Recent developments in $(Mn,Fe)_2(P,Si)$ materials

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Outline

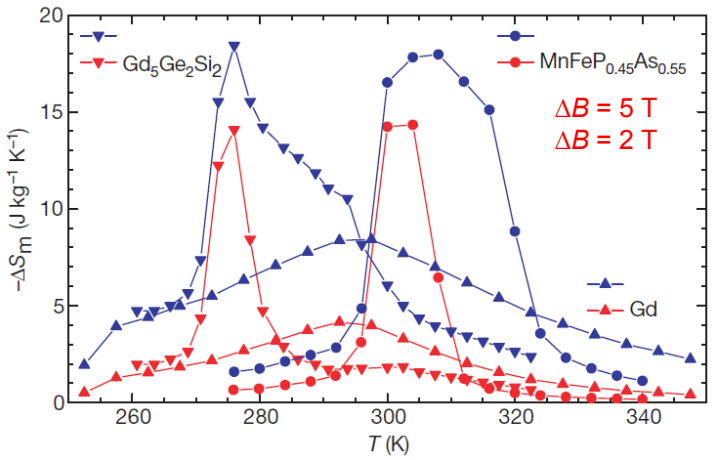
Part I:

- Parameters influencing the cyclability of the MCE in $(Mn,Fe)_2(P,Si,B)$ compounds
- Compositional mapping of magnetocaloric figure of merit
- Mechanical stability

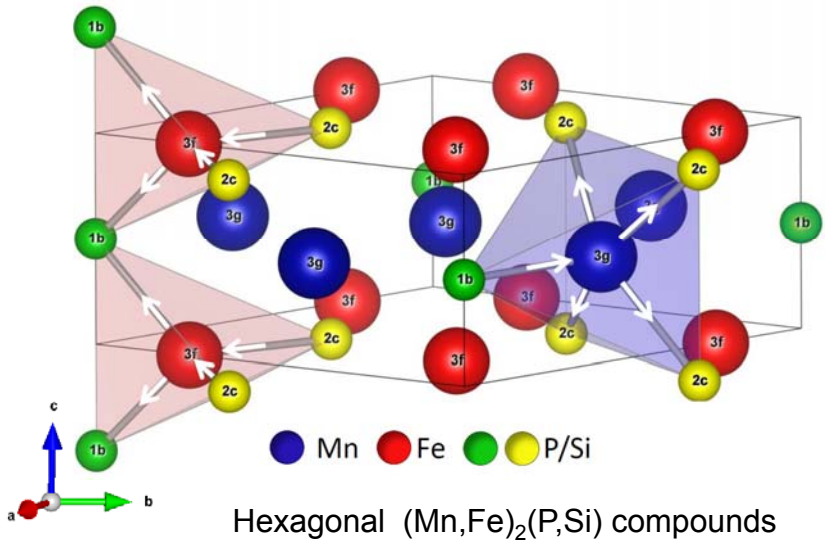
Part II:

- Growth of single-crystalline $(Mn,Fe)_2(P,Si)$
- Magnetocrystalline anisotropy
- Magnetic behaviour towards the ferromagnetic state

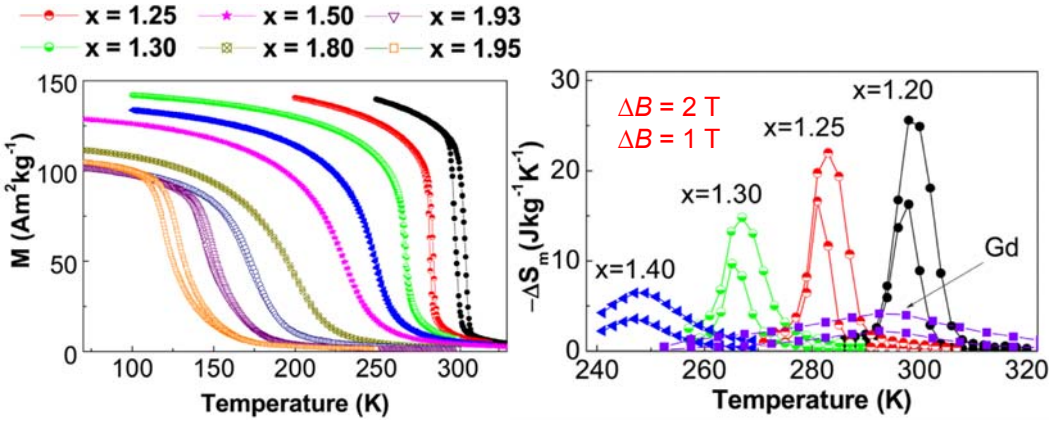
Fe_2P-based manganese compounds



Tegus *et al.*, Nature 415, 150 (2002)

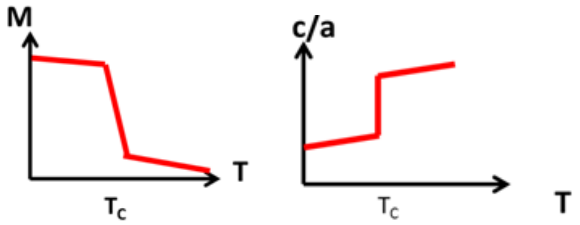


Hexagonal $(Mn,Fe)_2(P,Si)$ compounds



N.H. Dung *et al.*, Adv. Energy Mater. 1, 1215 (2011)

Magneto-elastic
First-order phase transition



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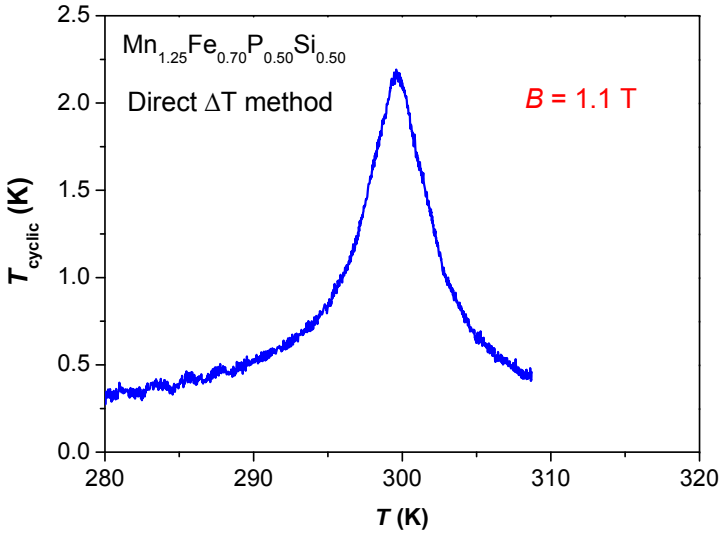
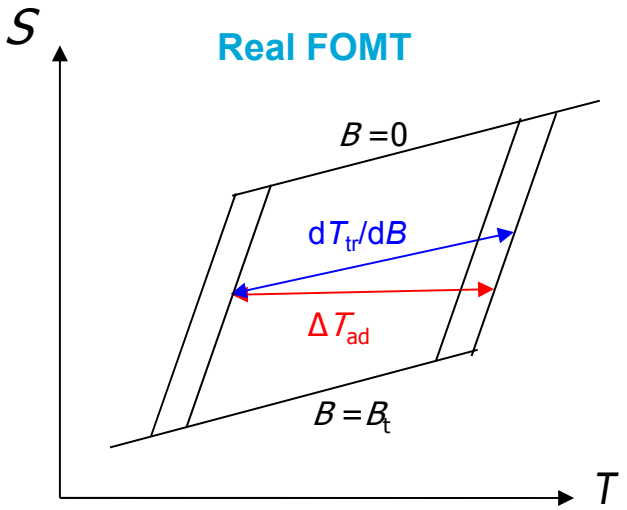
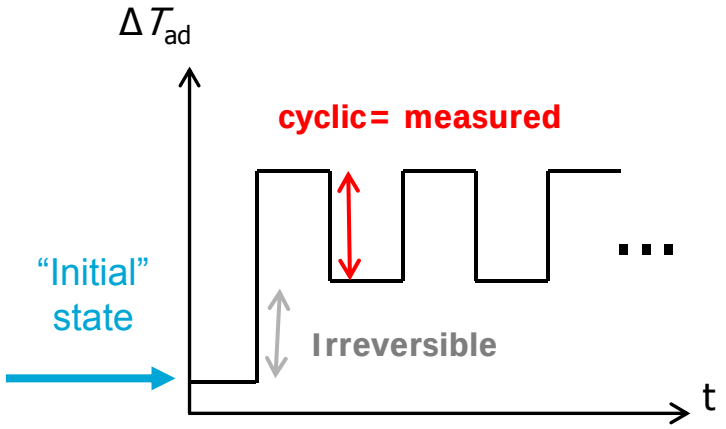
Cyclability of the MCE



H. Yibole *et al.*, J. Phys. D: Appl. Phys. 47, 075002(2014)





- Thermal hysteresis
- Finite transition width
- Shift of the transition due to the field

....

Cyclability is a complex question !

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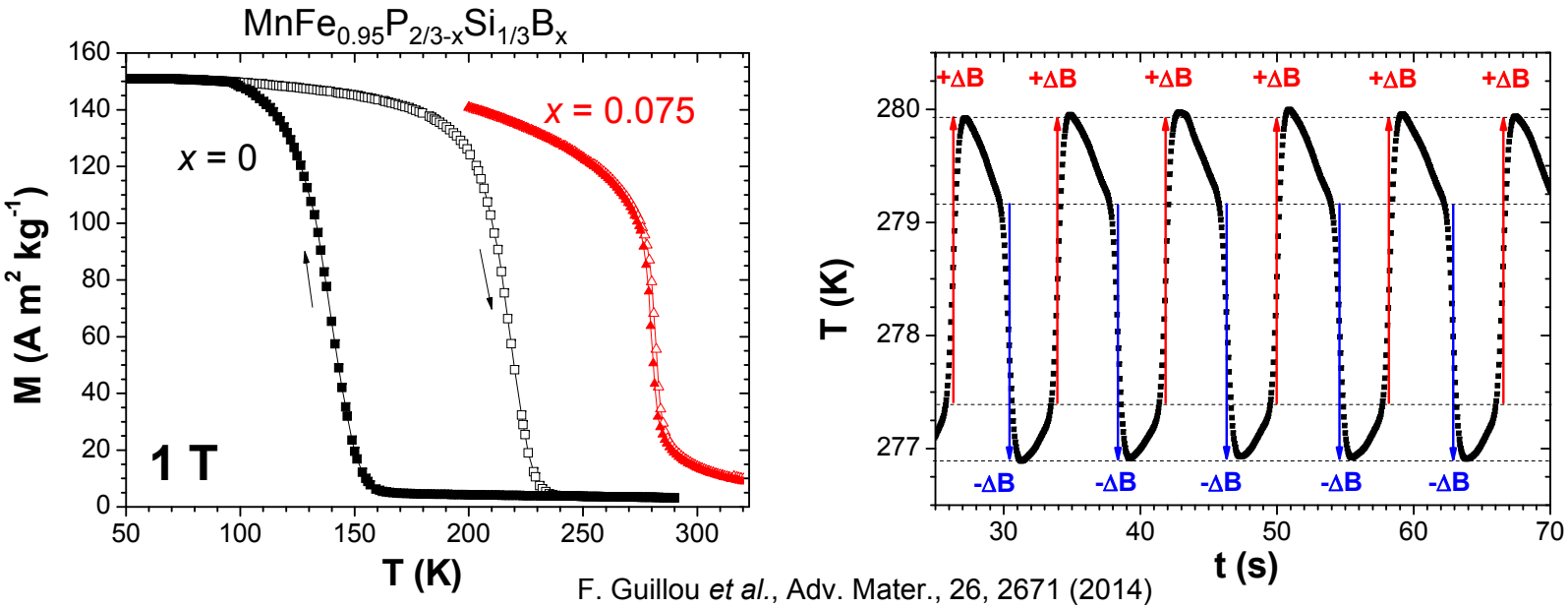
Boron doped $(Mn,Fe)_2(P,Si)$ materials



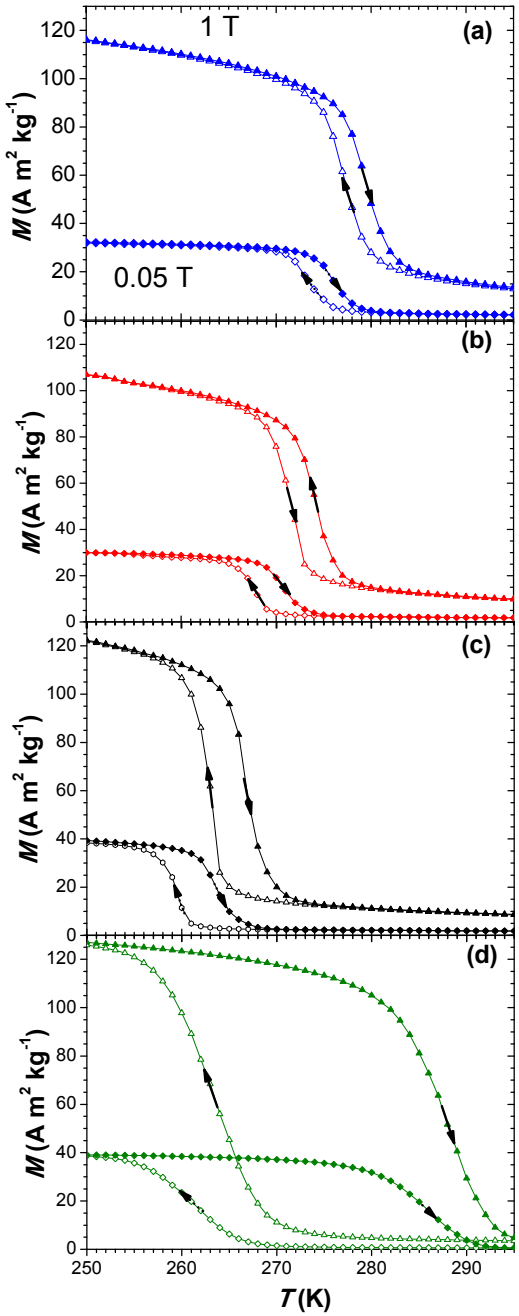
F. Guillou *et al.*, Adv. Mater., 26, 2671 (2014)

- Mn/Fe = 1, optimization of saturation *M*
- Metalloid site, controlling the phase transition

} Promising MCE properties

Other promising compositions in this system?

Influence of B content on hysteresis and sensitivity of transition to field



$MnFe_{0.95}P_{0.67-x}Si_{0.33}B_x$

x = 0.070	dT_{tr}/dB = 4.2 K/T dT_{tr}/dB (1T) > hysteresis
x = 0.065	dT_{tr}/dB = 4.1 K/T dT_{tr}/dB (1T) > hysteresis
x = 0.060	dT_{tr}/dB = 3.6 K/T dT_{tr}/dB (1T) ≈ hysteresis
x = 0, but Si=0.45	dT_{tr}/dB = 2.1 K/T dT_{tr}/dB (1T) < hysteresis

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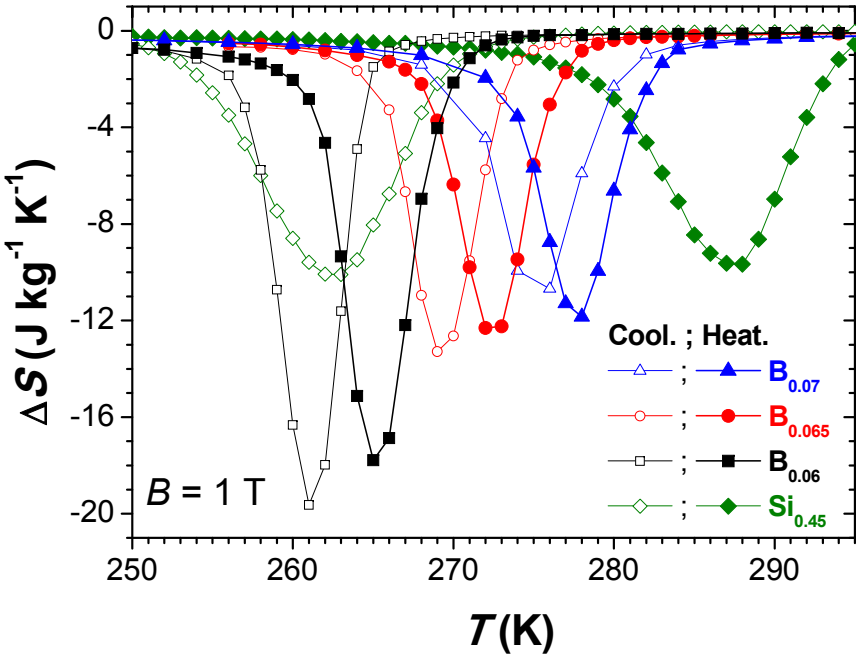
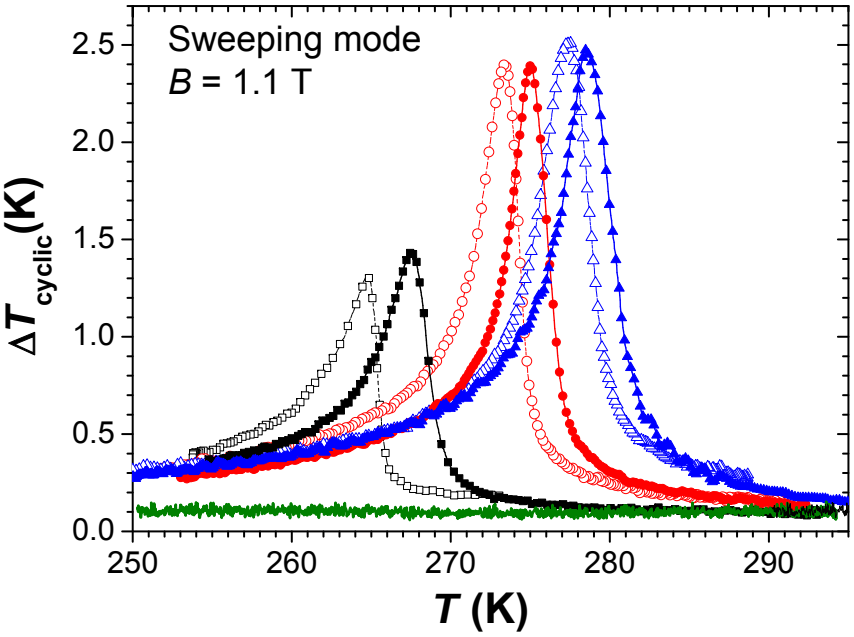
Magnetocaloric effect in *B* ~1 T

ΔS from Indirect method,
$M_B(T)$ using Maxwell equation



ΔT_{cyclic} from direct measurement



- dT_{tr}/dB (1T) > hysteresis, ΔT_{cyclic} is ensured
- dT_{tr}/dB (1T) ≈ hysteresis, ΔT_{cyclic} is reduced
- dT_{tr}/dB (1T) < hysteresis, ΔT_{cyclic} disappears

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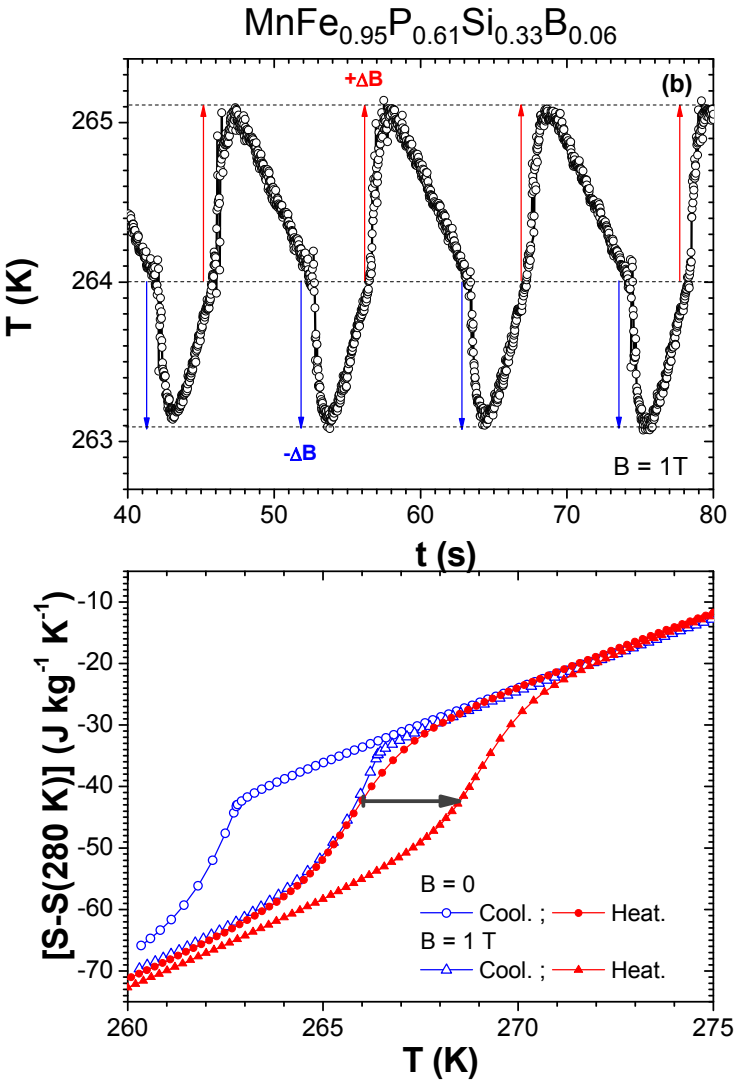
Threshold hysteresis for MCE cyclability



Direct method

ΔT_{cyclic} = 1.1 K

Indirect method

ΔT_{ad} = 2.65 K

- Distinction between ΔT_{ad} and ΔT_{cyclic} for materials with hysteresis.
- dT_{tr}/dB (1T) ≈ hysteresis: threshold for MCE cyclability.
- In $(Mn,Fe)_2(P,Si,B)$, $dT_{tr}/dB \approx 4.2$ K the **maximal hysteresis ≤ 4 K** for B ~1 T.

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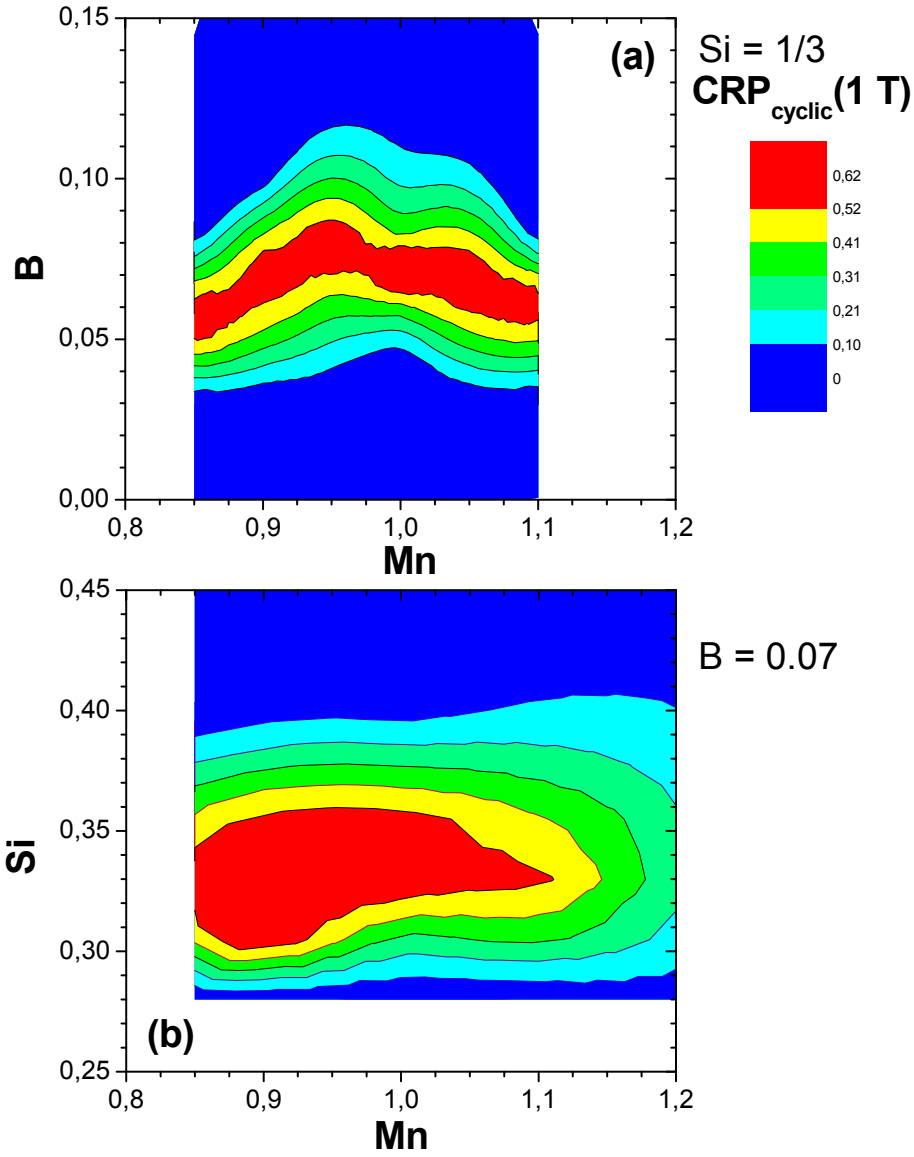
Mapping of magnetocaloric figure of merit

Coefficient of refrigerant performance (CRP)
(Wood and Potter 1985)

$$CRP = \frac{refrigerant\ capacity}{positive\ work\ on\ refrigerant} = \frac{\Delta S \Delta T}{\int_0^{B_{max}} M(T_C, B) dB'}$$

	Type of ΔT	CRP
$MnFe_{0.95}P_{0.595}Si_{0.33}B_{0.075}$ (hysteresis < 1 K)	ΔT_{ad}	0.62
	ΔT_{cyclic}	0.62
$MnFe_{0.95}P_{0.61}Si_{0.33}B_{0.060}$ (hysteresis = 3.5 K)	ΔT_{ad}	0.78
	ΔT_{cyclic}	0.37
Gd	ΔT	0.17



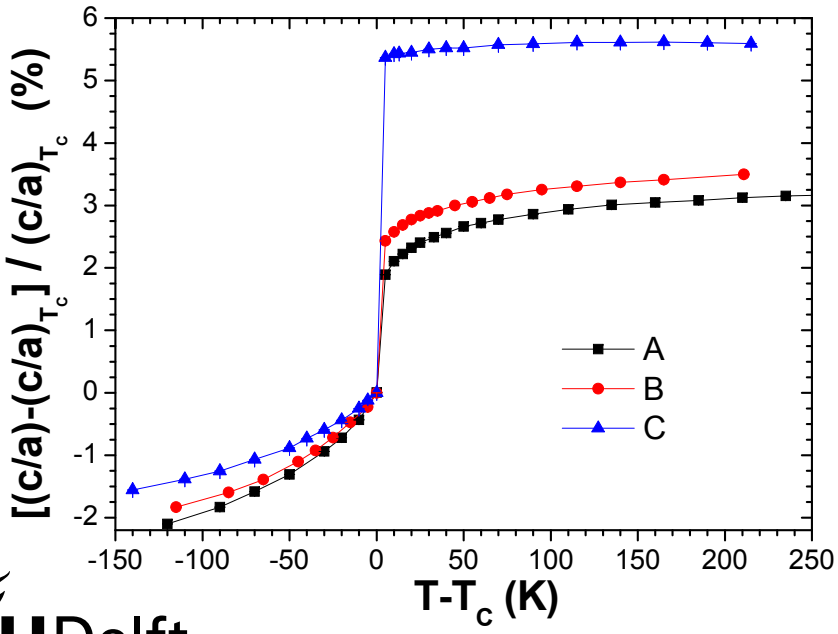
150 < T < 380 K.

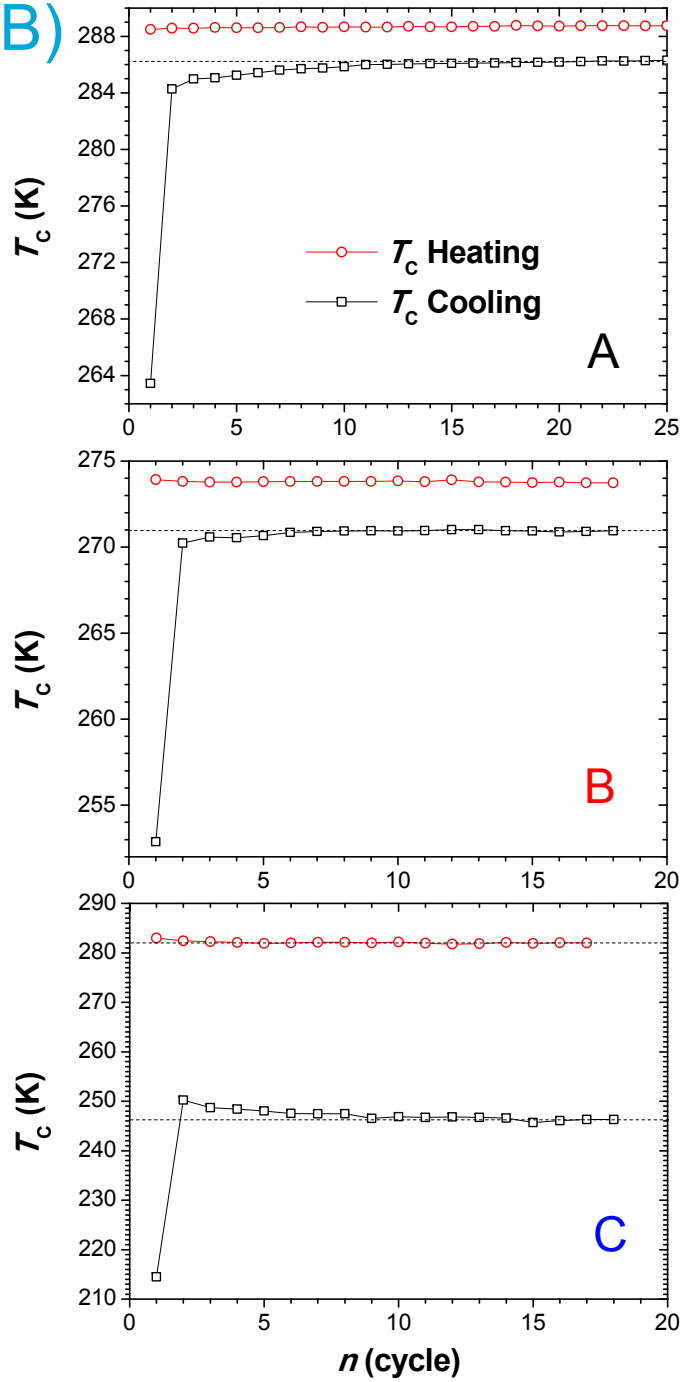
Mechanical stability of $(Mn,Fe)_2(P,Si,B)$

The degradation of material may result from:

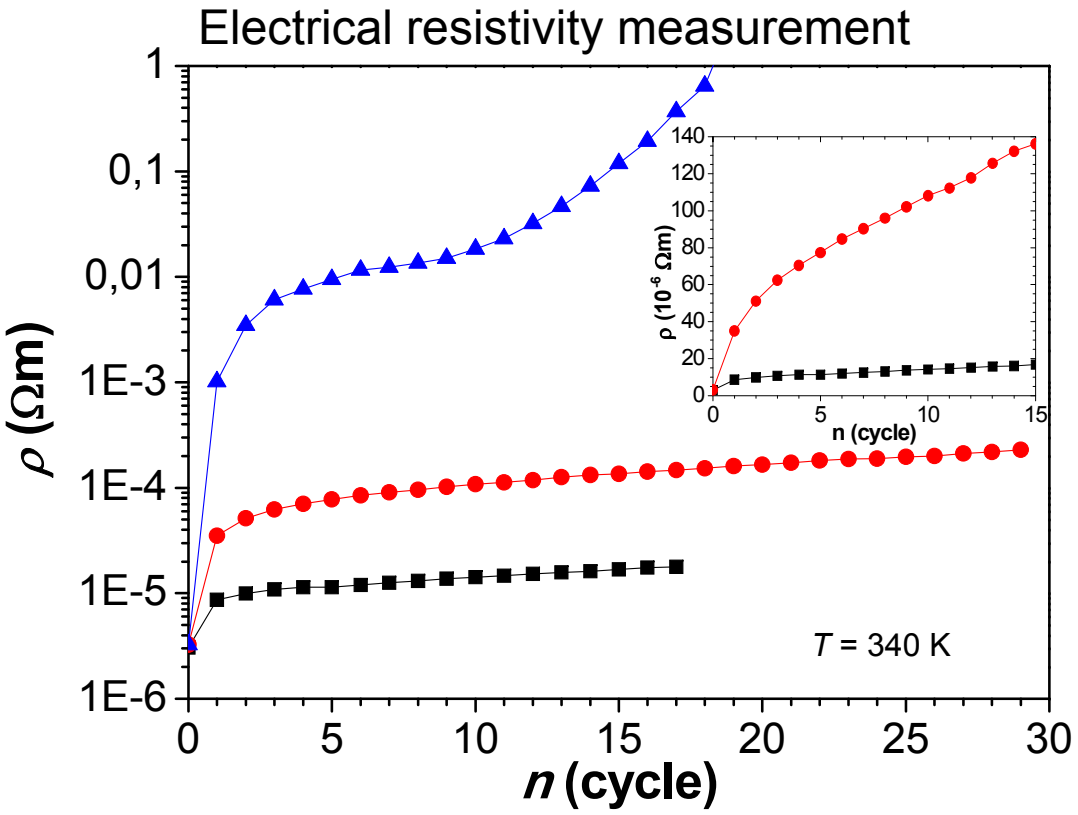
- The volumetric stress resulting from volume change
- Anisotropic internal stress

- Sample A: $MnFe_{0.95}P_{0.582}B_{0.078}Si_{0.34}$ (boron doped)
- Sample B: $Mn_{1.25}Fe_{0.7}P_{0.5}Si_{0.5}$ (Mn-rich)
- Sample C: $MnFe_{0.95}P_{0.55}Si_{0.45}$ (Mn/Fe = 1)

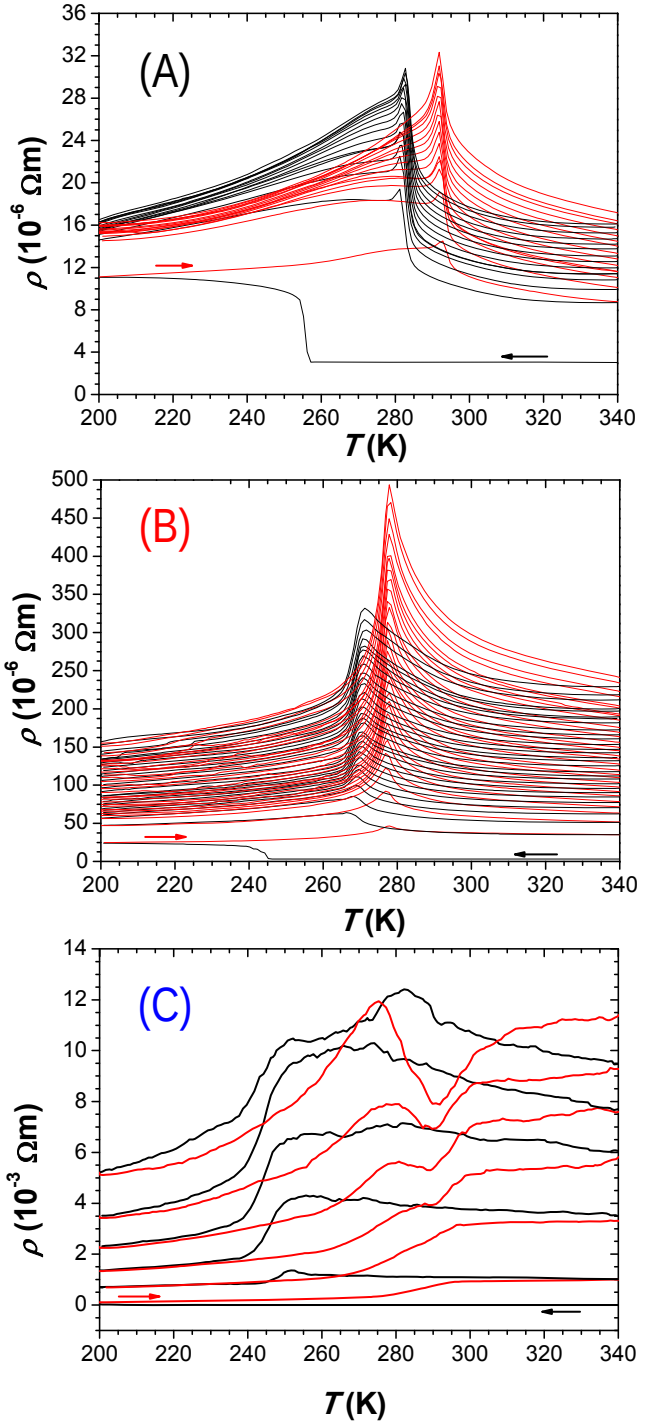




Mechanical stability



- Sample A: $MnFe_{0.95}P_{0.582}B_{0.078}Si_{0.34}$ (boron doped)
- Sample B: $Mn_{1.25}Fe_{0.7}P_{0.5}Si_{0.5}$ (Mn-rich)
- Sample C: $MnFe_{0.95}P_{0.55}Si_{0.45}$ (Mn/Fe = 1)



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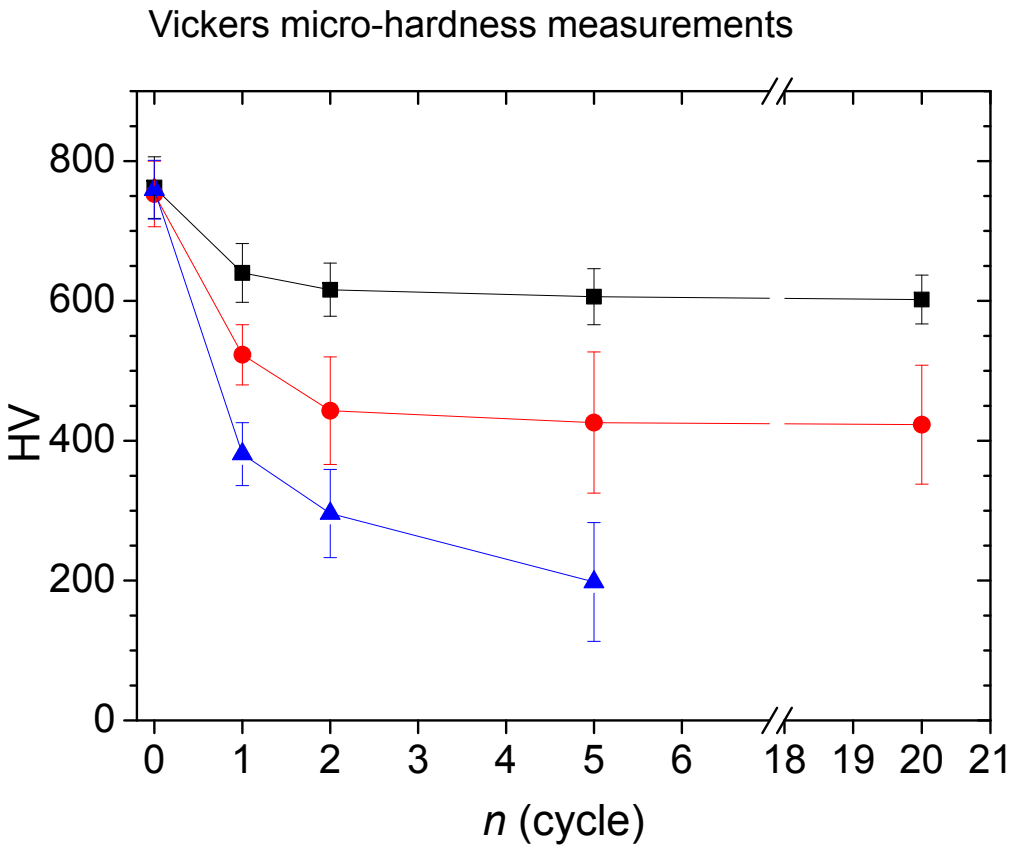
Mechanical stability



- $MnFe_{0.95}P_{0.585}Si_{0.34}B_{0.075}$
  ~ no ΔV, small $\Delta(c/a)$

- $Mn_{1.25}Fe_{0.7}P_{0.5}Si_{0.5}$
  limited ΔV, small $\Delta(c/a)$

- $MnFe_{0.95}P_{0.55}Si_{0.45}$
  limited ΔV, large $\Delta(c/a)$

Conclusions

Part I:

- Definition of a thermal hysteresis threshold ensuring the cyclic character of the MCE in the MnFe(P,Si,B) system

- Compositional mapping of the magnetocaloric performances : identification of MnFe(P,Si,B) compositions with promising performances on a broad temperature range 150 < T < 380 K.

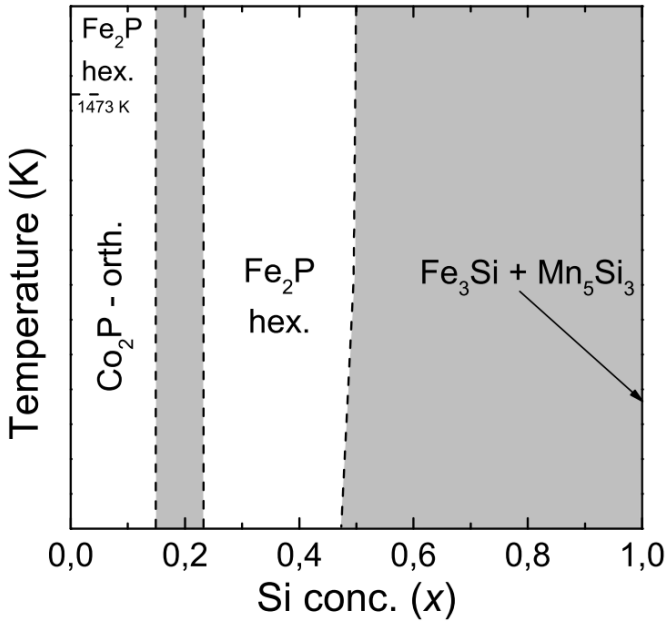
- Quantification of mechanical ageing due to cycling across the transition by DSC, resistivity micro-hardness. The mechanical degradation is highly dependent on the (c/a) change.

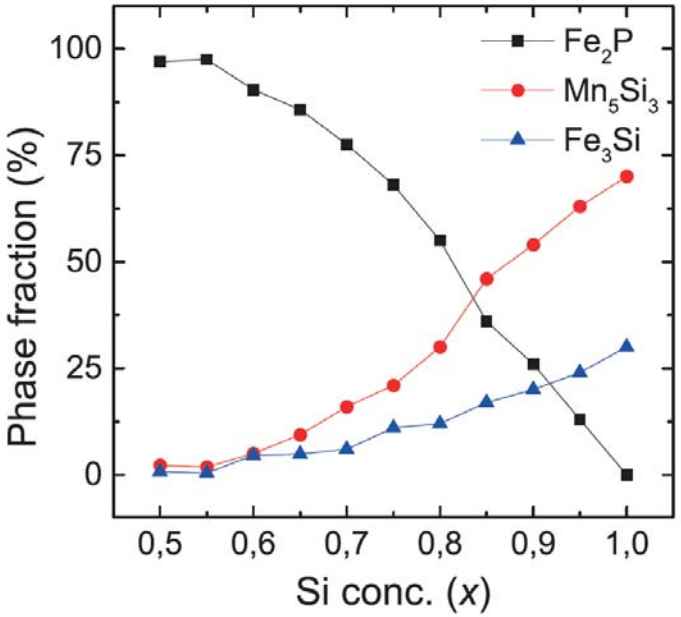
Part II: Single-crystalline $(Mn,Fe)_2(P,Si)$

$(Mn,Fe)_2(P,Si)$ Single Crystals

Needs for single crystals:

- Anisotropy
- Homogeneity
- Absence of grain boundaries

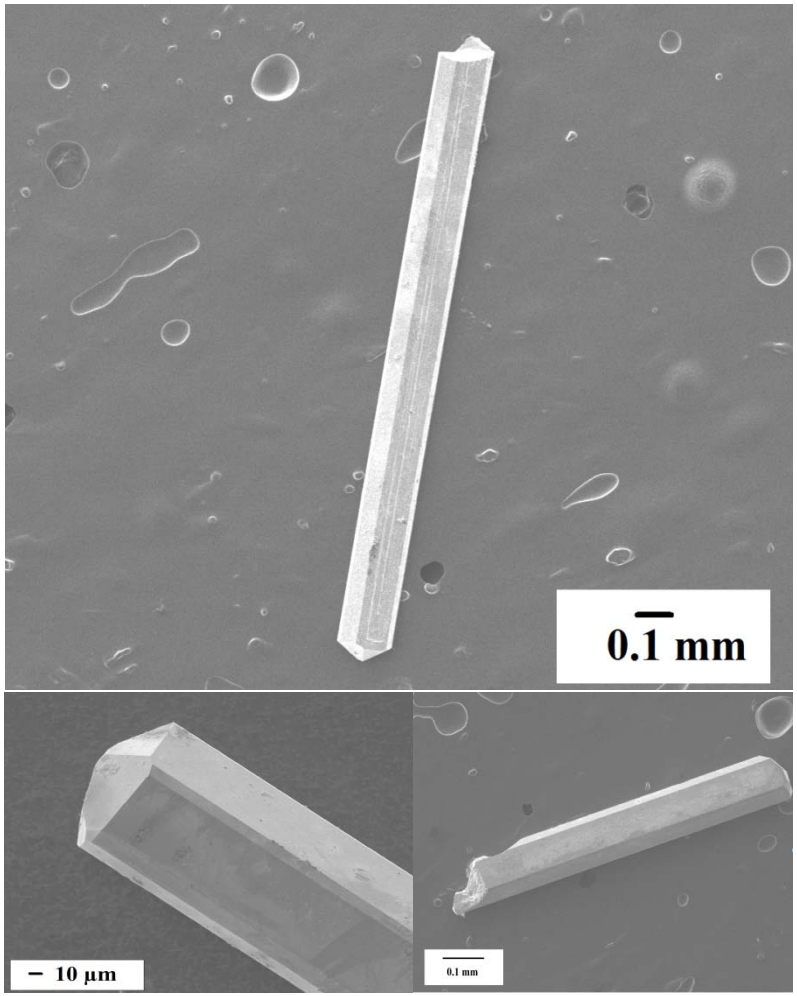




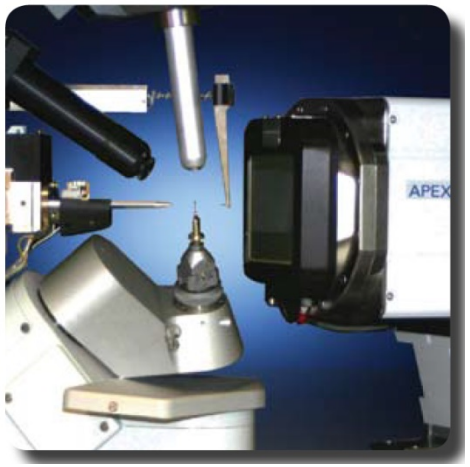
Viktor Hoglin, PhD Thesis, Uppsala Universitet.

$(Mn,Fe)_2(P,Si)$ Single Crystals

- Growth technique: Flux method
- Metallic flux: tin
- Crystal habit: prismatic
- Crystal surface: regular and homogeneous
- Average dimension: ~ $0.15 \times 0.15 \times 1.5$ mm^3
- Colour: metallic

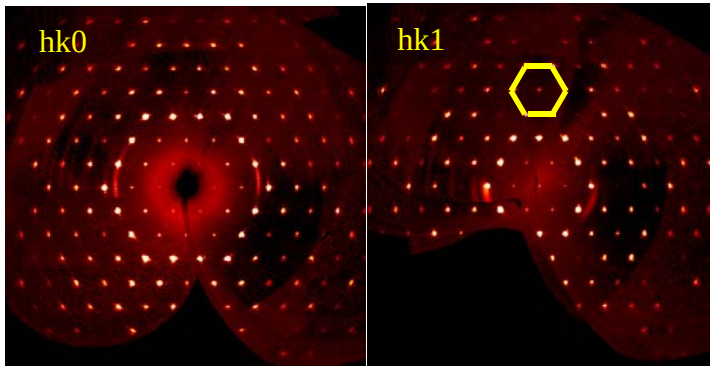


Single crystal diffraction and refinement



Bruker AXS Kappa APEX II Diffractometer

- Chemical composition (EDS): $Mn_{0.83}Fe_{1.17}P_{0.72}Si_{0.28}$
- Crystal structure: Hexagonal Fe_2P
- Space group: $P\bar{6}2m$
- Refinement method: full-matrix least-squares on F^2



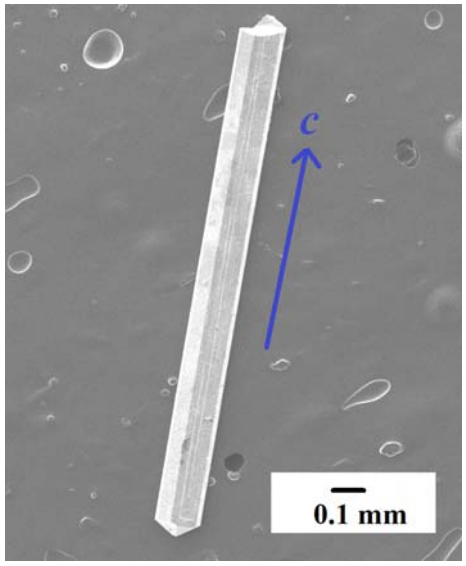
Reciprocal-Space mapping

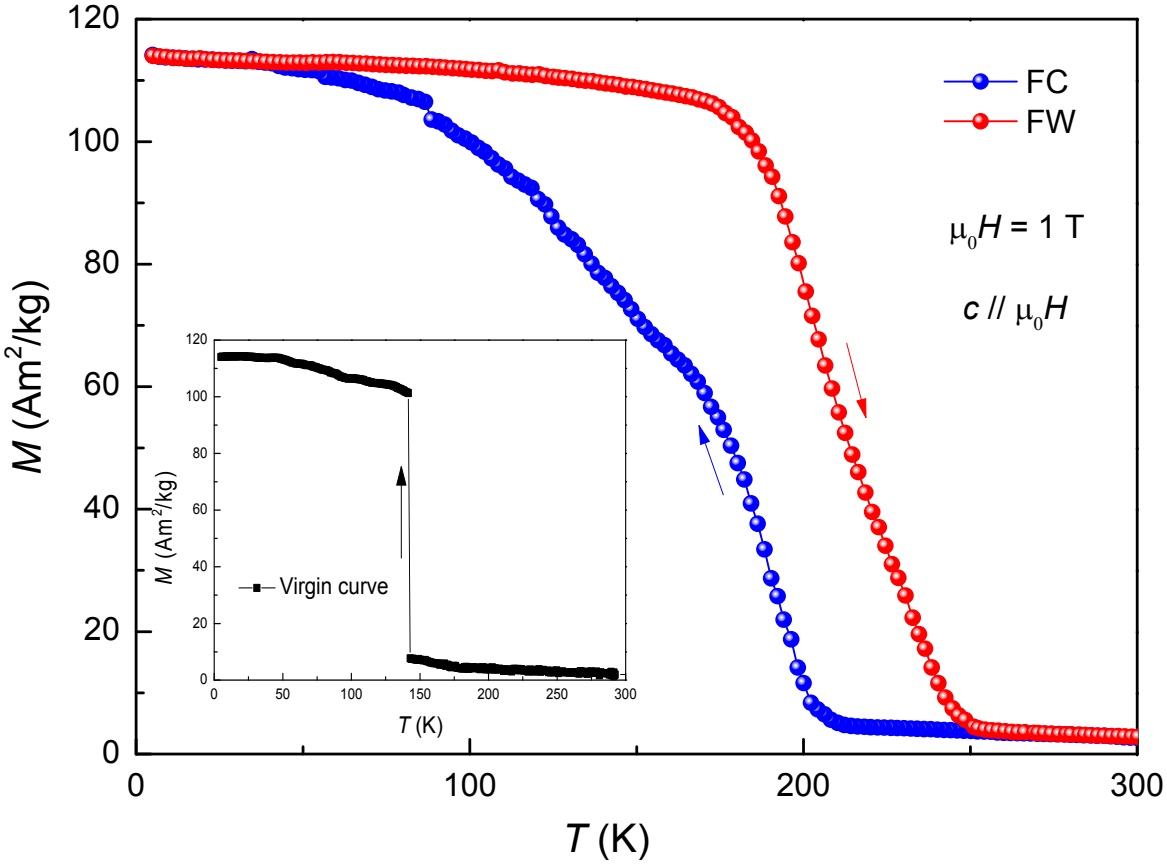
Atomic position:
3*g* (x_1, 0, 1/2); 3*f* (x_2, 0, 0); 2*c* (1/3, 2/3, 0); 1*b* (0, 0, 1/2)

Temperature (K)	100	280
a (Å)	6.0838(9)	5.997(6)
c (Å)	3.3556(5)	3.484(3)
Volume (Å^3)	107.56(4)	108.5(2)
x_1	0.5936(2)	0.5904(2)
x_2	0.2563(2)	0.2548(2)
Collected reflections	180	182
RF^2	0.0242	0.0243
Goodness-of-fit on F^2	1.096	1.050

Magnetic properties of ferromagnetic crystal

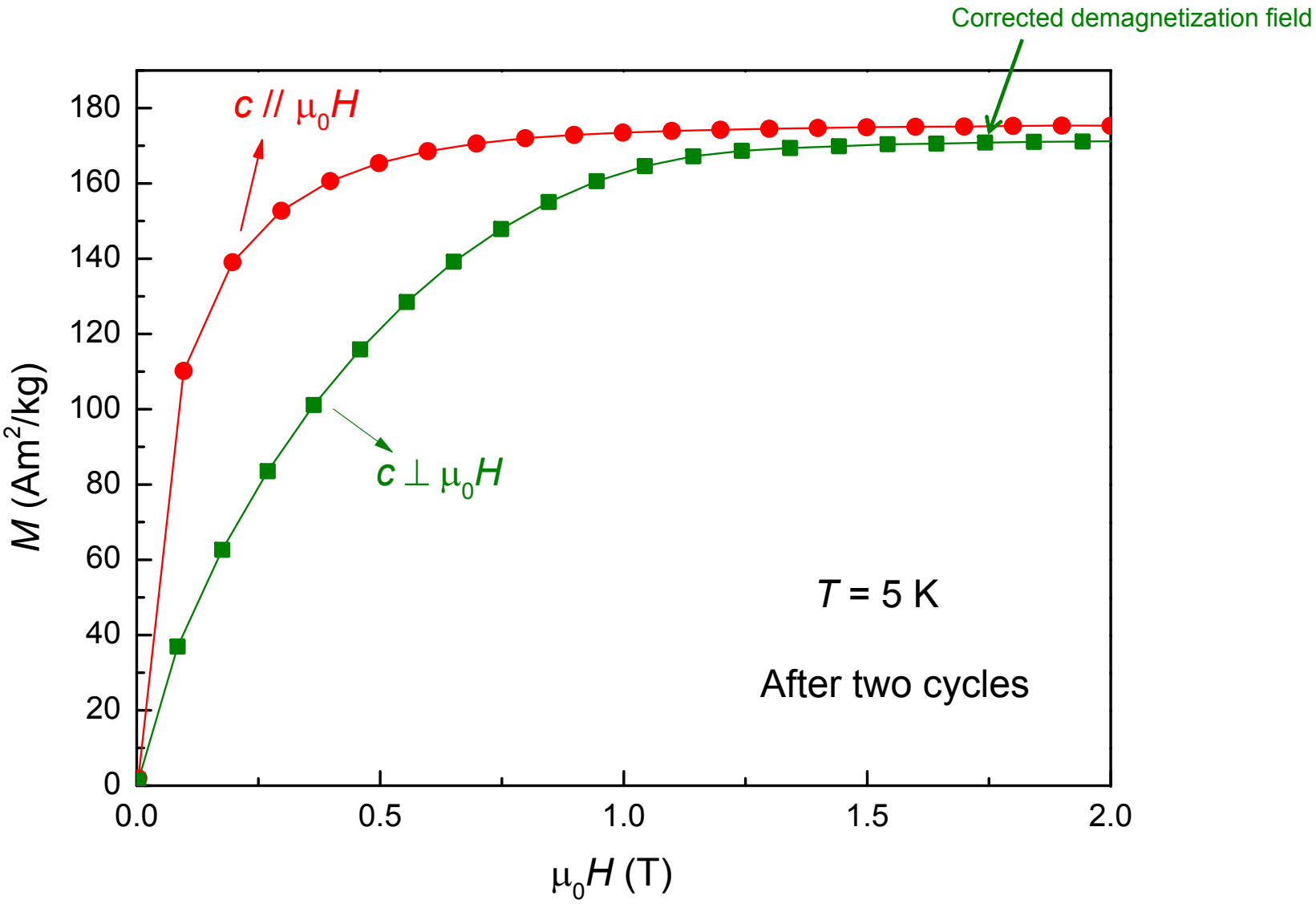
Chemical composition: $Mn_{0.83}Fe_{1.17}P_{0.72}Si_{0.28}$





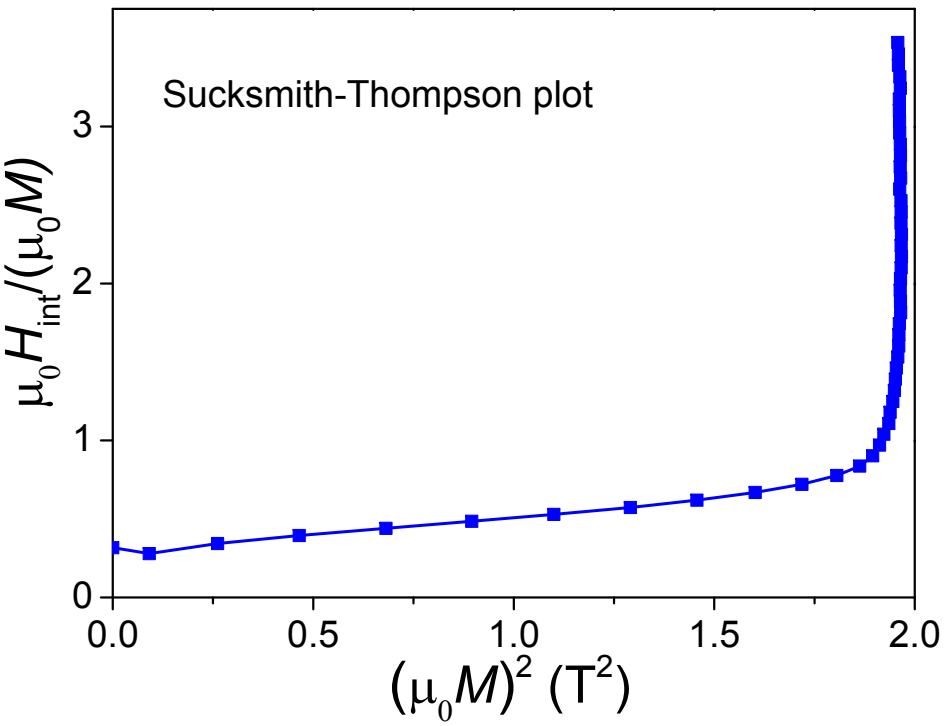
First-order ferromagnetic transition !

Mangetocrystalline anisotropy in $Mn_{0.83}Fe_{1.17}P_{0.72}Si_{0.28}$ crystal

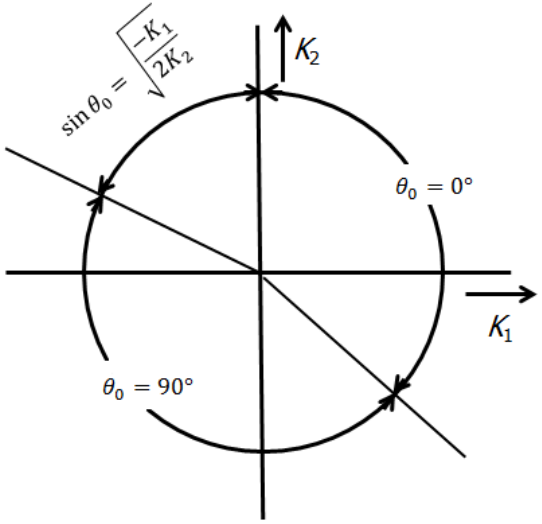


Mangetocrystalline anisotropy energy for hexagonal system

$$E \approx K_1 \sin^2\theta + K_2 \sin^4\theta$$



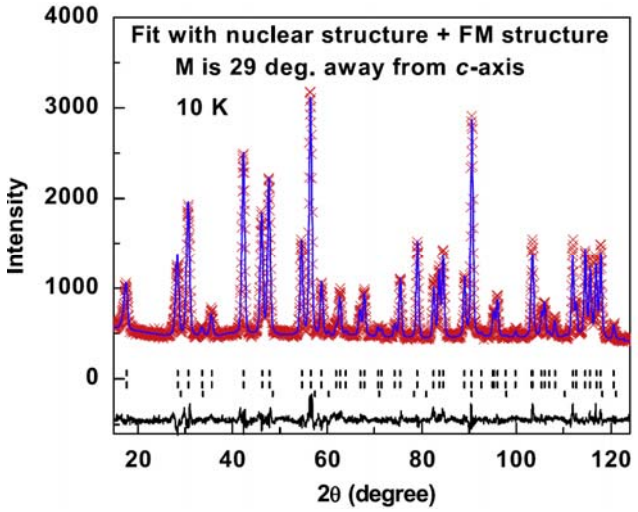
$$\begin{cases} K_1 = 0.28 \times 10^6\ J/m^3 \\ K_2 = 0.22 \times 10^6\ J/m^3 \end{cases}$$



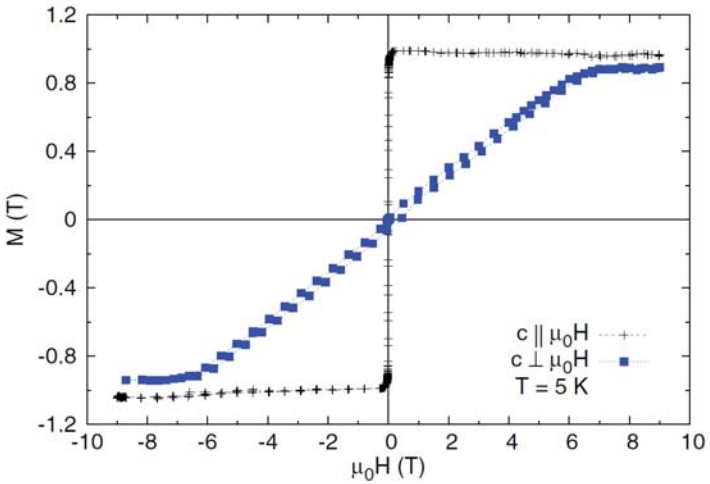
The preferred magnetization direction --- along the *c* axis !

Mangetocrystalline anisotropy of related polycrystalline compounds

Neutron powder diffraction



Fe_2P single crystal



L. Caron *et al*, PRB 88, 094440 (2013)

- Fe-rich $Mn_{0.66}Fe_{1.29}P_{1-x}Si_x$ (x = 0.42, 0.37,0.34)
  angle with *c*-axis 67˚, 46˚, 29˚
  Ou *et al*, J. Mag. Magn. Mater. 340, 80 (2013)

- $MnFeP_{0.5}As_{0.5}$
  along *c*-axis
  Bacmann *et al*, J. Mag. Magn. Mater. 134, 59 (1994)

- Mn-rich $Mn_{1.3}Fe_{0.64}P_{0.5}Si_{0.5}$ and $Mn_{1.1}Fe_{0.9}P_{0.8}Ge_{0.2}$
  (*a*,*b*) plane
  Dung *et al*, PRB 86, 045134 (2012);
  Liu *et al*, PRB 79, 014435 (2009);

Fe_2P

$$K_1 = 2.3 \times 10^6\ J/m^3$$

$Mn_{0.83}Fe_{1.17}P_{0.72}Si_{0.28}$

$$K_1 = 0.28 \times 10^6\ J/m^3$$

$$K_2 = 0.22 \times 10^6\ J/m^3$$

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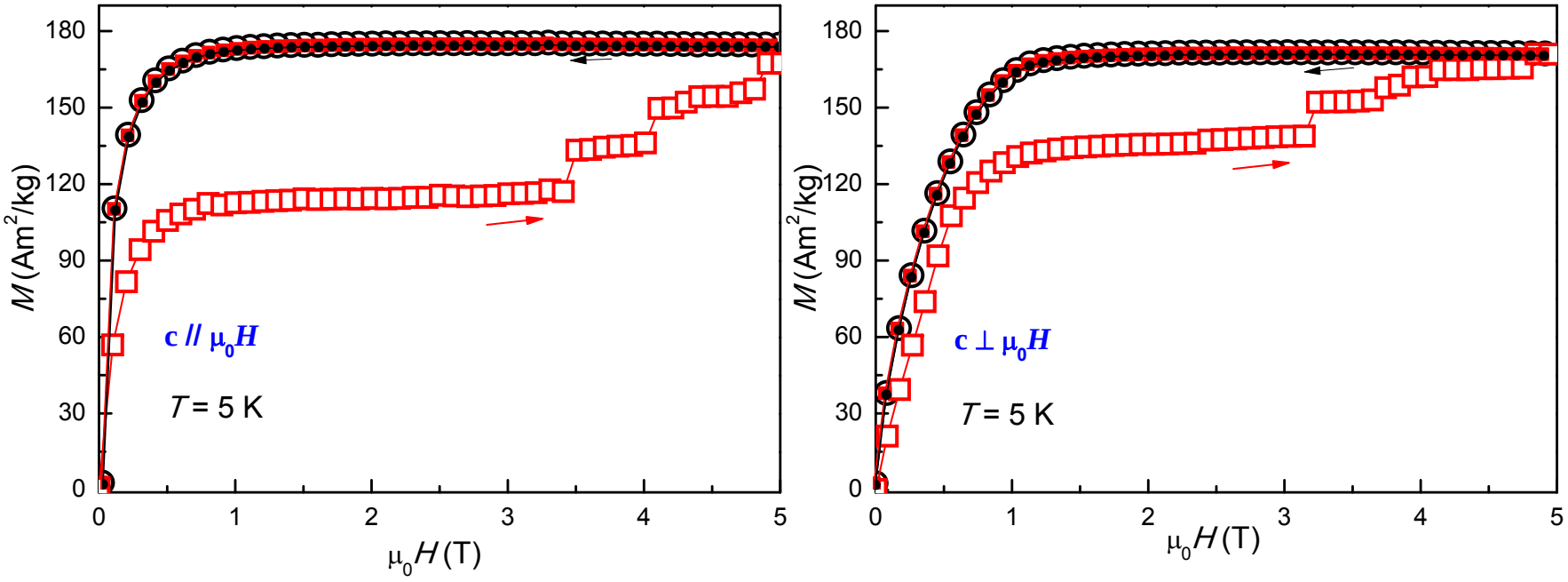
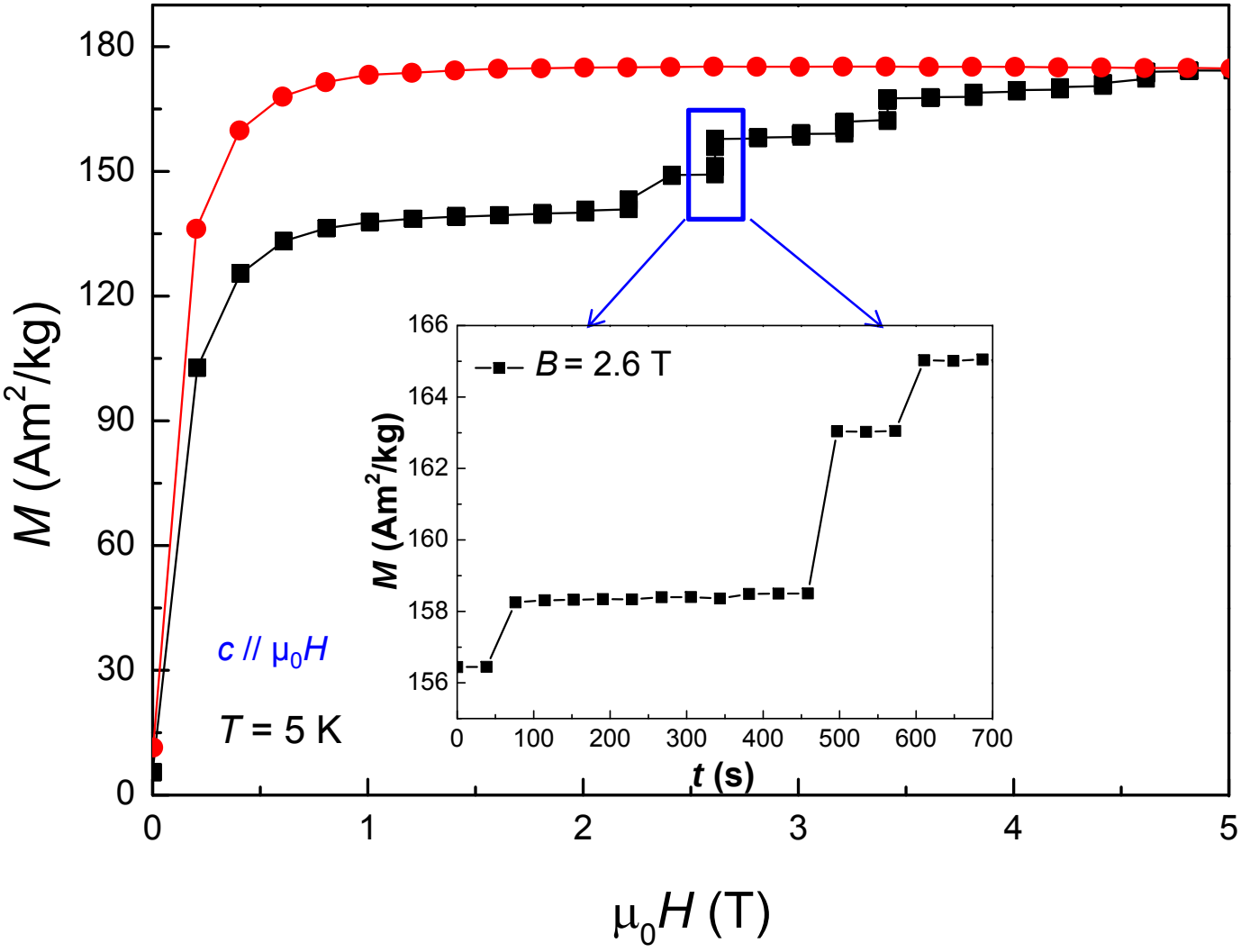
Peculiar magnetic behaviour towards ferromagnetic state



(After ZFC)

Spontaneous magnetization jumps

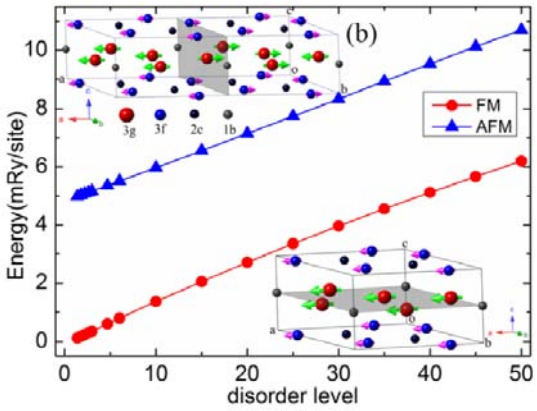


- Phase transition behaviour
- Not magnetic screening by eddy currents or domain wall movements

Possible interpretations for magnetization jumps

(i) An underlying antiferromagnetic order

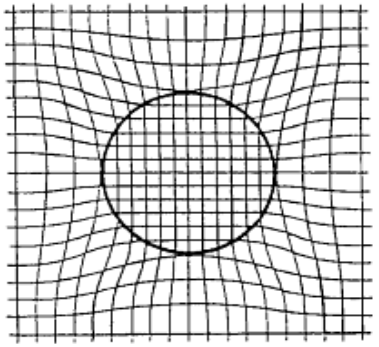
- Prompted by chemical disorder on 3*f* and 3*g* site



G. Li et al, Appl. Phys. Lett. 105, 262405 (2014).

(ii) A dynamical phase separation phenomenon

- General to a First-order phase transition
  (Manganites, Gd_5Ge_4, Heusler alloys, $CeFe_2$, FeRh,etc.)



(iii) A combination of both

Conclusions

Part II:

- $(Mn,Fe)_2(P,Si)$ single crystals presenting FOMT have been grown for the first time.
- Crystal structure and magnetic properties support the findings of previous works on polycrystals.
- The weakening of the magnetocrystalline anisotropy from Fe_2P to $Mn_{0.83}Fe_{1.17}P_{0.72}Si_{0.28}$ is beneficial for magnetocaloric application.
- The magnetization process toward the ferromagnetic state turns out to be complex.

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Zernike Institute for Advanced Materials

university of groningen

BASF
The Chemical Company

FOM

Thank you for your attention!

More details:

H. Yibole *et al.*, Appl. Phys. Lett. 107, 162403 (2015).

F. Guillou *et al.*, Adv. Mater. 26, 2671 (2014).

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F. Guillou *et al.*, J. Appl. Phys. 116, 063903 (2014).

F. Guillou *et al.*, J. Alloys & Compd. 617, 569 (2014).

F. Guillou *et al.*, Phys. status solidi (c) 11, 1007 (2014).

F. Guillou *et al.*, J. Alloys & Compd. 632, 717 (2015).