Damping the latent heat in MnFe(P,x) magnetocaloric materials

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An experimental report on MnFe(P,Si,B) MCE materials

Outline

1- Generalities

2- MnFe(P,Si,B) MCE

optimisation of M_{sat}
optimisation of ΔT_{ad}

3- B interstitial or substitution ?

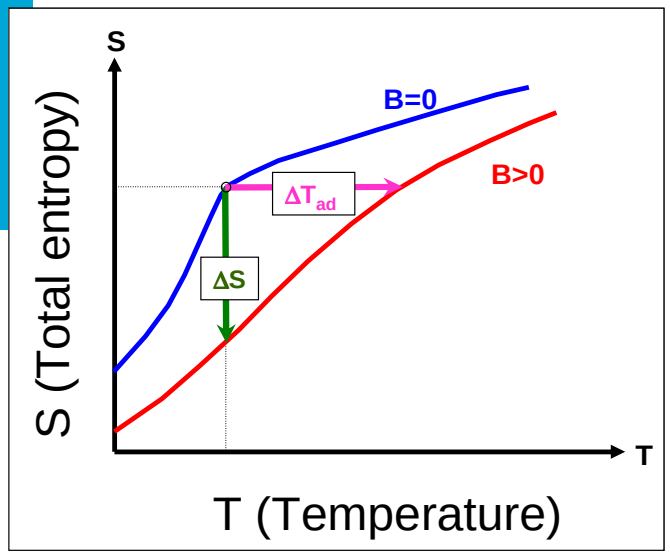
4- Mechanical stability

5- Origin of the "Boron effect" ?

(work in progress)

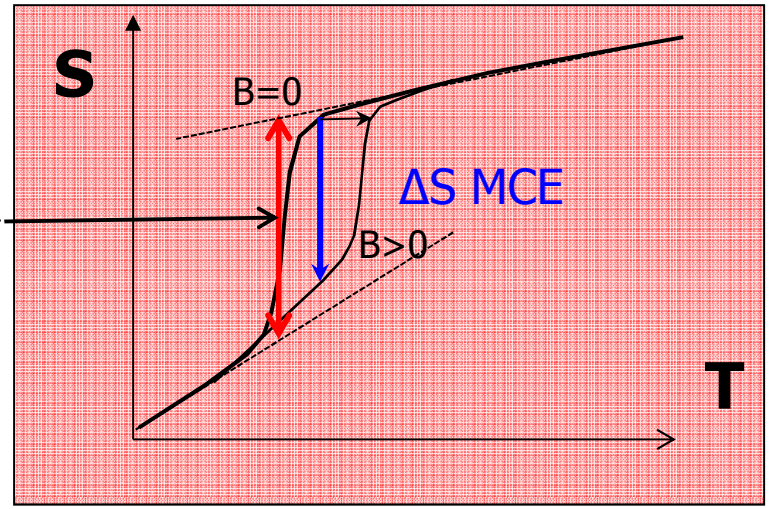
MCE // "Giant" MCE

Second Order Transition (SOT)



First Order Transition (FOT)

$$\Delta S_{tr} = \frac{L}{T_C}$$



Indirect : - Magnetization

$$\Delta S(T;\Delta B) = \frac{\partial}{\partial T}\int_0^B M(T,B')dB'$$

- Heat Capacity

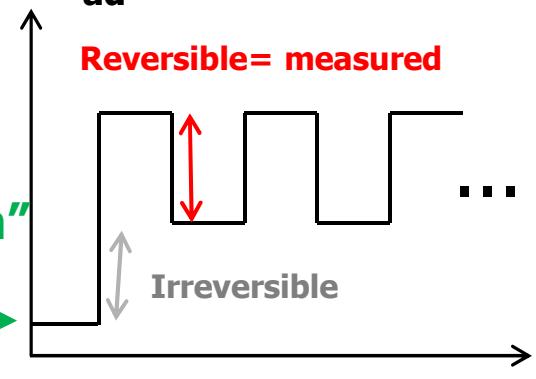
$$S(T,B) = \int_0^T \frac{C(T;B)}{T}dT$$

$$-\Delta S(T;\Delta B) = \left[S(T,B) - S(T,0)\right]$$

$$\Delta T_{ad}(T;\Delta B) = \left[T(S,B) - T(S,0)\right]_{S_0(T)}$$

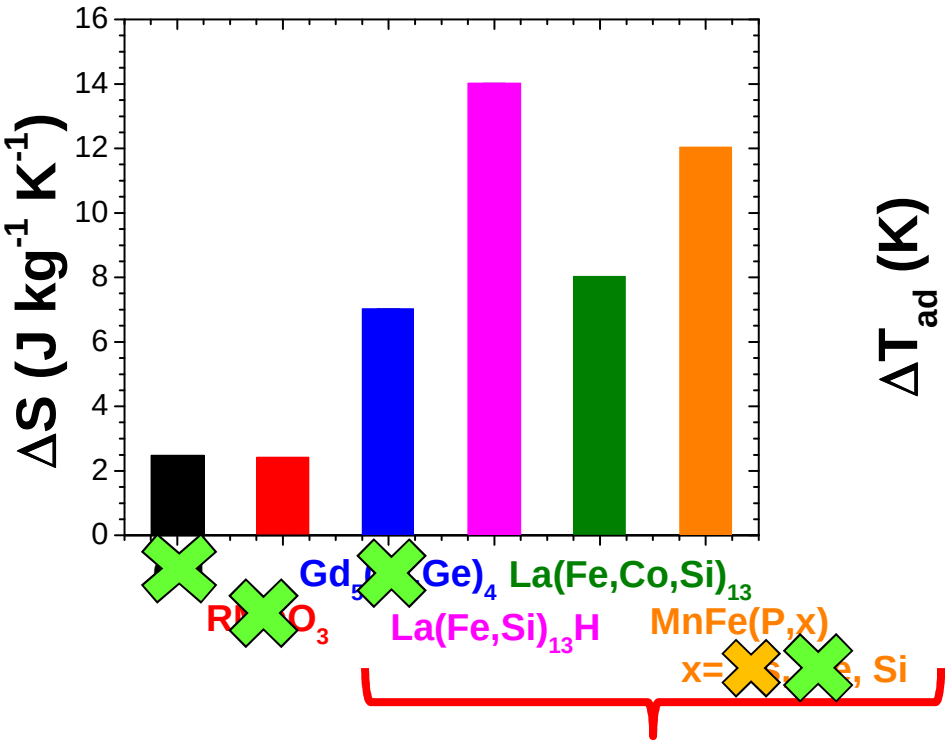
Direct : $\Delta T_{ad} = T_F(B) - T_i(0)$

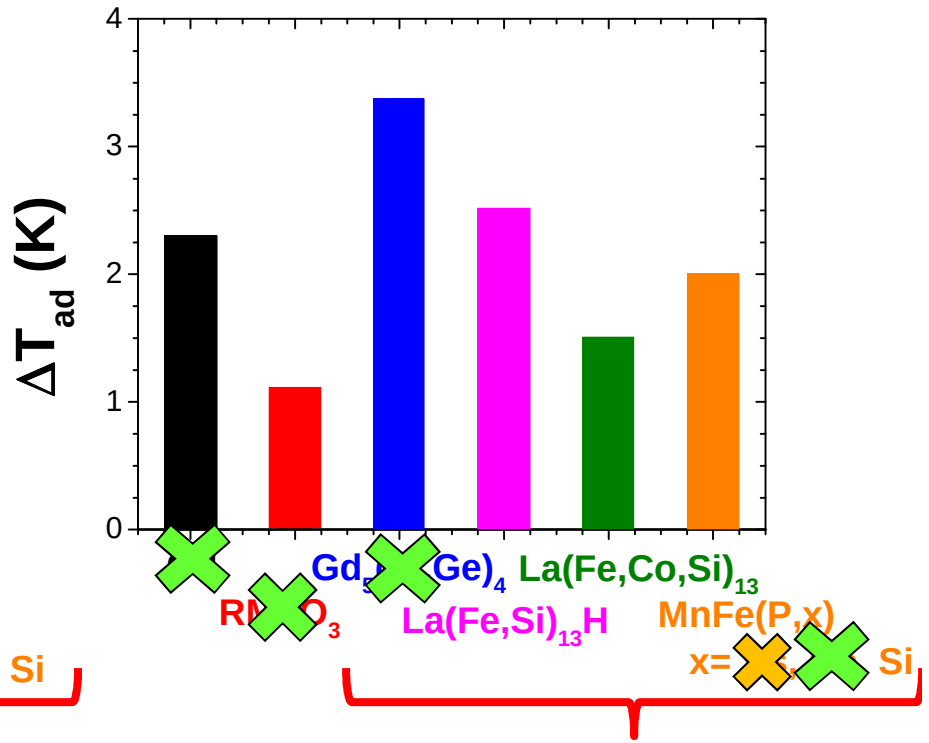
In our case cyclic,  for FOT



MCE Materials

At room temperature, for ΔB= 1 T (=available with permanent magnets)





"Giant" MCE: based on first order transitions

Large-Scale Applications:

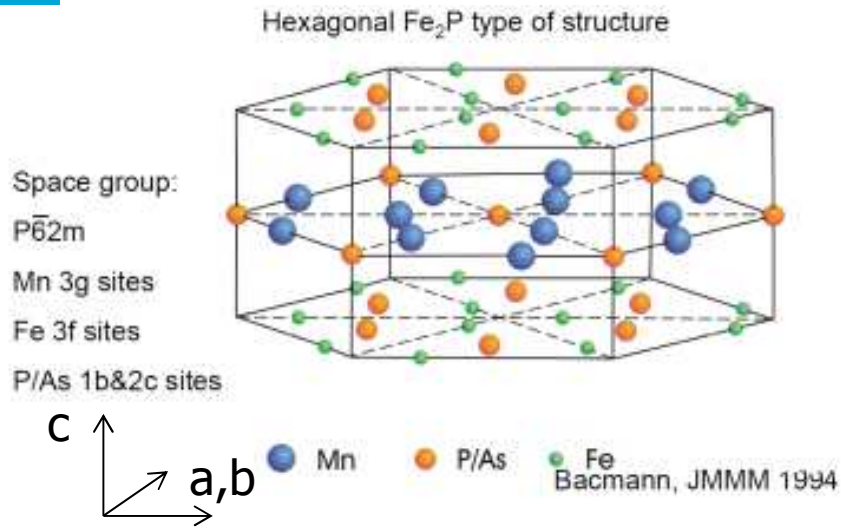
Toxicity

Cost + availability

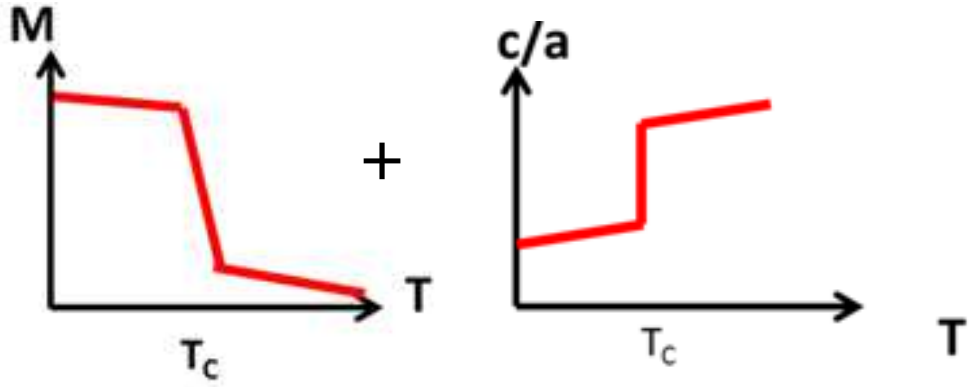
Other minor requirements (corrosion, mechanical resistance …)

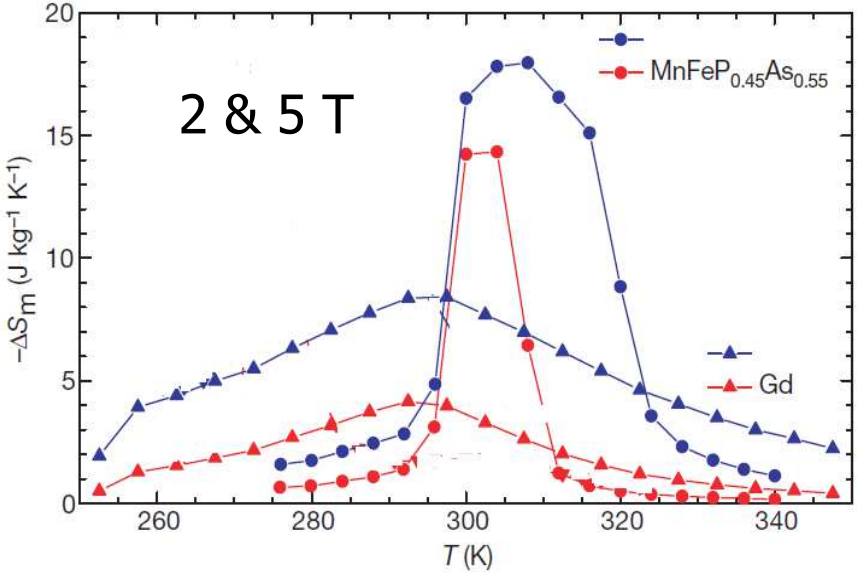
MnFe(P,As)

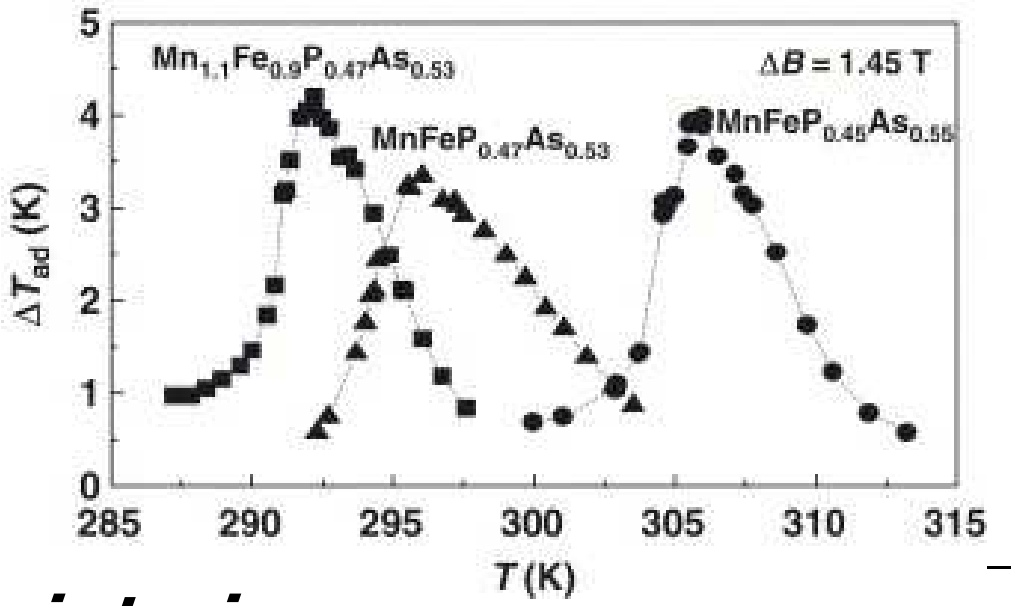
Delft, O. Tegus *et al.*, Nature 415, 150 **(2002)**



« Magneto-elastic » FOT



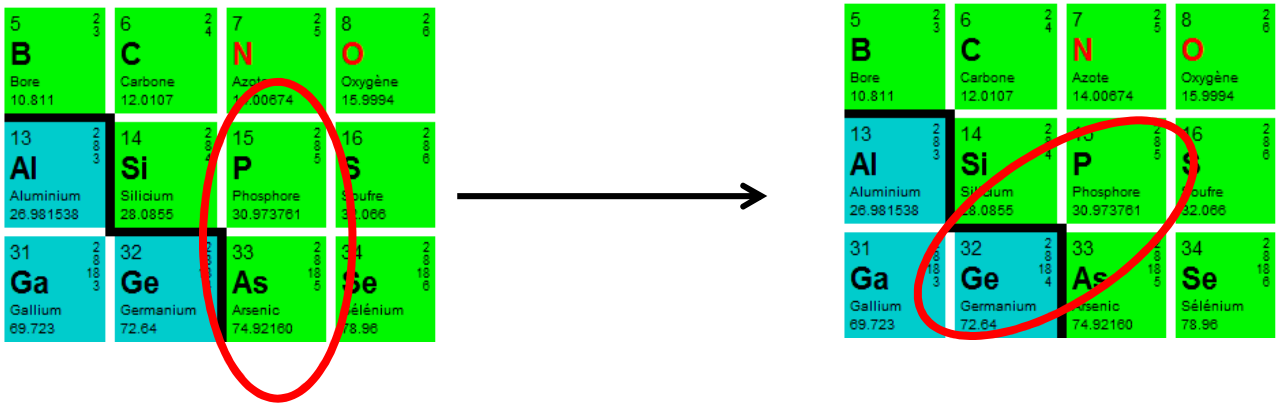




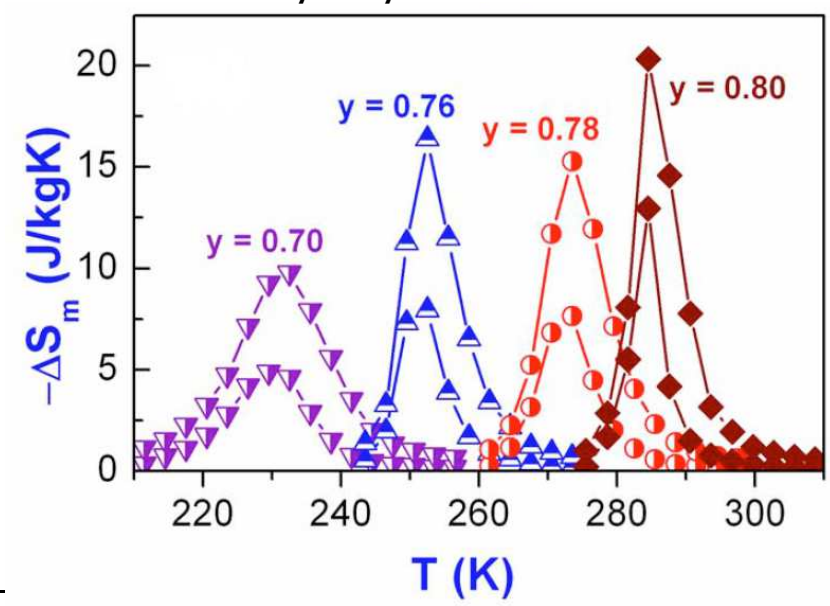
But, As is toxic…

MnFe(P,Ge)

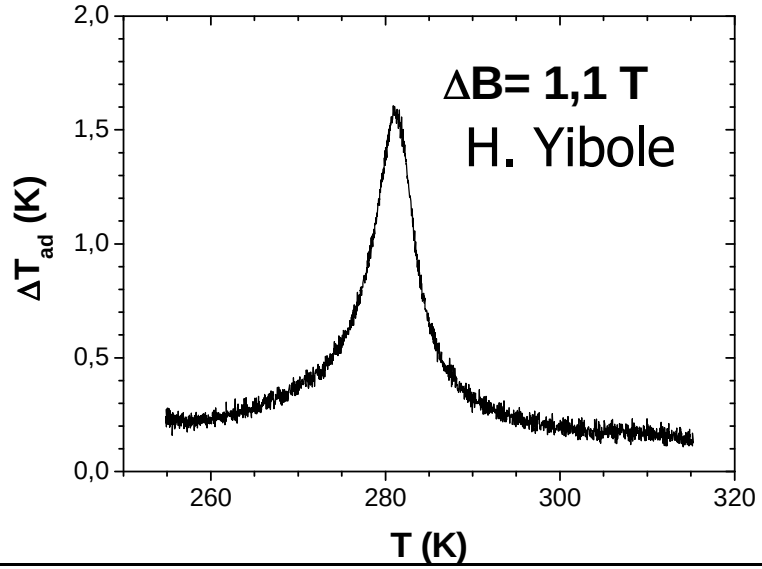
Delft, N.T. Trung *et al.*, Appl. Phys. Lett. 94, 102513 **(2009)**



$Mn_{2-y}Fe_yP_{0.75}Ge_{0.25}$



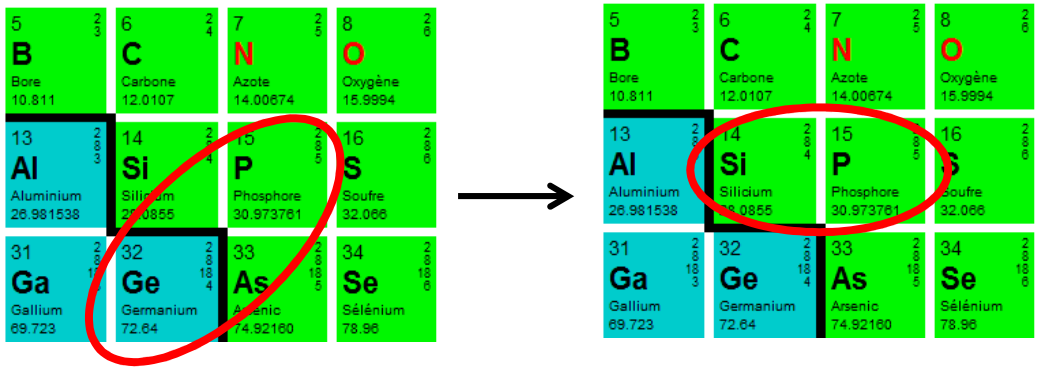
$Mn_{1.2}Fe_{0.8}P_{0.75}Ge_{0.25}$

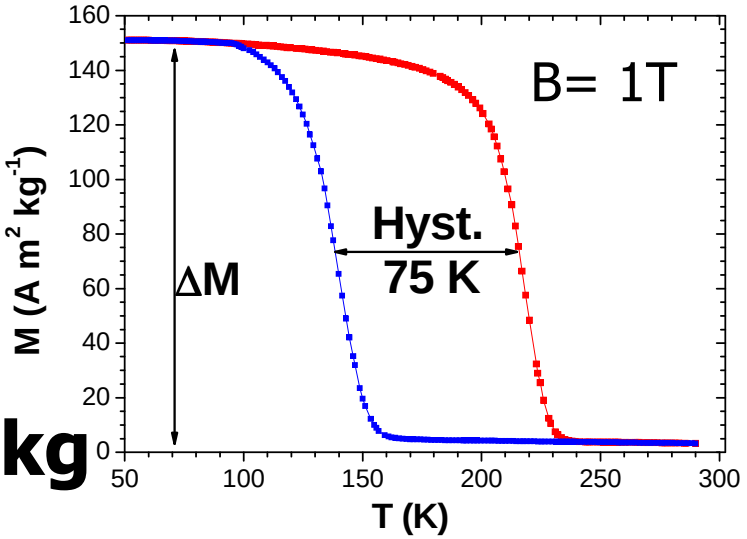


But, Ge is expensive...

MnFe(P,Si)

Delft, for more details see presentations: H. Yibole and X.F. Miao





$MnFeP_{2/3}Si_{1/3}$ L= 12 kJ/kg

P/Si

$MnFeP_{1-x}Si_x$

Si ↗	T_C (K) ↗	Hyst.(K) →
0.44	225	37
0.50	332	35
0.56	360	23
0.6	370	18

D. T. Cam Thanh (2008)

Mn/Fe

Extra Mn

Mn ↗	T_C (K) ↘	Hyst.(K) ↘
1	230	75
1.25	200	25
1.5	170	0

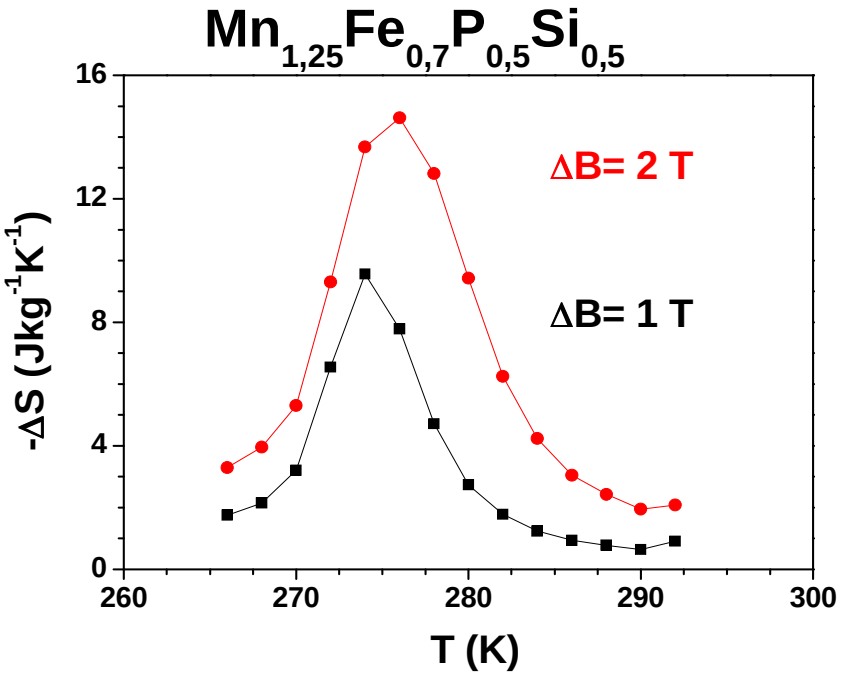
N. H. Dung (2011)

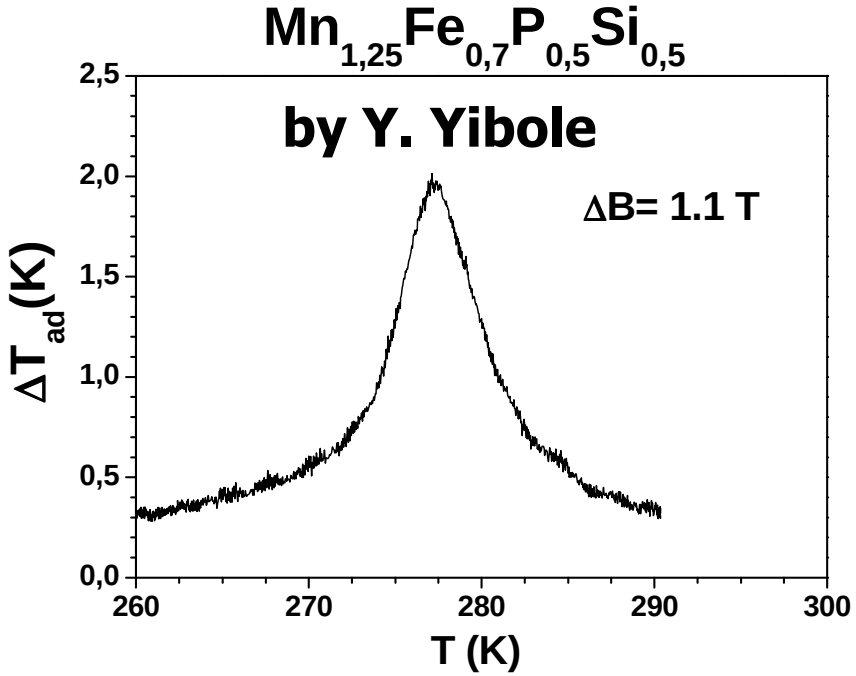
Extra Fe

Fe ↗	T_C (K) ↗	Hyst.(K) ↘
1	230	75
1.25	290	25
1.5	320	0

Z. Ou (2011)

"Mn rich" Best Si material (so far)





$\Delta B = 1$ T : $\Delta S \sim 10$ Jkg^{-1}K^{-1} $\Delta T_{ad} \sim 1,9$ K

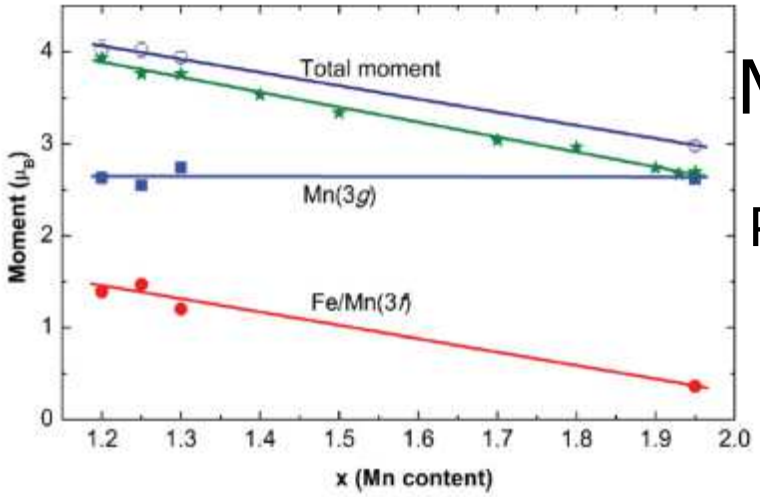
Properties still having to be optimized :

Room T. ΔB=1 T	ΔS^{max} (J kg^{-1} K^{-1})	ΔT^{max}_{ad} (K)
Gd	3	2,4
$LaFe_{11,6}Si_{1,4}H_1$	9,5 ??	2,6 ??
$Mn_{1,25}Fe_{0,7}P_{0,51}Si_{0,49}$	10,5	1,9

ΔT_{ad} + M_{sat} + Mechanical stability

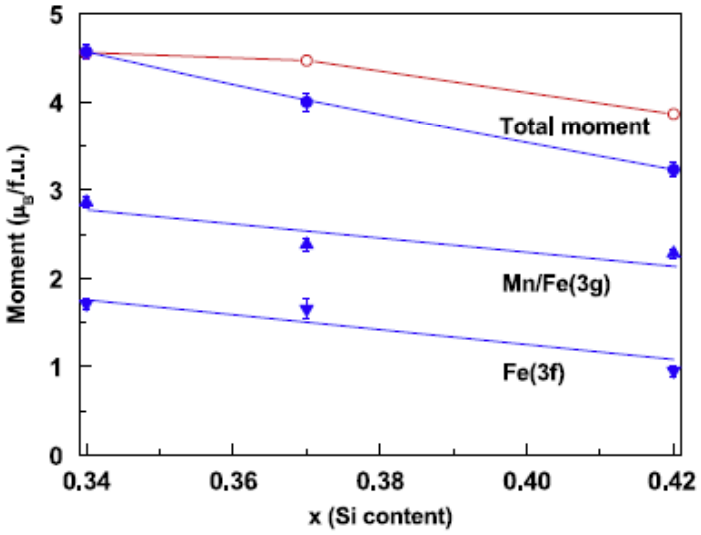
Optimization of M_{sat}

 # x: Mn

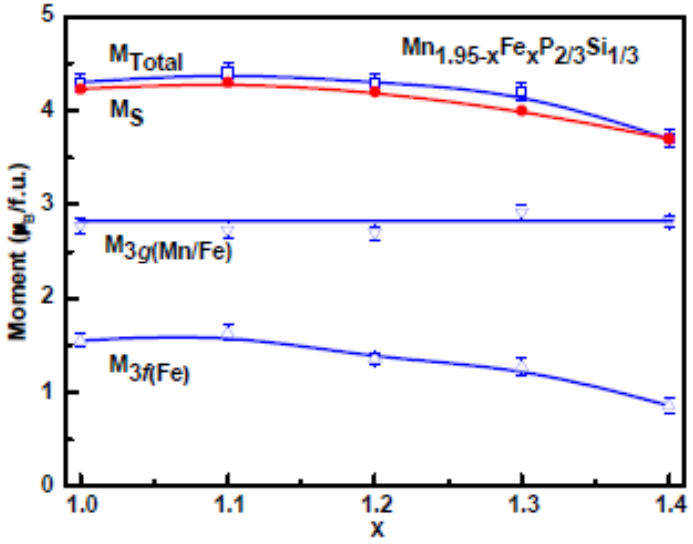


$Mn_xFe_{1,95-x}P_{0,5}Si_{0,5}$
N. H. Dung, *et al.*
Phys. Rev. B 86, 045134
(2012)

 # x: Si



 # x: Fe
Z. Q. Ou, *et al.*
Phd thesis
(2013)

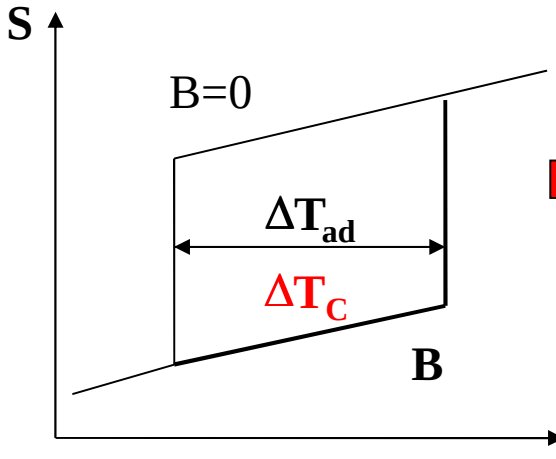


$Mn_{0,66}Fe_{1,29}P_{1-x}Si_x$
Z. Q. Ou, *et al.*
J. Mag. Mag. Matter. 340, 80 **(2013)**

Double optimum for M_{sat}:
Mn/Fe = 1 and **Si = 1/3**
($MnFeP_{0.67}Si_{0.33}$, hysteresis= 75K)
The best MCE material can not be a quaternary !

Optimisation of ΔT_{ad}

! Valid only in low B, $\Delta T_{ad} \sim L/C$

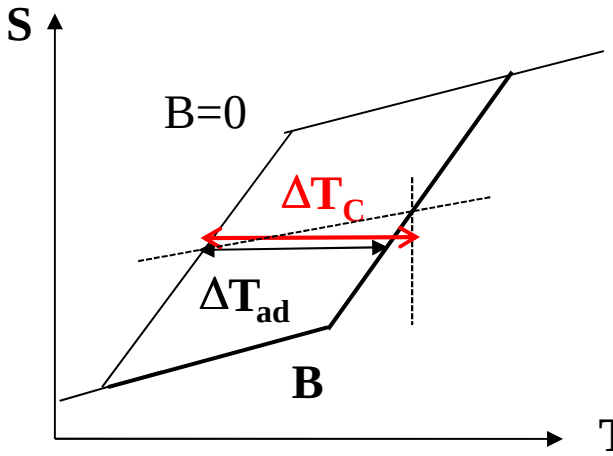


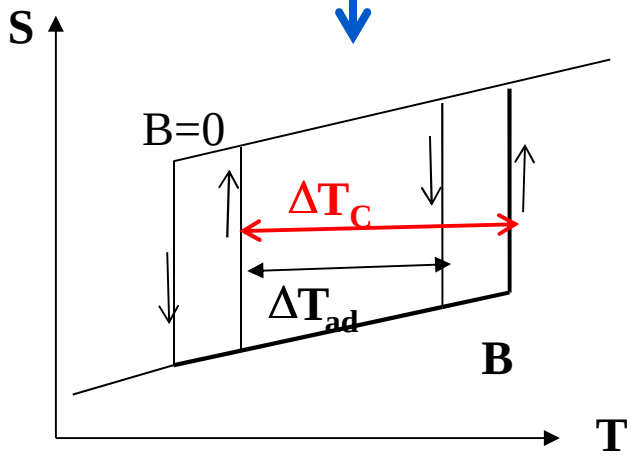
Ideal FOT

$\Delta T_{ad} = \Delta T_C$ Field induced shift of the transition

No transition width

No thermal hysteresis





Real FOT → $\Delta T_{ad} < \Delta T_C$

Hysteresis → Influence reversibility

$$\Delta T_C = \left(\frac{\partial T_C}{\partial B}\right)\Delta B \qquad \frac{\partial T_C}{\partial B} = \frac{T_C \Delta M}{L}$$

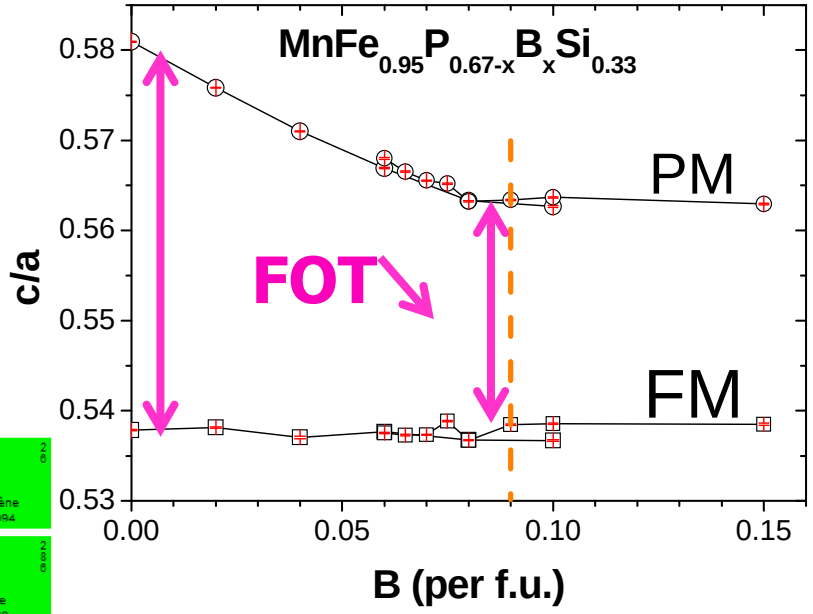
Taming the FOT in $MnFeP_{2/3}Si_{1/3}$ by Boron Substitution

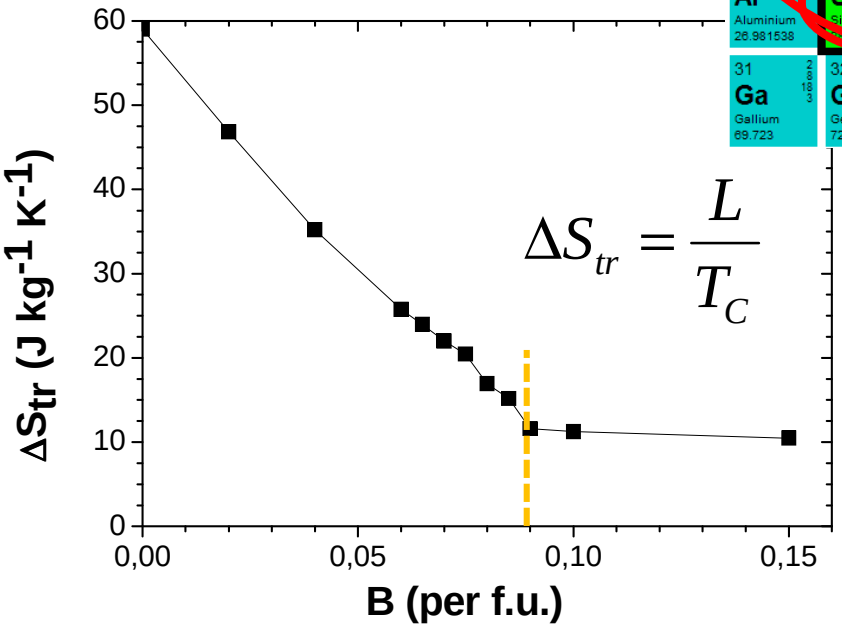
$Fe_2P_{1-x}B_x$

S. Rundqvist, Acta Chem. Scand. 16, 1 **(1962)** ;
A.Roger, phd Paris **(1970)**
R. Chandra *et al.*, J. SSC 34, 389 **(1980)**

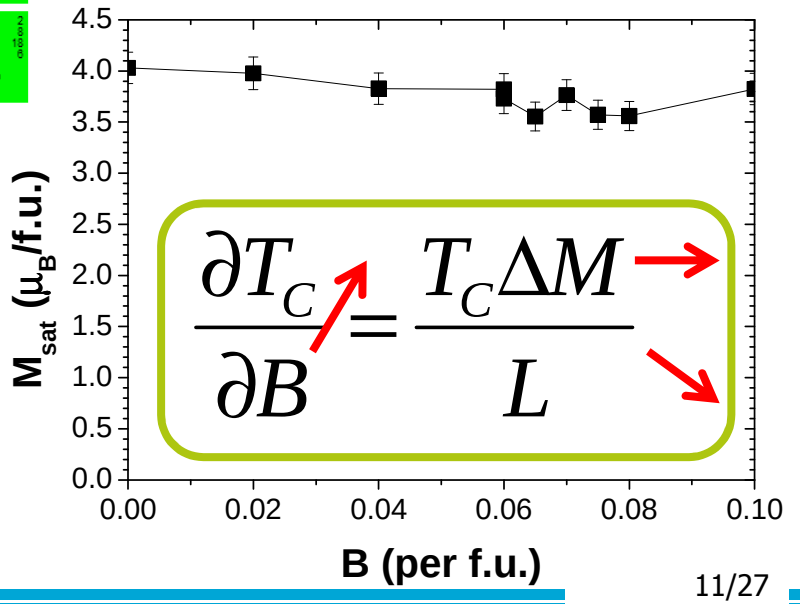
More recently:

E.K. Delczeg-Czirjak & Z. Gercsi *et al.* **2012 & 2013**
Phys. Rev. B 85, 224435 **(2012)**
Phys. Rev. B 86, 045126 **(2012)**
Phys. Rev. B 88, 024417 **(2013)**



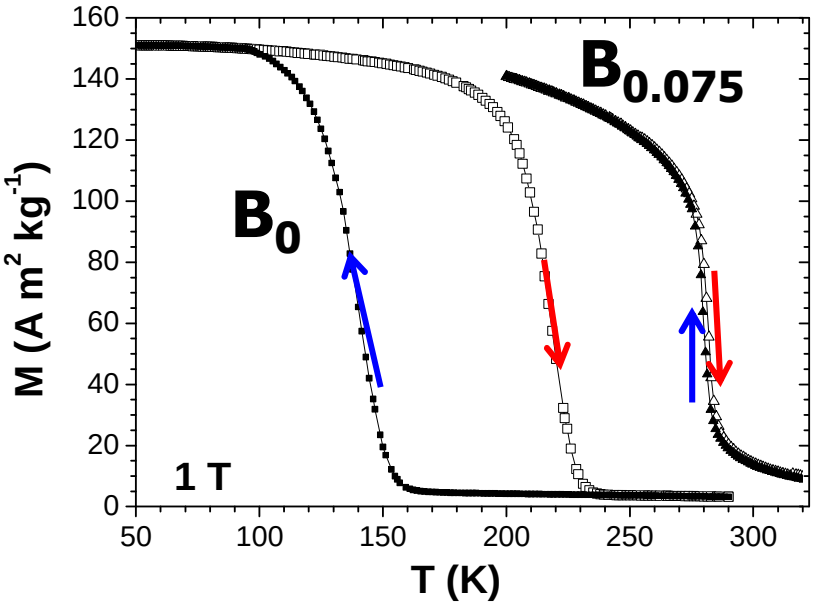


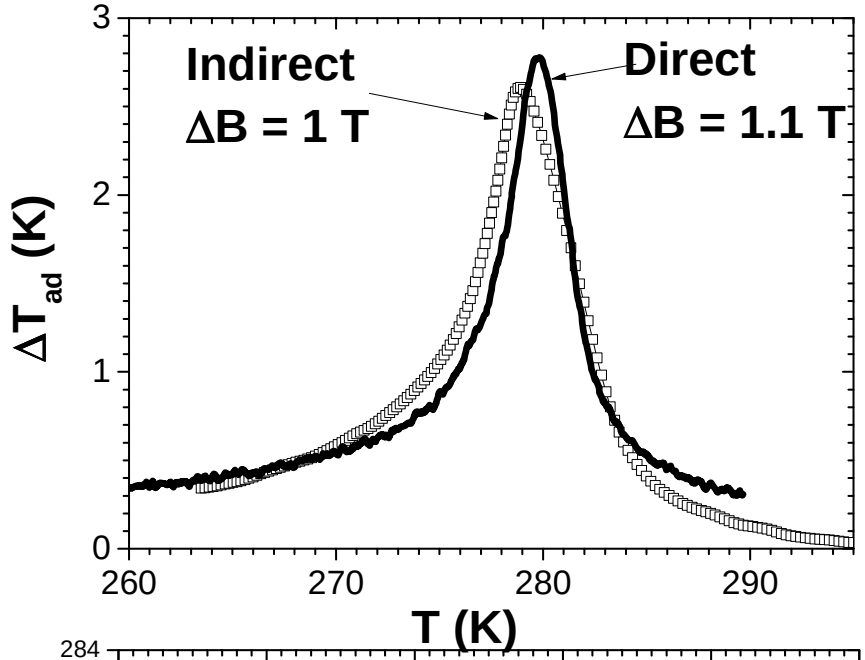
$$\Delta S_{tr} = \frac{L}{T_C}$$

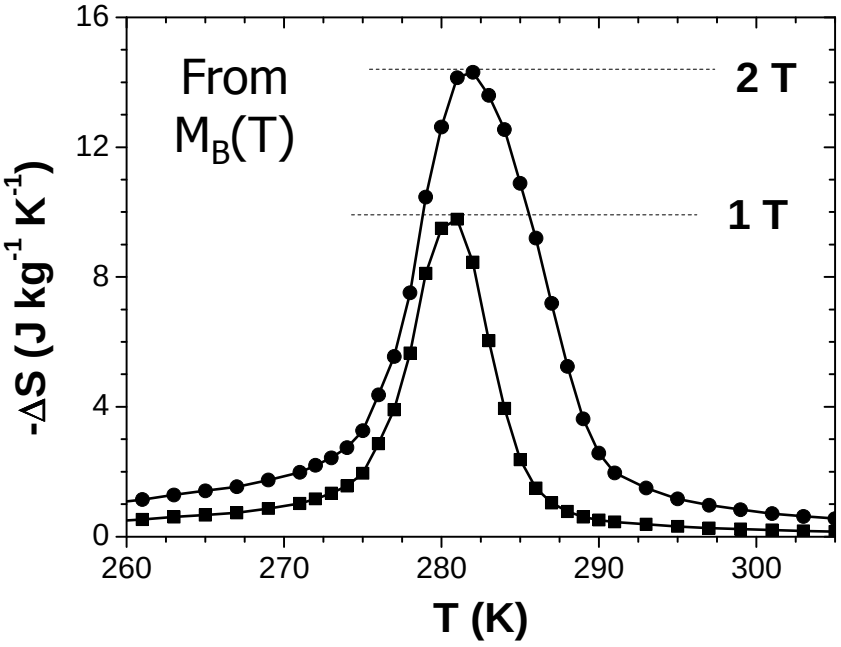


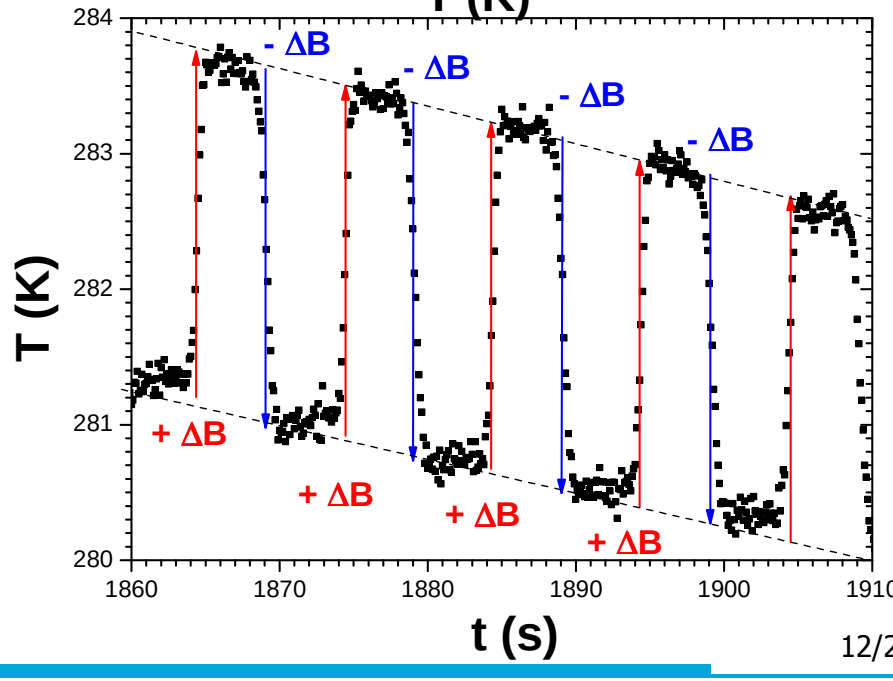
$$\frac{\partial T_C}{\partial B} = \frac{T_C \Delta M}{L}$$

$MnFe_{0.95}P_{0.595}B_{0.075}Si_{0.33}$

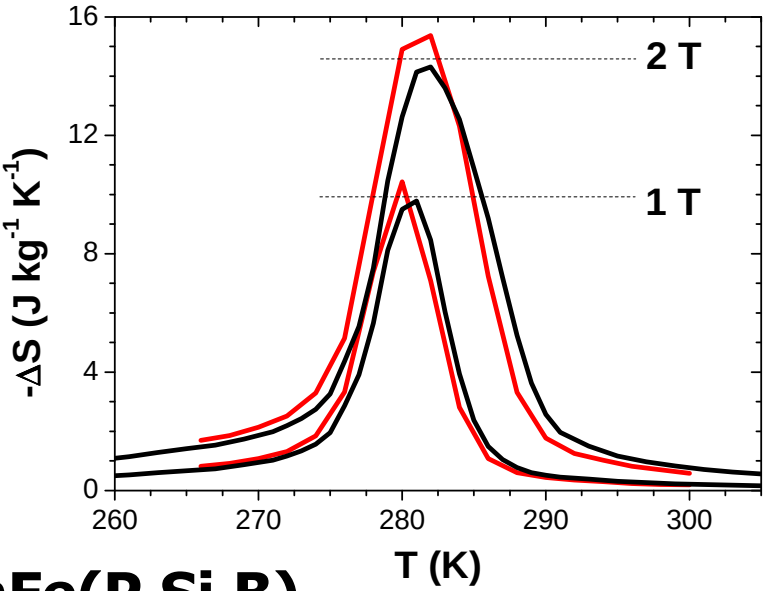


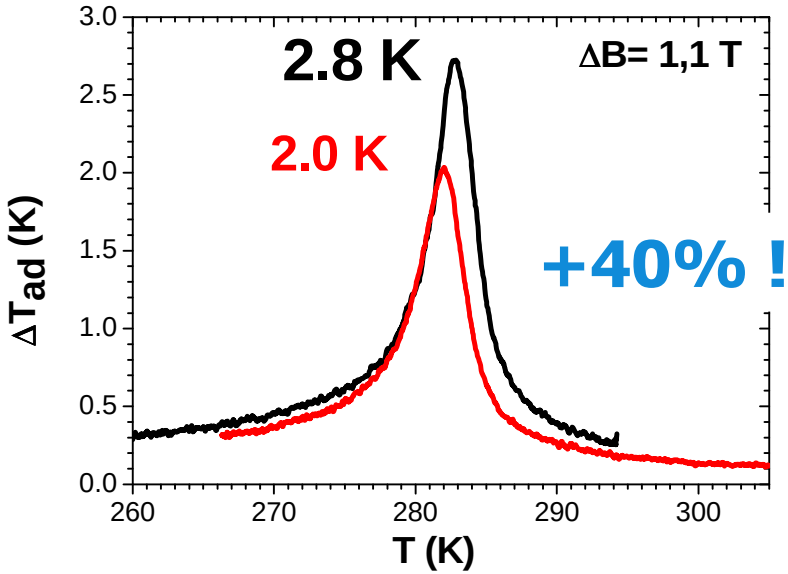






MnFe(P,Si,B) *vs* $Mn_{1.25}Fe_{0.7}P_{0.5}Si_{0.5}$





MnFe(P,Si,B)

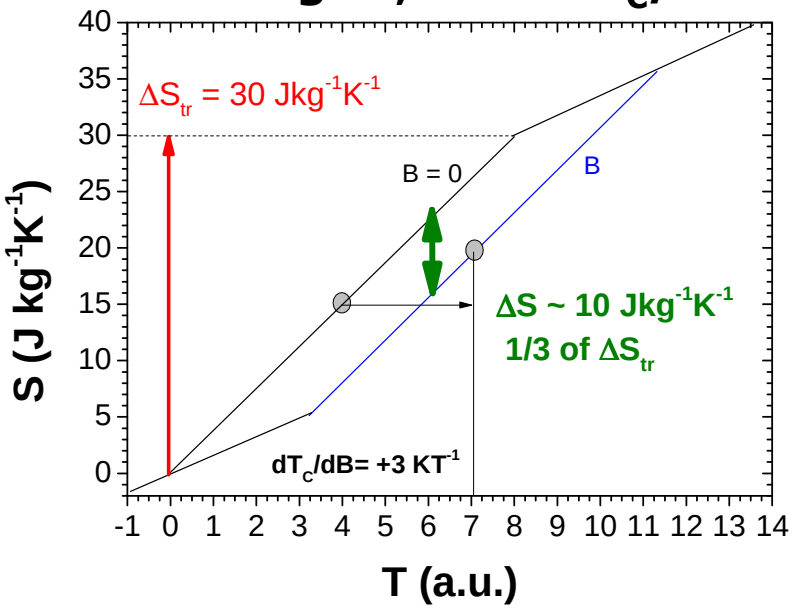
$Mn_{1,25}Fe_{0,7}P_{1/2}Si_{1/2}$

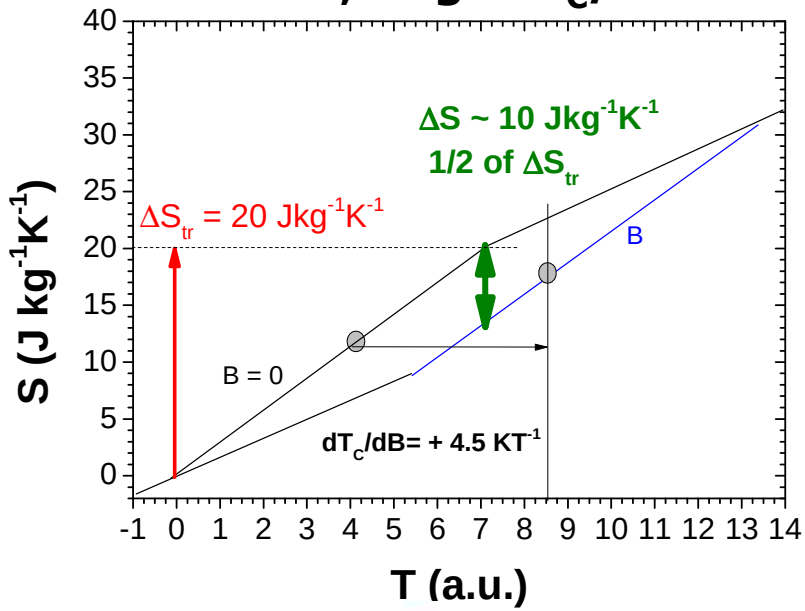
Reminder: $\frac{dT_C}{dB} = \frac{\Delta M}{\Delta S_{tr}} = \frac{\Delta M \,.T_C}{L}$

Sample	ΔS_{tr} = L/Tc (J kg^{-1} K^{-1})	ΔM (A m^2 kg^{-1})	dT_C/dB (K/T)	Transit. Width (K)	ΔS *MCE* B=1T (J kg^{-1} K^{-1})
Boron 7.5%	21,1	65	4,4 ±0,2	7,5	-10,5
	-36%	**+6%**	**+40%**		
Mn rich	29,8	61	3,2 ±0,2	8,0	-10,5

A personal point of view on materials design

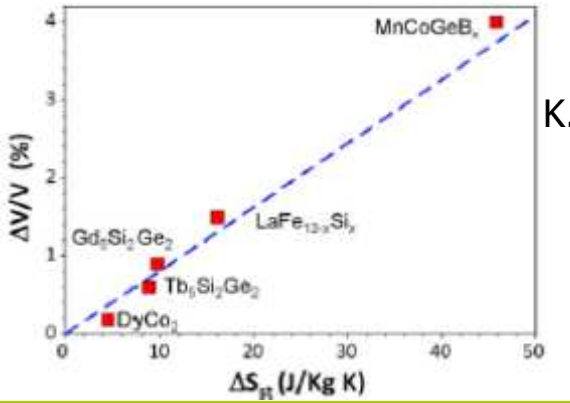
Large L, small dT_C/dB ***versus*** **Limited L, large dT_C/dB**





They have the same ΔS MCE !
But large L:
- amplifies all the FOT troubles
- gives lower ΔT_{ad}

Large L is only beneficial for high ΔB !



K.A. Gschneidner, Jr. *et al.* Scripta Mater. **(2012)**

Going toward "more first order" is not the only way to reach high MCE (at least for ΔB ≤ 2 T) !

Controversy about B addition: interstitial or substitution ???

 # $Fe_2P_{1-x}B_x$: (3 studies 80's; 3 studies since last year) **Substitution**

 # B in MnFe(P,Si): Patent CN 102881393A, filled 16/01/**2013**

$$Mn_{1.2}Fe_{0.8}P_{1-y}Si_yB_z$$

$$0.4 \leqslant y \leqslant 0.55, 0 \leqslant z \leqslant 0.05$$

Interstitial !

 # B in MnFe(P,Si,Ge): D.Wang *et al.*, Acta Metal. Sinica 47, 344 (2011)

$MnFeP_{0,63}Ge_{0,12}Si_{0,25}B_x$ x= 0- 0,03 **Interstitial !**

 # B in MnFe(P,As): Z. Q. Ou *et al.* , Results in Physics 2, 110 (2012)

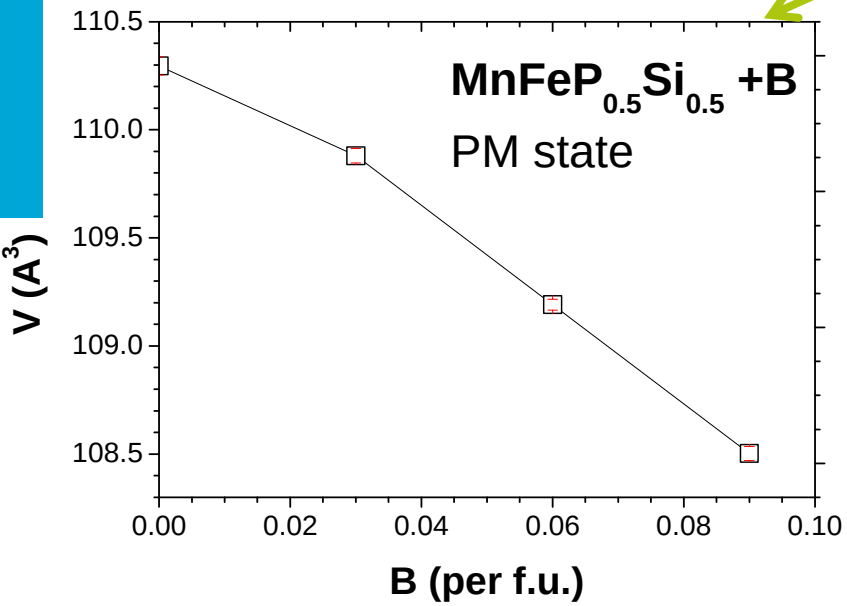
Compounds	V (Å^3)
$Mn_{0.95}Fe_{1.05}P_{0.5}As_{0.5}B_x$	(250 K/340 K)
$x = 0$	113.61/114.29
$x = 0.01$	113.70/114.46
$x = 0.02$	113.88/114.65
$x = 0.04$	113.97/114.74

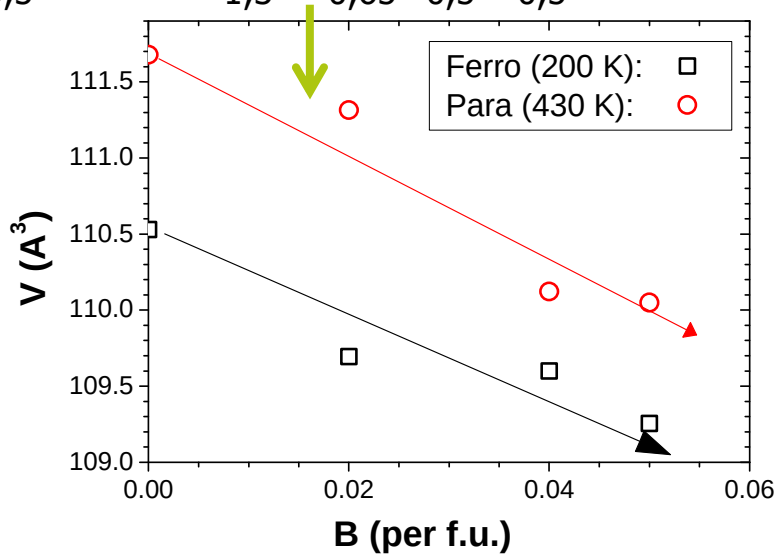
V ↗

Interstitial !

Interstitial Boron in MnFe(P,Si)

Two prototypical examples: $MnFeP_{0,5}Si_{0,5}$ and $Mn_{1,3}Fe_{0,65}P_{0,5}Si_{0,5}$

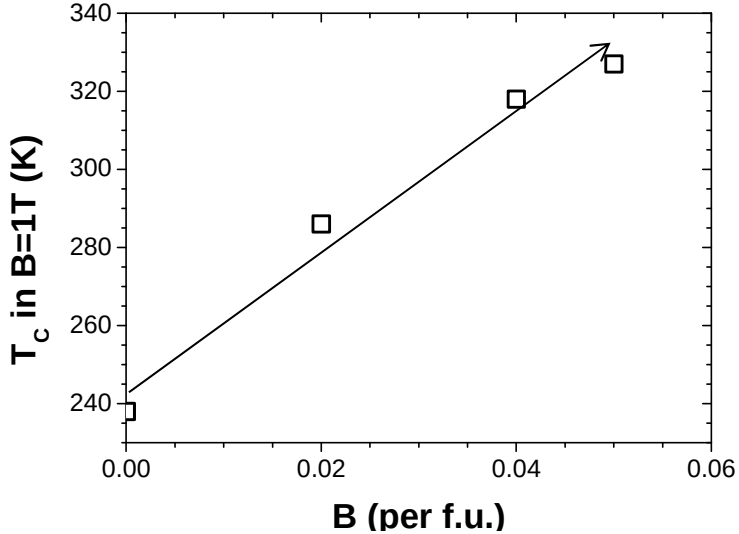




V ↘ ~~interstitial~~

T_C + 25 K / %B

~ -0,17 Å³ / %B



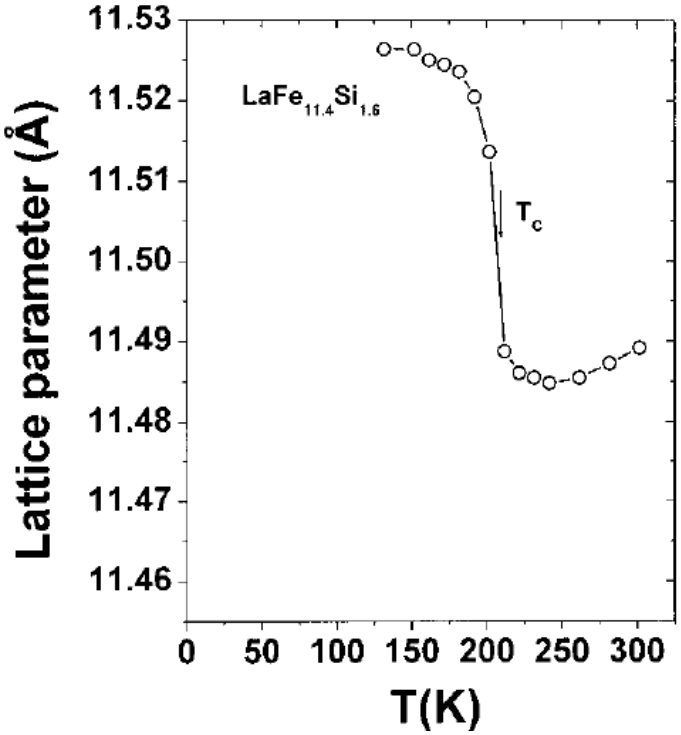
$Fe_2P_{1-x}B_x$: T_C + 20 K / %B

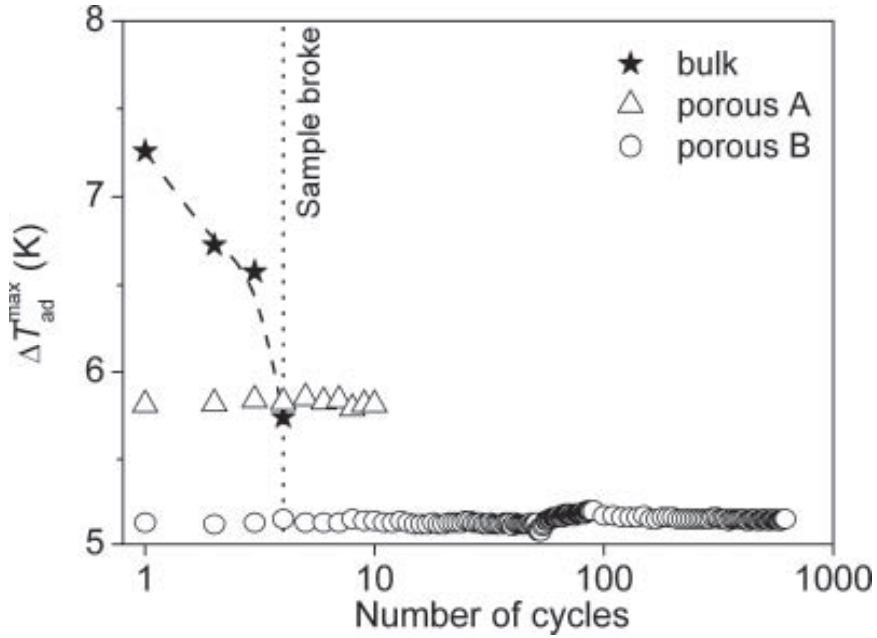
~ -0,13 Å³ / %B

In MnFe(P,Si) B is more probably a substitutional element !

Mechanical stability:

$La(Fe,Si)_{13}$ example





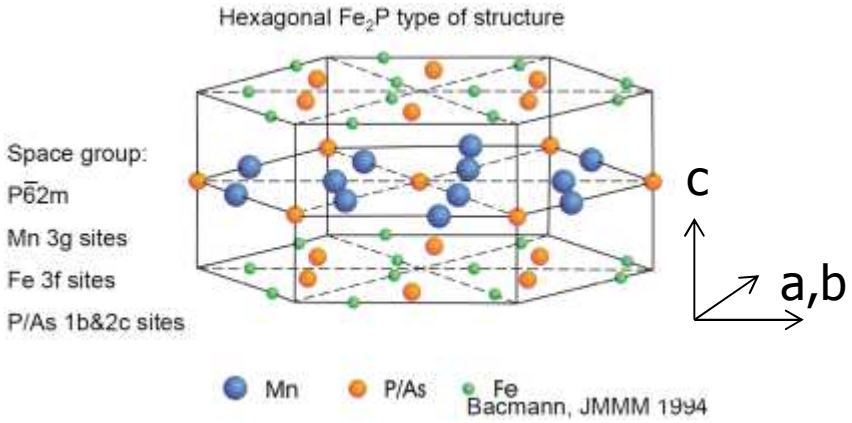
Cubic ΔV ≈ 3ΔL ≈ -1 %

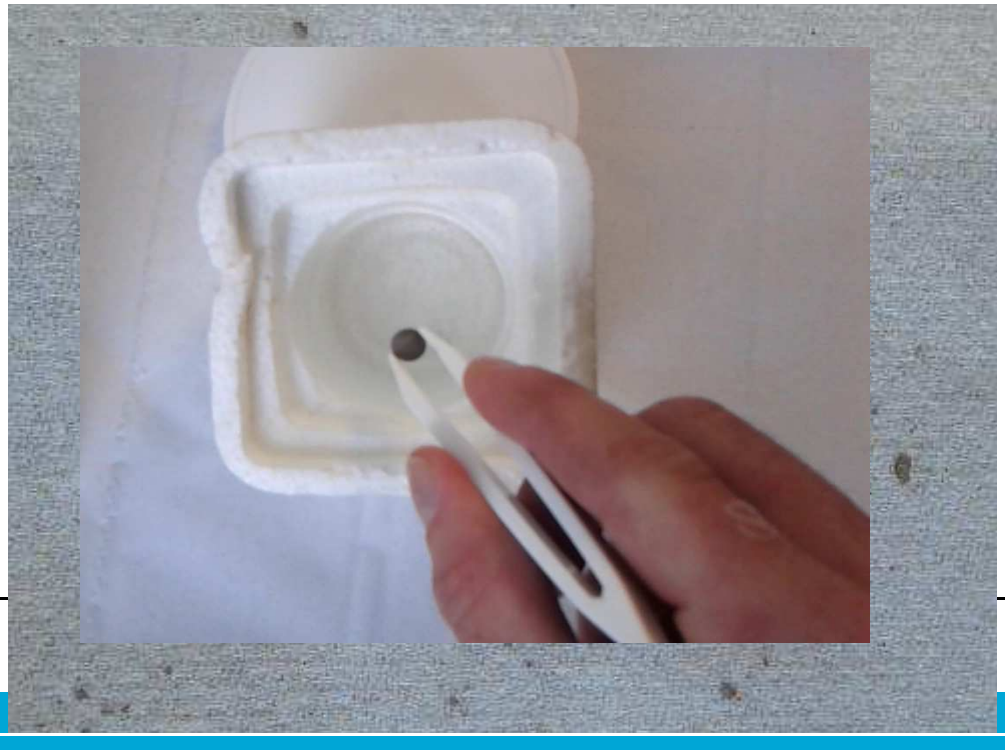
F.-X. Hu *et al.*,
Appl. Phys. Lett. **78**, 3675 (2001)

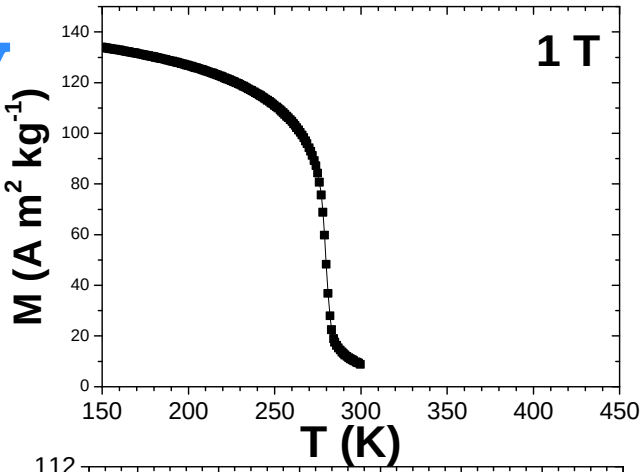
J. Lyubina *et al.*,
Adv. Mater. **22**, 3735 (2010)

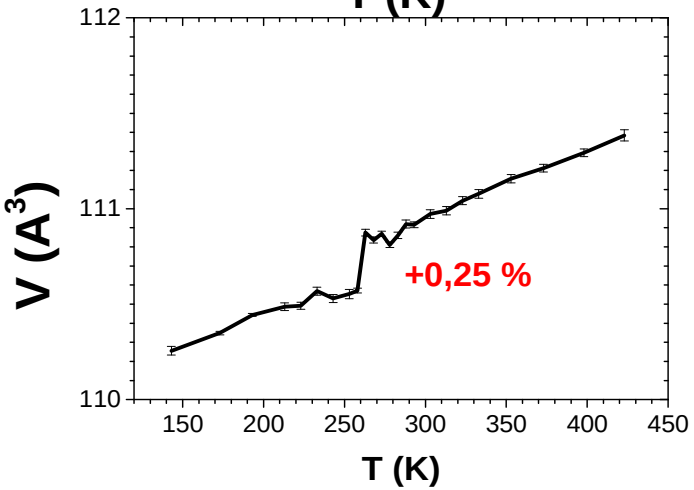
Mechanical stability

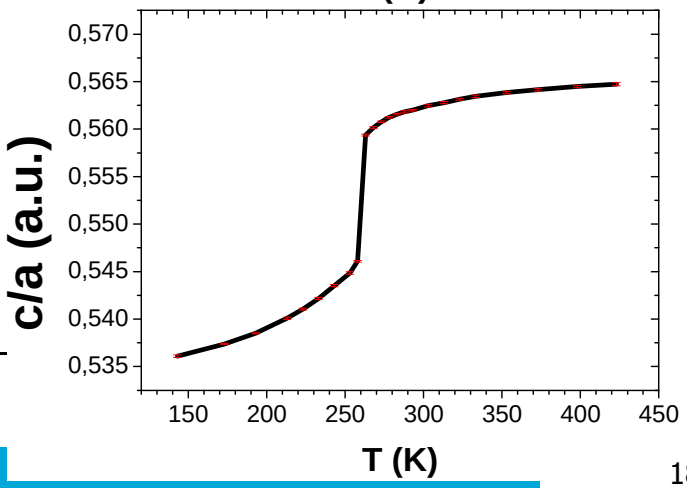
$Mn_{1,25}Fe_{0,7}P_{0,5}Si_{0,5}$



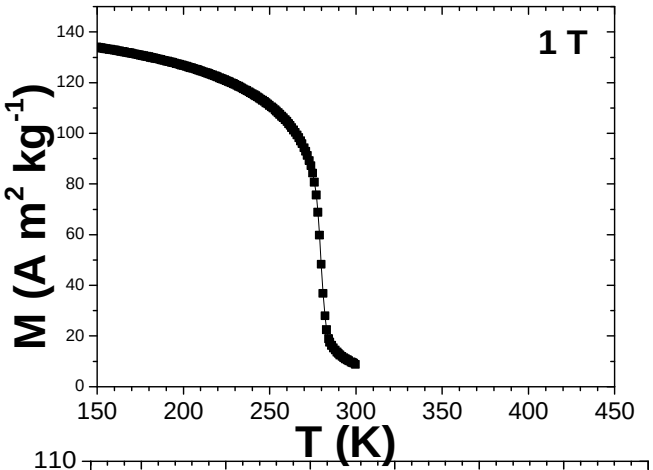


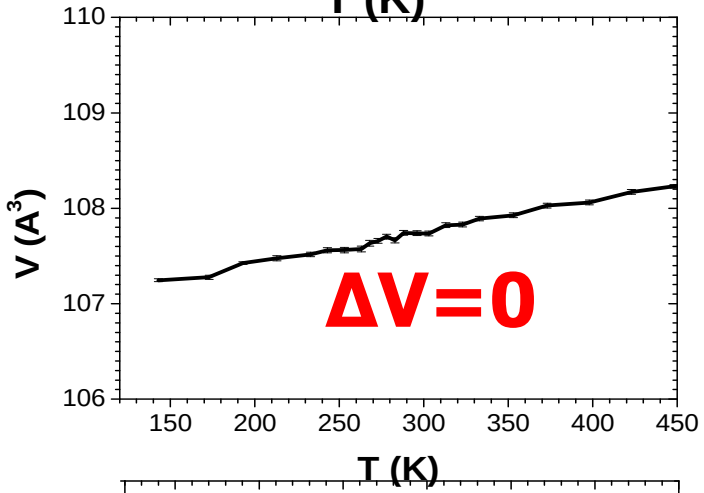


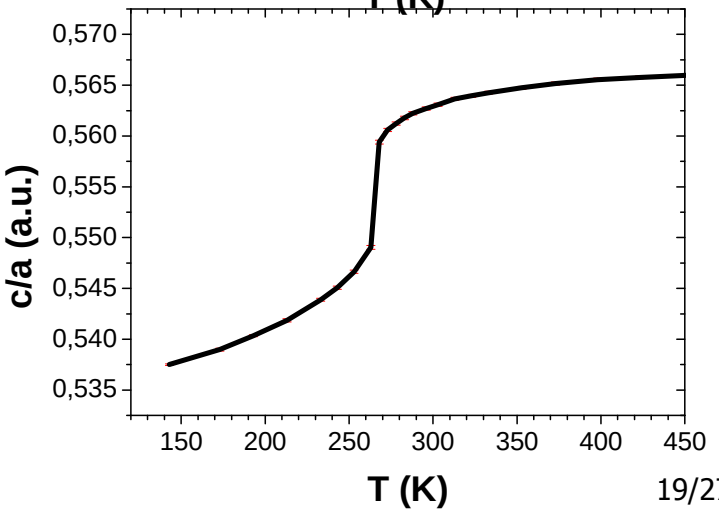




$MnFe_{0.95}P_{0.595}B_{0.075}Si_{0.33}$



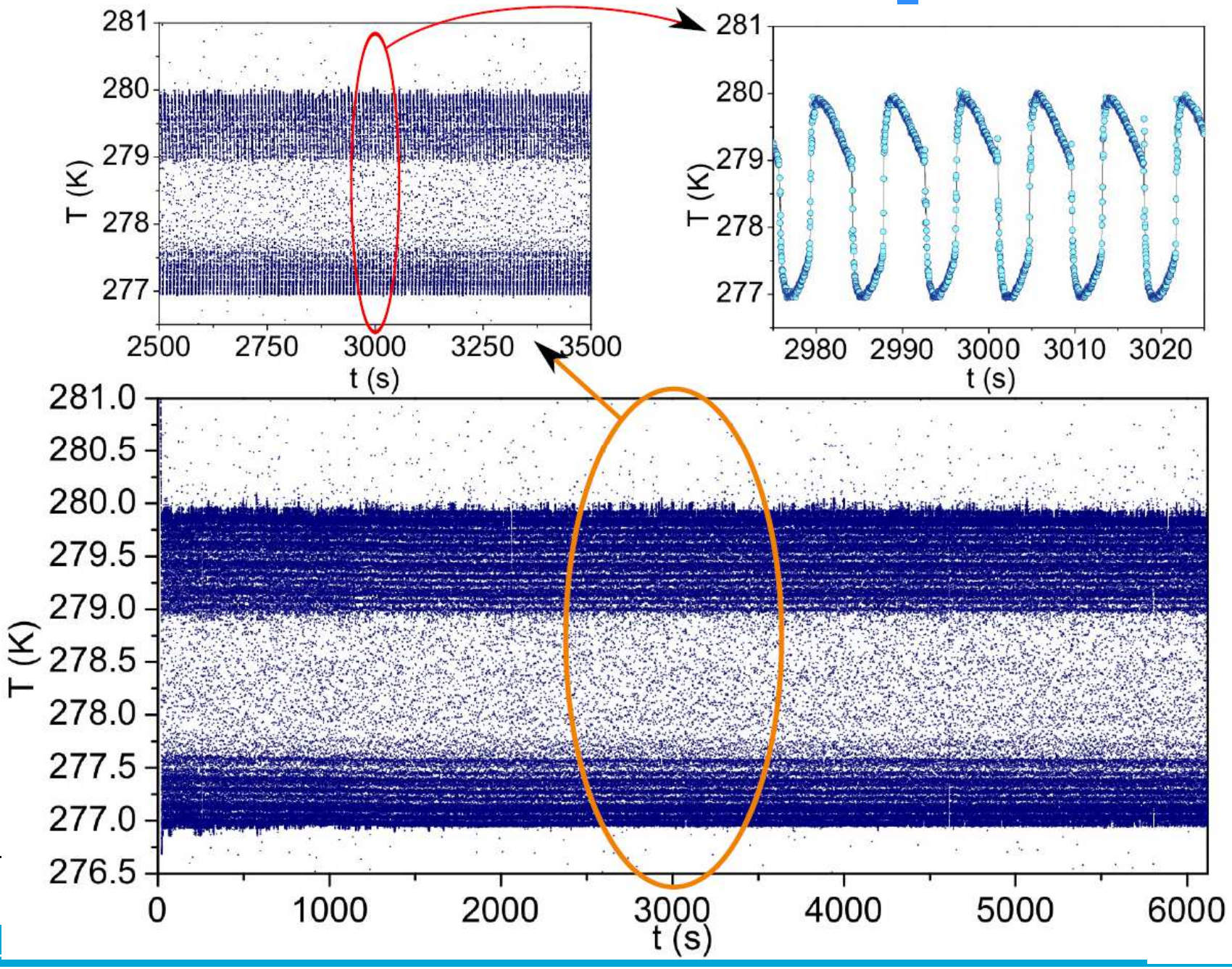




Note: This Sample survived to **10,000** magnetization/demagnetization cycles during ΔT_{ad} measurements !!

TU Delft

G. Porcari's Setup



1st Conclusion, MnFe(P,Si,B): a new generation of Fe_2P Giant-MCE materials

Room T. $\Delta B=1$ T	ΔS^{max} (J kg^{-1} K^{-1})	ΔT^{max}_{ad} (K)	
Gd	3	2,5	
$LaFe_{11,6}Si_{1,4}H_1$	~12	2,6	
$Mn_{1,25}Fe_{0,7}P_{0,51}Si_{0,49}$	10,5	1.9	
MnFe(P,Si,B)	10,5	2,8	←2013

- **Not toxic**
- **Not expensive**

(Boron only 0.5 wt%)

-Good mechanical stability

-Easy tunability of T_C

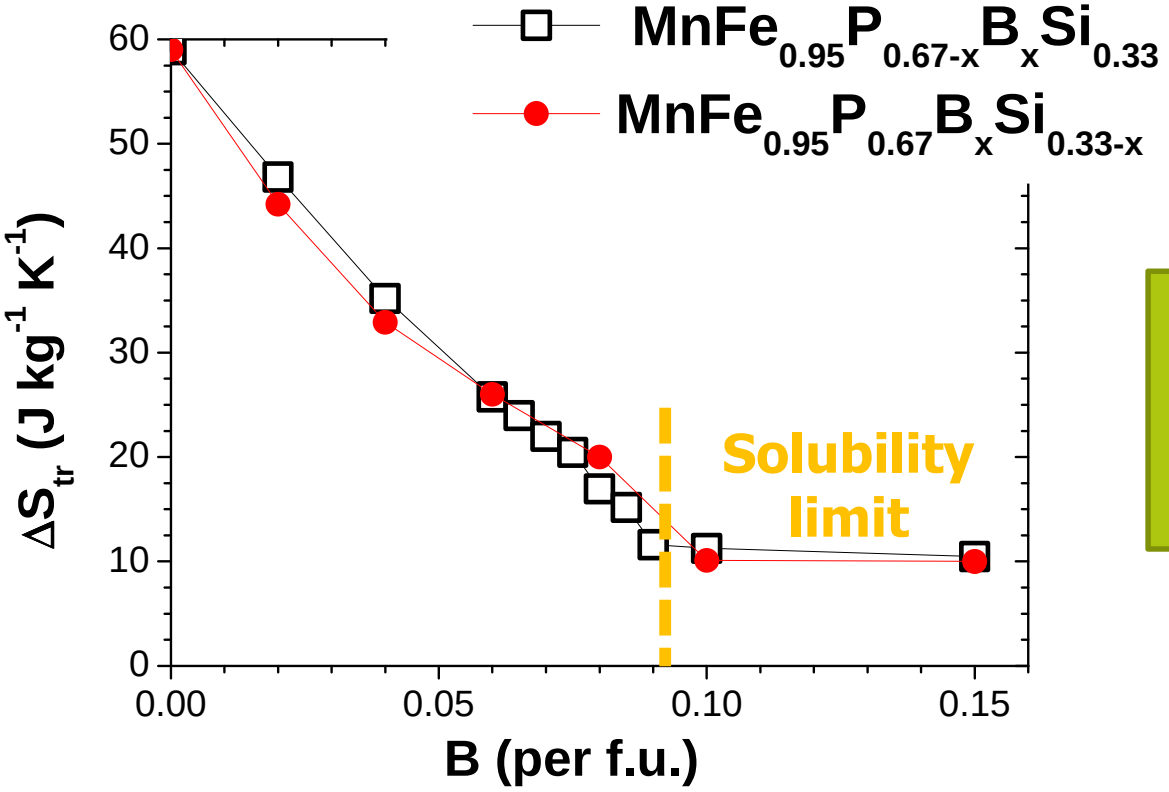
Mn/Fe + P/Si + B, from 130 K to 450 K

(will be developed during 58th MMM)

Some suggestions on the origin of the "Boron effect" in MnFe(P,Si) materials

(Work in progress, For more details on Fe_2P materials see also Z. Gercsi and L. Caron)

Reminder: MCE: positive effect of B substitution comes from his ability to decrease L (= $\Delta S_{tr} T_C$) and thermal hysteresis while keeping M_{sat} unmodified.

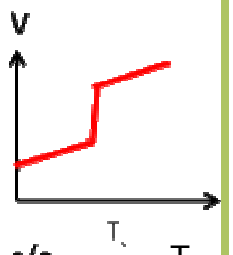


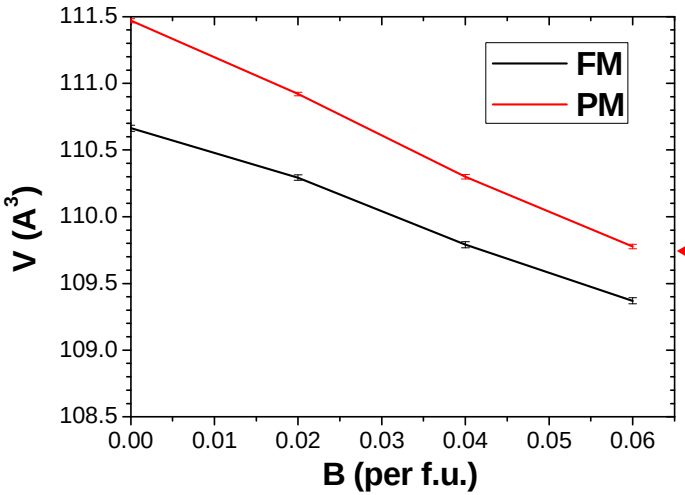
Note: in $MnFe_{0.95}P_{1-x}Si_x$ with $0.26 < x < 0.45$ ΔS_{tr} almost insensitive to P/Si ratio 50 +/- $Jkg^{-1}K^{-1}$

Boron substitutions in MnFe(P,Si)

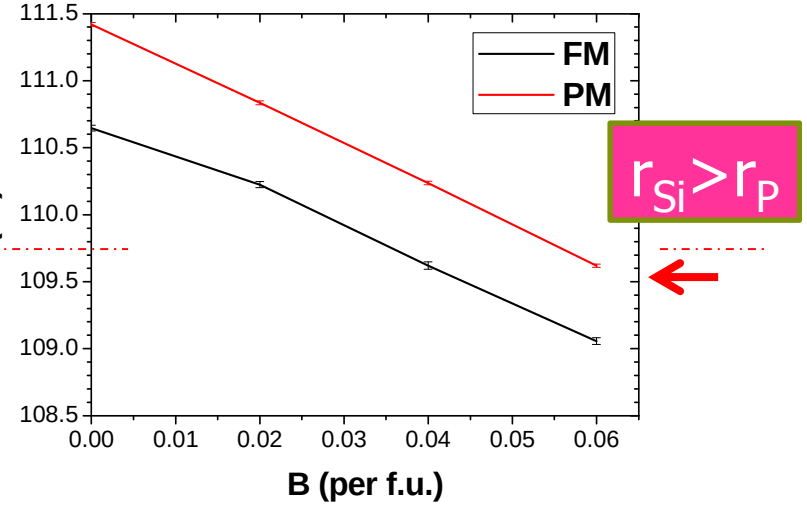
2 prototypical examples: MnFe(P, Si) and $Mn_{1,3}Fe_{0,65}P_{0,5}Si_{0,5}$

2 cases: **B on P** or **B on Si**

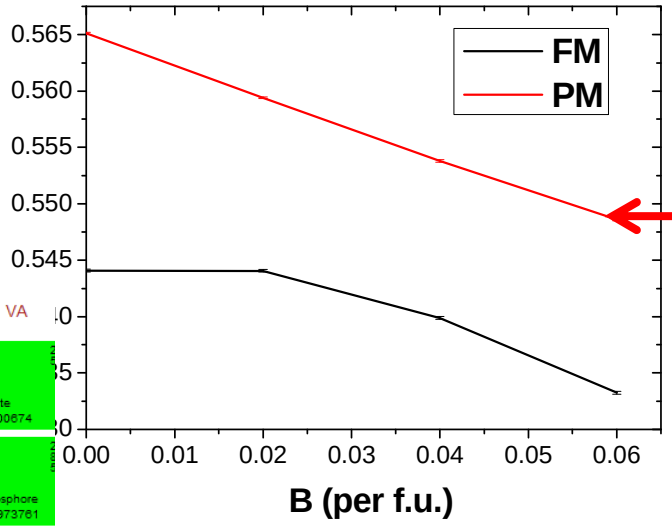




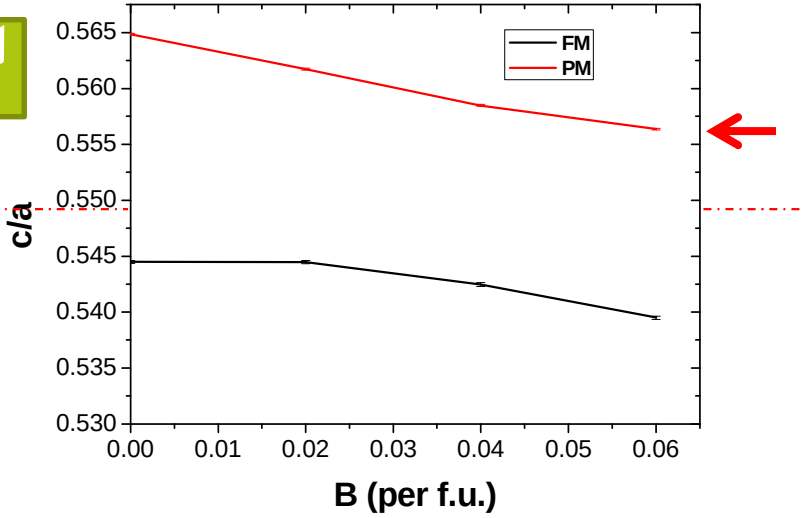
$T_C \neq Fe_2P$

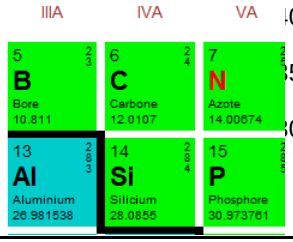


$r_{Si} > r_P$

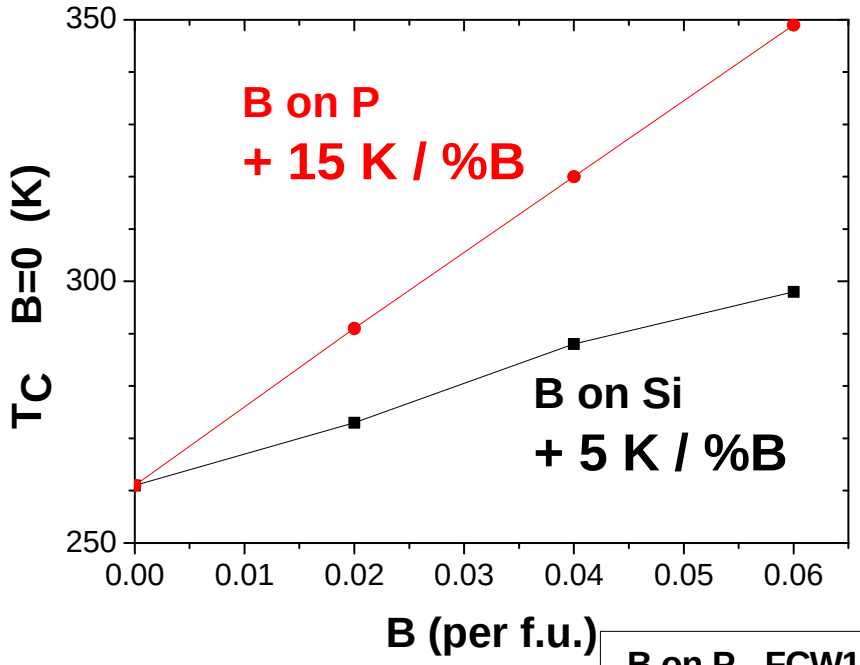


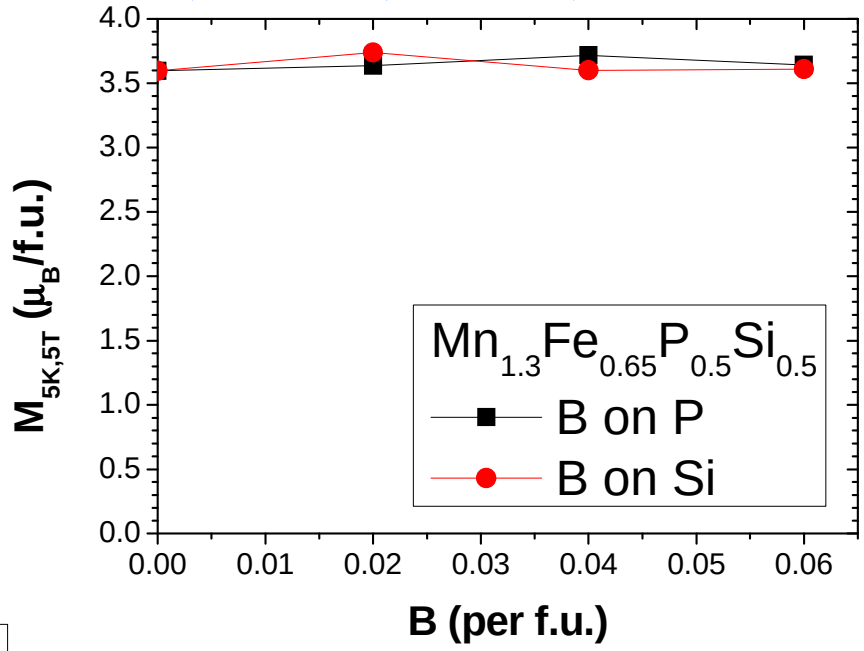
$T_C \nearrow$

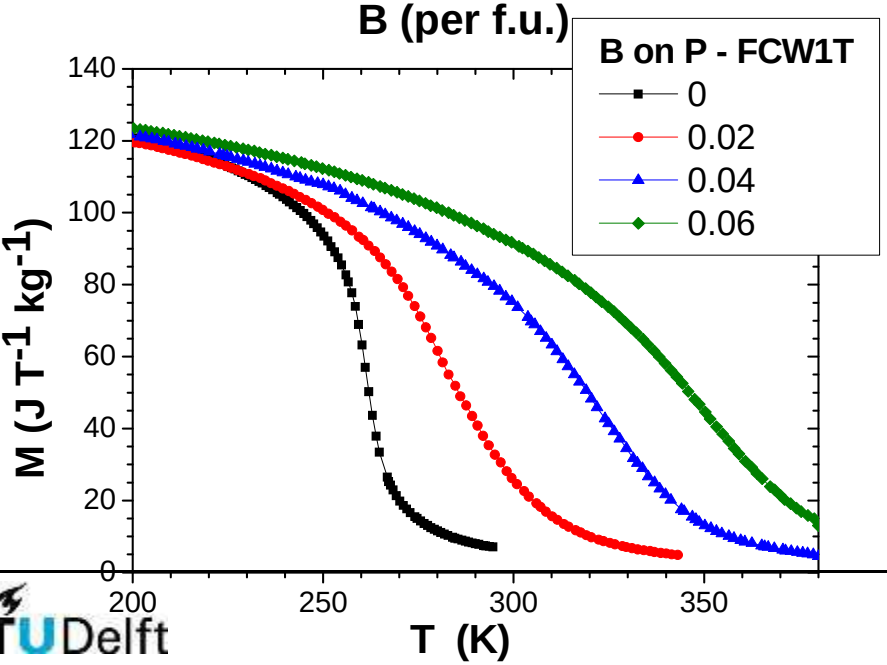




Boron in $Mn_{1,3}Fe_{0,65}P_{0,5}Si_{0,5}$





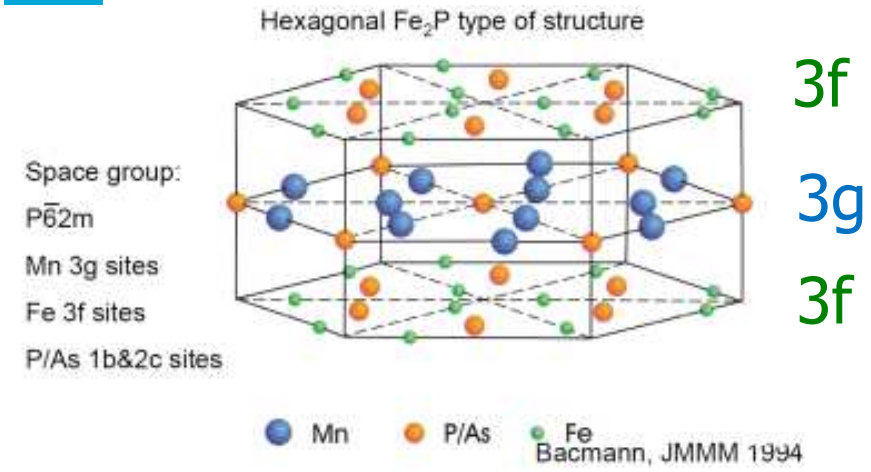


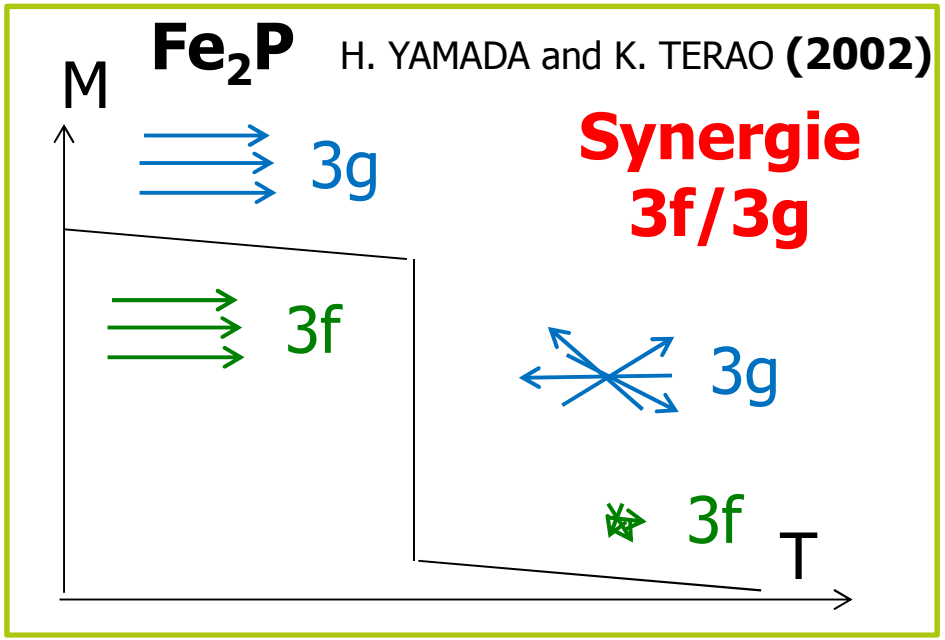
- Largest V evolution: B on Si
- Largest c/a: B on P
- Largest T_C shift: B on P
- L decrease: the same !
- M_{sat}: the same !

FOT properties not driven by "geometrical effects" !

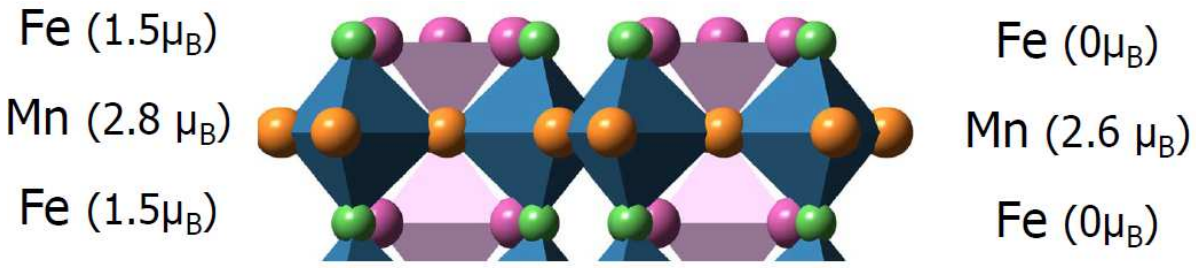
Origin of the FOT in MnFe(P,Si)

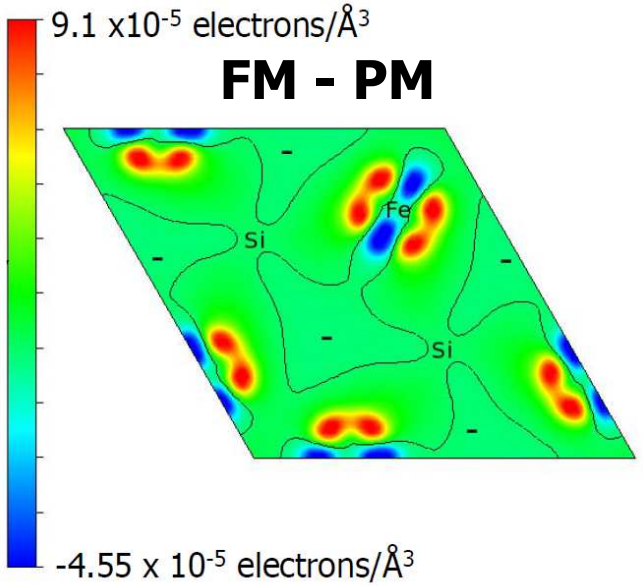
Fe_2P based material





MnFe(P,Si) Adv. Energ. Mater. **1**, 1215 **(2011)**





TUDelft

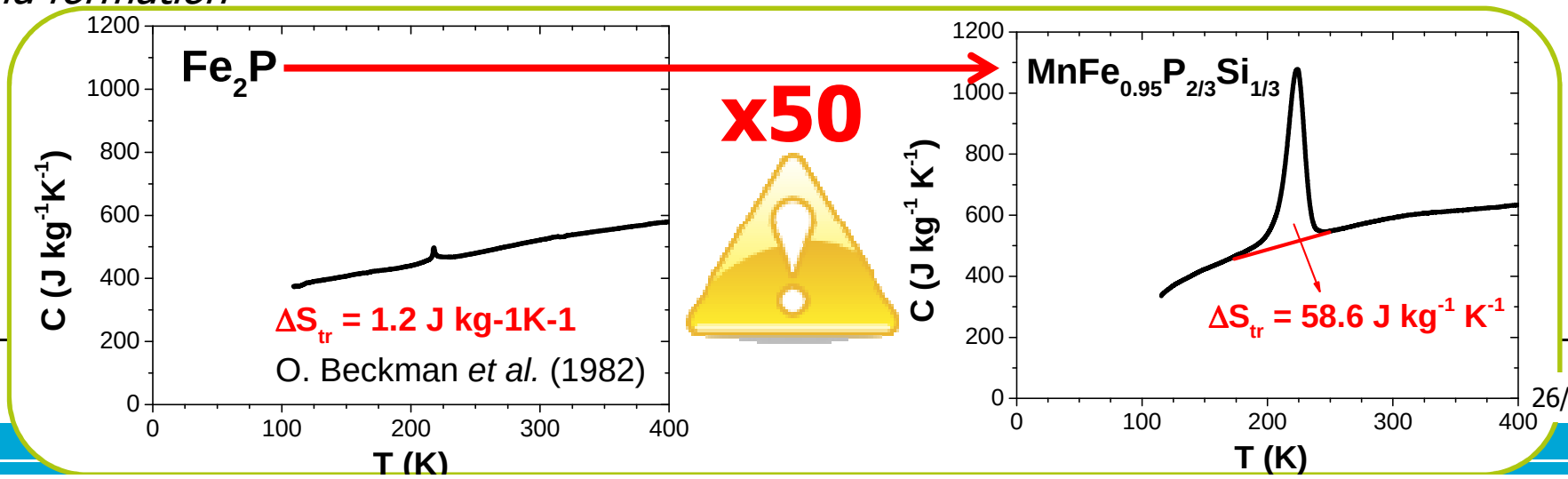
"B effect": the case of Fe_2P

When B substitutes P or Si in MnFe(P,Si):
- **Largest V evolution: B on Si** → $r_{Si} > r_P$
- **Largest c/a: B on P**
- **Largest T_C shift: B on P**
- **L decrease: the same !**
- **M_{sat}: the same !**

P.R.B 85, 224435 (2012):
- *"Decrease of c/a has an electronic origin"*
- *T_C driven by c/a*

P.R.B 86, 045126 (2012):
- *"in $Fe_2P_{0.92}B_{0.08}$ the 3f sublattice has a stronger tendency to form a finite-moment state compared to Fe_2P"*
- *"Coupling 3g -3f becomes less significant with increasing B at the P site"*

P.R.B 88, 024417 (2012) **Z. Gercsi**
- *"With doping* (-B) [...] *altering the balance between magnetic moment formation and bond formation"*



2nd Conclusion: General remarks

 # Be careful to B addition in "Fe_2P" materials

 # Role of B on the FOT in MnFe(P,Si) ?

 # Importance of L (or ΔS_{tr}) when designing new MCE materials !

More precisely, we are ↘ L !!!

 # Giant MCE with ΔV = 0

i) ≠ some predictions

Scripta Materialia, 67 (2012) 572-577, K.A. Gschneidner Jr. *et al.*

ii) Mechanical stability

 # Distinction between total/reversible MCE

Thank you for your attention

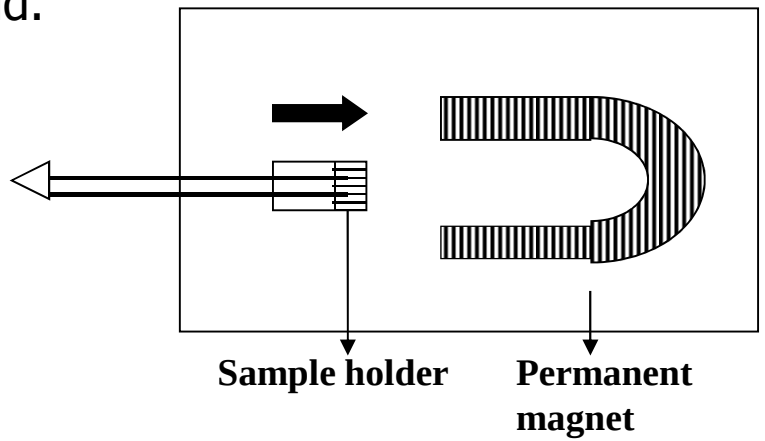
f.guillou@tudelft.nl

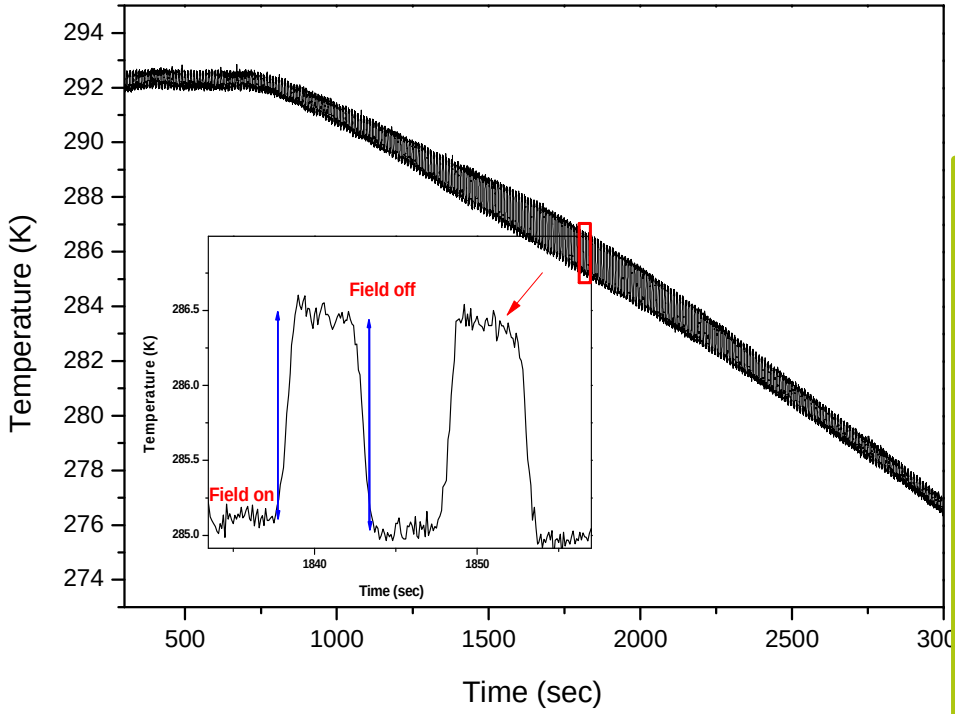
Thanks a lot in advance !

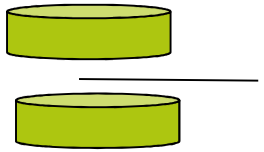
BASF Direct ΔT_{ad}

- Moving samples in and out of a magnetic field.
- Magnetic field: permanent magnet 1.1T.
- Sample size: Ø10 × 1-2 mm
- Temperature range 250 K ~ 320K.
- Sweeping mode: Quasi-adiabatic condition

Sweeping mode







a=b and c/a= 0,15
L/4π=M/4π= 0,10 and N/4π= 0,8 (Osborn tables)

With M_{FM}=7,2 10^5 ; M_{PM}=1,2 10^5 Am^{-1}

"B_{int} " = 1,04 T

ΔT_{ad} are "underestimated" by 5,4%