Improvement of magnetocaloric properties toward high efficiency cooling in $La(Fe_xSi_{1-x})_{13}$ by hydrogenation and partial substitution

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$La(Fe_xSi_{1-x})_{13}$ Compounds

Thermally induced first-order transition ($T = T_C$)

Itinerant-electron metamagnetic transition ($T > T_C$)

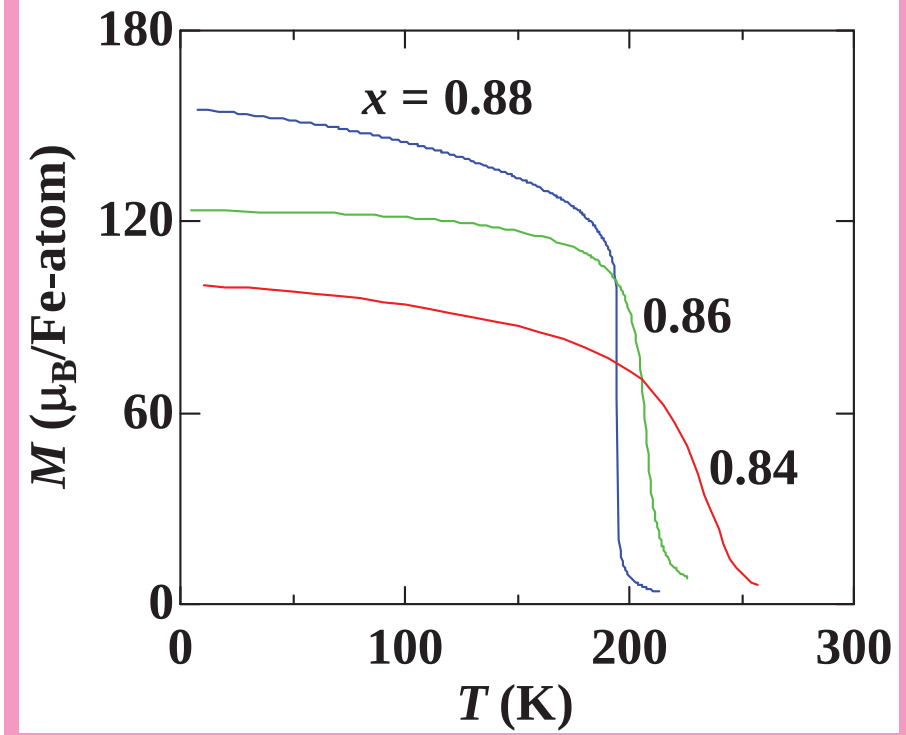
→ Large magnetocaloric effects (MCEs) around $T_C \sim 200$K

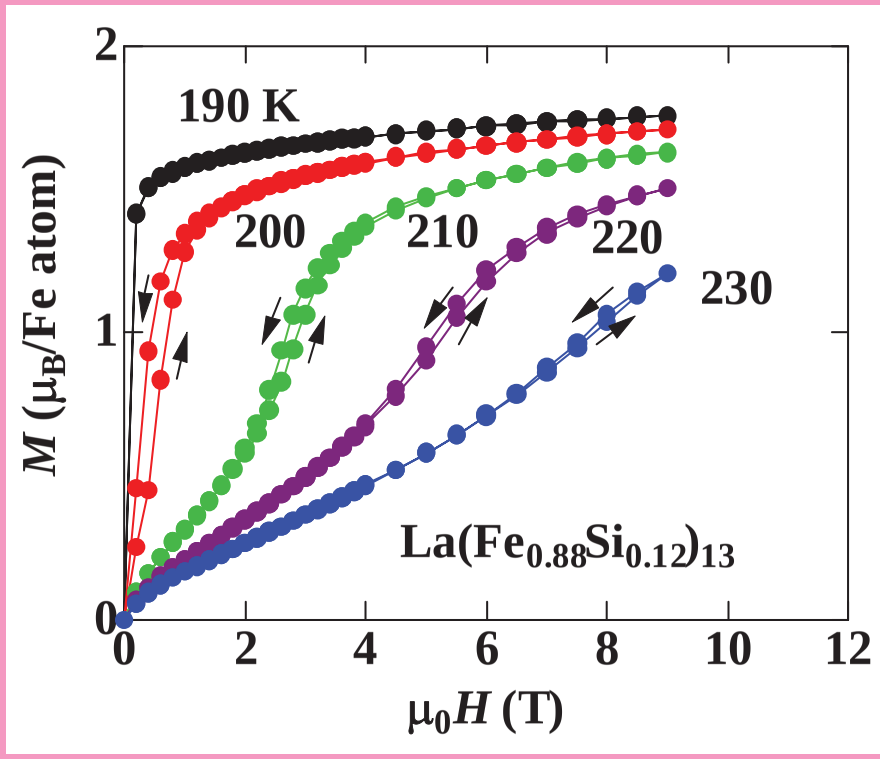
1) Control of T_C

2) Temperature span and cooling power

3) Hysteretic behavior

Magnetic properties of $La(Fe_xSi_{1-x})_{13}$



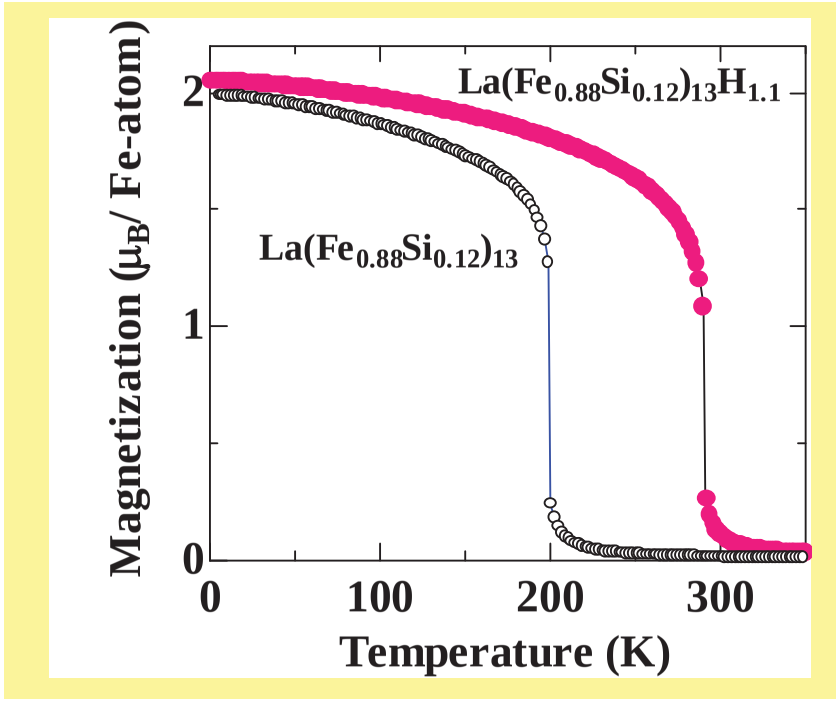


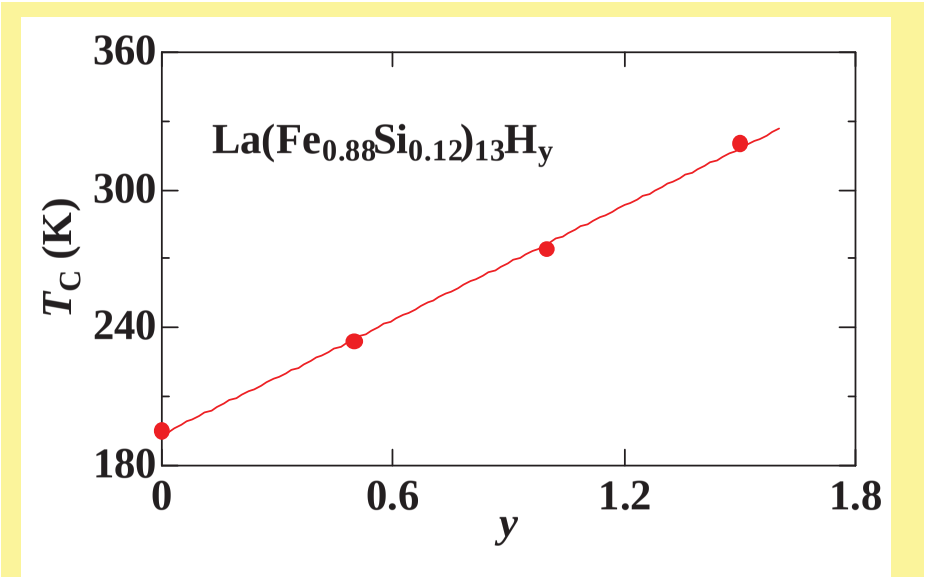
Thermally induced first-order transition ($x \geqq 0.86$)

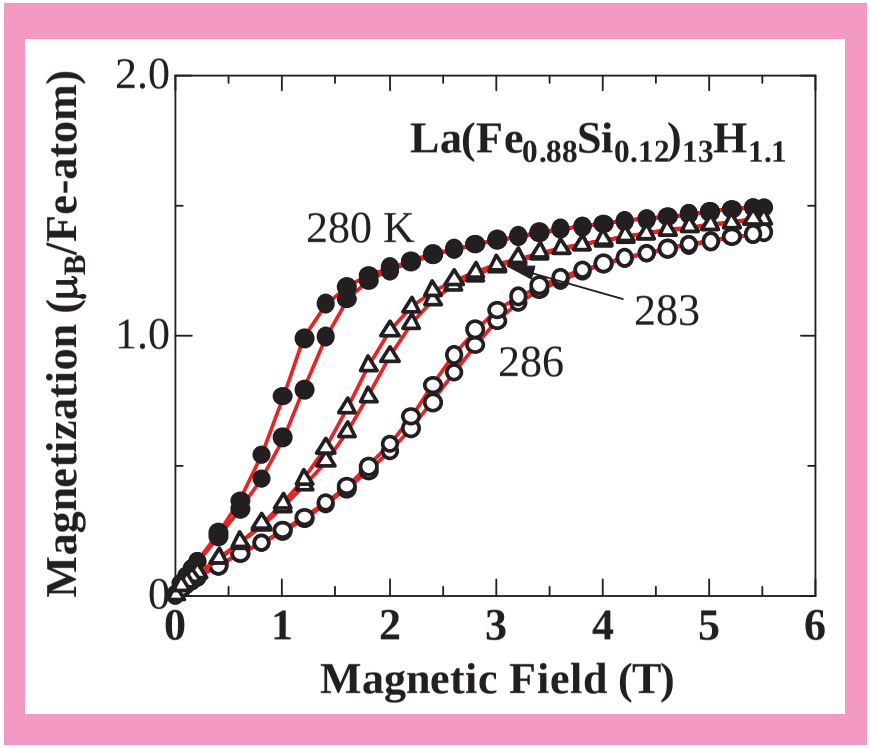
Itinerant-electron metamagnetic transition

A. Fujita, Y. Akamatsu and K. Fukamichi, J. Appl. Phys. **85** (1999) 4756.

Control of T_C by hydrogenation for $La(Fe_xSi_{1-x})_{13}H_y$

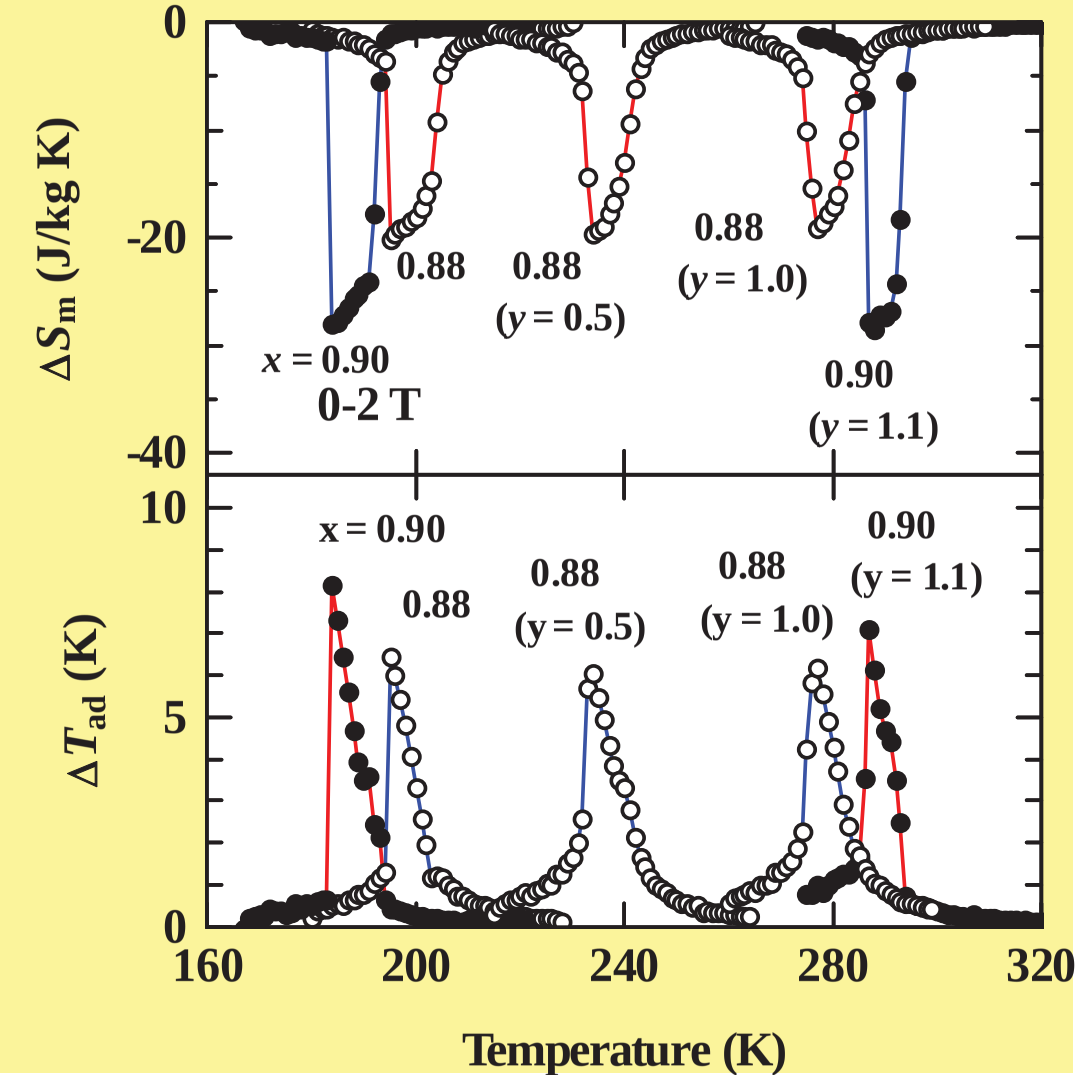






A. Fujita, S. Fujieda, Y. Hasegawa and K. Fukamichi, Phys. Rev. B **67** (2003) 104416.

Temperature dependence of ΔS_m and ΔT_{ad} for $La(Fe_xSi_{1-x})_{13}H_y$

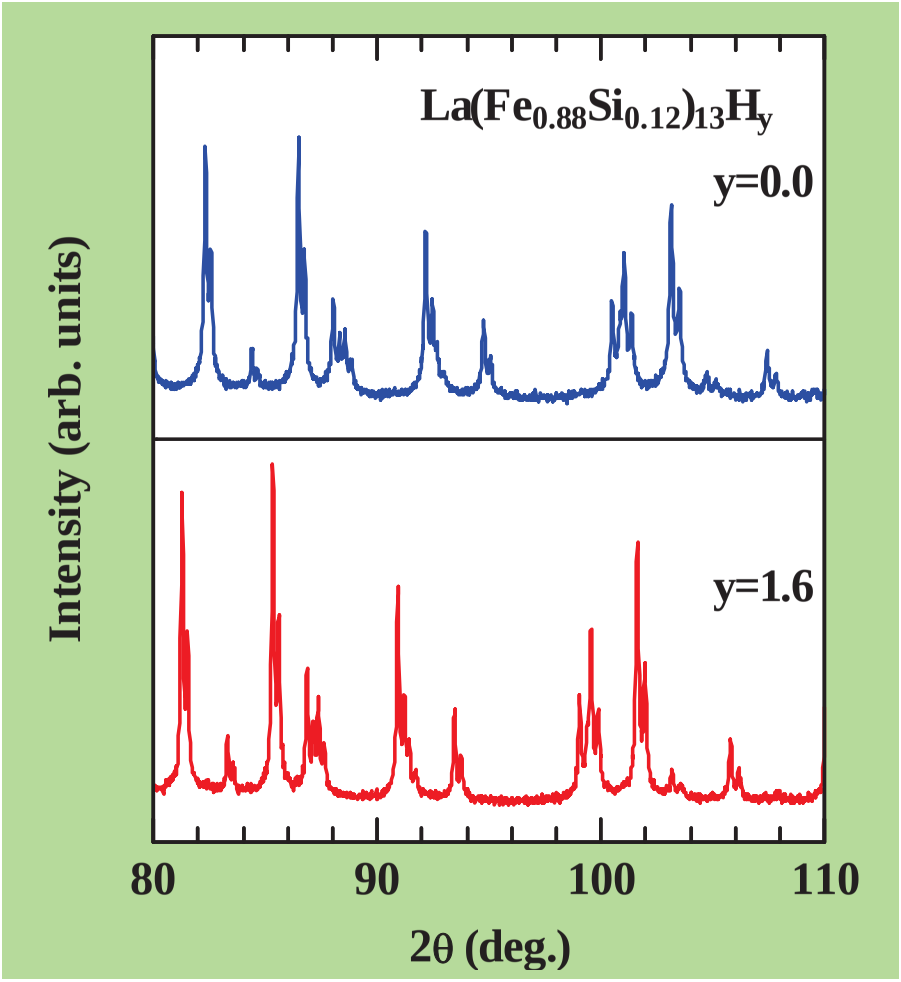


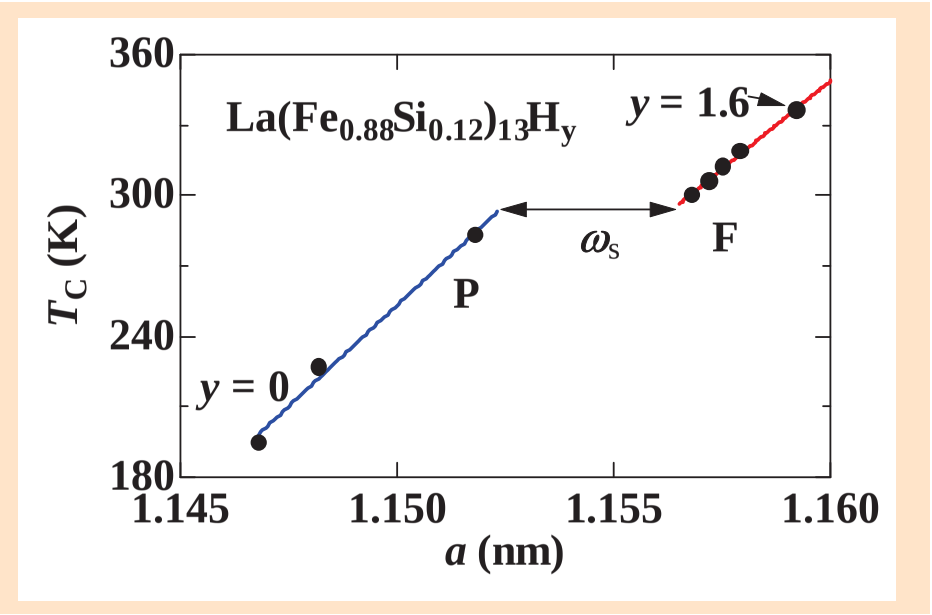
Same magnitude of MCEs are maintained at higher temperatures.

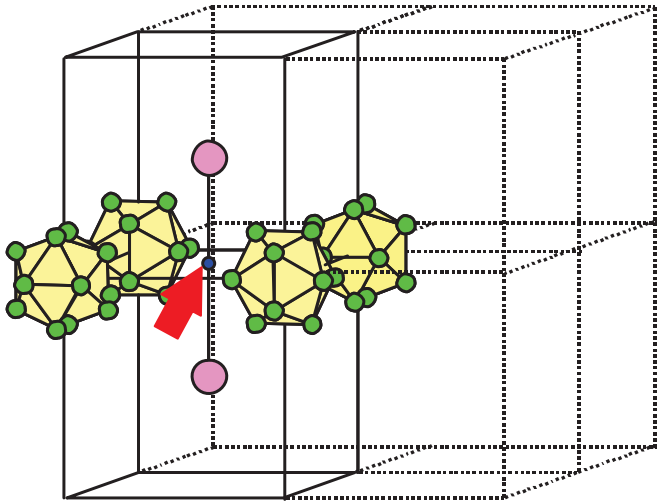
With increasing *x*, MCEs becomes larger

A. Fujita, S. Fujieda, Y. Hasegawa and K. Fukamichi,
Phys. Rev. B **67** (2003) 104416.

Influence of hydrogen absorption on T_C of $La(Fe_{0.88}Si_{0.12})_{13}H_y$

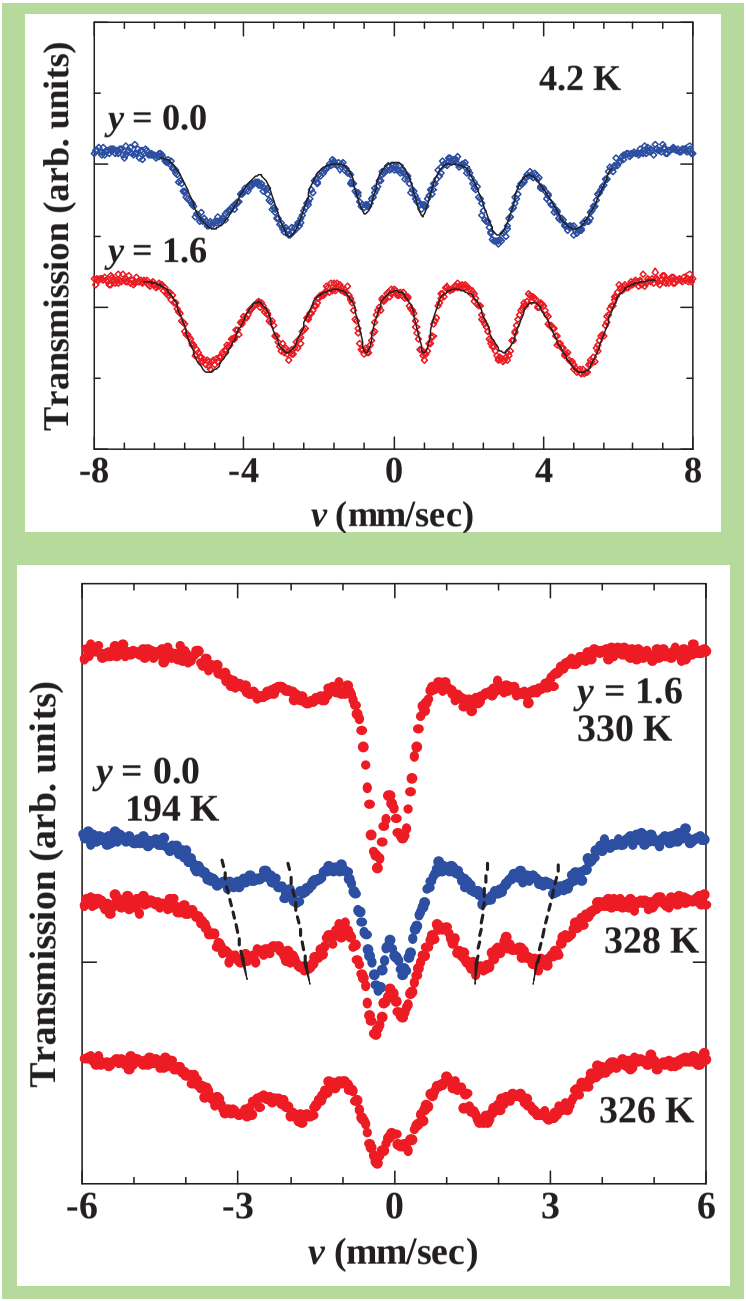


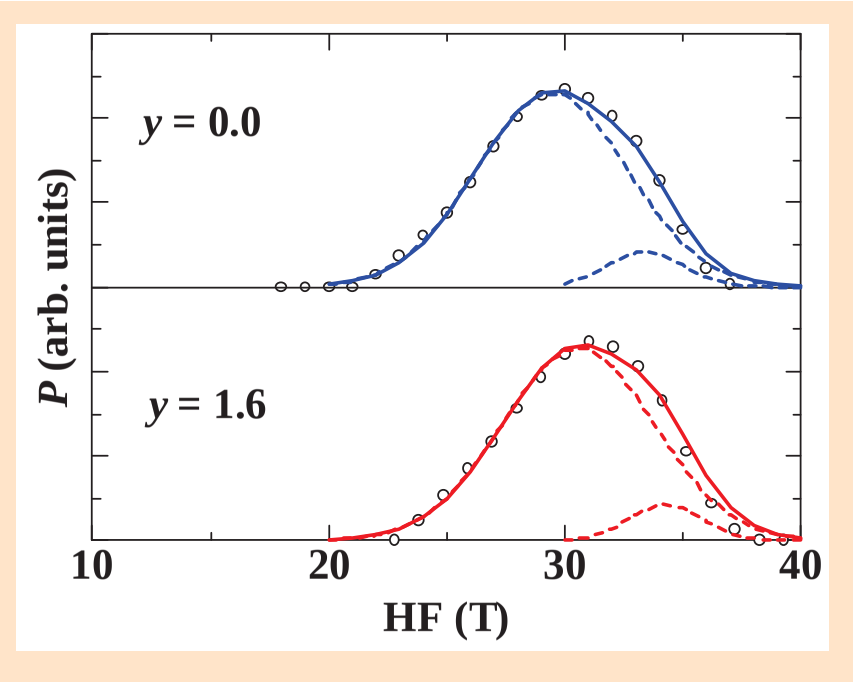




Increase in lattice parameter ⇒ **Increase in T_C above RT**

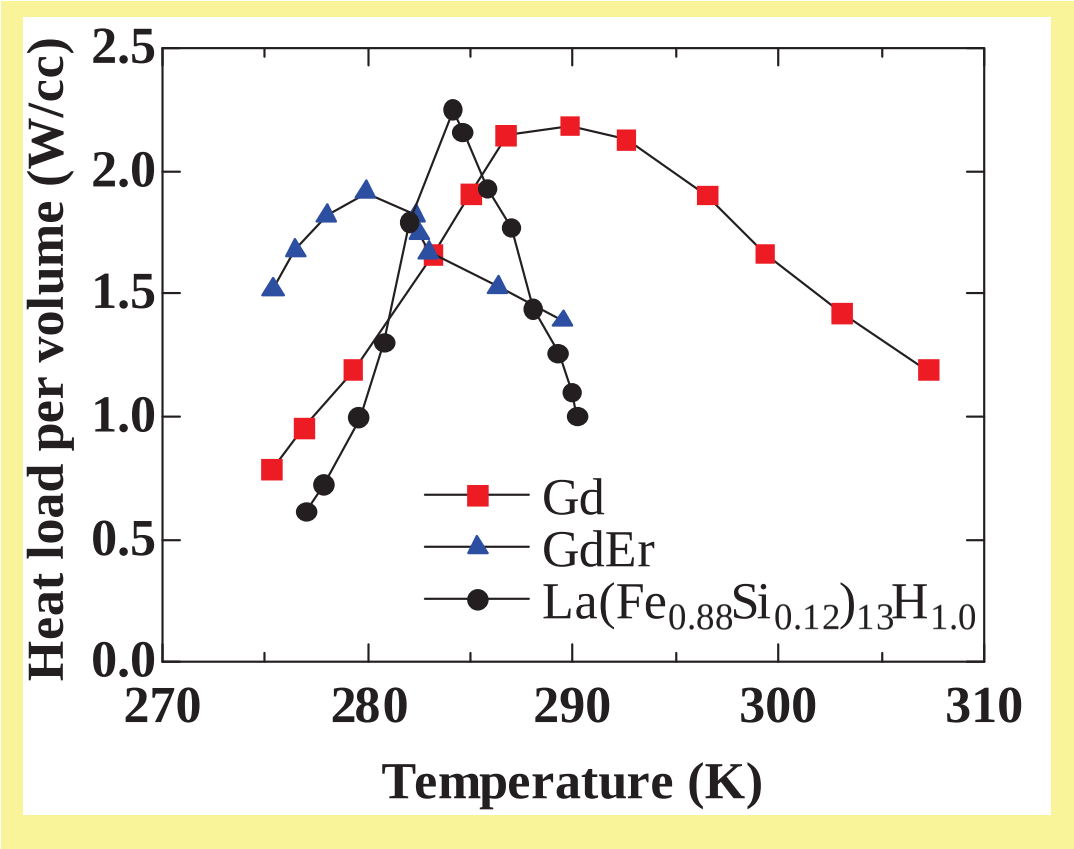
Mössbauer effect for hydride compound





	δ_{IS} (mm/sec)	HF: Fe^{I} (T)	HF: Fe^{II} (T)	H_{av} (T)	M_s (μ_B)	T_C (K)
$y = 0.0$	-0.01	25.7	30.4	29.9	2.05	195
$y = 1.6$	+0.12	26.9	31.6	31.2	2.15	330

Test results in AMR-type module 1

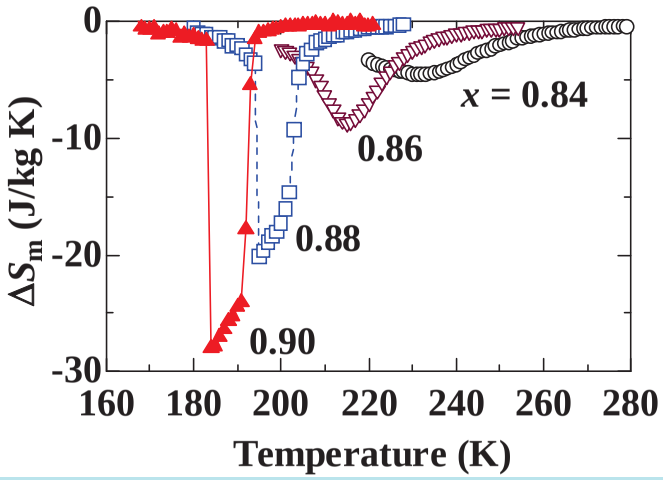


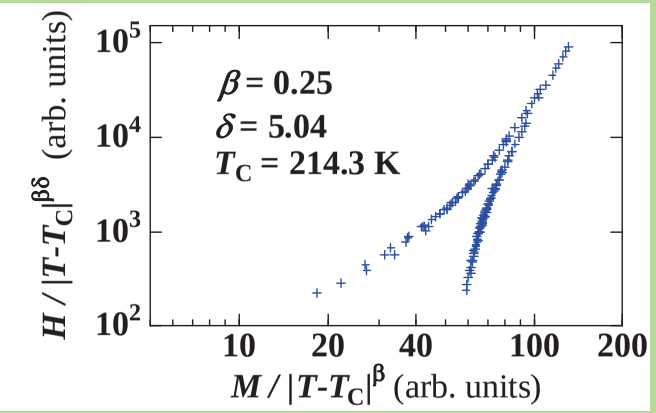
The maximum cooling power is superior to that of Gd

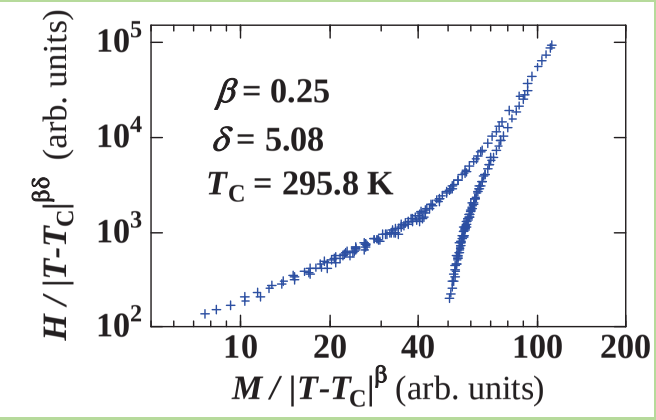
Cooling curve is sharp and narrow

Astronautics and Tohoku Univ.
Int. J. Refrg., **29**, 1302 (2006)

Test results in AMR-type module 2

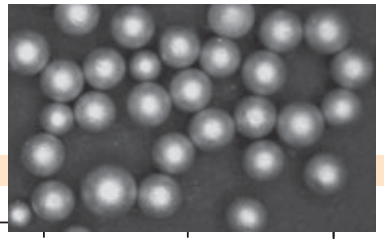


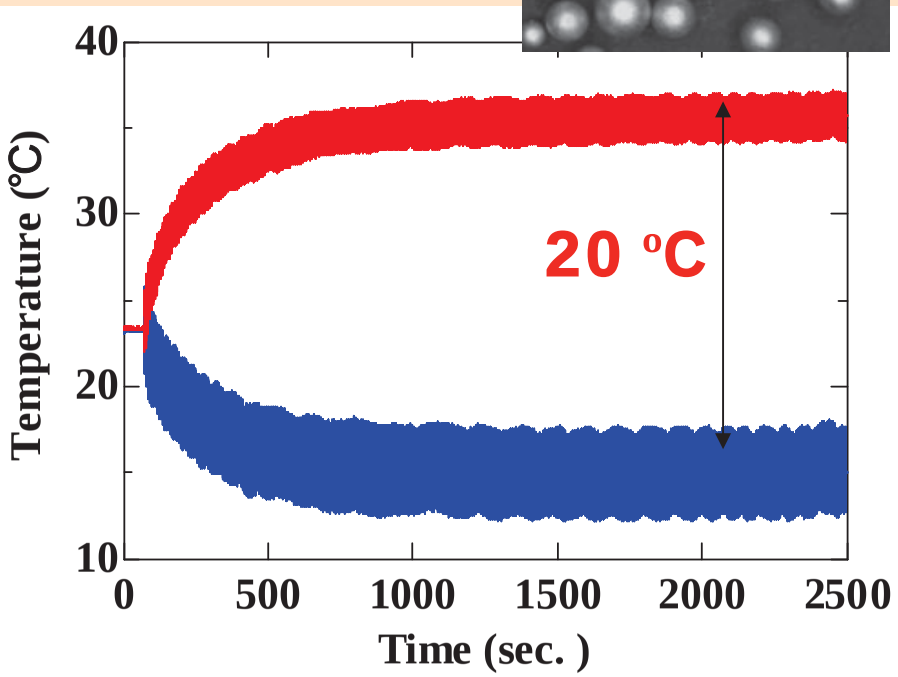




Tricritical concentration
***x* = 0.85**

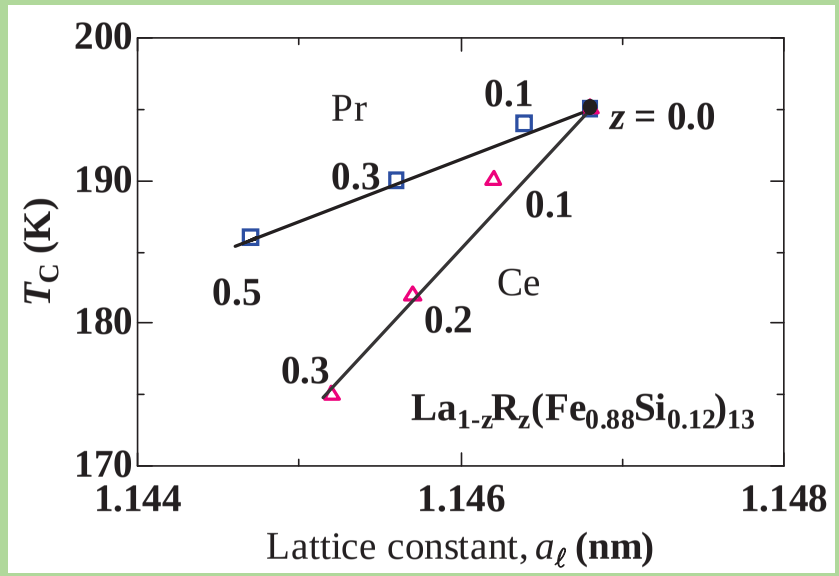
Spherical shape
(Rotating Electrode Process)

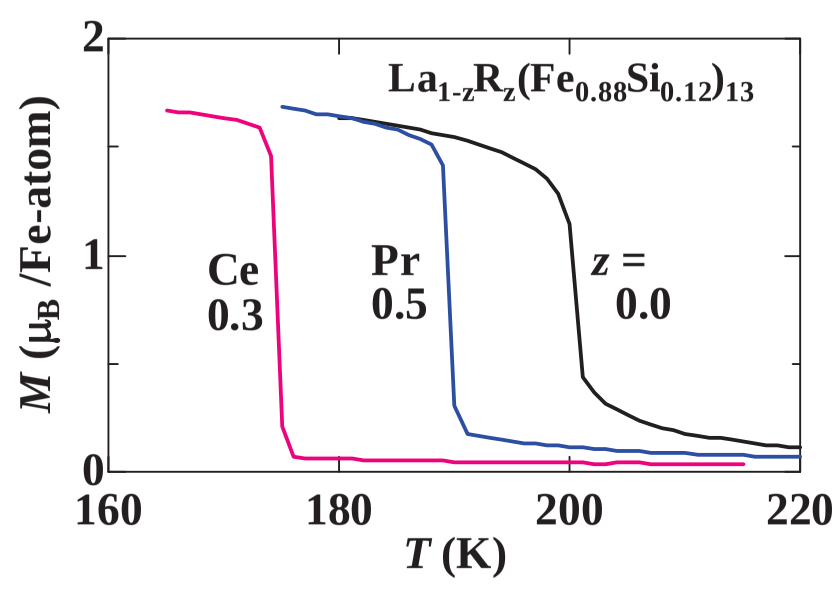


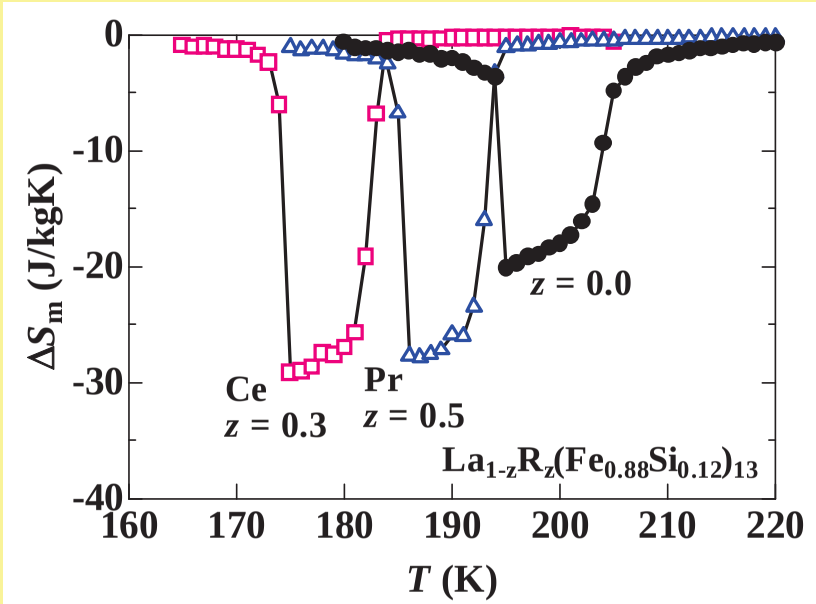


Toshiba and Tohoku Univ.
Jpn. J. Appl. Phys. 46, L154 (2007)

Partial substitution: $La_{1-z}R_z(Fe_{0.88}Si_{0.12})_{13}$



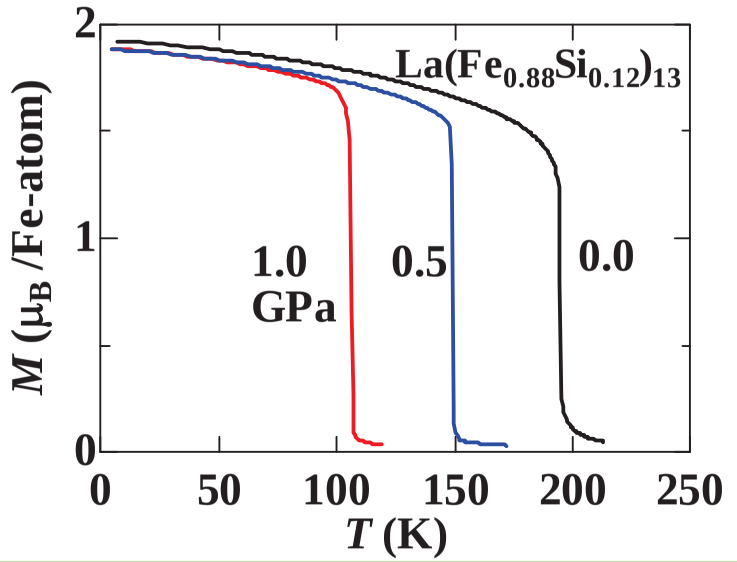


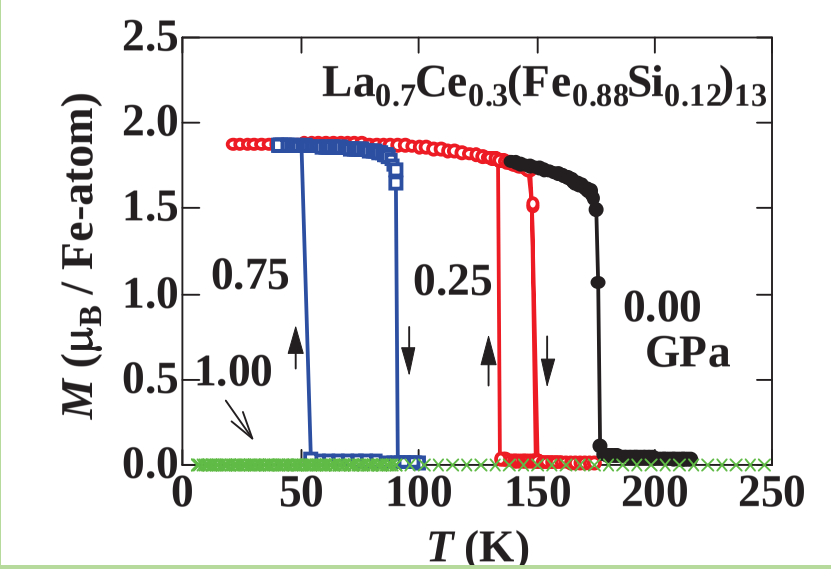


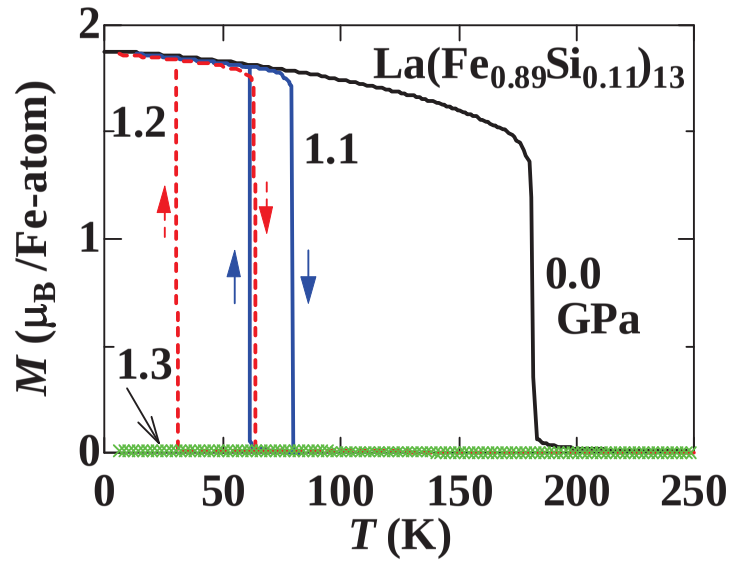
Lattice contraction

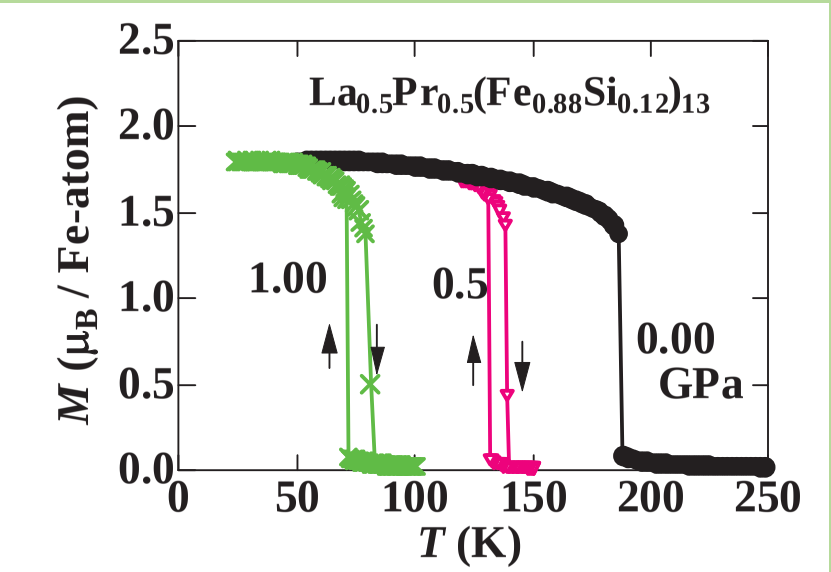
Band hybridization

Do partial substitutions correspond to “chemical pressure” ?

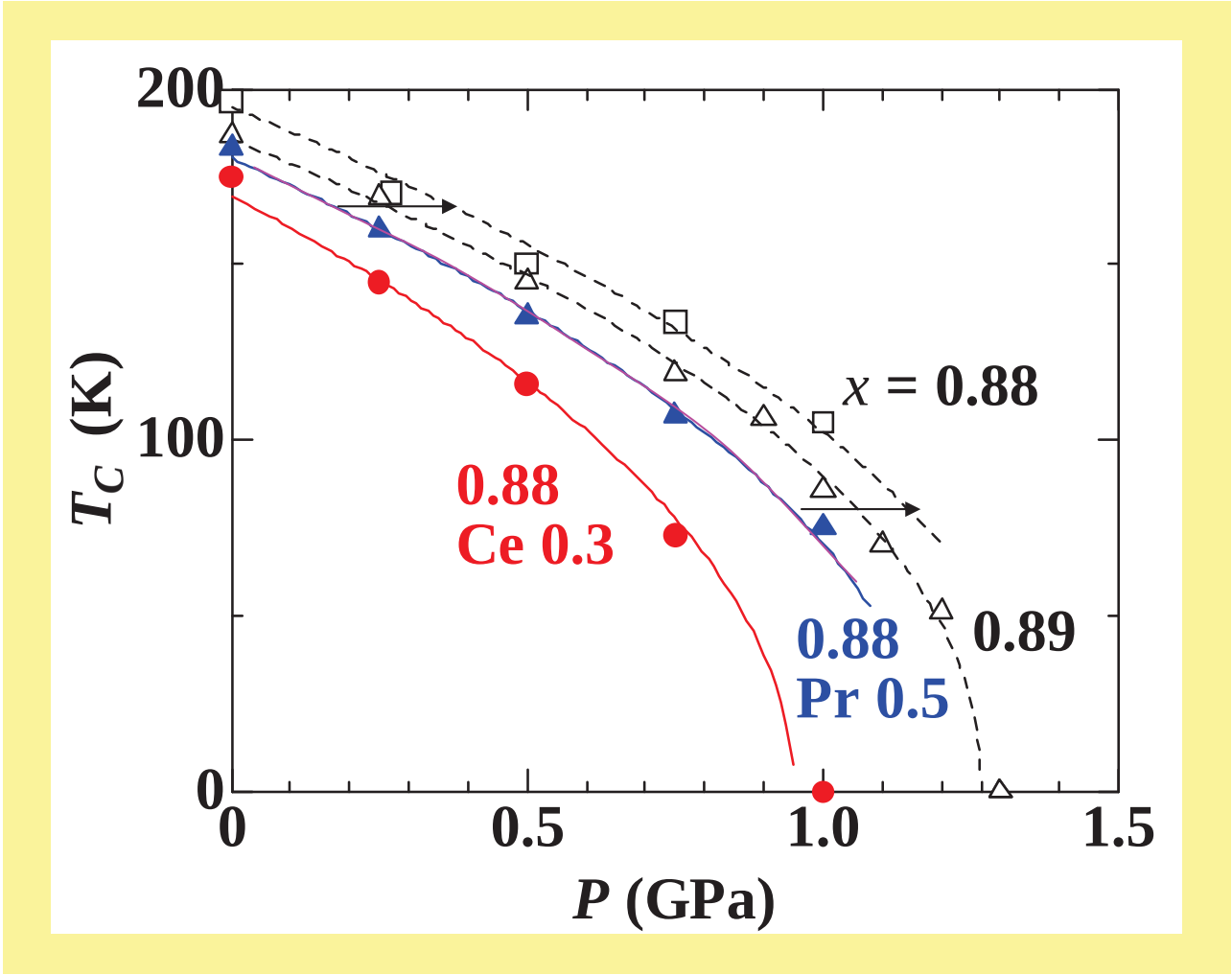




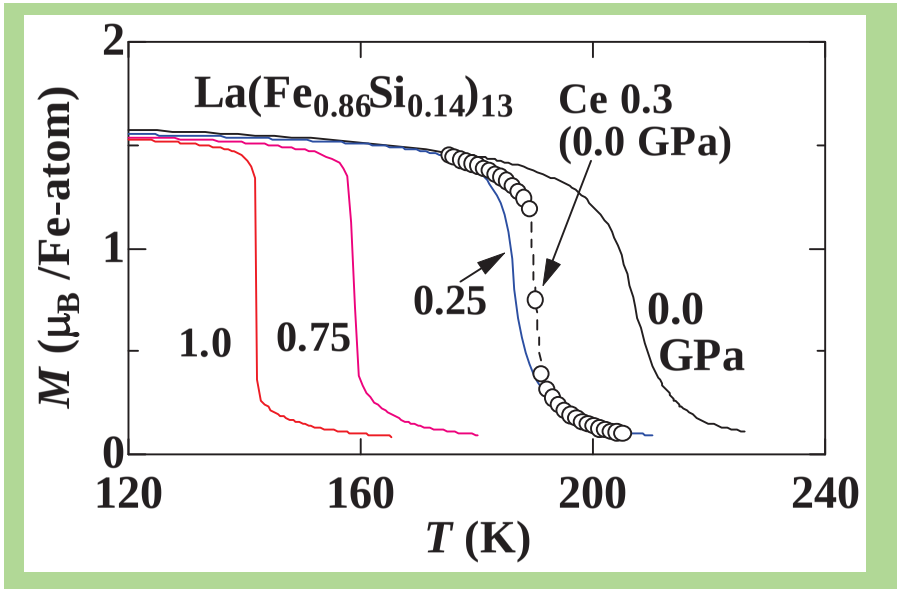


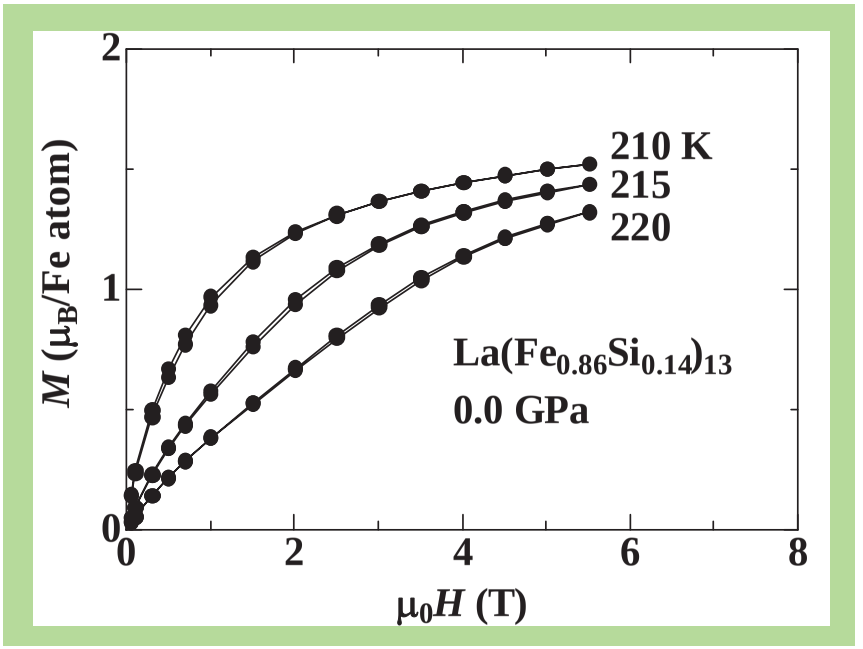


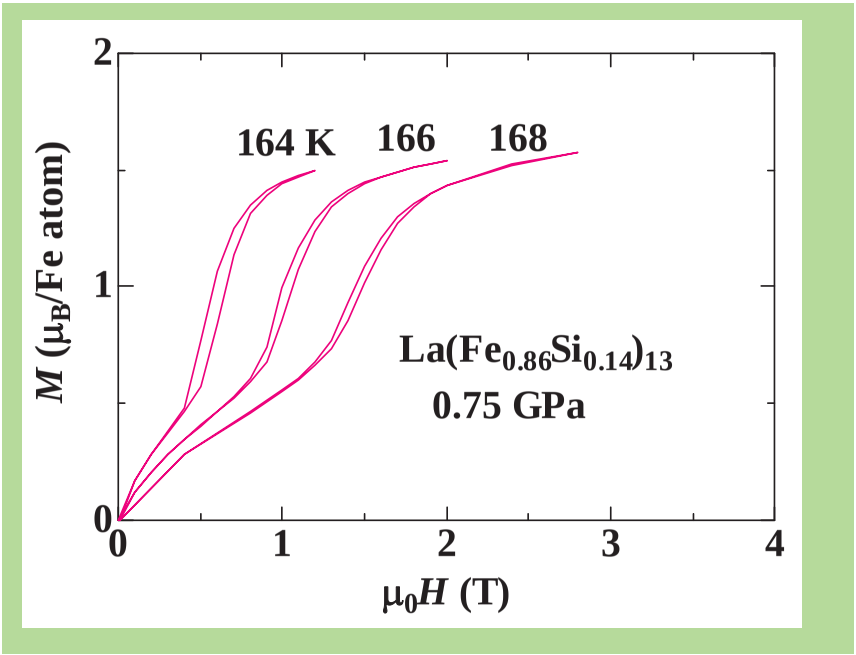
Phase diagram of $La_{1-z}R_z(Fe_{0.88}Si_{0.12})_{13}$ under pressure

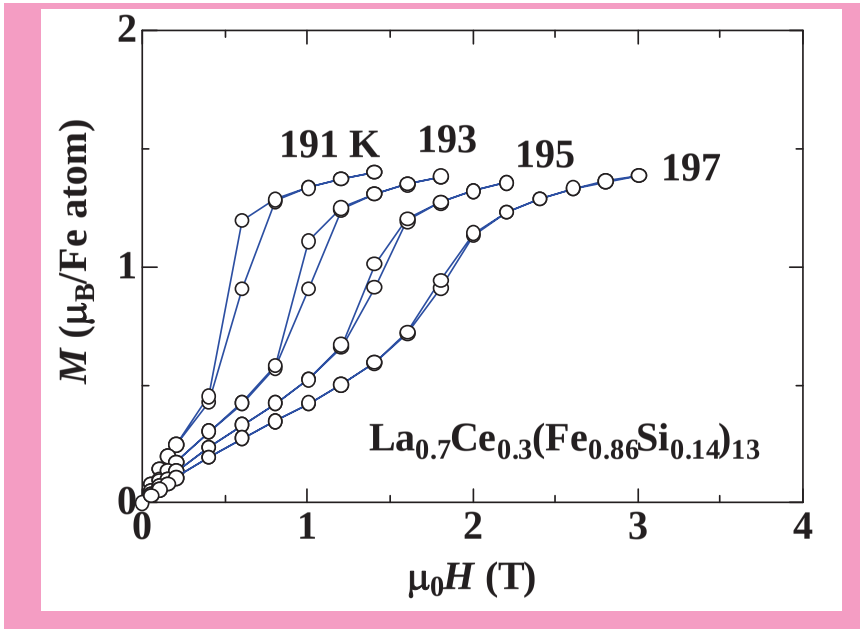


The IEM transition after partial substitution of Ce in $La(Fe_{0.86}Si_{0.14})_{13}$





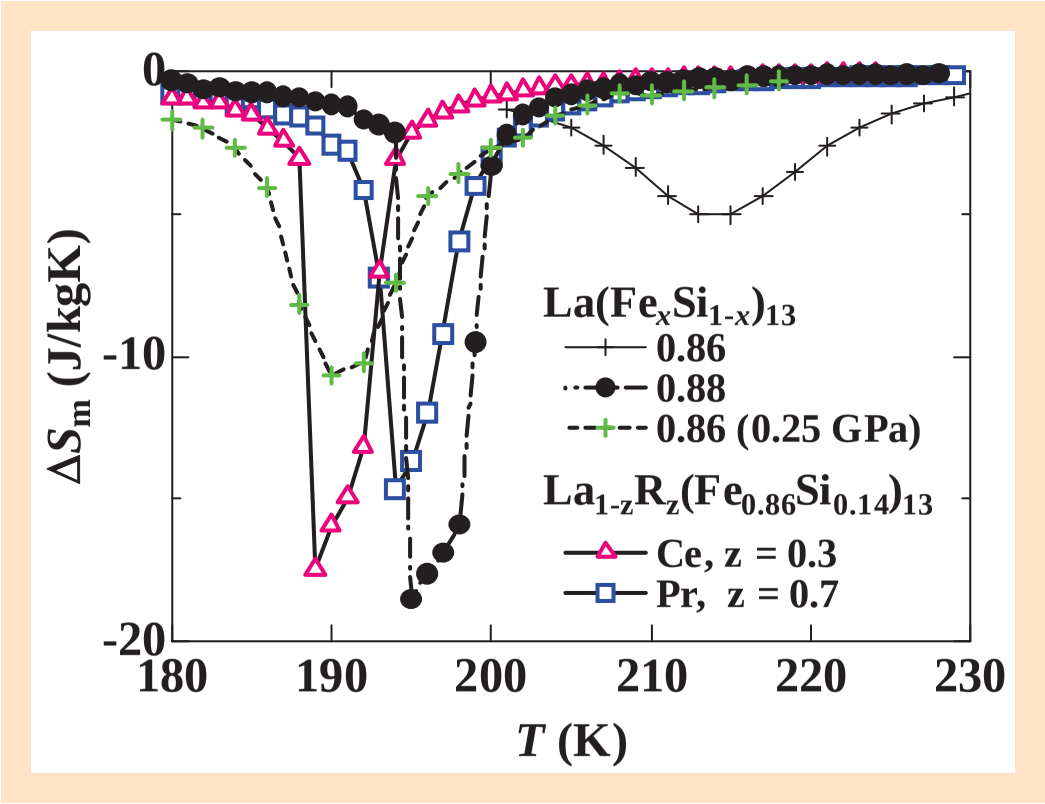




A. Fujita et al, J. Appl. Phys.,**93**(2003), 7263

S. Fujieda et al, IEEE Trans. Mag ,**41**(2005), 2787

Enhancement of ΔS_m in $La_{1-z}R_z(Fe_{0.88}Si_{0.12})_{13}$

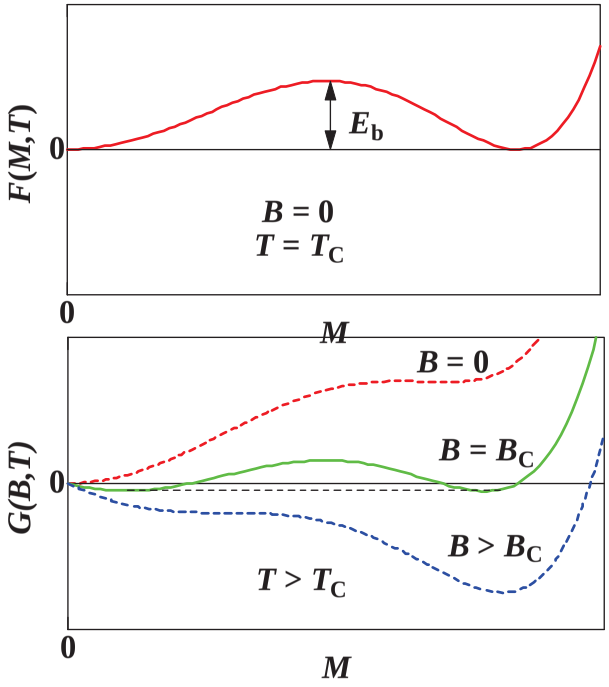


The IEM transition becomes sharp

ΔS_m is enhanced

due to both the magnetovolume and band hybridization effects

Reduction of hysteresis loss by partial substitutions



$$F(M,T) = \frac{1}{2}A(T)M^2 + \frac{1}{4}B(T)M^4 + \frac{1}{6}C(T)M^6 \ ,$$

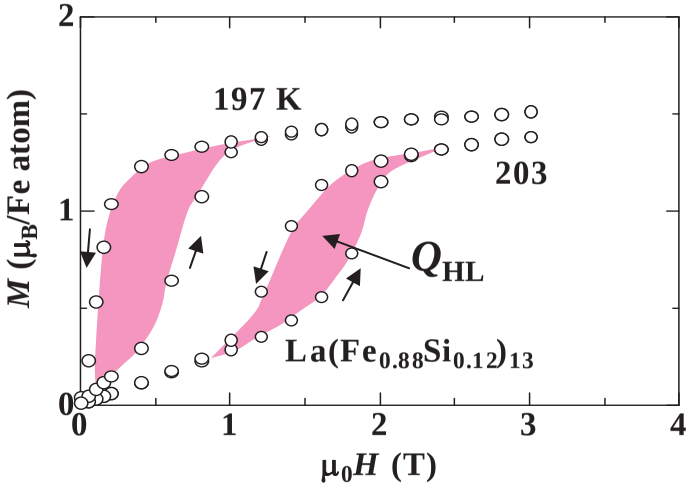
$$A(T) = a + \frac{5}{3}b\xi(T)^2 + \frac{35}{9}c\xi(T)^4 - 2\kappa C_{mv}^2\xi(T)^2 + 2C_{mv}\omega$$

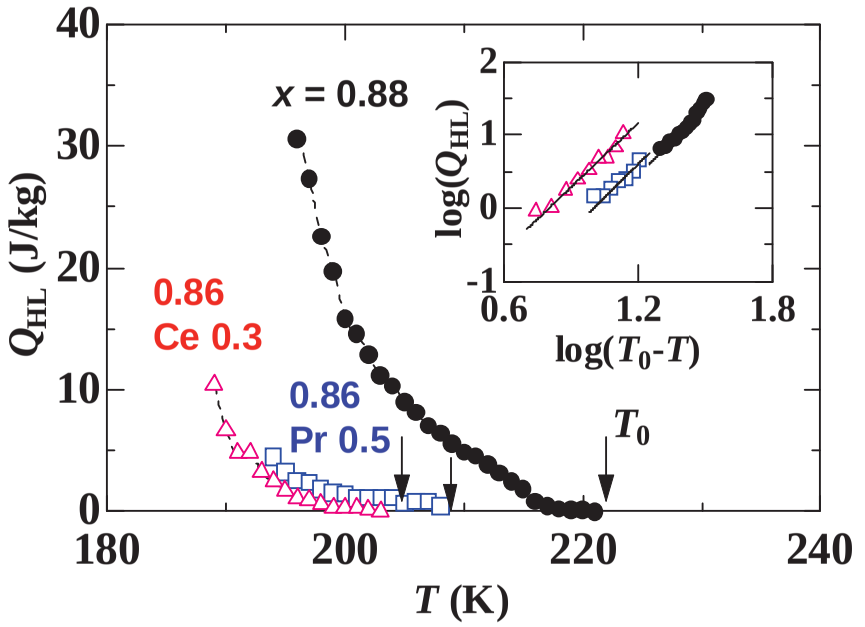
$$B(T) = b + \frac{14}{3}c\xi(T)^2 - 2\kappa C_{mv}^2, \quad C(T) = c,$$

$$E_b = |B(T)|^3 / 96C(T)^2 \ .$$

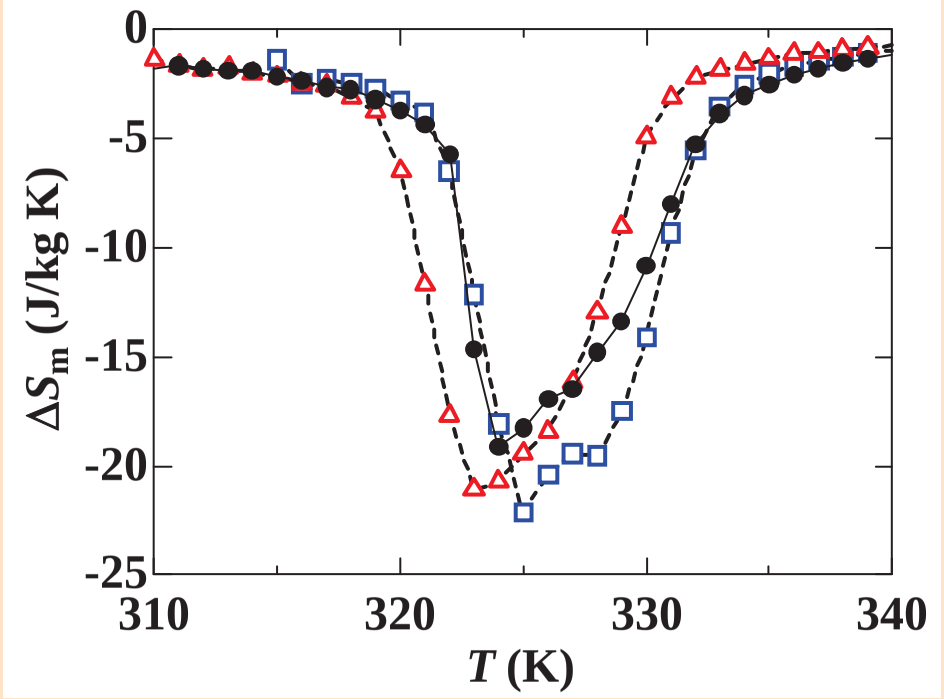
$$G(B,T) = F(M,T) - BM$$

$$F(M_C,T) - B_C M_C = 0$$





Partial substitution and hydrogenation



- $La(Fe_{0.88}Si_{0.12})_{13}H_{1.5}$
- $La_{0.7}Ce_{0.3}(Fe_{0.88}Si_{0.12})_{13}H_{1.7}$
- $La_{0.5}Pr_{0.5}(Fe_{0.88}Si_{0.12})_{13}H_{1.6}$

By hydrogenation after partial substitution,

Enhancement of ΔS_m is remained.

T_C is elevated above room temperature.

Summary

Improvement of magnetocaloric properties in $La(Fe_xSi_{1-x})_{13}$ by hydrogenation and partial substitution has been investigated:

1. The Curie temperature T_C of $La(Fe_xSi_{1-x})_{13}$ is increased by hydrogen absorption, while decreased by the partial substitution of Ce or Pr for La.

2. Superiority of hydrogenated specimens has been confirmed by tests in AMR-type modules.

3. Reduction of hysteretic behavior with maintaining large MCEs is established by partial substitutions.

4. By combining the hydrogenation and partial substitutions, enhancement of MCEs are established at room temperature.

Various improvements of the MCEs increase further potential of $La(Fe_xSi_{1-x})_{13}$ compounds as magnetic refrigerants working around room temperature with high efficiency and low hysteresis loss.