

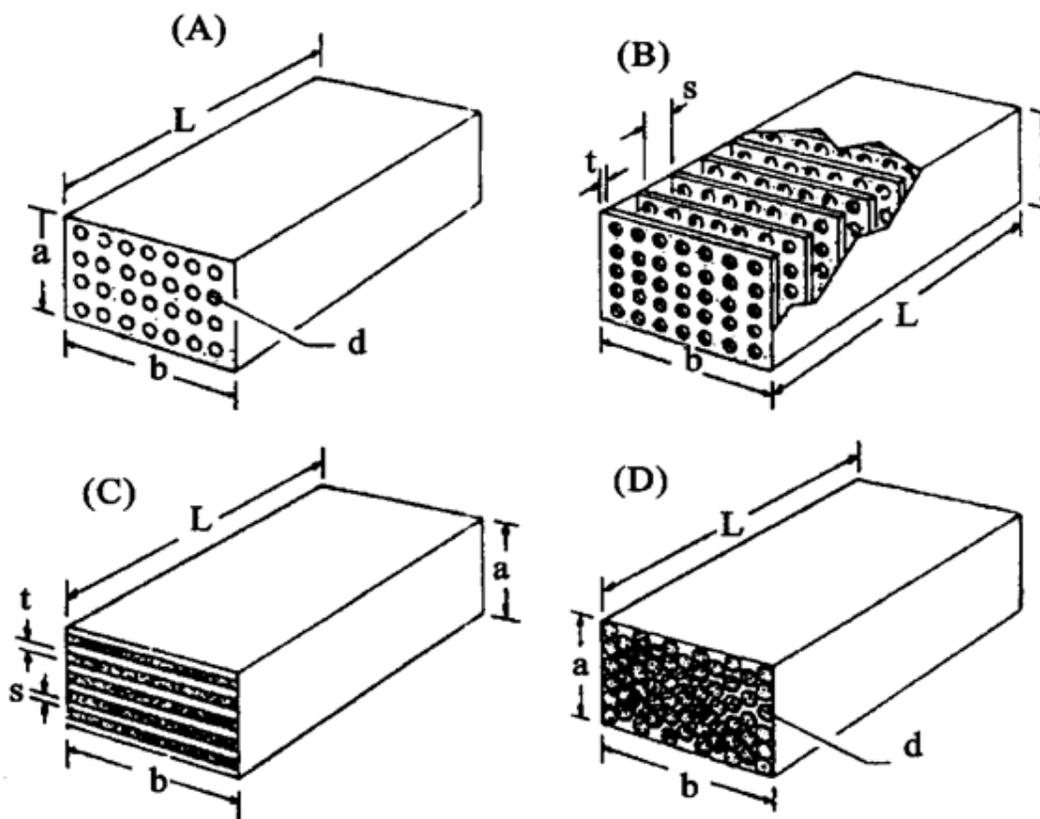
Solid Hydrogenation (SH) Process for Massive $\text{La}(\text{Fe}, \text{Co}, \text{Mn}, \text{Si})_{13}\text{H}_x$ parts

Delft Days on Magnetocaloric 2011
M. Katter, V. Zellmann, A. Barcza
Oct. 2011

outline

- Introduction
- solid hydrogenation of sintered $\text{La}(\text{Fe},\text{Co},\text{Si})_{13}$
- tuning of T_C by partial hydrogenation
- instability of partially hydrogenated $\text{La}(\text{Fe},\text{Si})_{13}$
- tuning of T_C of fully hydrogenated $\text{La}(\text{Fe},\text{Mn},\text{Si})_{13}\text{H}_x$ by varying Mn
- conclusions

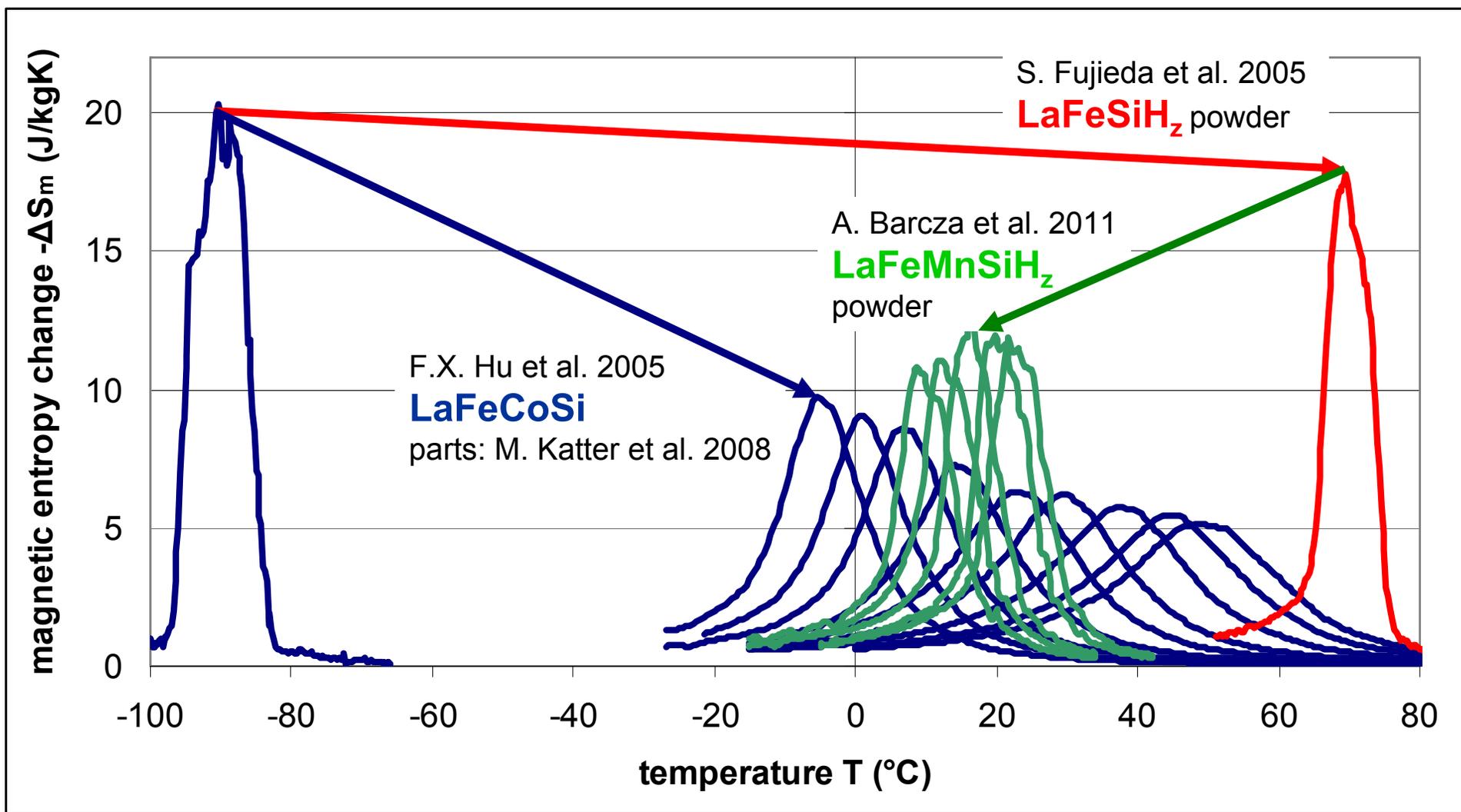
Designs for active magnetic regenerators



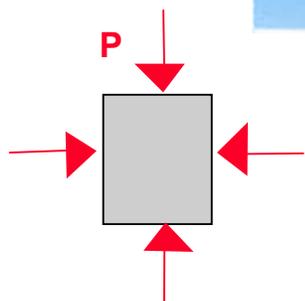
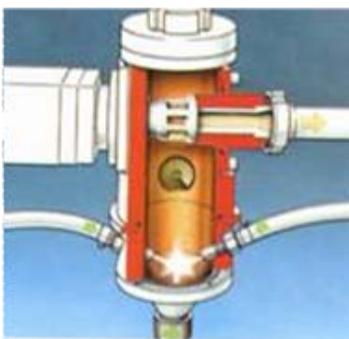
large pressure drops
in powder beds?

J.A. Barclay and S. Sarangi 1984 in A.M. Tishin and Y.I. Spichkin 2003

LaFeSi-based magnetocaloric materials, @ 16 kOe



Powder Metallurgical (PM) Processing of La-Fe-Si, M. Katter et al. 2008



isostatic pressing

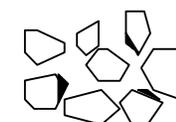
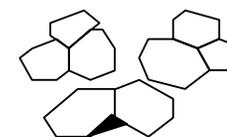
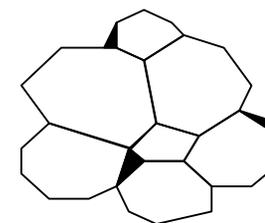
Vacuum Induction Alloying and Casting

Crushing

Milling

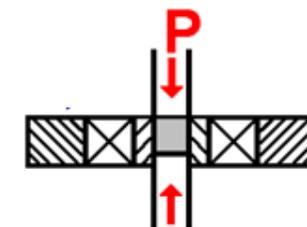
Blending

Pressing:
CIP - die

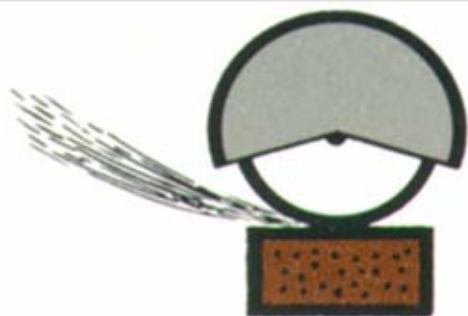
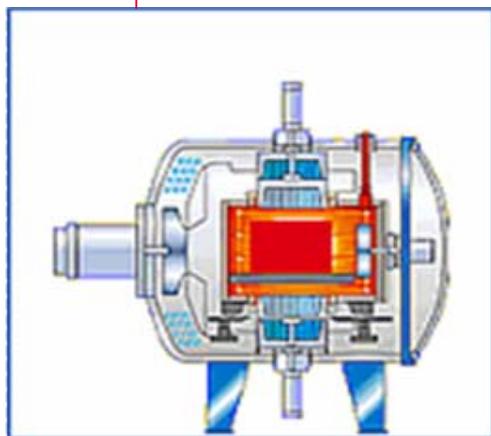
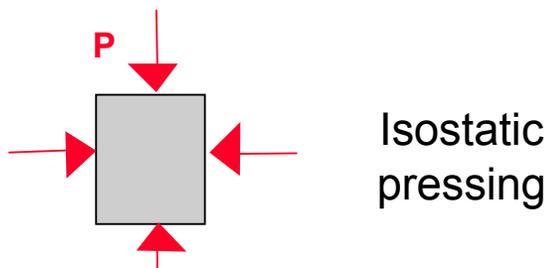


elemental powders

die-pressing



Powder Metallurgical (PM) Processing of La-Fe-Si

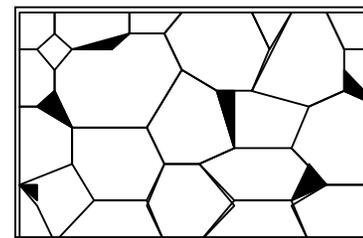
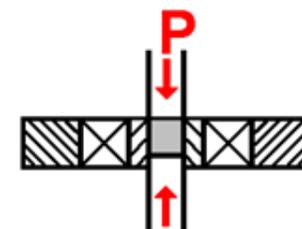


Pressing:
CIP - die

Reactive Sintering
+ thermally induced
decomposition

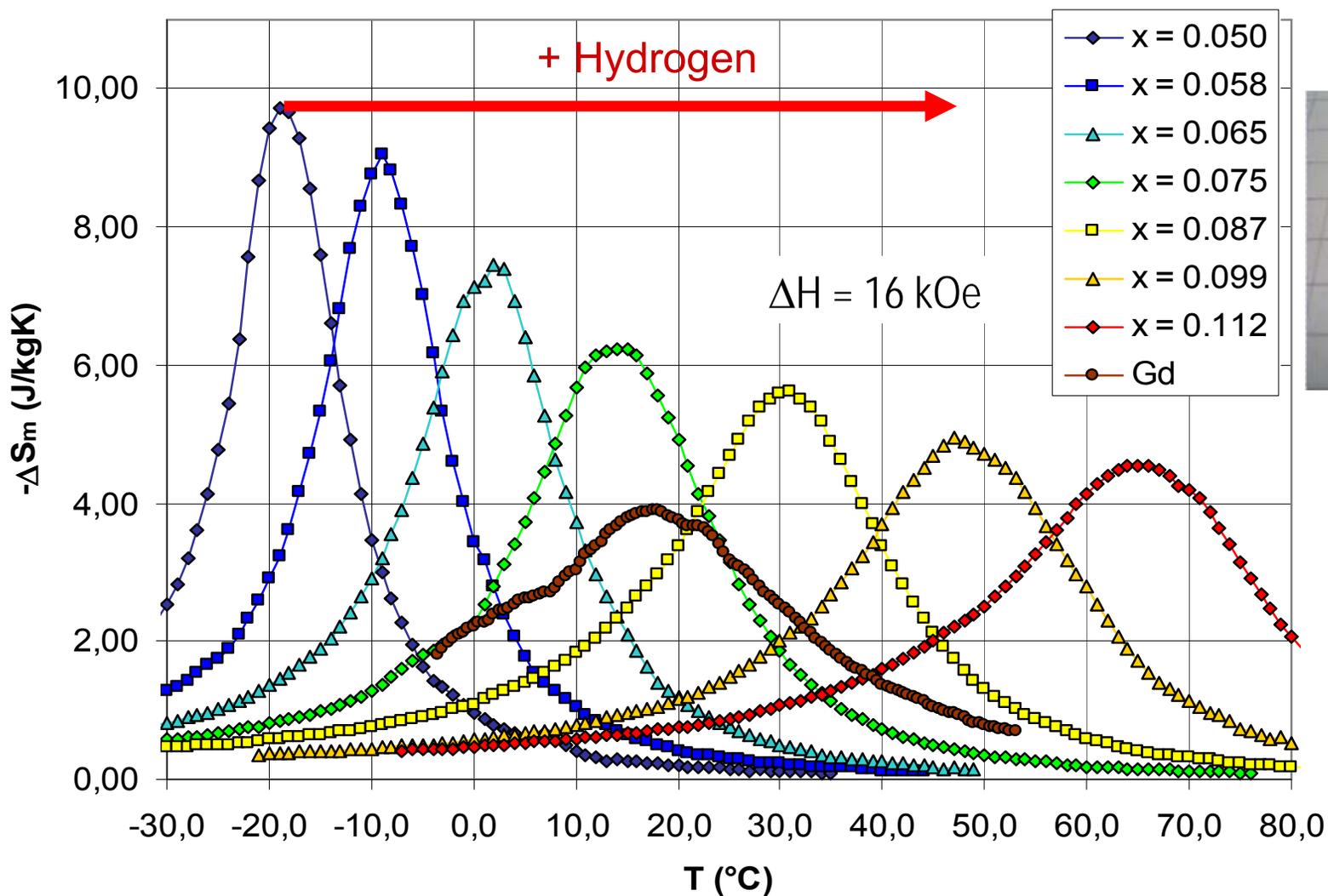
Machining
+ recombination
heat treatment

die-
pressing



TDR process, M. Katter et al. 2009

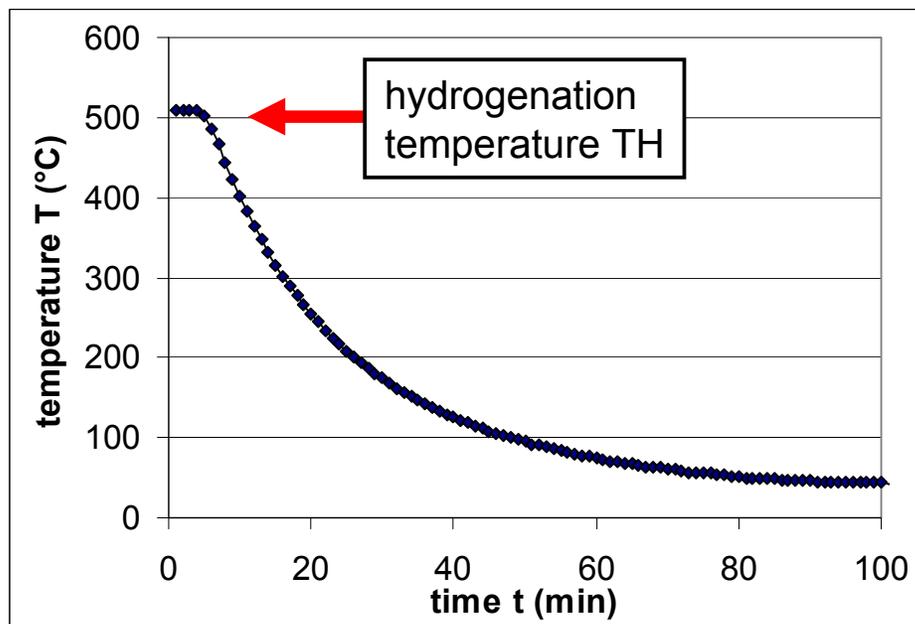
Starting material: sintered $\text{La}(\text{Fe}_{0.915-x}\text{Co}_x\text{Si}_{0.085})_{13}$



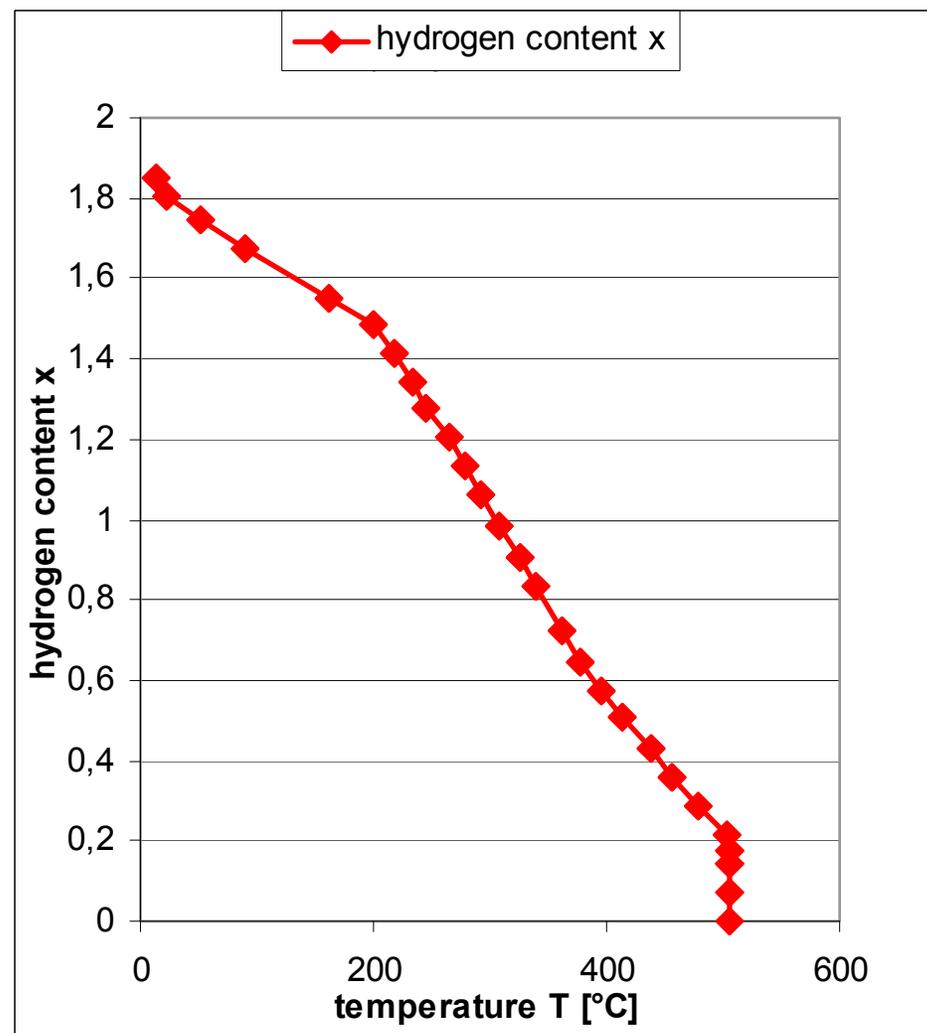
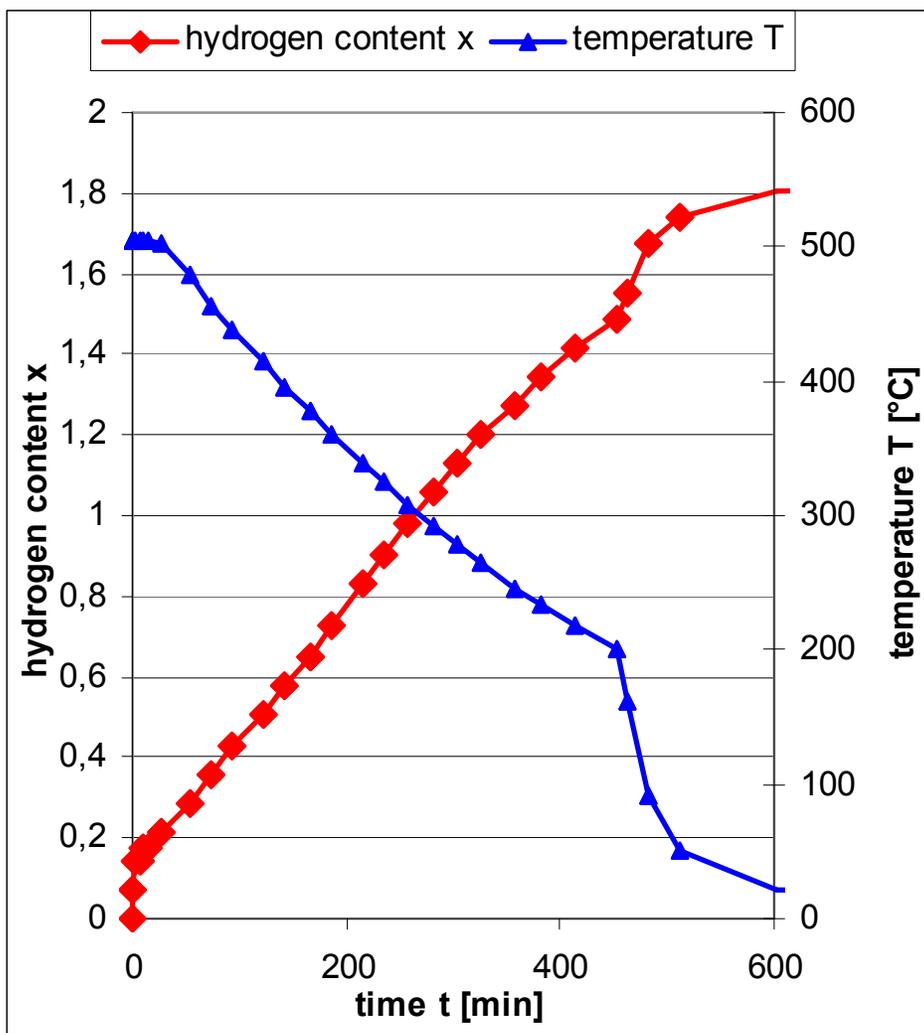
cut and homogenized plates ca. 12x6x0.6 mm

Solid Hydrogenation SH process

- heating under Argon to TH
- 2h/1.9 bar hydrogen at TH
- rel. slow cooling in 1.9 bar H₂ to RT

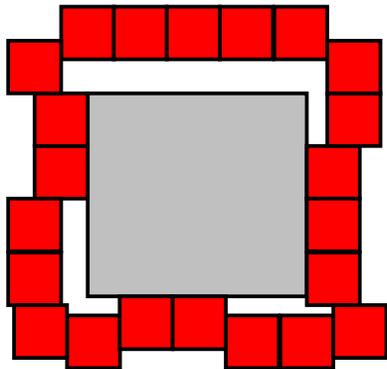


hydrogen uptake of 360 g 12x6x0.6 mm $\text{LaFe}_{11.25}\text{Co}_{0.65}\text{Si}_{1.11}\text{H}_x$ platlets



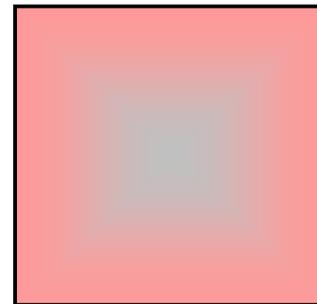
model for the SH process

hydrogenation at RT



- high hydrogen content in surface region
- slow diffusion of hydrogen
- shell-like decrepitation

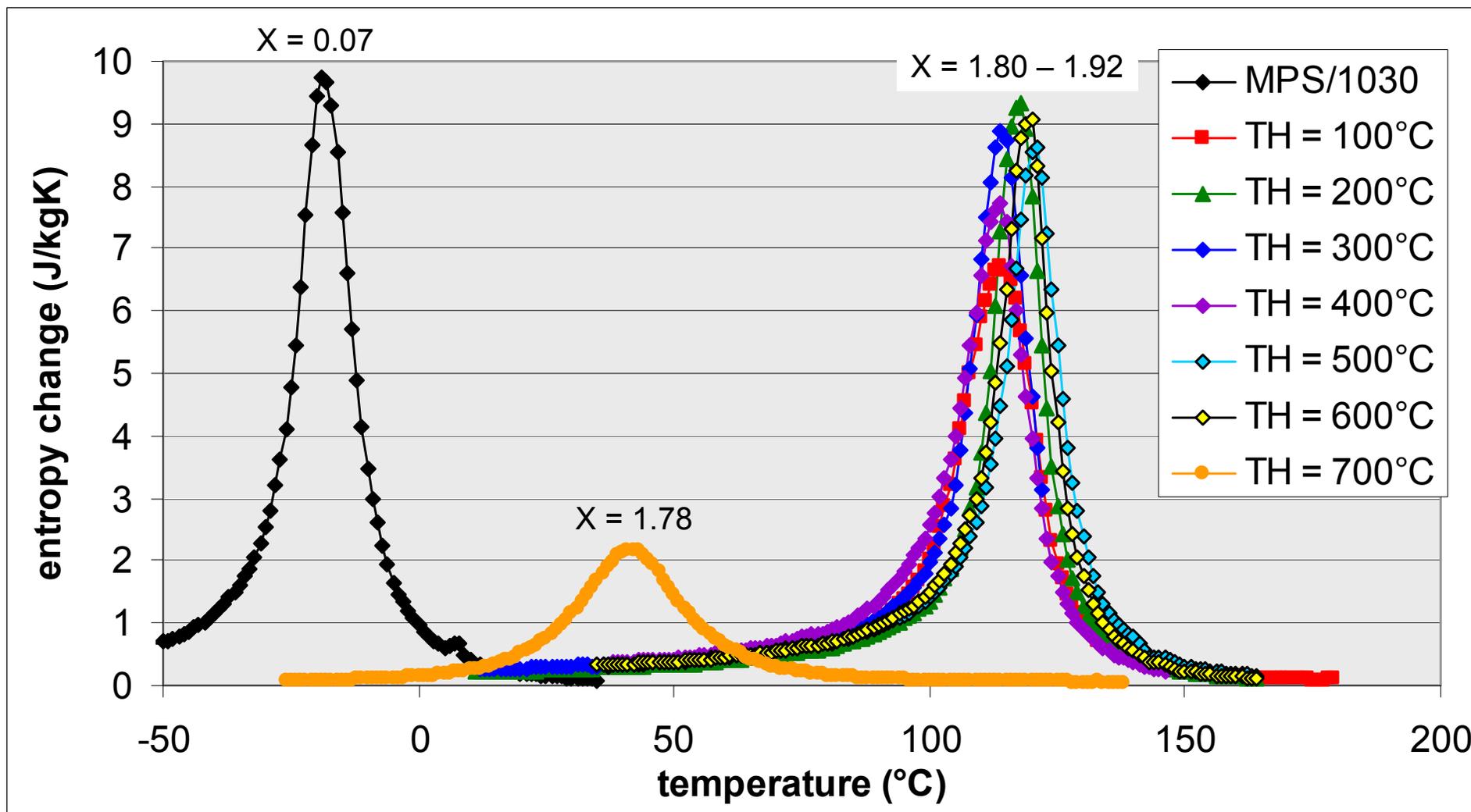
hydrogenation at 500°C



- low hydrogen content in surface region
- fast diffusion of hydrogen
- no decrepitation

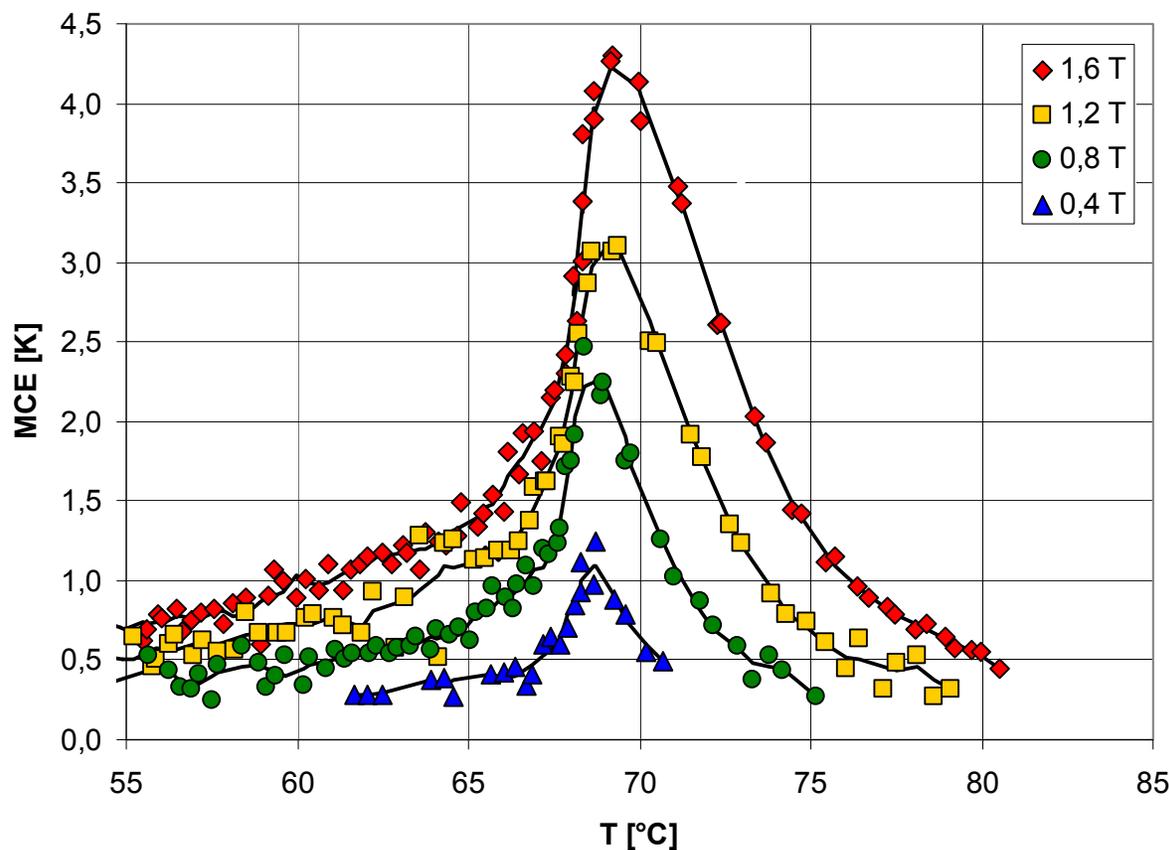
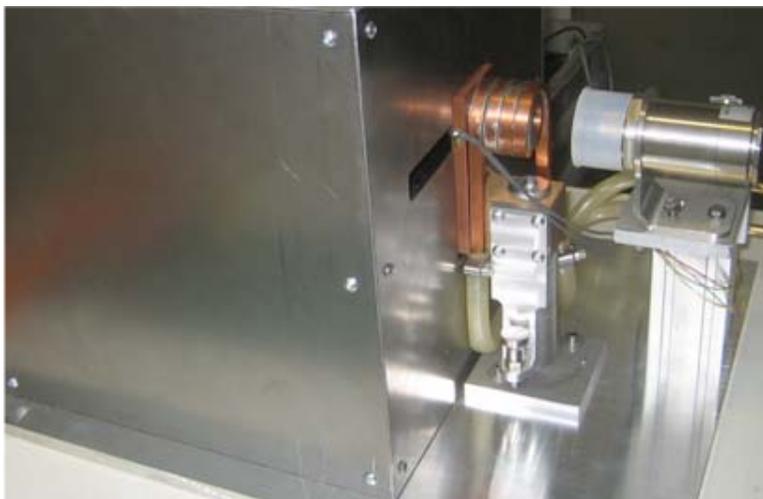
Similar process described by O. Gutfleisch, N. Martinez, M. Verdier and I.R. Harris, "Development of microstructure of the disproportionated material during HDDR-process in a Nd₁₆Fe₇₆B₈ alloy", J. Alloys Comp. 204 (1994) L21-L23

sintered and solid hydrogenated $\text{LaFe}_{11.25}\text{Co}_{0.65}\text{Si}_{1.11}\text{H}_x$



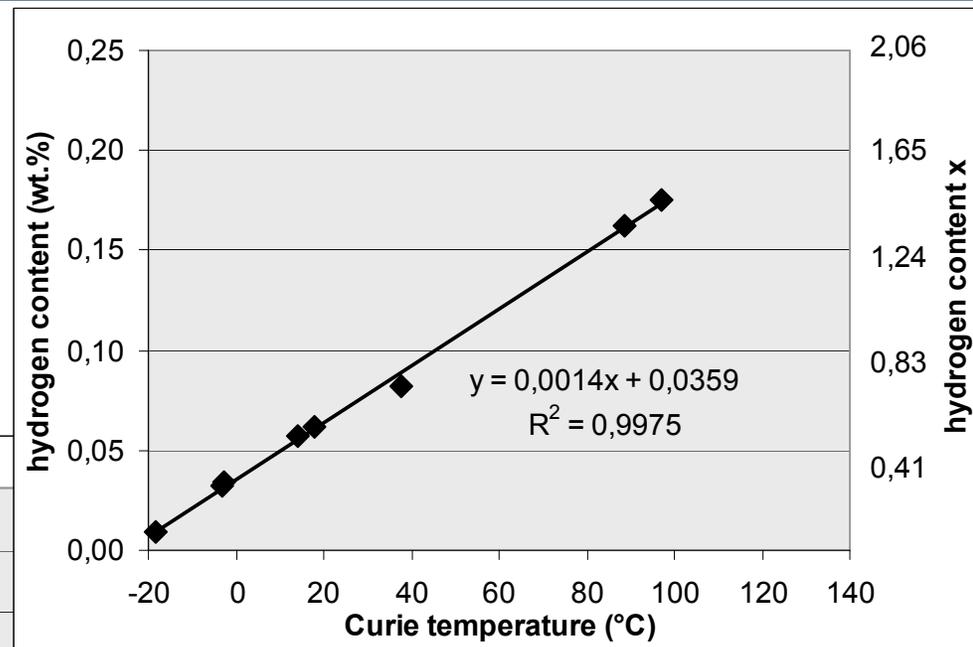
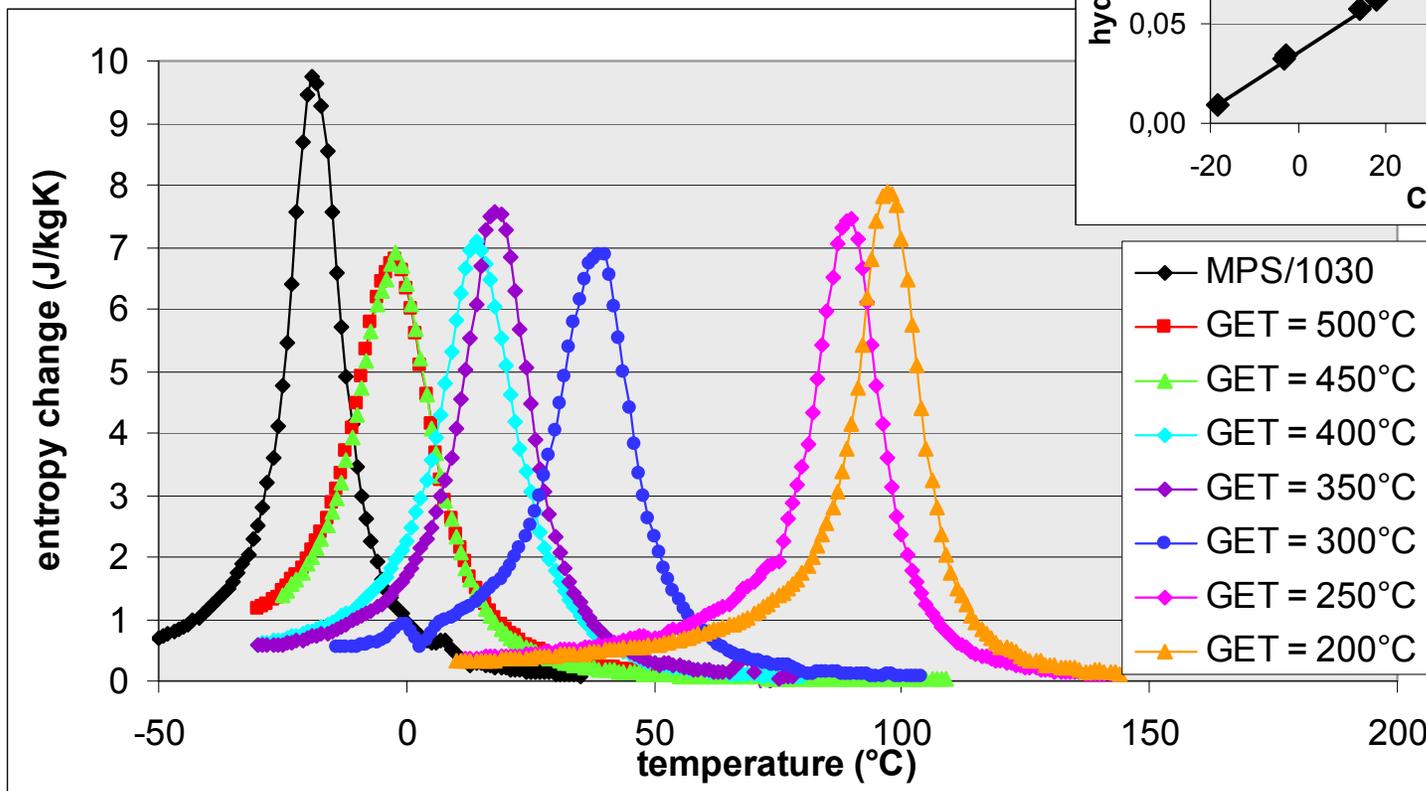
Temperature change of SH-treated La-Fe-Si-H_x D6 x 1.5 mm

- Temperature change of representative sample was measured with IR sensor
- Maximum temperature change of 4 K upon application of 1.6 T at 70°C.



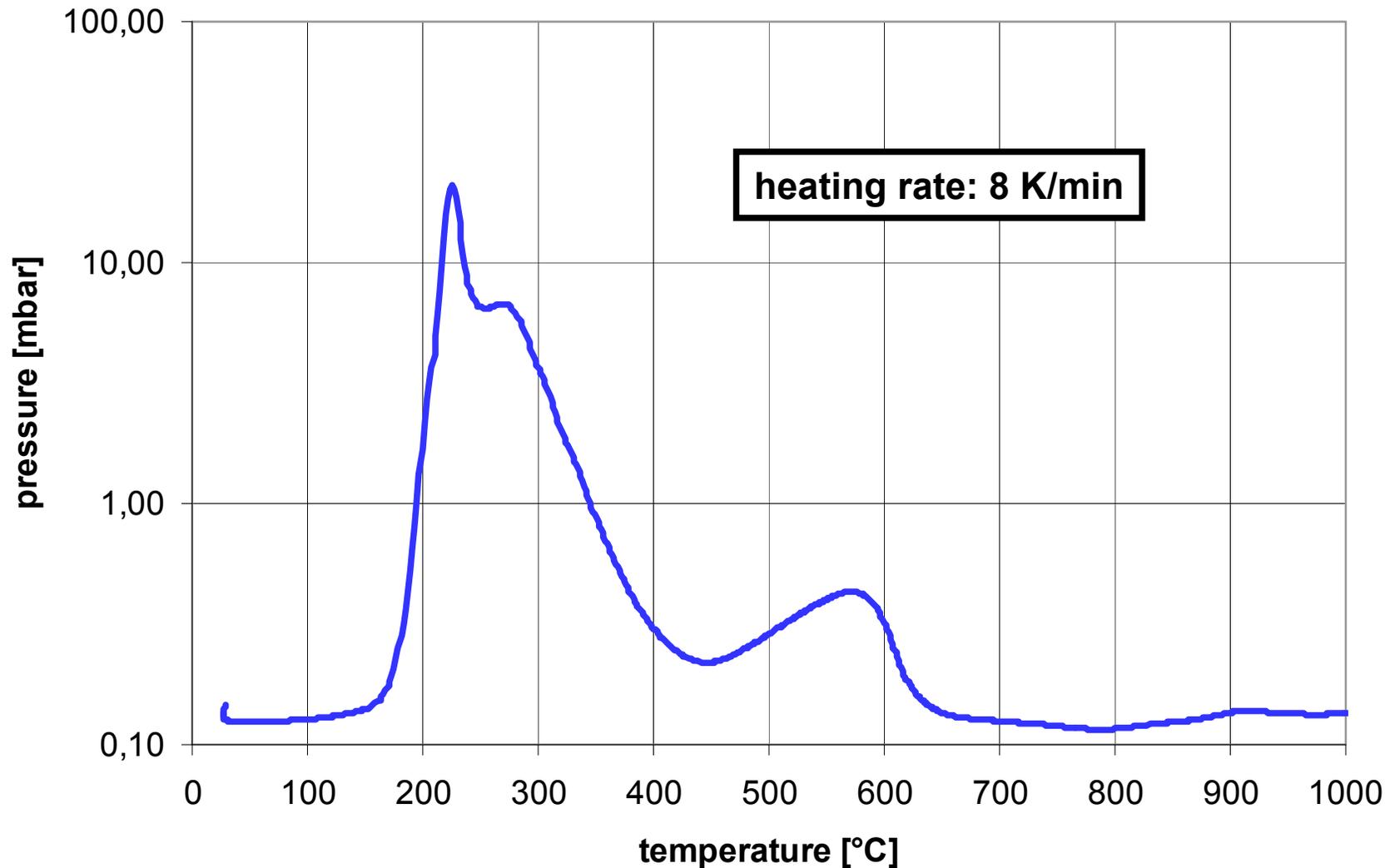
Tuning of T_c of Solid La-Fe-Co-Si- H_x by gas exchange

- heat in Argon to 500°C
- hold at 500°C in 1.9 bar H_2 for 2 h



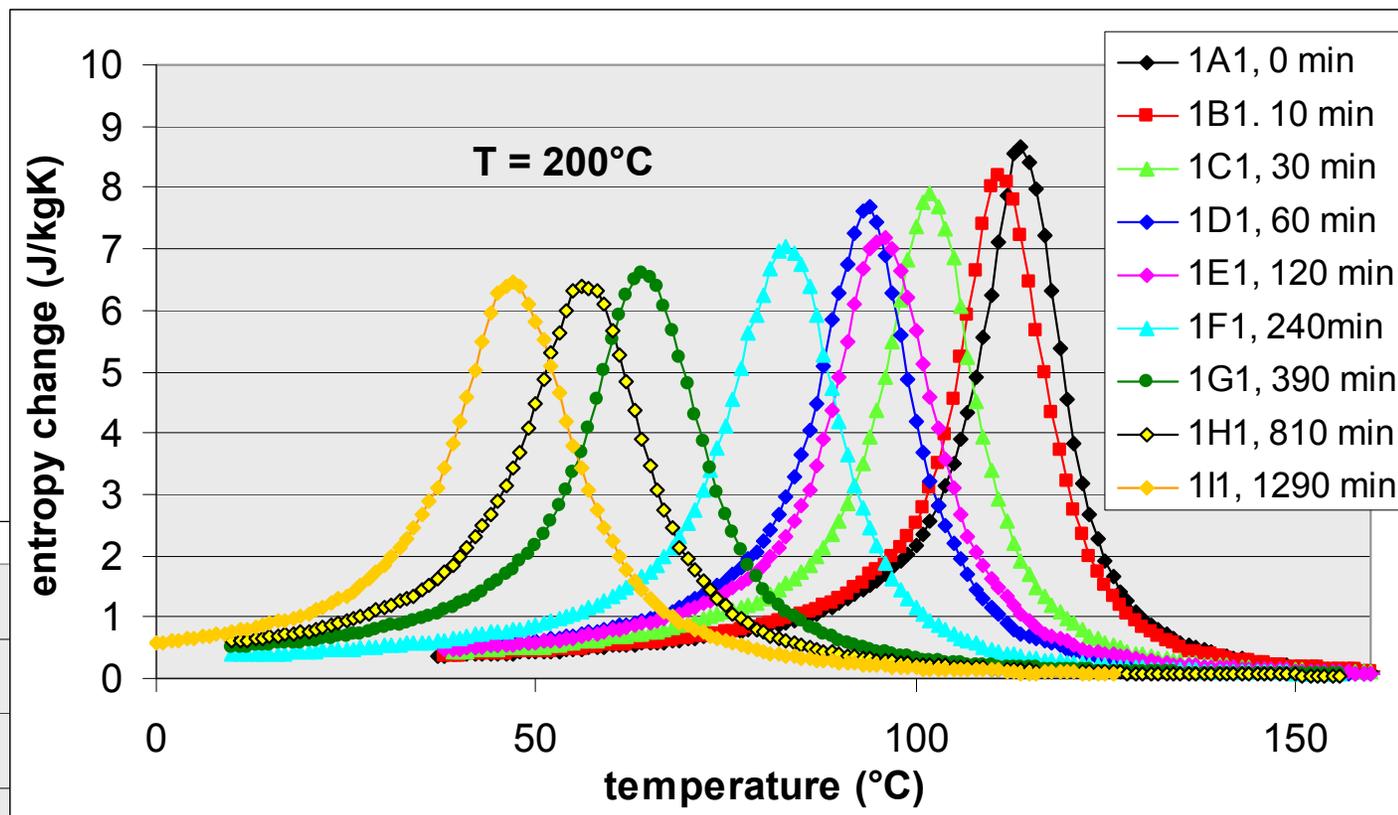
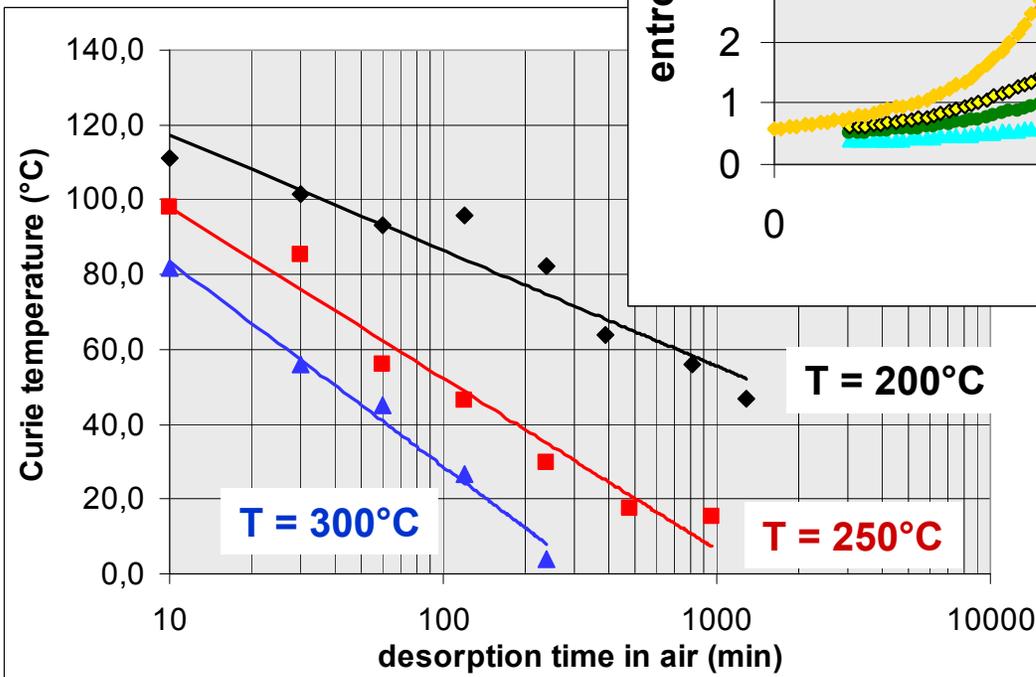
- cool in 1.9 bar H_2 to GET
- exchange H_2 by Argon
- quench to RT

degassing of 360 g 12x6x0.6 mm $\text{LaFe}_{11.25}\text{Co}_{0.65}\text{Si}_{1.11}\text{H}_x$ platlets



Tuning of T_C of solid La-Fe-Co-Si-H_x by desorption

- SH at 500°C
- cooled to RT in hydrogen



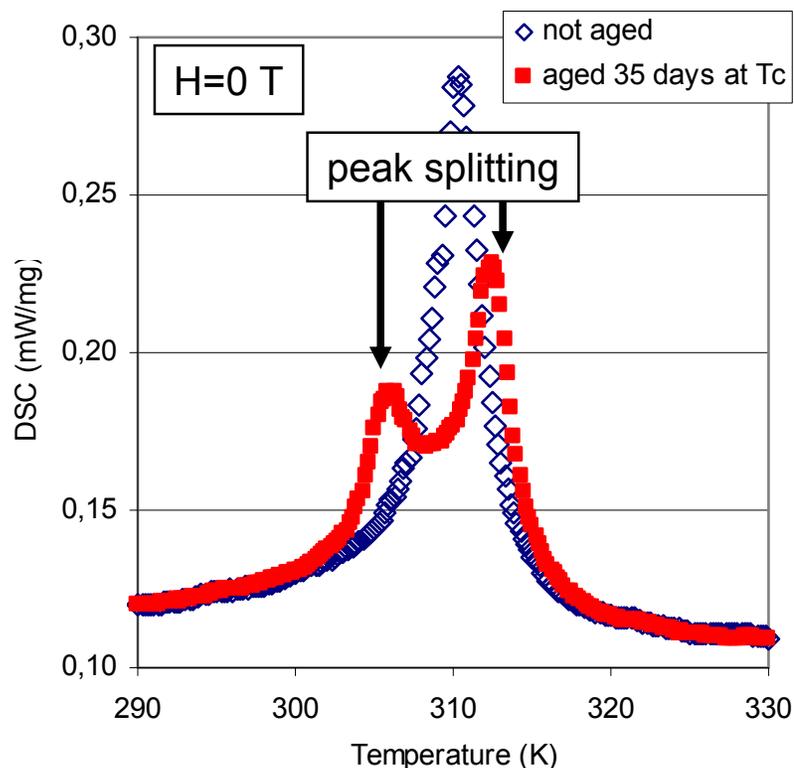
- desorption in air at $200 - 300^\circ\text{C}$

Aging of partially hydrogenated La-Fe-Si-H_x alloys when held at T_C

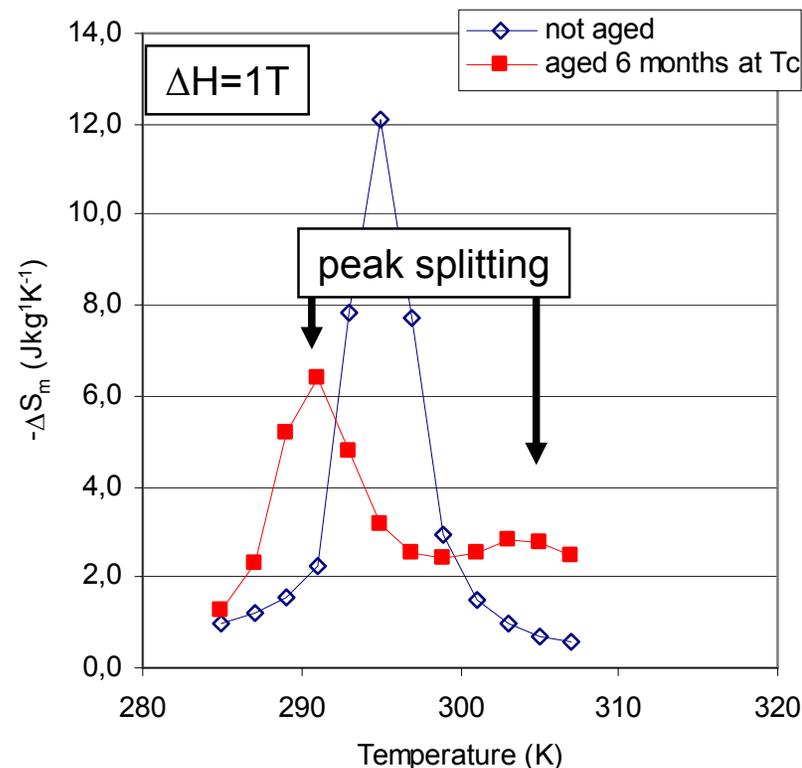
A. Barcza, V. Zellmann, M. Katter, C. Zimm, S. Jacobs, S. Russek, Intermag 2011



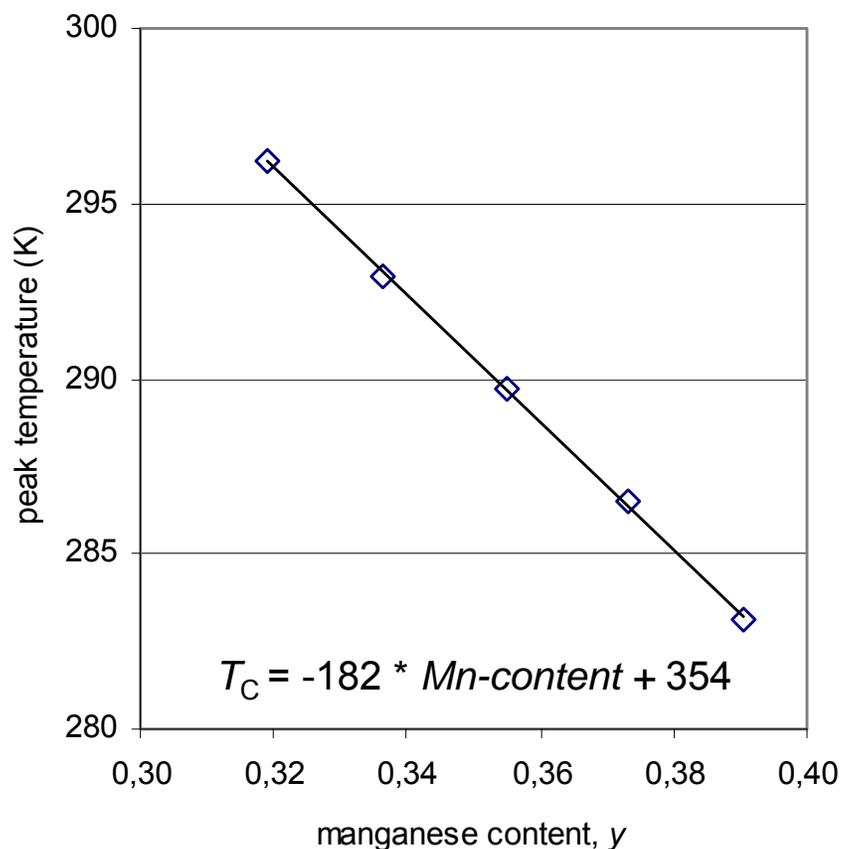
- Produced by induction melting.
- Hydrogenated at 514 K.
- Stored in air at T_C for 35 days.



- Produced by rapid solidification.
- Similar hydrogenation conditions.
- Stored in air at T_C for 6 months.



Mn-substitution to adjust T_C in fully hydrogenated $\text{LaFe}_{13-y-x}\text{Mn}_y\text{Si}_x\text{H}_{1.5}$

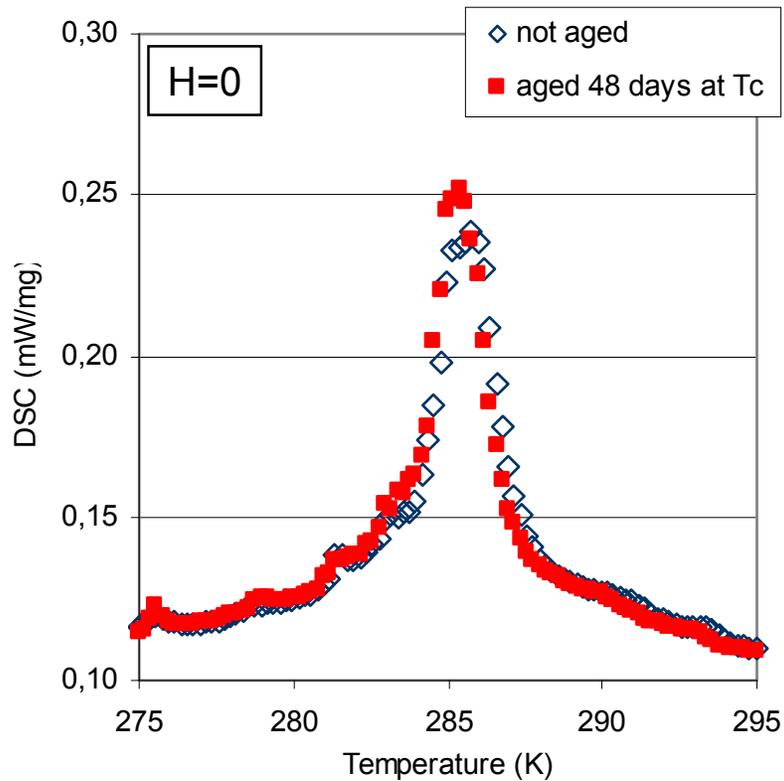


Mn content, y	0.390	0.373	0.356	0.338	0.322
H content, z	1.525	1.524	1.523	1.539	1.530
T_C (K)	283.1	286.5	289.7	293.0	296.2
$-\Delta S_m$ (J/kgK) for $\Delta H = 1.6\text{T}$	10.7	11.0	12.4	11.8	11.6

- T_C is tailored by Mn-concentration.
- Hydrogen content is kept constant at saturation.
- Isothermal entropy change is reduced.

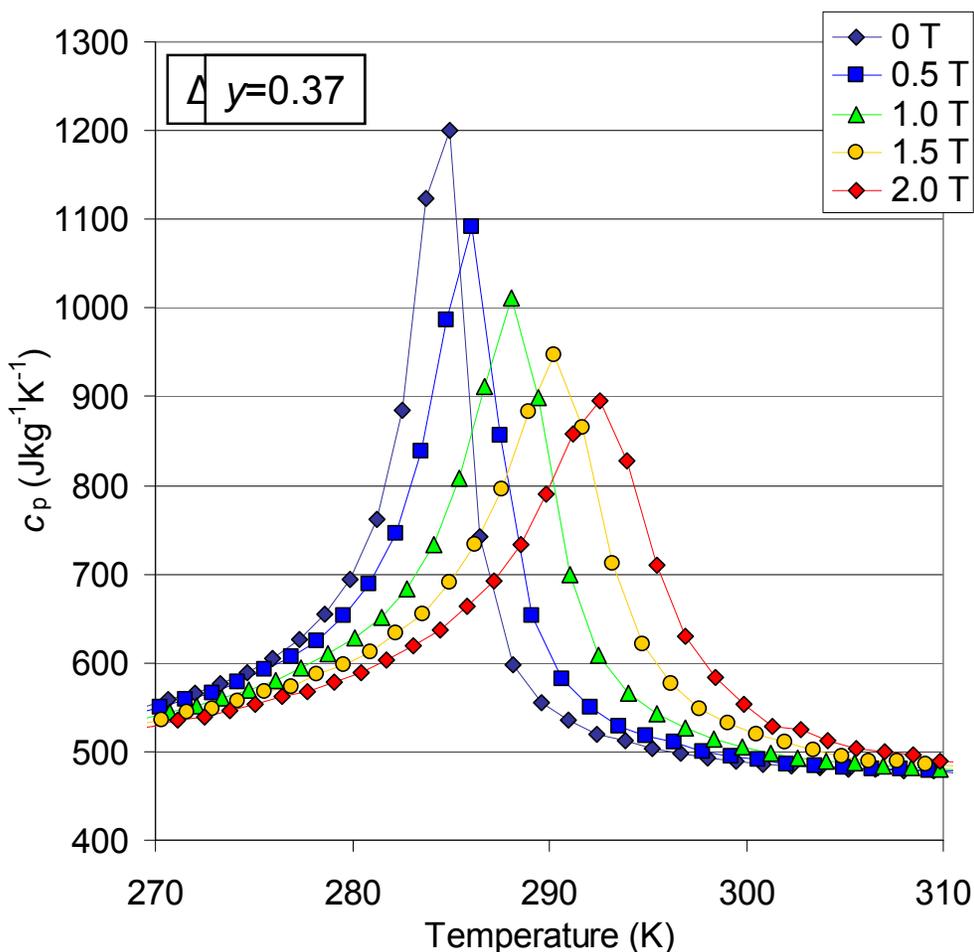
Similar results obtained by C. Wang, Y. Long, T. Ma, and X. Li, 55th Annual Conference on Magnetism & Magnetic Materials, Atlanta, 2010, BQ-10.

Aging behaviour of $\text{LaFe}_{11.74}\text{Mn}_{0.38}\text{Si}_{1.26}\text{H}_{1.53}$



- Sample was produced by powder metallurgy.
- Material is fully hydrogenated.
- T_C precisely adjusted to a specified temperature.
- Aging treatment for over a month do not alter properties.

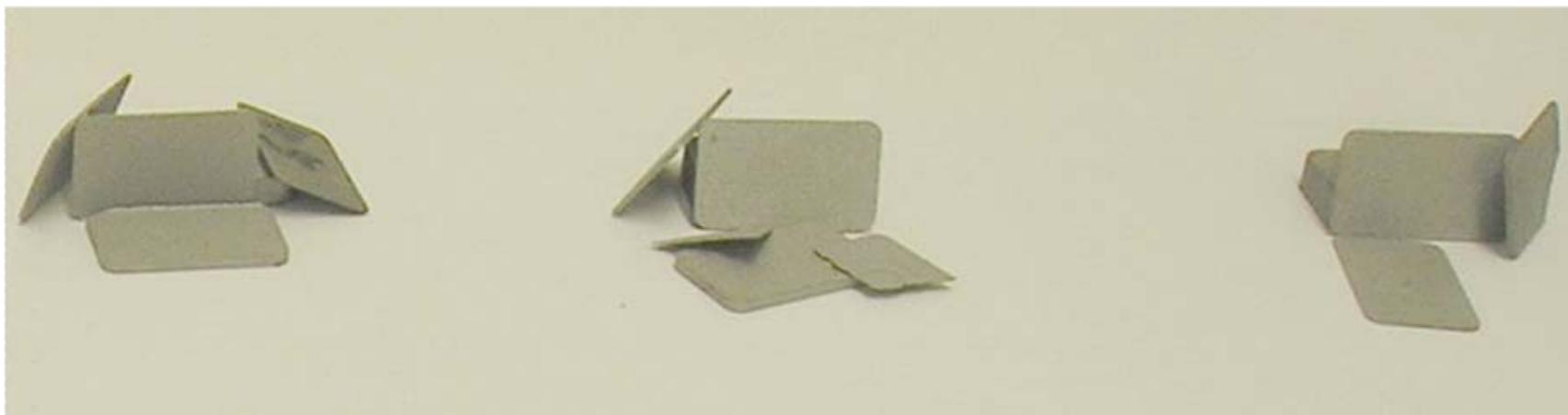
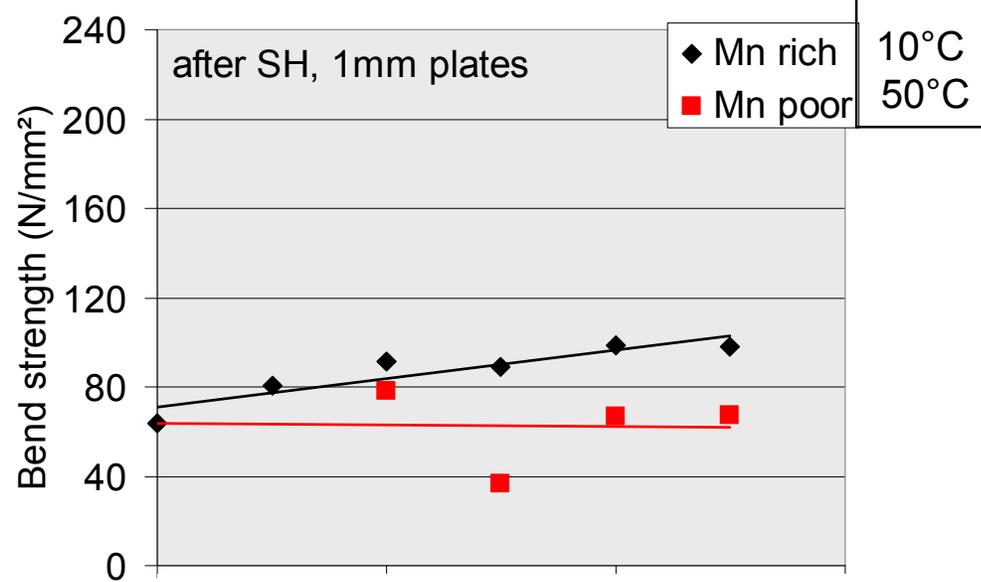
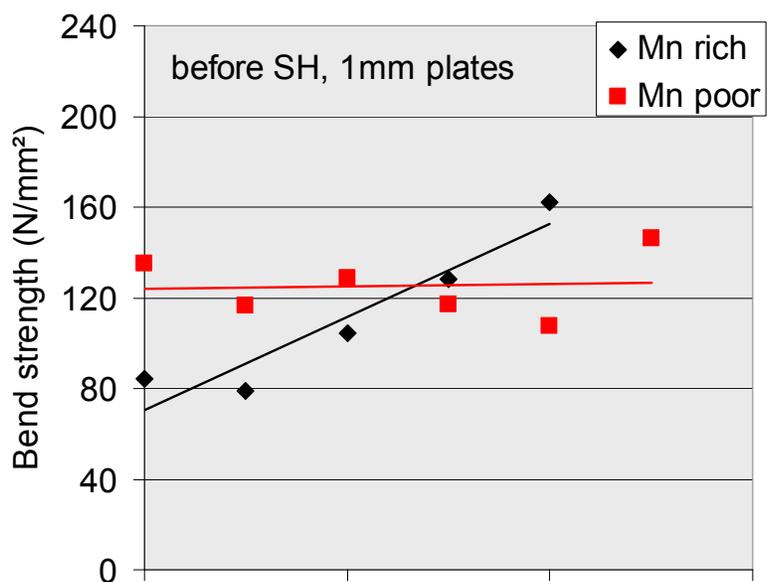
Magnetocaloric properties of stable $\text{LaFe}_{11.74-y}\text{Mn}_y\text{Si}_{1.26}\text{H}_{1.53}$



- Precisely adjustable Curie temperatures by varying Manganese content.
 - Stable magnetocaloric properties when operated at T_C .
 - $c_p(T, H)$ has been measured on one sample.*
 - Coarse powders have been tested under real operating conditions.
 - Performance is better than Gd:
- ➔ S. Russek et al., Proceedings of Thermag IV, Baotou, China, 2010.

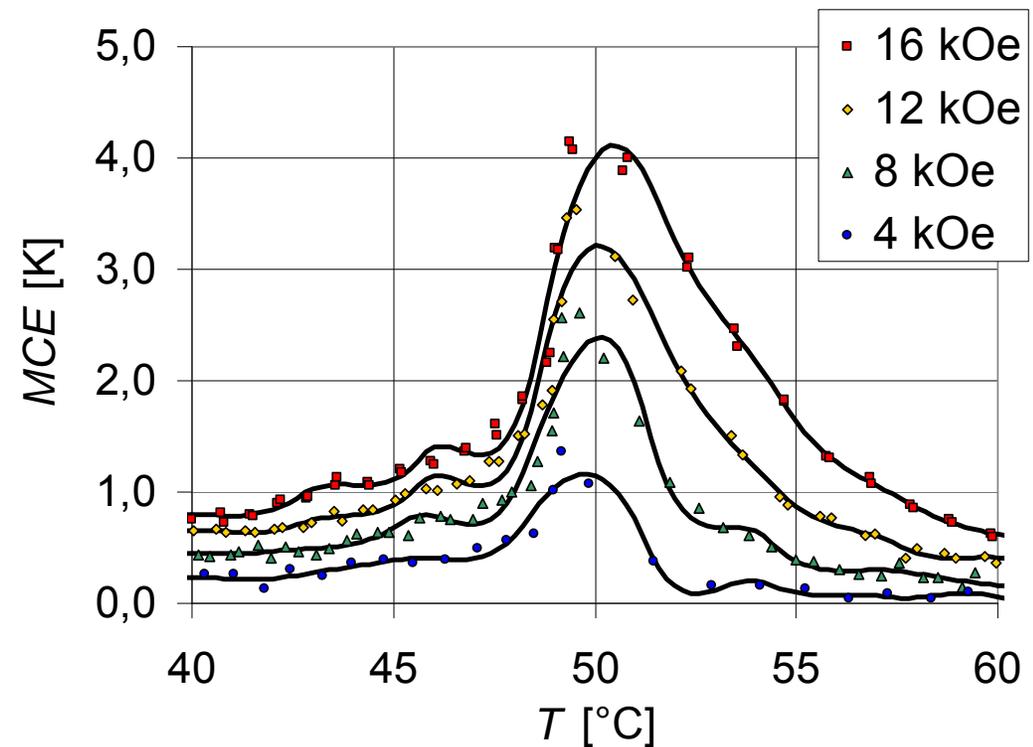
*Yaroslav Mudryk, Ames Lab

mechanical properties of SH-treated $\text{La}(\text{Fe},\text{Mn},\text{Si})_{13}\text{H}$ – platlets



Adiabatic temperature change of SH-treated $\text{La}(\text{Fe},\text{Mn},\text{Si})_{13}\text{H}_{1.53}$

- ΔT_{ad} was measured using automated rig with IR sensor
- Mn-poor samples exhibit larger temperature changes than Mn-rich:
 - Mn-rich: $\Delta T_{\text{ad}} \approx 3.5 \text{ K}$ ($\Delta H=1.6 \text{ T}$)
 - Mn-poor: $\Delta T_{\text{ad}} \approx 4.0 \text{ K}$ ($\Delta H=1.6 \text{ T}$)

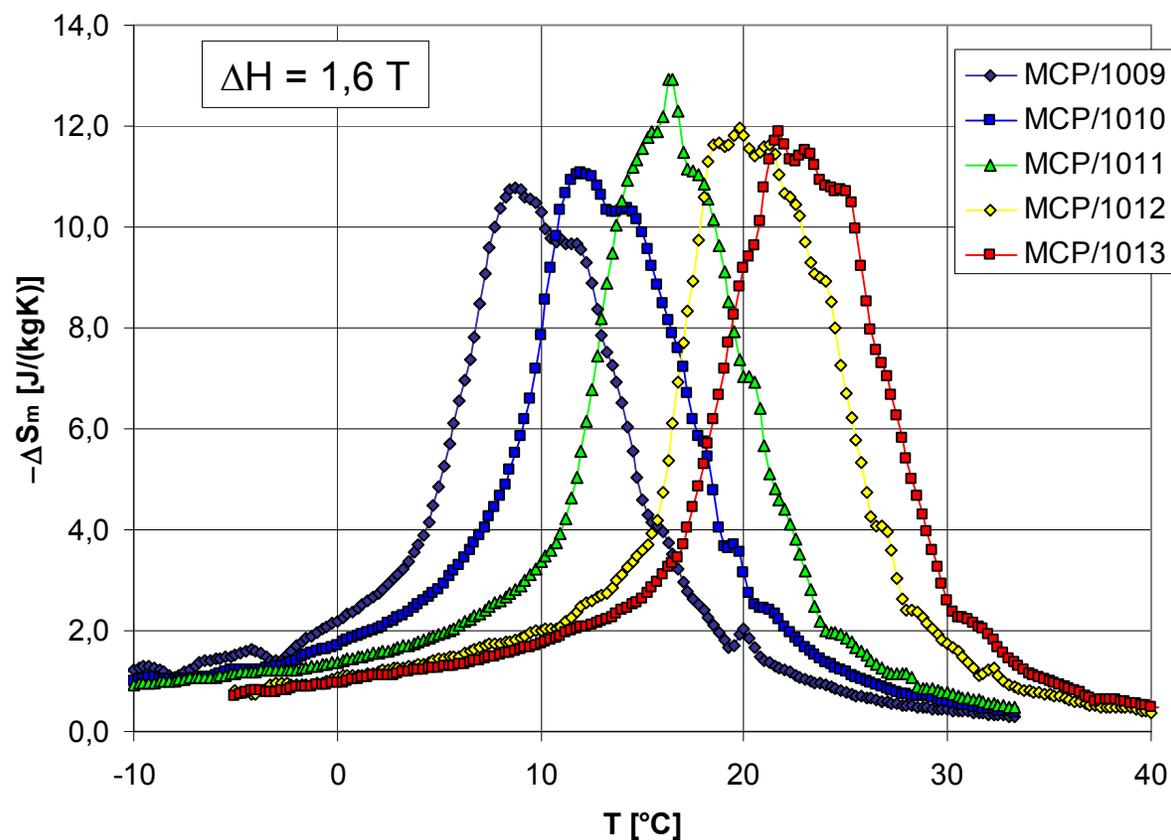


Entropy change of fully hydrogenated $\text{La}(\text{Fe}_{1-x-y}\text{Mn}_y\text{Si}_x)_{13}\text{H}_z$

Mn concentration



- Large entropy change in the relevant temperature range.
- Narrow peaks with a FWHM of about 10 K.



Conclusions

- Massive sintered $\text{La}(\text{Fe}, \text{Co}, \text{Mn}, \text{Si})_{13}\text{H}_x$ parts can be produced by the SH process
- For the SH process hydrogenation has to start at about 500°C followed by cooling under hydrogen atmosphere
- T_C could be tuned by varying the hydrogen content by interrupting the SH process or partial degassing
- But, partially hydrogenated $\text{La}(\text{Fe}, \text{Si})_{13}\text{H}_x$ with $x \ll 1.5$ exhibits peak splitting when kept at T_C .
- Fully hydrogenated $\text{La}(\text{Fe}, \text{Co}, \text{Mn}, \text{Si})_{13}\text{H}_x$ is stable during application.
- T_C of fully hydrogenated $\text{La}(\text{Fe}, \text{Co}, \text{Mn}, \text{Si})_{13}\text{H}_x$ parts can be tuned by variation of the Co and/or Mn content
- Mechanical properties of SH-treated parts are sufficient for practical application