



Soft magnetic materials for magnetic refrigeration: field dependence and a universal curve

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Soft magnetic amorphous alloys for magnetic refrigeration

- Low cost (compared to materials in this session)
 - 15x less than GdSiGe
- Performance
 - Modest peak entropy change (40% of Gd) $\Delta T_{ad} \approx 3.2$ K for 5T
 - Not so small RC
 - Up to 78% of that of $\text{Gd}_5\text{Ge}_{1.9}\text{Si}_2\text{Fe}_{0.1}$ *for the same temperature span*
- Adequate properties
 - Mechanical
 - Electrical
 - ...
- Good testing ground to analyze the physics behind MCE

Structure of this talk

- Compositional effects
 - Magnetic entropy change
 - Refrigerant capacity
- Field dependence of ΔS_M
 - Different temperature regions
 - Universal curve behavior
 - Extension to alloy series?
- How can we use the universal curve?
 - Enhancement of resolution
 - Extrapolations in field or temperature
 - Simple screening procedure for materials selection

Experimental techniques

➤ Magnetic measurements

- VSM (RT -700 K; 15 kOe)
 - Magnetic entropy change

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

- Refrigerant capacity: Wood and Potter

➤ Specific heat

- DSC (zero field)
 - Estimate of ΔT_{ad}

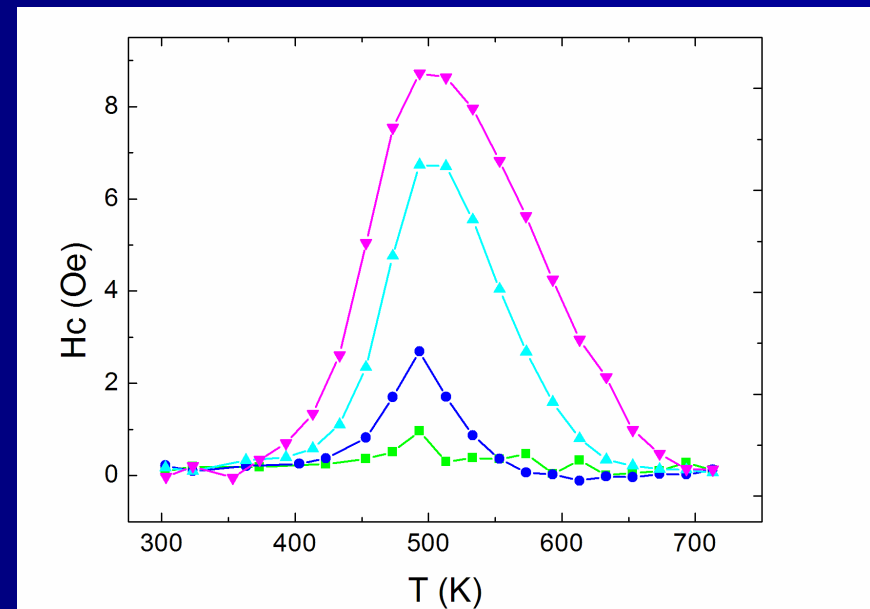
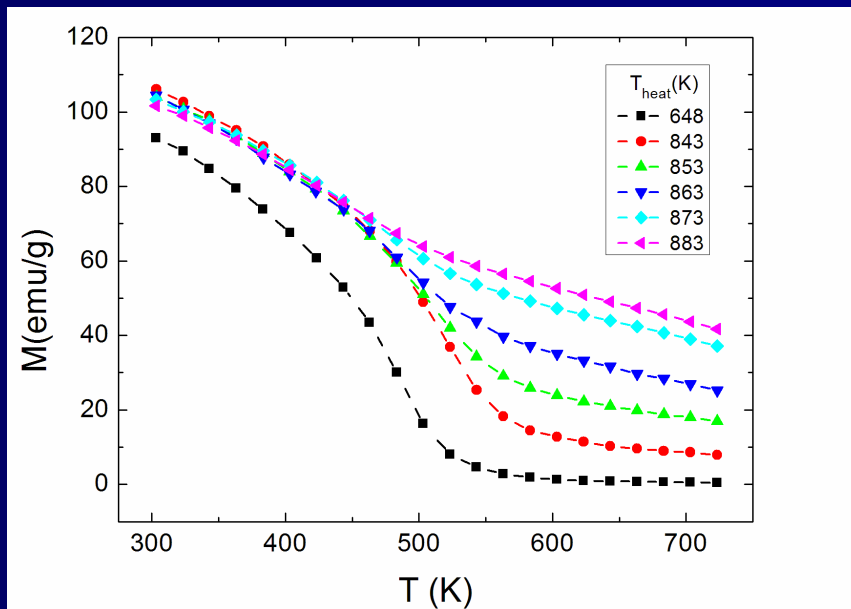
Alloys

- Ribbons prepared by melt spinning
 - Pre-heated for stress relaxation
- Compositional series
 - FINEMET: 5 at. % Mo
 - NANOPERM
 - Co addition
 - Fe/B ratio
 - HITPERM
 - Mn addition
 - Bulk amorphous alloys
 - Co addition
 - Cr/Mo ratio

Alloy compositions

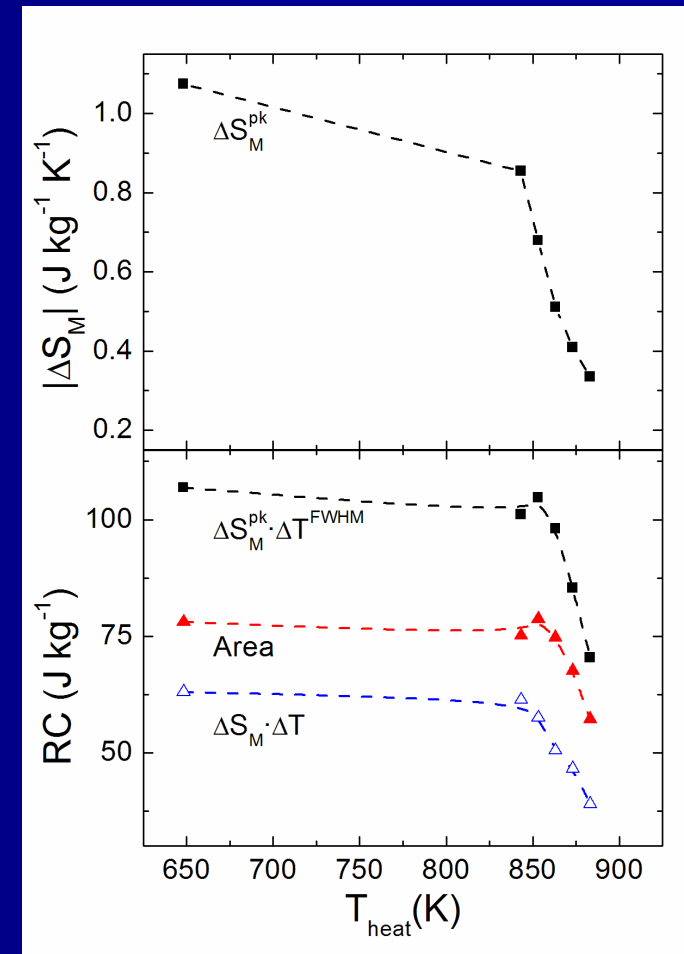
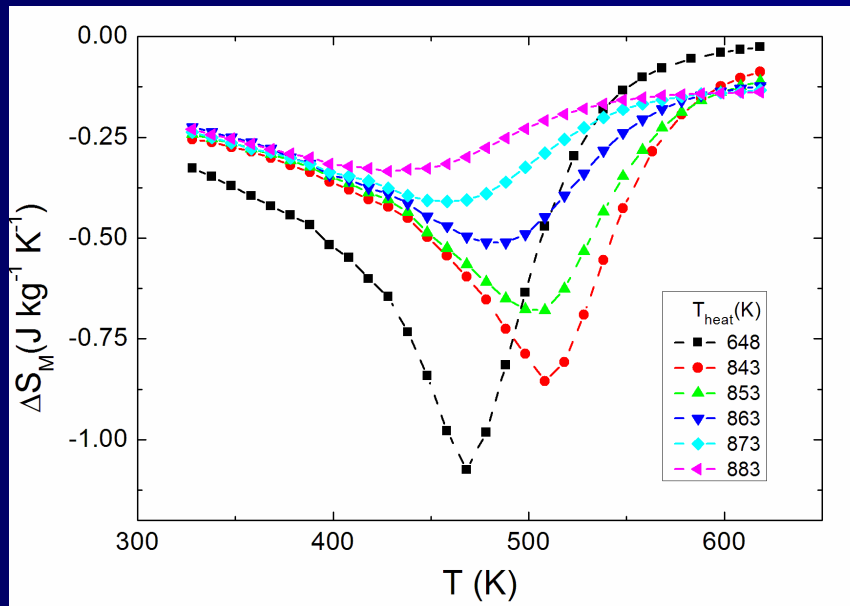
- $\text{Fe}_{68.5}\text{Mo}_5\text{Si}_{13.5}\text{B}_9\text{Cu}_1\text{Nb}_3$, denoted as MoFinemet
- $\text{Fe}_{83-x}\text{Co}_x\text{Zr}_6\text{B}_{10}\text{Cu}_1$ ($x=0, 5$), denoted as CoNanoperm
- $\text{Fe}_{91-x}\text{Mo}_8\text{Cu}_1\text{B}_x$ ($x=15, 17, 20$), denoted as BNanoperm
- $\text{Fe}_{60-x}\text{Mn}_x\text{Co}_{18}\text{Nb}_6\text{B}_{16}$ ($x=0, 2, 4$), denoted as MnHiTperm
- $(\text{Fe}_x\text{Co}_y\text{B}_z\text{C}_u)\text{Si}_3\text{Al}_5\text{Ga}_2\text{P}_{10}$ ($x,y,z,u=70,0,5,5; 56,14,6,4; 43,26,8,3; 29,40,9,2; 17,52,10,1; 5,63,12,0$), denoted as CoBAA
- $\text{Fe}_{65.5}\text{Cr}_{4-x}\text{Mo}_{4-y}\text{Cu}_{x+y}\text{Ga}_4\text{P}_{12}\text{C}_5\text{B}_{5.5}$ ($x, y=0; 0.5; 1, x+y \leq 1$), denoted as CrMoBAA

Nanocrystallization of Mo-Finemet



Smaller values of coercivity → More reduced dipolar interactions

MCE of nanocrystalline Mo-Finemet

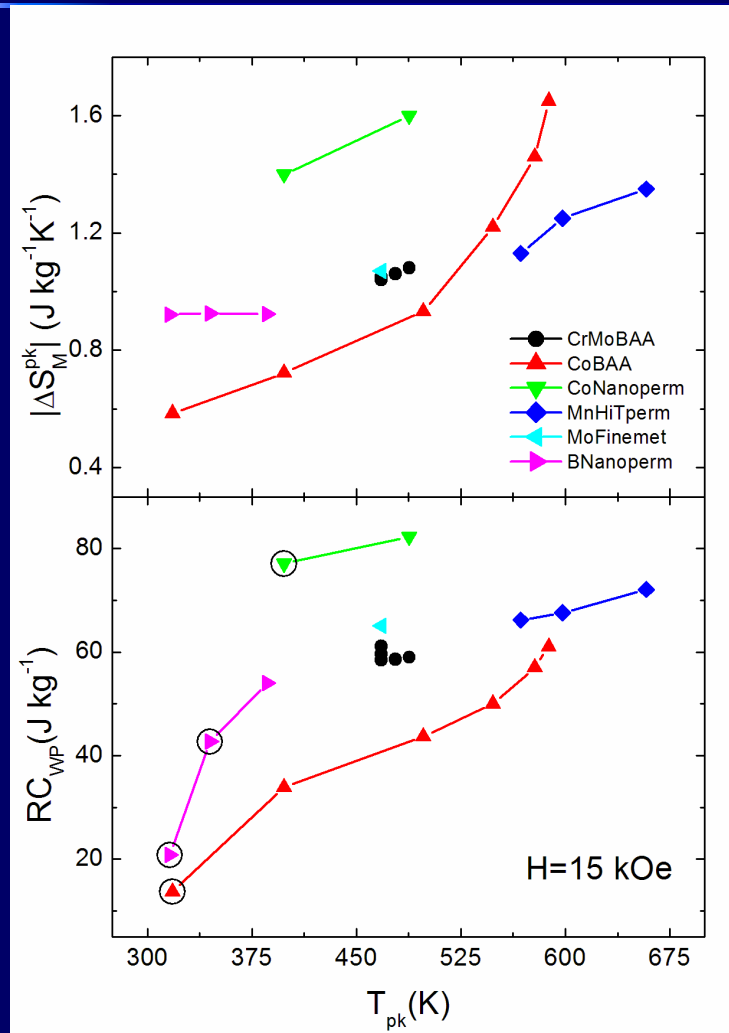


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Compositional effects in amorphous alloys

- MCE due to a second order magnetic phase transition
 - Tune T_{Curie} close to the working temperature
- For a given transition temperature
 - Maximization of both ΔS_M^{pk} and RC
- Minimize dependence with T_{Curie}
 - composites

Compositional effects in amorphous alloys (results)

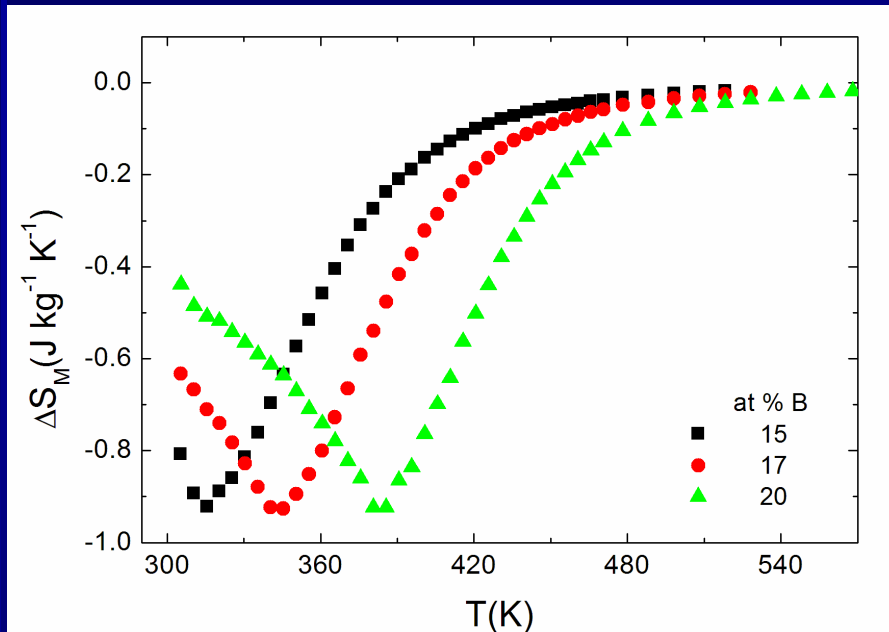


- Nanoperm-type alloys are among the best
 - Estimate:

$$\Delta T_{ad} \approx 1.3 \text{ K for } 1.5 \text{ T;} \\ 3.2 \text{ K for } 5\text{T}$$

- Co addition has different effects for low and high metalloid content
- A constant $|\Delta S_M^{pk}|$ can be obtained by altering the Fe/B ratio

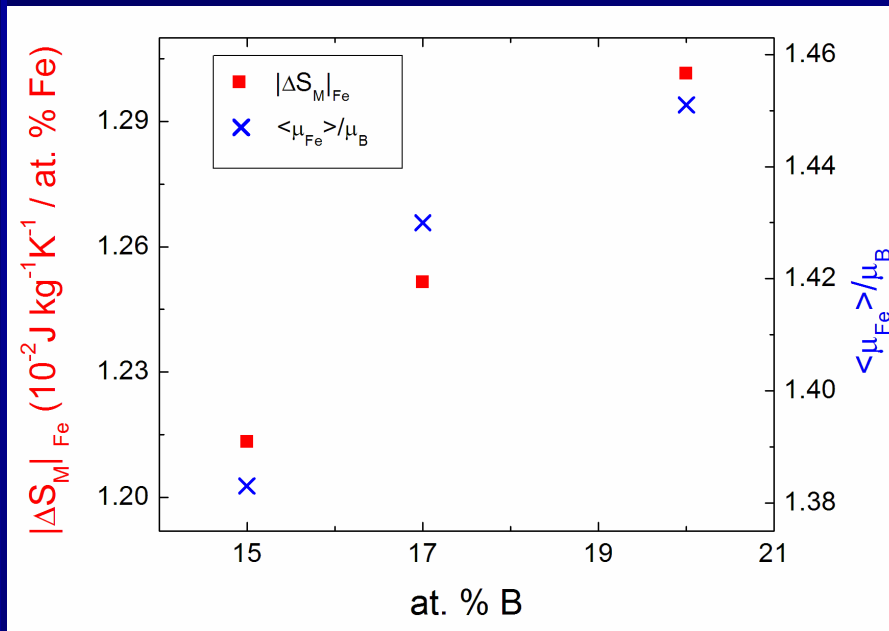
$\text{Fe}_{91-x}\text{Mo}_8\text{Cu}_1\text{B}_x$ ($x=15, 17, 20$)



- T_C can be tuned without altering the magnitude of $|\Delta S_M^{pk}|$

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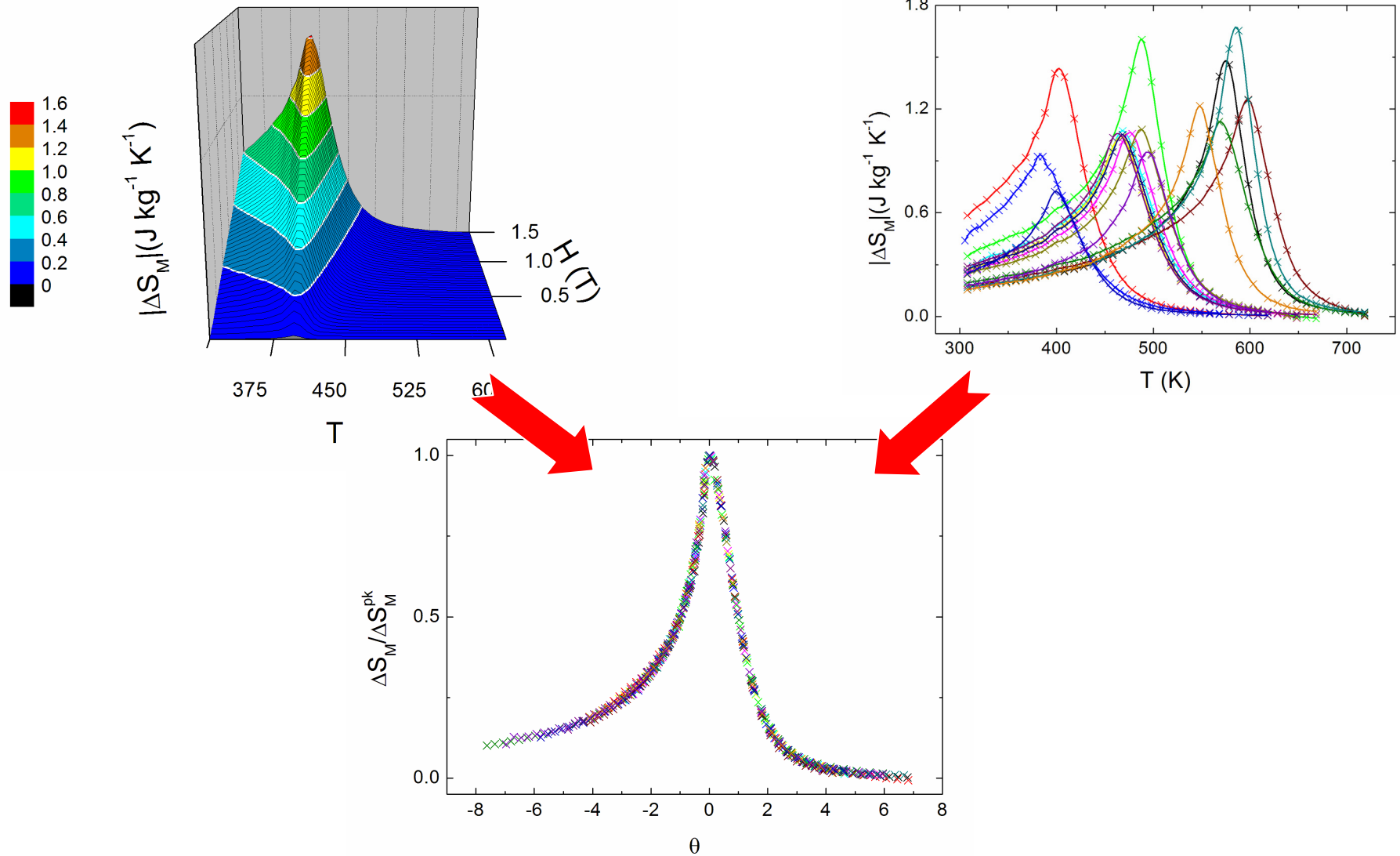
$\text{Fe}_{91-x}\text{Mo}_8\text{Cu}_1\text{B}_x$ ($x=15, 17, 20$)



- Increasing contribution per Fe atom
- Correlated with the low-temperature average magnetic moment of Fe

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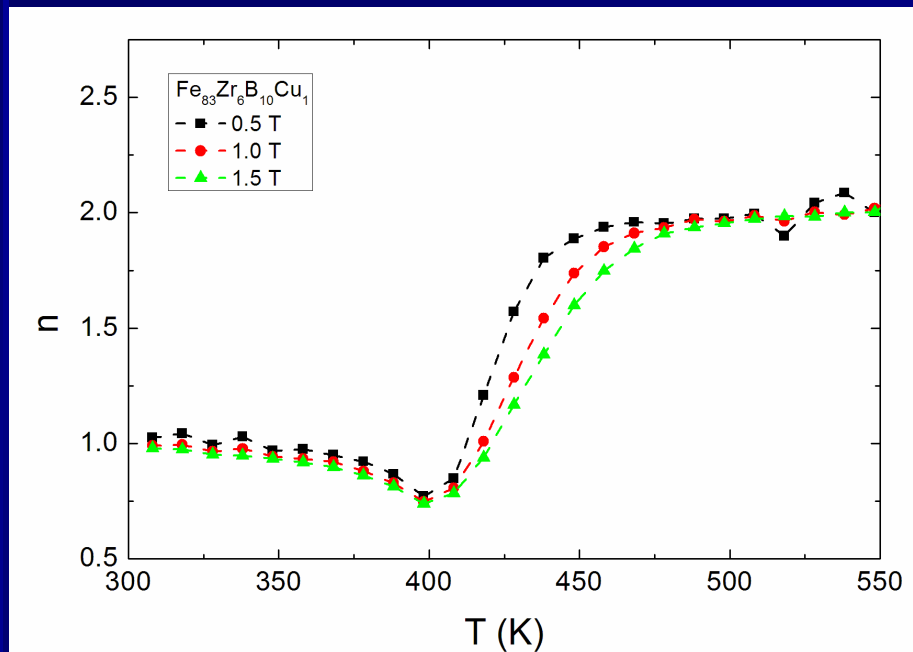
Field dependence of ΔS_M



Field dependence of ΔS_M

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

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



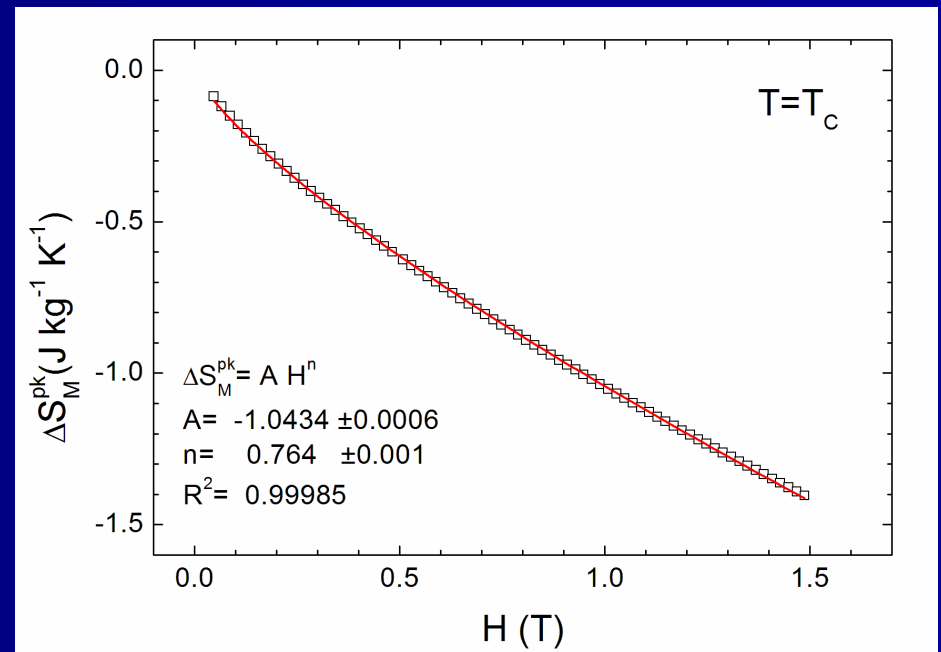
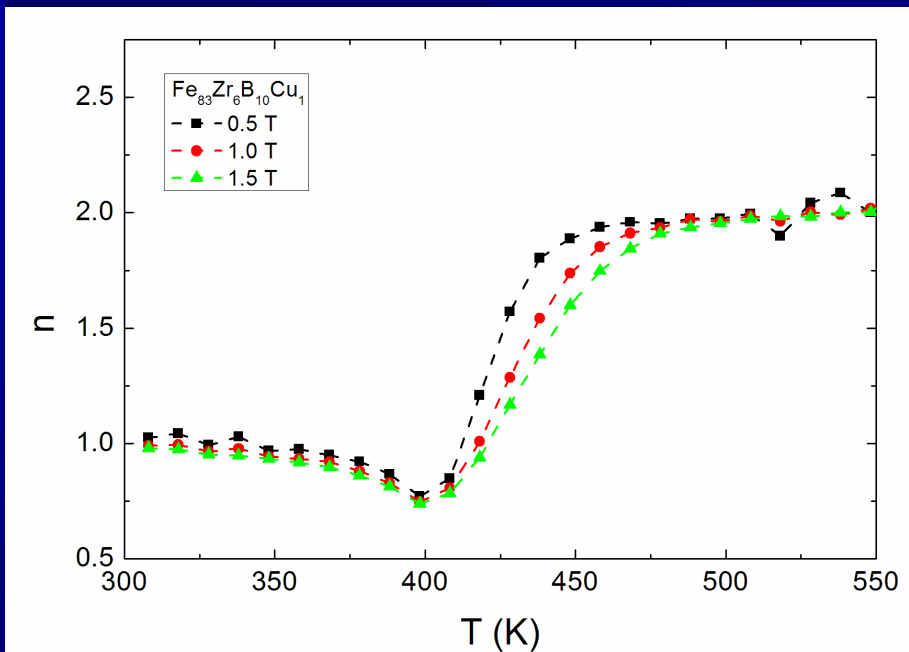
- $T \ll T_C$: $n=1$
- $T \gg T_C$: $n=2$
- $T = T_C$: $n \sim 0.75$
 - Not compatible with a mean field approach ($n=2/3$)

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n from two methods

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

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



Field dependence at T_c

- Arrott-Noakes equation of state

$$H^{\frac{1}{\gamma}} = a(T - T_c)M^{\frac{1}{\gamma}} + bM^{\frac{1}{\beta} + \frac{1}{\gamma}}$$

- At $T = T_c$

$$n = 1 + \frac{1}{\delta} \left(1 - \frac{1}{\beta} \right)$$

- Good description of experimental results

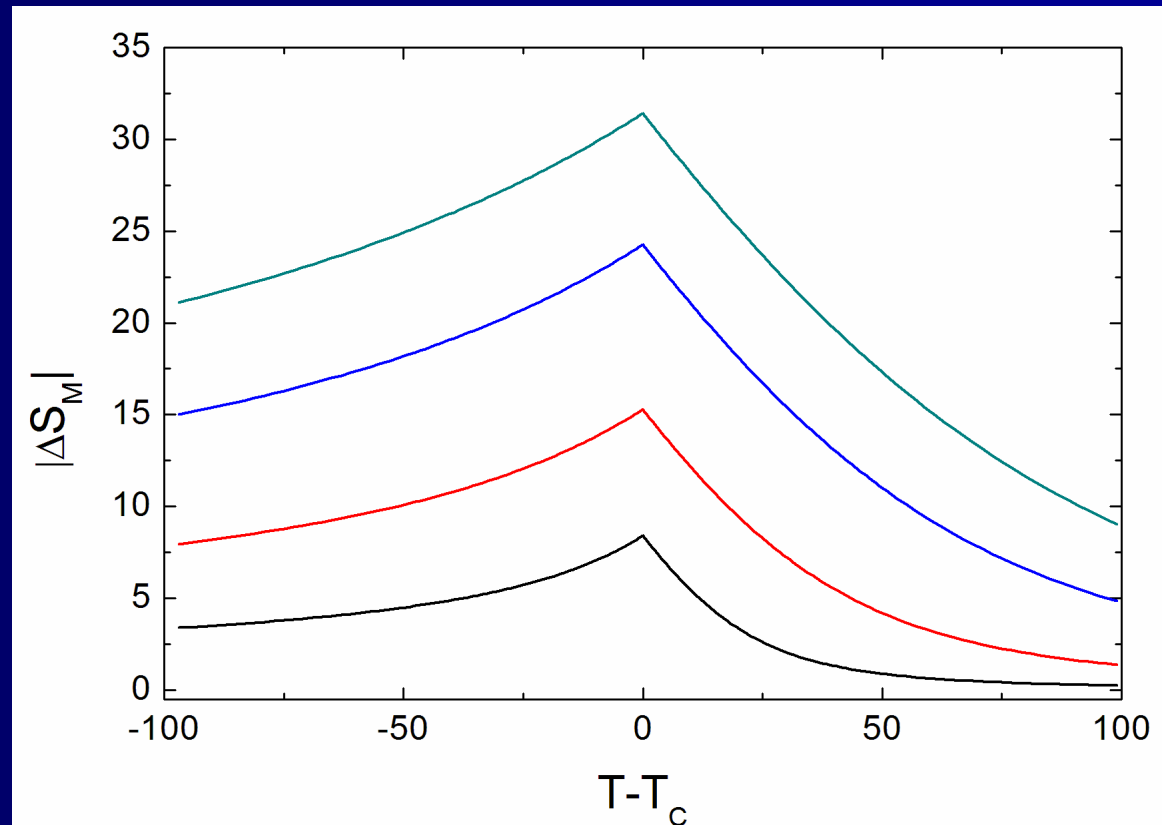
V. Franco, J.S. Blázquez, and A. Conde, Appl. Phys. Lett. 89 (2006) 222512

Master curve for the field dependence?

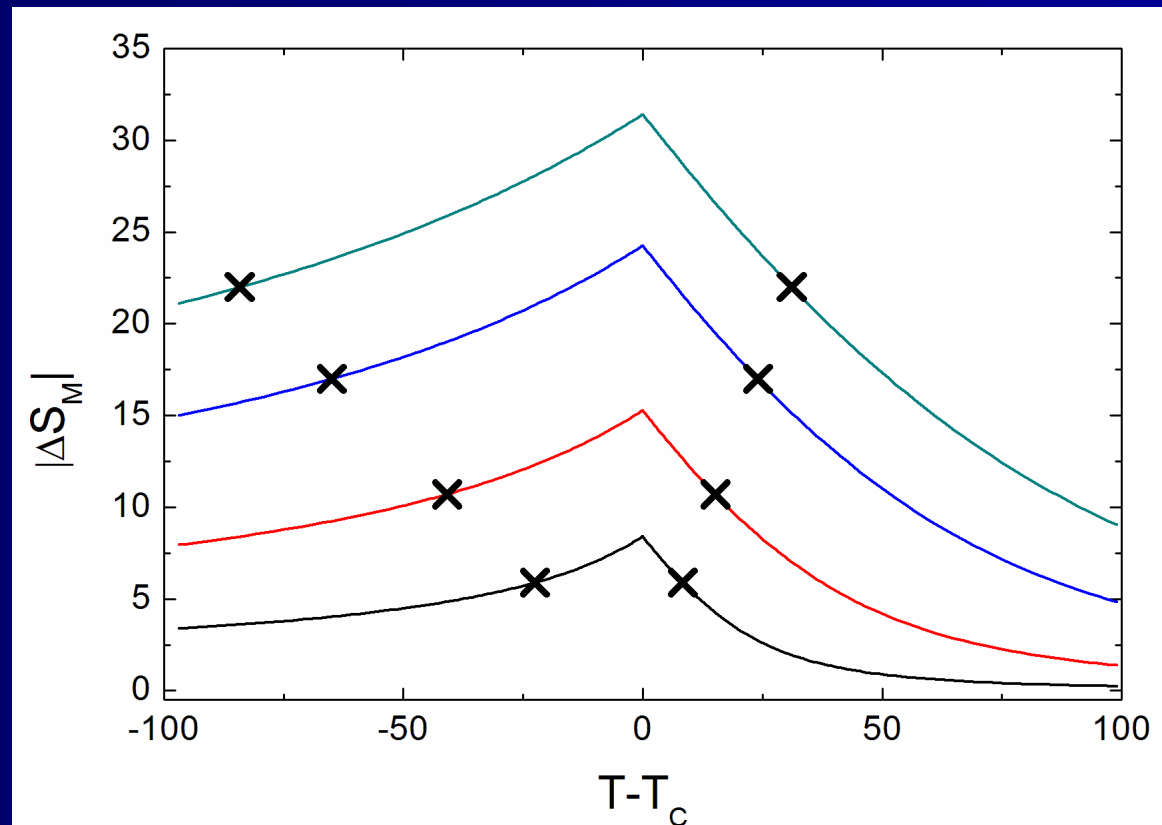
- Different characteristic regions of n
- The temperature dependence of ΔS_M also changes above and below T_C
- Phenomenological master curve:
 - Normalization of ΔS_M
 - Rescaled temperature using 2 reference points

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

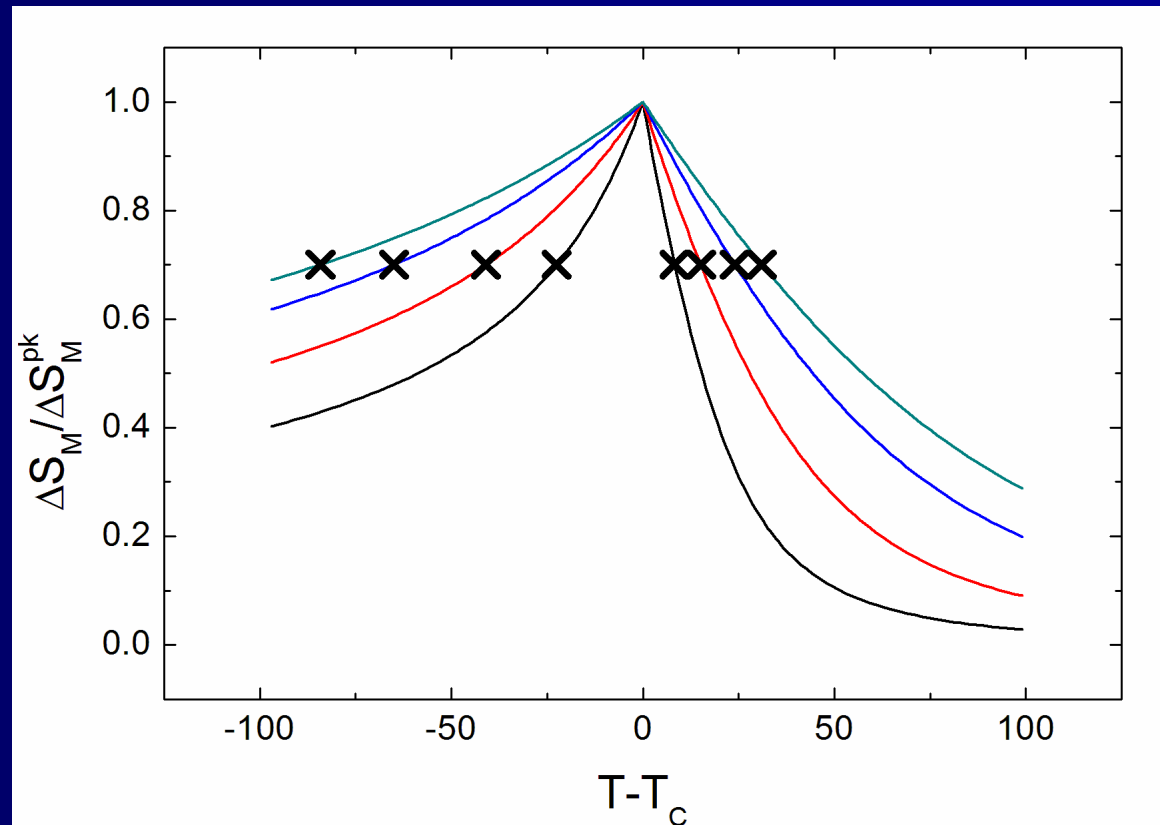
“Measurements” for different applied fields



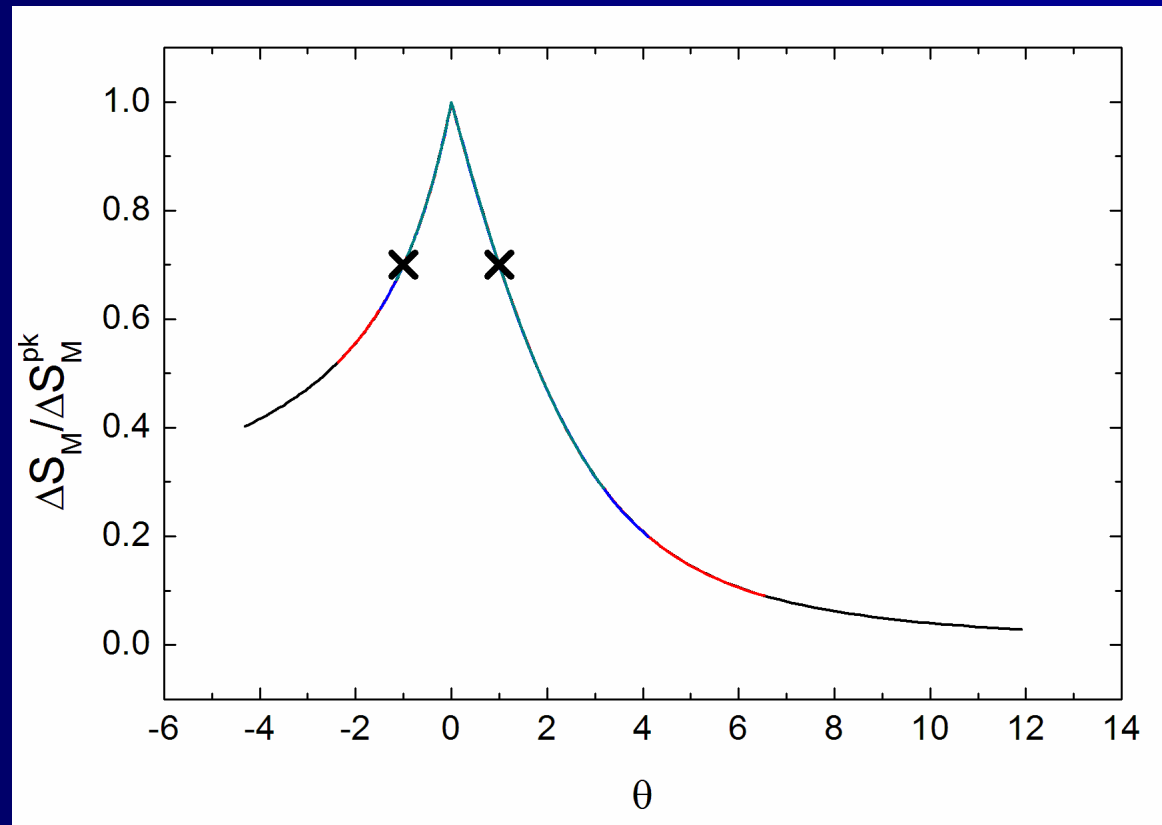
Selection of equivalent points (with respect to the peak)



Rescale (normalize) the vertical axis



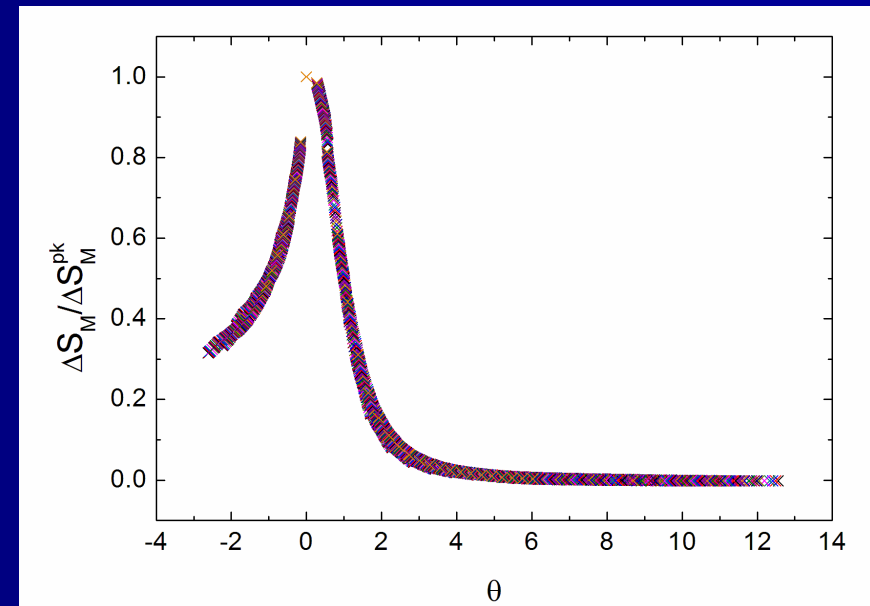
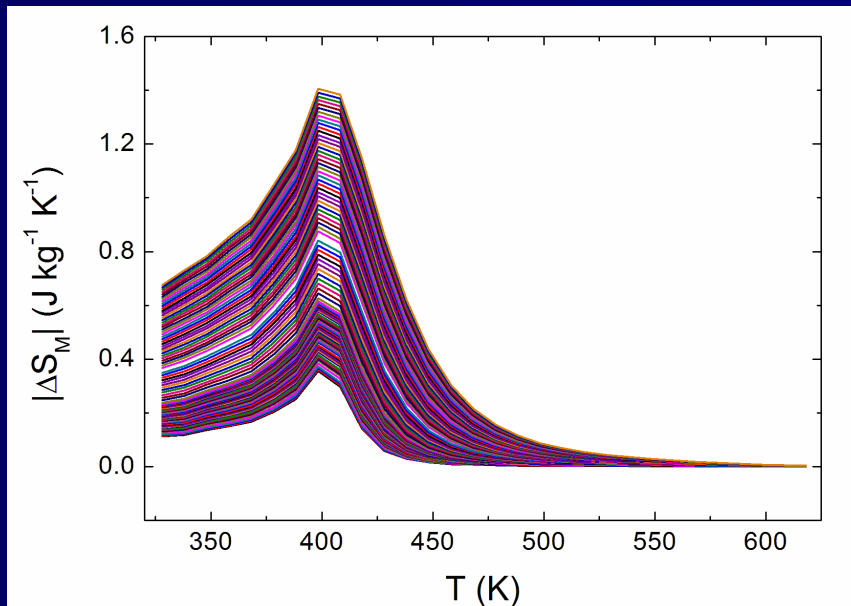
Rescale the temperature axis



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

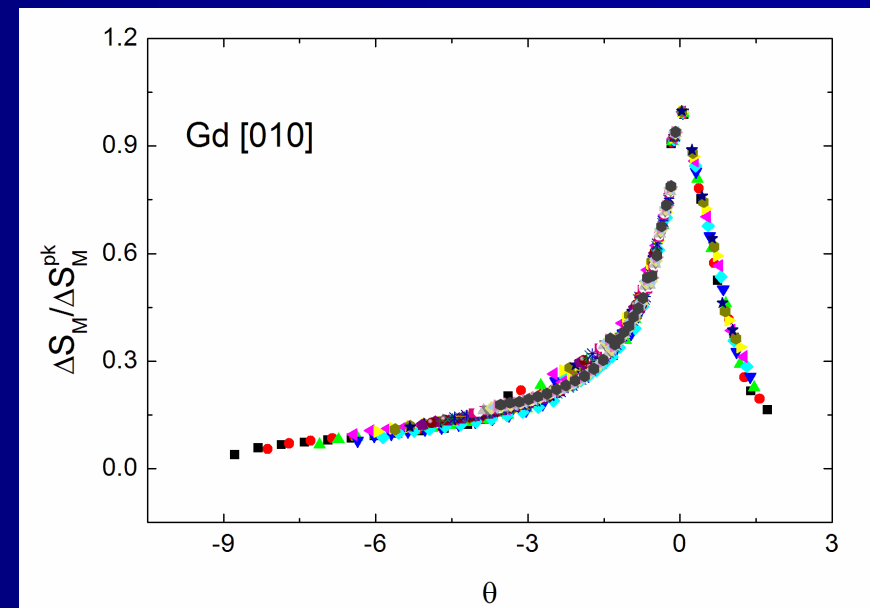
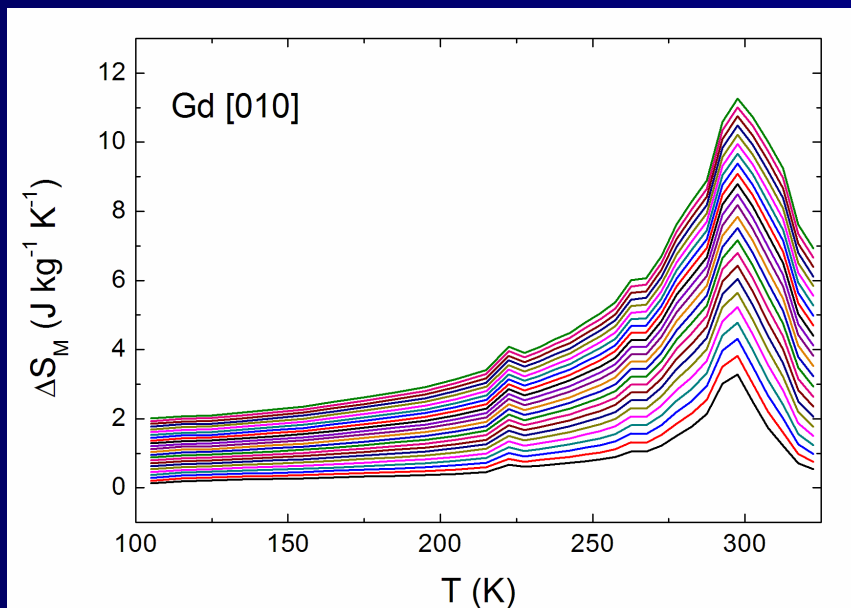
Master curve for the field dependence

96 curves; 0.25 – 1.5 T



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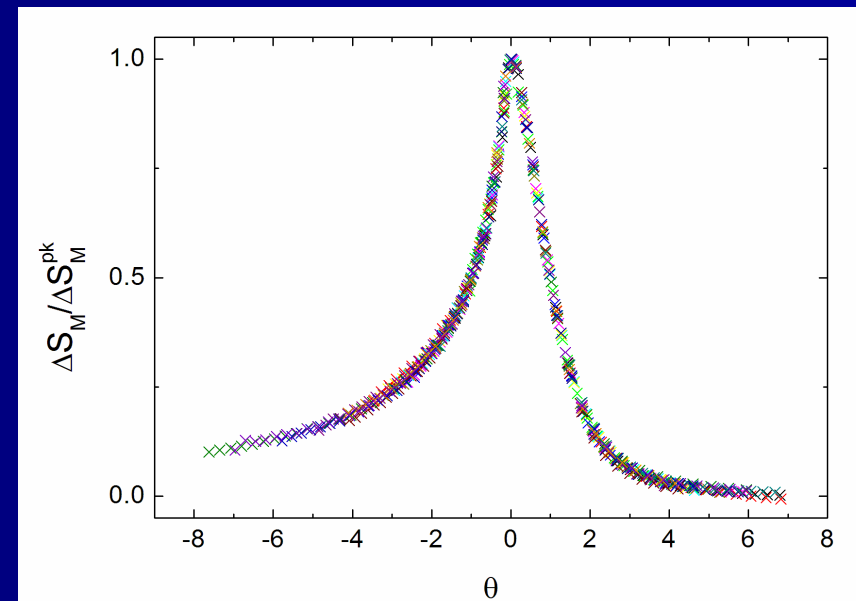
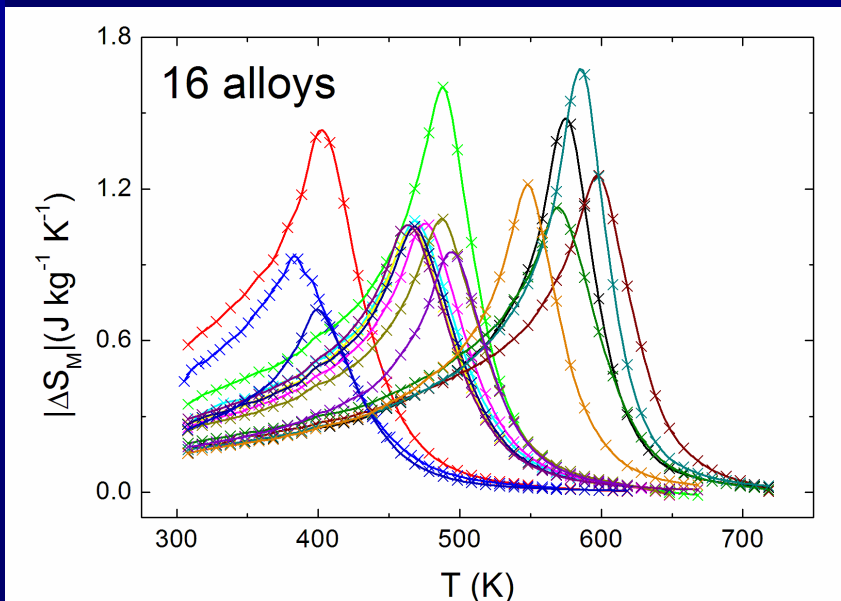
Only for Fe-based soft magnets?



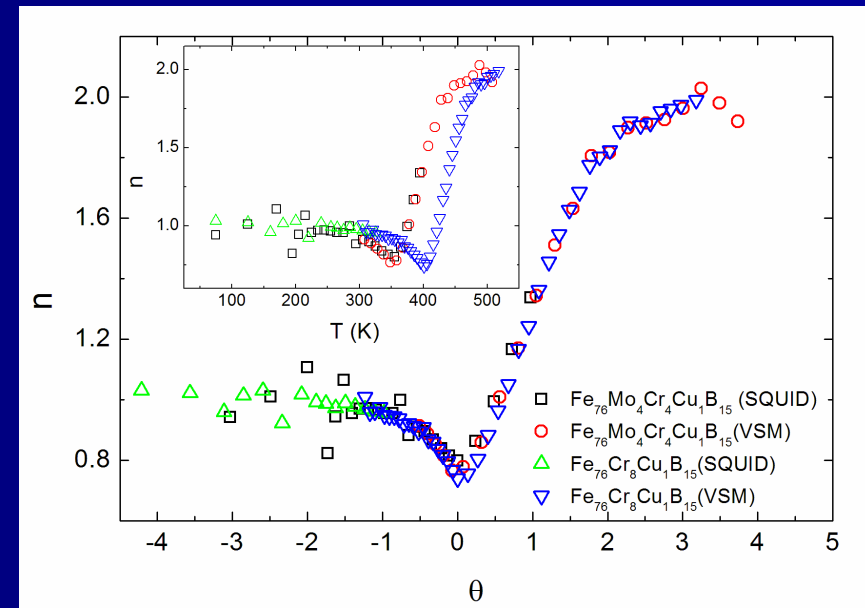
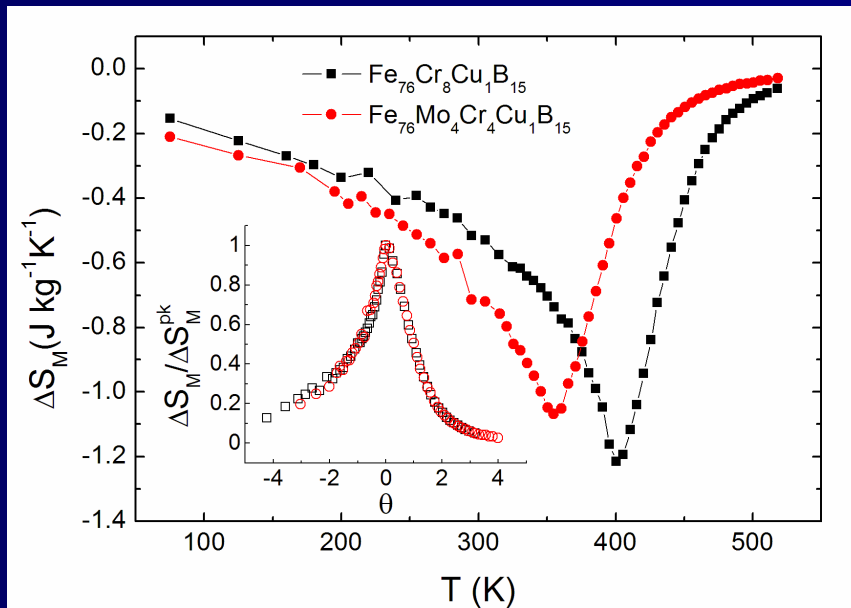
V. Franco, A. Conde, V.K. Pecharsky, K.A. Gschneidner, Jr. *Europhys. Lett.* 79 (2007) 47009

MCE of different alloy series

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

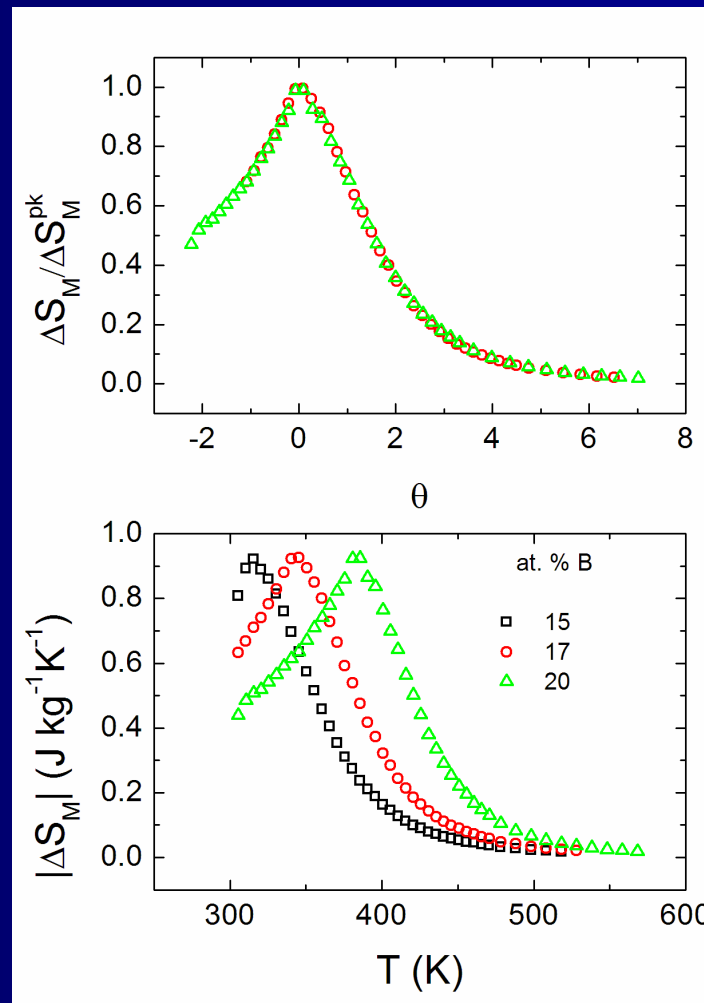


n also collapses

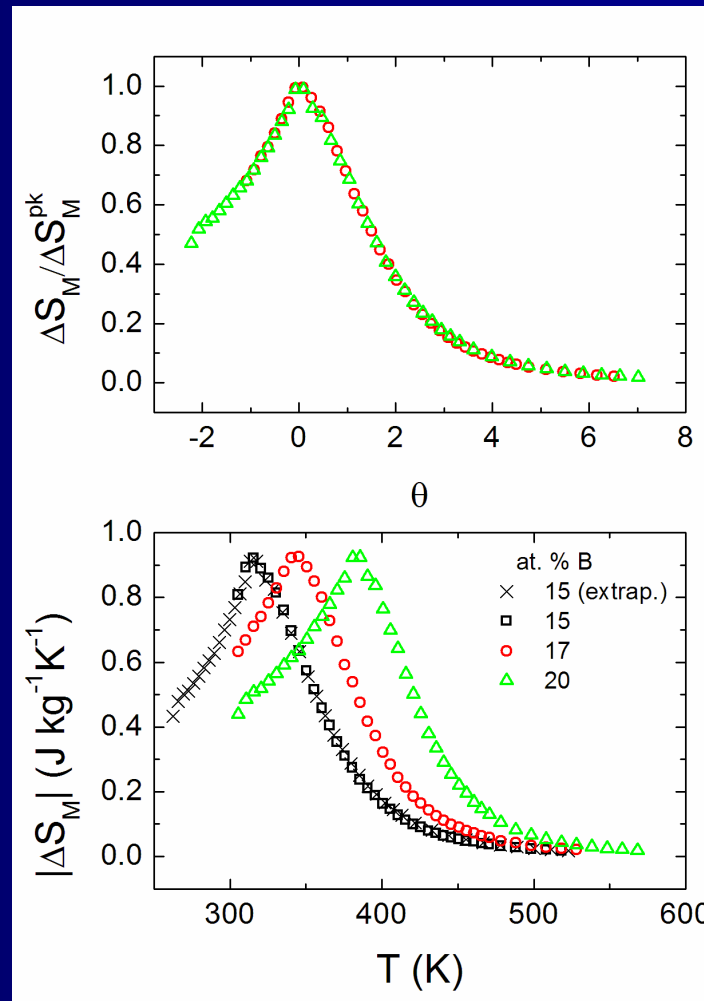


V. Franco, C.F. Conde, A. Conde, L.F. Kiss, Appl. Phys. Lett. 90 (2007) 052509

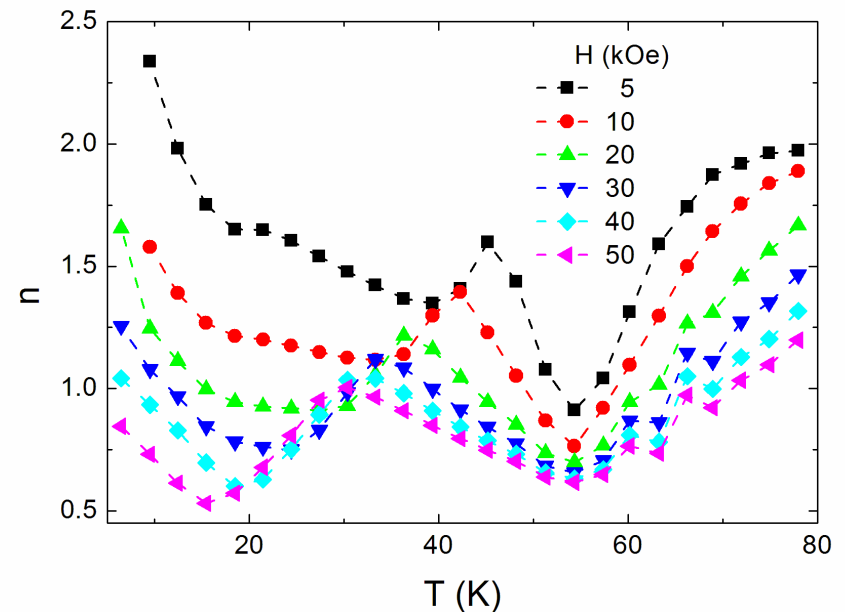
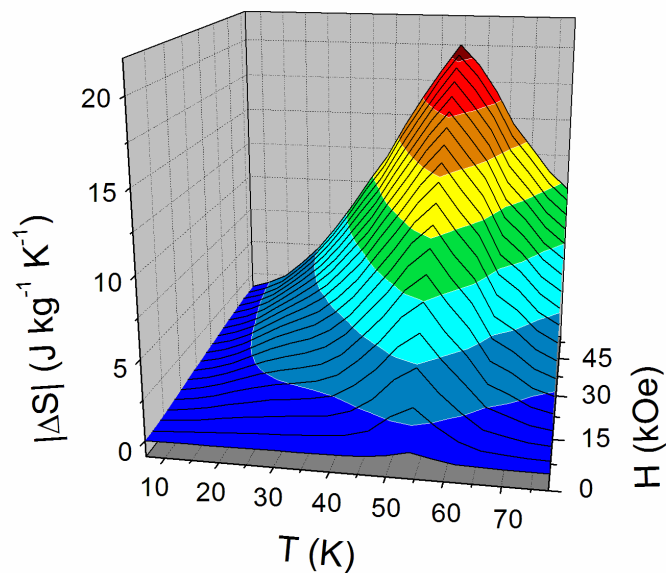
Extrapolation using the universal curve



Extrapolation using the universal curve

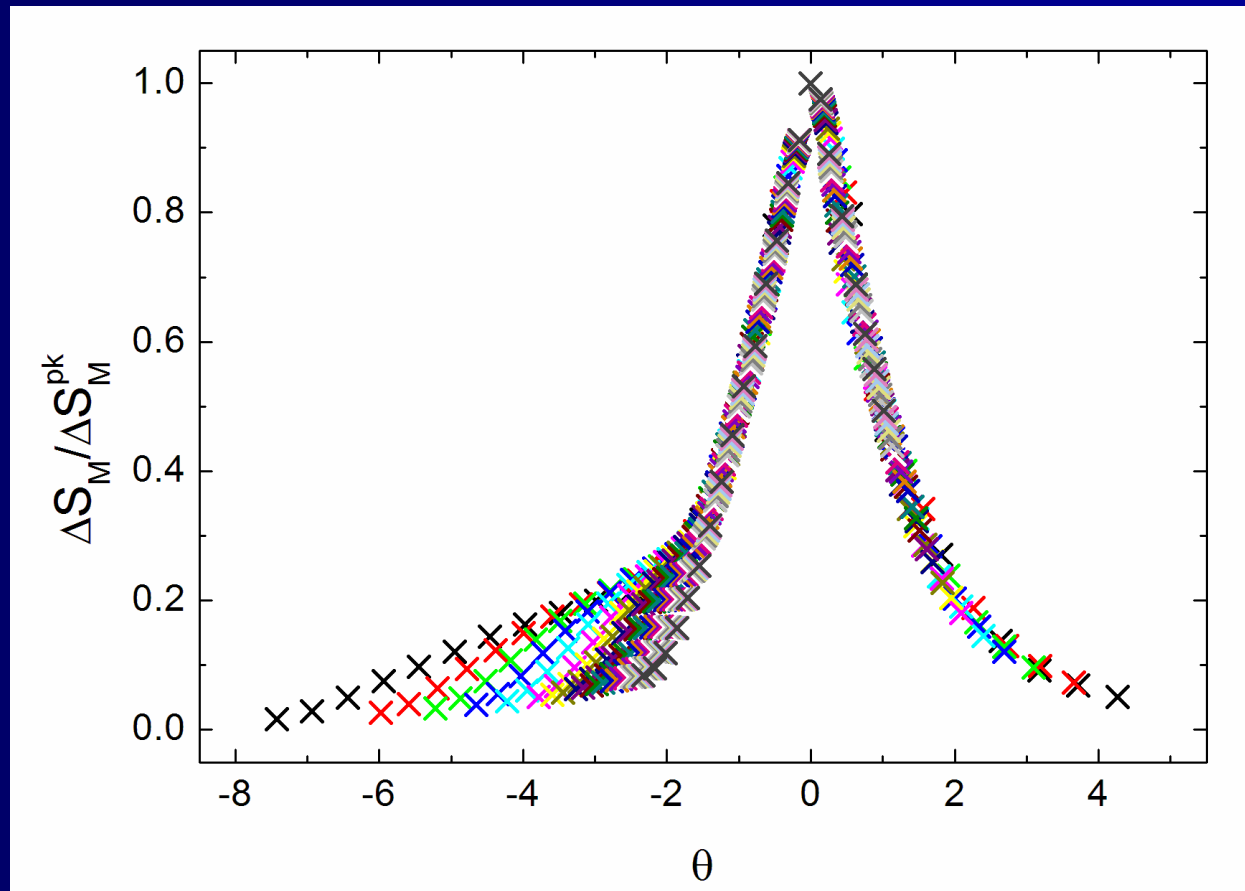


Overlapping magnetic phenomena: the use of n



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

Overlapping magnetic phenomena



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

Conclusions

- Soft magnetic amorphous alloys for MCE refrigeration
 - Low cost (at least 15x less than Gd-based materials)
 - Modest peak entropy change (40% of Gd); $\Delta T_{ad} \approx 3.2$ K for 5T
 - Refrigerant capacity comparable to that of $\text{Gd}_5\text{Ge}_{1.9}\text{Si}_2\text{Fe}_{0.1}$
- Field dependence of ΔS_M
 - Three characteristic regions
 - $n=1$ for $T \ll T_C$
 - $n=2$ for $T \gg T_C$
 - $n = 1 + \frac{1}{\delta} \left(1 - \frac{1}{\beta} \right)$ at T_C
- Experimental data show a universal curve for ΔS_M
 - For different applied fields
 - For different alloys with similar critical exponents
- It can be used for
 - Enhancing of the resolution of the data
 - Extrapolating curves in temperature or field
 - Simple screening of the performance of materials

Our publications on this subject

- V. Franco, J. S. Blázquez, C.F. Conde, A. Conde.
"A Finemet-type alloy as a low-cost candidate for high-temperature magnetic refrigeration"
Applied Physics Letters **88** (2006) 42505
- V. Franco, J.M. Borrego, A. Conde, S. Roth.
"Influence of Co addition on the magnetocaloric effect of FeCoSiAlGaPCB amorphous alloys"
Applied Physics Letters **88** (2006) 132509
- V. Franco, J. S. Blázquez, A. Conde.
"The influence of Co addition on the magnetocaloric effect of Nanoperm-type amorphous alloys"
Journal of Applied Physics **100** (2006) 064307
- V. Franco, J. M. Borrego, C.F. Conde, A. Conde, M. Stoica, S. Roth.
"Refrigerant capacity of FeCrMoCuGaPCB amorphous alloys"
Journal of Applied Physics **100** (2006) 083903
- V. Franco, J. S. Blázquez, A. Conde.
"Field dependence of the magnetocaloric effect in materials with a second order phase transition: a master curve for the magnetic entropy change"
Applied Physics Letters **89** (2006) 222512
- V. Franco, C.F. Conde, A. Conde, L.F. Kiss.
"Enhanced magnetocaloric response in Cr/Mo containing Nanoperm-type amorphous alloys "
Applied Physics Letters **90** (2007) 052509
- V. Franco, J. S. Blázquez, M. Millán , J.M. Borrego , C.F. Conde, A. Conde.
"The magnetocaloric effect in soft magnetic amorphous alloys"
Journal of Applied Physics **101** (2007) 9C503
- V. Franco, C.F. Conde, J. S. Blázquez, A. Conde, P. Švec, D. Janičkovič, L.F. Kiss.
"A constant magnetocaloric response in FeMoCuB amorphous alloys with different Fe/B ratios"
Journal of Applied Physics **101** (2007) 93903
- V. Franco, C.F. Conde, J.S. Blázquez, M. Millán, A. Conde
"Magnetocaloric effect in Mn-containing Hitperm-type alloys"
Journal of Applied Physics **102** (2007) 13908
- V. Franco, A. Conde, V.K. Pecharsky, K.A. Gschneidner, Jr.
"Field dependence of the magnetocaloric effect in Gd and $(Er_{1-x}Dy_x)Al_2$: Does a universal curve exist?"
Europhysics Letters **79** (2007) 47009

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- Non-crystalline solids group. Sevilla University
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- Slovak Academy of Sciences
 - Dr. P. Svec
- IFW-Dresden
 - Dr. S. Roth
- Ames Laboratory
 - Prof. V.K. Pecharsky
 - Prof. K.A. Gschneidner