Pressure effects on the thermal hysteresis in MnFe(P,Ge) compounds

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Delft days on magnetocalorics, 31 Oct. 2008

- Introduction

Experimental results

- Theoretical model and Experimental results

- Conclusions

Pressure

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Tuning of molar volume

⇩

Modification of intermolecular interactions

⇩

Destabilization of intermolecular bonds

⇩

Phase transitions

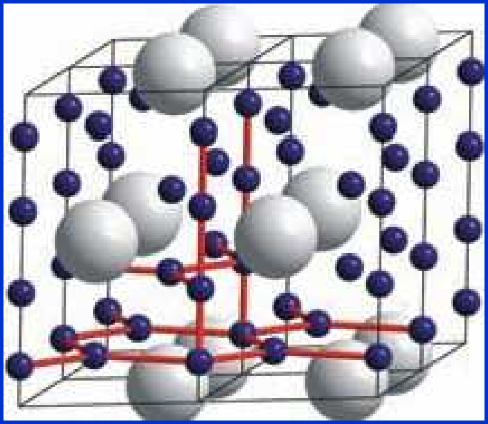
Examples: Pressure effect

Iron becomes superconductor(<2 K): 10-30 GPa

Hydrogen becomes metal: 400 GPa
(static pressure 1 Matm, dynamic pressure 10 Matm)

Silane becomes Superconductor: 50 GPa

SiH_4



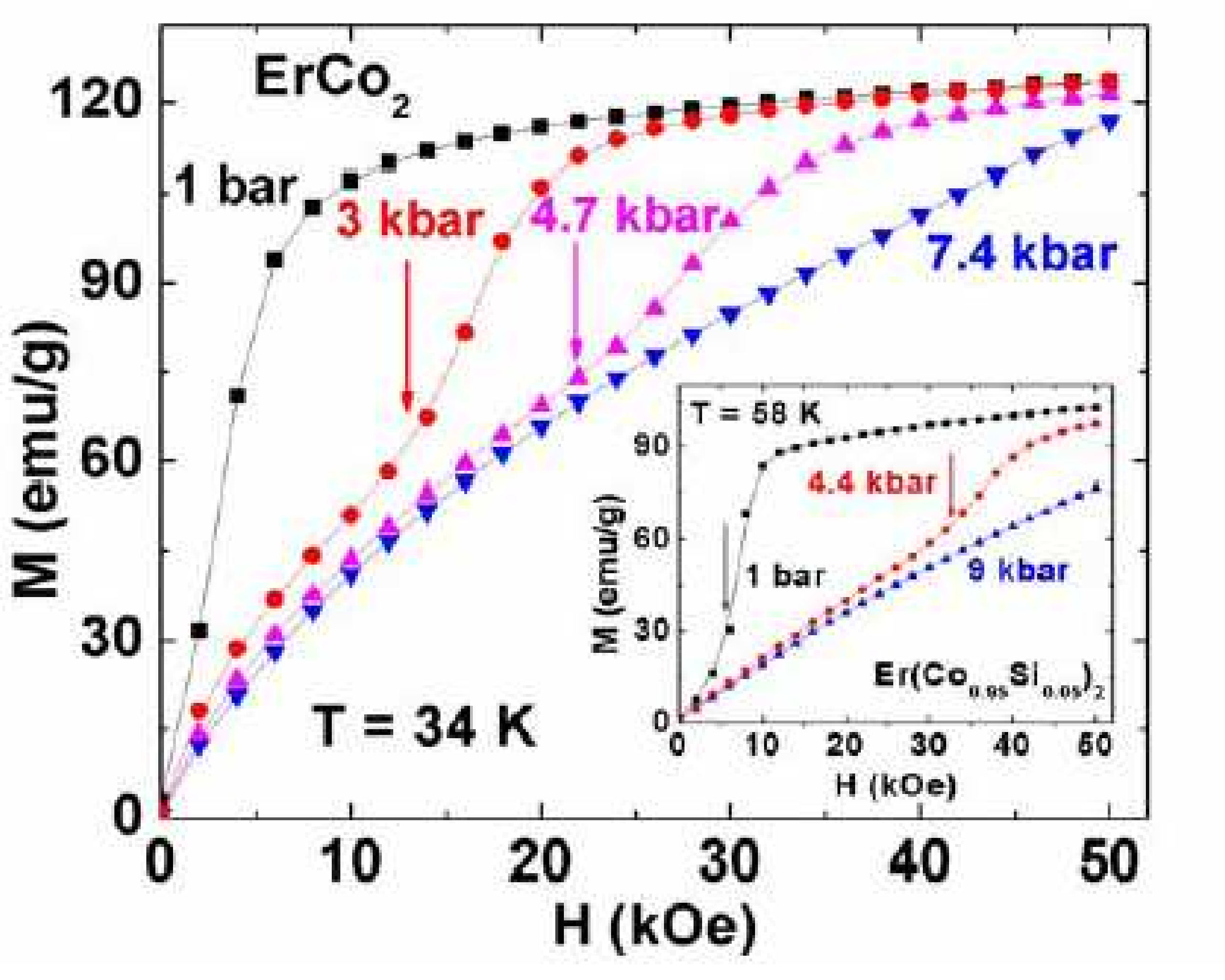
Effects of pressure on magnetism

Pressure effects on magnetization

$ErCo_2$

1storder phase transition

$T_c = 32$ K

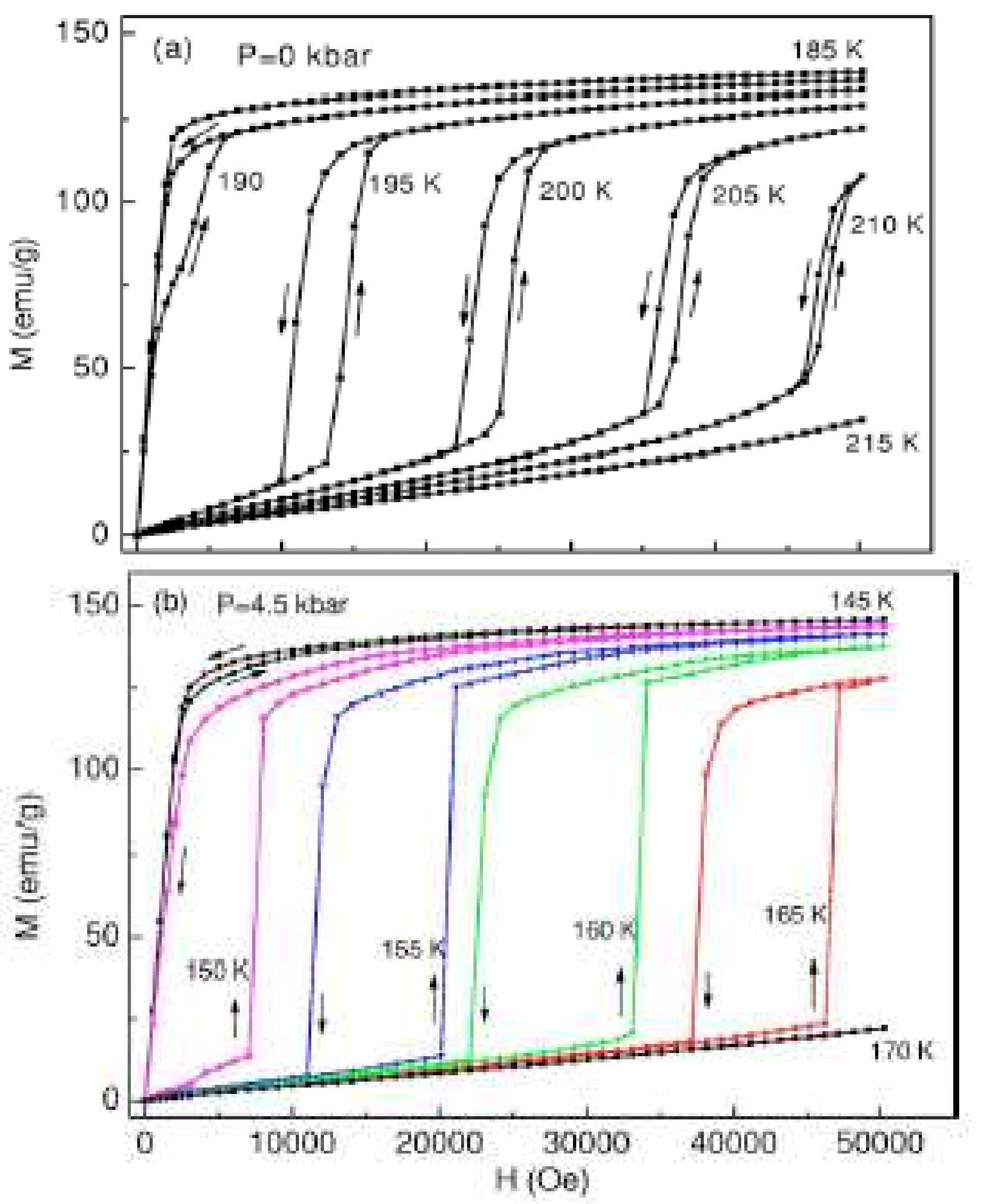


$\mathrm{LaFe_{11.6}Si_{1.4}}$

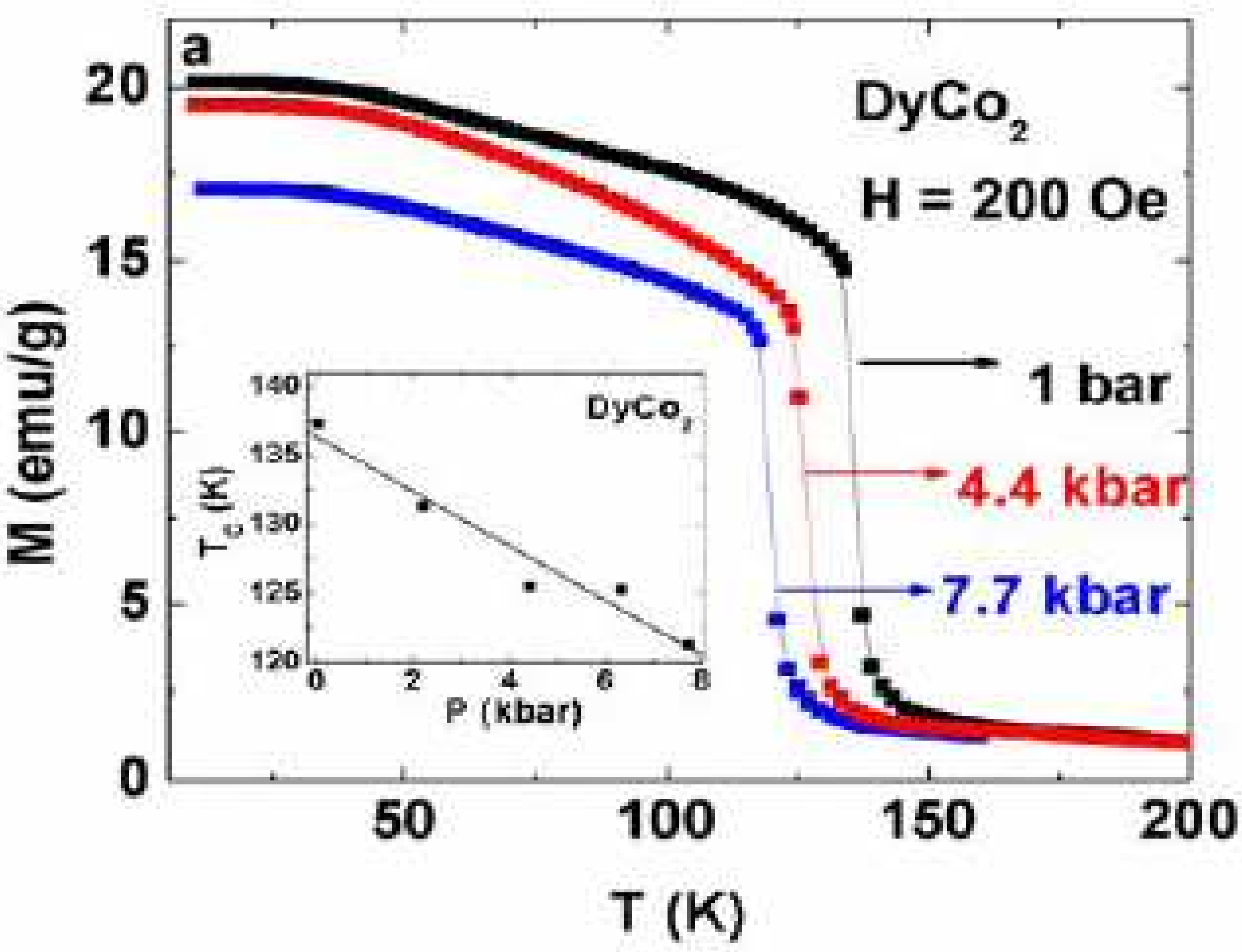
P = 0 kbar

P = 4.5 kbar

1st order phase transition



Pressure effects on exchange interactions

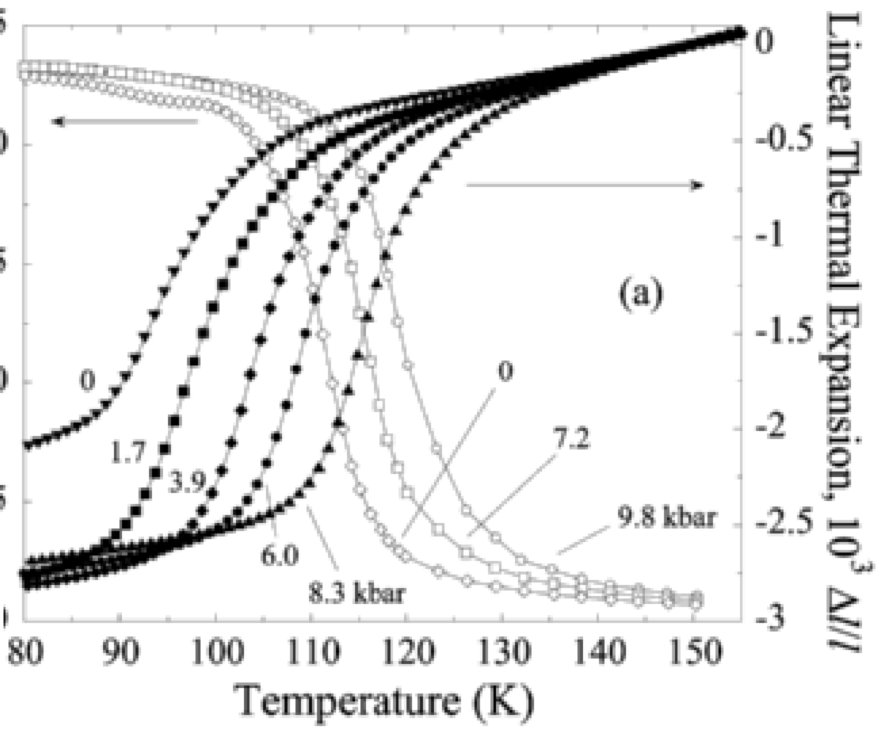


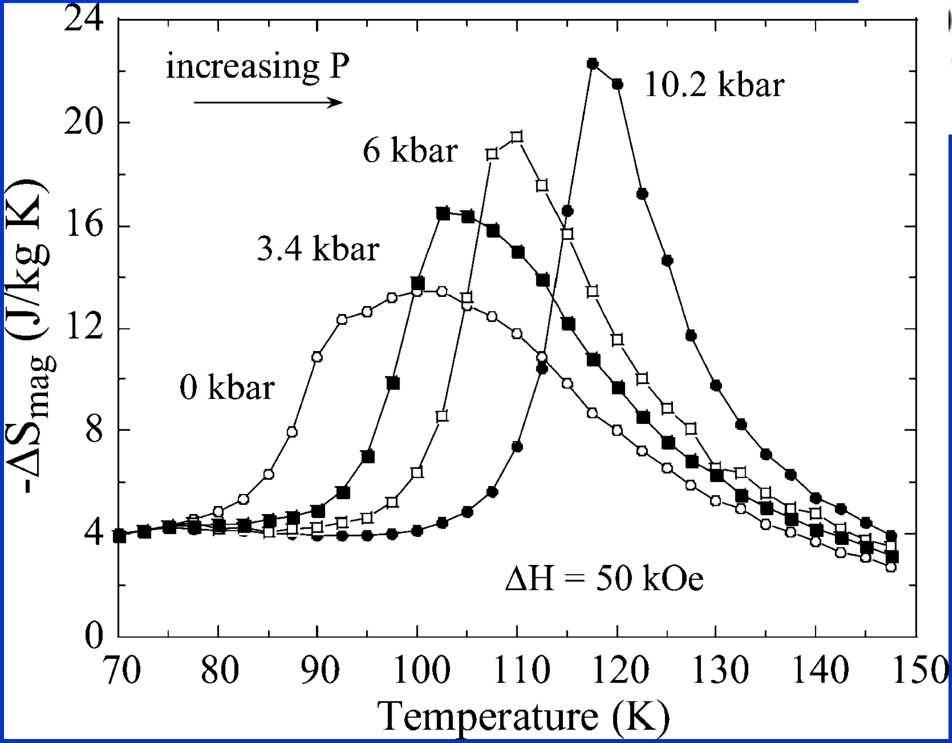
T_h decreases with increasing p

$Tb_5Ge_2Si_2$

1st order phase Transition

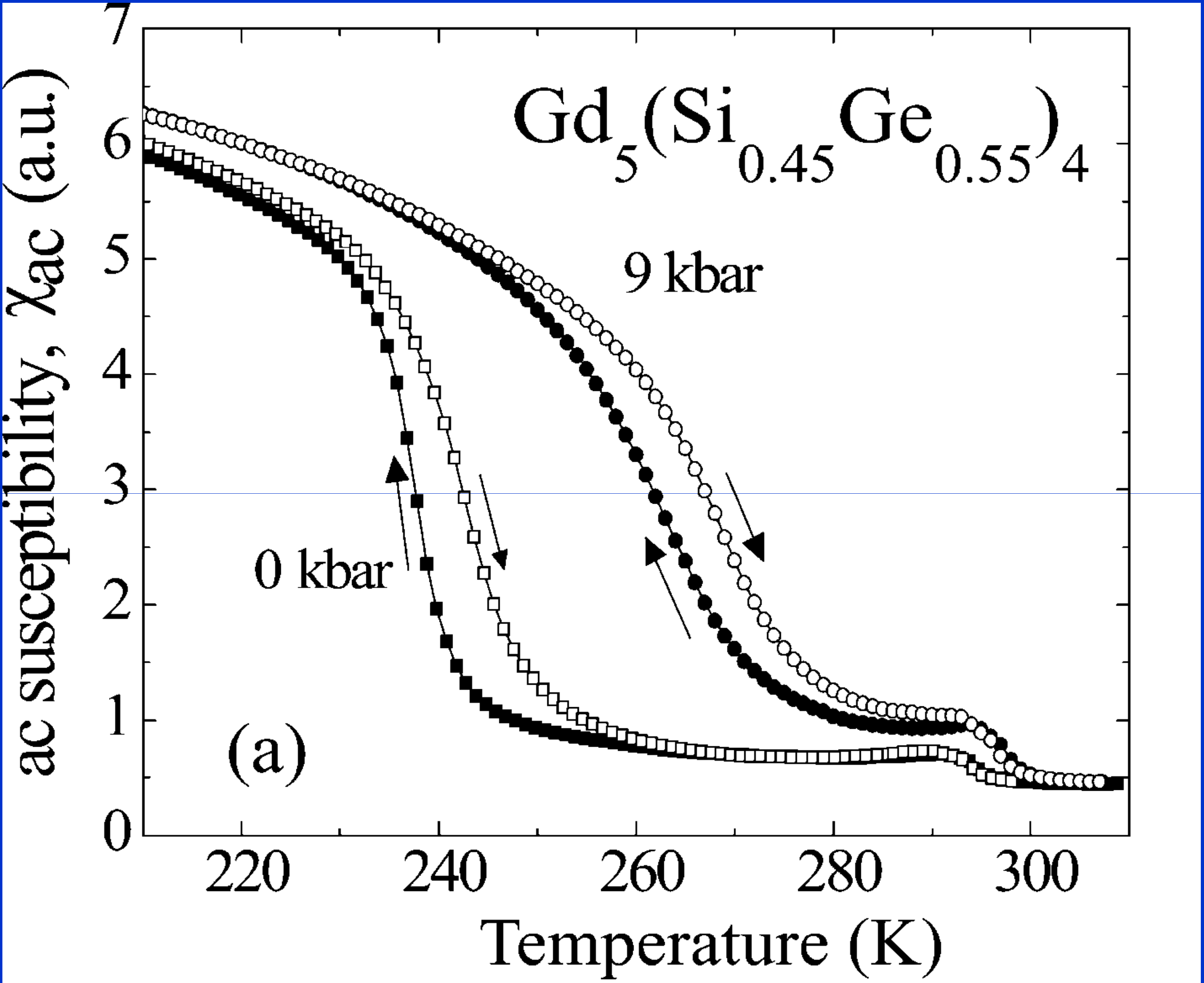
T_c = 105 K





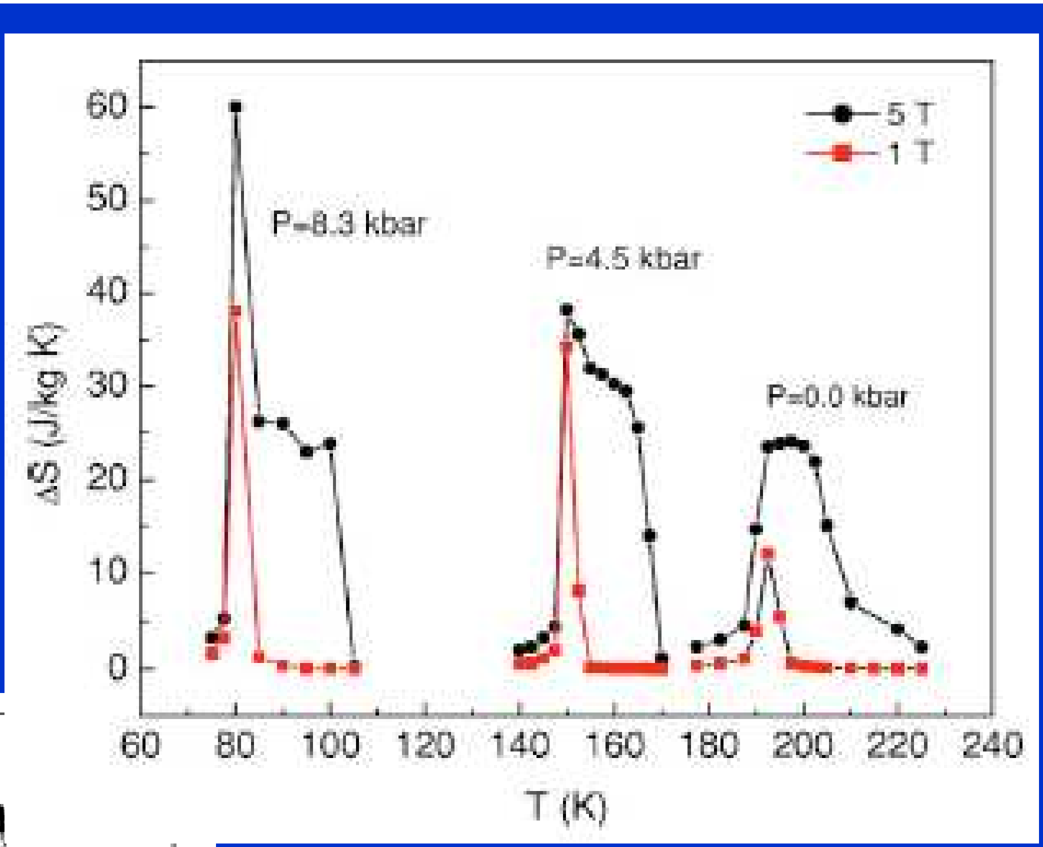
dT_C/dp = 2.64 K/kbar

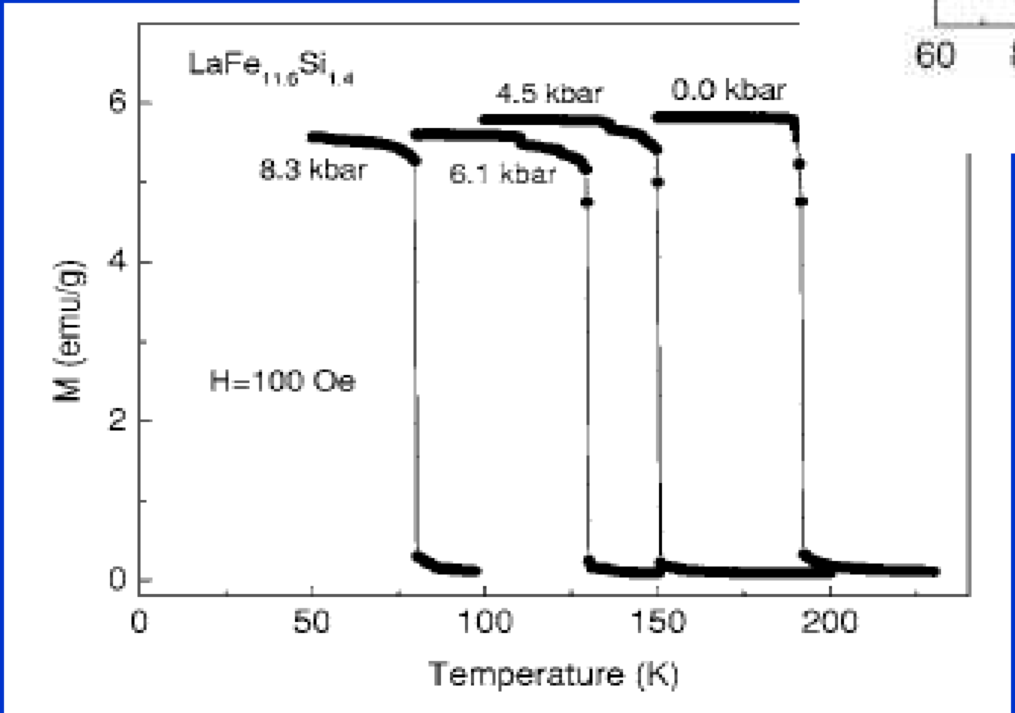
Morellon *et al. PRL 93(2004)*



$dT_C/dp = +3.0$ K/kbar

$LaFe_{11.6}Si_{1.4}$





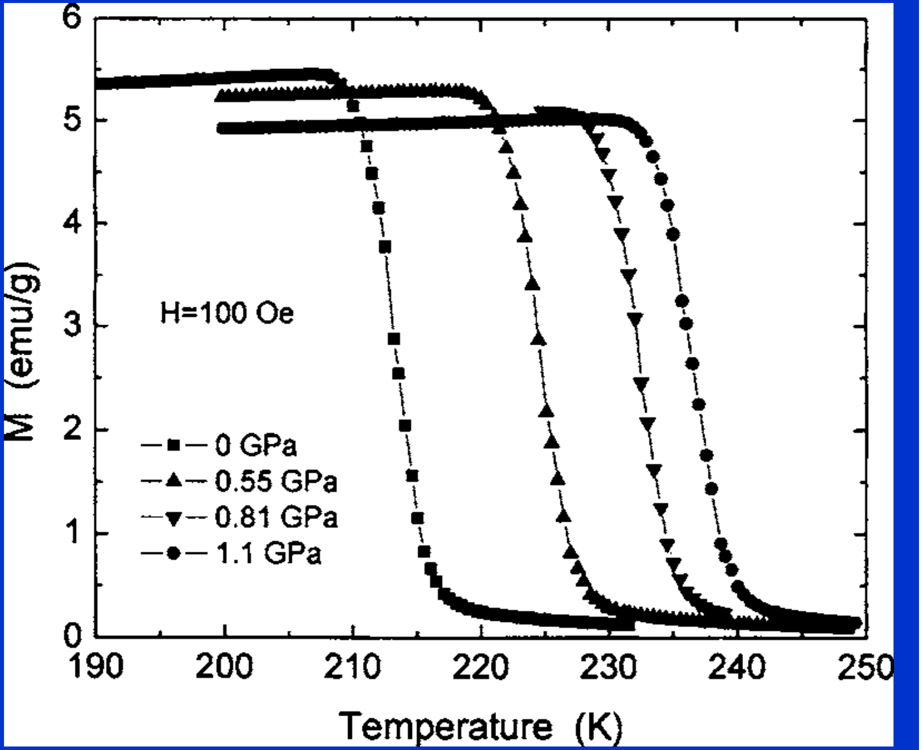
Curie temperature becomes lower!

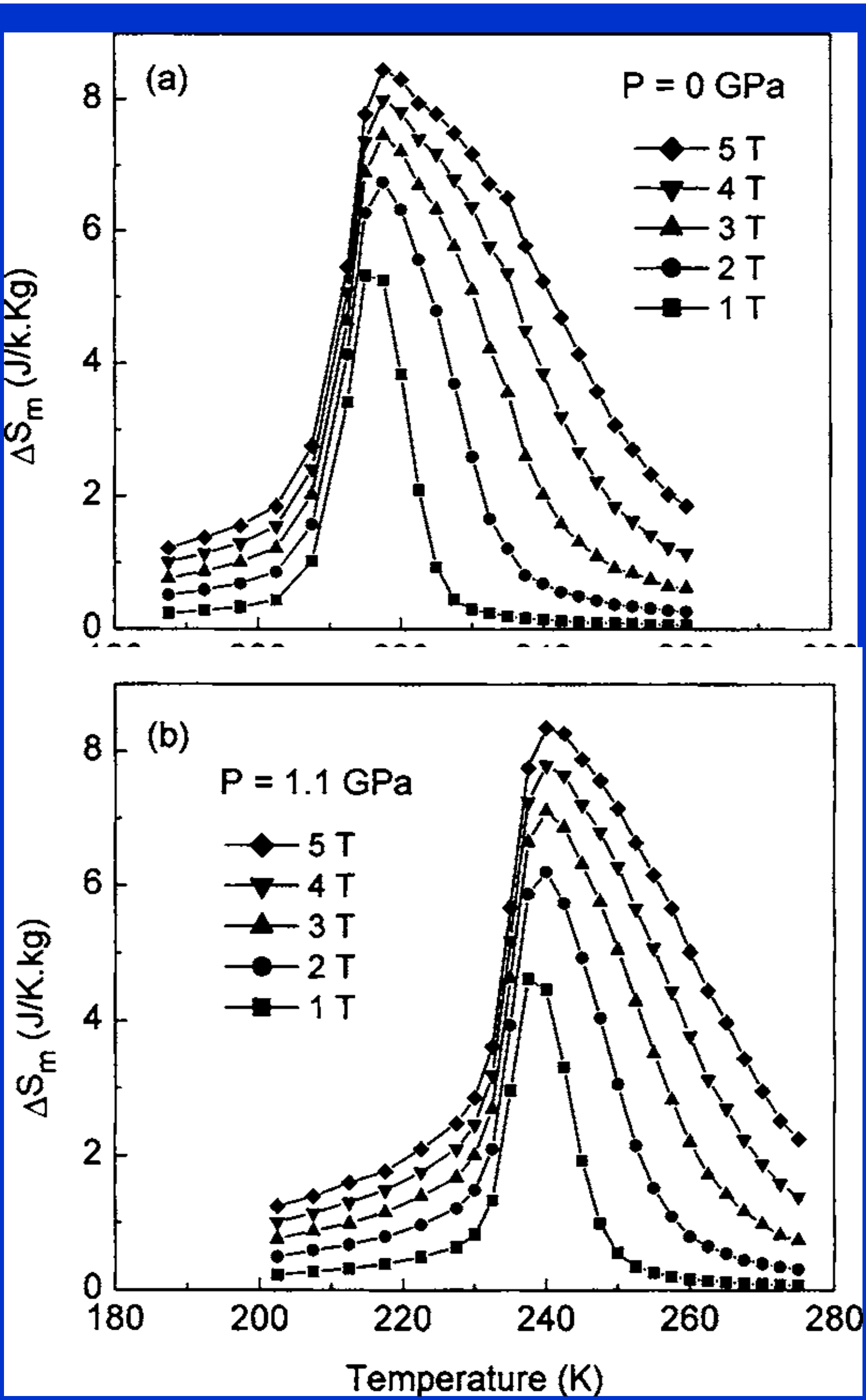
MCE becomes higher!

(La,Ca)MnO$_3$

T$_h$ increases with *p*

Y. Sun et al. APL 88 (2006)



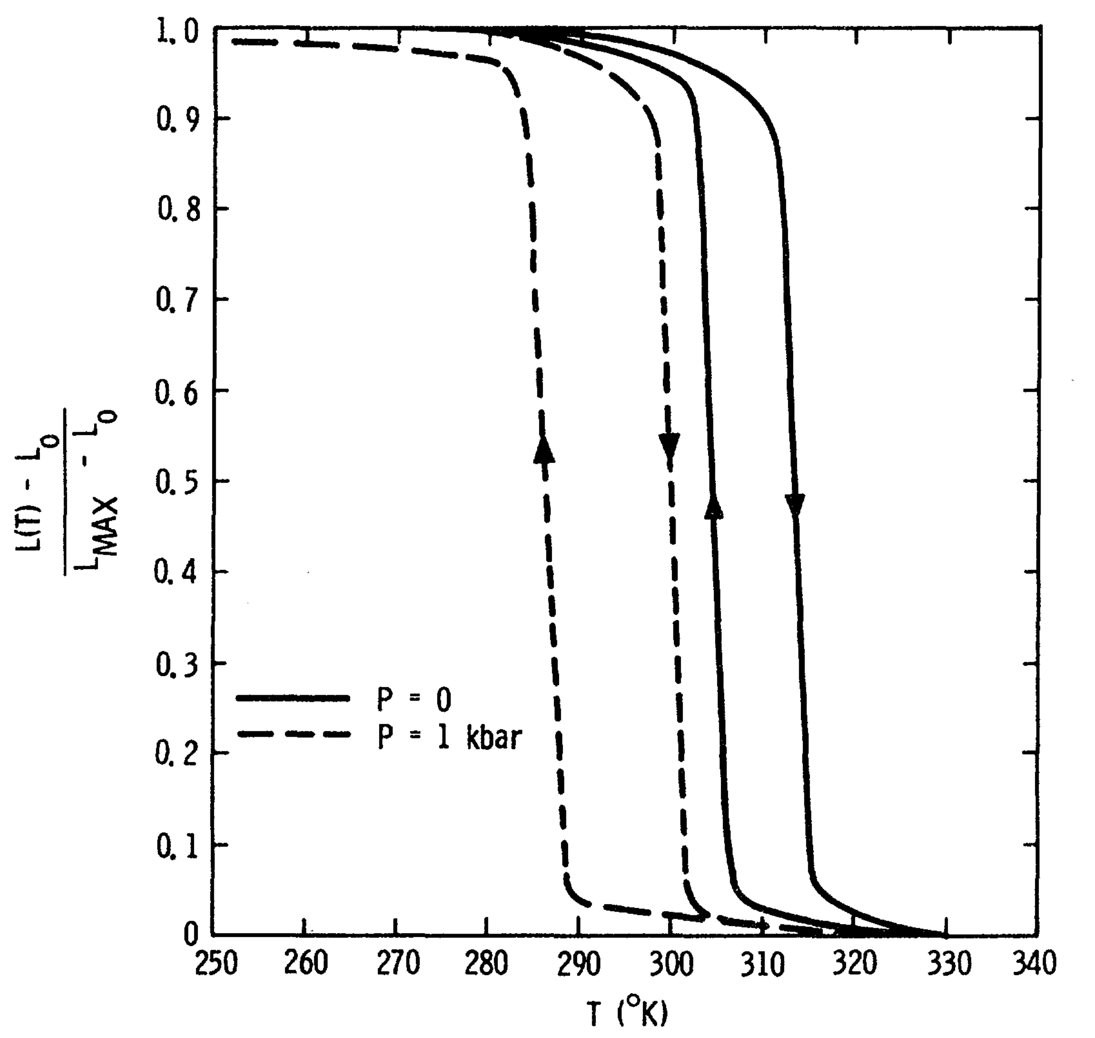


$MnAs_{0.9}Sb_{0.1}$

Hex. FM

Orthor. PM

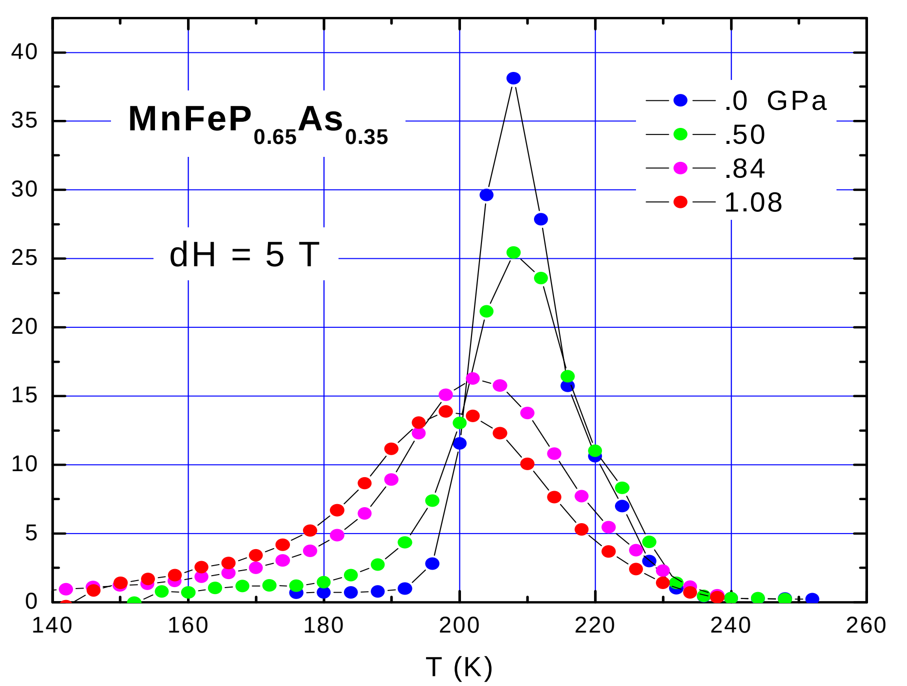
dT_c/dp = - 3.0 K/kba

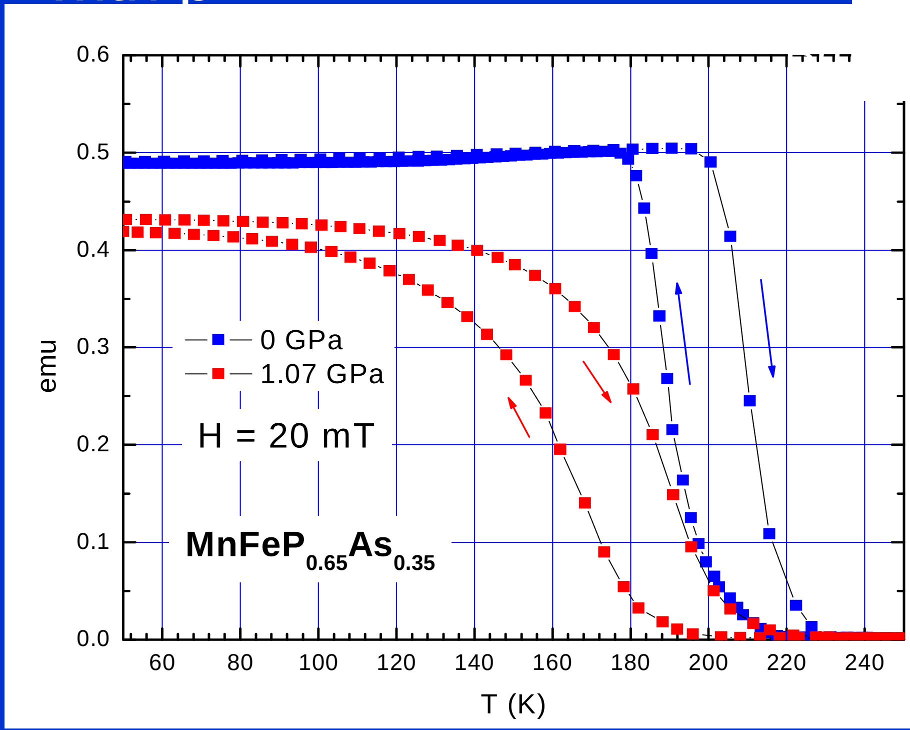


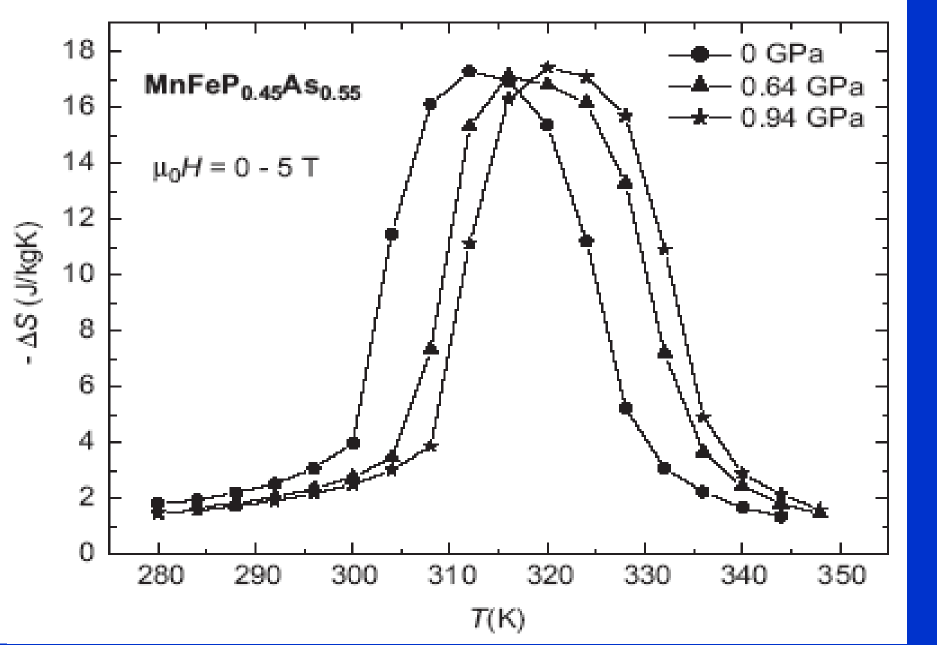
Edwards PRB (1972)

Pressure effect on
MnFe(P,As)
Brück et. al.

$MnFeP_{0.65}As_{0.35}$
dT_c/dp decreases with p
$MnFeP_{0.45}As_{0.55}$ increases with p







To summarize

compound	T_c (K)	dTc/dp (K/GPa)
$Ni_{2.15}Mn_{0.85}Ga$	335	4.7
$ErCo_2$	33	-16.6
$Gd_5Si_2Ge_2$	276	30
$MnAs_{0.9}Sb_{0.1}$	>300	-30
$La_{0.69}Ca_{0.31}MnO_3$		21.4
$La(FeSi)_{13}$		-90
MnFe(P,Ge)		negative

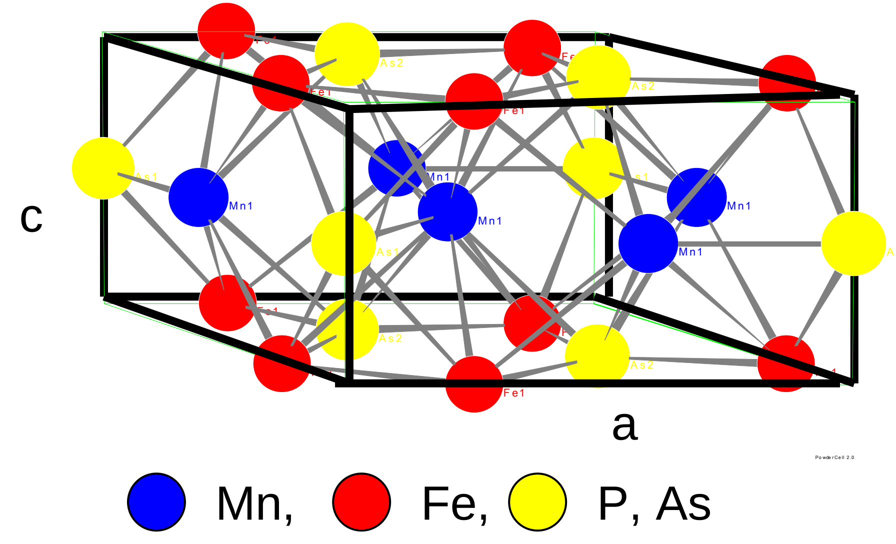
dT_C/dp depends on pressure

Thermal hysteresis also depends on pressure.

$MnFeP_{1-x}As_x$ compounds

- $MnFeP_{1-x}As_x$ (0.2 < x< 0.66)
  - Hexagonal Fe_2P-type structure

    Zach et al. (1990)
  - A first order transition from FM to PM state with a hysteresis at T_C.
  - No structural change



- X ~ 0.5: T_C ~ RT

- A large magnetocaloric effect at RT --> magnetic refrigerant

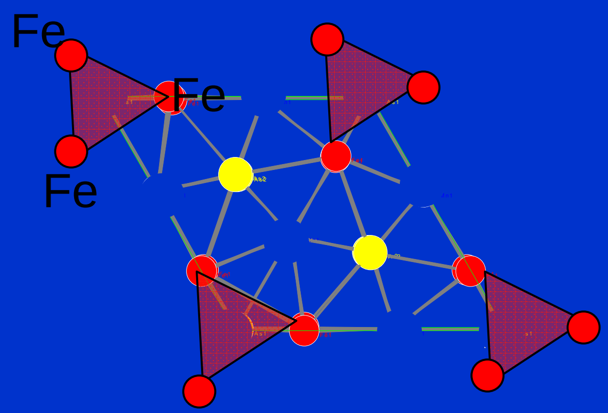
Tegus et al. Nature 415 (2002) 150.

$MnFeP_{1-x}As_x$ compounds

Magnetic moments in $MnFeP_{0.5}As_{0.5}$

- Neutron diffraction Bacmann et al. (1994)

Magnetic moments at 200 K
Mn: $m_{Mn} = 2.02\ \mu_B$ Fe : $m_{Fe} = 1.48\ \mu_B$



in c-plane

- Band structure calc. by Yamada & Terao (2002)

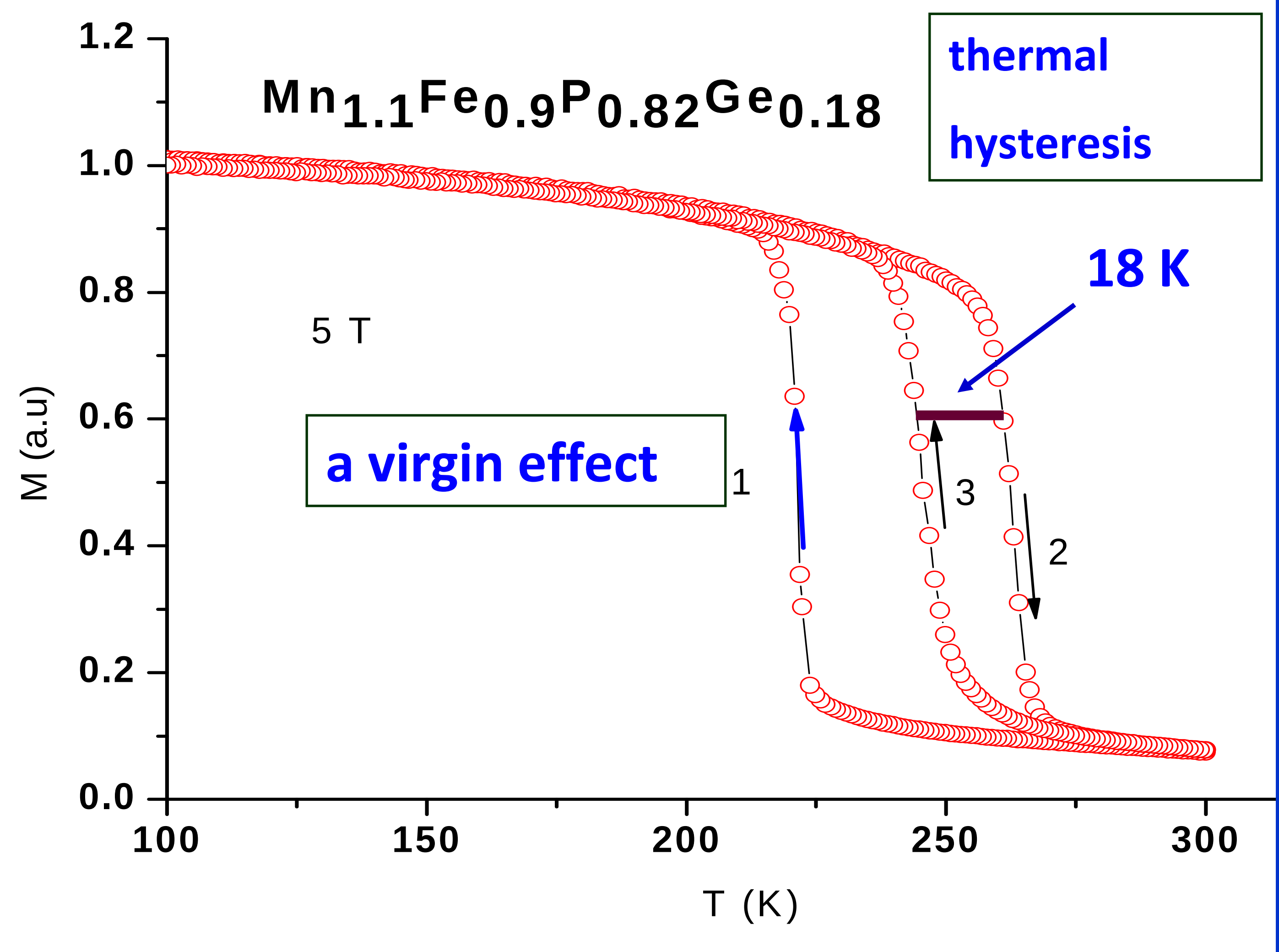
  - hybridization of Fe(3d)-Fe(3d) in c-plane
    --> suppresses (unstable) m_{Fe}
  - (interlayer) hybridization of Fe(3d)-Mn(3d)
    --> enhances (stable) m_{Fe}

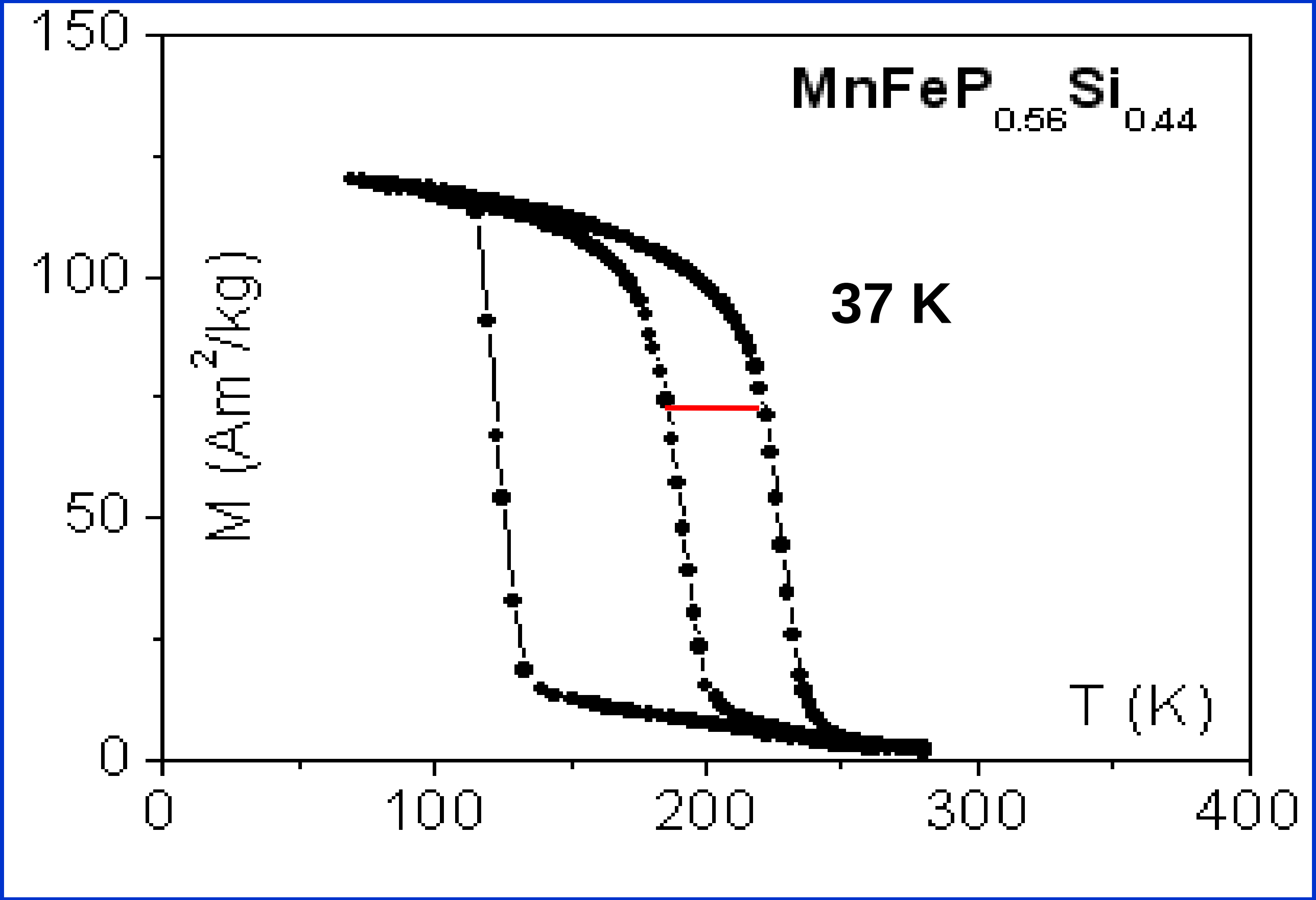
Applying pressure

a decreases and *c* increases → FM state becomes unstable

Problems & Purpose of this study

MnFe(P,As) → MnFe(P,Ge) → MnFe(P,Si)





Cam
Thanh
et. al.

1. **New phenomenon: low transition point, irreversible, why?**

2. **Large thermal hysteresis, what is the mechanism?**

Theoretical model

including the coupling between the strain and magnetization

Gibbs free energy of the system

$$g = g_0 + A\sigma^2 + B\sigma^4 + C\sigma^6 + D\omega\sigma^2 + E\omega\sigma^4 + p\omega + \frac{1}{2K}\omega^2$$

σ **: spontaneous magnetization,**
ω **: relative volume change,**
K: **the compresibility,**
p: **applied pressure.**

$$\omega = \frac{V - V_0}{V_0}$$

***A*, *B*, and *C* are the Landau coefficients**

***D* and *E* represent coefficients of the third and fifth order coupling between strain and magnetization.**

The equilibrium conditions

$$\frac{\partial g}{\partial \sigma} = 0$$

$$A + 2(B + E\omega)\sigma^2 + 3C\sigma^4 + D\omega = 0$$

$$\frac{\partial g}{\partial \omega} = 0$$

$$p + \frac{\omega}{K} + D\sigma^2 + E\sigma^4 = 0.$$

The solution of σ

$$\sigma^2 = \frac{-B' + (B'^2 - 4A'C')^{1/2}}{2C'}$$

where

$$A' = A - DKp$$

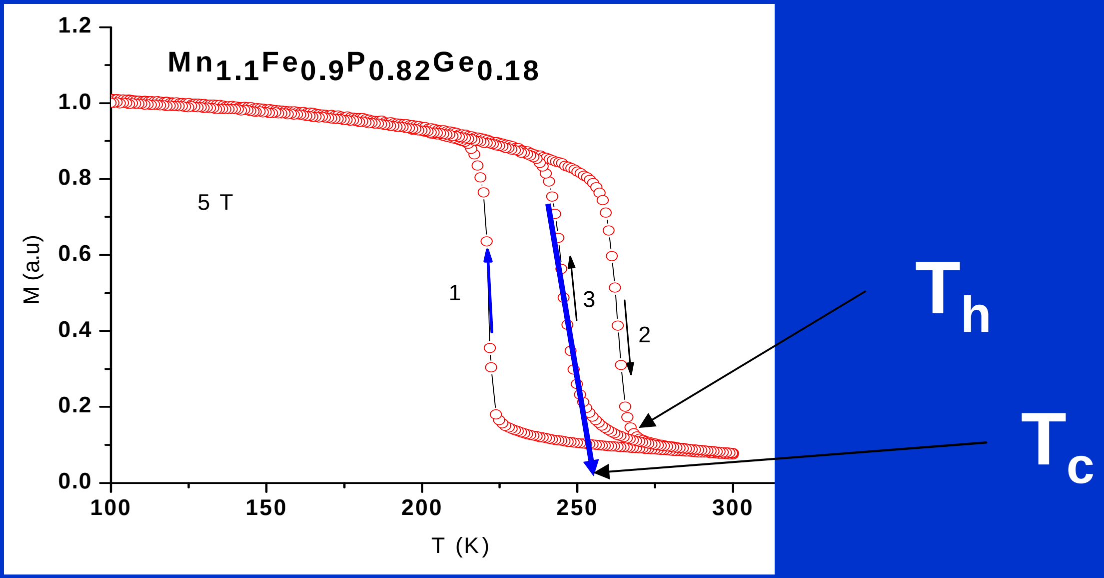
$$B' = 2B - D^2K - 2EKp$$

$$C' = 3(C - EDK)$$

T_0 - At which the theoretical magnetic susceptibility becomes infinite;

T_h - the highest temperature for which
the ferromagneticc phase can exist as a metastable state

T_c - the lowest temperature for which
the paramagnetic phase can exist as a metastable state.

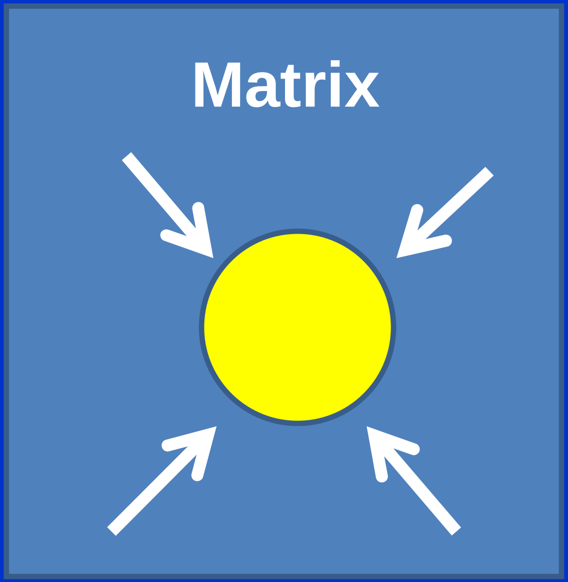


The high-temperature paramagnetic phase remains metastable until $A' = 0$, taken $A = A_0(T-T_0)$

$$T_c = T_0 + \frac{DK}{A_0} p \qquad \frac{dT_c}{dp} = \frac{DK}{A_0}.$$

T_c linearly depends on pressure
If DK > 0 T_c increases with *p*
If DK < 0 T_c decreases with *p*
If D = 0 T_c = $T_{0,}$ no *p* dependent.
Experiment show that T_c depends on P, therefore, D ≠ 0, indicating third-order coupling between strain and magnetization should exist.

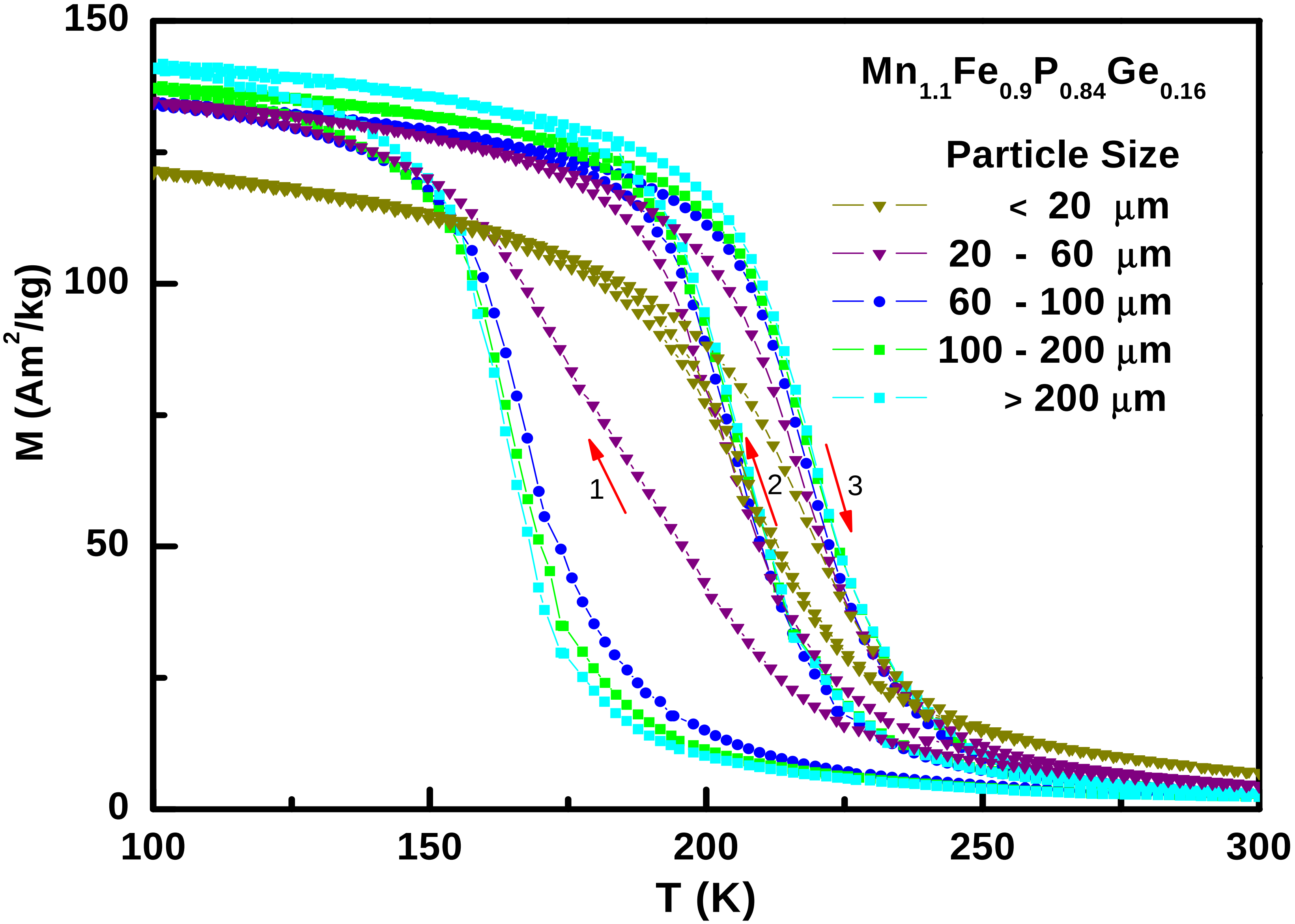
A possible explanation of the virgin effect



$$T_c = T_0 + \frac{DK}{A_0} p$$

DK < 0

Misfit strain exists.
Additional elastic energy
Product phase becomes powder, or occurs microcracks
Release misfit strain, disconnected
Only exist in cooling, and once!



$Mn_{1.1}Fe_{0.9}P_{0.84}Ge_{0.16}$
Particle Size
< 20 μm
20 - 60 μm
60 - 100 μm
100 - 200 μm
> 200 μm
1
2
3
150
100
50
0
M (Am^2/kg)
100
150
200
250
300
T (K)

The low-temperature ferromagnetic phase remains metastable until $B'^2 = 4A'C'$

$$T_h = T_c + \frac{(2B - D^2K - 2EKp)^2}{12A_0(C - EDK)}$$

T_h is not linearly dependent on p.

If E = 0

$$T_h = T_c + \frac{(2B - D^2K)^2}{12A_0(C - EDK)} = T_0 + \frac{(2B - D^2K)^2}{12A_0C} + \frac{DK}{A_0}p$$

Then T_h also linearly depends on p

The spread of the thermal hysteresis

$$\Delta T = T_h - T_c = \frac{(2B - D^2K - 2EKp)^2}{12A_0(C - EDK)}$$

P **dependent**

If E = 0

$$\Delta T = T_h - T_c = \frac{(2B - D^2K)^2}{12A_0C}$$

P **independent**

E ≠ 0 ; indicates the fifth order coupling between the strain and magnetization should exist.

The pressure dependence of the thermal hysteresis is caused by the fifth order coupling between the strain and the magnetization.

When p = 0, then

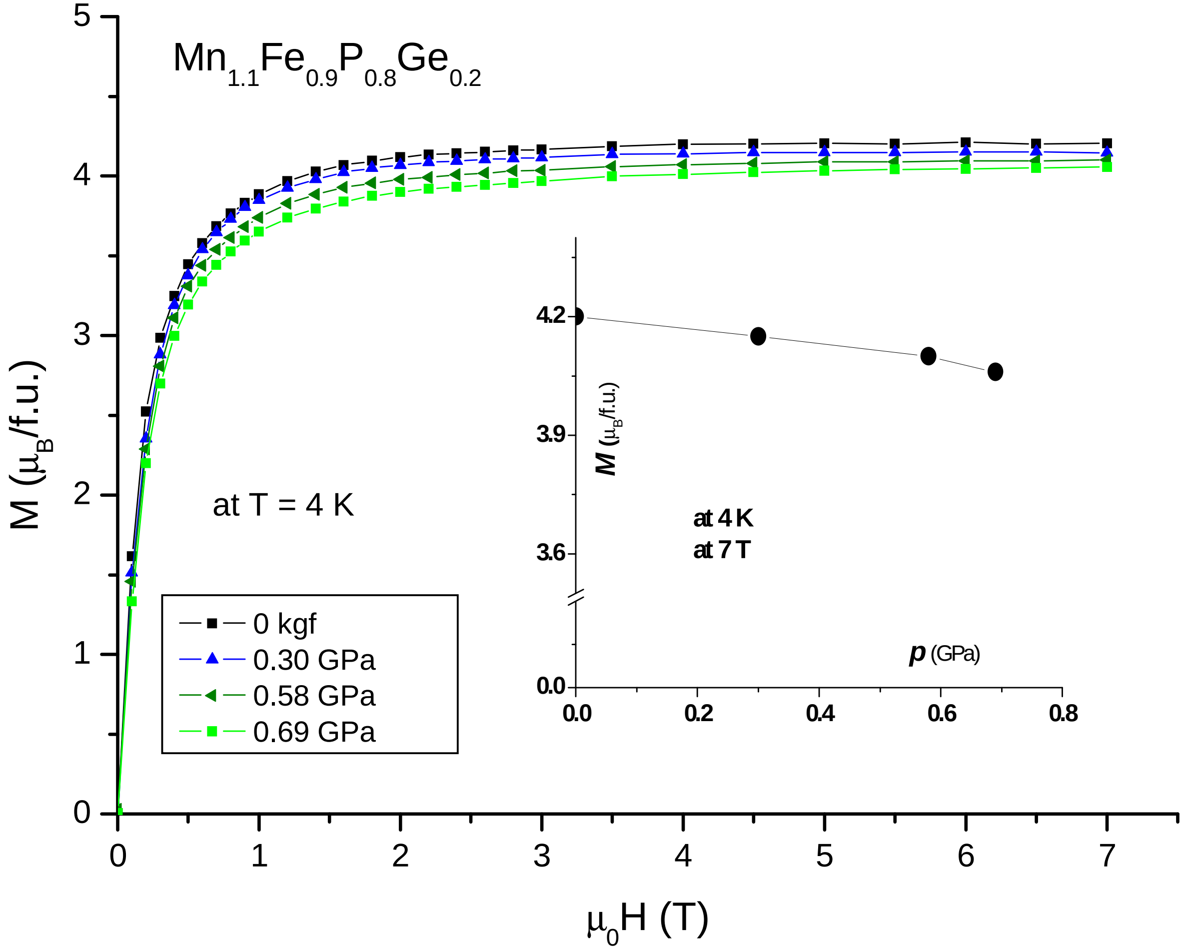
$$\Delta T = T_h - T_c = \frac{(2B - D^2 K)^2}{12A_0(C - EDK)}$$

Without coupling between strain and magnetization

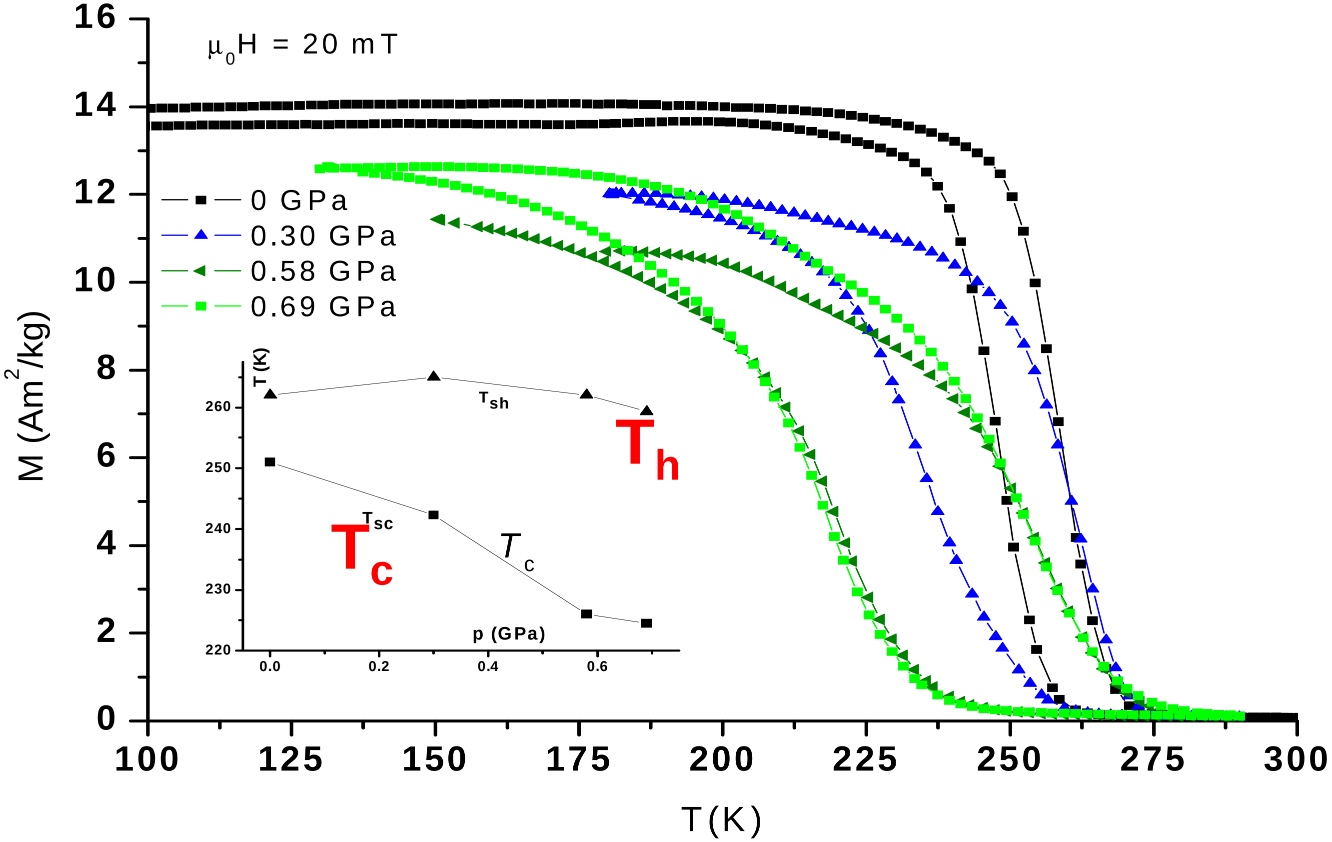
$$\Delta T = T_h - T_c = \frac{B^2}{3A_0 C}$$

Experimental results

Pressure effect on magnetization



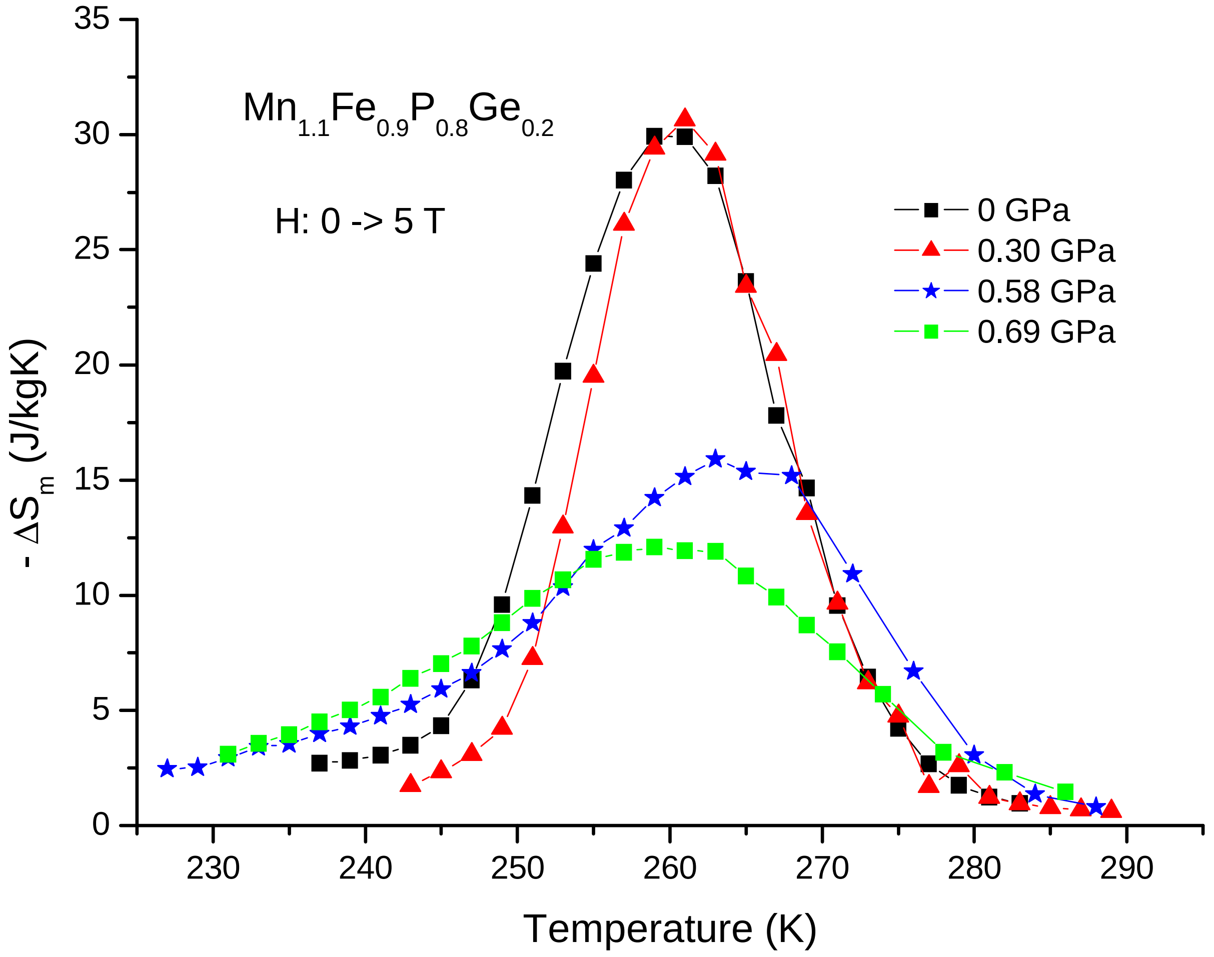
Pressure effects on thermal hysteresis



$$T_c = T_0 + \frac{DK}{A_0} p$$

$$T_h = T_0' + \alpha p + \beta p^2$$

Pressure effects on MCE



Conclusions

1. The T_c, M, ΔS_m decrease with increasing pressure

2. The thermal hysteresis increases.

3. These pressure dependence of the behaviors can be understood in the framework of Landau theory, but the Gibbs free energy should include the third and fifth order couplings between strain and magnetization.

4. The third order coupling leads to a decrease of T_c and the fifth order coupling results in the increase of thermal hysteresis.

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Thank you for your attention!