Phase transitions
Experimental studies on magnetic materials

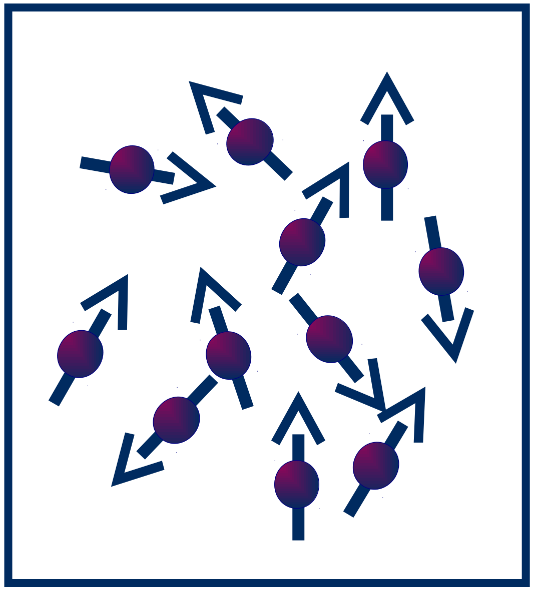
Ekkes Brück, Fundamental Aspects of Materials and Energy, TNW
27-08-11

Outline

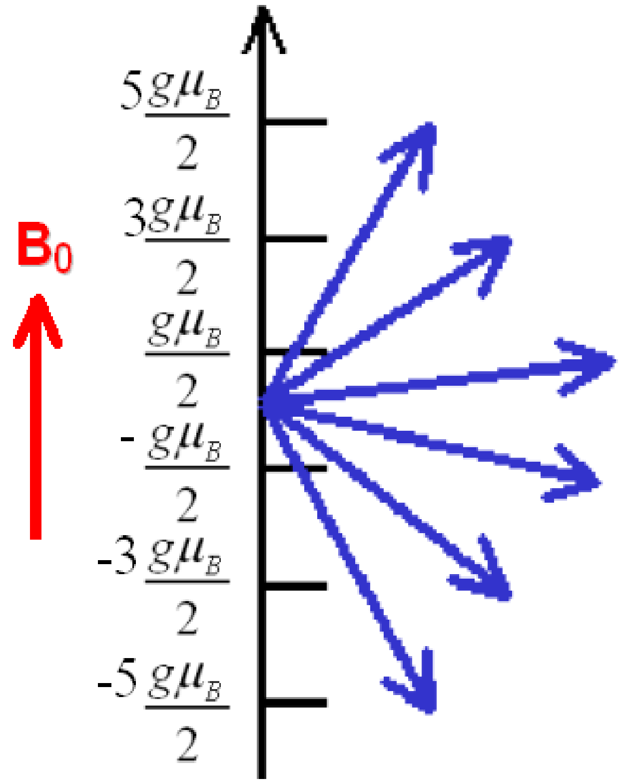
- **Basic magnetics (classical)**
- Origin of first order transition?
- Magnetic materials
- $Gd_5Ge_2Si_2$ magnetic Rare-Earth
- MnFe(P,Si) magnetic transition metals
- $TbFe_4Al_8$ magnetic RE & TM

Magnetization processes

Magnetic (spin) moments



no field
no net moment

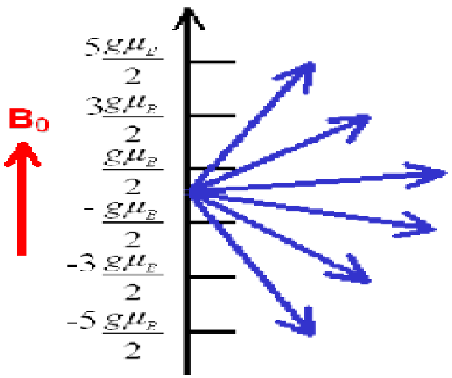


$$e^{-E/k_BT}$$

$- \mu B_0$

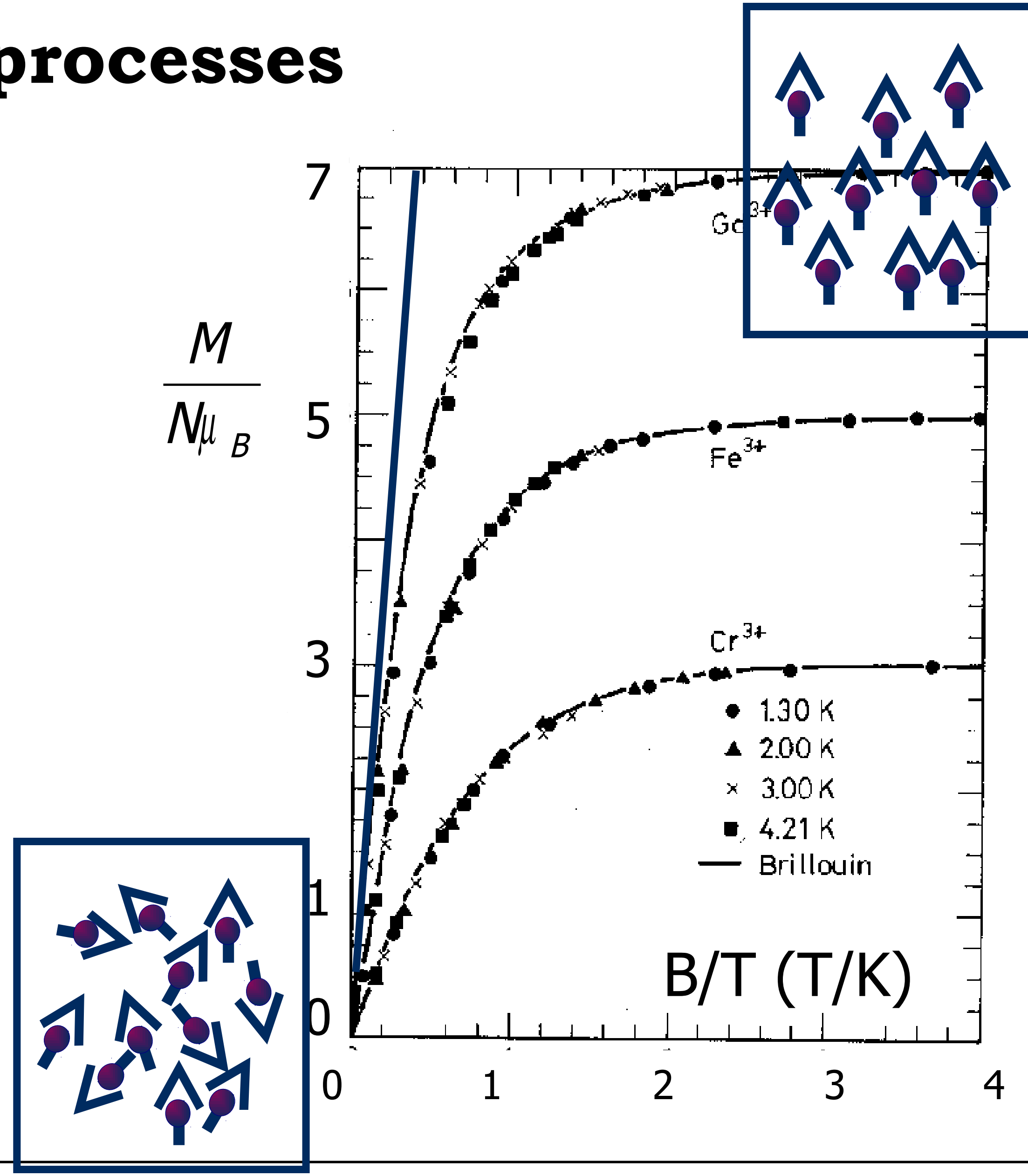
Effect of temperature. Classical statistical physics:
probability of finding atomic dipole in state with energy E:

Magnetization processes



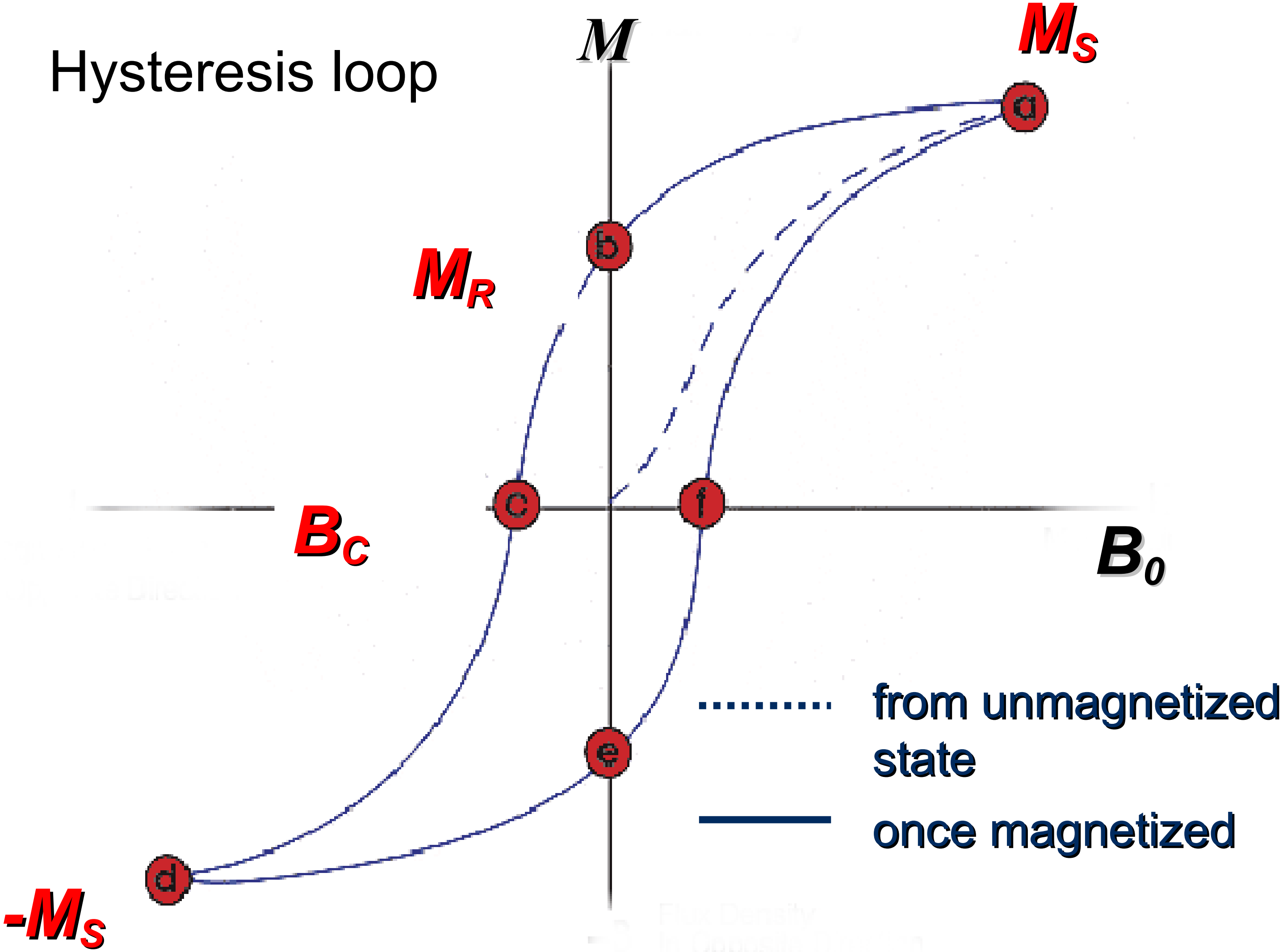
$$e^{-E/k_BT}$$

$-\mu B_0$



Magnetization processes

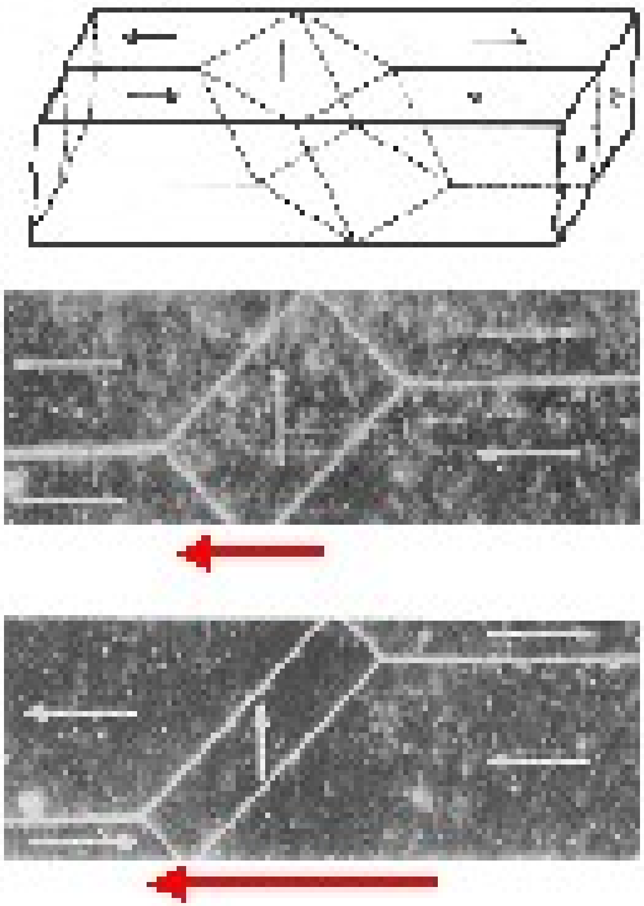
Hysteresis loop

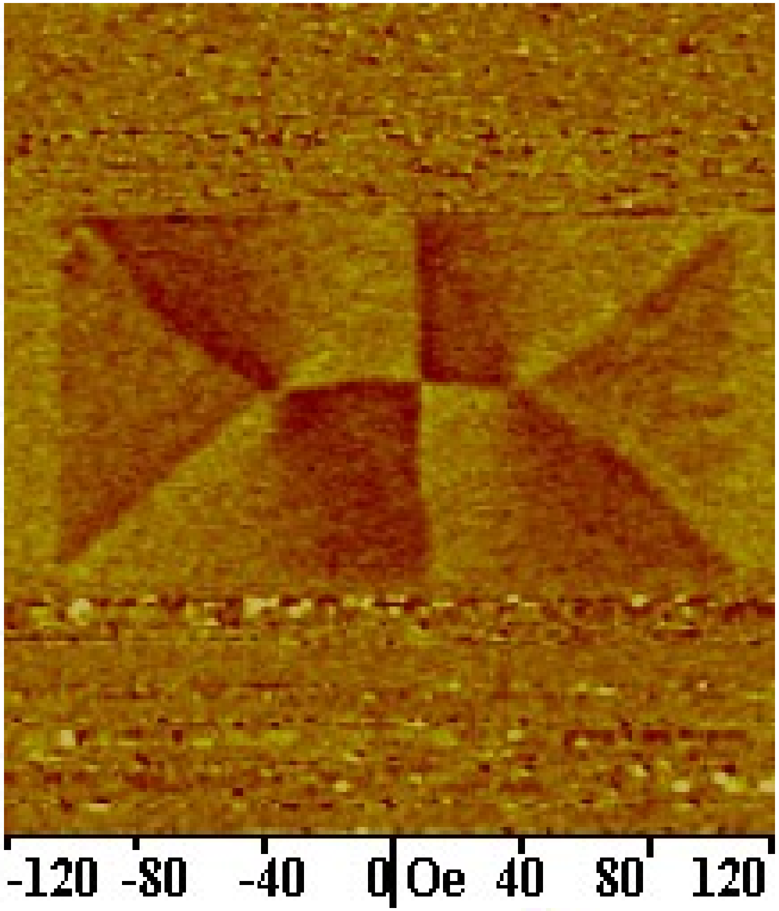


Magnetization processes

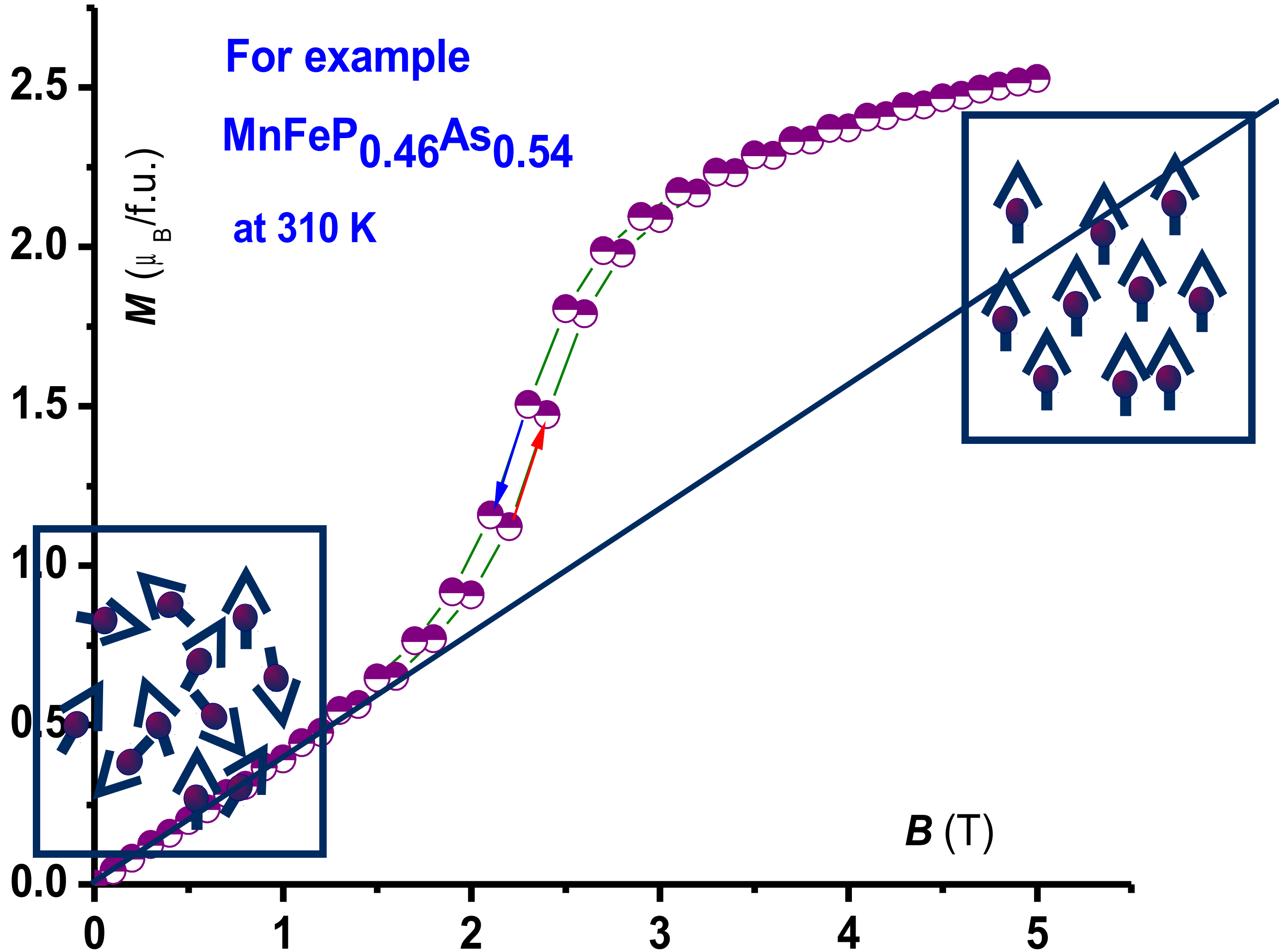
Ferromagnetic domains

www.ee.umd.edu/~rdgomez/permalloy.htm





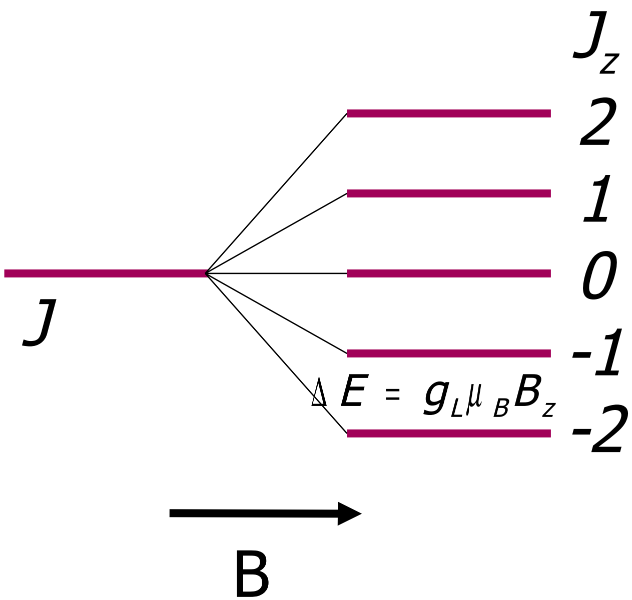
Magnetization processes



Materials with field induced first order phase transition.

Zeeman effect for state with total moment J

- Ground state J is 2J+1 times degenerated: $J_z = -J, -J+1, \ldots J$
  - Splits in magnetic field into sublevels



$$H_P = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z \cdot B$$

$$E = \langle H_P \rangle = g_{Lande} \mu_B J_z B_z$$

$$g_{Lande} = \frac{3}{2} - \frac{L(L+1) - S(S+1)}{2J(J+1)}$$

- Spectroscopic splitting factor g_{Landee} depends on L, S, and J
  - Splitting at B=1 Tesla in the order of meV
- Atom behaves as if it has effective moment: $\mu_{eff} = -g_L \mu_B \mathbf{J}$

Statistical physics description

When a system, in contact with a heat bath at temperature **T** can be in a state with energy **E**, the probability for this is given by the Gibbs rule:

$$p(E) = \frac{e^{-\beta E}}{Z}, \qquad \beta = \frac{1}{kT},$$

where *k* is Boltzmann's constant. **Z** is called the partition sum,

$$Z = \sum_E e^{-\beta E}$$

Z is needed to have the proper normalization

$$\sum_E p(E) = 1.$$

The strength of statistical physics is that by calculating **Z** a lot of information about the system can be derived.

The Helmholtz free energy is:

$$F = U - TS = -kT \log Z$$

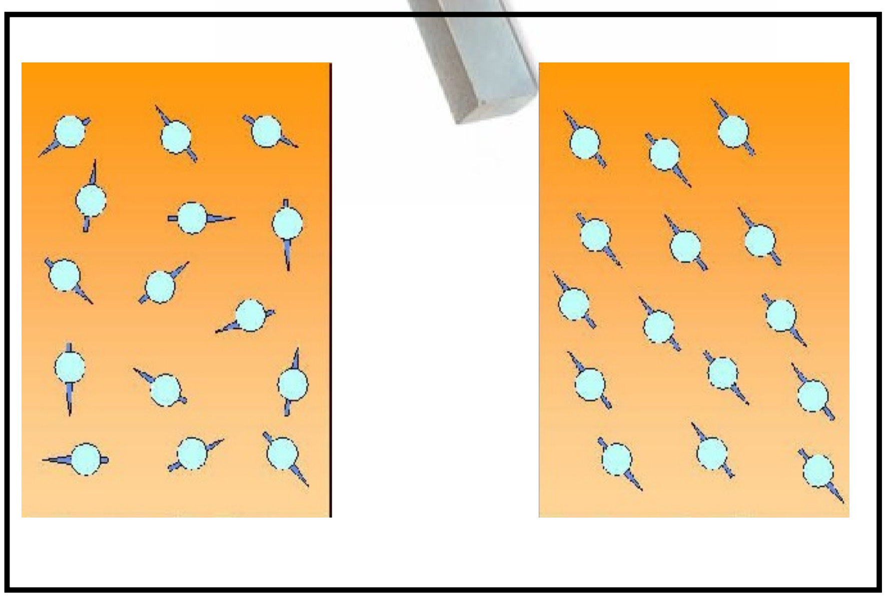
while the Gibbs free energy is:

$$G = U - TS + pV$$

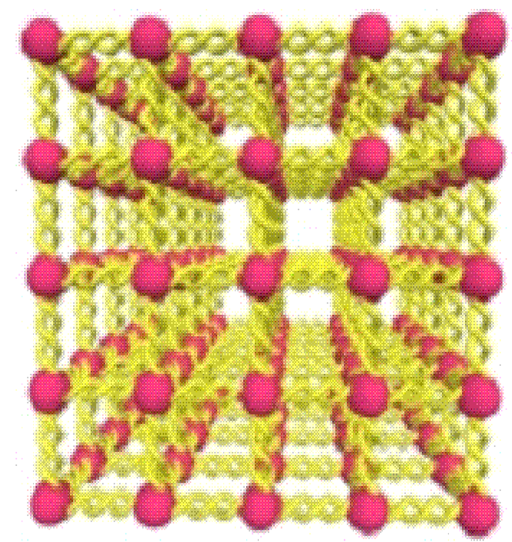
Basic magnetocalorics

Two energy reservoirs

spins → lattice

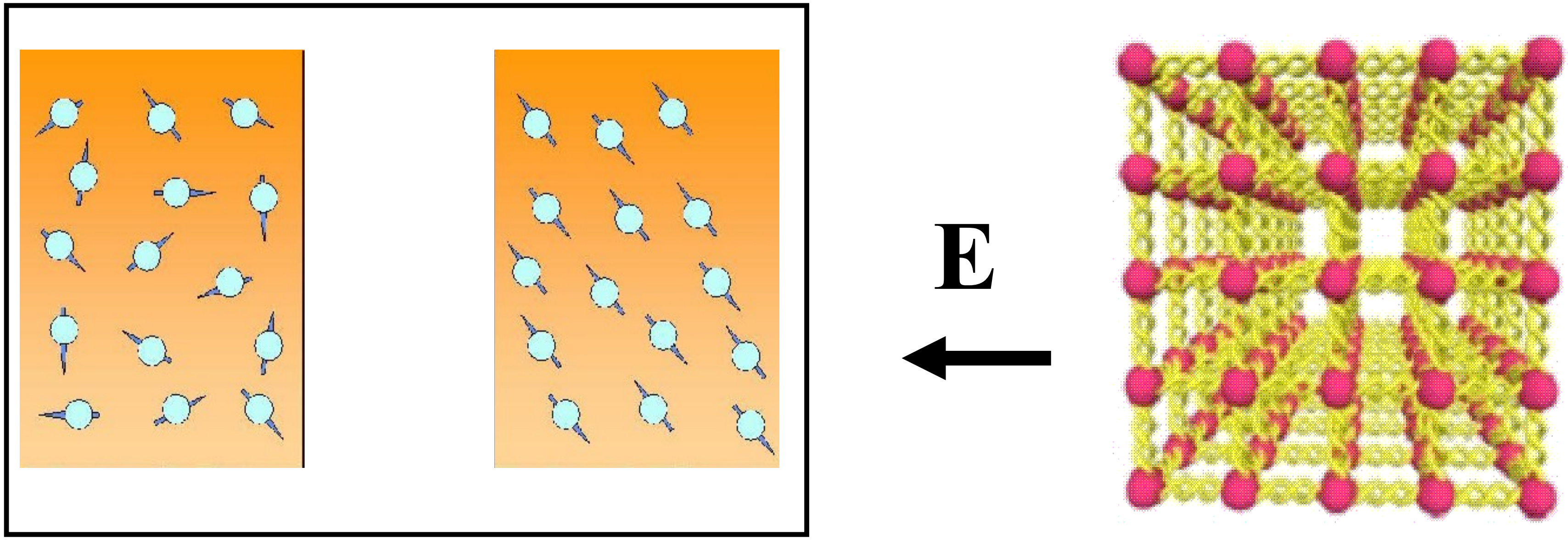


E →



Basic magnetocalorics

spins ← lattice



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.

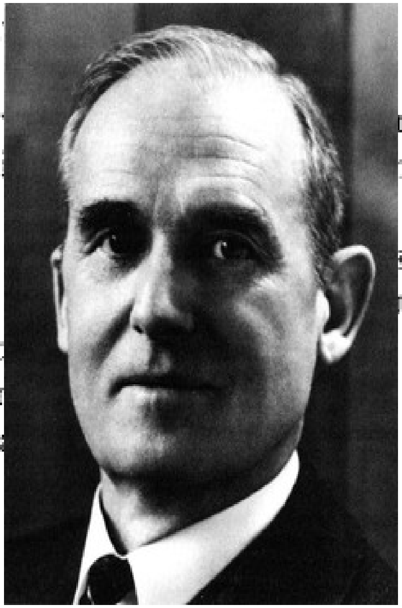
An iron-free solenoid producing a field of about 8000 gauss was used for all the measurements. The amount of $Gd_2(SO_4)_3 \cdot 8H_2O$ was 61 g. The observations were checked by many repetitions of the cooling. The temperatures were measured by means of the inductance of a coil surrounding the gadolinium 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, espec nagnetizations are utilized.

GALL

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



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

Nobel prize 1949

Thermodynamic relations:

Differential of Gibbs free energy

$$S(T,B,p) = -\left(\frac{\partial G}{\partial T}\right)_{B,p},\quad M(T,B,p) = -\left(\frac{\partial G}{\partial B}\right)_{T,p},\quad V(T,B,p) = -\left(\frac{\partial G}{\partial p}\right)_{T,B}$$

Entropy Magnetization Volume

Differential of entropy

$$dS = \left(\frac{\partial S}{\partial T}\right)_{B,p} dT + \left(\frac{\partial S}{\partial B}\right)_{T,p} dB + \left(\frac{\partial S}{\partial p}\right)_{T,B} dp$$

Identification of terms

$$dS = \frac{C_{B,p}}{T} dT + \left(\frac{\partial S}{\partial B} \right)_{T,p} dB - \alpha V dp$$

Adiabatic process at constant pressure

$$dT = -\frac{T}{C_{B,p}} \left(\frac{\partial S}{\partial B} \right)_{T,p} dB$$

Maxwell relations

$$\left(\frac{\partial S}{\partial B} \right)_T = \left(\frac{\partial M}{\partial T} \right)_B$$

Magnetic entropy

$$\Delta S_m = \int_0^B \left(\frac{\partial M}{\partial T} \right)_B dB$$

From definition of specific heat

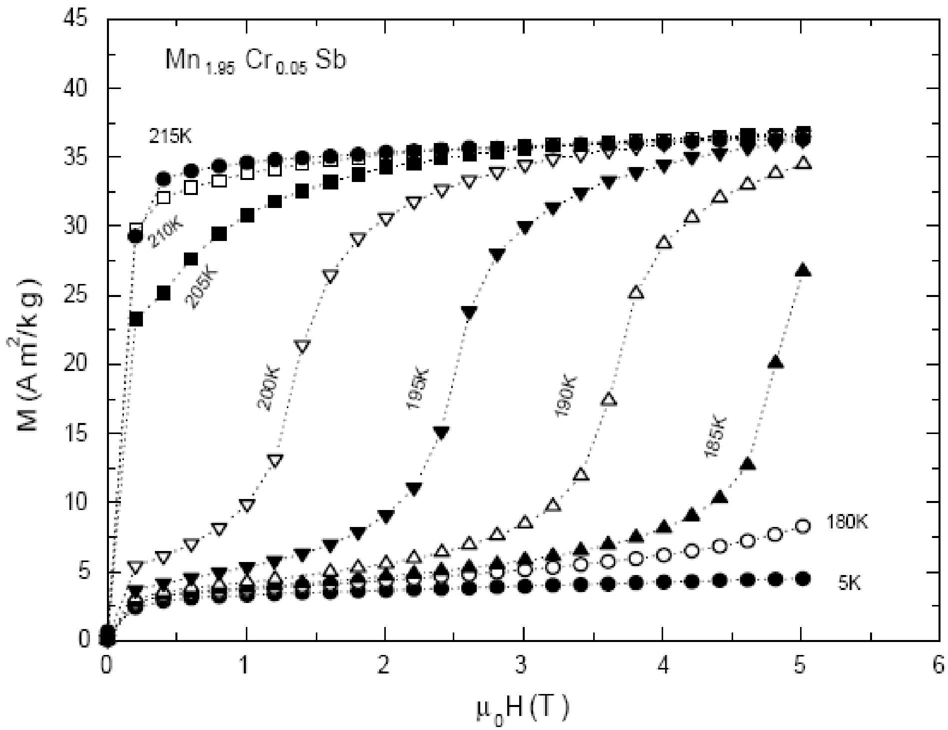
$$S(T,B) = S_0 + \int_0^T \frac{c_p(T',B)}{T'} dT'$$

S_0 can be set to zero because it is not depending on field

$$\Delta S(T,\Delta B) = \int_0^T \frac{c_p(T',B_f) - c_p(T',B_i)}{T'} dT$$

Experimental determination from magnetic measurements

$$\Delta S_m(T,B) = \sum_i \frac{M_{i+1}(T_{i+1},B) - M_i(T_i,B)}{T_{i+1} - T_i}\Delta B$$



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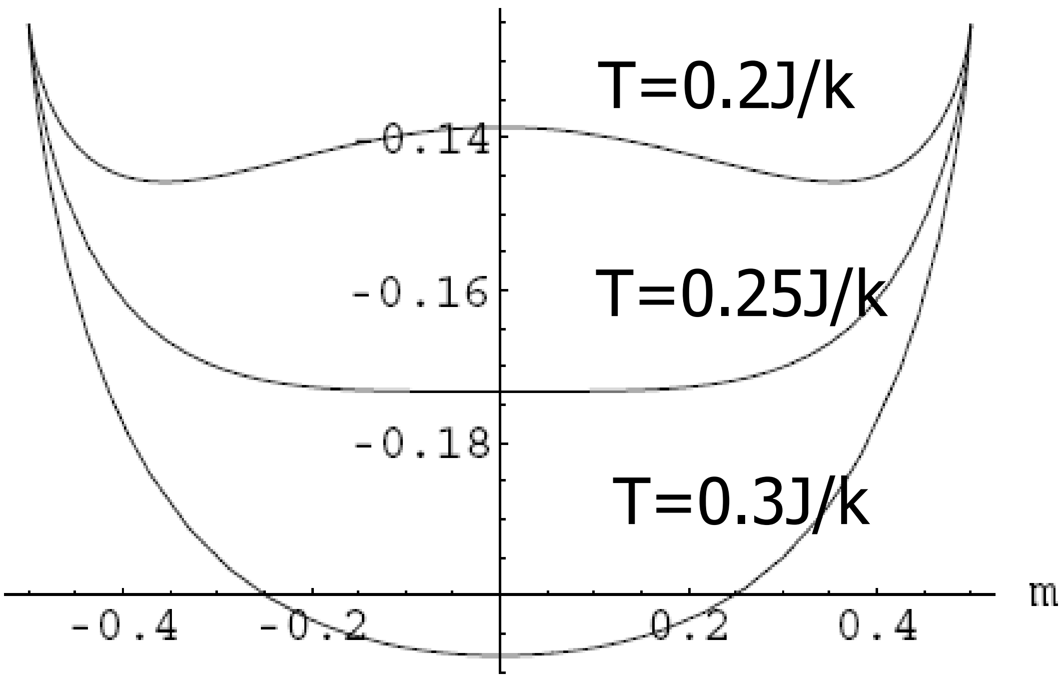
Continuous phase transition

In the absence of an external field, H=0, the system with exchange interaction J/k=1may spontaneously order.

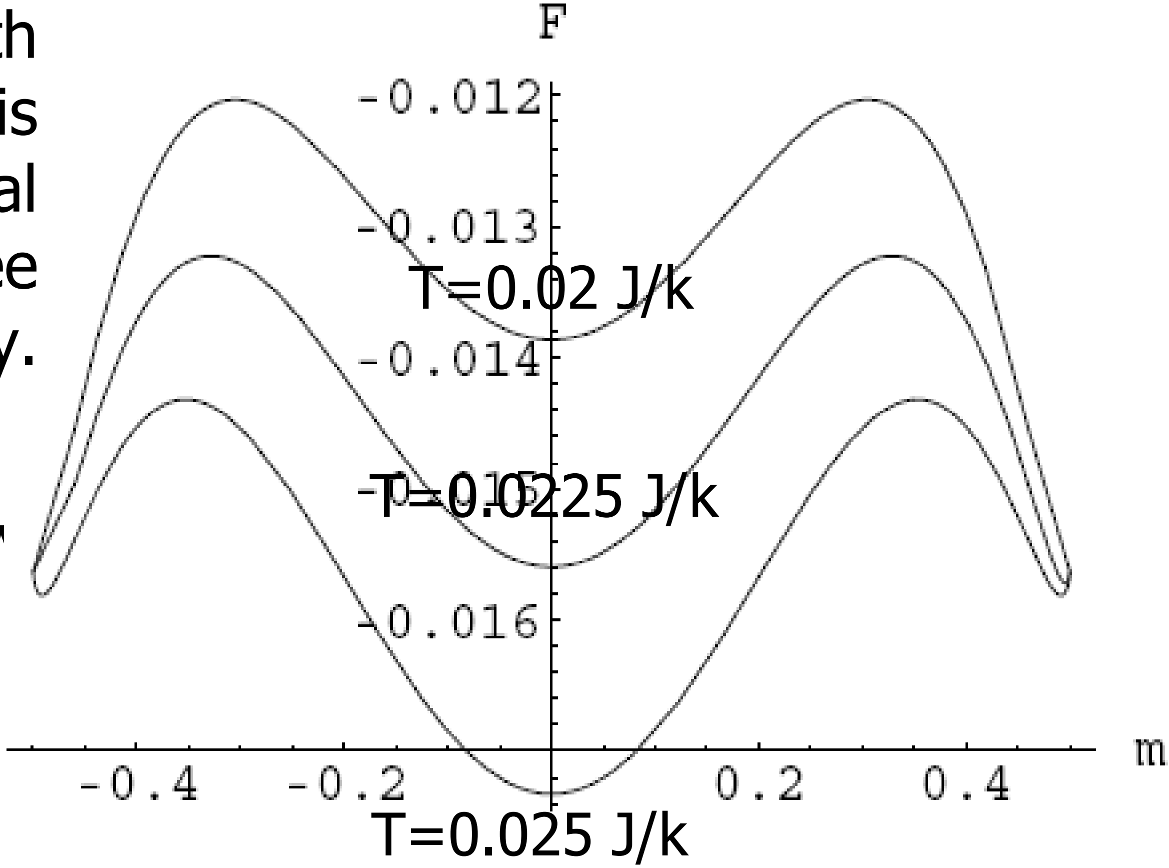
$$F = -\frac{1}{2}NJm^2 - NHm + NT\left[(\frac{1}{2}-m)\ln(\frac{1}{2}-m)+(\frac{1}{2}+m)\ln(\frac{1}{2}+m)\right]$$



First order phase transition

If interactions with quartets play a role this may result in local minima in the free energy.

$$F = -\frac{1}{2} NJm^4 - NHm + 1$$



Reason for first order transition

Ansatz $T_C = T_0[1 + ß(V - V_0)/V]$,

(Bean and Rodbell, 1962).

T_C Curie temperature,

T_0 Curie temperature if lattice incompressible.

V_0 volume in absence of exchange interaction,

β effect of volume change on Curie temperature.

Gibbs energy

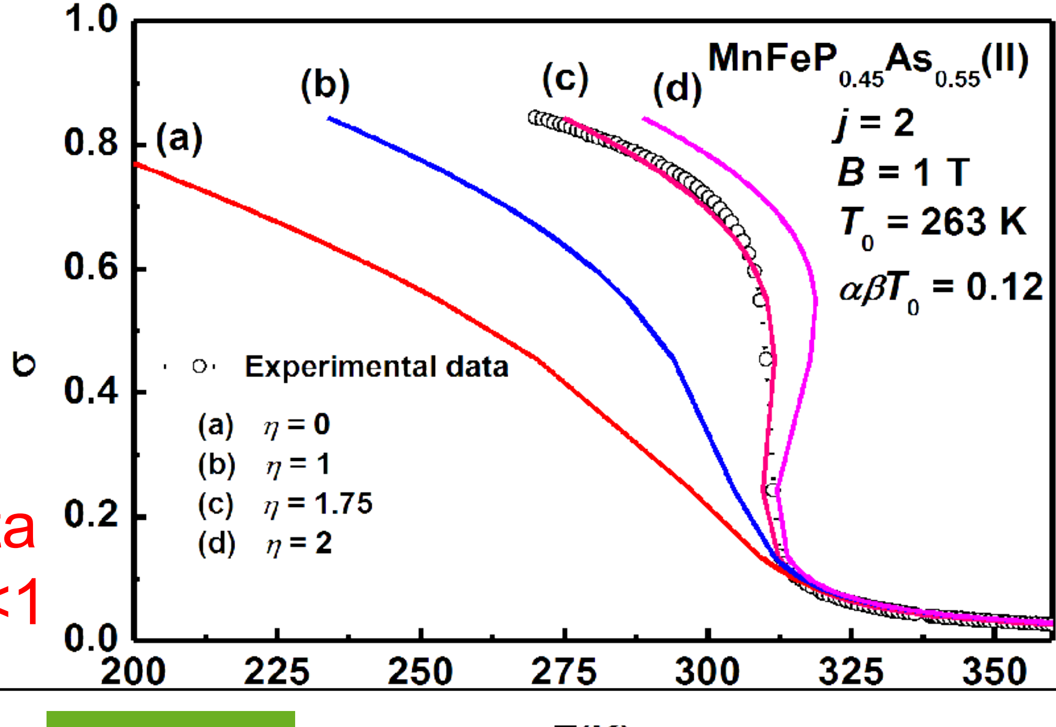
$$G = -\frac{1}{3}\left(\frac{j}{j+1}\right)NkT_C\sigma^2 - B\sigma_0\sigma + \frac{1}{2K}\left(\frac{V-V_0}{V_0}\right)^2 - T(S_j + S_l) + pV$$

N number of magnetic atoms per unit mass,
k Boltzmann constant,
σ_0 saturation magnetization,
σ relative magnetization,
K the compressibility,
S_j entropy of spin sublattice,
S_l entropy of lattice subsystem

State equation

$$\frac{T}{T_0} = \frac{2\sigma - 0.867\eta\,\sigma^2 + B\sigma_0 / NkT_0}{2\sigma + 0.867\sigma^3 + 0.606\sigma^5 - 2\alpha\,\beta\,T_0\sigma}.$$

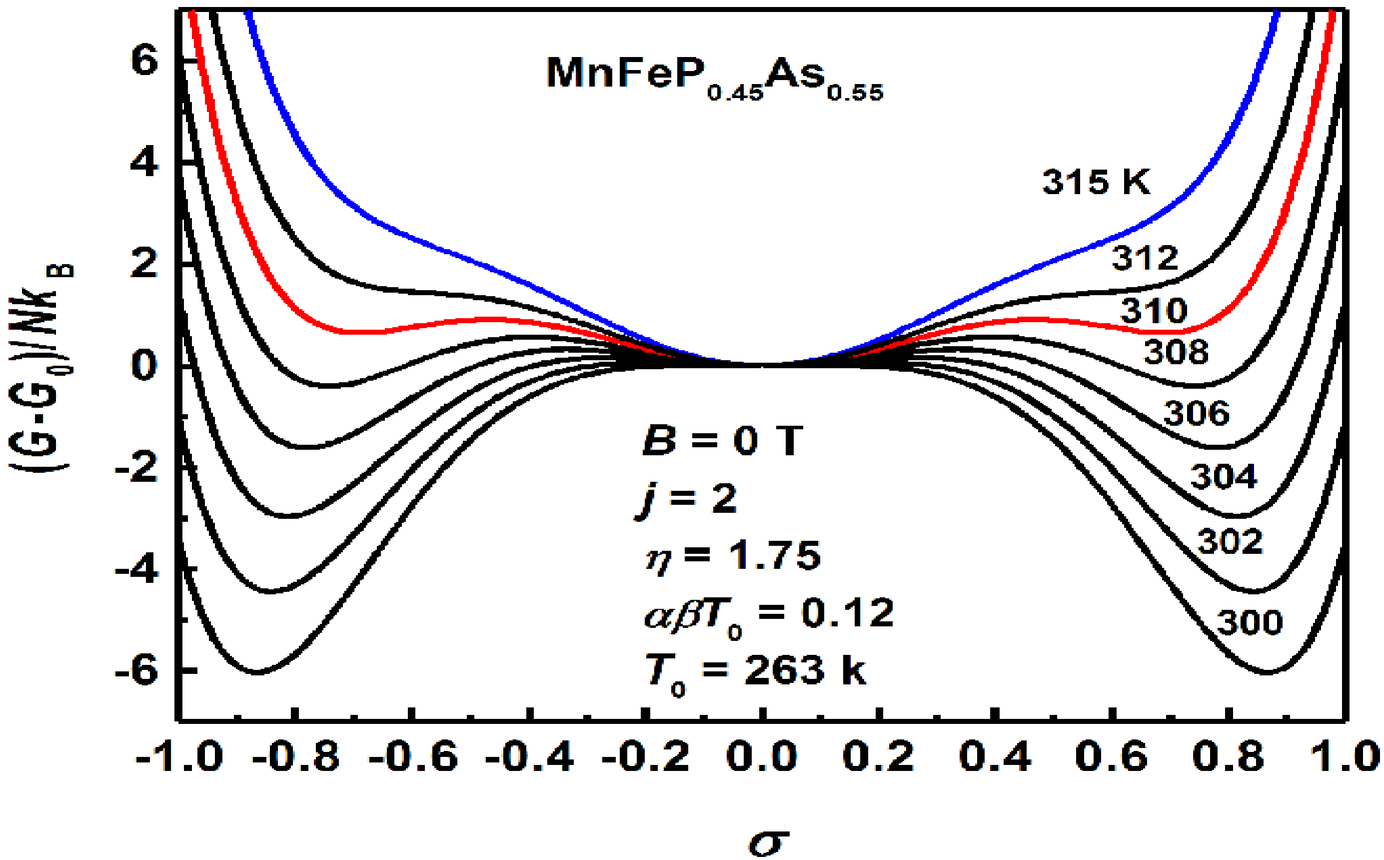
α Thermal expansion



Good agreement with exp. data

Second order transition for η <1

Gibbs energy as function of σ



Local minimum near Tc

⇒ First order transition

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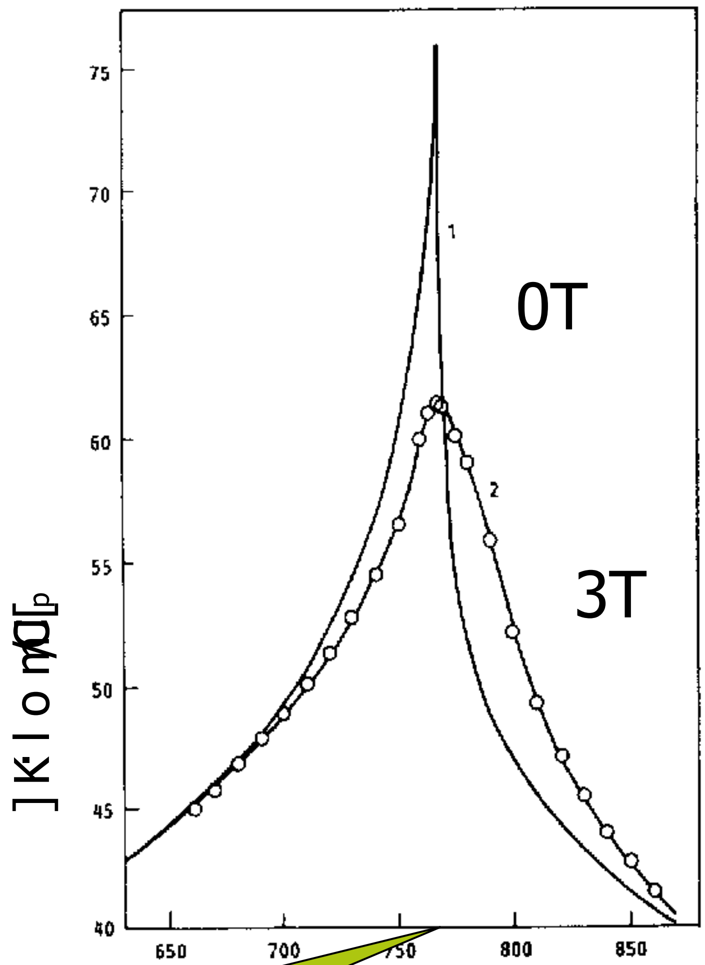
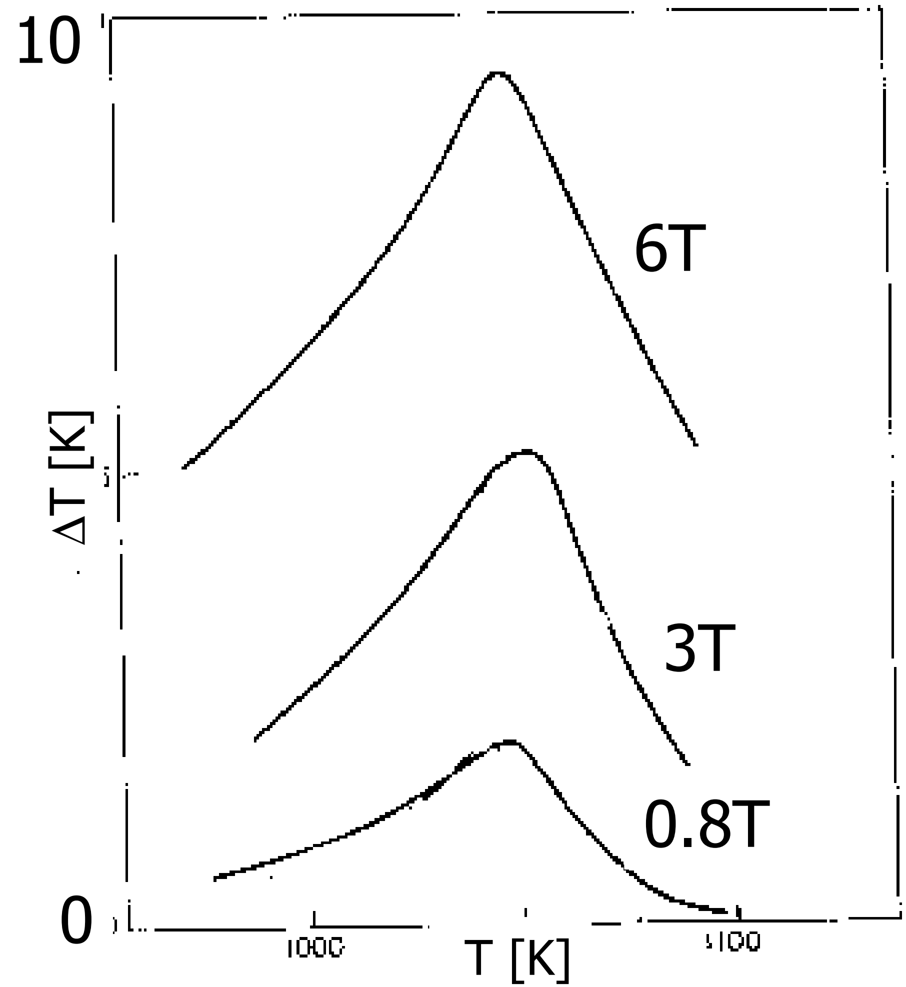
Phase transition in iron

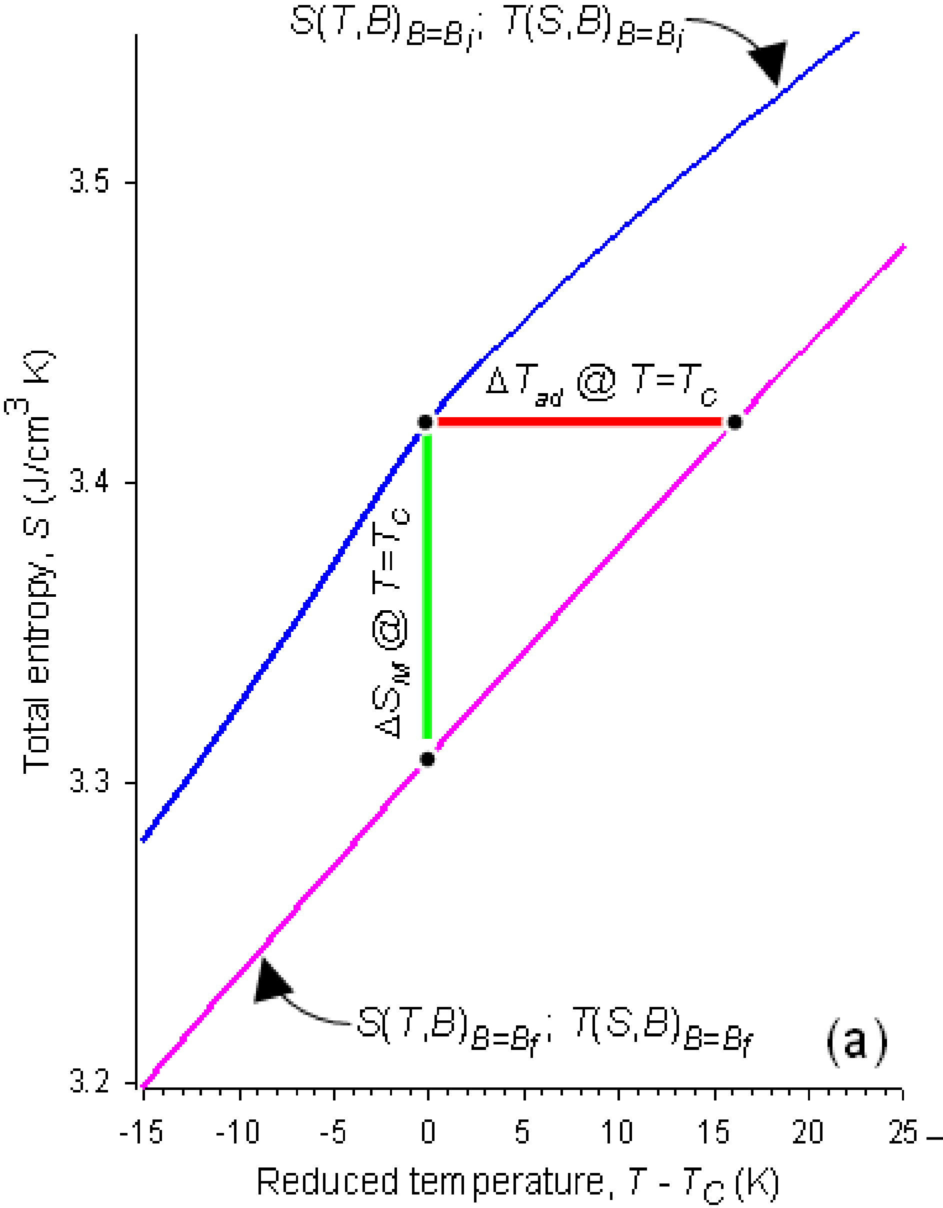




Magnetic ordering T

MCE in gadolinium

Total entropy vs reduced temperature of gadolinium in low field (blue) and high field 9T (purple) (Gschneidner et al)



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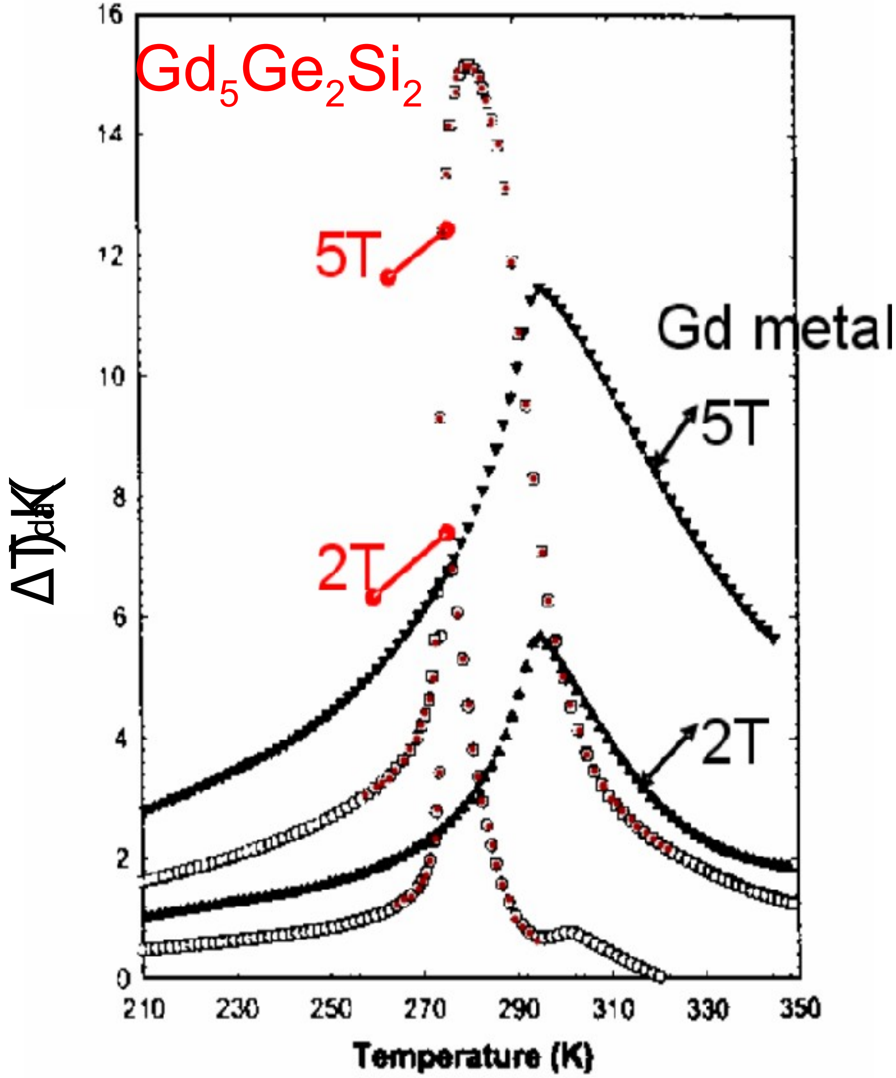
Giant magnetocaloric effect in

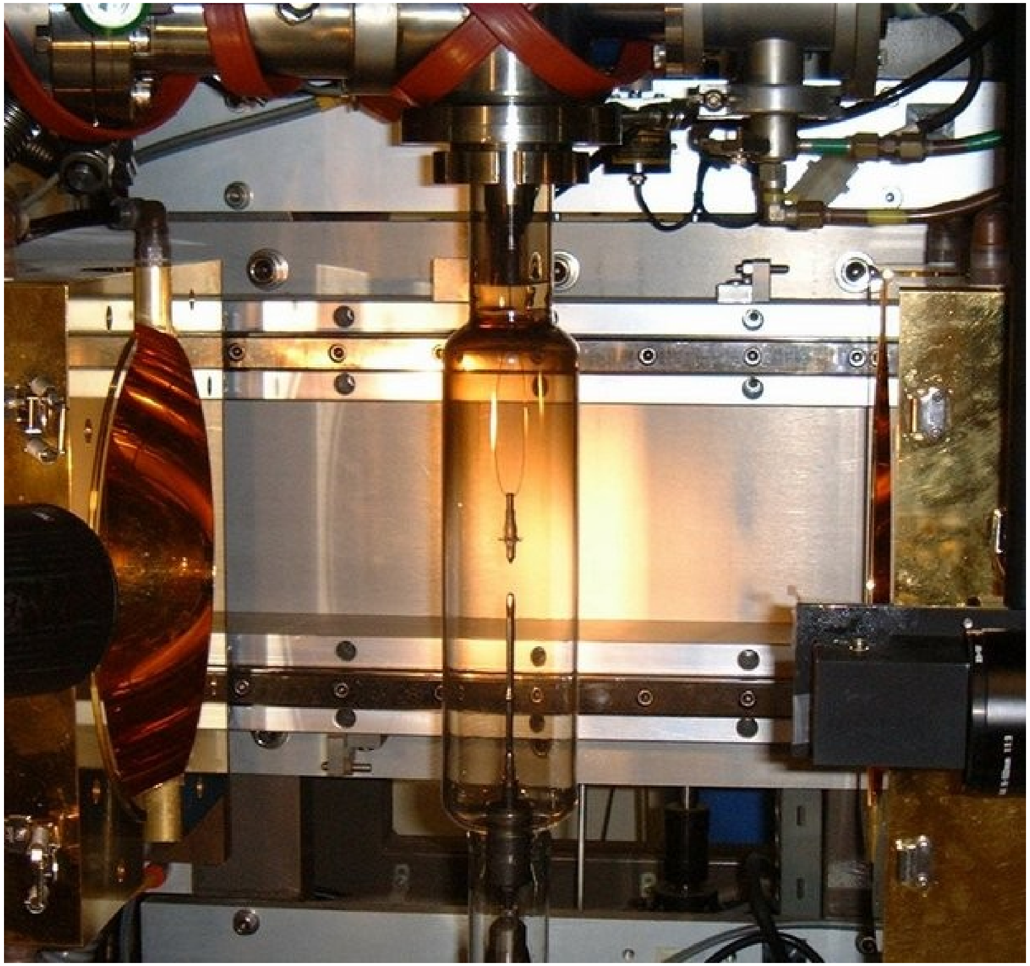


Magnetically dilute yet higher effect

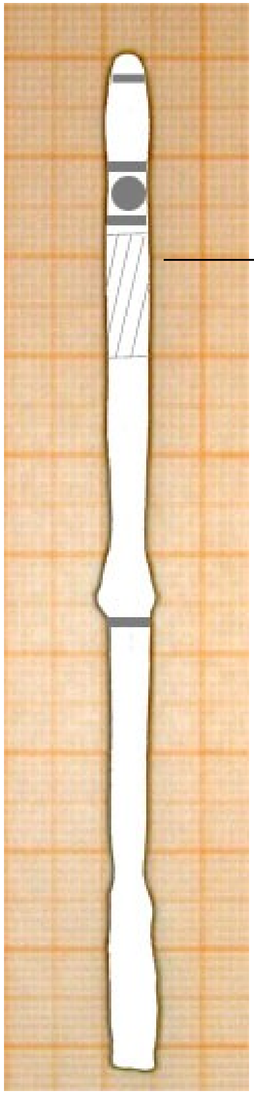
double transition?

Pecharsky & Gschneidner
PRL 78 (1997) 4494

Crystal growth



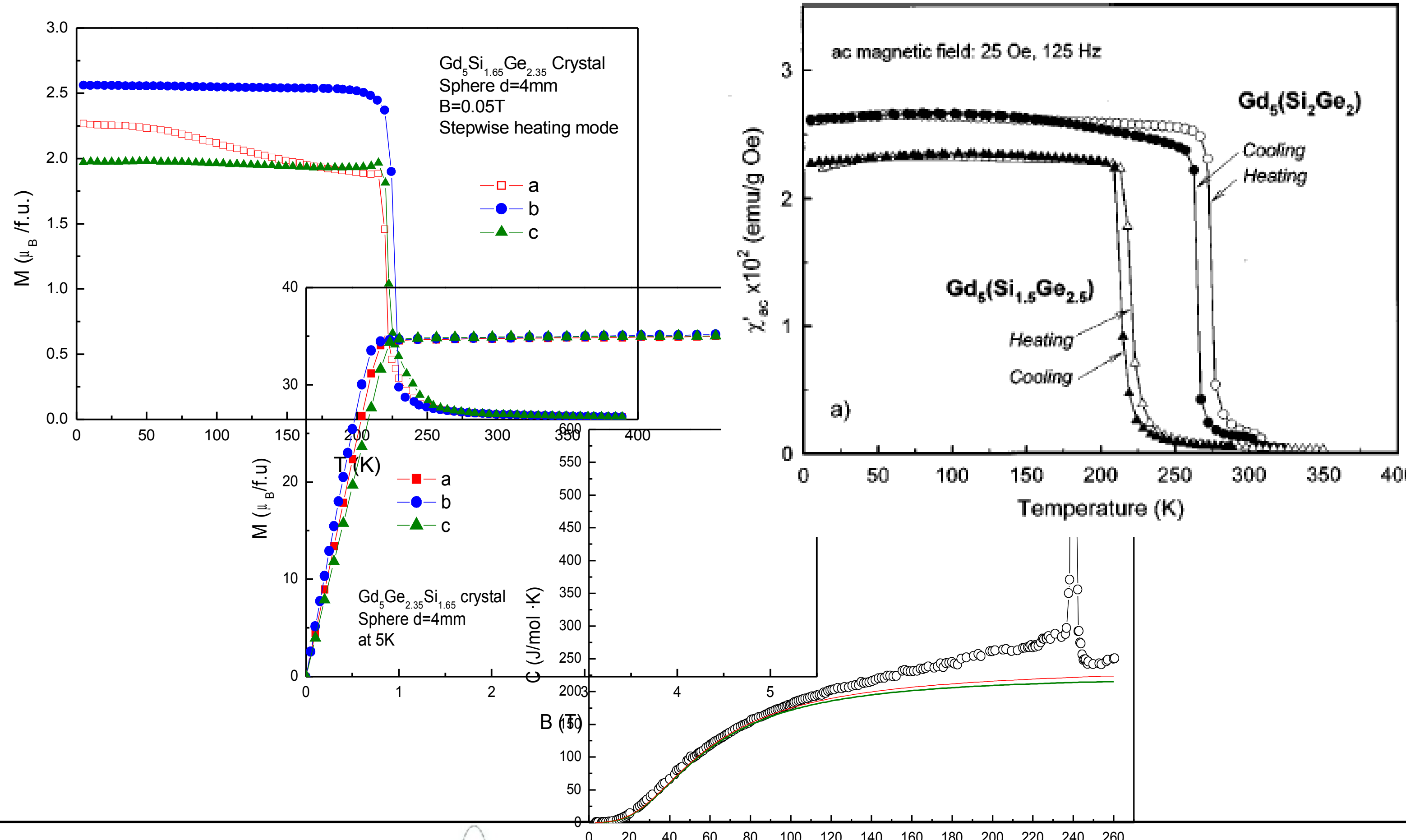
Crystal was grown in a mirror furnace by means of traveling solvent floating zone method



D=4mm Sphere was cut by spark erosion from as grown rod

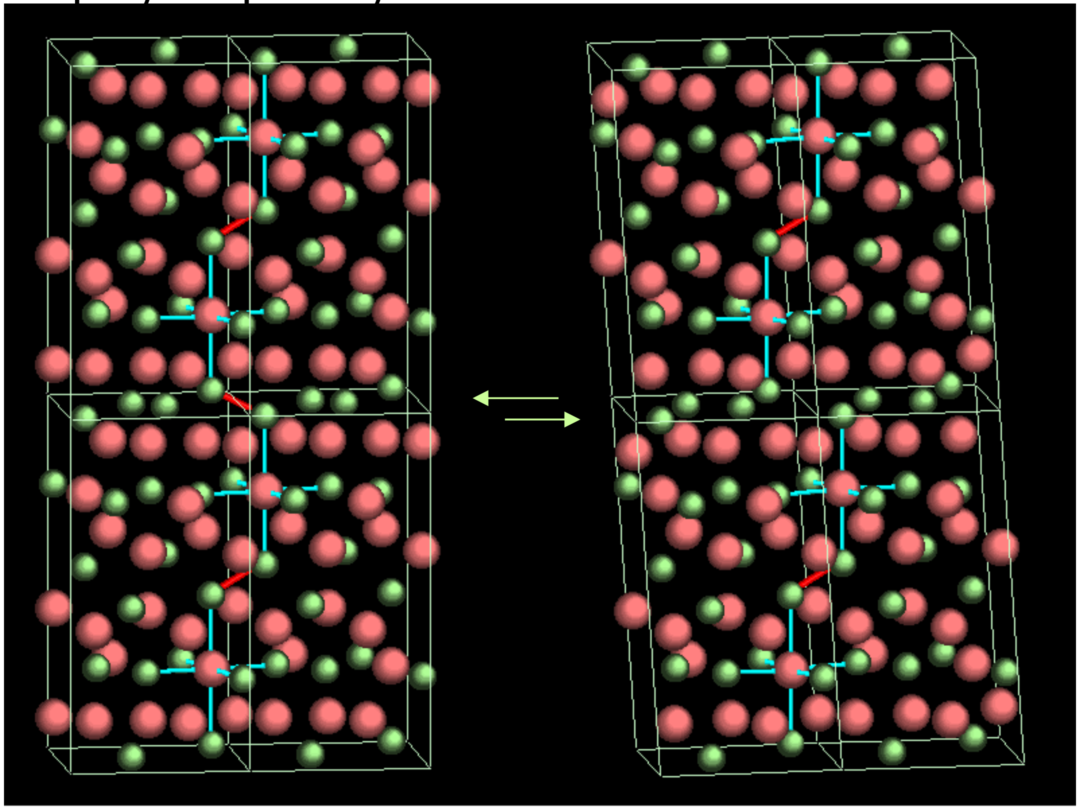
Unusual behavior

- Extraordinary magnetic behavior: first-order character of the paramagnetic-ferromagnetic transition.



Unusual behavior

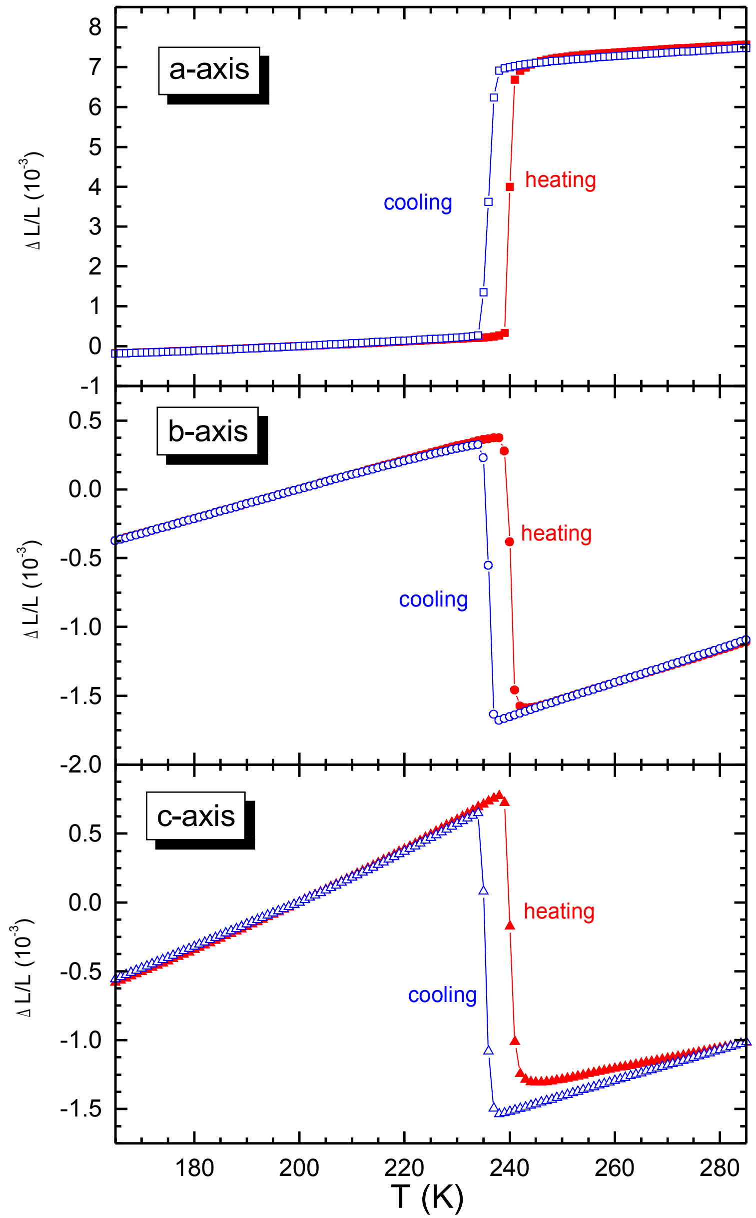
- The high temperature paramagnetic monoclinic phase transforms to the low temperature ferromagnetic orthorhombic phase. The low temperature phase has a higher symmetry than the high temperature, which is the opposite of what is normally observed for other polymorphic systems.



<T_c: Pnma, No.62 >T_c: $P112_1/a$, No.14

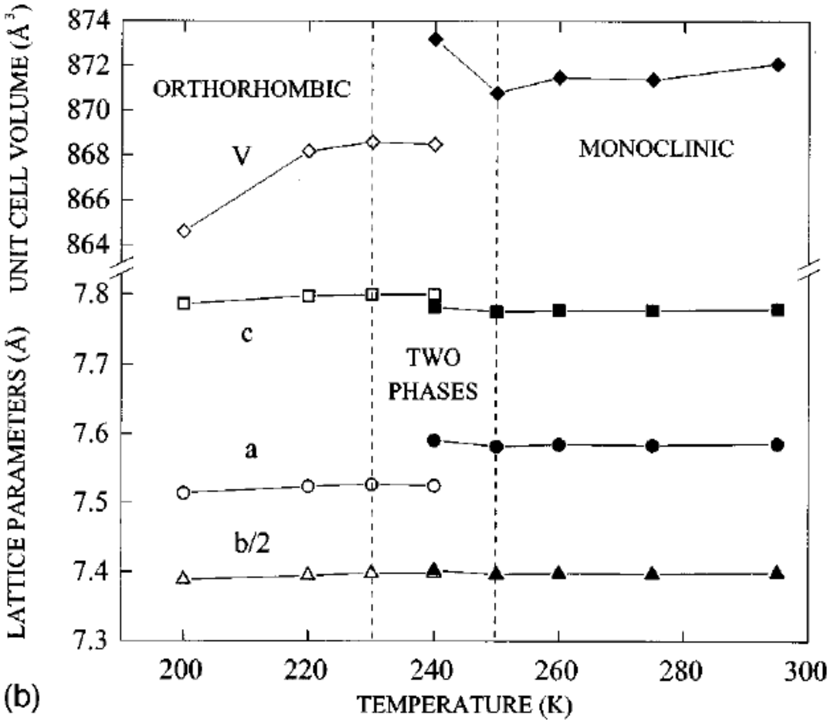
Crystallographic data comes from W Choe PRL v84, n20, p4617, 2000

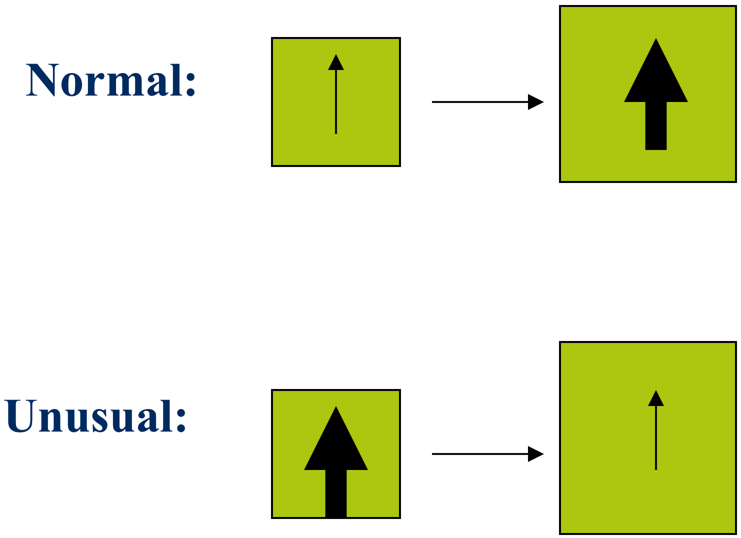
thermal expasion of $Gd_5Ge_{2.4}Si_{1.6}$

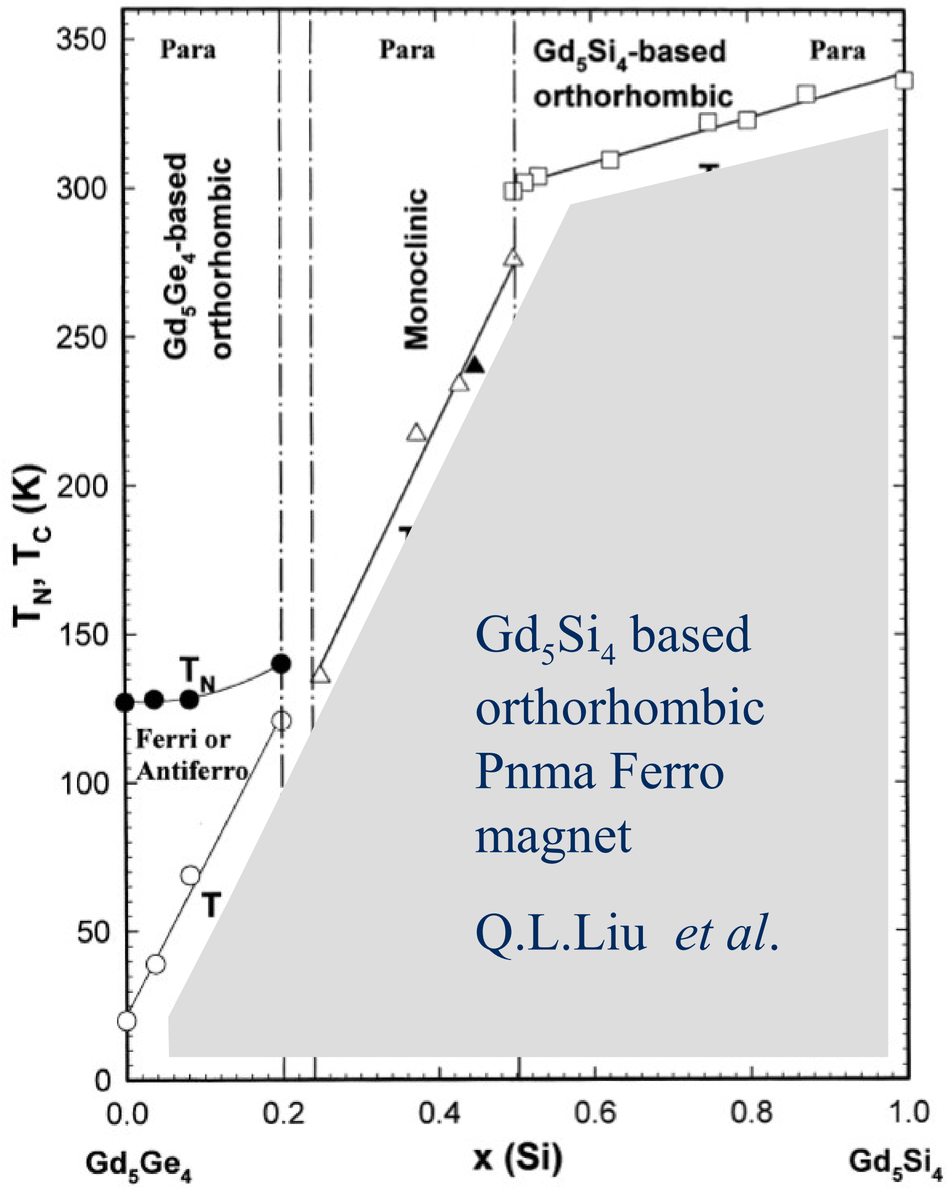


Unusual behavior

- Volume decreases when cooling through the transition, i.e., the cell volume in the low-temperature ferromagnetic phase is smaller ($\Delta v > 0.4\%$) than in the high-temperature paramagnetic one. This is in contrast with the general physical picture of the magnetovolume effects which are transtions from a low-volume low-moment to a high-volume high-moment state.





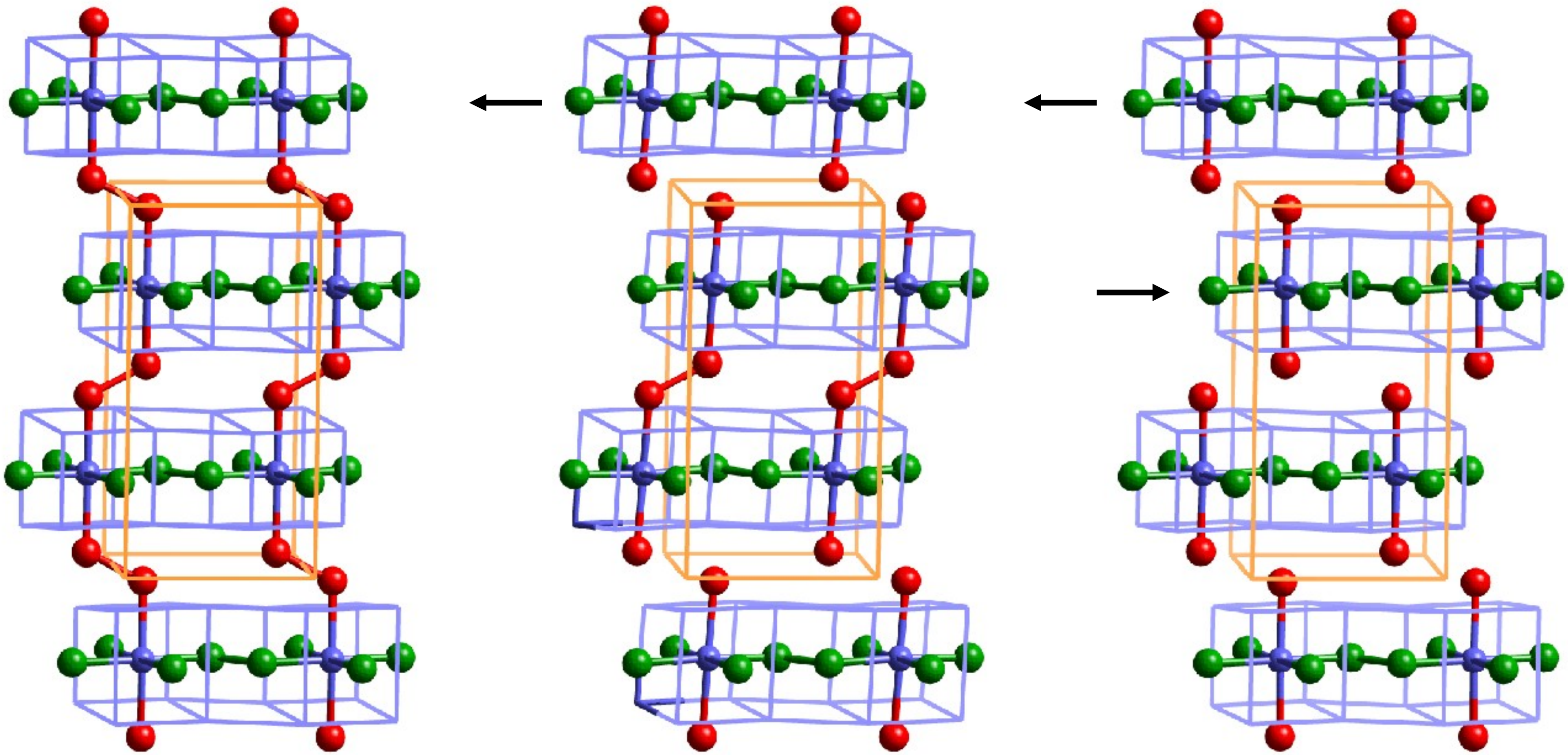


Unusual behavior

- Recent XRD investigation reported that $Gd_5(Si_xGe_{1-x})_4$ alloys form a completely miscible solid-solution crystallized in the Gd_5Si_4-type *Pnma* structure below T_C regardless of the composition. Ground state is low temperature (Gd_5Si_4–based) orthorhombic ferromagnet

- Temperature of structural phase transition always coincides with Curie temperature T_C.

What is responsible for the unusual behaviors?



x > 0.5	0.4 < x < 0.5	x < 0.3
Gd_5Si_4 type *Pnma*	$Gd_5Si_2Ge_2$ type $P112_1/a$	Gd_5Ge_4 type *Pnma*

T=Si, Ge **$(Gd^{3+})_5(T_2^{6-})_2(3e^-)$** **$(Gd^{3+})_5(T_2^{6-})_{1.5}(T^{4-})(2e^-)$** **$(Gd^{3+})_5(T_2^{6-})\ (T_2^{6-})_2\ (1e^-)$**

Breaking and making bond RKKY or superexchange

V. K. Pecharsky and K. A. Gschneidner, Jr., *J. Alloys Compd.* 260, 98-106 (1997)

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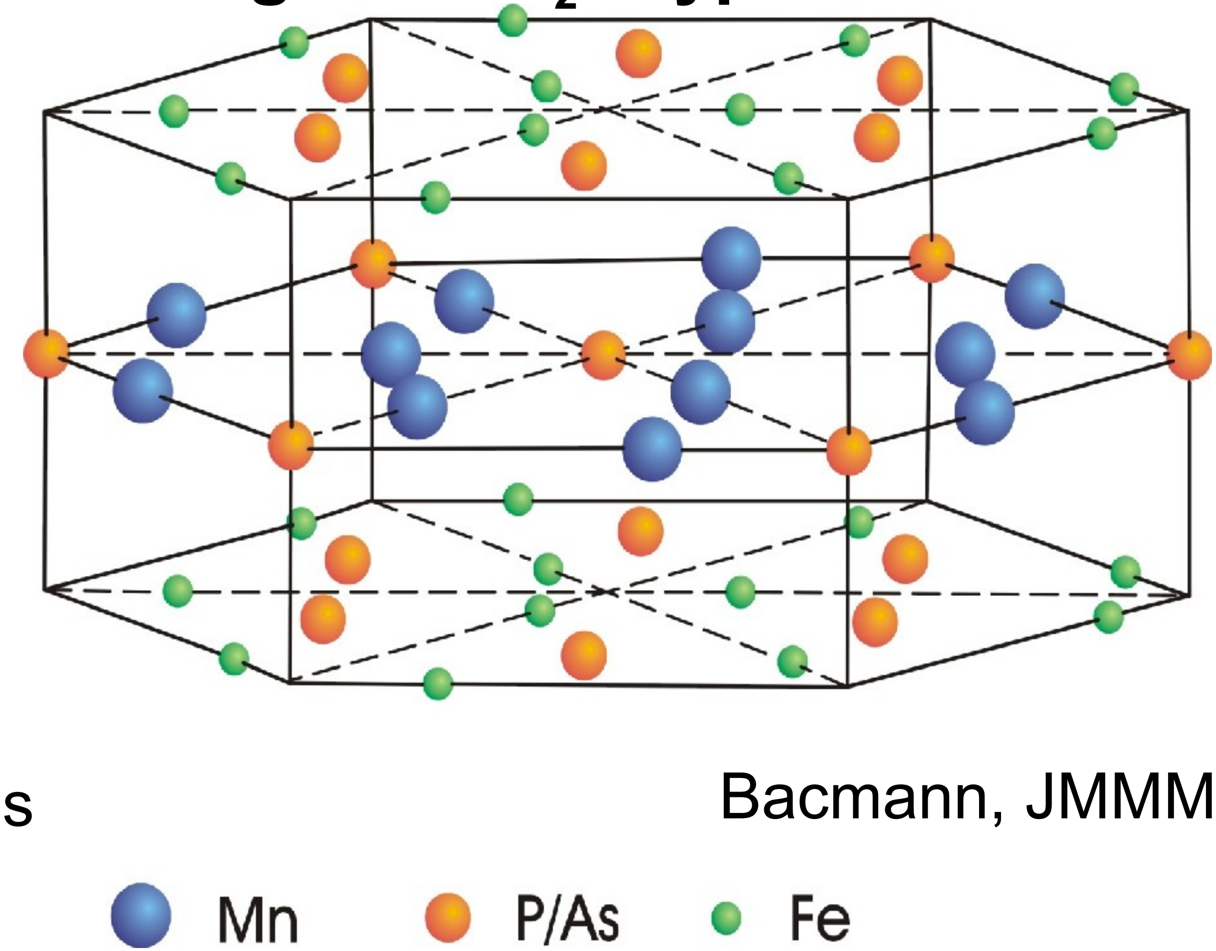
$MnFeP_{1-x}Si_x$

Hexagonal Fe_2P type of structure



Space group:

$P\bar{6}2m$

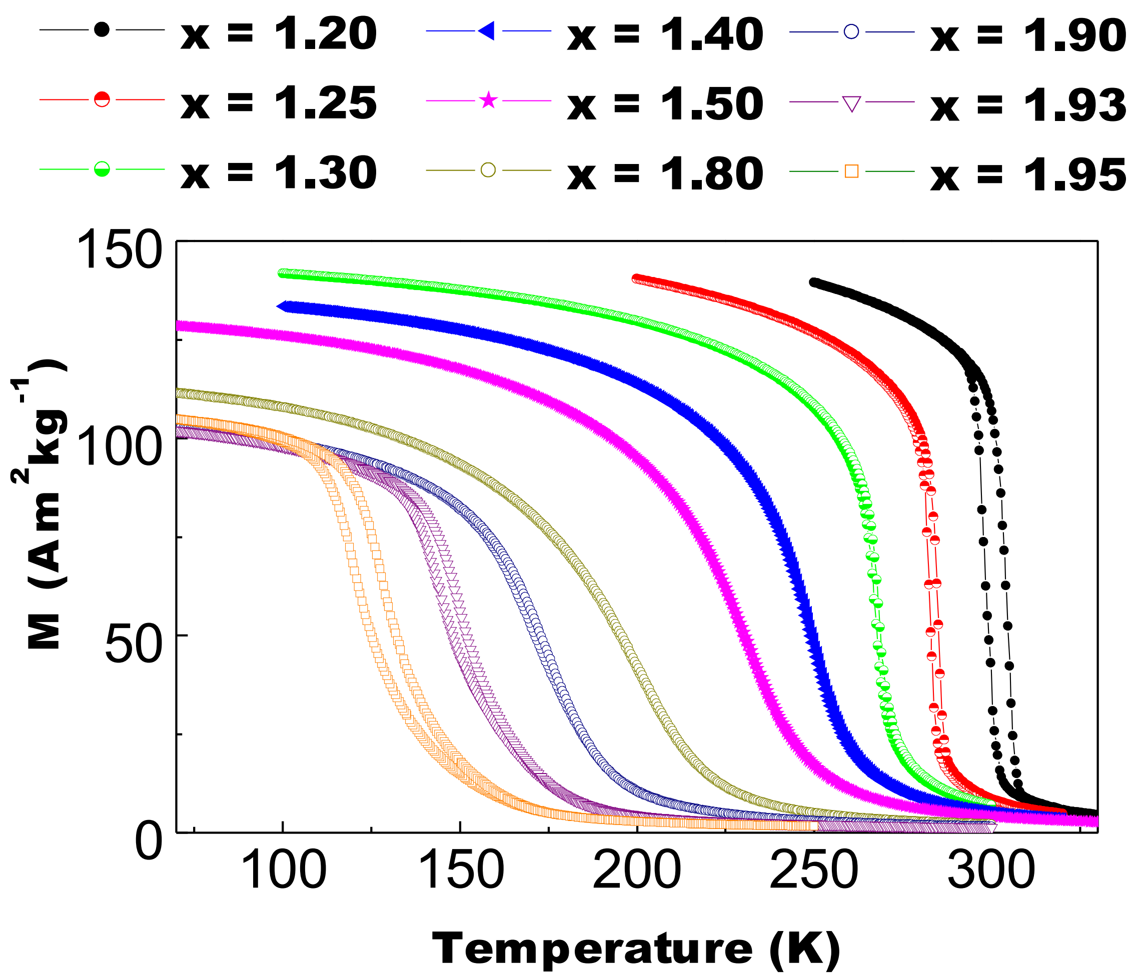
Mn 3g sites

Fe 3f sites

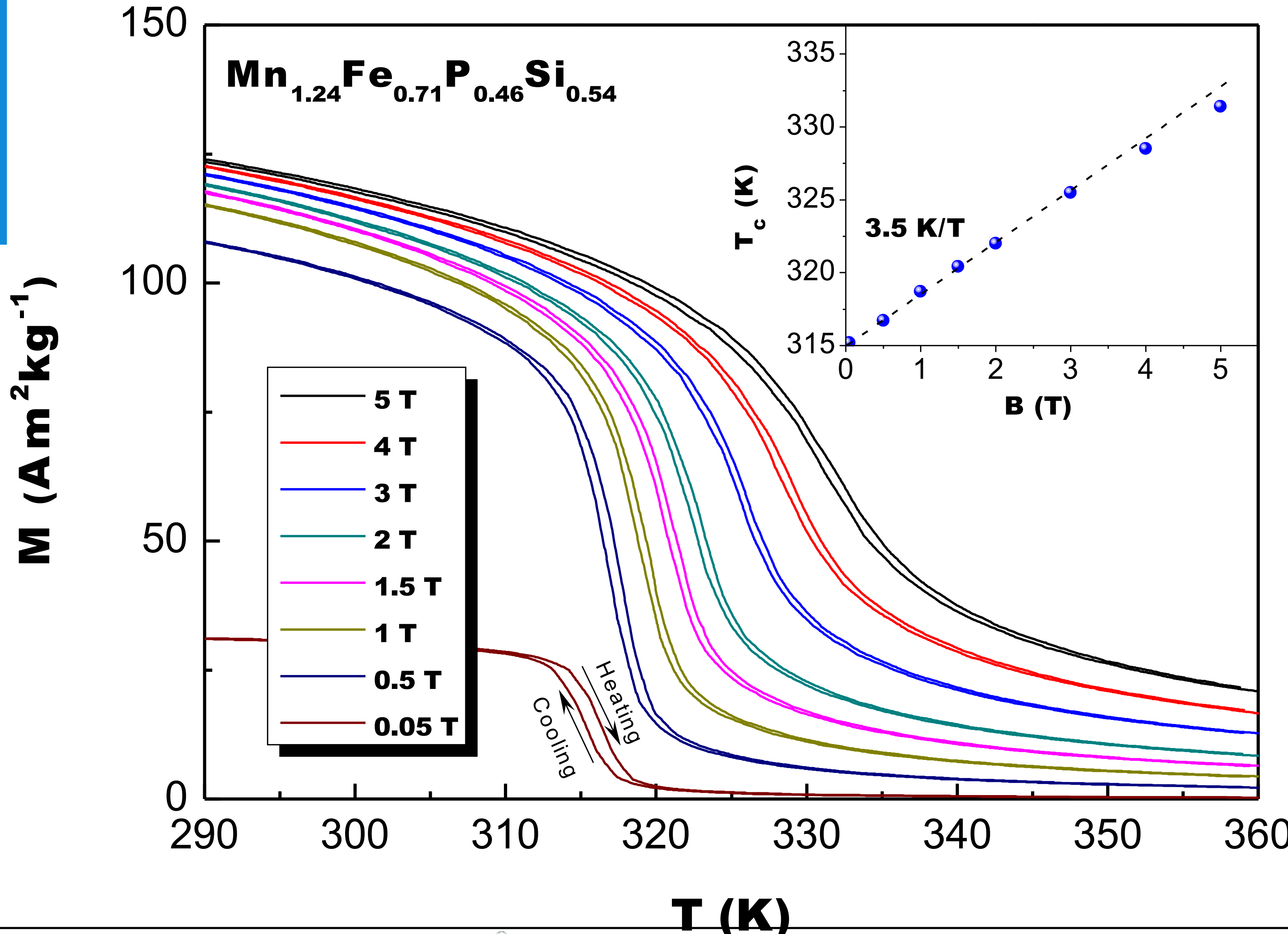
P/Si 1b&2c sites

Bacmann, JMMM 1994

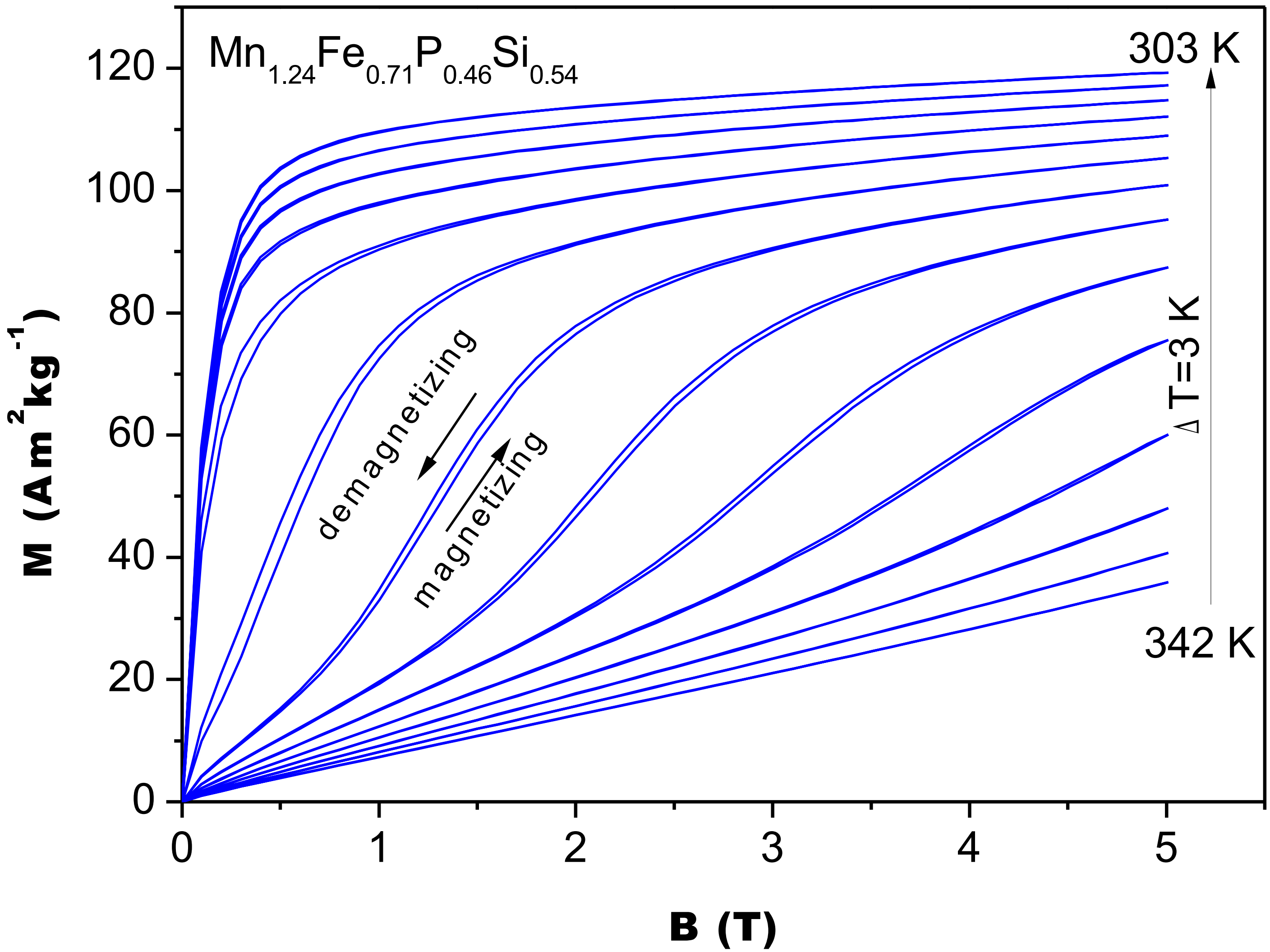
Magnetic response of $Mn_xFe_{2-x}P_{0.5}Si_{0.5}$ in 1T



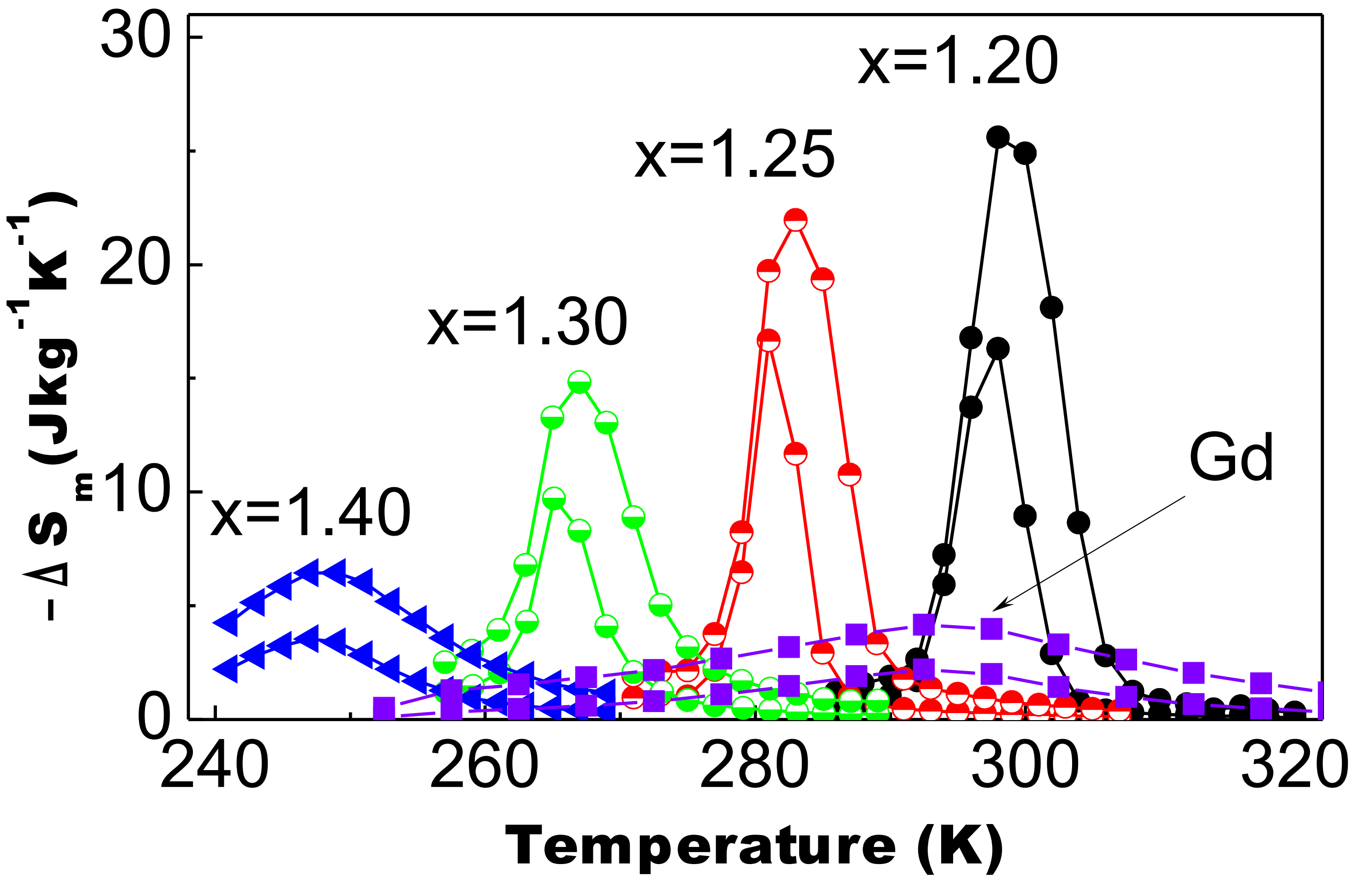
Different fields



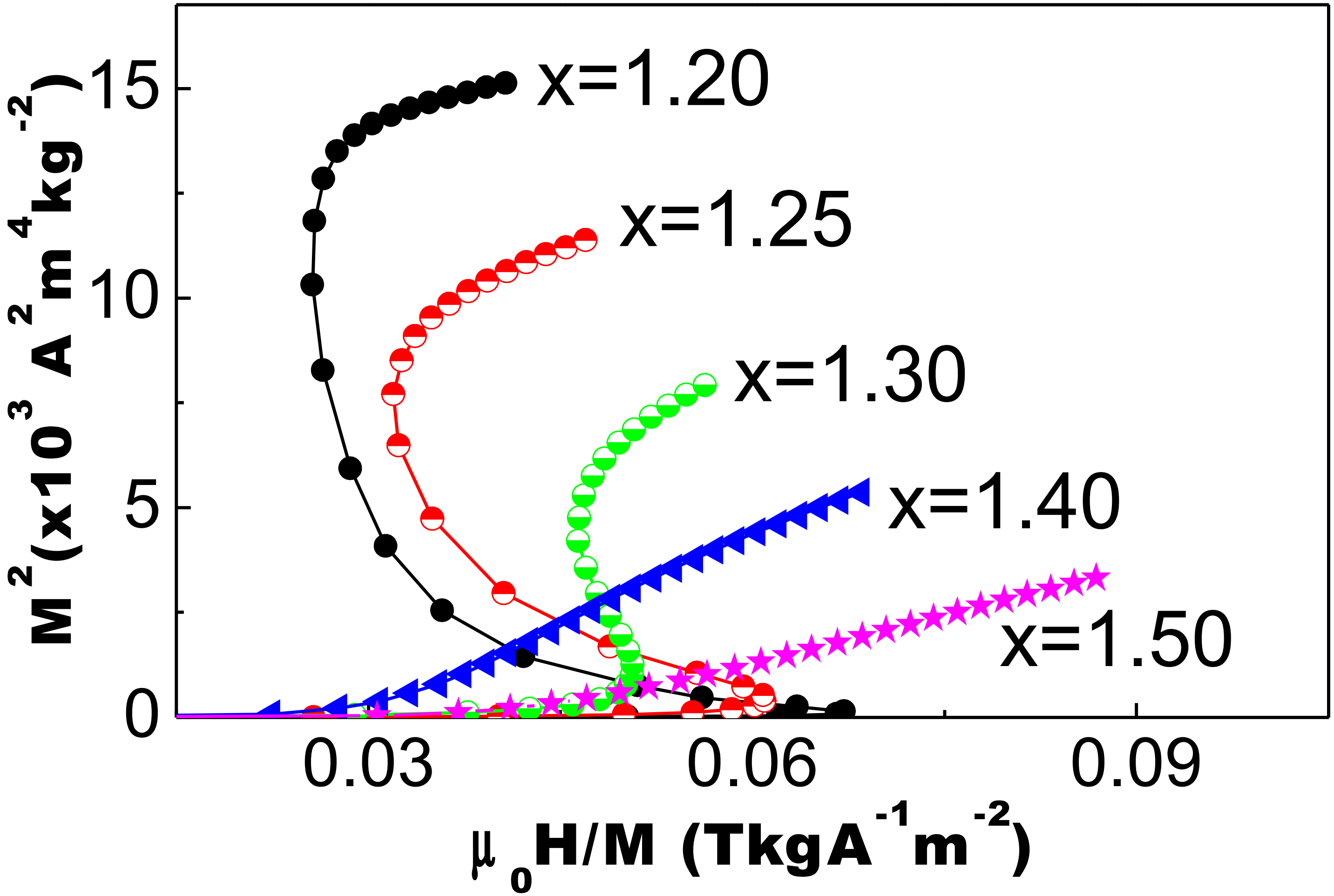
Magnetization isotherms



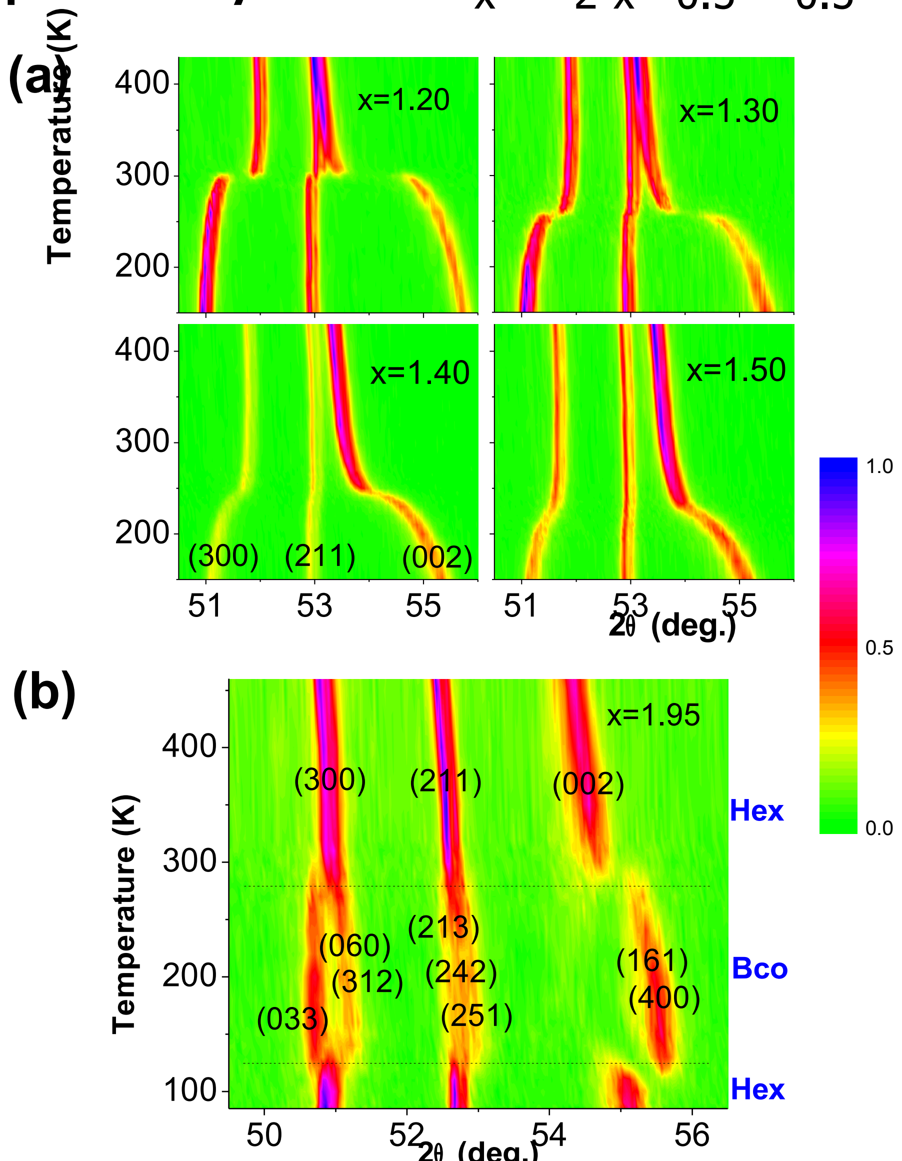
MCE of $Mn_xFe_{2-x}P_{0.5}Si_{0.5}$ in 1 and 2 T



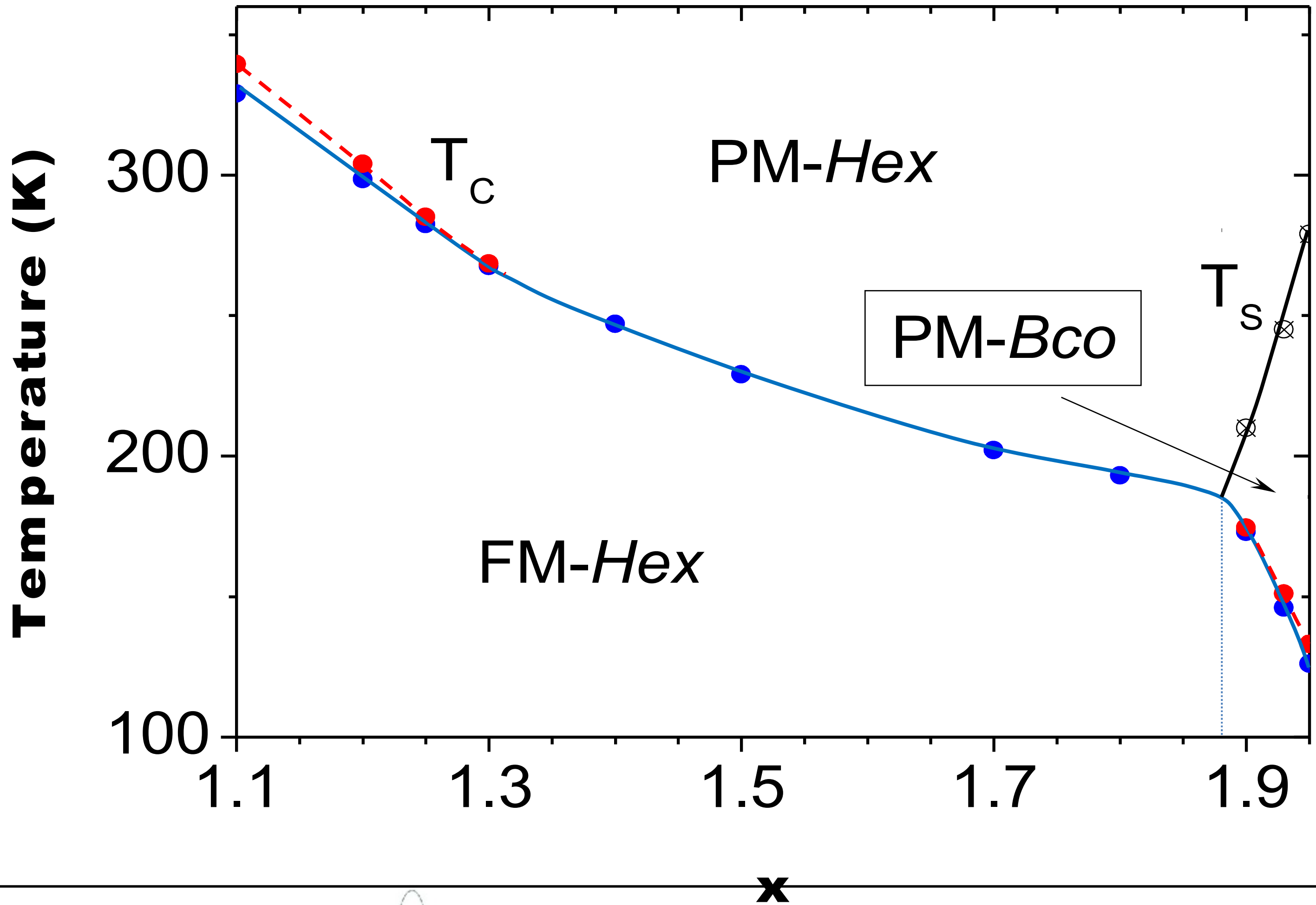
Arrot plots of $Mn_xFe_{2-x}P_{0.5}Si_{0.5}$



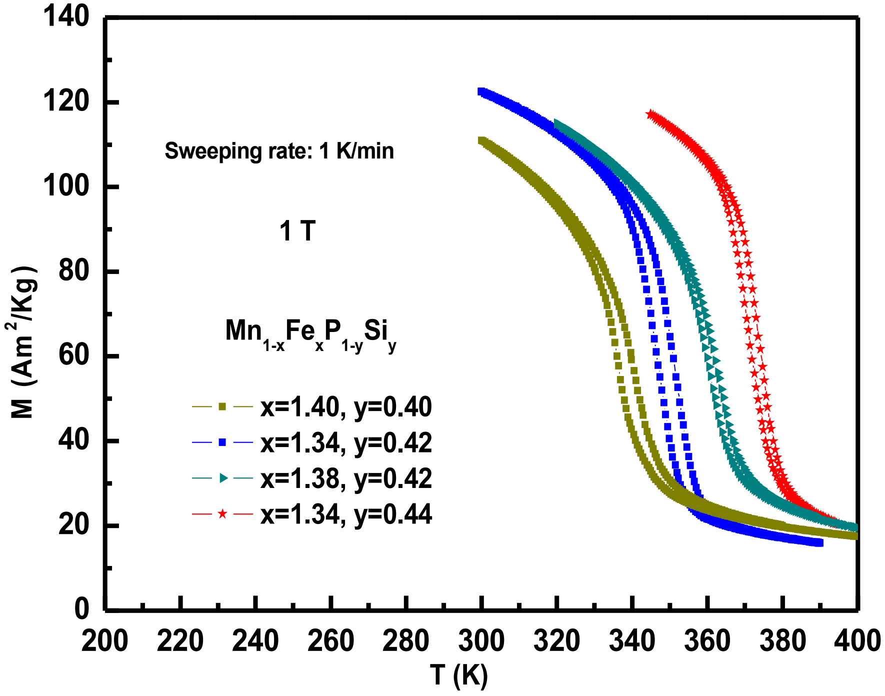
Temp dep. X-ray of $Mn_xFe_{2-x}P_{0.5}Si_{0.5}$



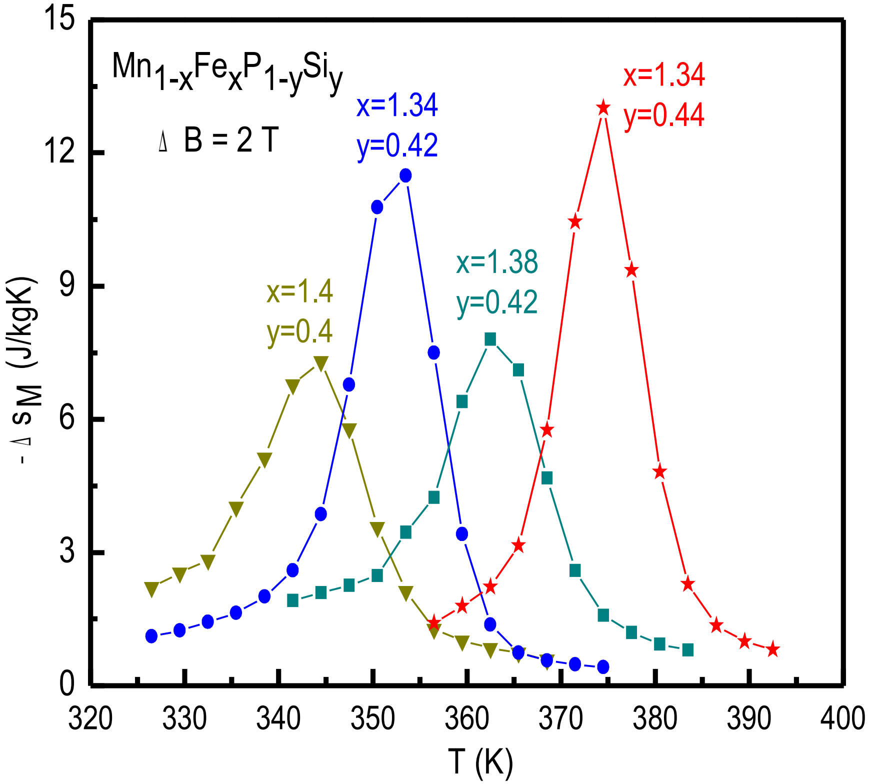
Phases of $Mn_xFe_{1.95-x}P_{0.5}Si_{0.5}$



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

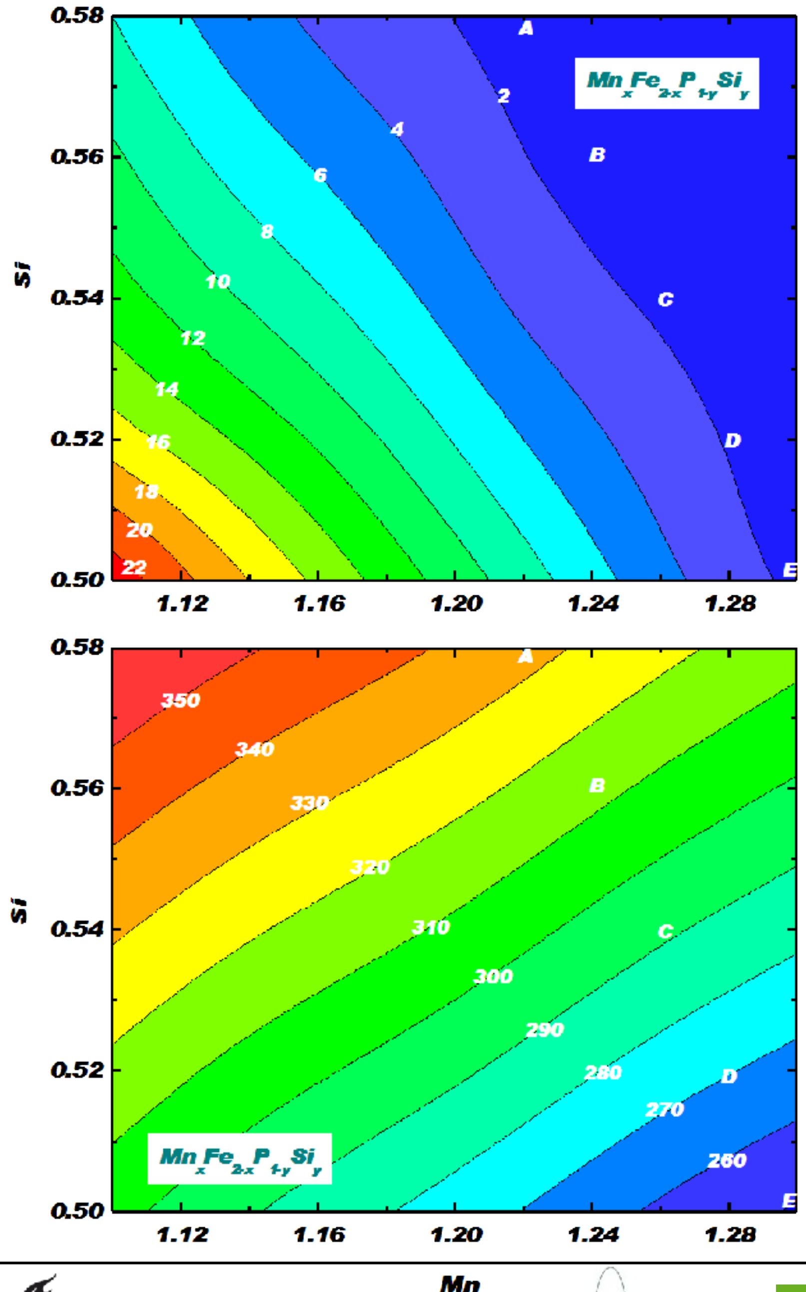


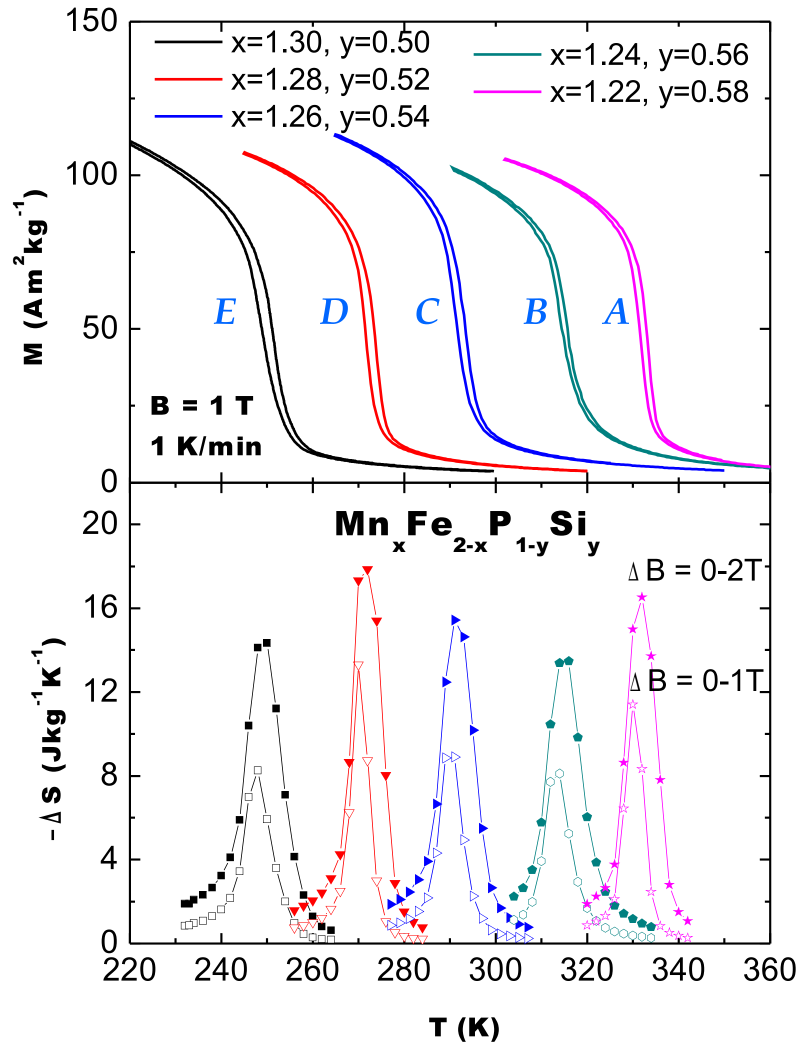
M *vs.* T



Magnetic entropy change for a field change of 2 T.

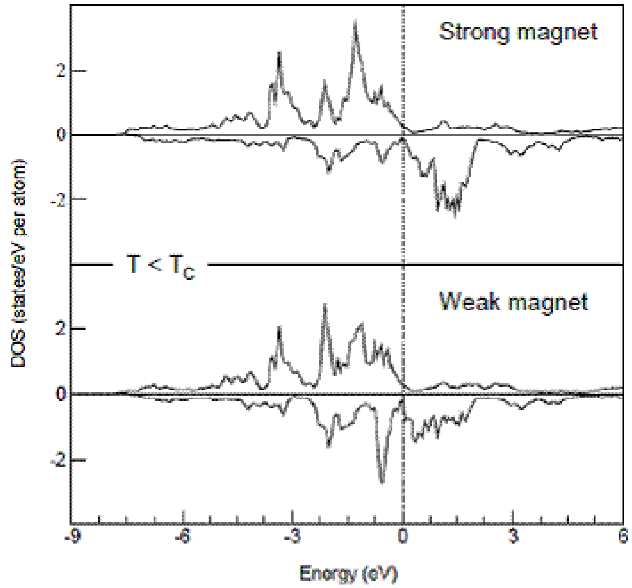
Partial phase-diagram

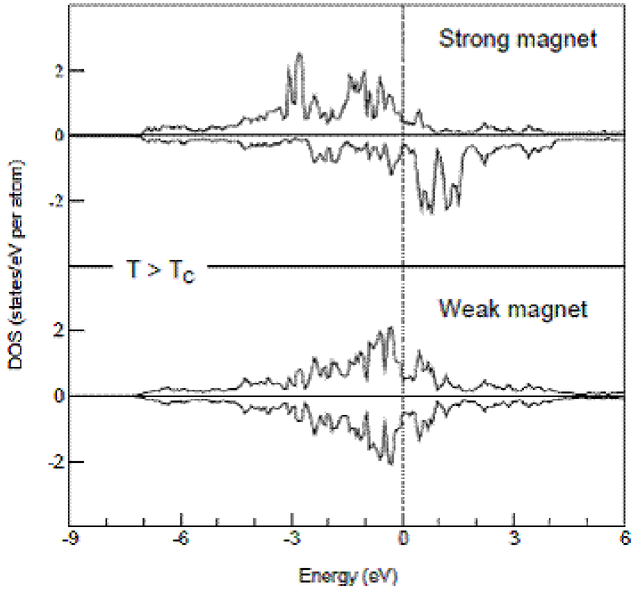




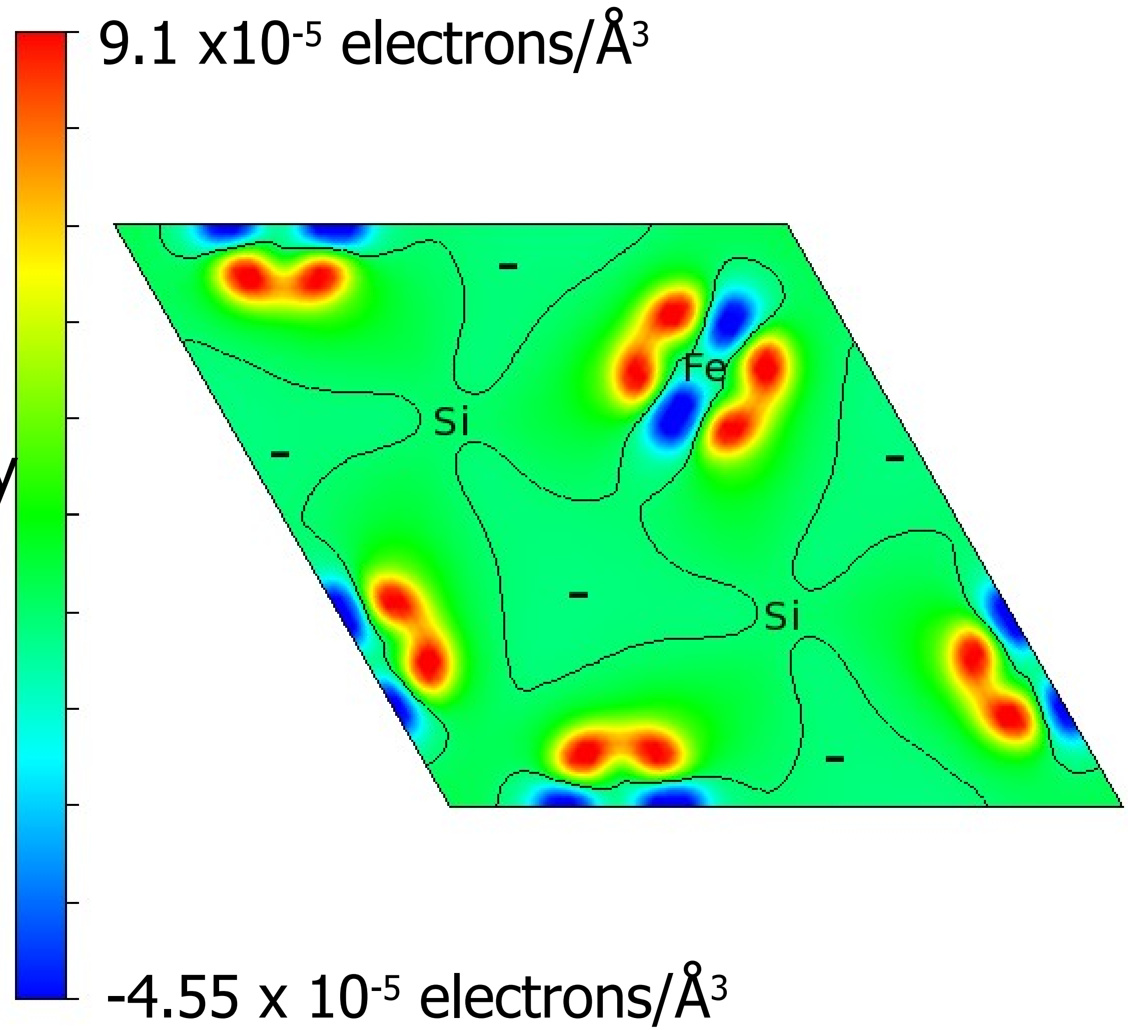
Theoretical progress

Novel type of magnetism:
Intercallation of strong and weak magnetism





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



Summary Mn & Fe rich Si compounds

- **Magneto-elastic and magneto-structural transition 1st order**
- **Increased Mn or Fe content strongly reduces hysteresis**
- **Increased Si content strongly reduces hysteresis**
- **Ferromagnetic state prefers hex structure?**
- **Combining variation of Mn and Si content results in desired properties**

- **T_C of $(Mn,Fe)_{2+z}(P,Si)$ compounds above 400 K**

Outline

- Basic magnetics (classical)
- Origin of first order transition?
- Magnetic materials
- $Gd_5Ge_2Si_2$ magnetic Rare-Earth
- MnFe(P,Si) magnetic transition metals
- **$TbFe_4Al_8$ magnetic RE & TM**

Magnetic properties of single-crystalline

$TbFe_4Al_8$

Fe- or Co-rich 1:12 compounds candidates for permanent-magnet materials

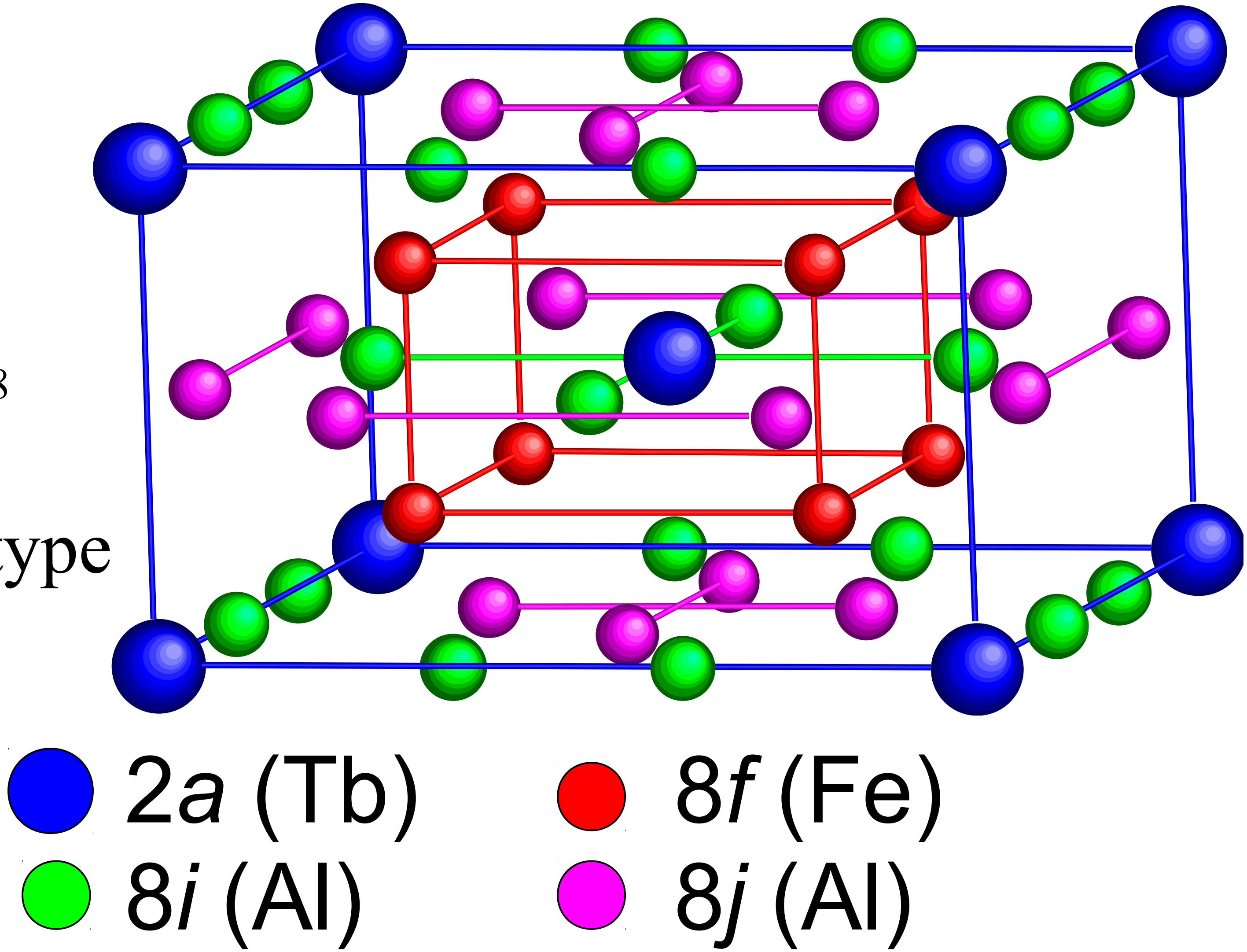
Preferential occupation of different sites

R-R interactions

AF Fe-Fe interactions

$TbFe_4Al_8$

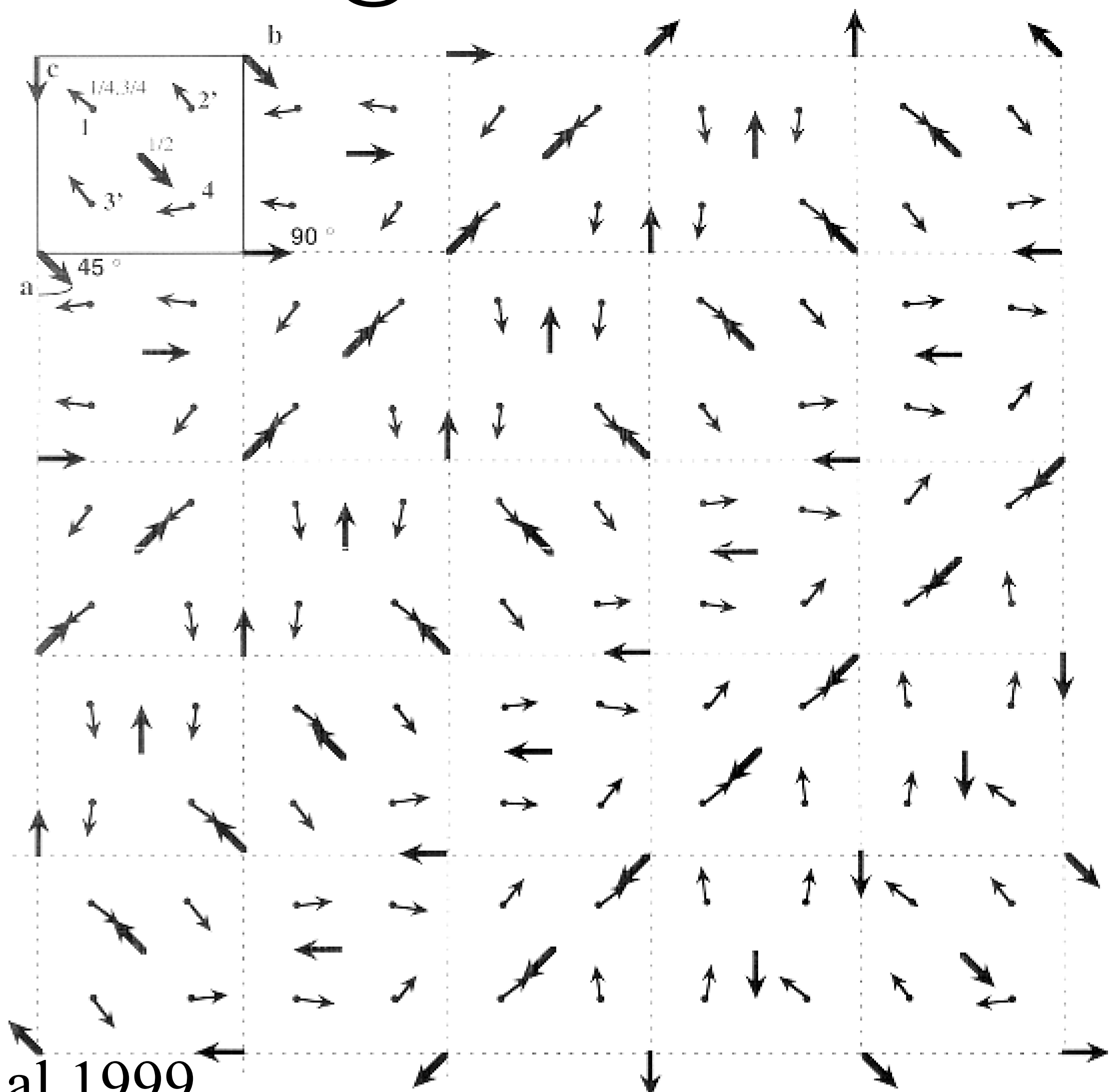
$ThMn_{12}$ type



Magnetic structure @ 8K

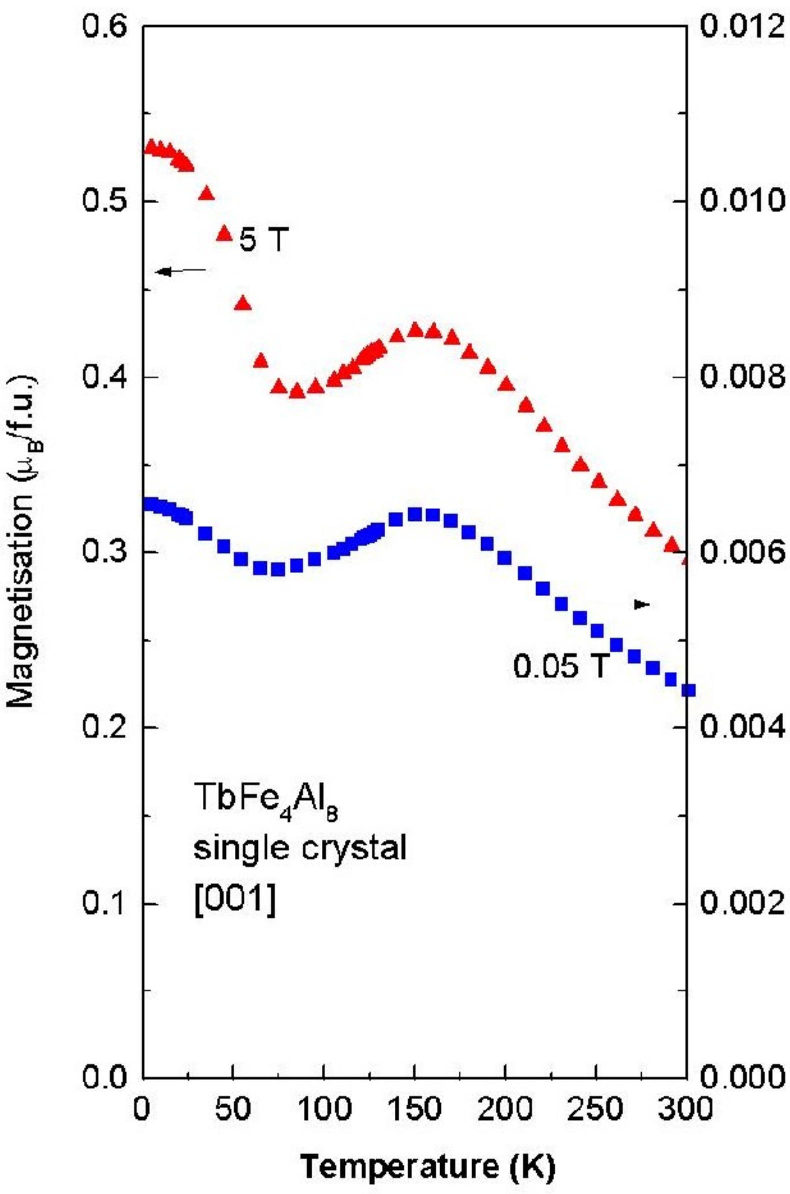
canted spiral
with ferromagnetic
component

only half of the
moments shown



Schobinger-Papamantolos et al 1999

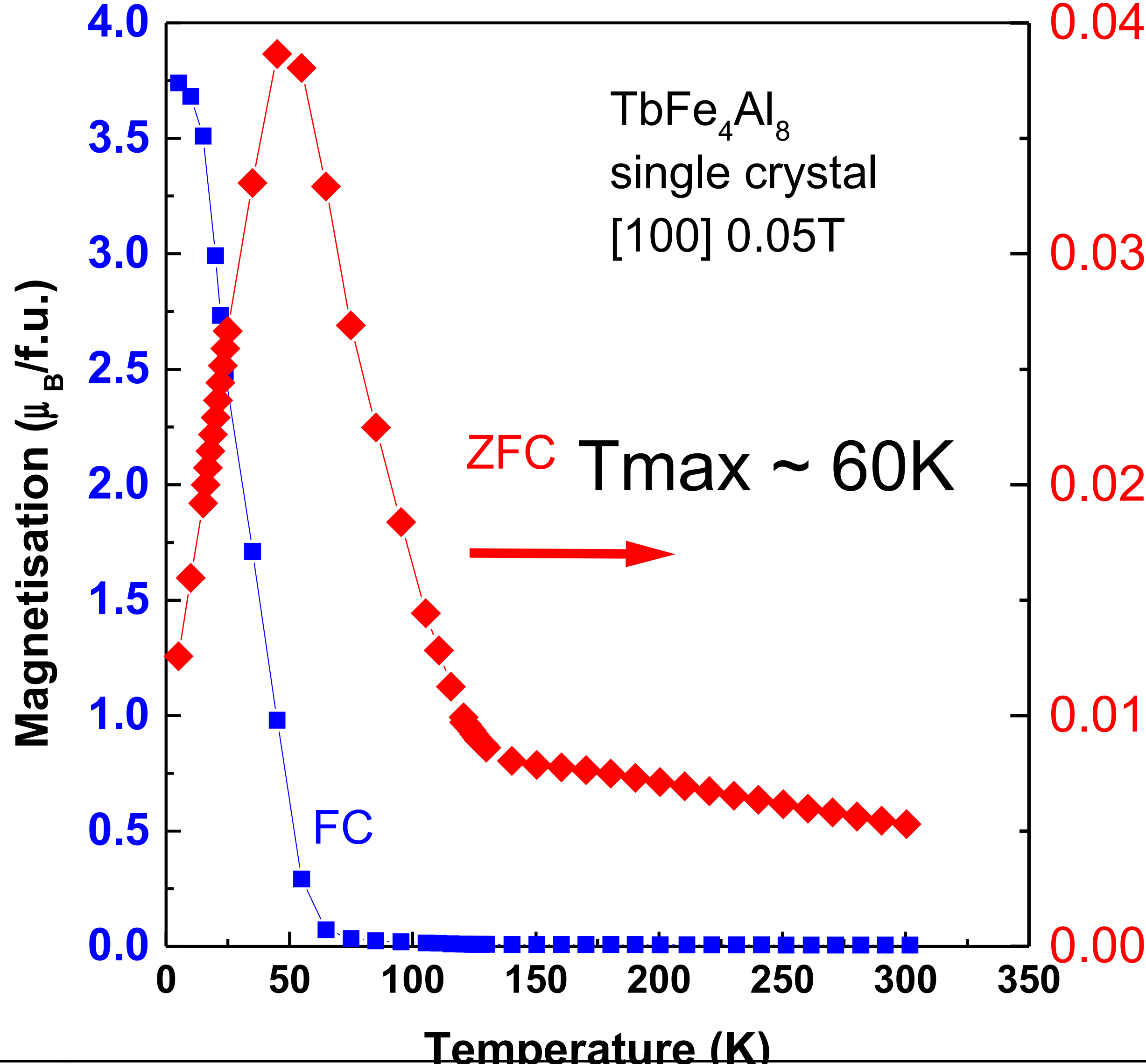
Temperature dependence of magnetisation with B//c-axis



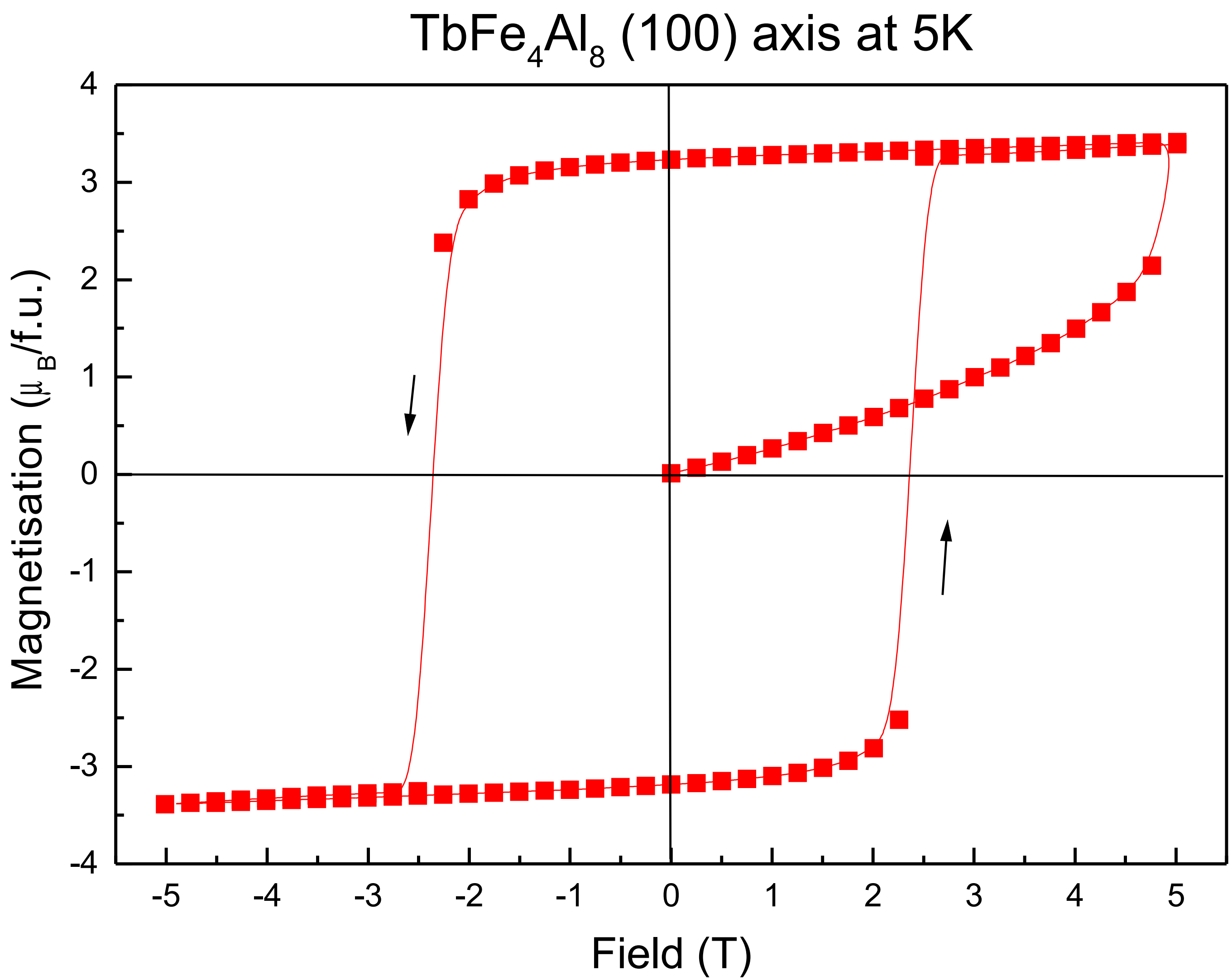
TUDelft stw FOM

Spin glass?

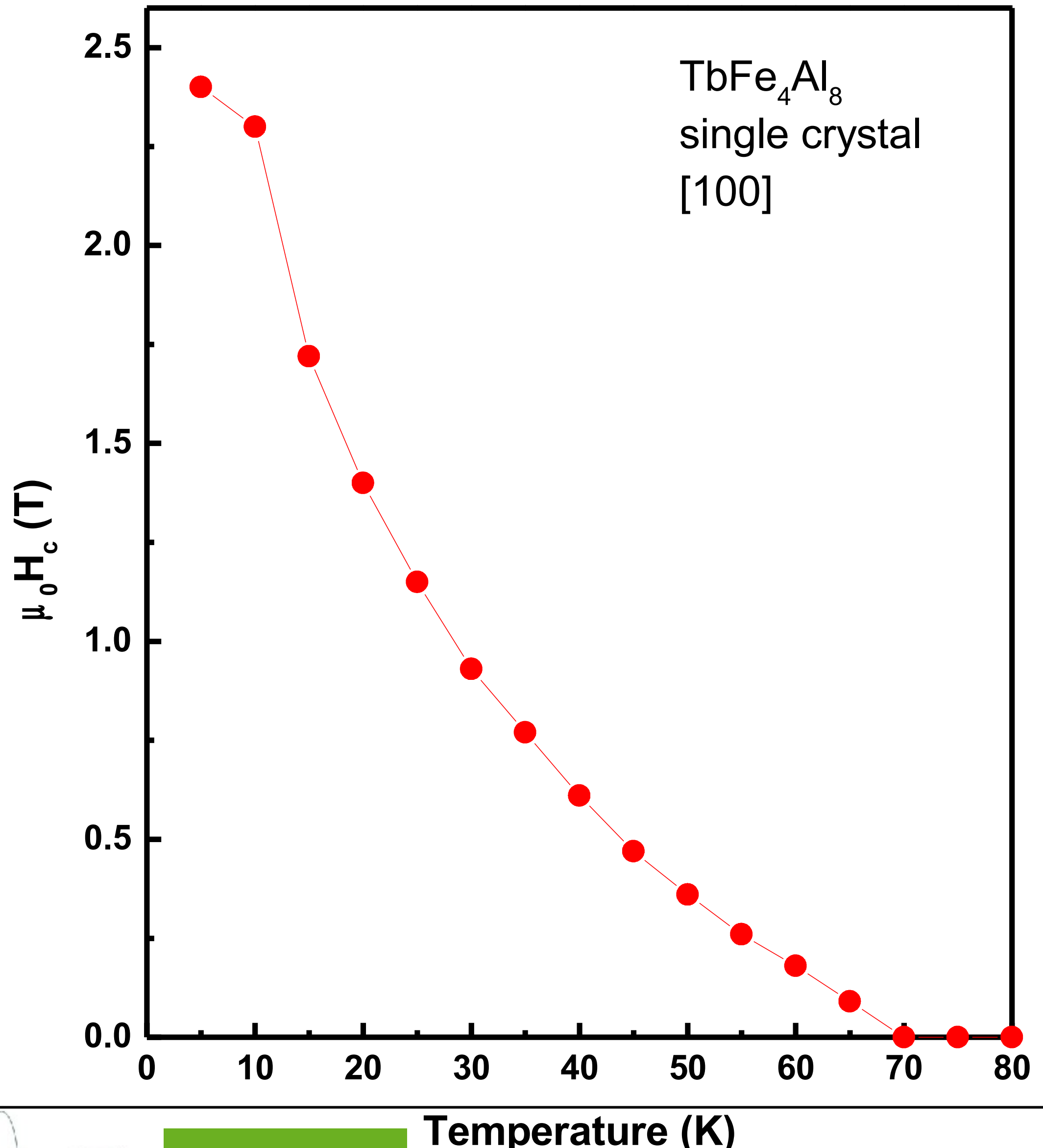
Temperature dependence of magnetisation with B//a-axis



“Hysteresis” loop of ZFC sample

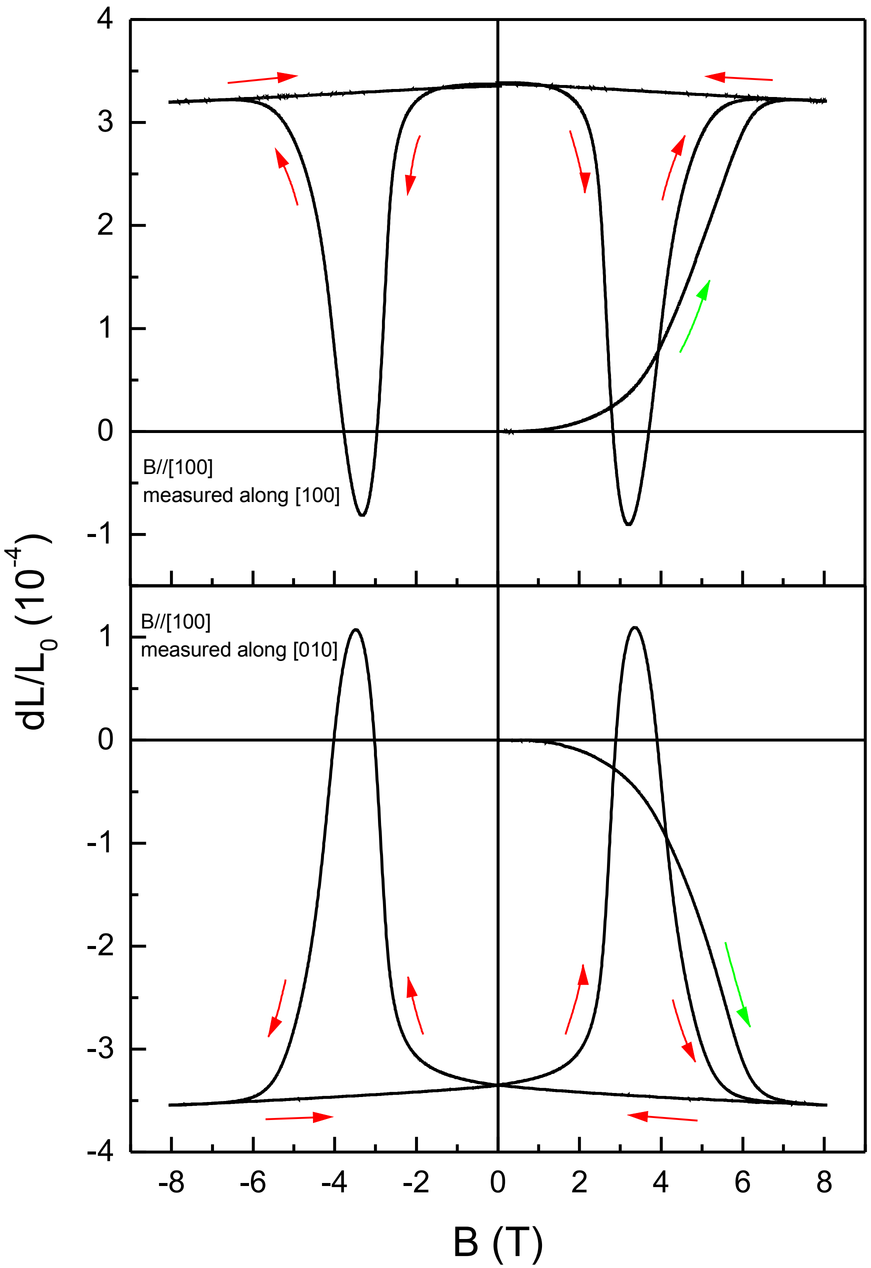


Temperature dependence of coercive field



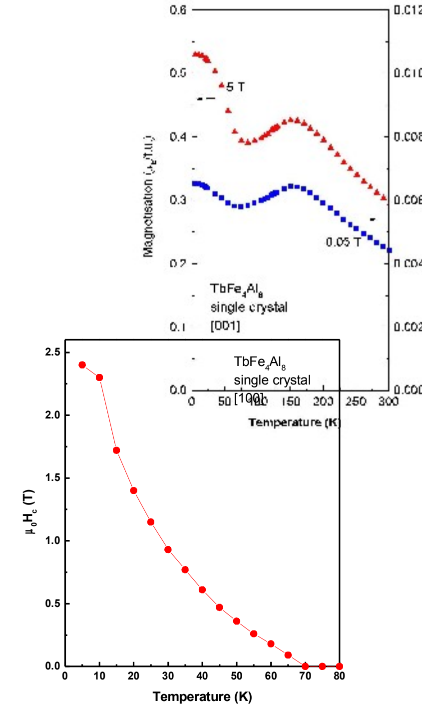
longitudinal and transversal magnetostriction

B//[100]



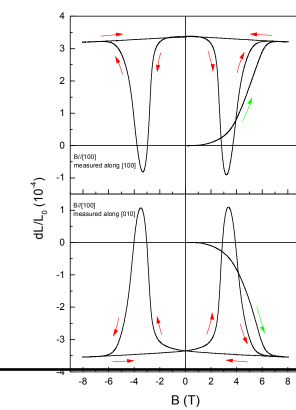
Four relevant energies:

T_N iron = 160 K
T_O terbium = 110 K
T_c coercivity = 70 K
T_F ferrimagnetic = 25 K



Peculiar magnetization not related to AF order or CantedSpiral order.

Magnetoelastic effect (orthorhombic)



People involved in project

Delft

- Senior scientists: Jürgen Buschow, Niels van Dijk
- Pos docs: Lian Zhang, Luana Caron, Cam Thanh Dinh
- PhD students: Thanh Trung Nguyen, Zhiqiang Ou, Huu Dung Nguyen, Jose Leitao
- Technician: Anton Lefering

Gilles de Wijs en Rob de Groot, Nijmegen

Thank you, mercie

postdoctoral fellowship vacancy no. TNWRRR11-018
PhD student position vacancy no. TNWRRR11-019