Magnetocaloric materials

not only for cooling applications

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Outline:

Introduction to magnetism and MCE

Giant MCE in Fe_2P type materials

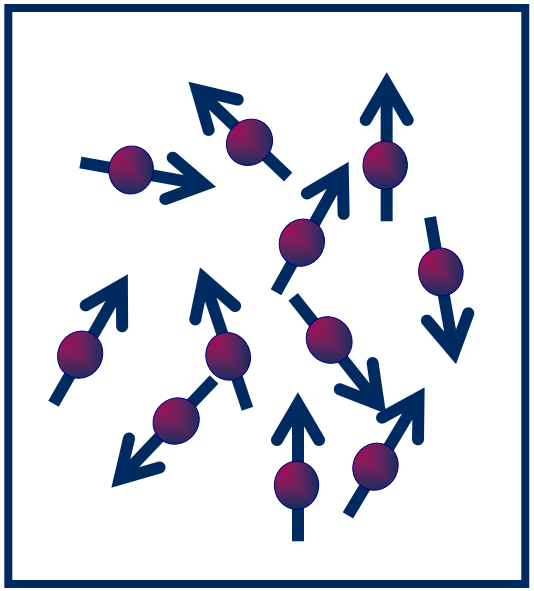
Tailoring properties by substitutions

Electronic structure and phase-transition

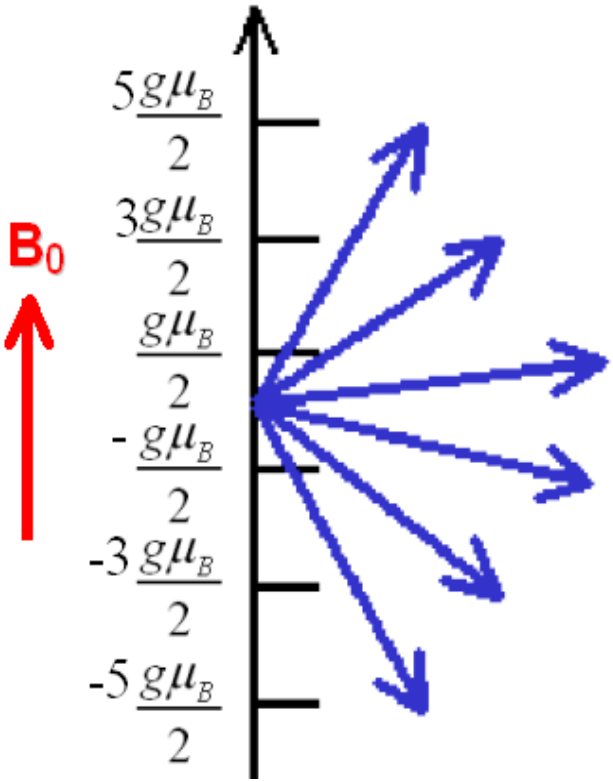
Conclusions

Magnetization processes

Magnetic (spin) moments



no field
no net moment

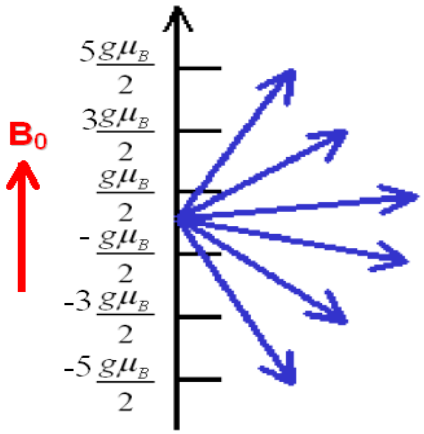


$$e^{-E/k_BT}$$

$-\mu B_0$

Effect of temperature. Classical statistical physics:
probability of finding atomic dipole in state with energy E:

Magnetization processes



$$e^{-E/k_BT}$$

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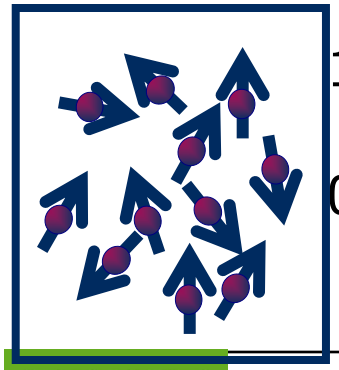
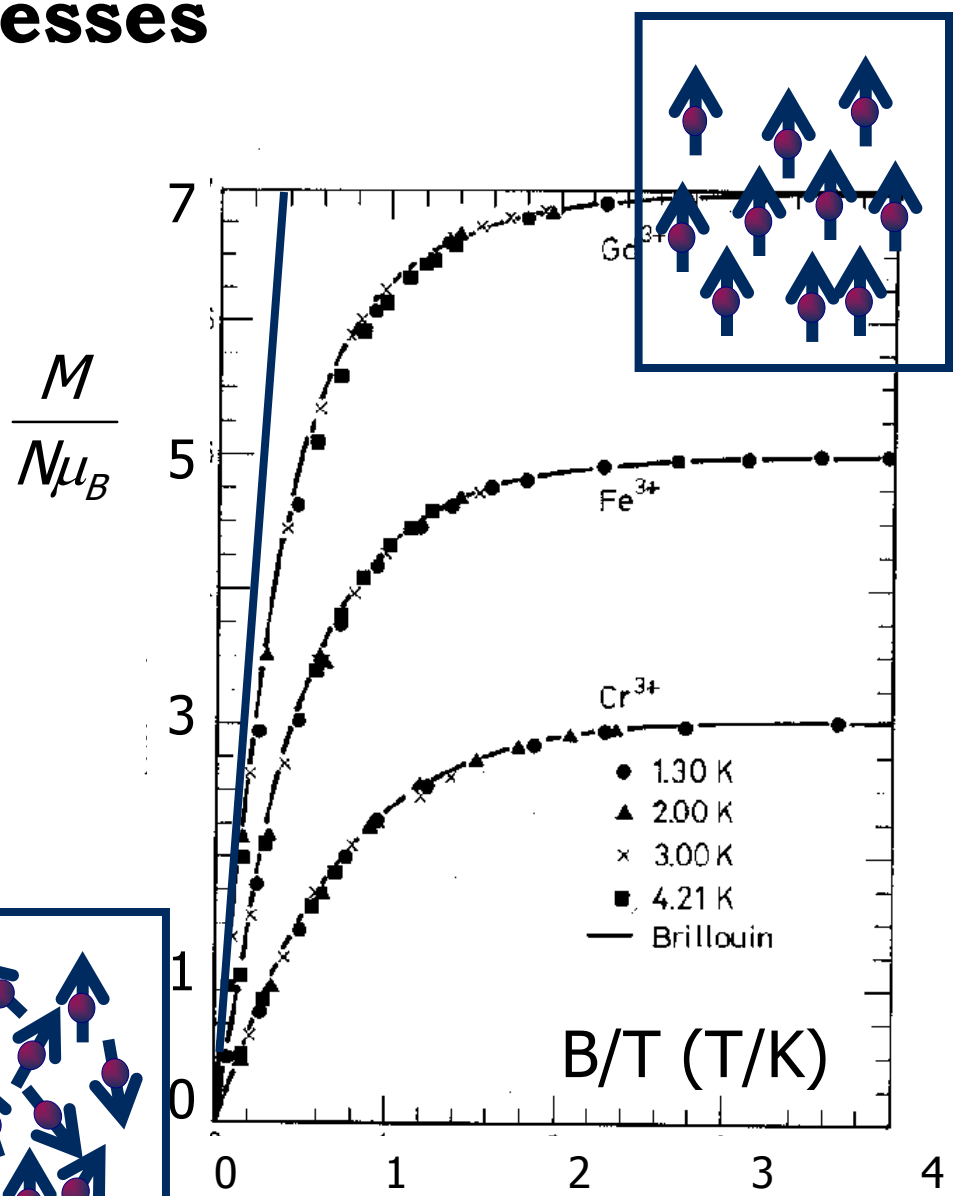
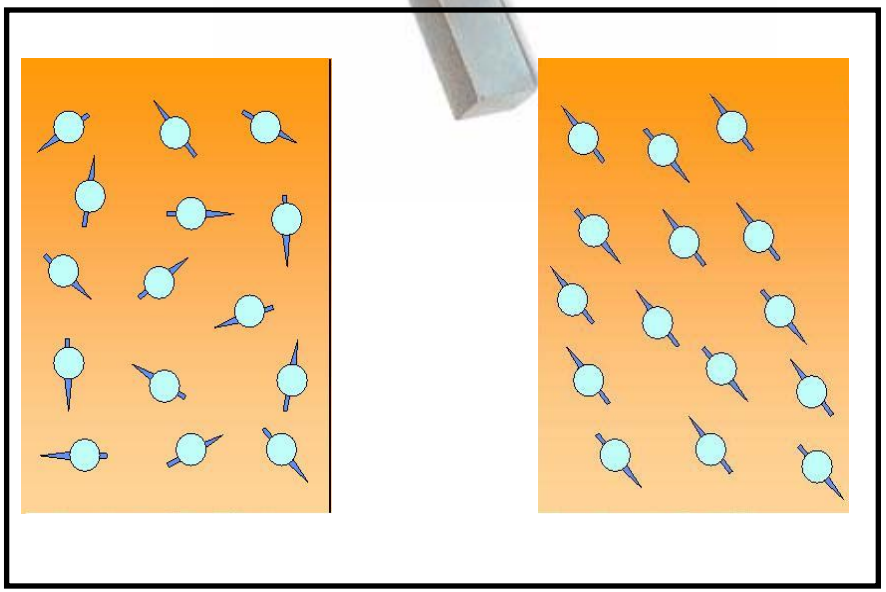




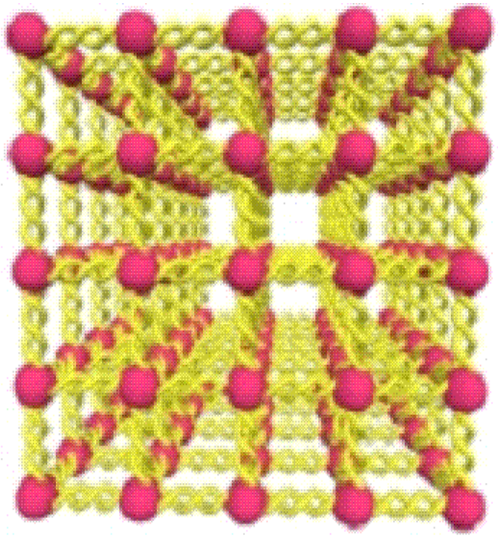
Basic magnetocalorics

Two energy reservoirs

spins → lattice

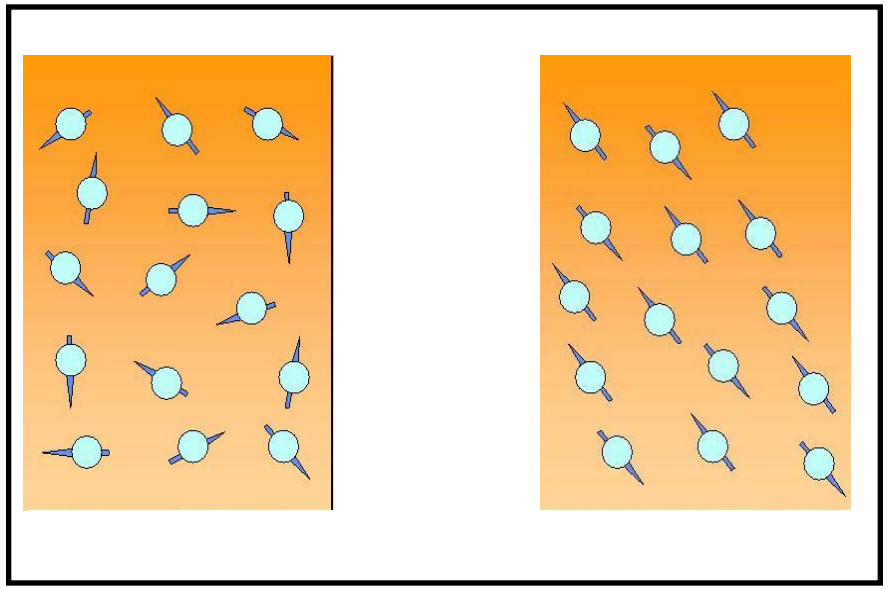


E →

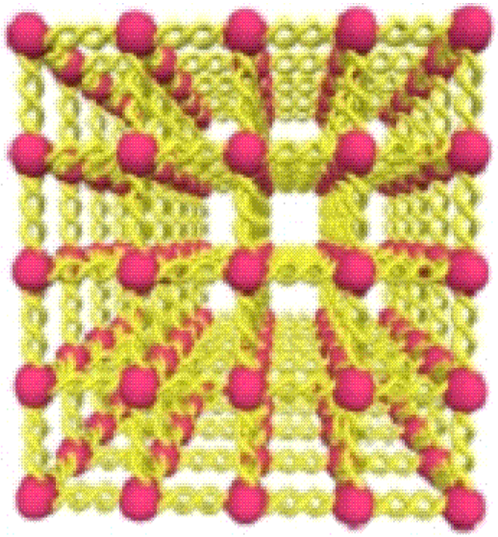


Basic magnetocalorics

spins ← lattice



E ←



Magnetic cooling: Debye and Giauque 1926

768 LETTERS TO THE EDITOR

Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$

We have recently carried out some preliminary experiments on the adiabatic demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$ at the temperatures of liquid helium. As previously predicted by one of us, a large fractional lowering of the absolute temperature was obtained.

An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $Gd_2(SO_4)_3 \cdot 8H_2O$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium sulfate. The coil was immersed in liquid helium and isolated from the gadolinium by means of an evacuated space. The thermometer was in excellent agreement with the temperature of liquid helium as indicated by its vapor pressure down to 1.5°K.

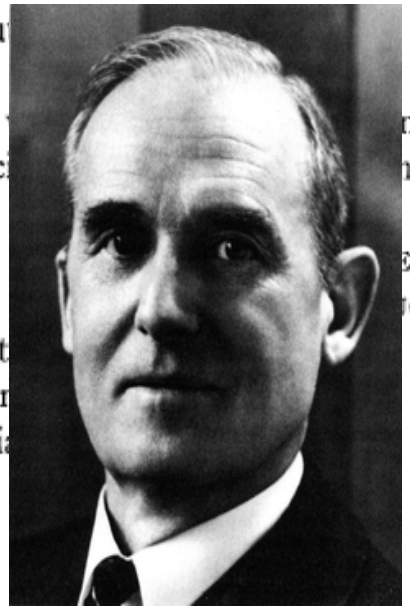
On March 19, starting at a temperature of about 3.4°K, the material cooled to 0.53°K. On April 8, starting at about 2°, a temperature of 0.34°K was reached. On April 9, starting at abou 0.25°K was attained.

It is apparent that it n much lower temperatures, especi nagneti-zations are utilized.

E

GALL

Department of Chemist
University of Califor
Berkeley, Californi
April 12, 1933.

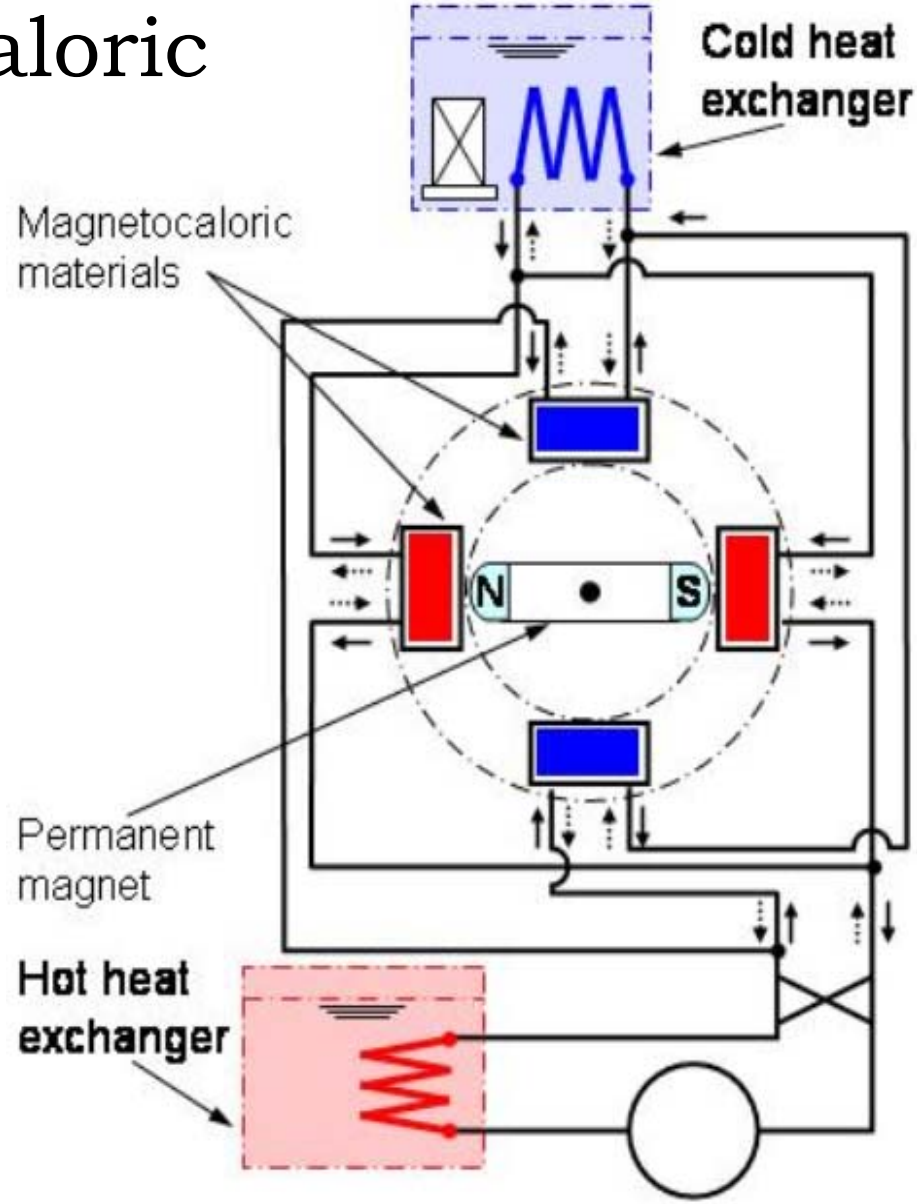


61g $Gd_2(SO_4)_3 \cdot 8H_2O$, ΔB=0.8T, 1.5K $\rightarrow$0.25K

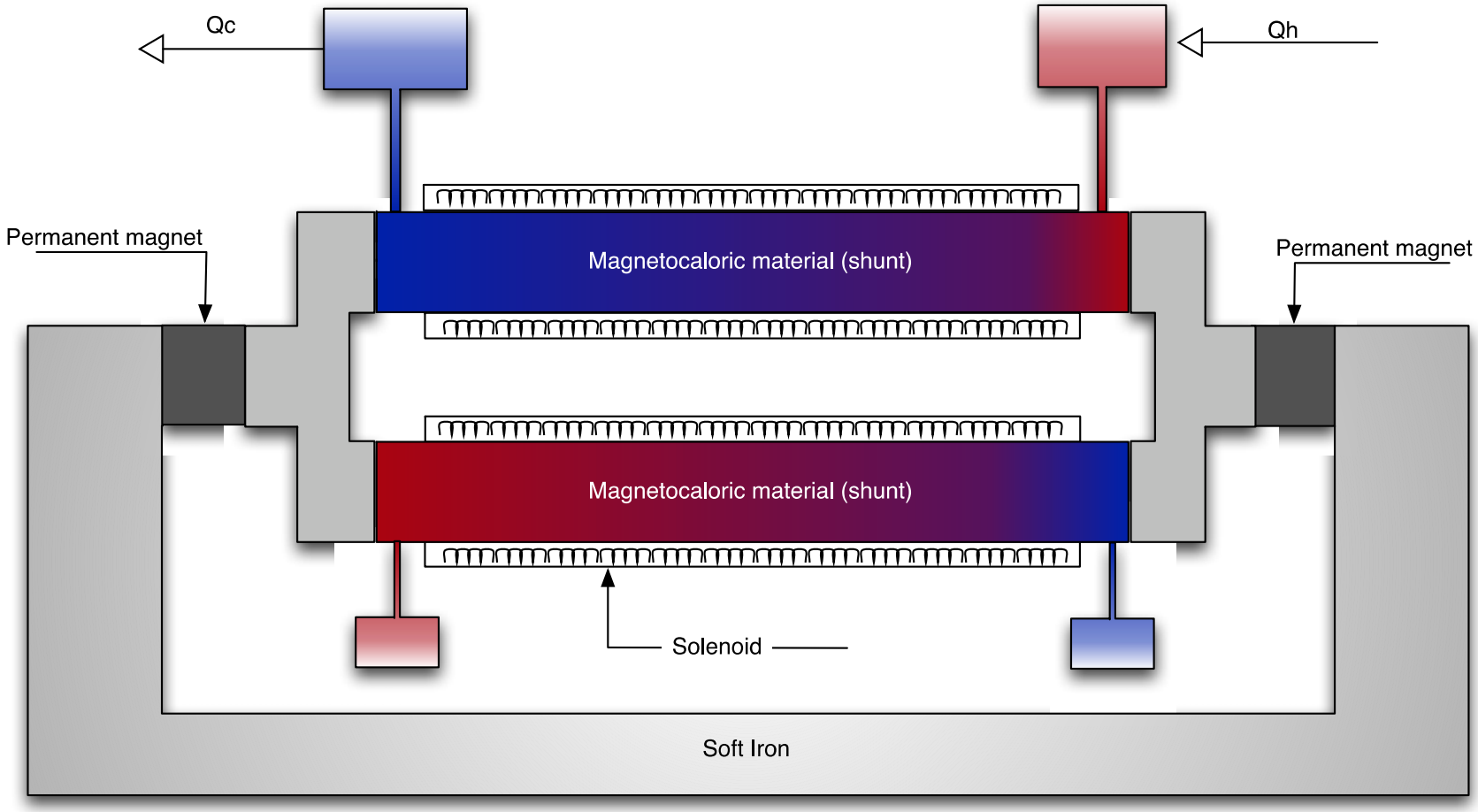
Nobel prize 1949

Active Magnetocaloric Regenerator

Chubu and Toshiba schematic



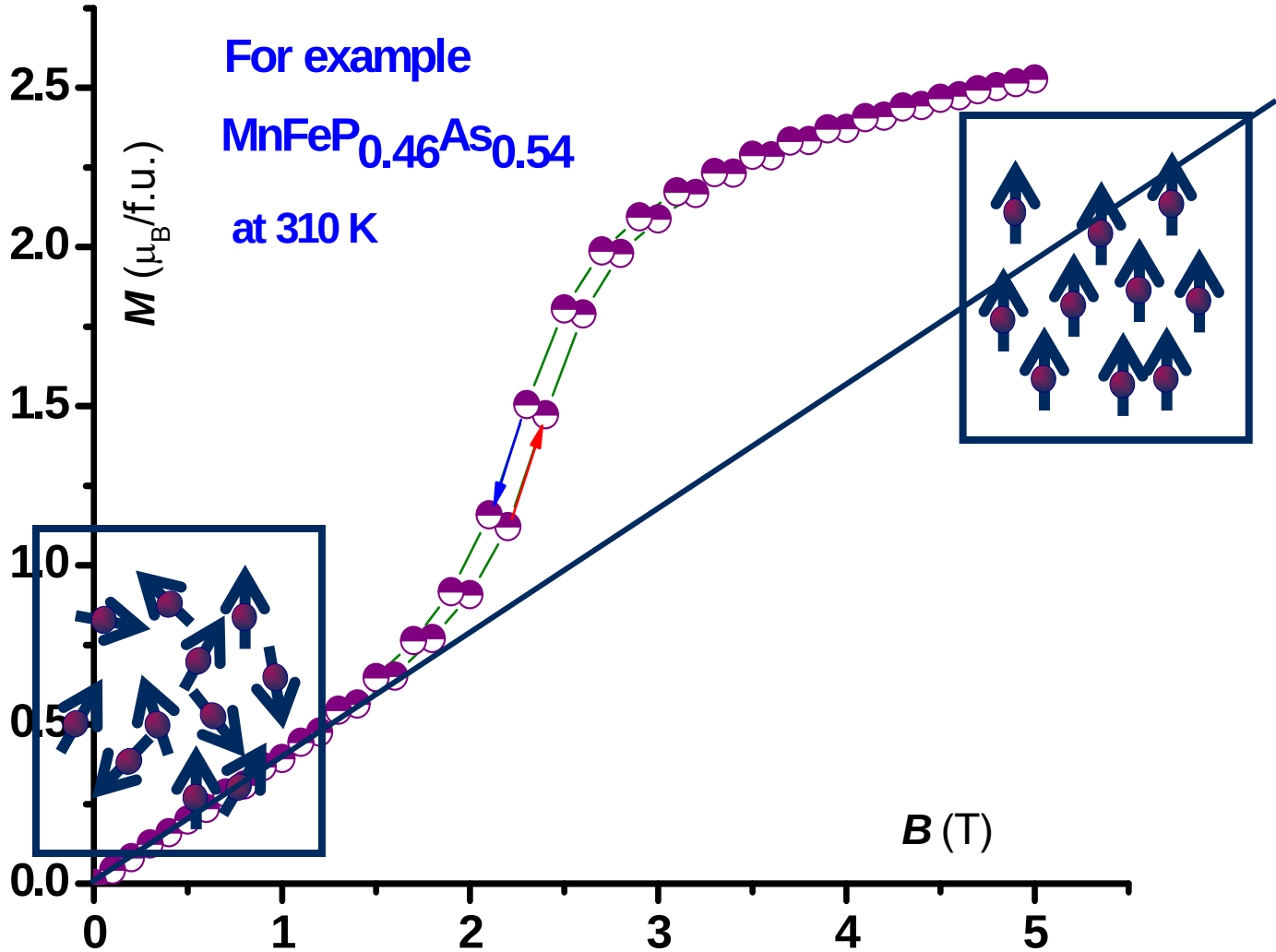
Magnetocaloric power generation



Huu Dung et. al. Adv. Energy Mat. (2011)

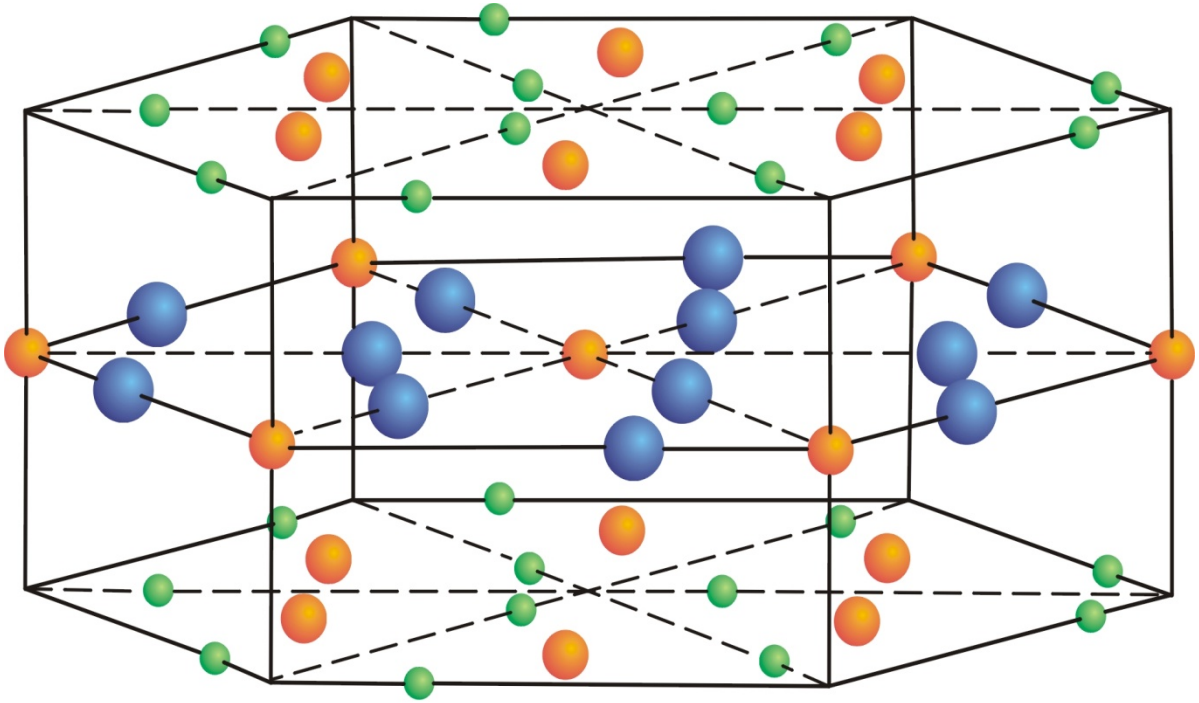
Magnetization processes

Materials with field induced first order phase transition.



$MnFeP_{1-x}As_x$

Hexagonal Fe_2P type of structure



Space group:

$P\bar{6}2m$

Mn 3g sites

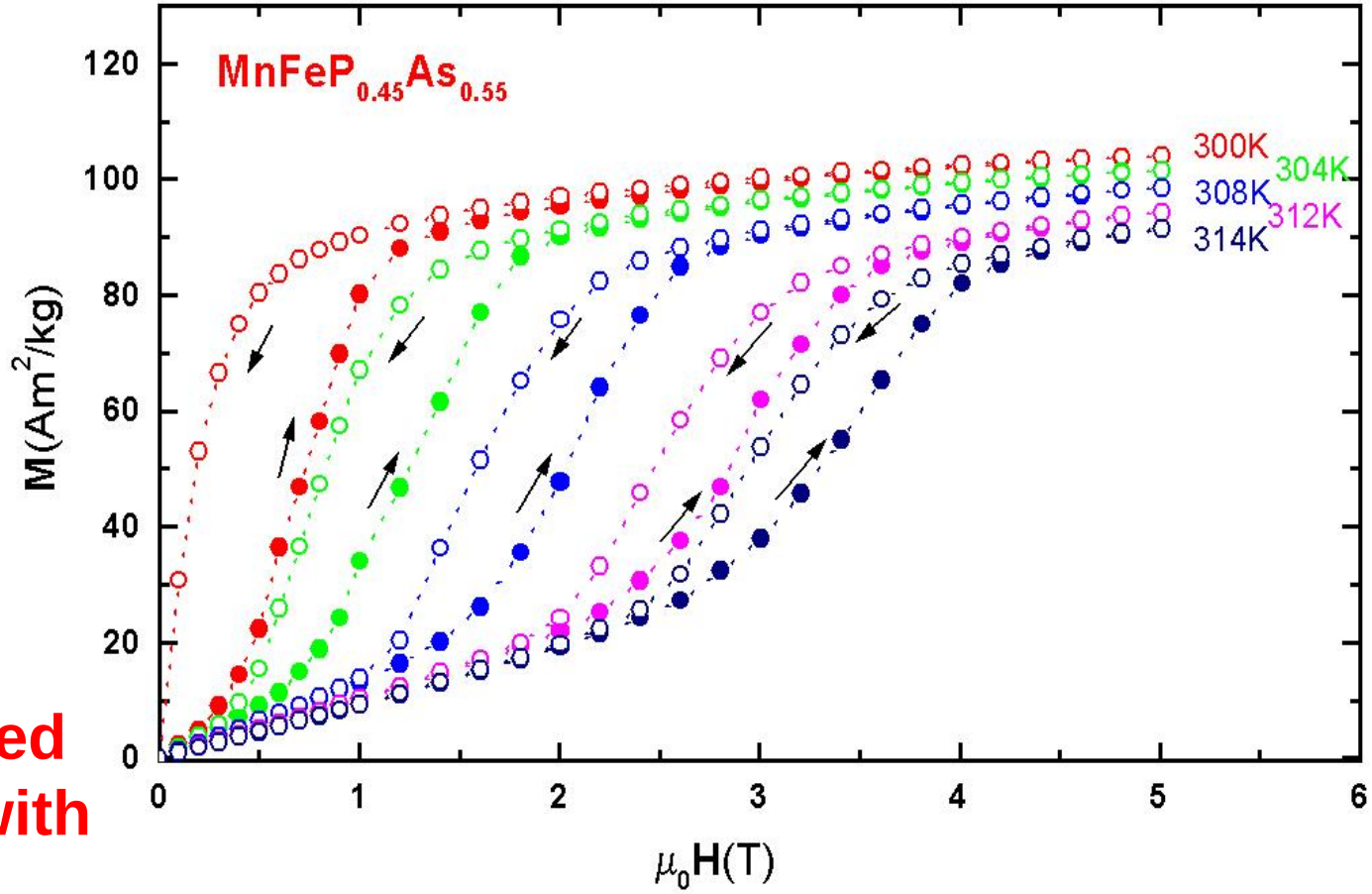
Fe 3f sites

P/As 1b&2c sites

Bacmann, JMMM 1994

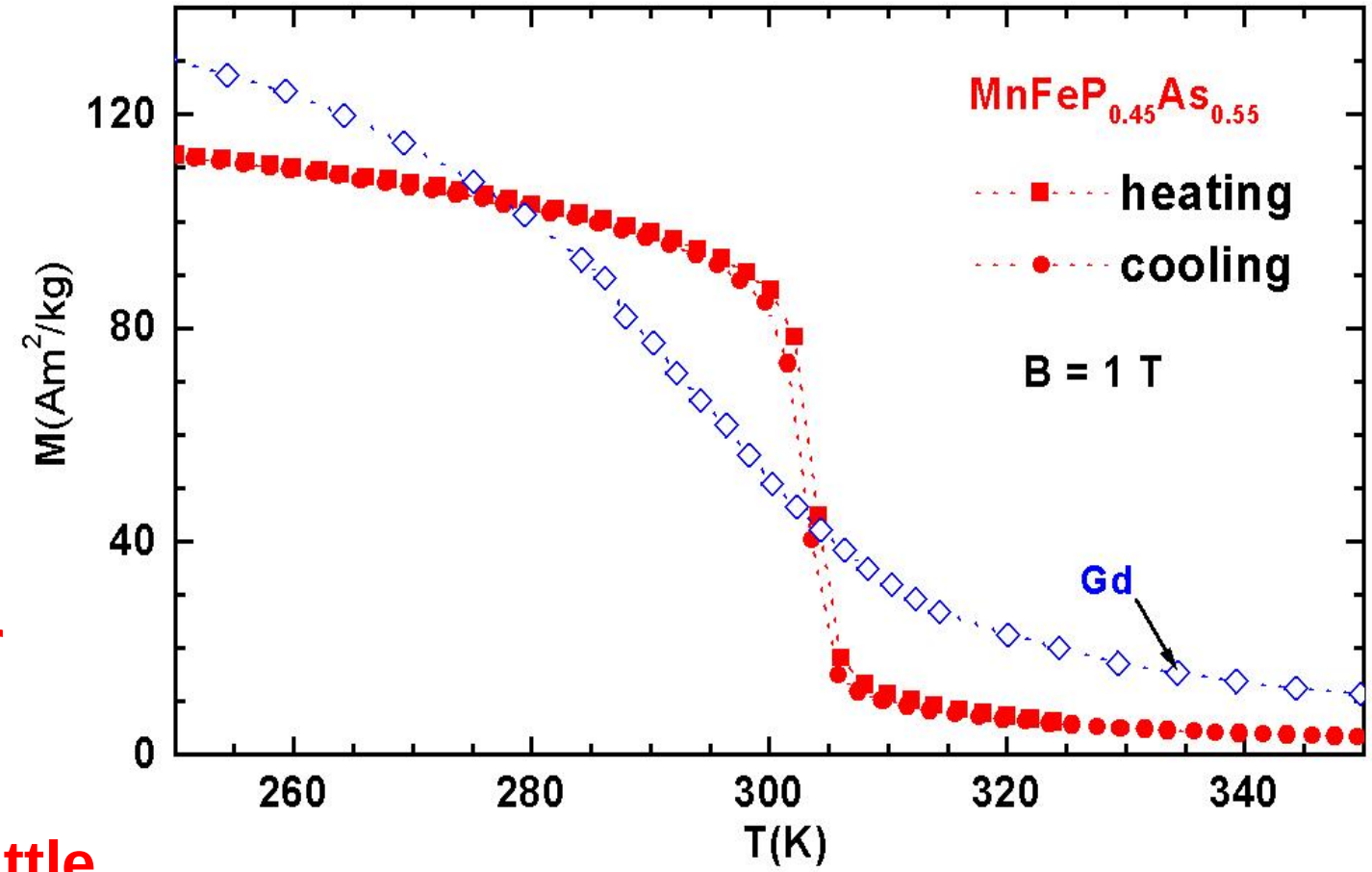
Mn P/As Fe

Magnetization process near T_c



Field induced transition with small hysteresis

Temperature dependence of Magnetization

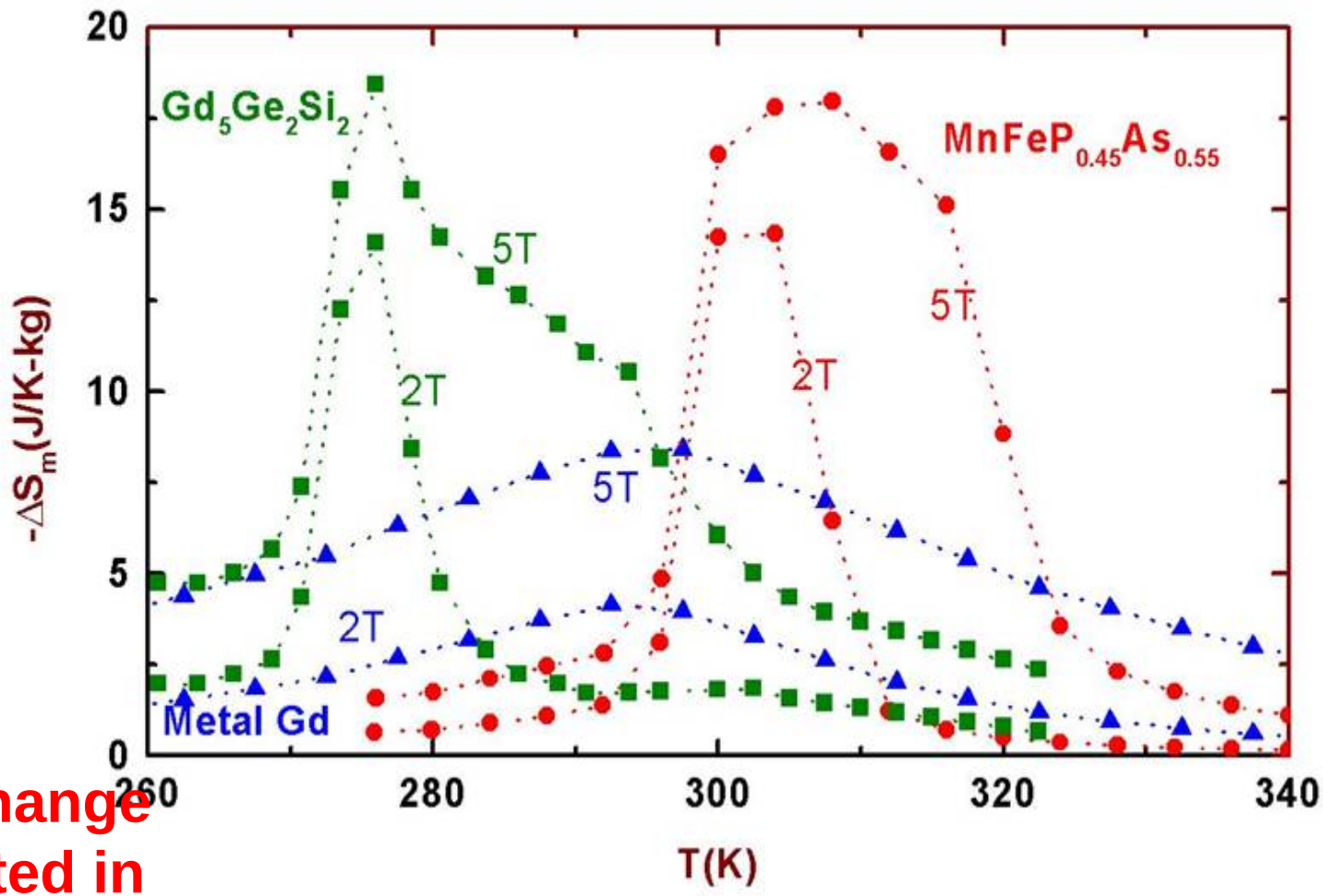


Step-like transition

first order

but very little hysteresis

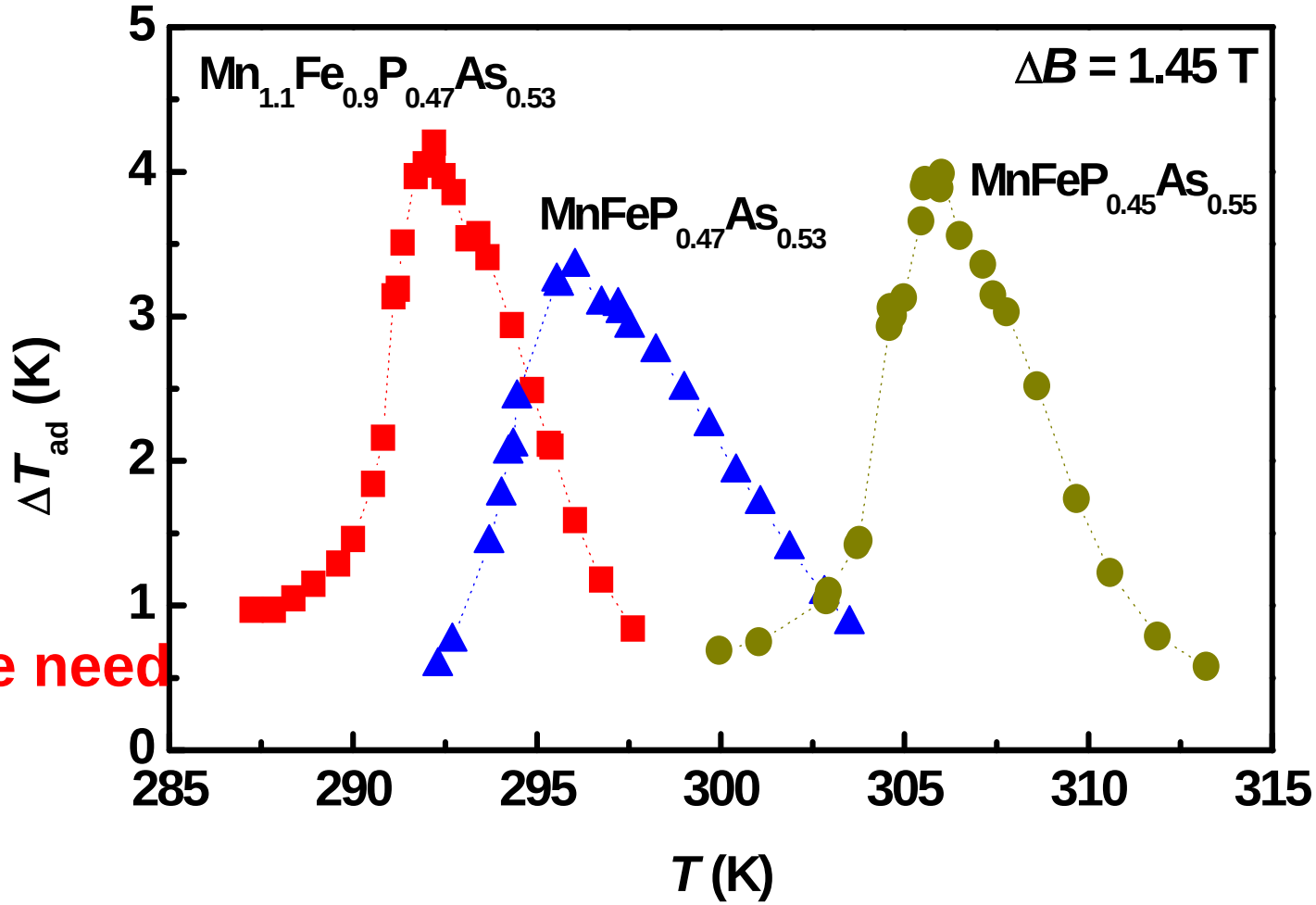
Comparison of magnetocaloric effect in different materials



Entropy change concentrated in relevant T interval

Tegus et al. Nature 415

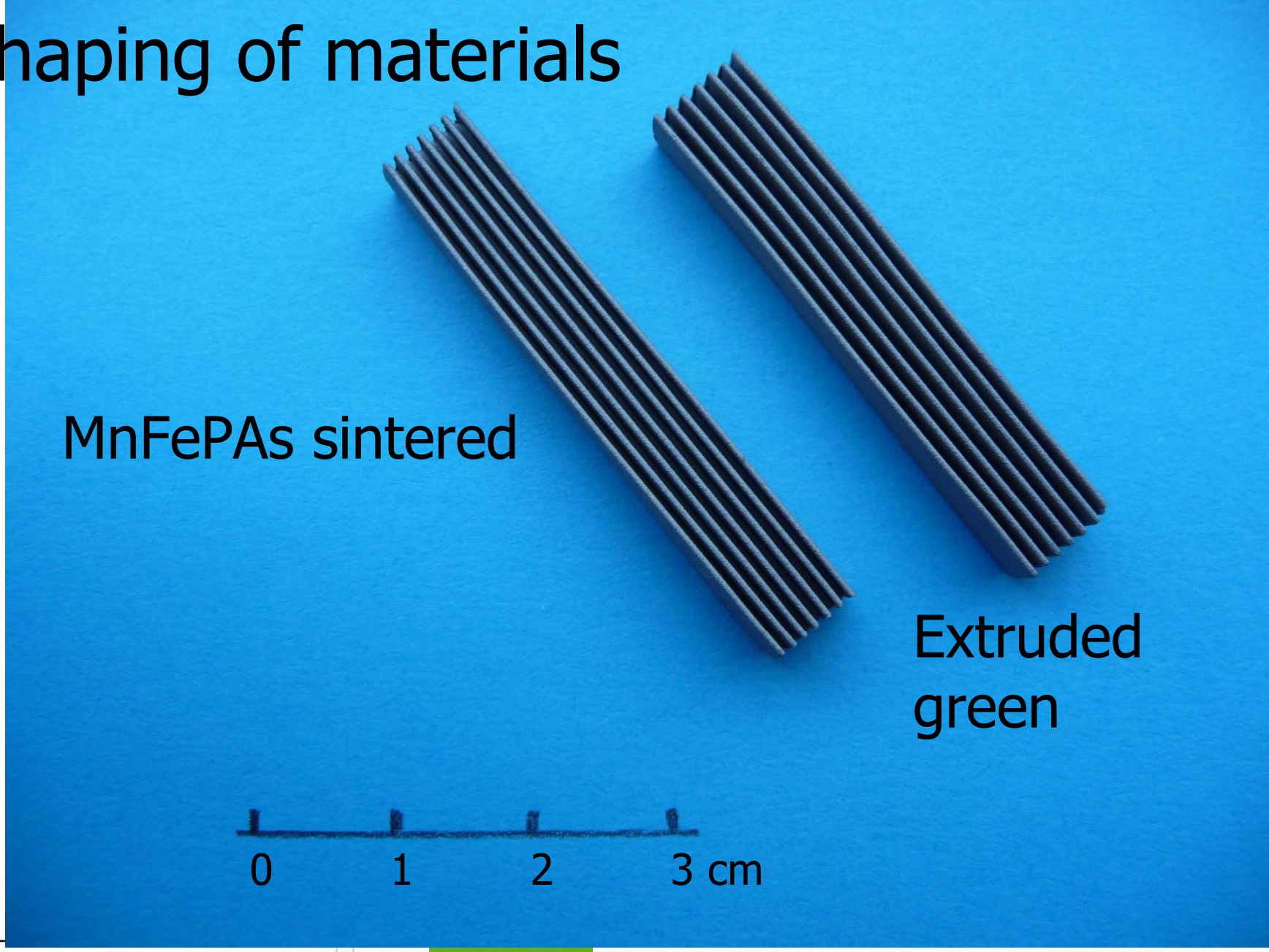
Adiabatic temperature-change



Sample dependence need for careful preparation

Direct measurements MSU

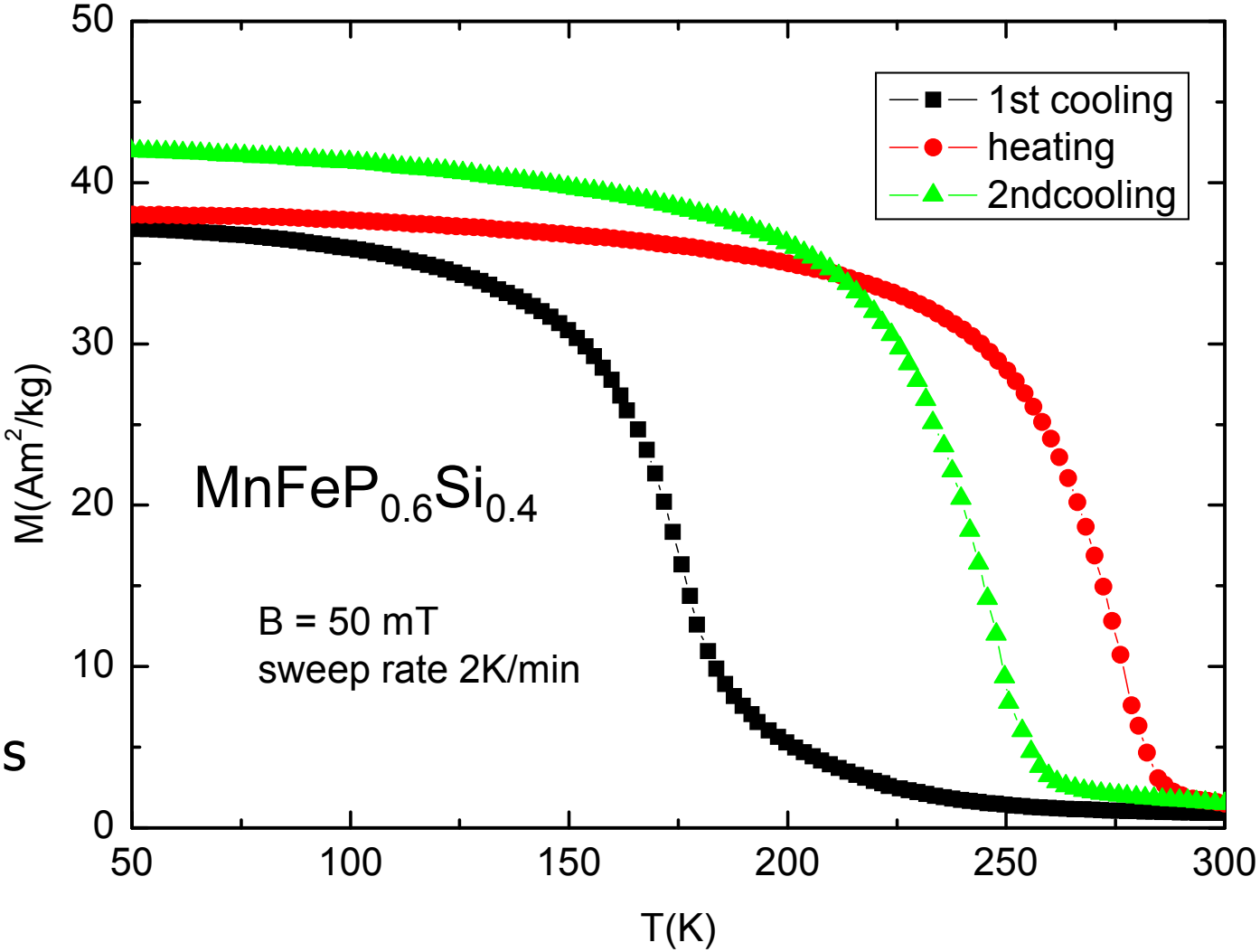
Shaping of materials



Challenges with Fe_2P materials

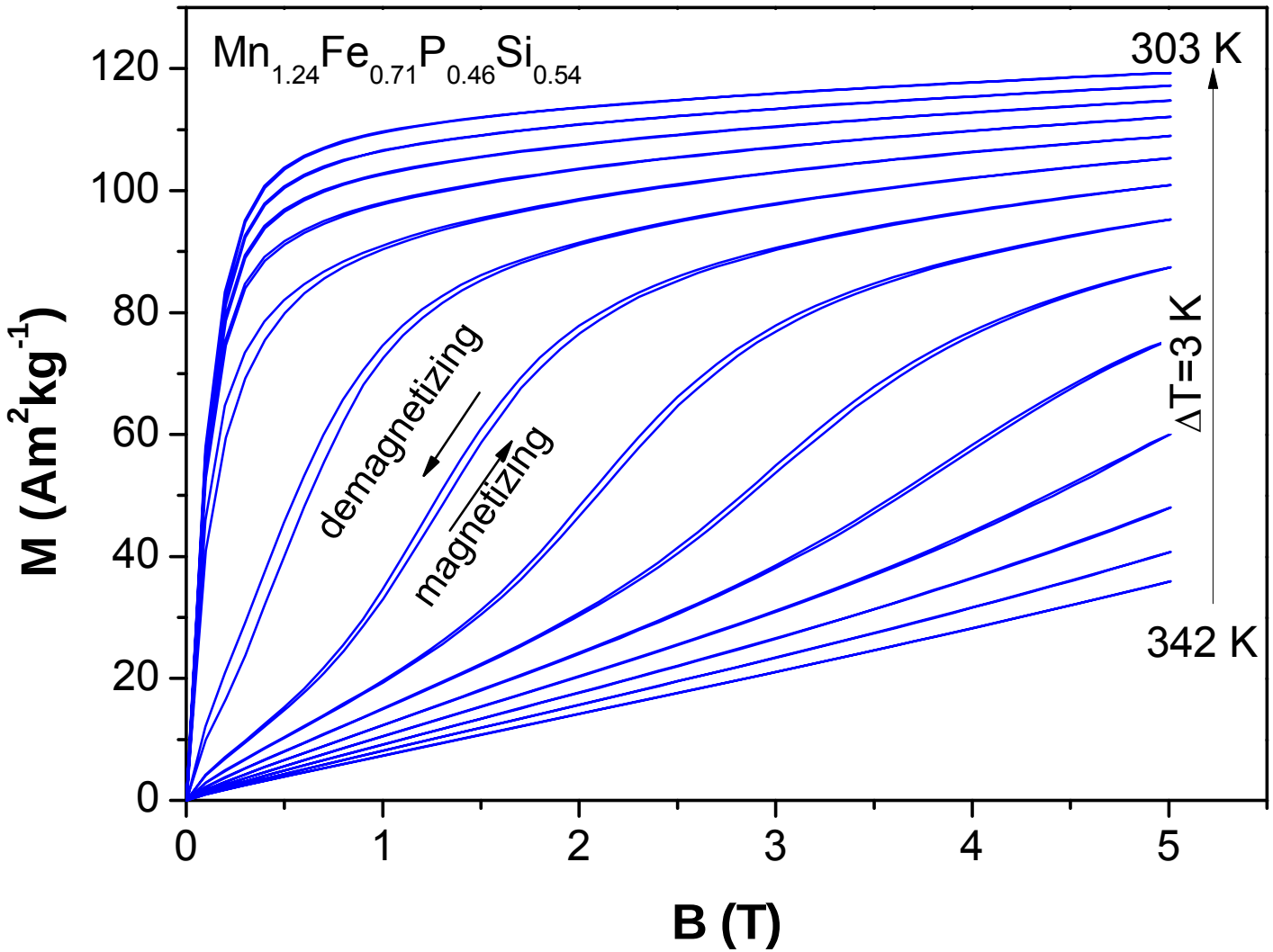
- As — bad reputation
- Ge — expensive
- Si or Al — could be perfect

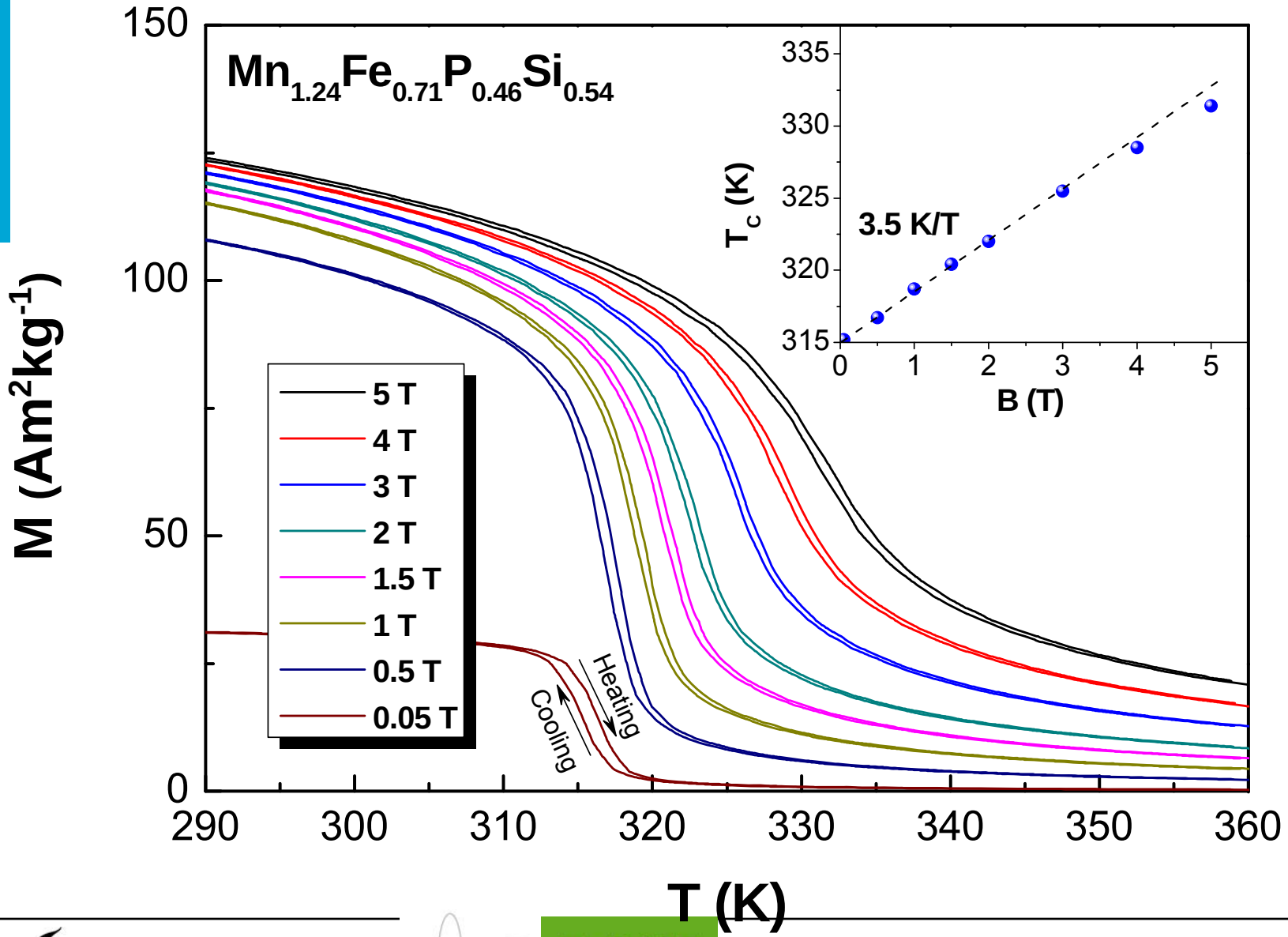
MnFe(P,Si) first samples



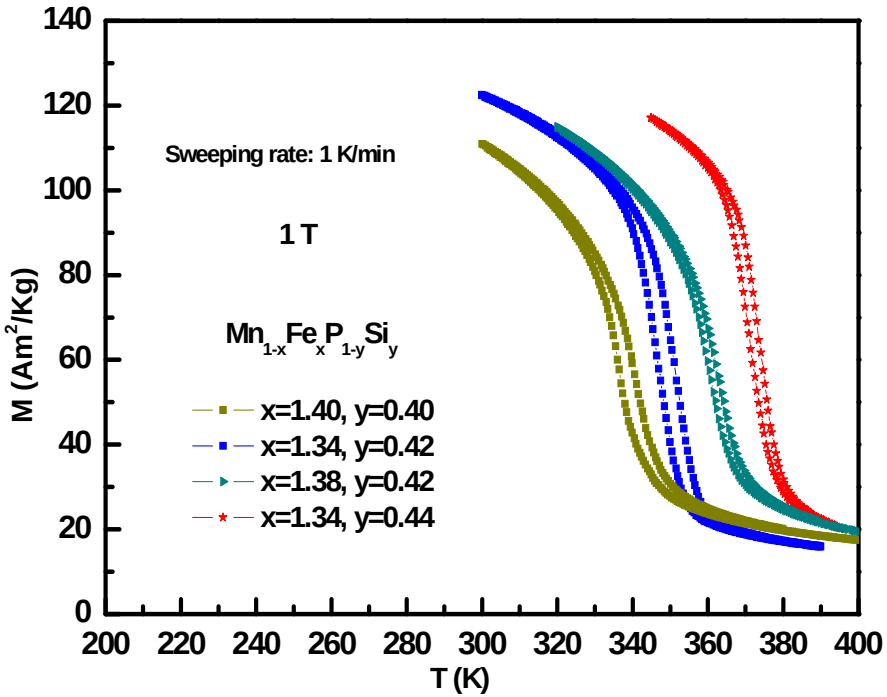
Large hysteresis

Sample with 25% extra Mn

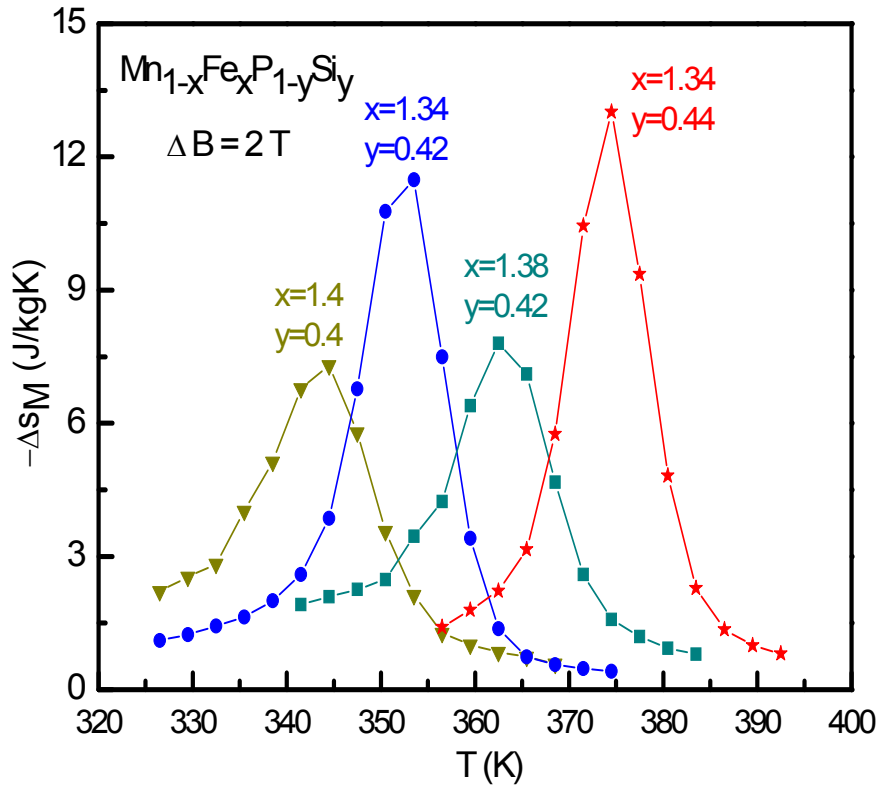



$Mn_{1.24}Fe_{0.71}P_{0.46}Si_{0.54}$
M (Am^2kg^{-1})
T (K)
150
100
50
0
290
300
310
320
330
340
350
360
5 T
4 T
3 T
2 T
1.5 T
1 T
0.5 T
0.05 T
Heating
Cooling
T_c (K)
B (T)
3.5 K/T
335
330
325
320
315
0
1
2
3
4
5

$Mn_{2-x}Fe_xP_{1-y}Si_y$ 30-40% extra iron

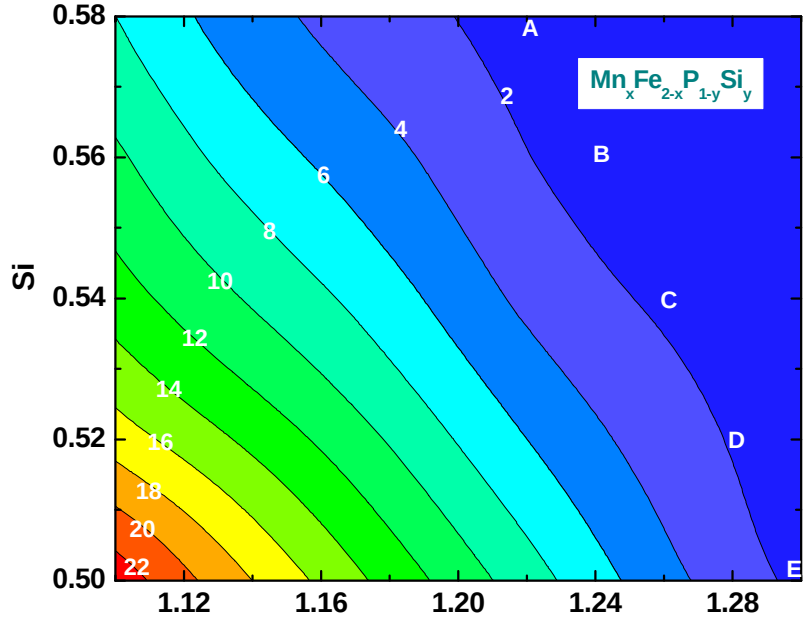


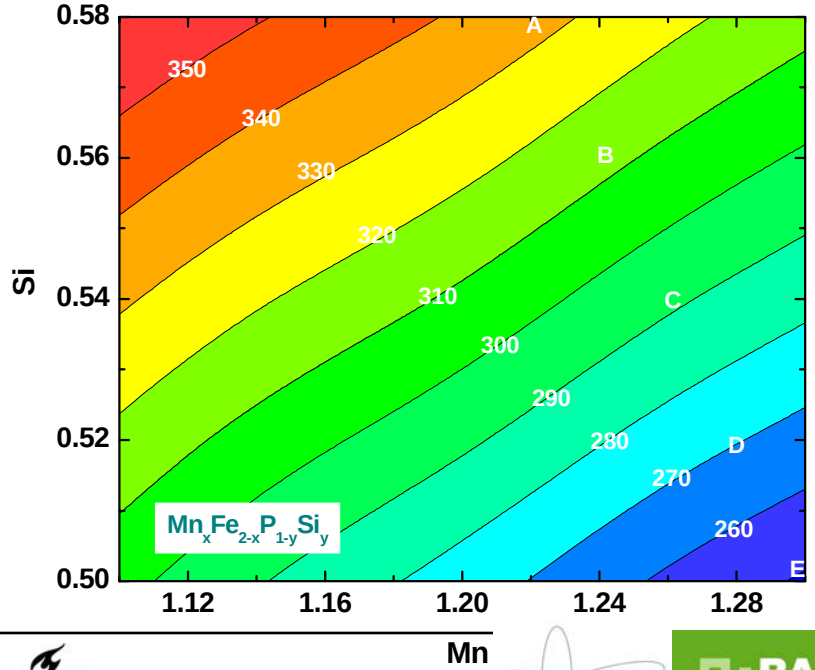
M *vs.* T

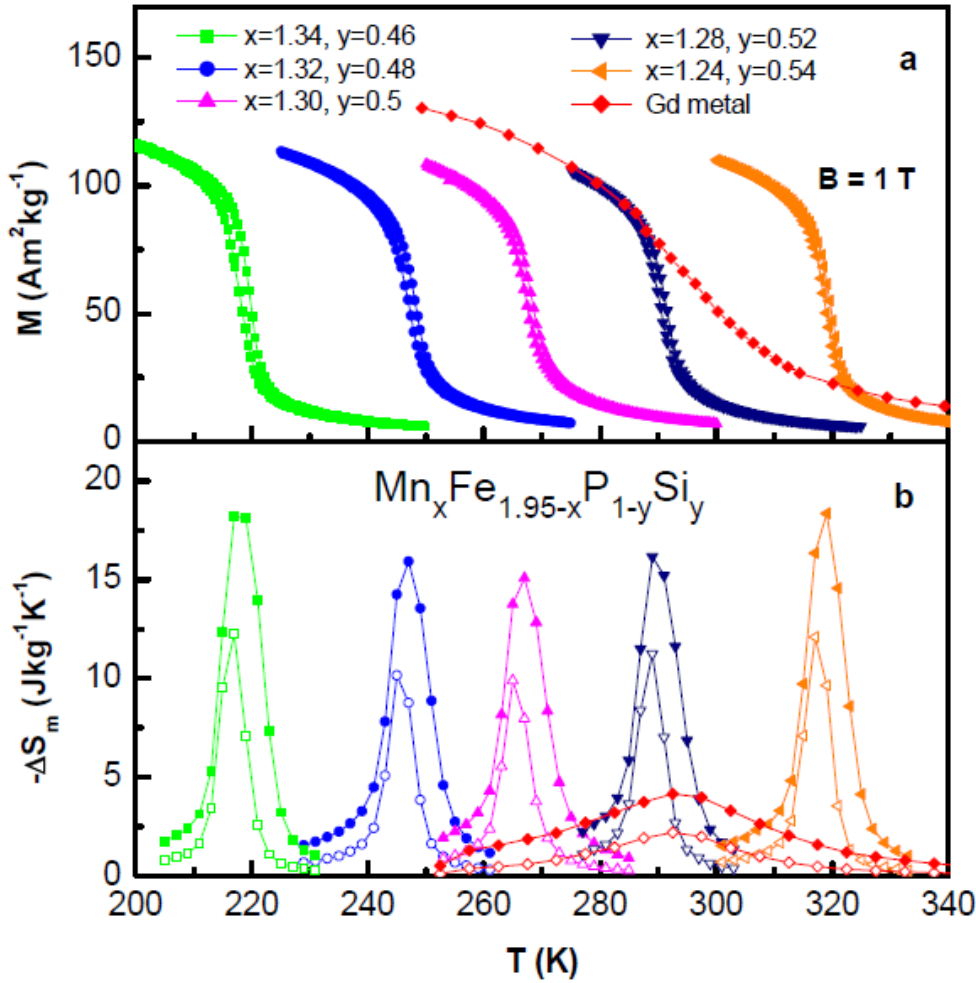


Magnetic entropy change for a field change of 2 T.

Partial phase-diagram



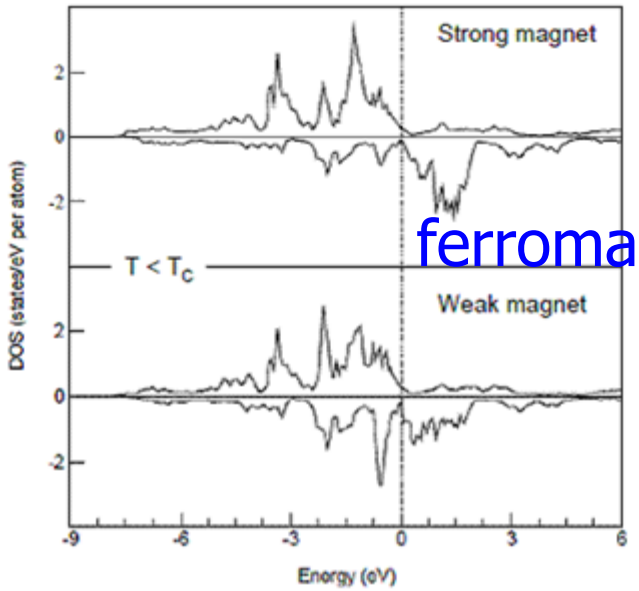




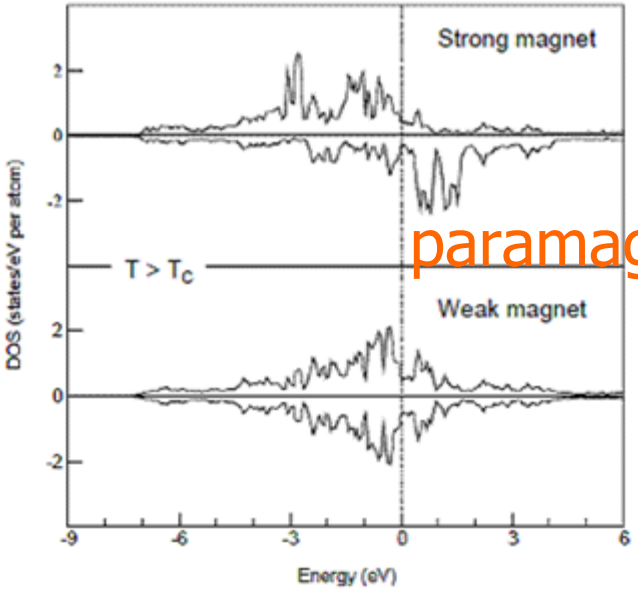
≈ 6.3 g/cm^3

Electronic structure

Novel type of magnetism: Intercallation of strong and weak magnetism



ferromagnetic



paramagnetic

Electronic structure

Fe ($0\mu_B$)

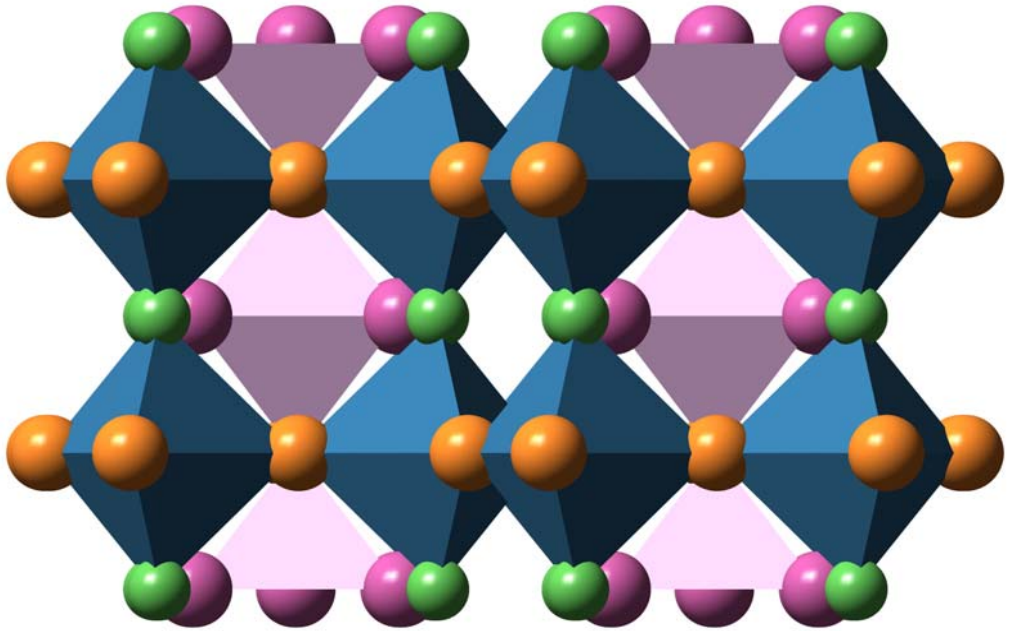
Mn ($2.6\ \mu_B$)

Fe ($0\mu_B$)

Mn ($2.6\ \mu_B$)

Fe ($0\mu_B$)

paramagnetic



Fe (P,Si)

Mn (P,Si)

Fe (P,Si)

Mn (P,Si)

Fe (P,Si)

Closer look at the layers

Electronic structure

Fe ($0\mu_B$)

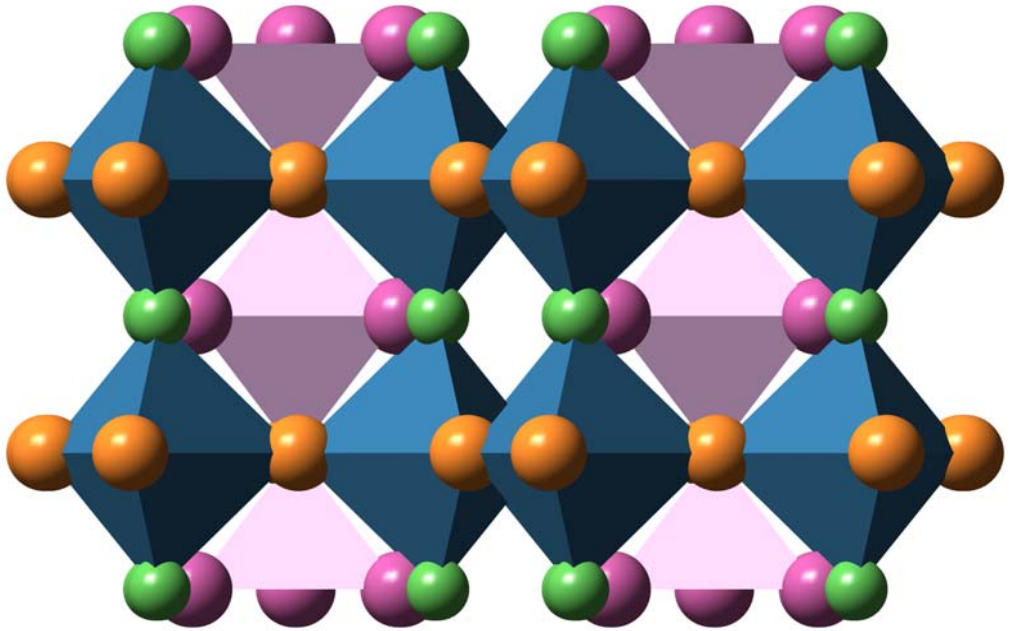
Mn ($2.6\ \mu_B$)

Fe ($0\mu_B$)

Mn ($2.6\ \mu_B$)

Fe ($0\mu_B$)

paramagnetic



Fe ($1.5\mu_B$)

Mn ($2.8\ \mu_B$)

Fe ($1.5\mu_B$)

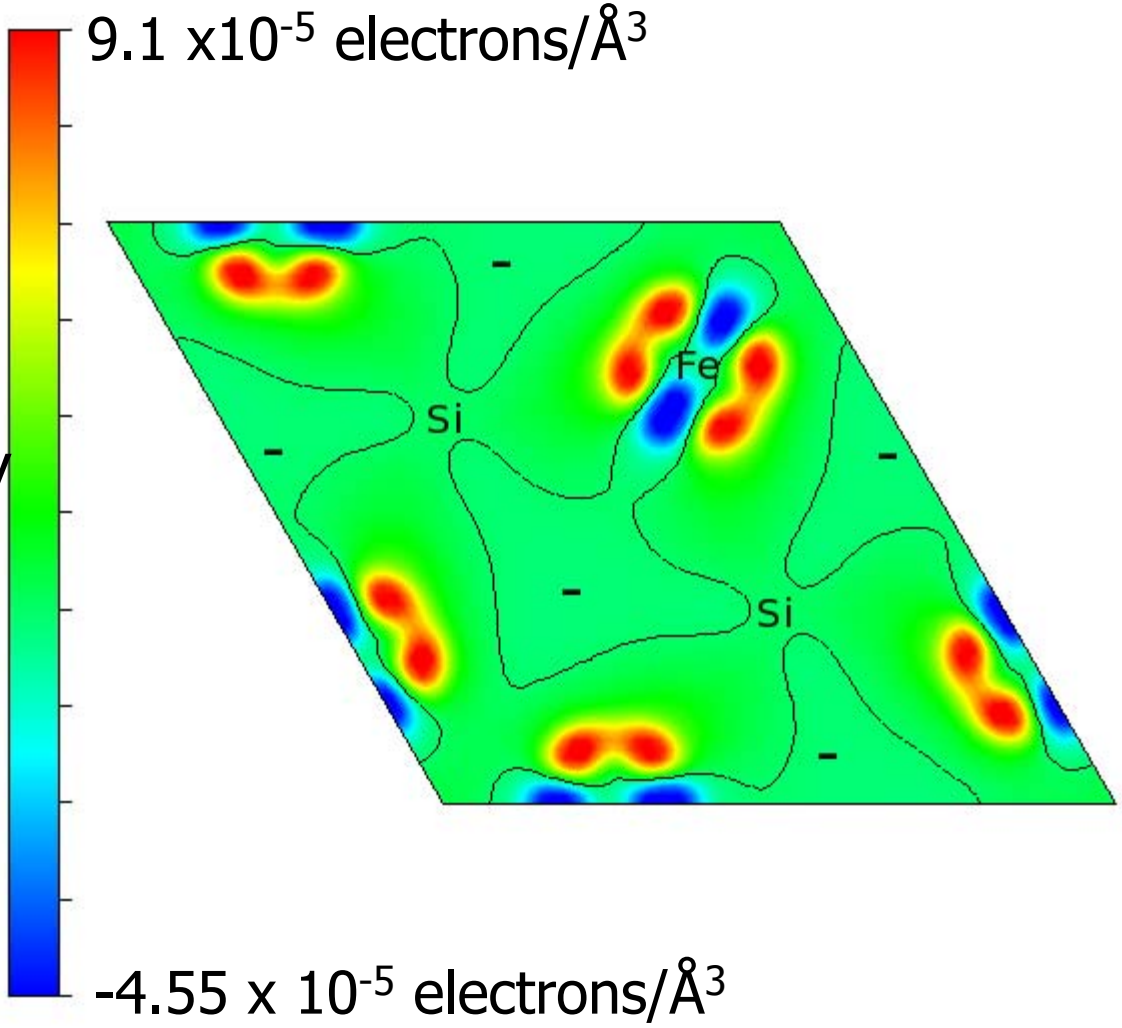
Mn ($2.8\ \mu_B$)

Fe ($1.5\mu_B$)

ferromagnetic

Closer look at the layers

Change in electron density at the phase transition ferromagnetic density subtracted from paramagnetic density.



Conclusions:

- **Magnetoelastic transition enhances MCE in low fields**
- **Combining variation of Mn and Si content results in desired properties**
- **Change in electronic structure at basis of Magnetoelastic transition**
- **Materials with high Curie-temperatures may be suited for waste–heat recovery**
  - **T_C of $(Mn,Fe)_{2+z}(P,Si)$ compounds above 400 K**

Thank you