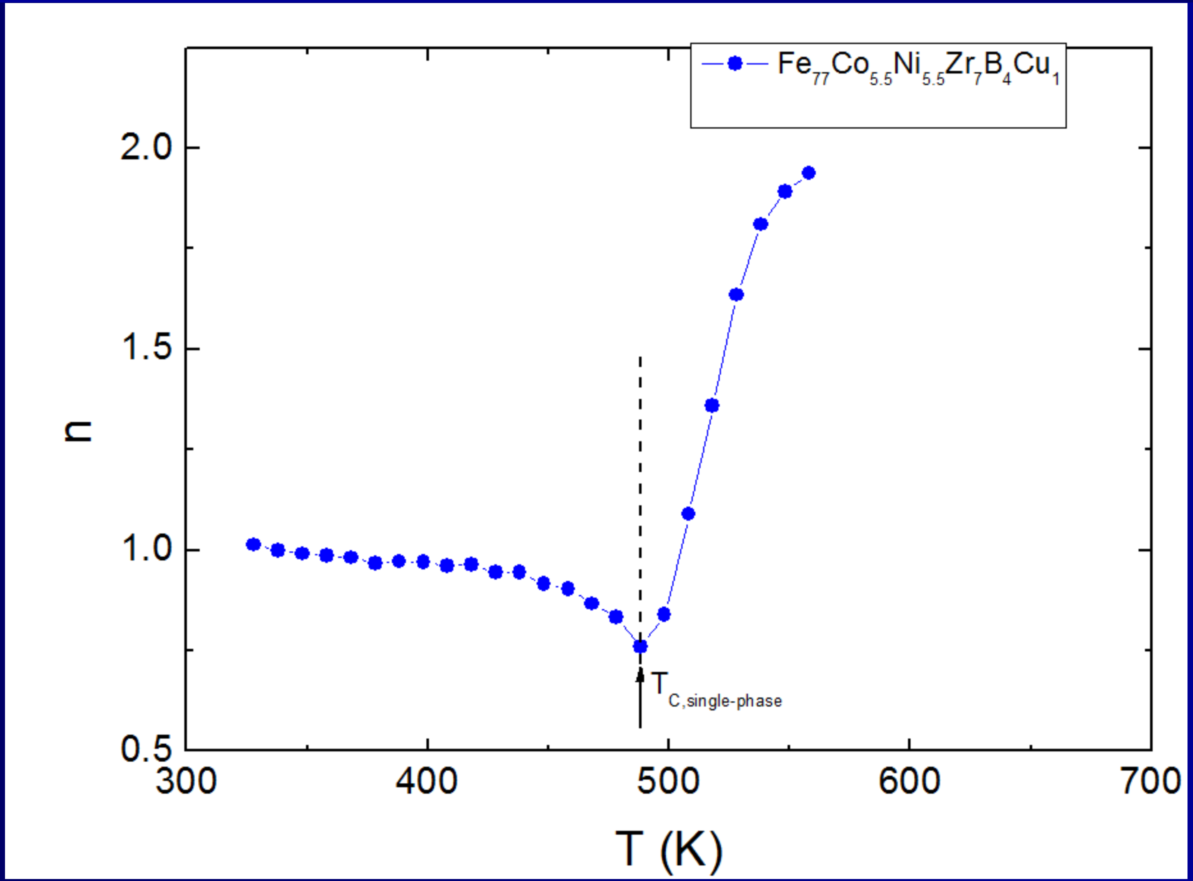
Field dependece at the peak



A linear field dependence of the peak is achieved

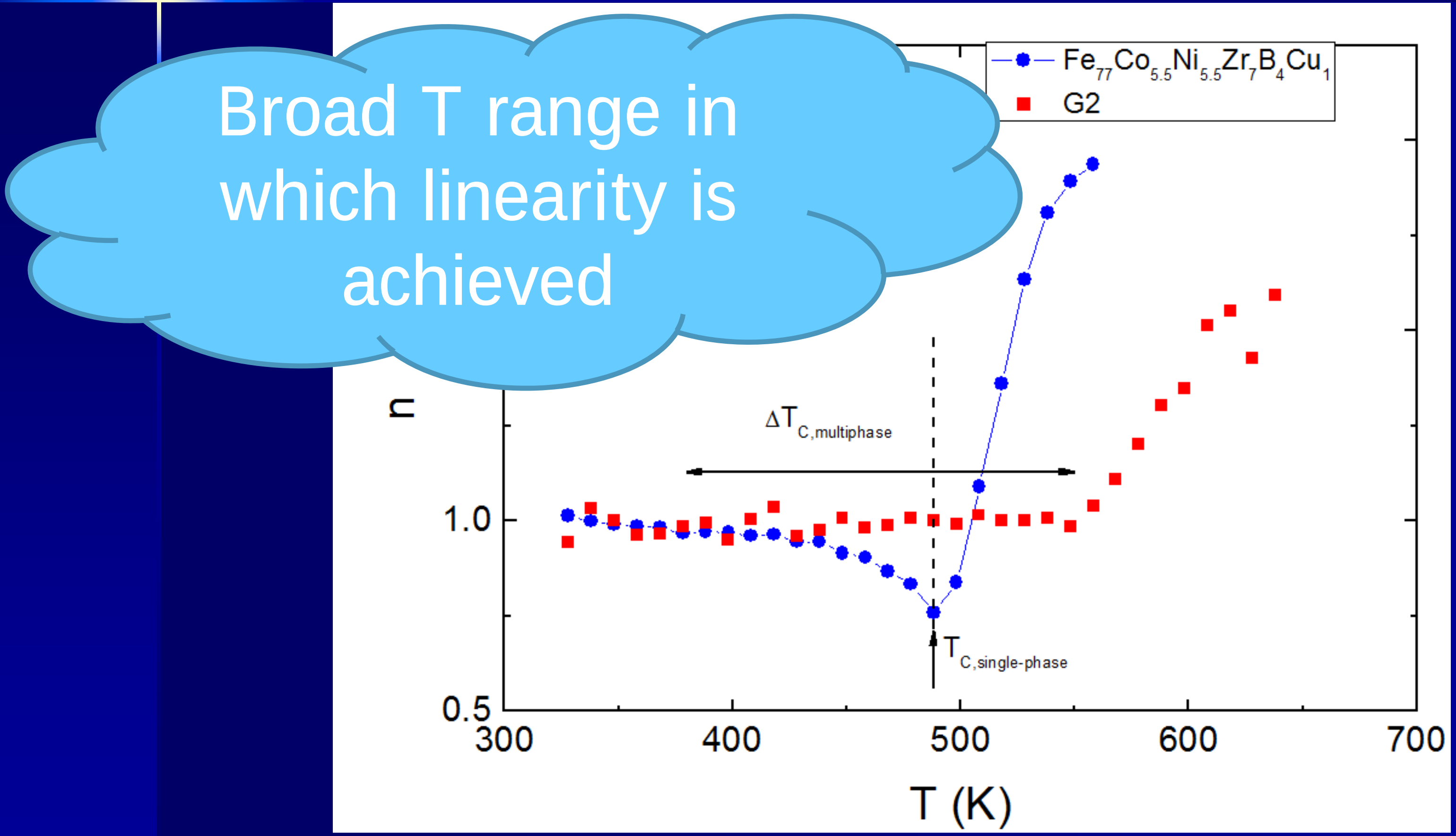
R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
Journal of Nanoscience and Nanotechnology 12 (2012) 7432

Field dependence in an extended T range



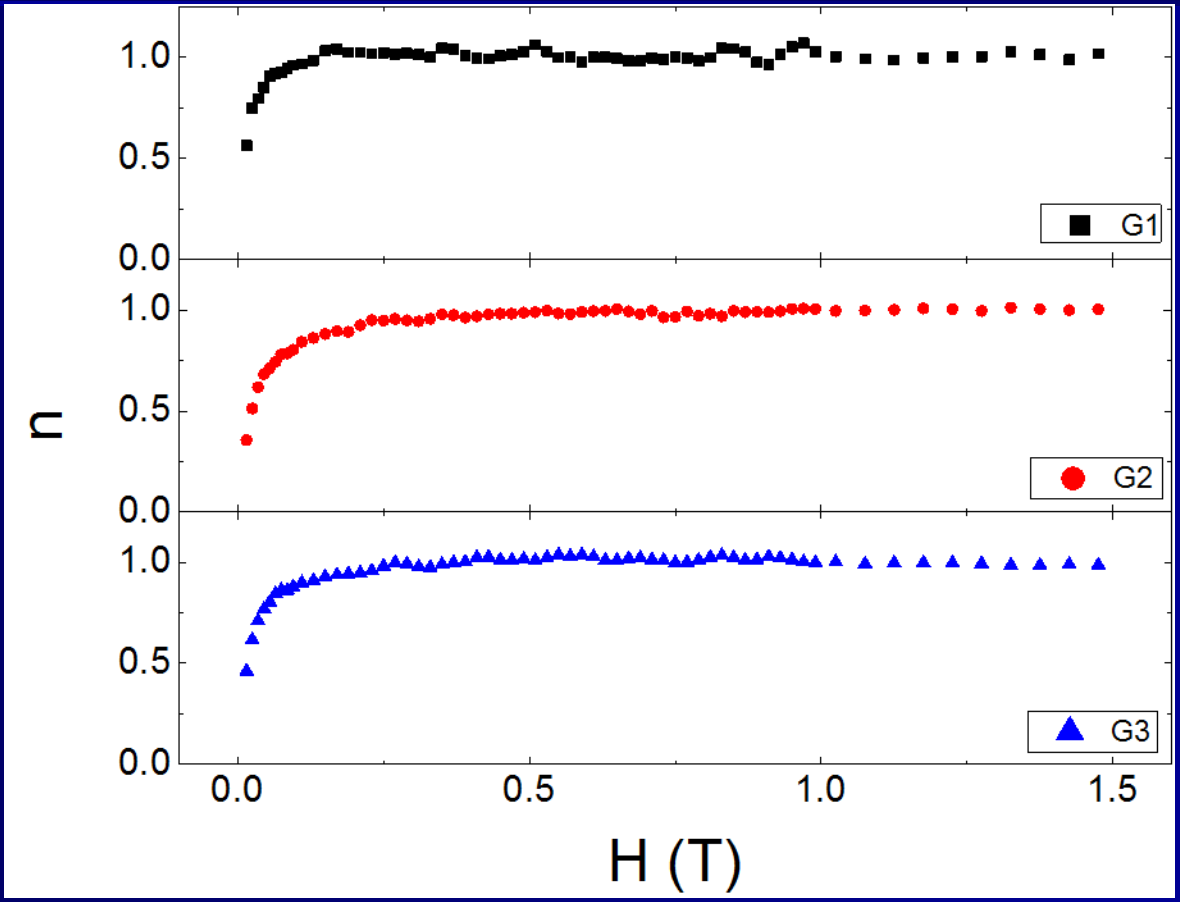
R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi
Journal of Nanoscience and Nanotechnology 12 (2012) 7432

Field dependence 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

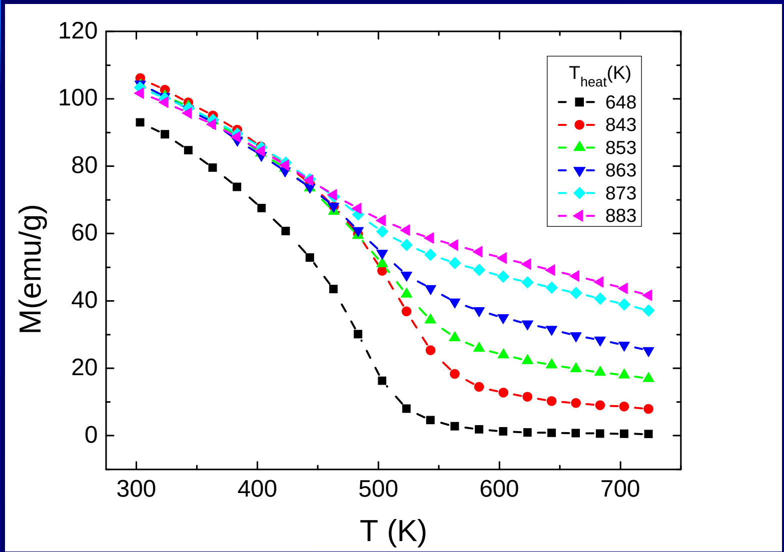


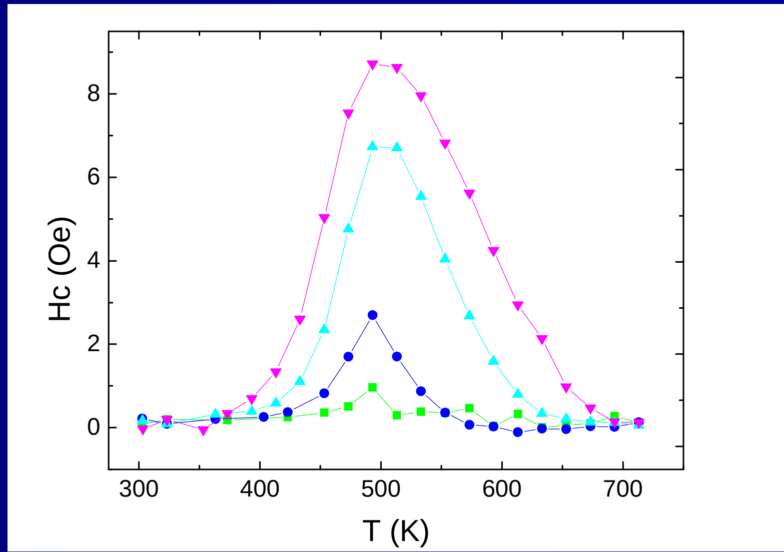
Difference with bulk composites (H independent)

MCE IN NANOCRYSTALLINE ALLOYS:

NOT AS GOOD AS INITIALLY EXPECTED

Nanocrystallization of Mo-Finemet

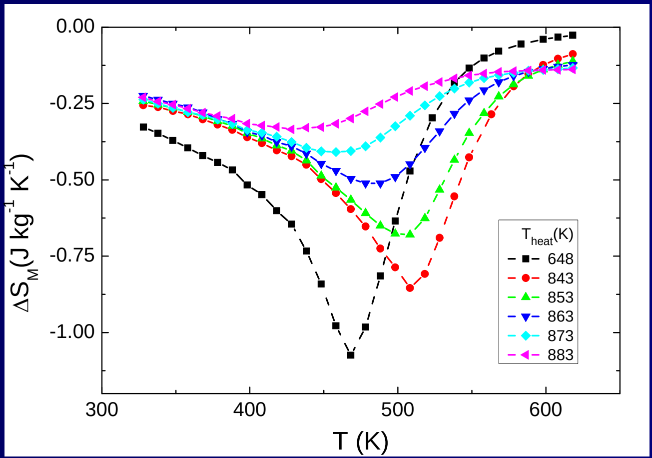


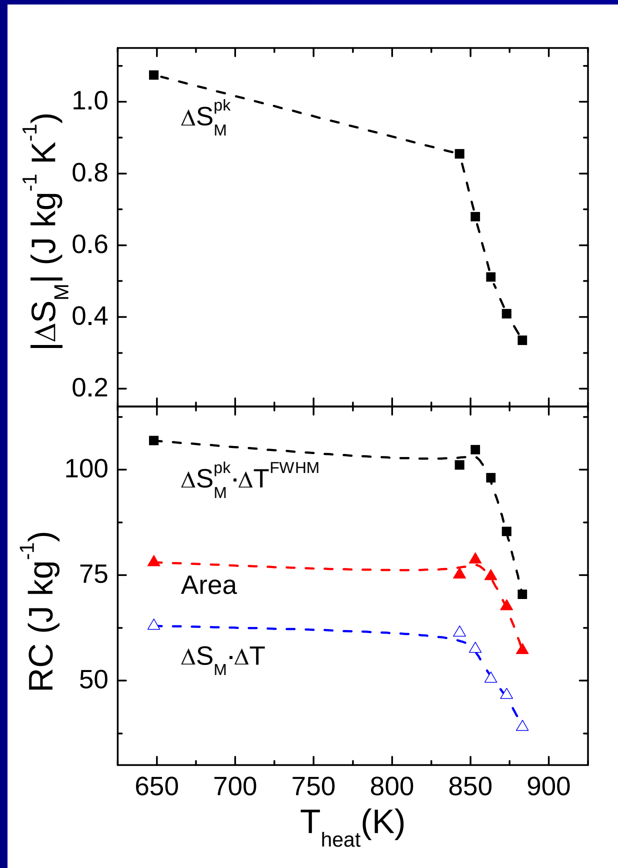


Smaller values of the coercivity peak → More reduced dipolar interactions

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

MCE of nanocrystalline Mo-Finemet





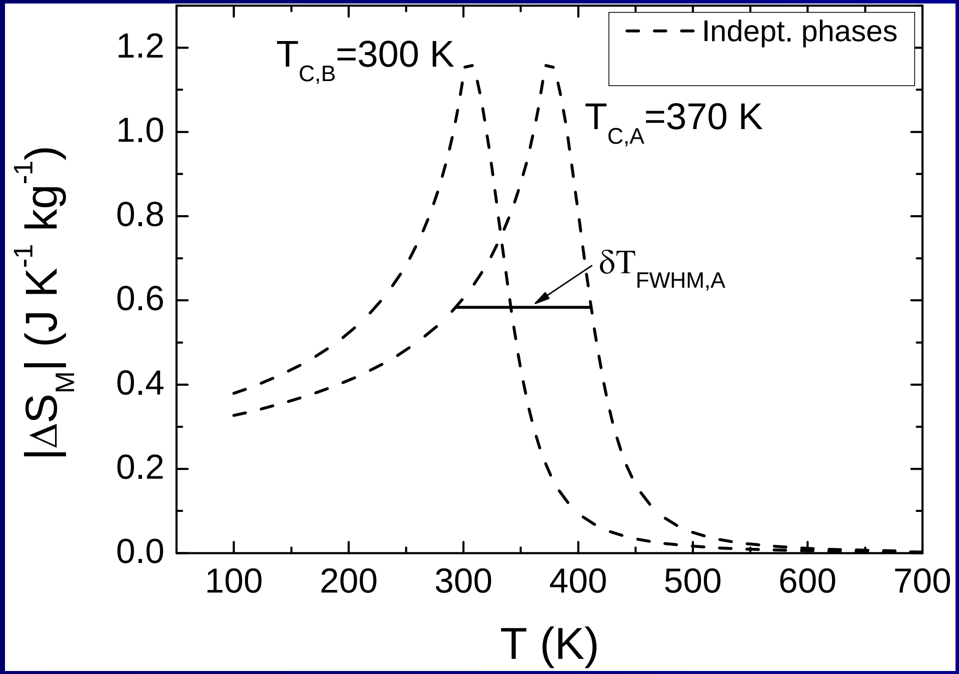
- SPM better than paramagnets
- The peak is broadened due to different T_C (sum rule)
- RC does not increase

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

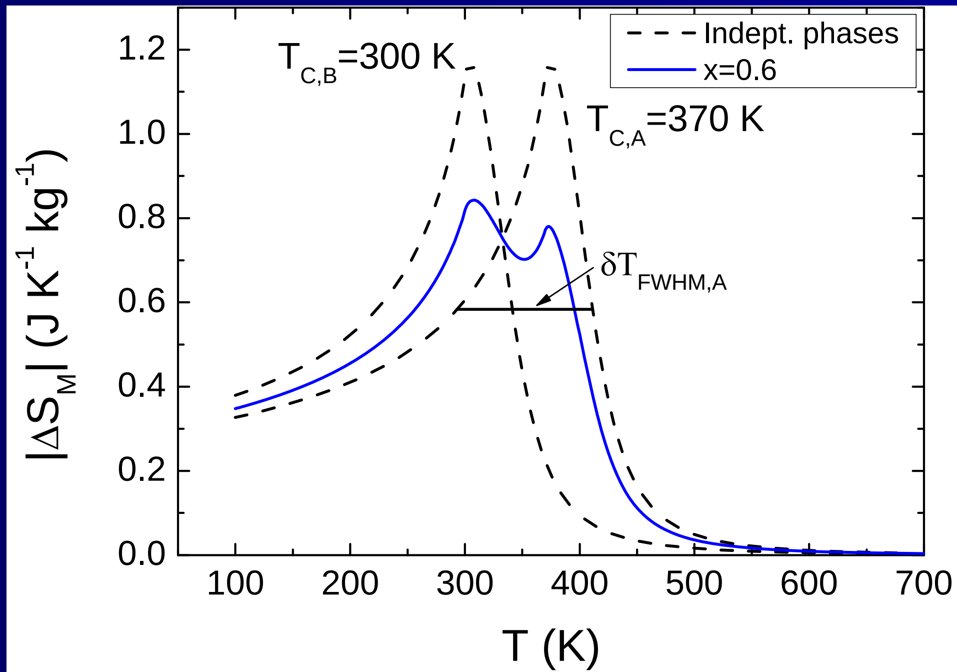
MCE IN MULTIPHASE MATERIALS:

IS THERE A WAY OF INCREASING RC?

Non-interacting composite (calculations)

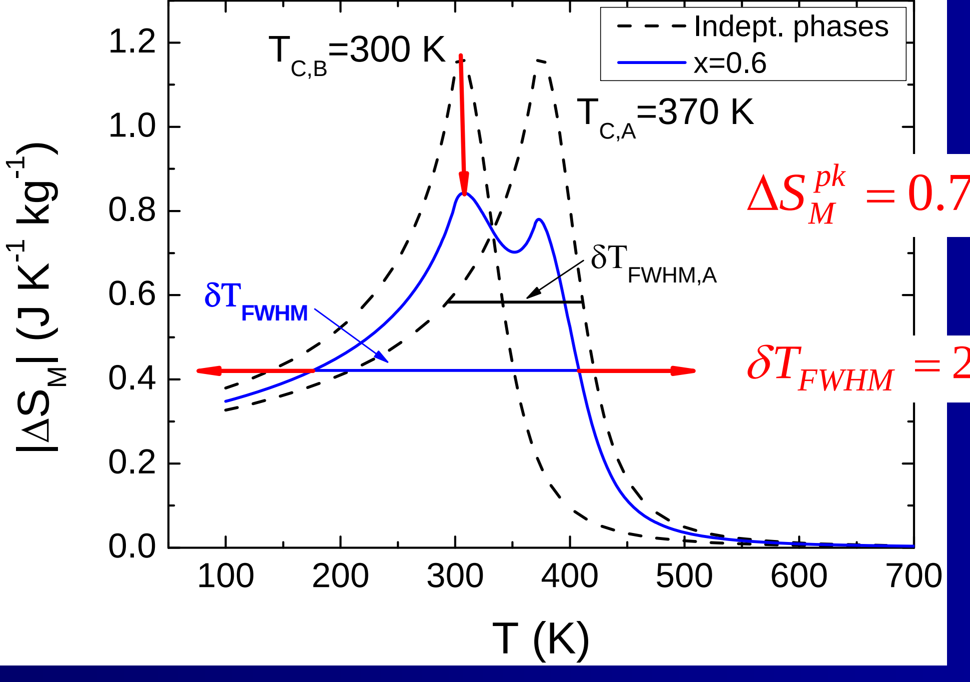


Non-interacting composite (calculations)



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

Non-interacting composite (calculations)

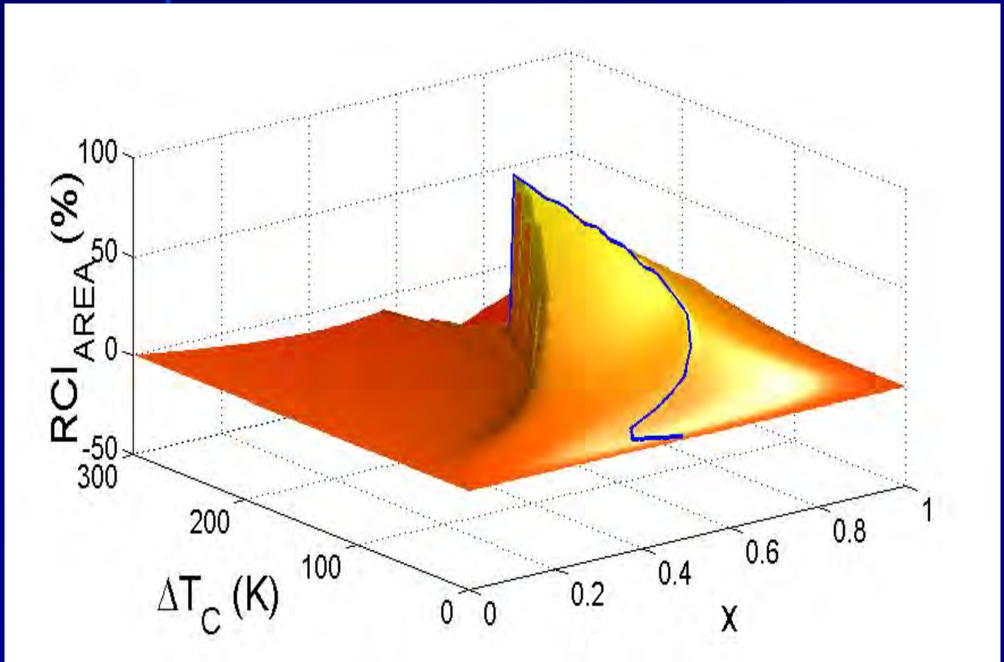


$$\Delta S_M^{pk} = 0.72\ \Delta S_{M,A}^{pk}$$

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

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

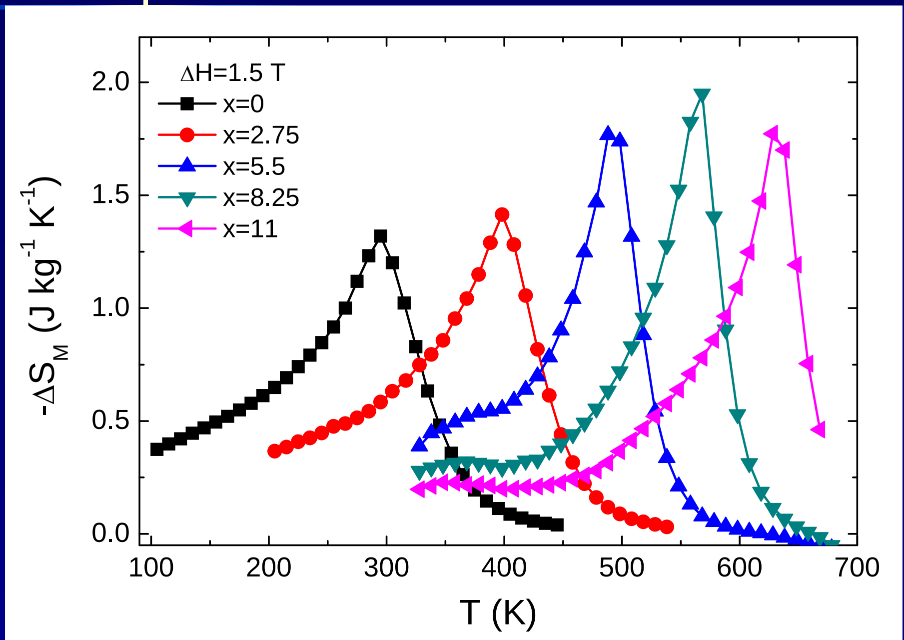
Improvement of RC

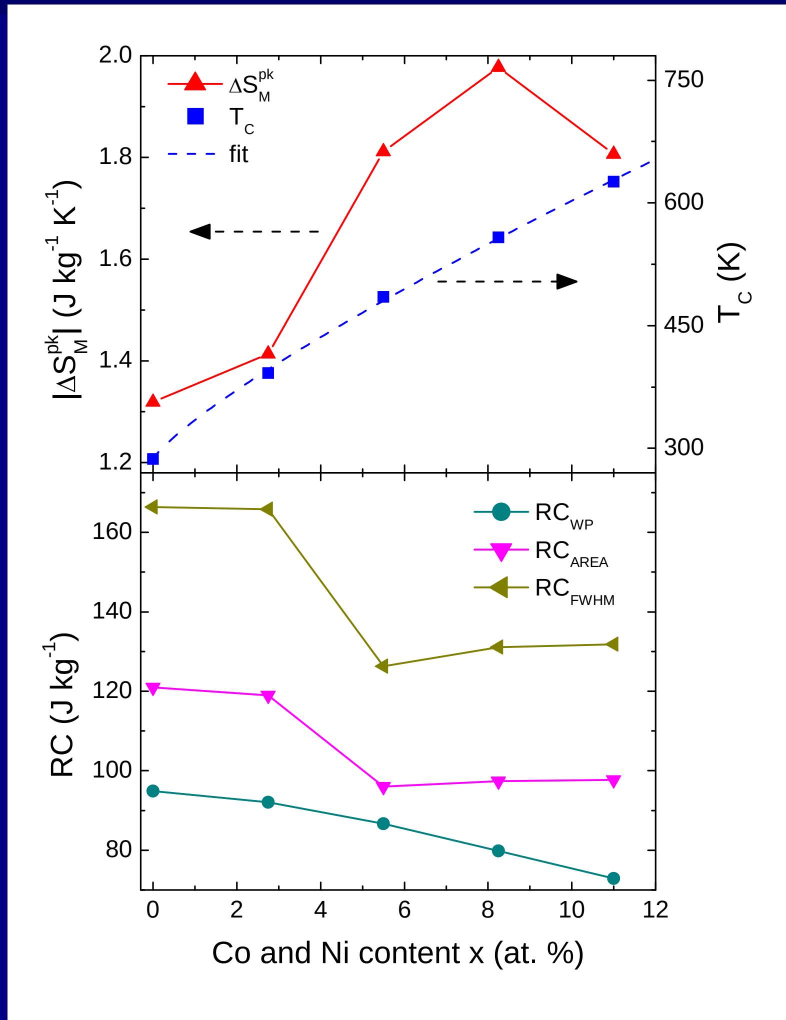


R. Caballero-Flores, V. Franco, A. Conde, K. E. Knipling, and M. A. Willard. Appl. Phys. Lett. 98 (2011) 102505

- 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}

Amorphous alloys for rt-MCE $Fe_{88-2x}Co_xNi_xZr_7B_4Cu_1$

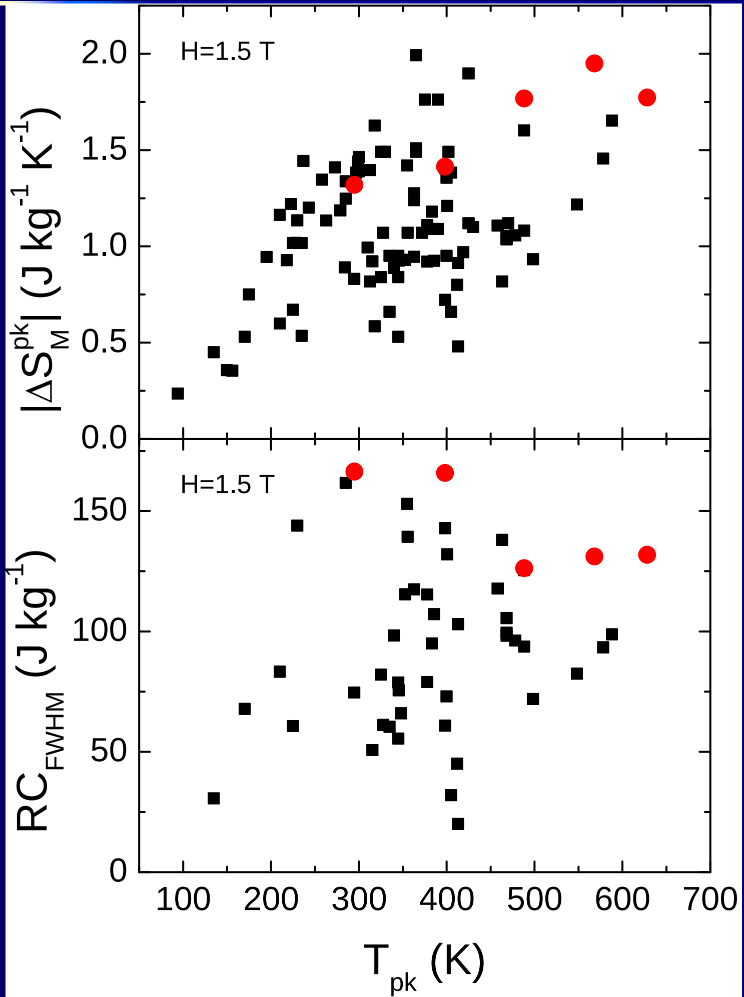




RC ~40% larger than $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ and ~15% larger than Fe-based amorphous alloys

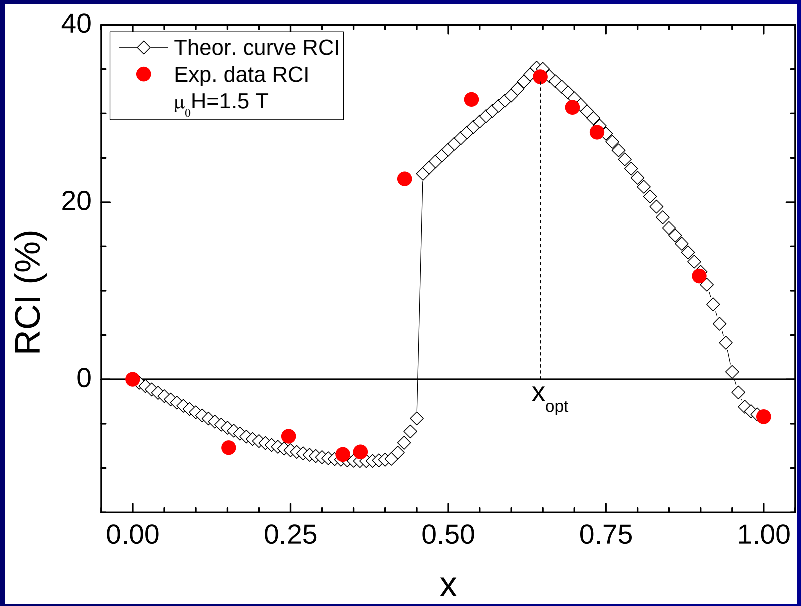
R. Caballero-Flores, V. Franco, A. Conde, K. E. Knipling, and M. A. Willard. Appl. Phys. Lett. 96 (2010) 182506

Compositional effects in amorphous alloys



- Nanoperm-type (FeZrB based) alloys are among the best
- The influence of alloying elements is different for low and high metalloid content
- For amorphous alloys there is a trend of increasing $\left|\Delta S_M^{pk}\right|$ for increasing T_c
- That trend is not evident for RC

RC of composite: Comparison with experiments



- 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

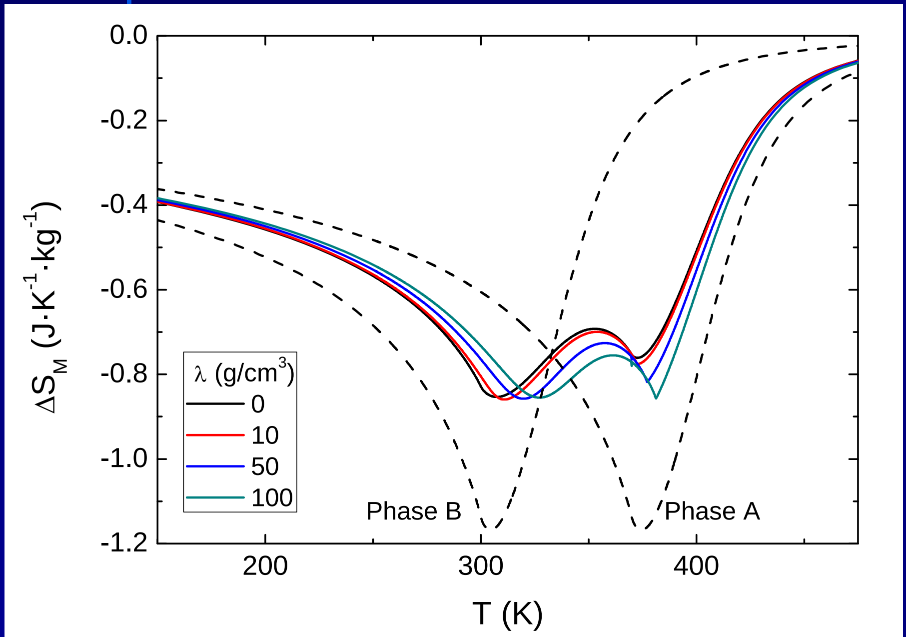
$$M = xM_A + (1-x)M_B$$

- Interactions (mean field)

$$H_{eff} = H + \lambda M$$

- ΔS_M calculated from Maxwell relation

Influence of interactions

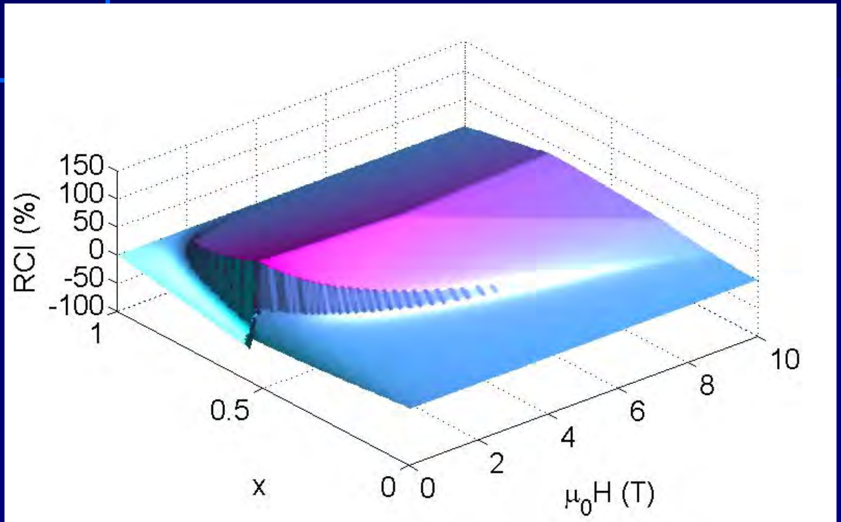


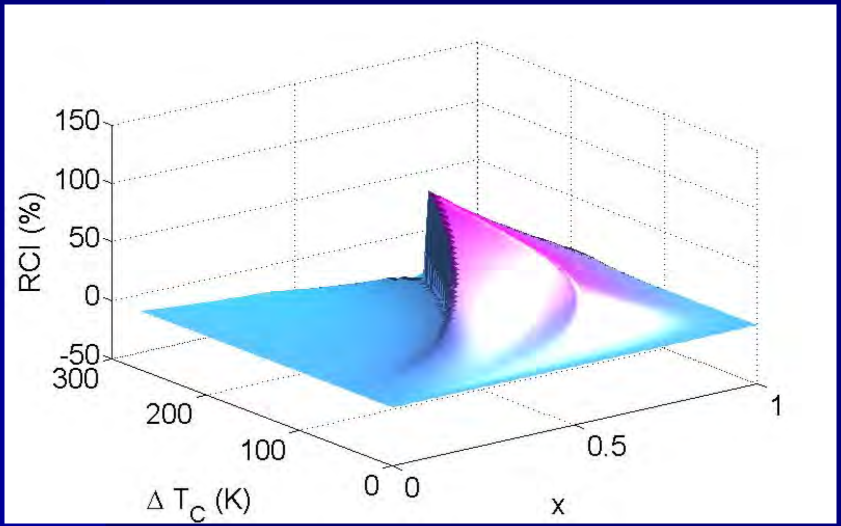
- Peak temperatures are shifted with increasing interaction strength
- Table-like character is enhanced

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

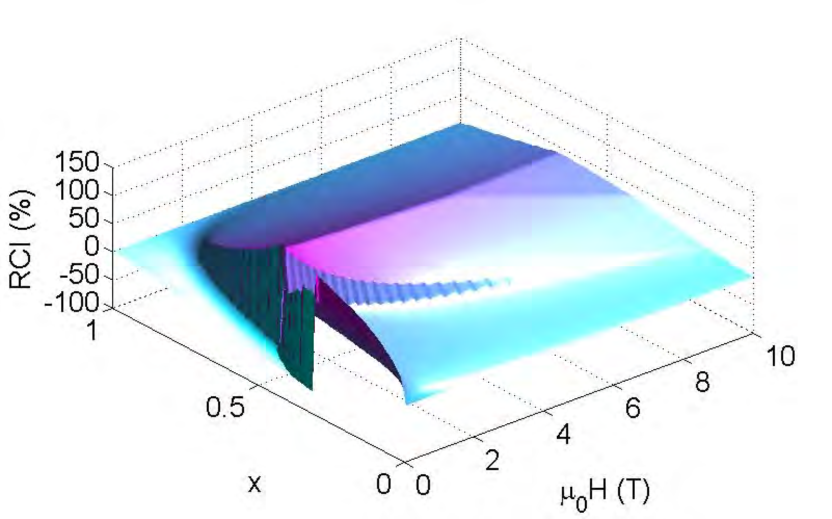
RCI

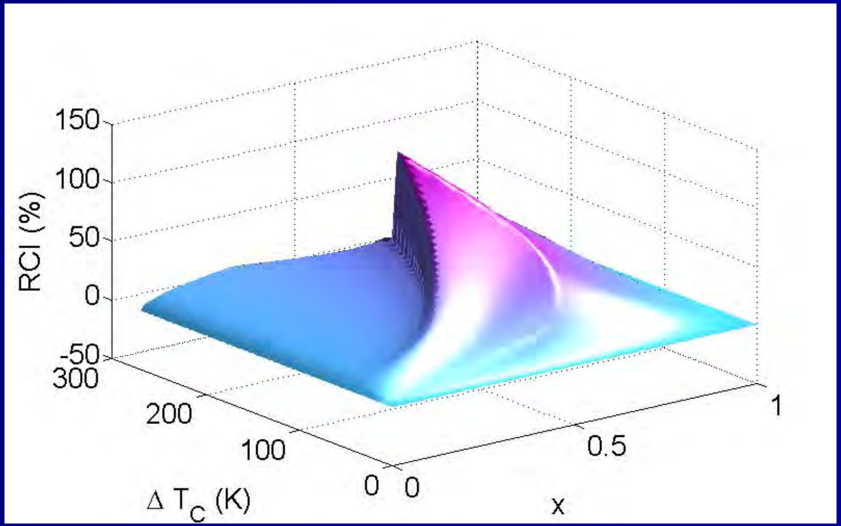
$\lambda = 0\ g/cm^3$





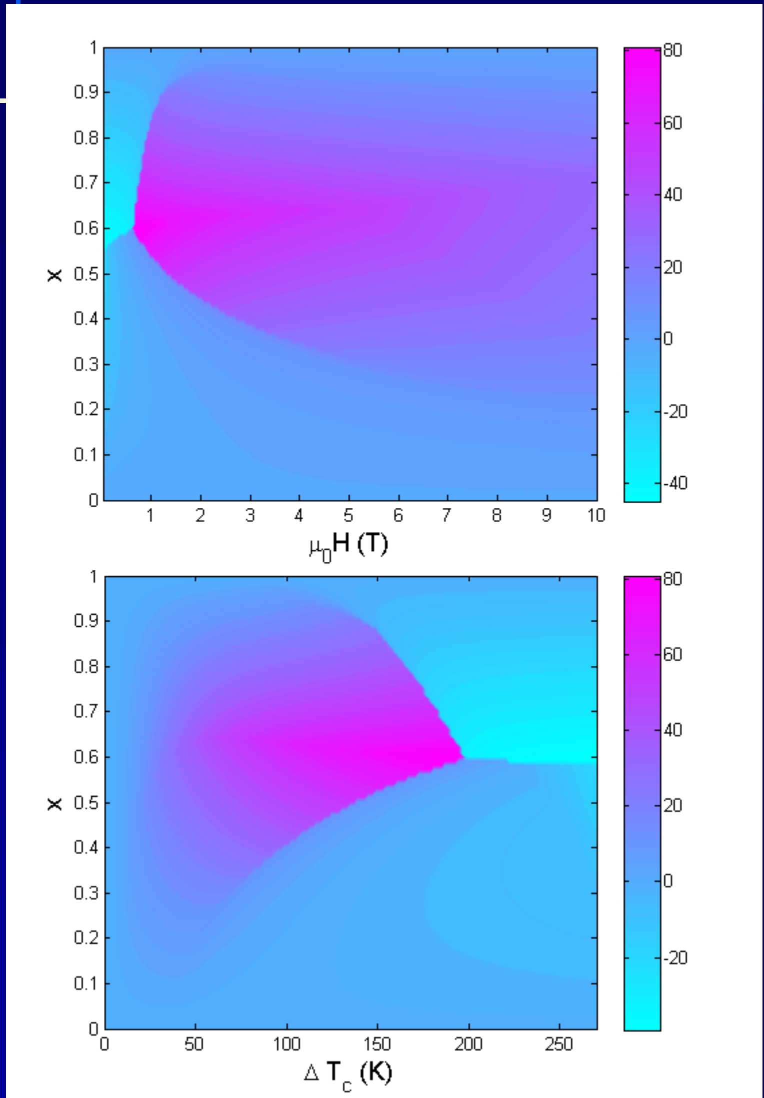
$\lambda = 100\ g/cm^3$

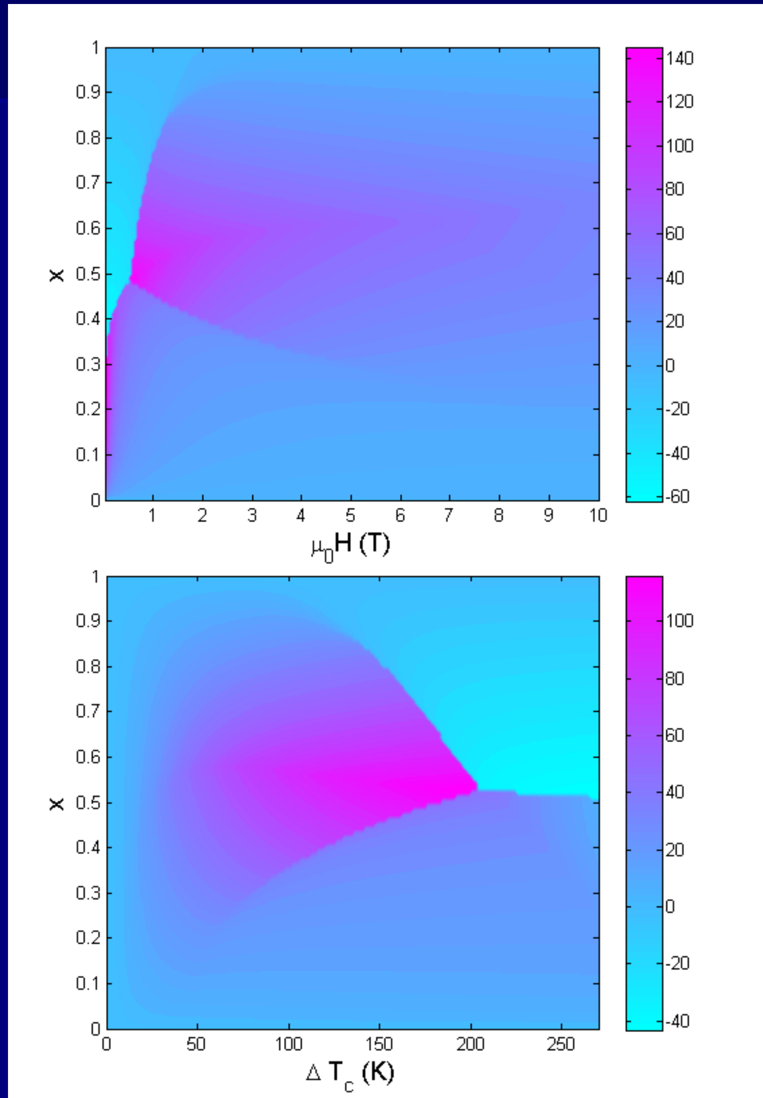


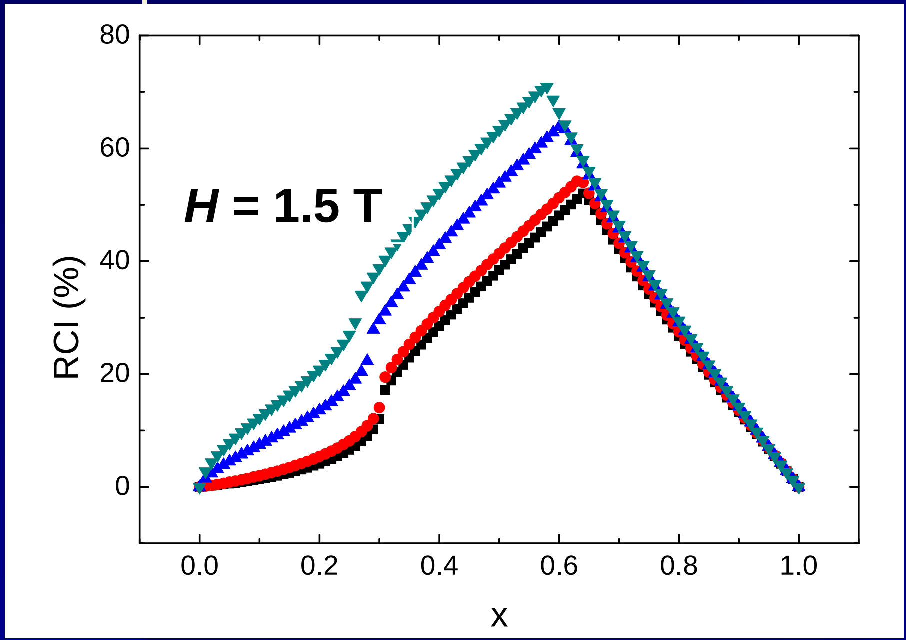


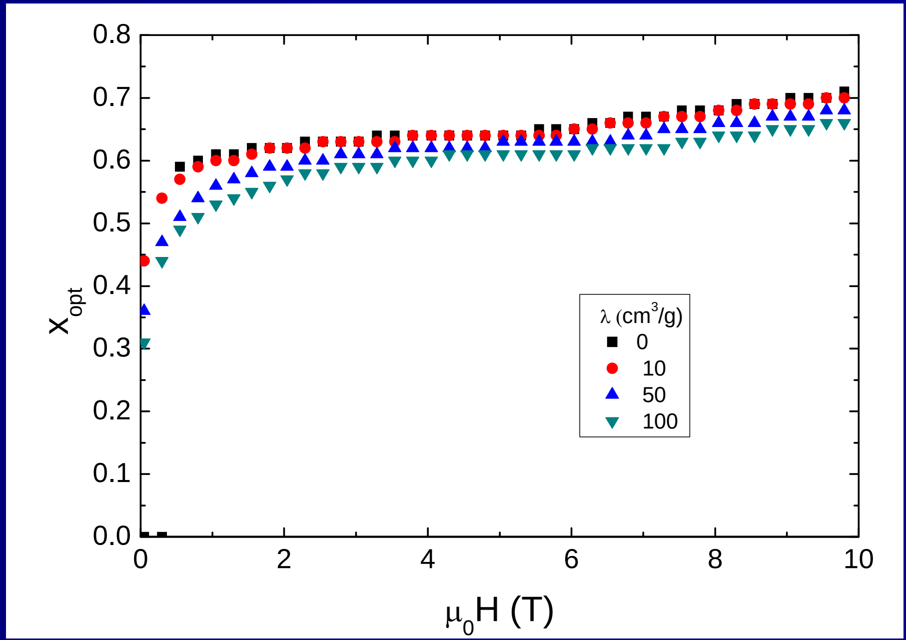
RCI

λ = 0 g/cm^3 | λ = 100 g/cm^3



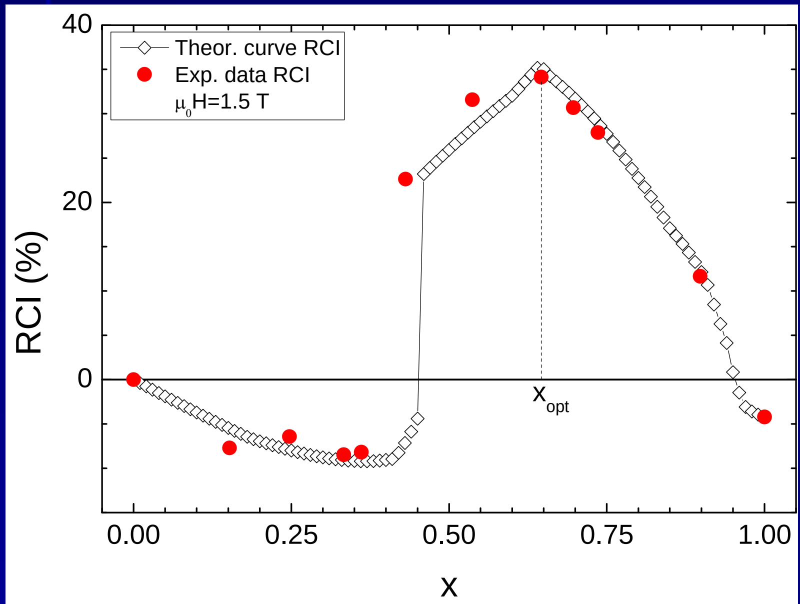






- There is no qualitative change of the curves due to interactions
- There is a shift of x_{opt} to lower values

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

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Conclusions

- For comparing experimental data, it is necessary to determine the appropriate field dependence of ΔS_M
  - Mean field predictions are not the optimal for all cases
  - We can obtain critical exponents from MCE
- Phase transitions and critical phenomena can be studied by analyzing the magnetocaloric response
  - Even when conventional methods do not work
- Composites are a good strategy to enhance the refrigerant capacity of materials
  - Interactions between phases alter the optimal compositions
- Nanostructuring allows us to control the field responsiveness of magnetocaloric materials
  - Multilayers composed of different phases exhibit a linear field dependence of ΔS_M in a broad temperature range
    - In contrast to bulk composites, this behavior remains for an extended field range