materials for magnetic refrigeration

Ekkes Brück

Introduction

Magnetic cooling

Giant magnetocaloric effect

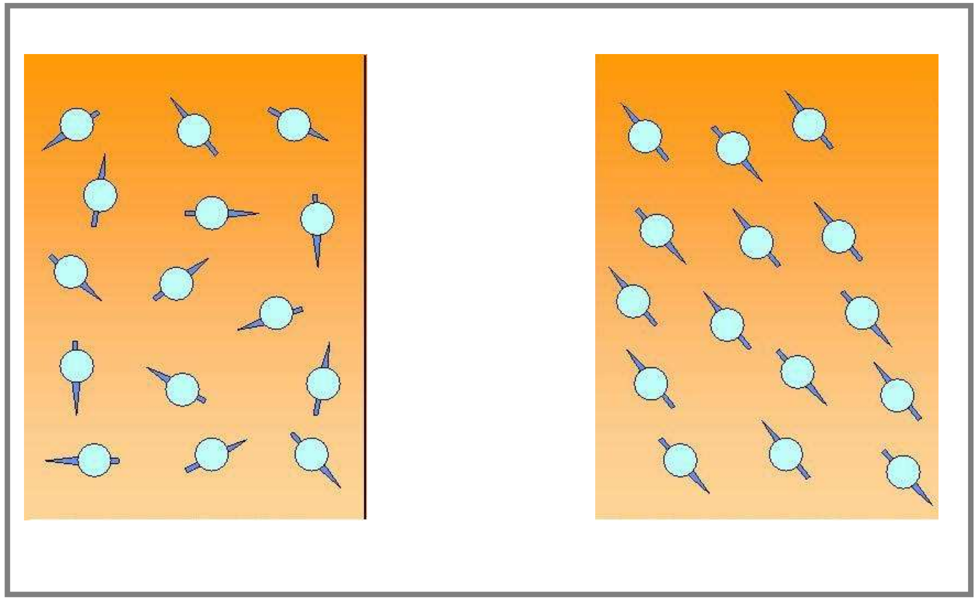
Outlook

Review: E. Brück, Magnetic refrigeration near room temperature, Handbook of magnetic materials Vol 17 chapt. 4 (2007) ed. K.H.J. Buschow

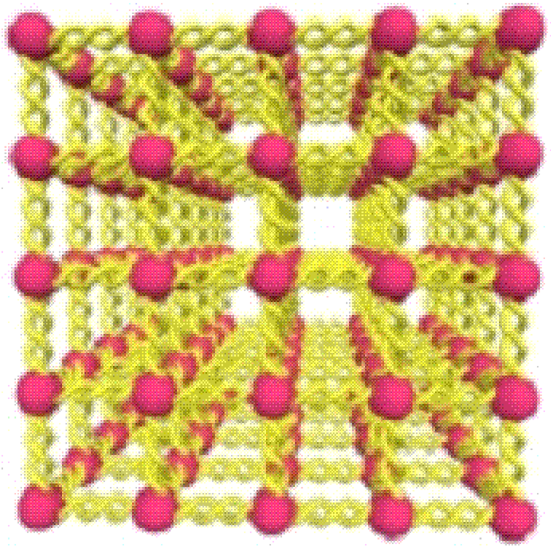
Basic magnetocalorics

Two energy reservoirs

spins → lattice

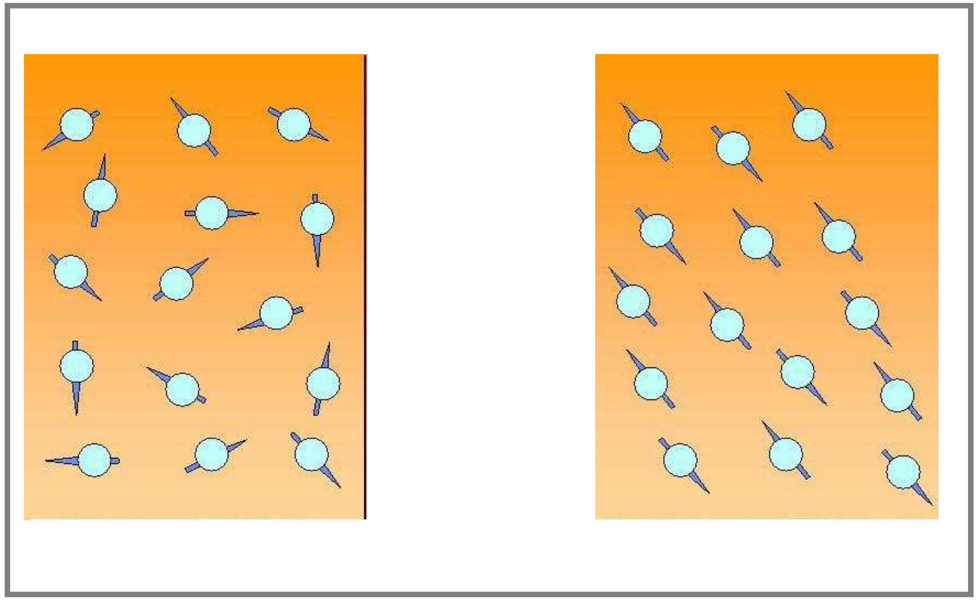


E →



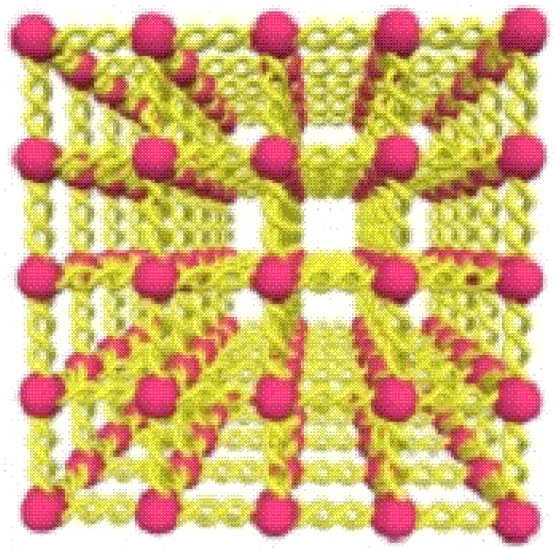
Basic magnetocalorics

spins ← lattice

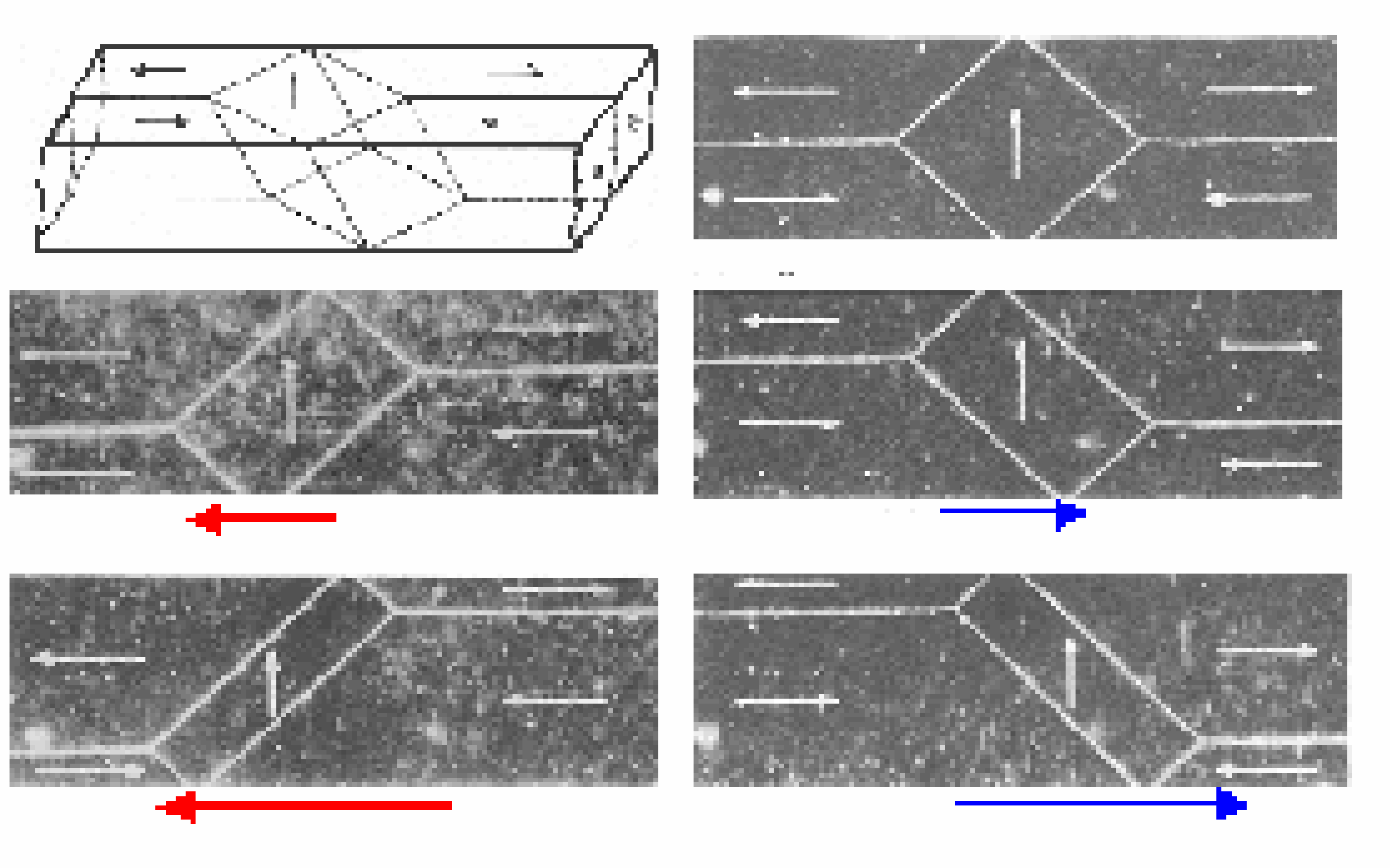


E

←



Domain movement



Magnetic cooling: Debye and Giauque 1926

768 LETTERS TO THE EDITOR

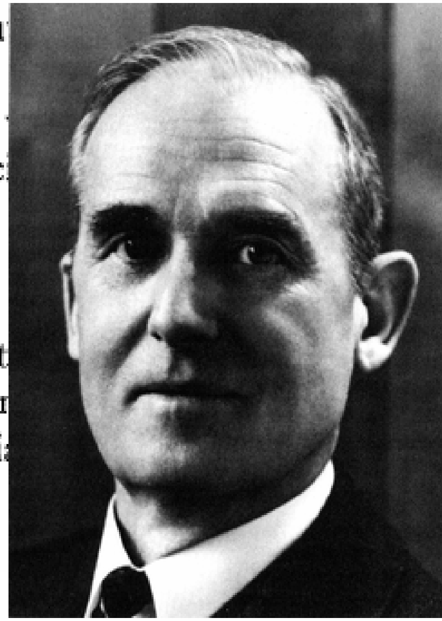
Attainment of Temperatures Below 1° Absolute by Demagnetization of $Gd_2(SO_4)_3 \cdot 8H_2O$

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.



E
GALL

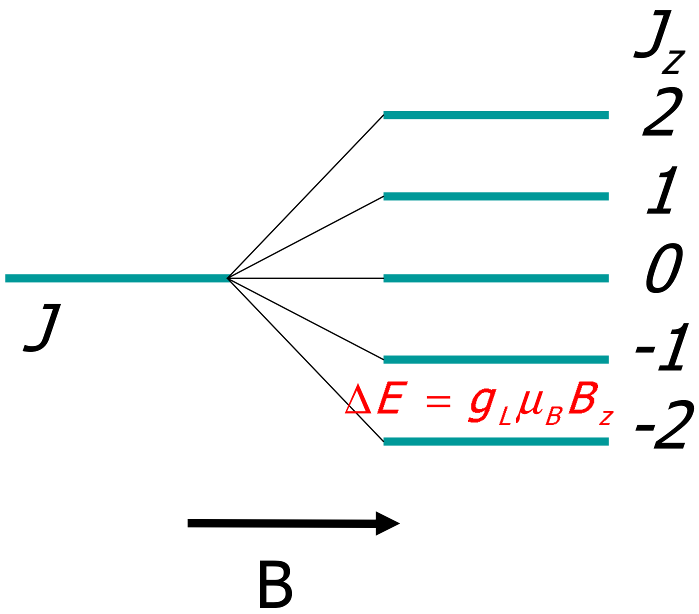
Department of Chemist
University of Califor
Berkeley, Californi
April 12, 1933.

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

Nobel prize 1949

Zeeman effect for state with total moment J

- Ground state J is 2J+1 times degenerated: J_z=-J, -J+1, … 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:

$$G = U - TS + pV$$

Thermodynamic relations:

Differential of Gibbs free energy

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

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

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

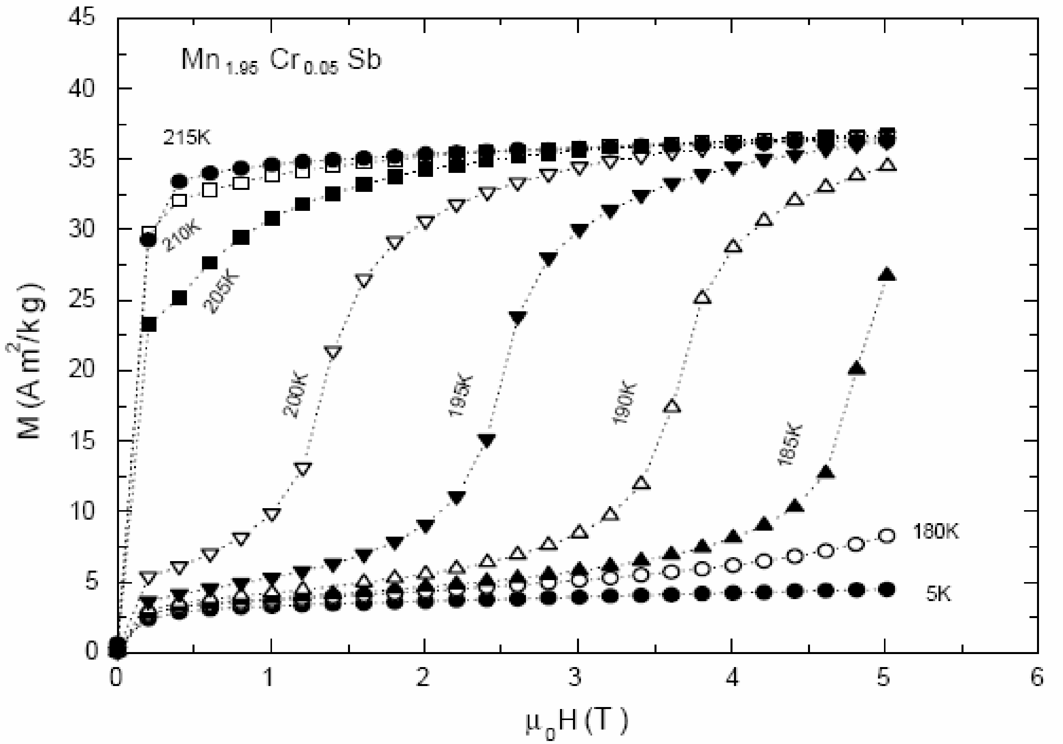
S_0 can be set to zero because it is not depending on field

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

Easy measurable

Experimental determination from magnetic measurements

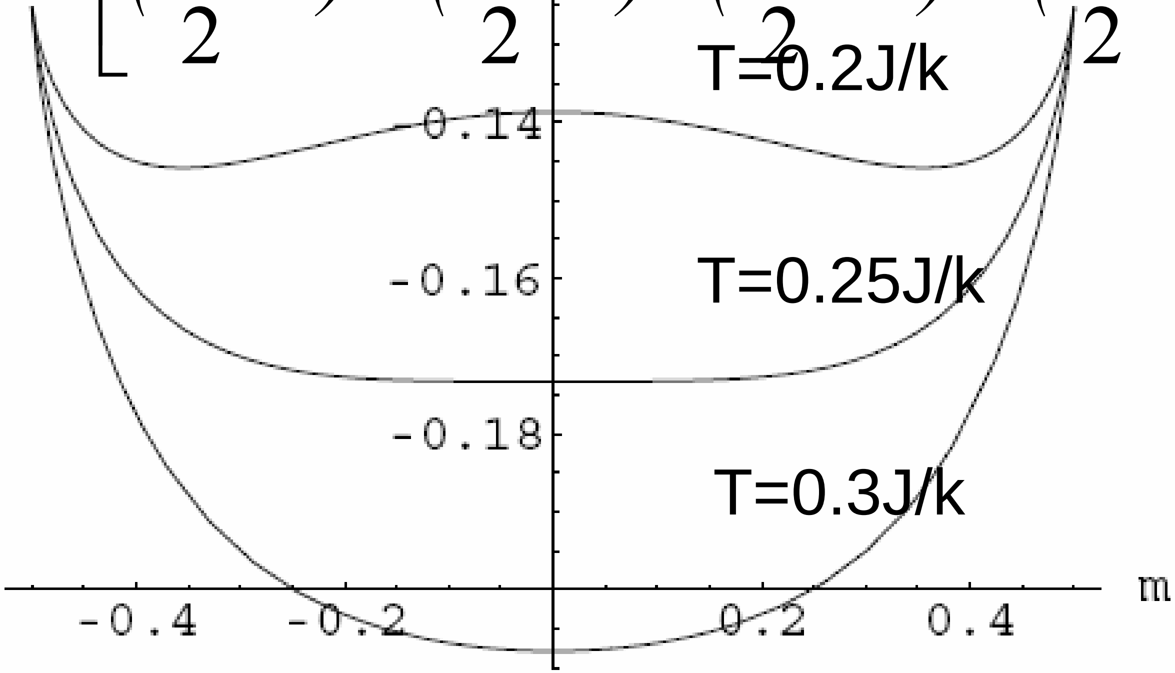
$$\Delta S_m(T,B) = \sum_i \frac{M_{i+1}(T_{i+1},B) - M_i(T_i,B)}{T_{i+1} - T_i} \Delta B$$



Continuous phase transition

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

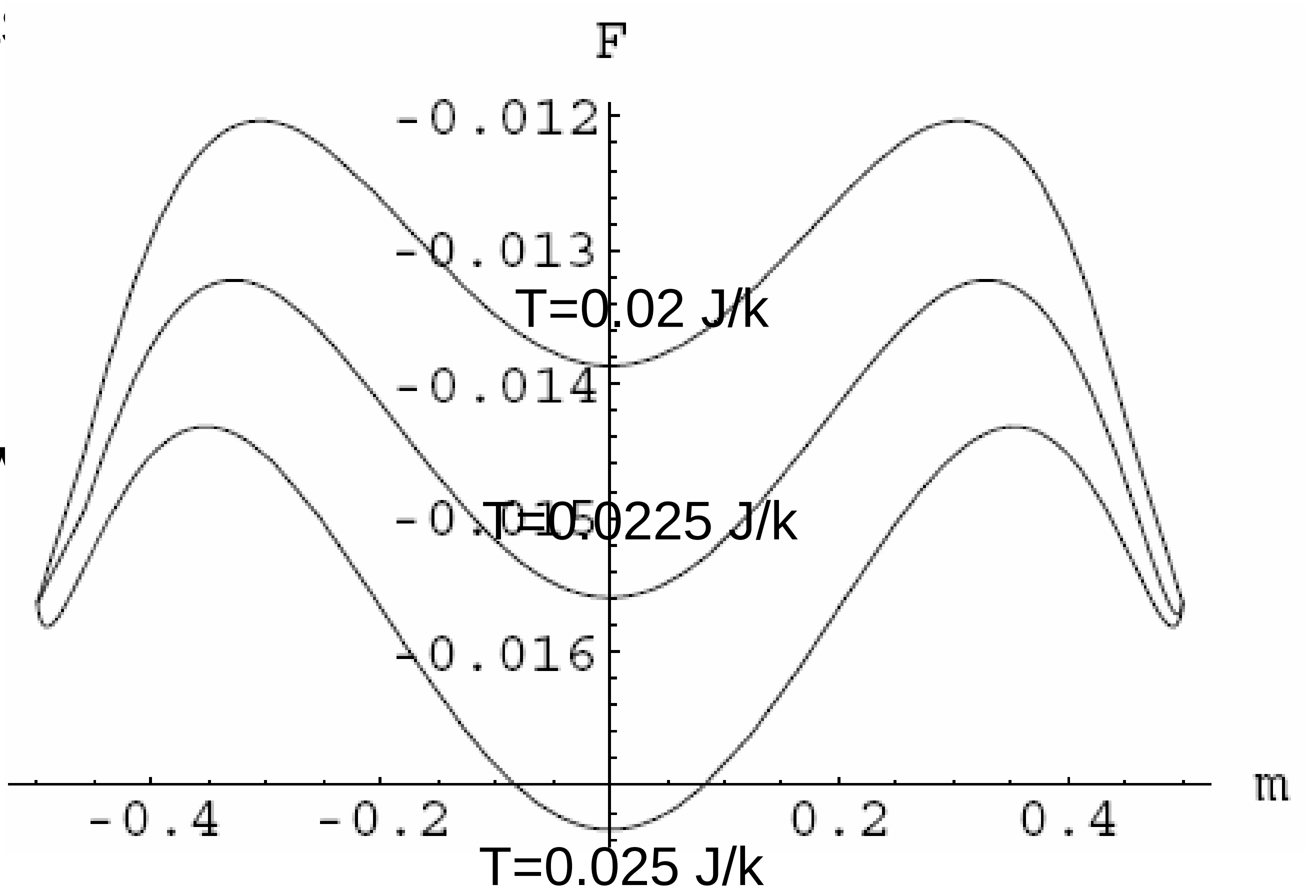
$$F = -\frac{1}{2}NJm^2 - NHm + NT\left[\left(\frac{1}{2}-m\right)\ln\left(\frac{1}{2}-m\right)+\left(\frac{1}{2}+m\right)\ln\left(\frac{1}{2}+m\right)\right]$$



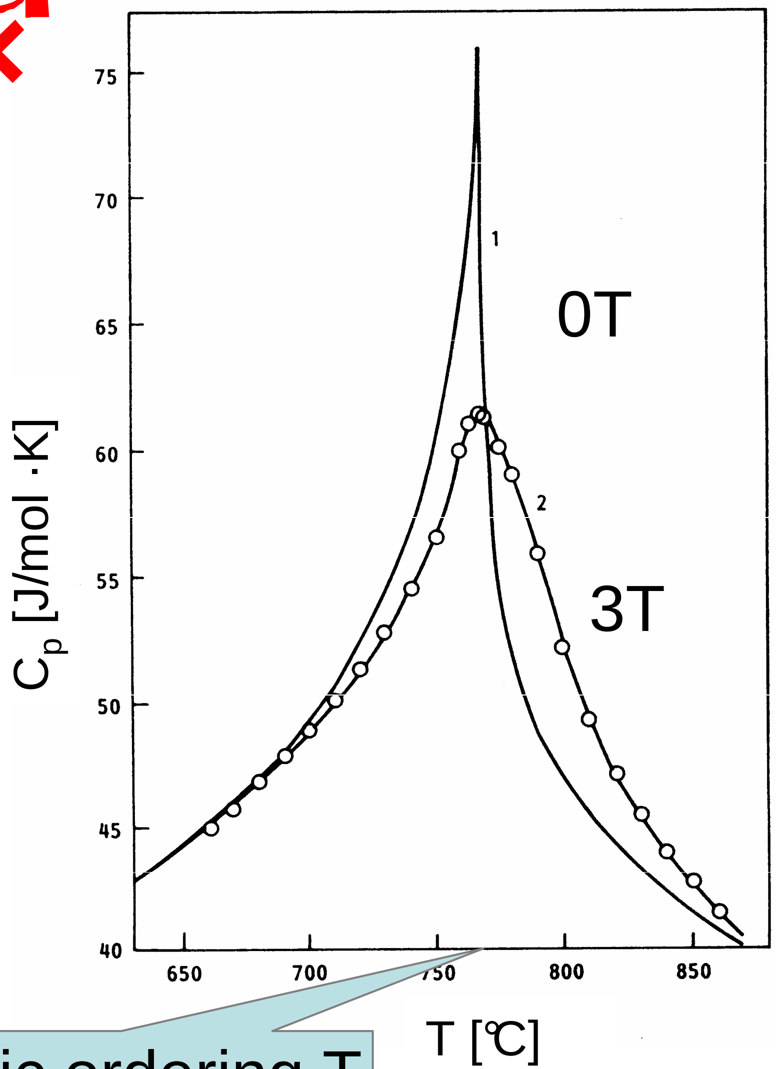
First order phase transition

If interactions with quartet[s]
play a role this may result
in local minima in the free
energy.

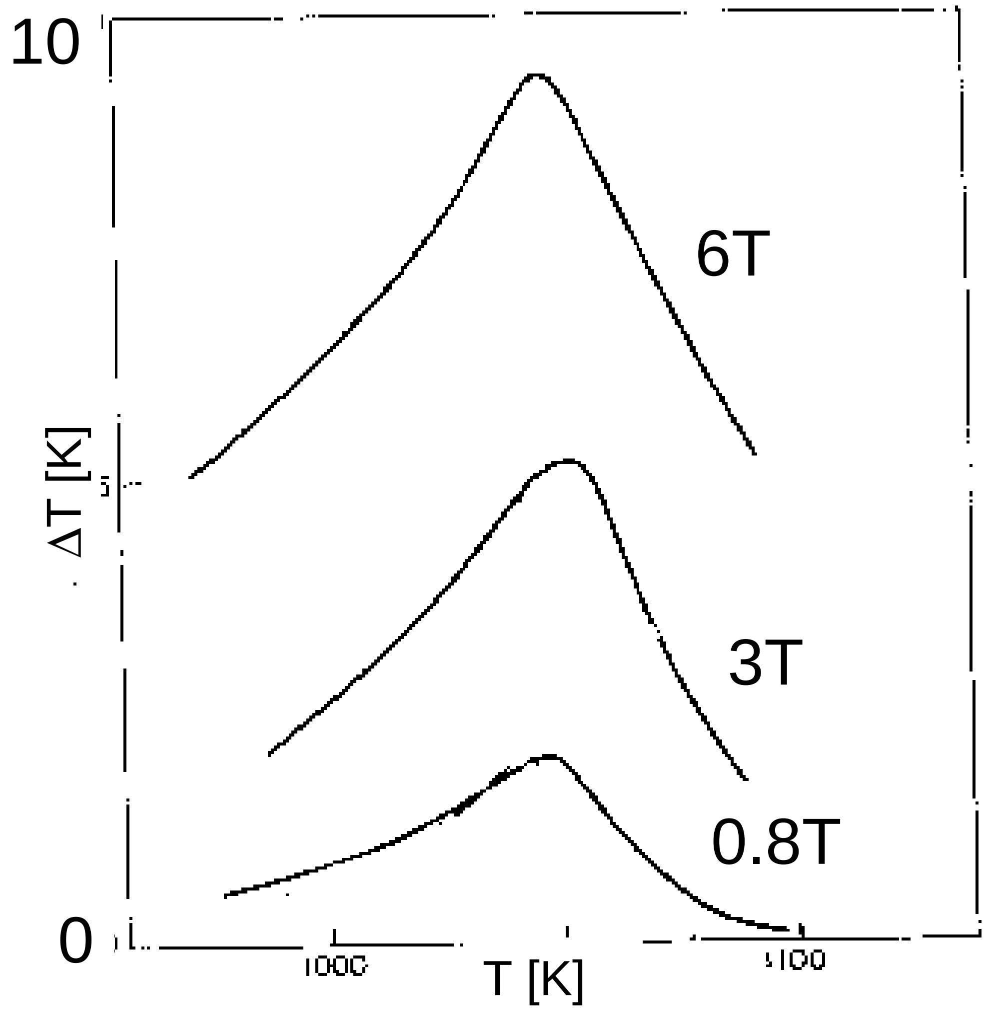
$$F = -\frac{1}{2} NJm^4 - NHm + N$$



MCE in iron

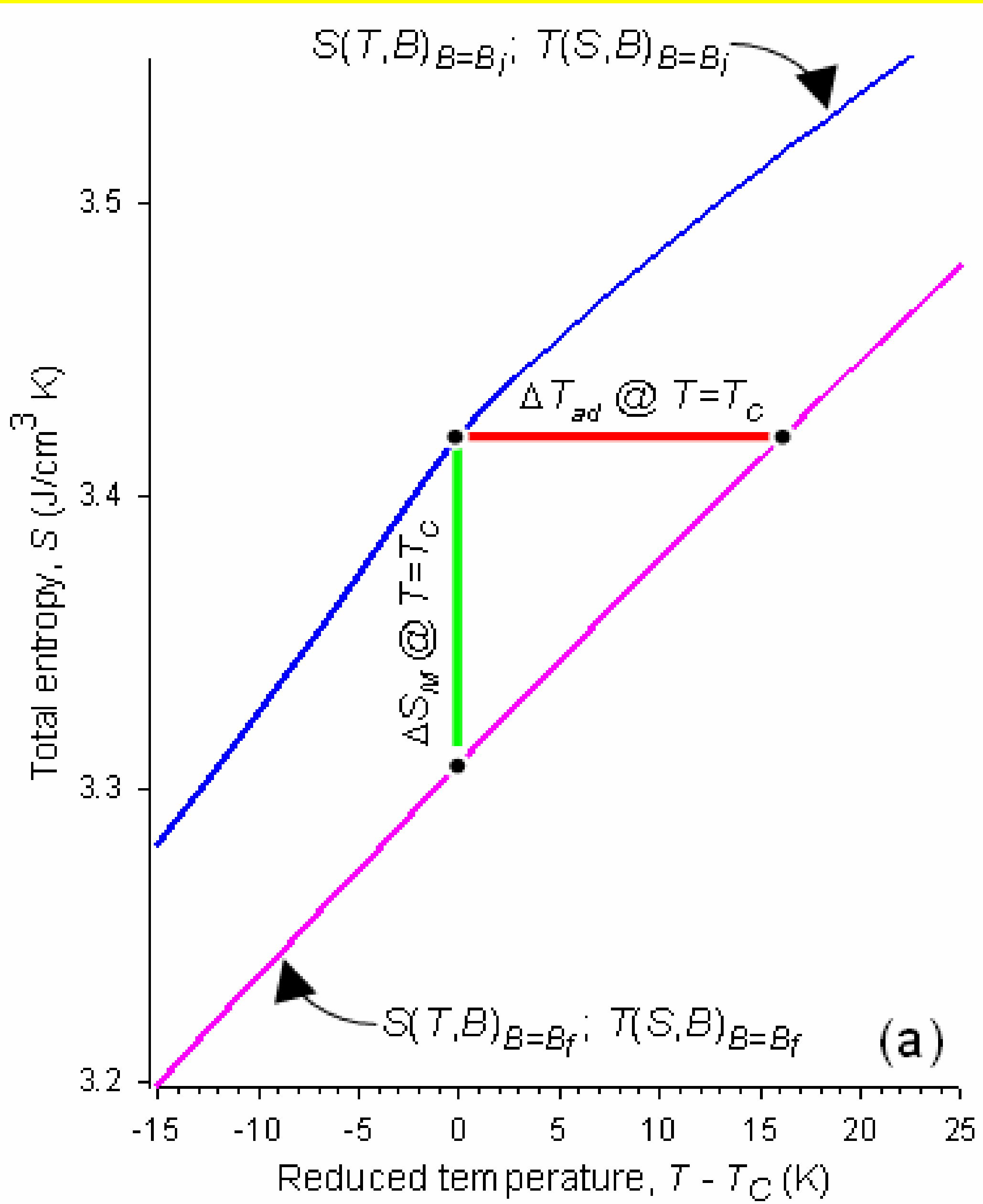


Magnetic ordering T



MCE in gadolinium

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

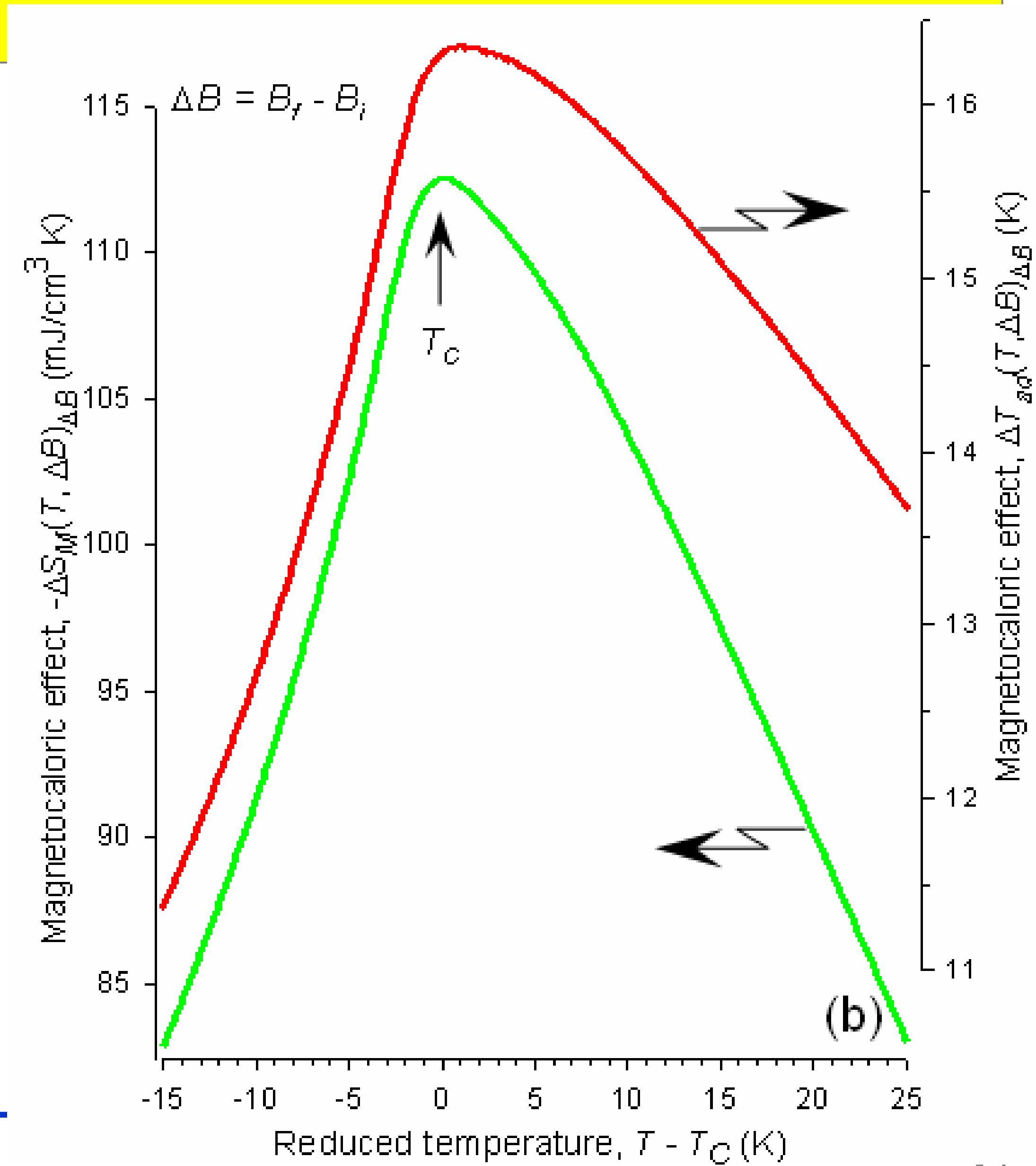


MCE in gadolinium

Magnetic entropy change (green left scale) and

Temperature change (red right scale)

Derived from specific heat data. (Gschneidner et al)



The magnetocaloric properties of selected binary intermetallic compounds

Compound	T_C (K)	$-\Delta S_M$ (mJ/cm^3K) 0-2T	$-\Delta S_M$ (mJ/cm^3K) 0-5T	ΔT_{ad} (K) 0-2T	ΔT_{ad} (K) 0-5T	Dens. (g/cm3)
Gd_4Bi_3	332	15	27	2.2	4.2	10.073
$Gd_4(Bi_{2.25}Sb_{0.75})$	308	27	47	3.7	6.8	9.679
$Gd_4(Bi_{1.5}Sb_{1.5})$	289	24	47	3.1	6.5	9.259
$Gd_4(Bi_{0.75}Sb_{2.25})$	273	26	49	3.2	6.4	8.834
Gd_4Sb_3	265	29	55	3.2	6.4	8.414
Gd_2In	194	18.5	37	2.0	4.4	8.316
Gd_2In	~50[a]	-12	-4	-0.7	-0.2	8.316

[a]Temperature at which ΔSM has the largest positive value and ΔTad has largest negative MCE value

Ilyn M I, Tishin A M, Gschneidner K A Jr, Pecharsky V K and Pecharsky A O 2001 *Cryocoolers 11* ed R G Ross Jr (New York: Kluwer Academic/Plenum) p 457

Niu X J, Gschneidner K A Jr, Pecharsky A O and Pecharsky V K 2001 *J. Magn. Magn. Mater.* **234** 193

The magnetocaloric properties of selected binary intermetallic compounds

Comp.	T_C (K)	$-\Delta S_M$ (mJ/cm^3K)		ΔT_{ad} (K)		Density (g/cm^3)
		0-2T	0-5T	0-2T	0-5T	
Nd_2Fe_{17}	325	25	46	1.9	4.0	7.797
Gd_7Pd_3	323	22	57	3.0	8.5	8.707
TmAg	~12[b]	11	74[c]	0.8	4.2[c]	10.169
TmAg	~ 7[a]	-26	-55[c]	-0.4	-0.9[c]	10.169
TmCu	~10[b]	25	118[c]	0.6	3.6[c]	9.692
TmCu	6.7[d]	-68	-131[c]	-0.4	-1.8[c]	9.692

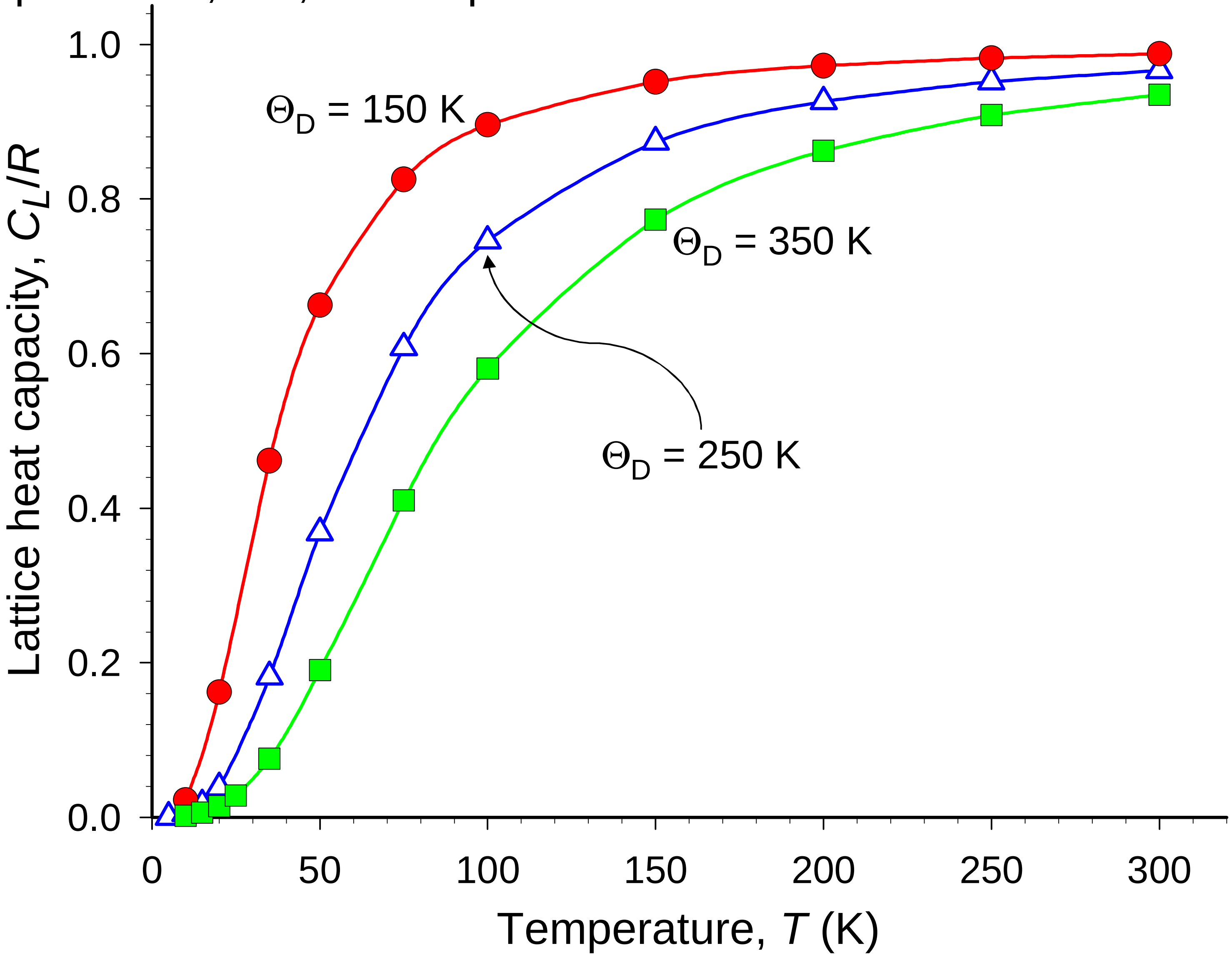
[a]Temperature at which ΔSM has the largest positive value and ΔT_{ad} has largest negative MCE value
[b]Maximum in MCE (no magnetic ordering observed at this temperature) [c]Interpolated [d]Néel temperature

Dan'kov S Yu, Ivtchenko V V, Tishin A M, Gschneidner K A Jr and Pecharsky V K 2000 *Adv. Cryog. Engin.* **46** 397
Canepa F, Napoletano M and Cirafici S 2002 *Intermetallics* **10** 731
Rawat R and Das I 2001 *J. Phys.: Condens. Matter* **13** L379

The magnetocaloric properties of selected ternary intermetallic compounds.

	T_C[a]	$-\Delta S_M$ (mJ/cm^{3}K)		ΔT_{ad} (K)		Dens. (g/cm^3)
Compound		0-2T	0-5T	0-2T	0-5T	
GdCoAl	100	37	79	---	---	7.575
TbCoAl	70	41	80	---	---	7.649
DyCoAl	37	70	125	---	---	7.619
$GdPd_2Si$	17	42	142	3.2	8.6	9.358
HoCoAl	10	100	171	---	---	7.961

Zhang X X, Wang F W and Wen G H 2001 *J. Phys.: Condens. Matter* **13** L747 dimensionlless lattice heat capacity of three solids with different Debye temperatures, ΘD, vs. temperature



Rules for magnetocaloric effect

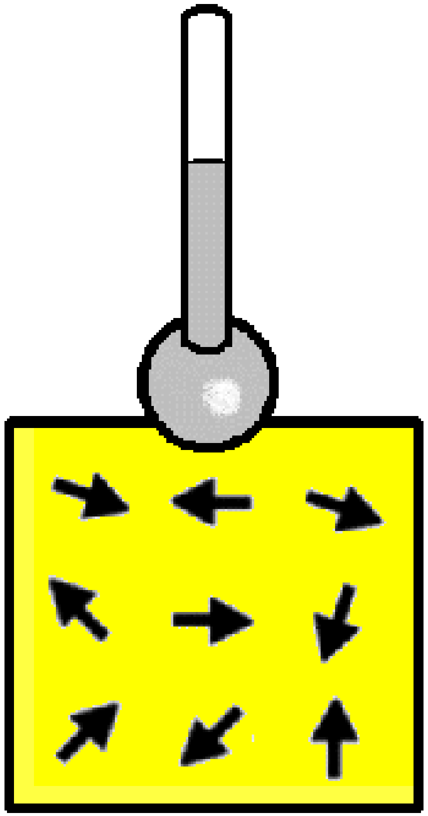
Larger moment $\Rightarrow$ larger ΔS & ΔT

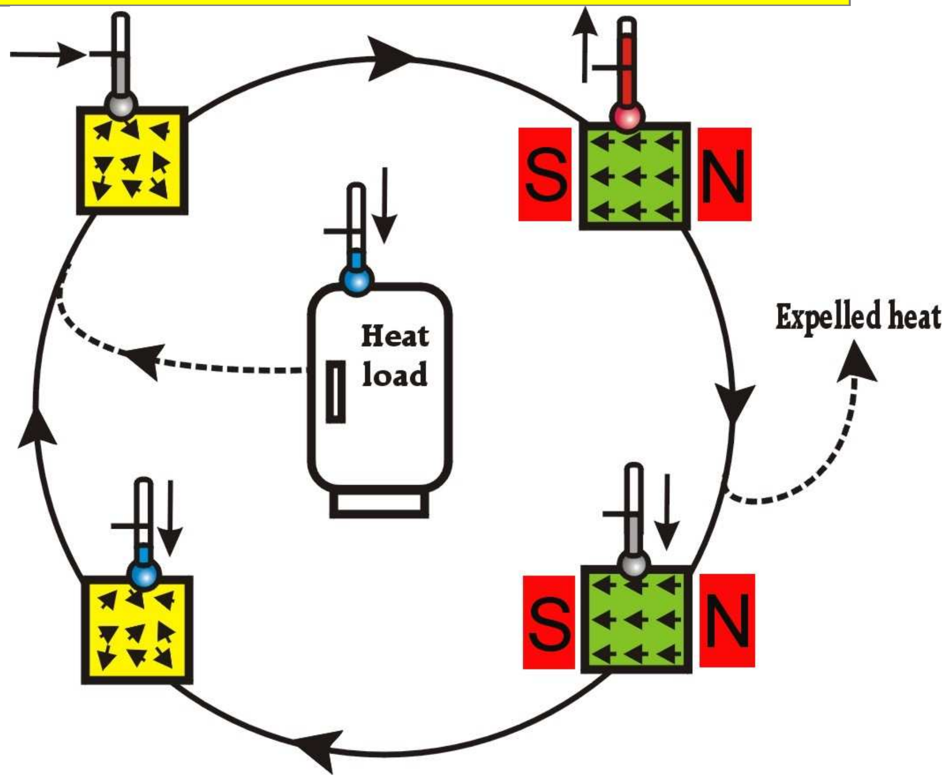
$S_{mag} \approx J$

Lower temperature $\Rightarrow$ larger ΔS & ΔT

Lower thermal agitation

Lower heat capacity





No CFCs, easy scalable, high efficiency, permanent magnets

Chubu and Toshiba Refrigerator 2003

Gd metal

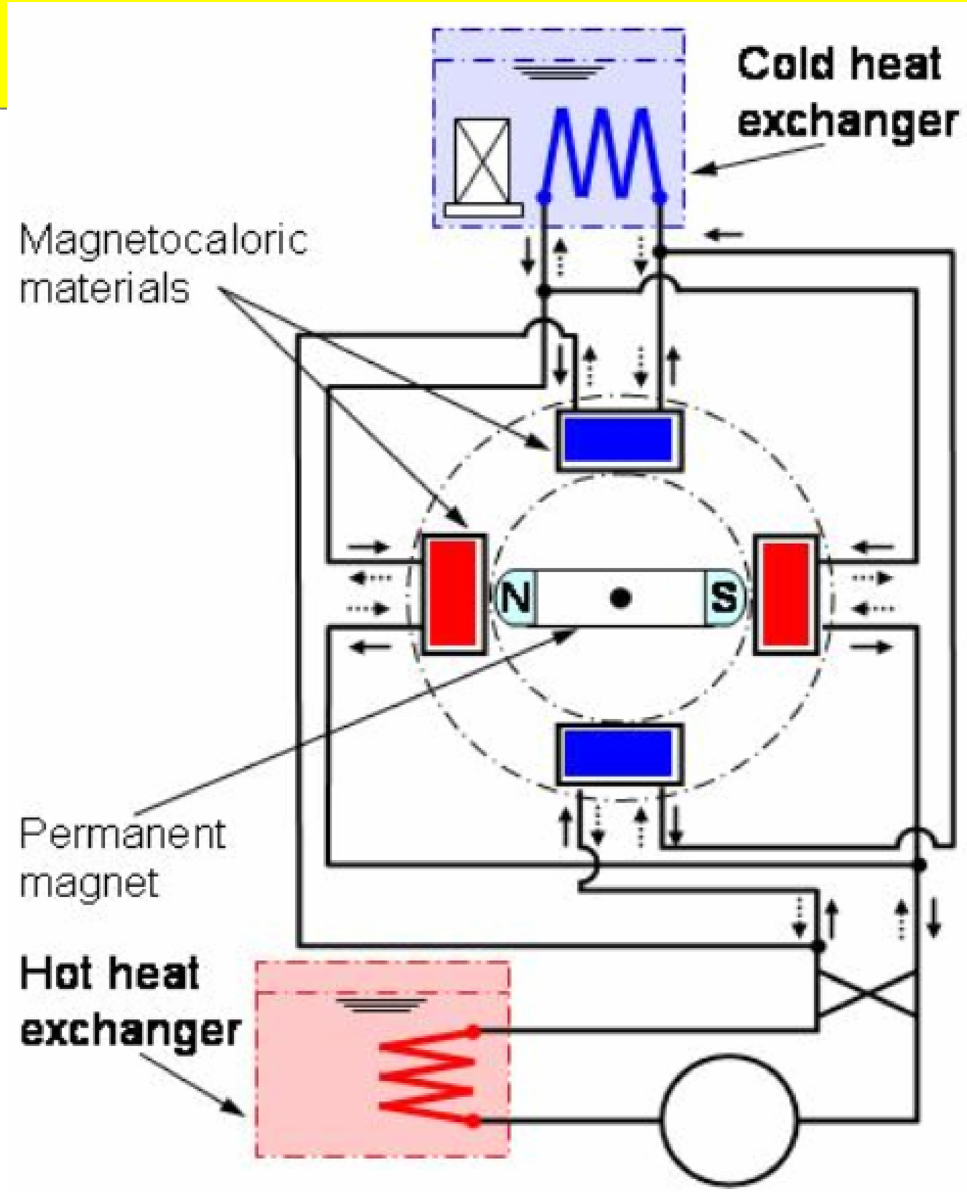
Rotating magnet

0.76 T

Cooling power

60 W

T span 20 K


Cold heat exchanger
Magnetocaloric materials
N
S
Permanent magnet
Hot heat exchanger

Other AMR prototypes

Name	AMR Type	AMR Material	Magnetic Field (T)	Remarks	Ref.
Ames Laboratory/ Astronautics	reciprocatin g	Gd spheres	5 (S)	COP[T] 10	(Zimm et al. 1998)
Barcelona	rotary	Gd foil	0.3 (P)	Olive oil	(Bohigas et al. 2000)
University of Victoria	reciprocatin g	Gd , $Gd_{.74}Tb_{.26}$	2 (S)	epoxy bonded pucks	(Richard et al. 2004)
Lab. Electric Grenoble	reciprocatin g	Gd foil	0.8 (P)	COP[R] 2.2	(Clot et al. 2003)
Astronautics	rotary	Gd, Gd-Er, spheres LaFeSiH particles	1.5 (P)	4 Hz	(Zimm et al. 2006)
Natl Inst. Appl. Sci. / Cooltech	rotary	Gd plates	1 (P)	Torque 10 Nm	(Vasile et al. 2006)
Xian Jiaotong Univ.	reciprocatin g	Gd spheres; $Gd_5(Si,Ge)_4$ pwdr.	2.18 (E)	COP[T] 25	(Gao et al. 2006)
University of Victoria	reciprocatin g	Gd , $Gd_{.74}Tb_{.26}$ $Gd_{.85}Er_{.15}$	2.0 (S)	ΔT 50K	(Rowe et al. 2006)

Replace Gd with material with large MCE

1990 FeRh (Nikitin et al.)

1997 $Gd_5Si_2Ge_2$ ((Percharsky & Gschneidner Jr.)

1998 RCo_2 (Foldeaki et al.)

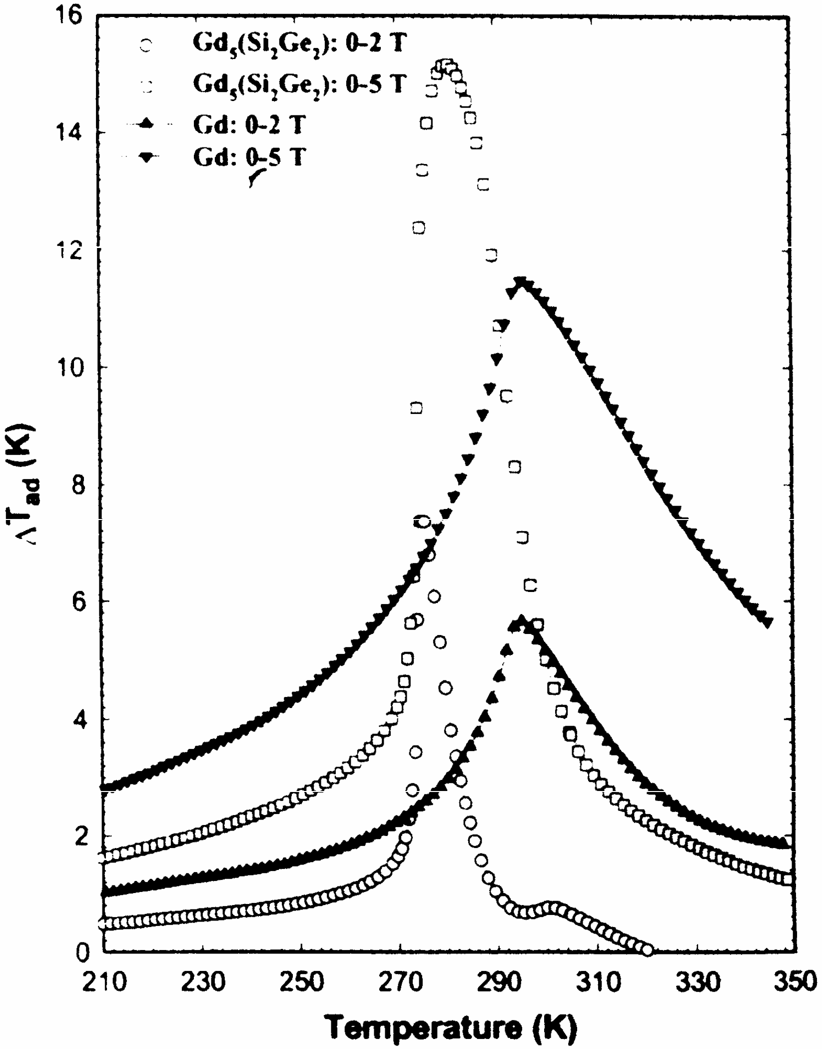
2000-2002 $La(Fe,Si)_{13}$ (Zhang et al., Fukamichi et al.)

2001 $MnAs_{1-x}Sb_x$ (Wada et al.)

2002 MnFe(P,As) (Tegus et al.)

2003 $Co(S_{1-x}Se_x)_2$ (Yamada & Goto)

Giant magnetocaloric effect in $Gd_5Ge_2Si_2$

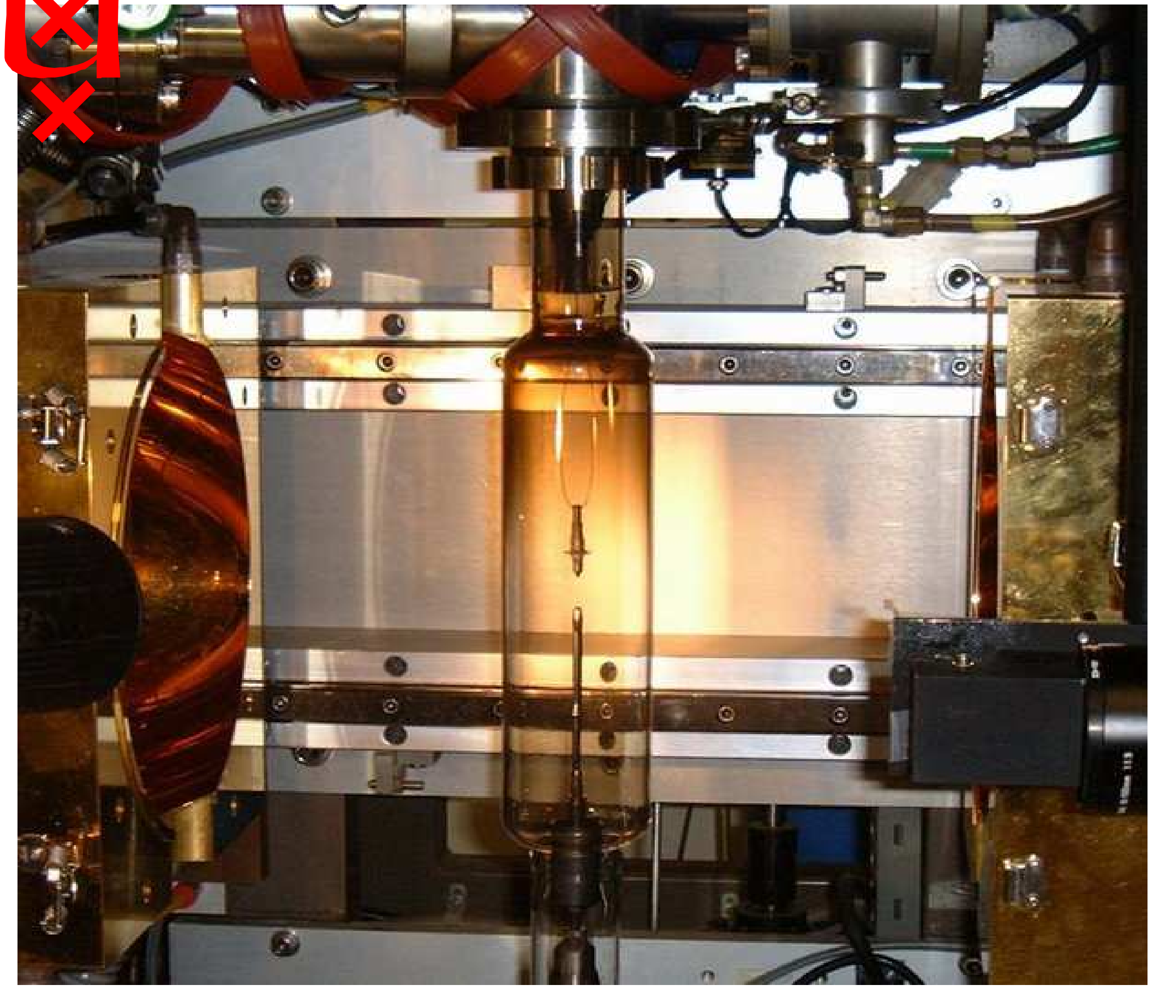


Magnetically dilute yet higher effect

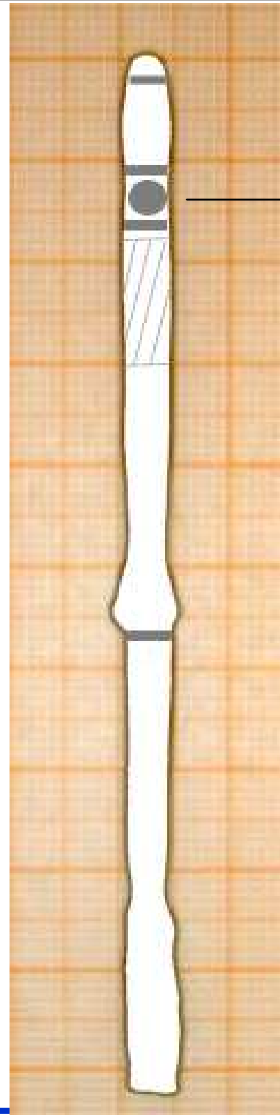
double transition?

Pecharsky & Gschneidner
PRL 78 (1997) 4494

Crystal growth



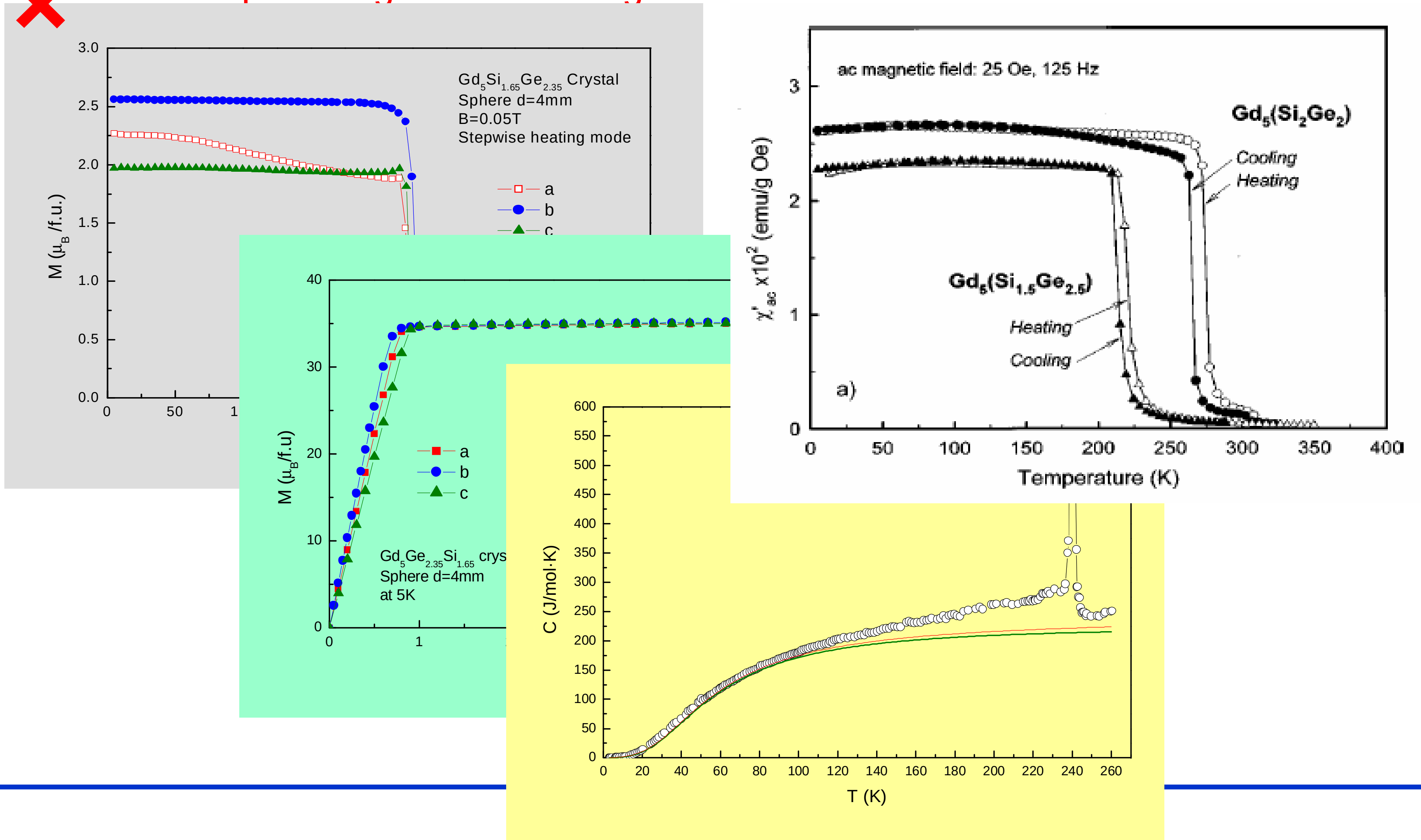
Crystal was grown in a mirror furnace by means of traveling solvent floating zone method



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

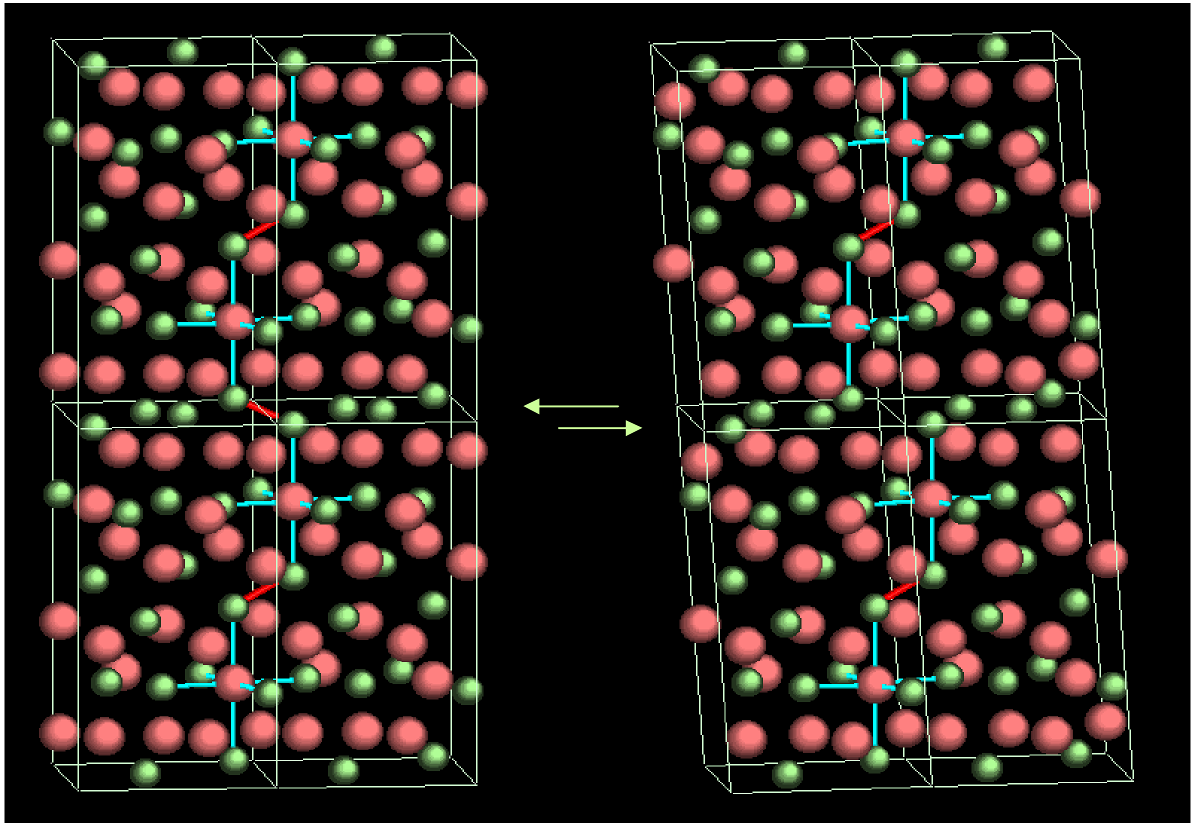
Unusual behavior

- 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.

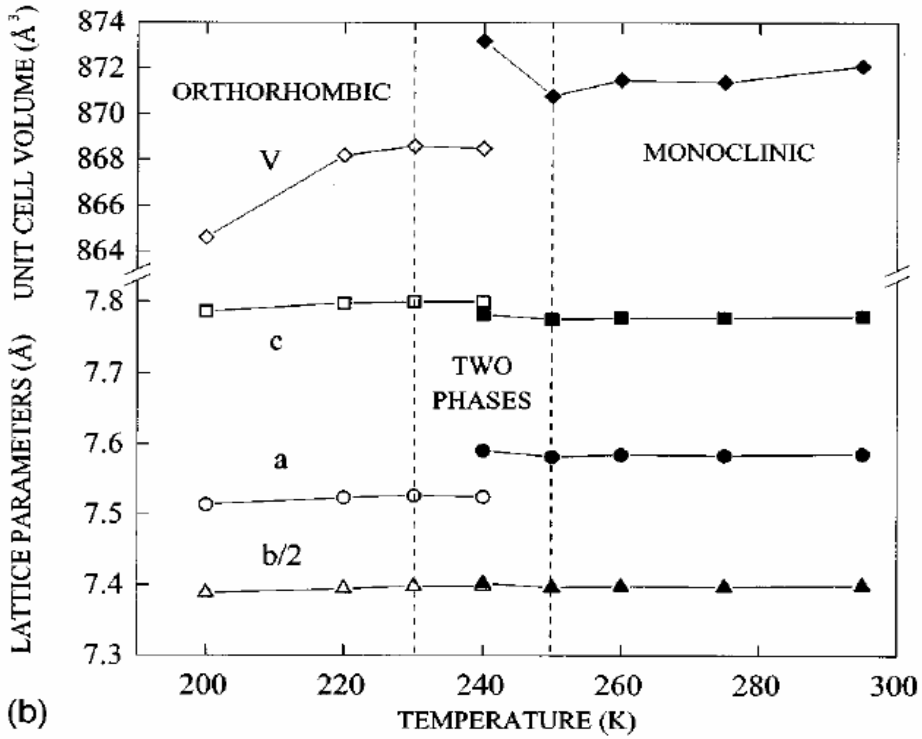


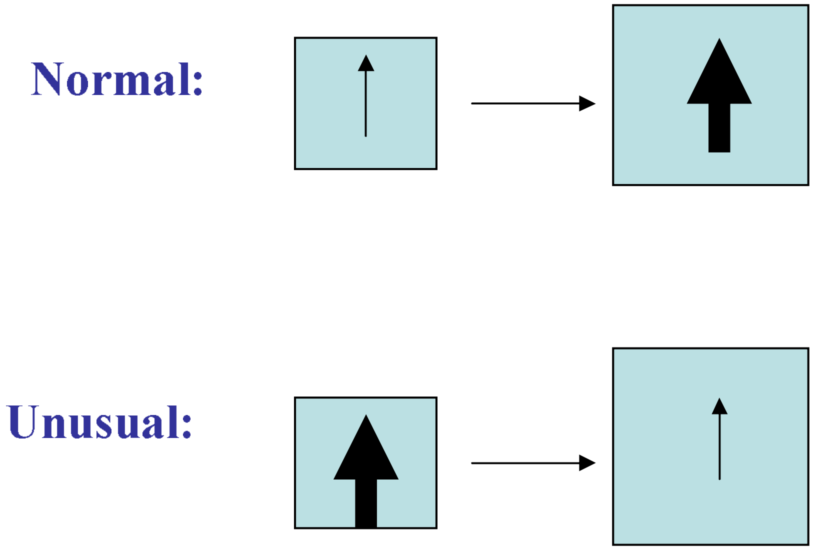
<T_c: Pnma, No.62   >T_c: $P112_1/a$, No.14

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

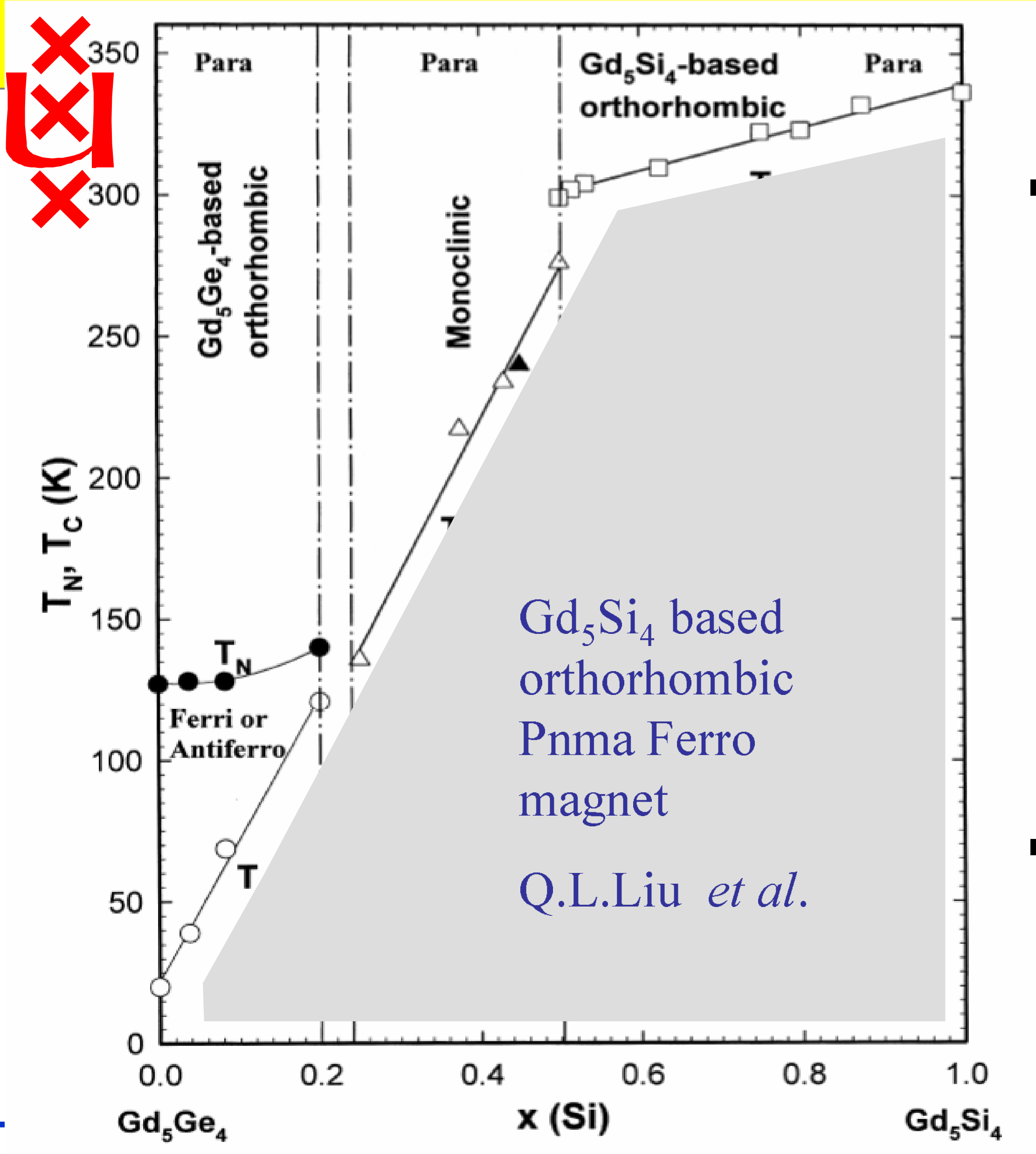
Unusual behavior

- 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

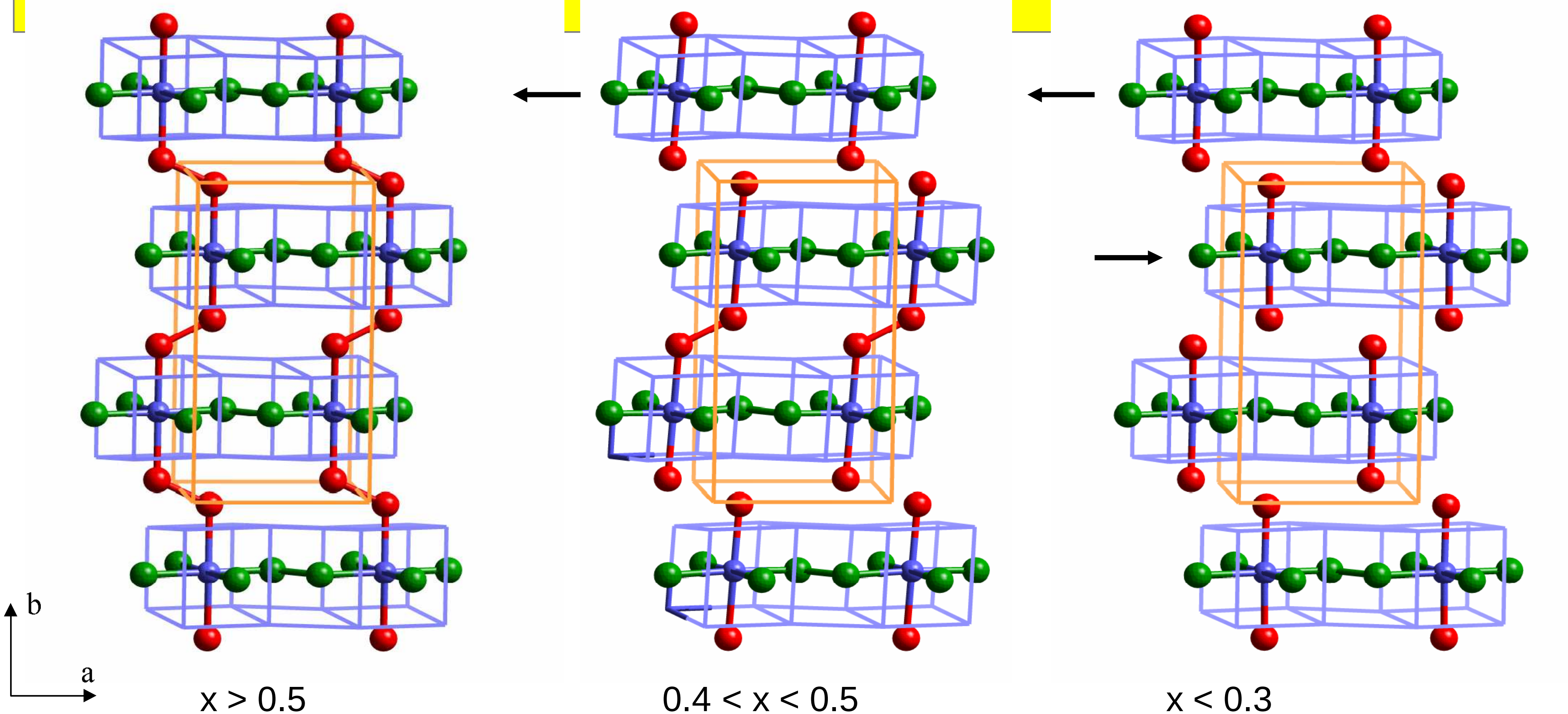


- Recent XRD investigation reported that $Gd_5(Si_xGe_{1-x})_4$ alloys form a completely miscible solid-solution crystallized in the Gd_5Si_4-type *Pnma* structure below T_C regardless of the composition. Ground state is low temperature (Gd_5Si_4–based) orthorhombic ferromagnet

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

Magnetocaloric effect

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)

Summary $Gd_5Ge_2Si_2$

Magnetically driven 1st order structural transition below 270 K.

$Gd_5Ge_2Si_2$ monoclinic above magnetic transition

orthorhombic below.

Anisotropy on X-tals. Exceptional coupling of lattice with s-state 4f-magnetism.

Hysteretic transition: locking of structure?
Mechanical stability?

Transition-metal compounds

other alternative

High abundance (low price)

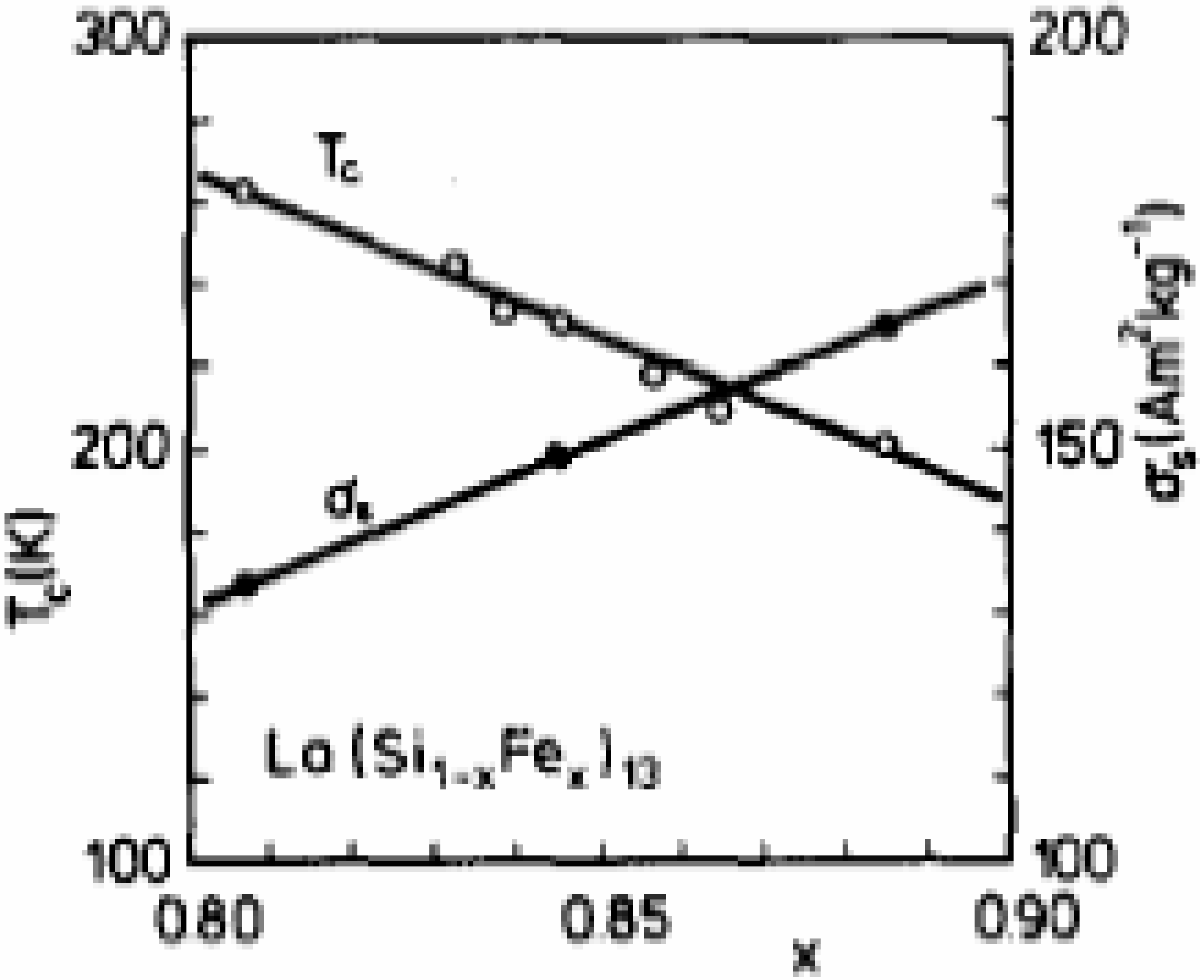
Intermediate magnetic moment (moderate MC effect)

Strong coupling to lattice (Simultaneous magnetic and structural transitions or metamagnetism)

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

Cubic $CaZn_{13}$ type of structure stabilized by addition of 10% Si
(Kripyakewich et al. 1968)
Invar type of behavior and unusual magnetic transition
(Palstra et al 1983)
Difficult to obtain single phase.

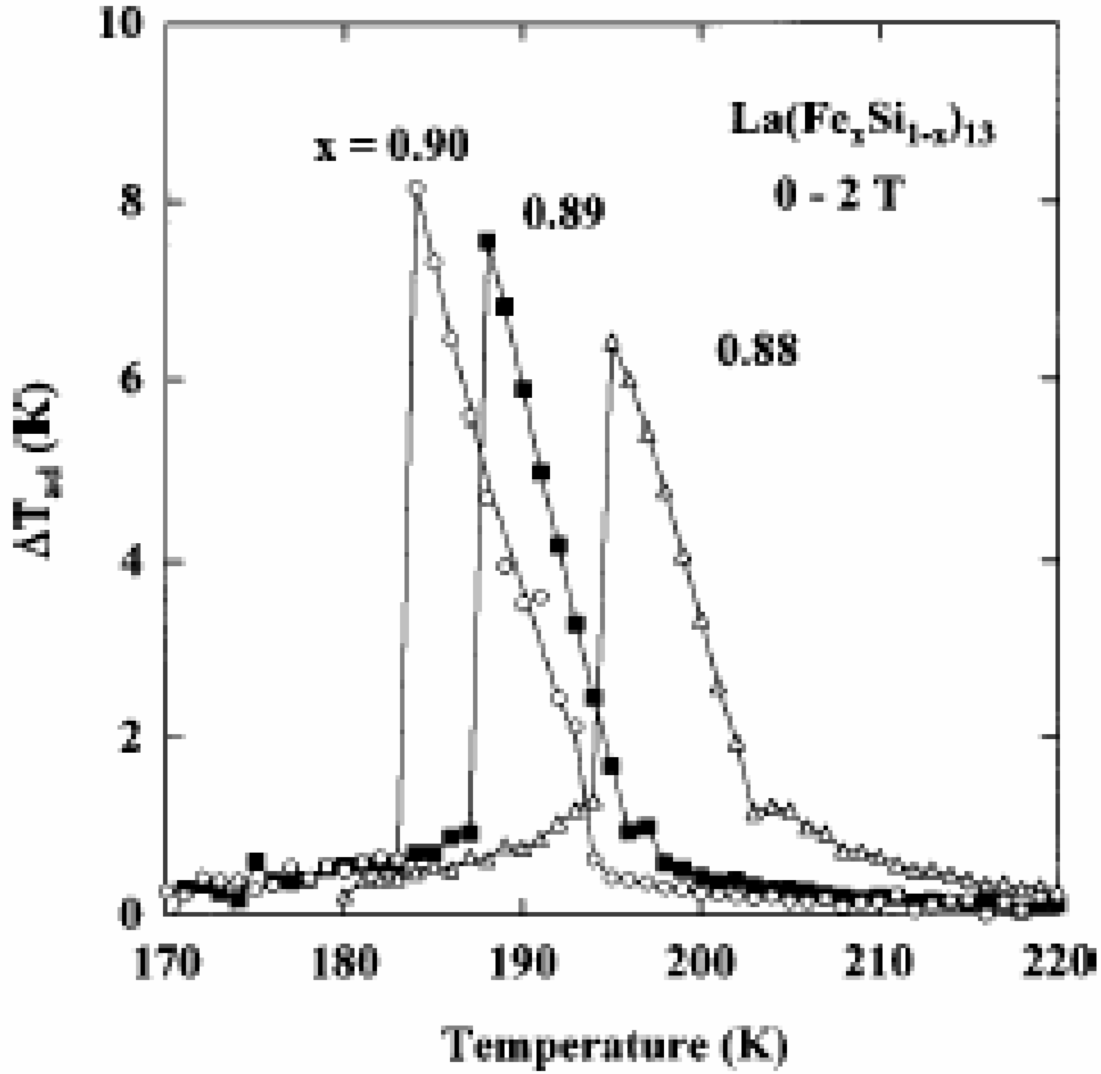
Concentration dependence of Curie temperature and moment



Tc increase
with dilution

Palstra et al. 1983

$LaFe_{13}$ system

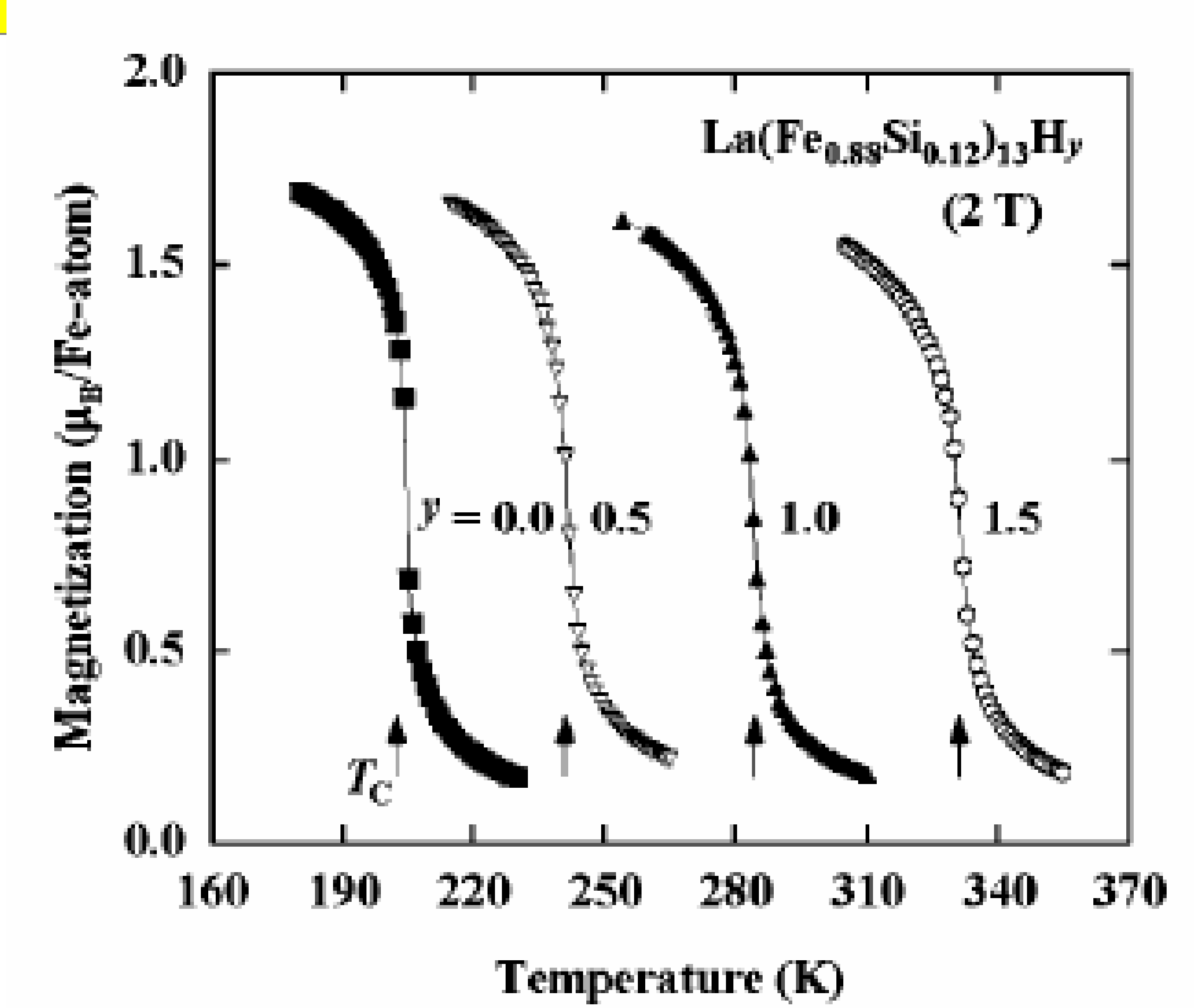


MCE decrease
with dilution

APL Zhang et al 2000

Fujieda et al 2002

$LaFe_{13}$ system with hydrogen

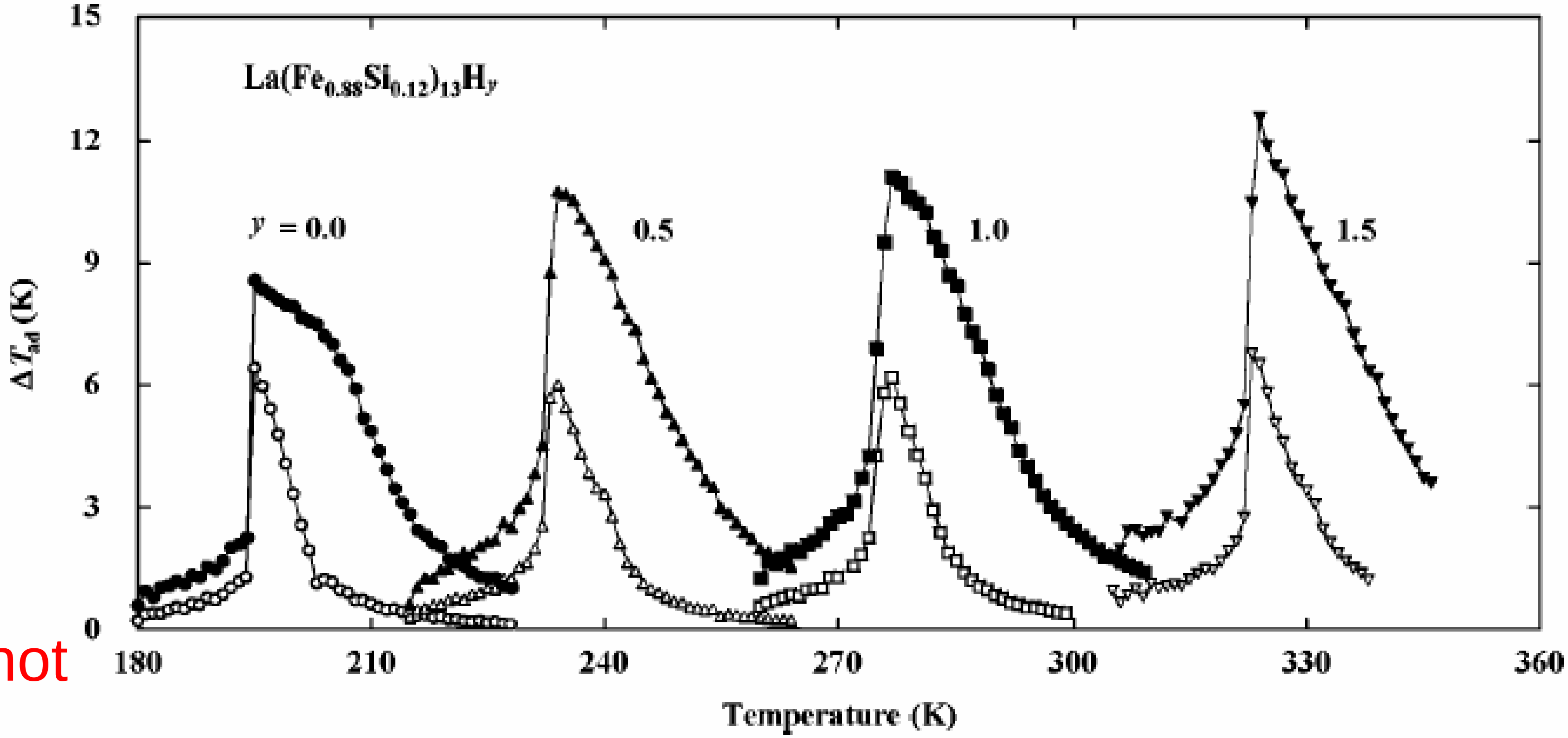


Tc increase with hydrogen!

Sharp transition maintained!

PRB Fujita et al 2003

$LaFe_{13}$ system with hydrogen



MCE almost not affected with hydrogen

PRB Fujita et al 2003

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

Field driven 1st order metamagnetic transition around 200 K .

La(Fe,Si)$_{13}$ cubic above magnetic transition

cubic below

volume change 1.5%.

Low Tc can be increased by addition of Cobalt or Hydrogen.

Hysteretic transition: powder after hydrogenation?
Mechanical stability?

$MnFeP_{1-x}As_x$

Hexagonal Fe_2P type of structure

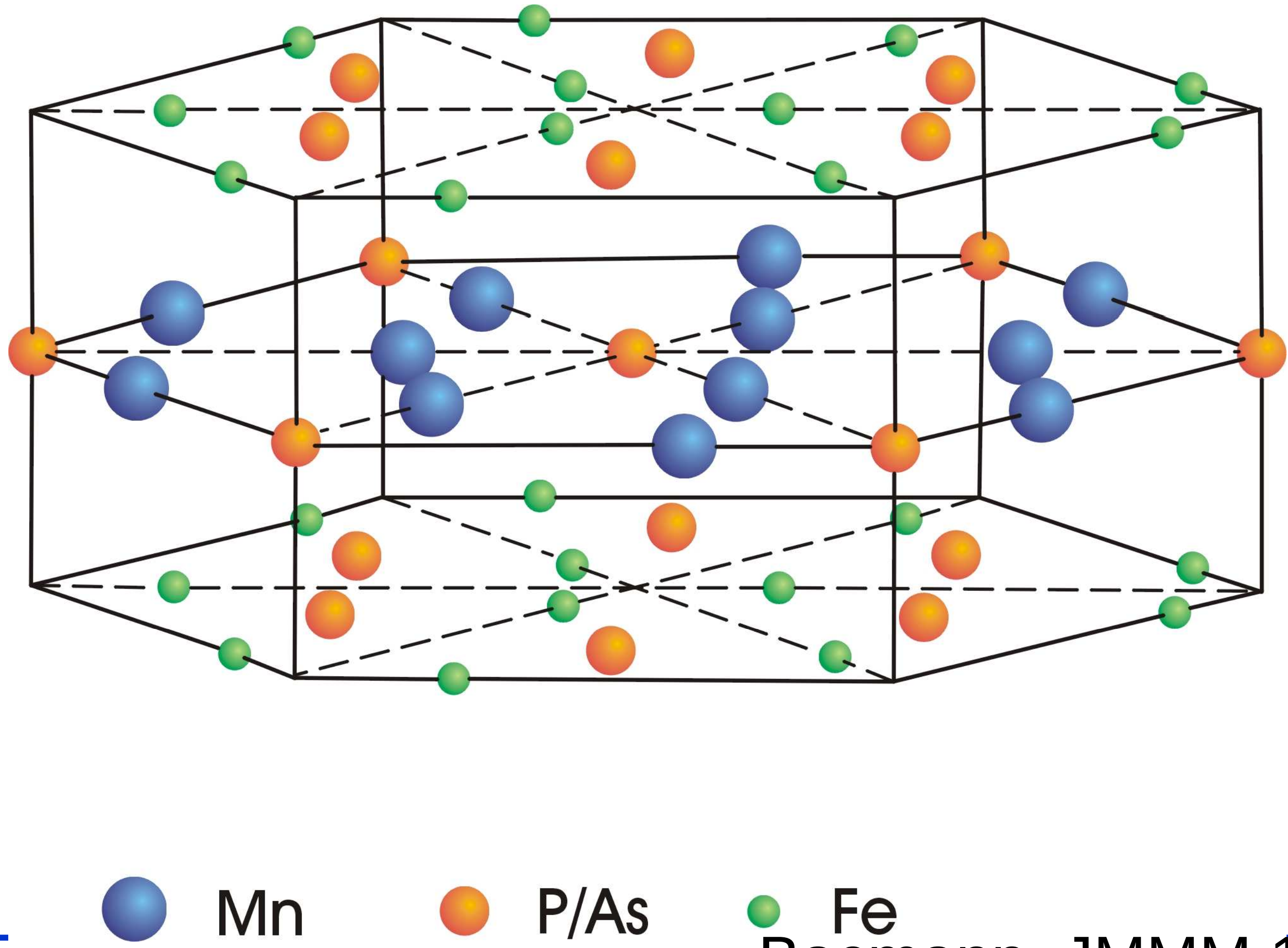
Space group:

$P\bar{6}2m$

Mn 3g sites

Fe 3f sites

P/As 1b&2c sites



Bacmann, JMMM 1994

Sample preparation

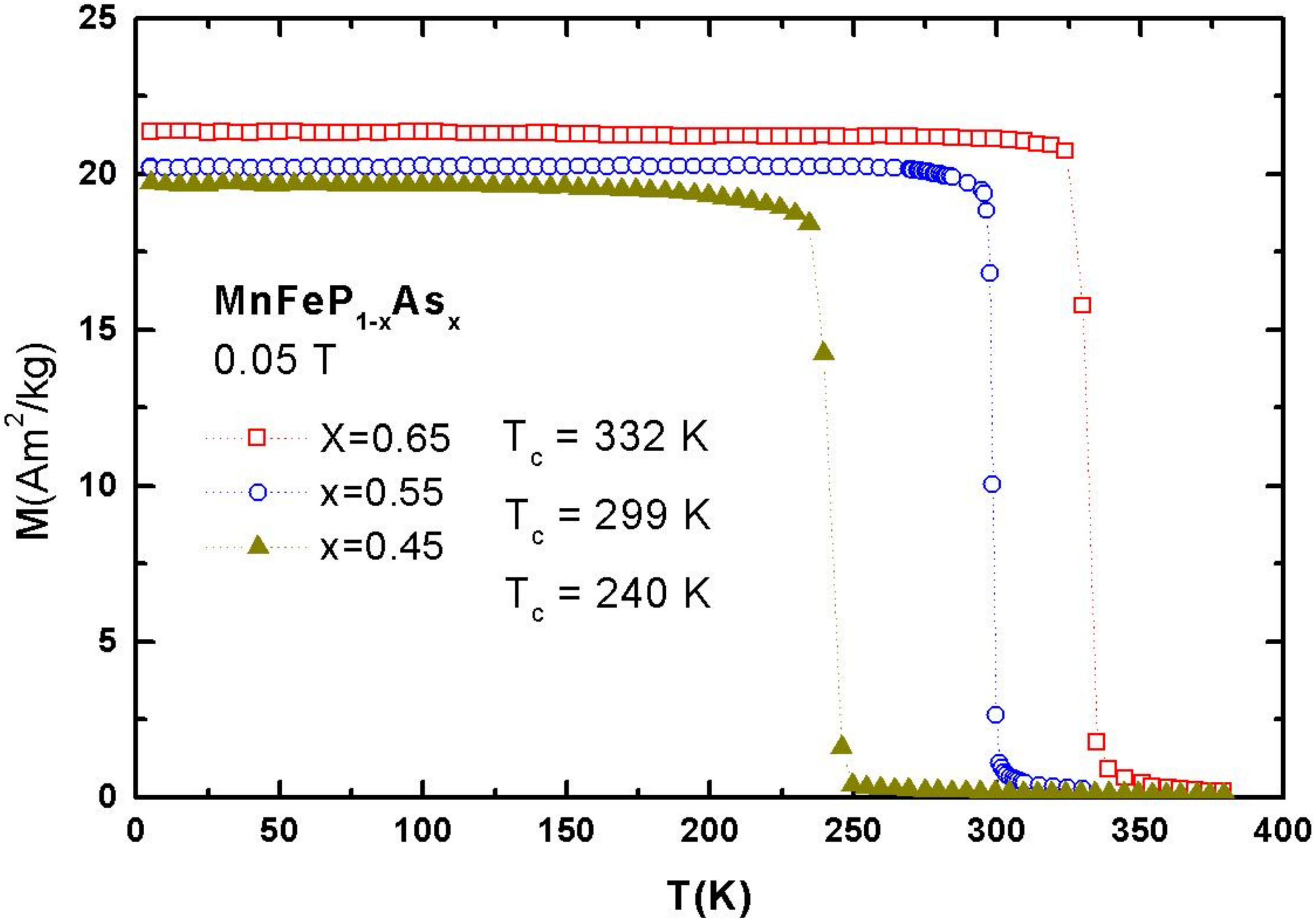
Starting Fe_2P, Mn_2As_3, Mn & P

mechanical alloying

sintering 1000°C

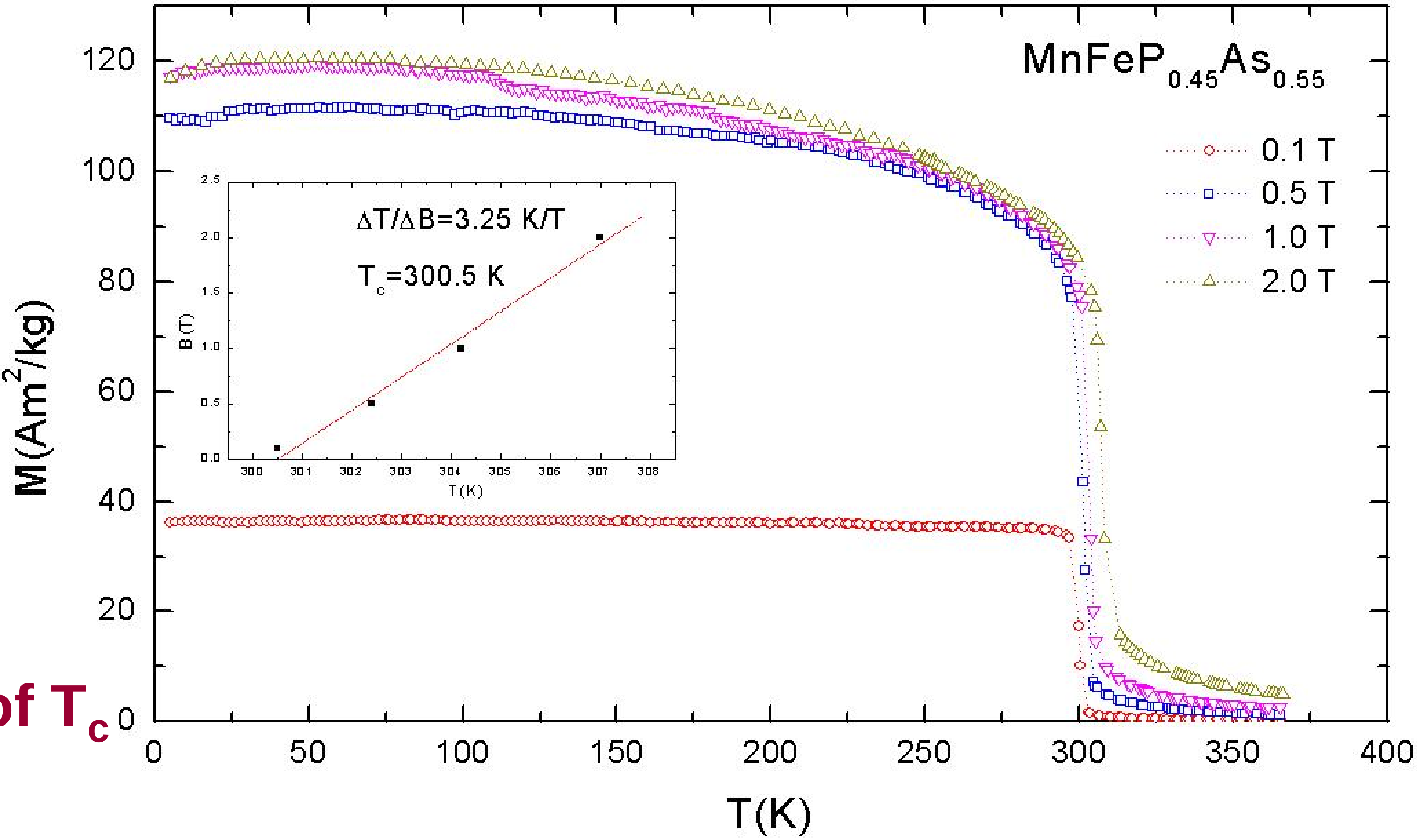
annealing 800°C

Temperature dependence of magnetization with different compositions



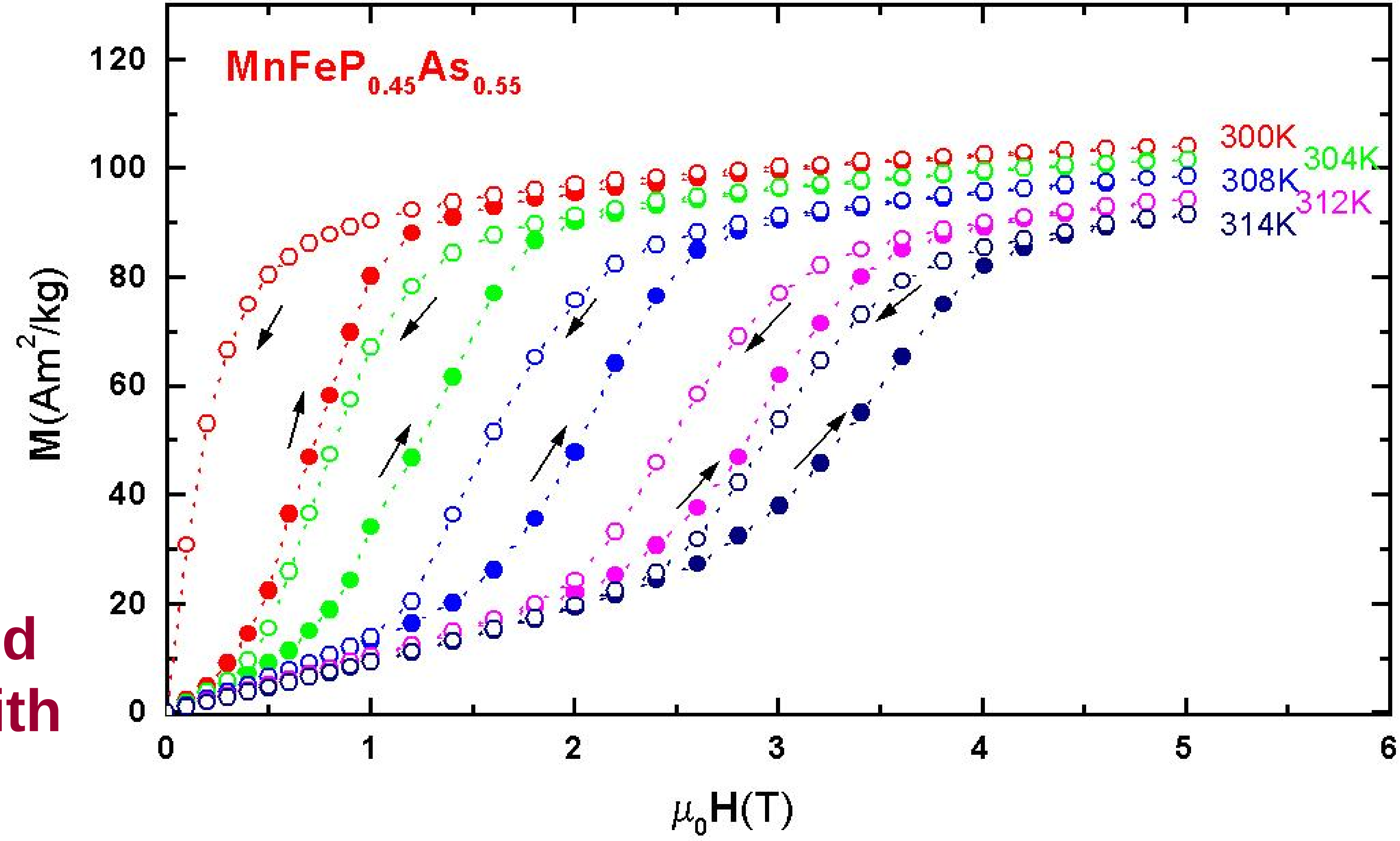
T_c tunable

Temperature dependence in different fields



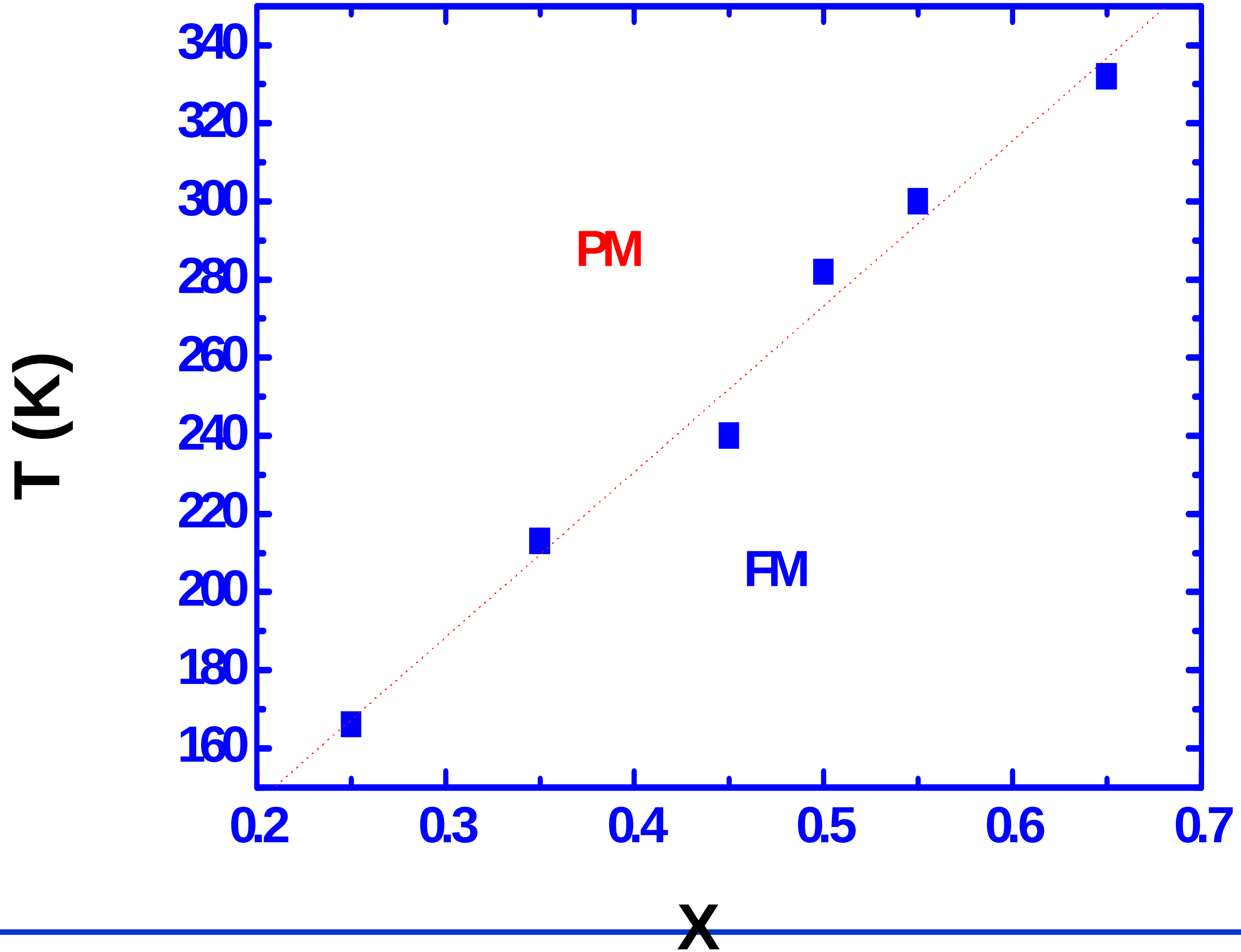
Strong shift of T_c with field

Magnetization process near Tc



Field induced transition with small hysteresis

Concentration dependence of T_C for $MnFeP_{1-x}As_x$



Somewhat higher T_C compared with lit.

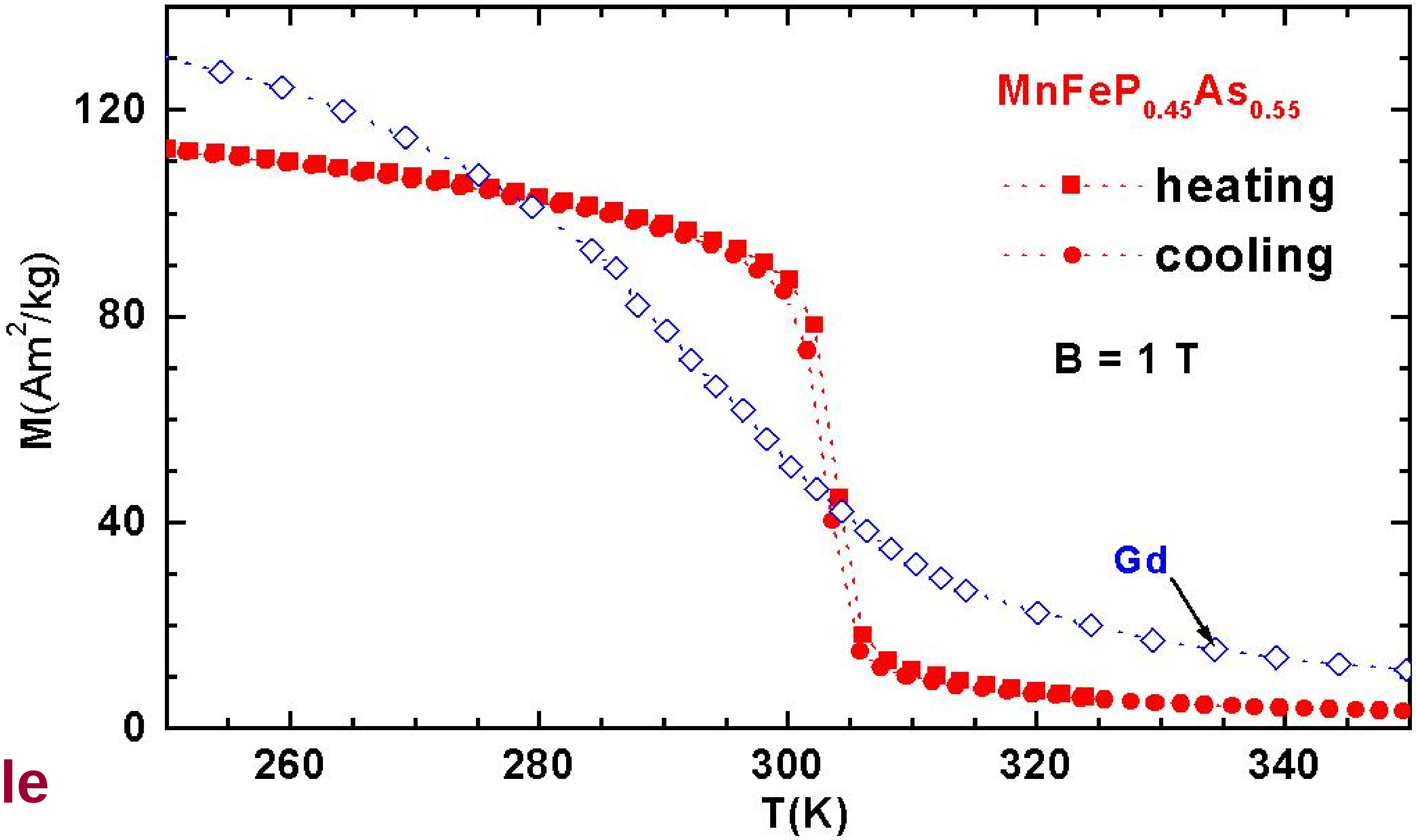
Almost linear concentration dependence.

Comparison with Gd metal

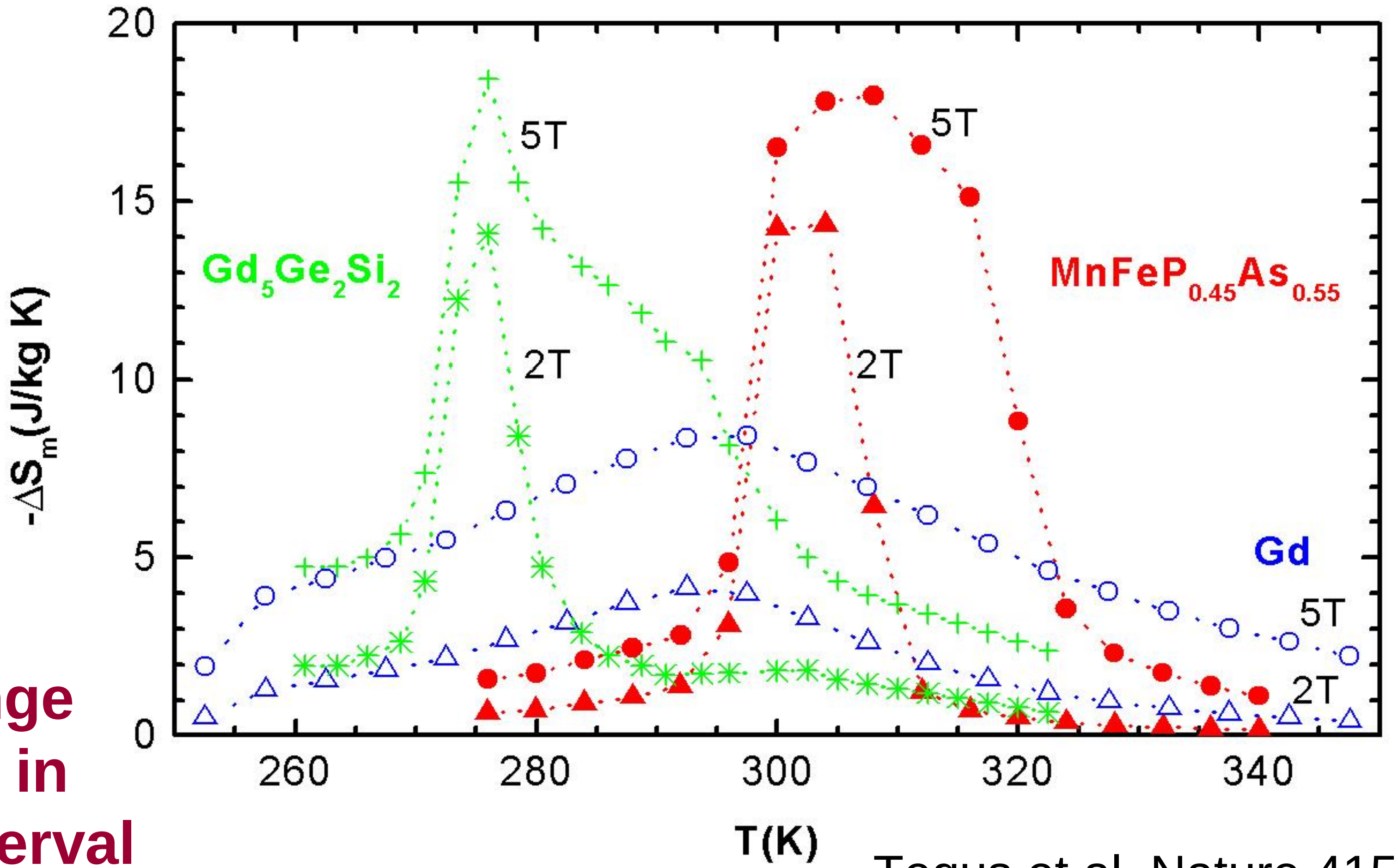
Step-like transition

first order

but very little hysteresis



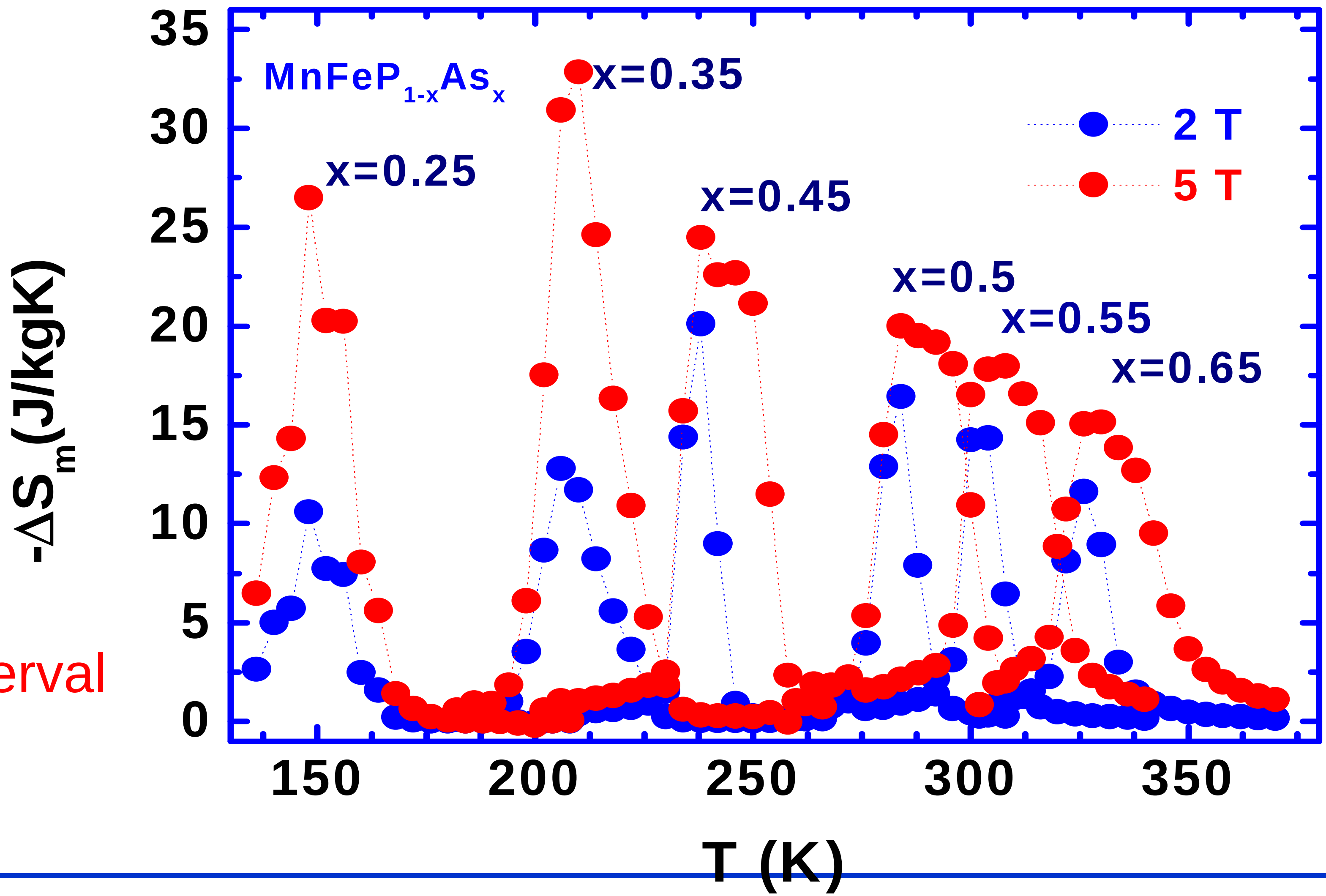
Comparison of magnetocaloric effect in different materials



Entropy change concentrated in relevant T interval

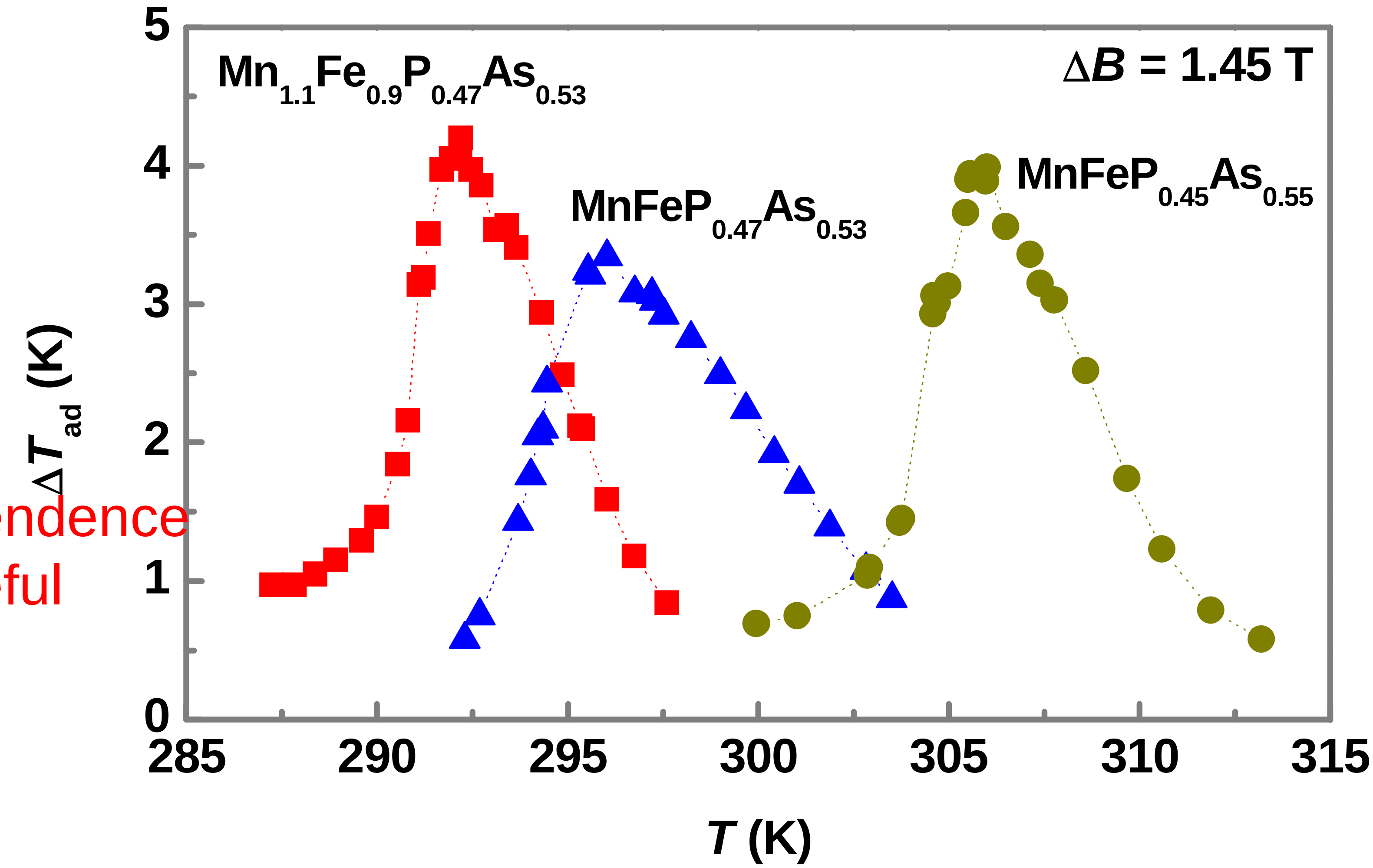
Tegus et al. Nature 415

MCE as function of composition



Broad T interval covered

Adiabatic temperature-change



Sample dependence
need for careful
preparation

Direct measurements MSU

Summary MnFe(P,As)

Field driven 1st order magnetoelastic transition
150 K < Tc < 450 K .

MnFe(P,As) hexagonal above magnetic transition

hexagonal below.

Hardly any volume change(0.1 %) but change of c/a.

Hysteretic transition: Hysteresis depends on grain size?
High chemical stability allows As content?

Conclusions

- First order magnetic transition common to the different systems!
- Structural transition may cause extra hysteresis.
- Control of hysteresis very important.
- Evaluation of entropy change needs care.
- Fe and Mn based systems with much lower materials costs.
- Relevant T range covered by $La(Fe,Si)_{13}H_x$ and MnFe(P,As,Si,Ge).
- Sample preparation simplest for MnFe(P,As) with As replaced by other element.

Outlook

Cooltech current N°4 Prototype

Registered Patents, Brand and Models

IMPORTANT issues:

1 – The **AMRR** Cycle (Active Magnetic Regenerator Refrigeration): with Gd inserts as cross-flow plate heat-exchangers.

2 - Amplification of ΔT by accumulation of cycles.

3 - Reduction in torque (10 Nm) obtained by ensuring a ferromagnetic continuity on the disc.

4 - Very low level of noise and vibrations (< 25 dB)

5 - Creation of magnetic fields of 0.7 to 2 Tesla with standard permanent magnets.

6 - Low thermal losses, completely separate “hot” and “cold” fluid circuits.

Availability

	Limiting ingredient	Estimated availability	Total availability of MC material
Gd metal	Gd	1000	1000t
Gadolinium Silicon alloys $Gd_4(Si_{1-x}Ge_x)_5$	Ge	WW prod=90t, avail 10t ?	**140t**
Manganese alloys $Mn(As_{1-x}Sb_x)$ $MnFe(P_{1-x}As_x)$	**none**	**none**	**No limitation for an industrial production**
Lathanum alloys $La(Fe_{13-x}M_x)$	La	4000	22000t
Manganites $LaMnO_3$	La	4000	7000t
$Ni_{0.501}Mn_{0.227}Ga_{0.258}$	Ga	WW prod=90t, avail 10t ?	60t?

Data : Cooltech source and USGS.GOV

Increased T span with active magnetic regenerator containing different materials with tailored T_C