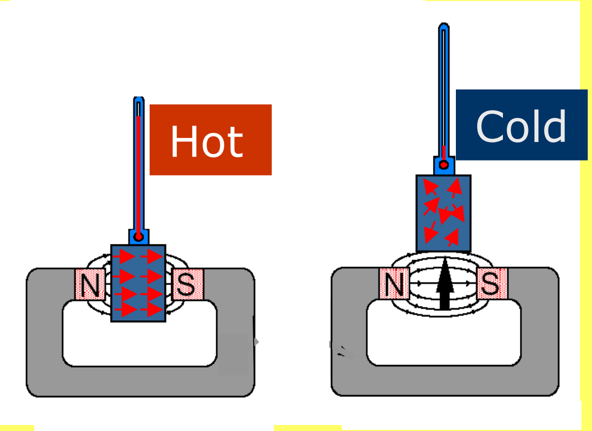
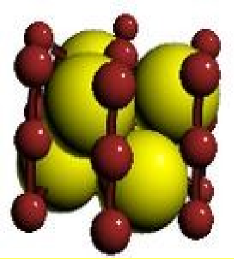
European Network of Excellence

Sixth Framework Programme

## European School in Materials Science

$$\Delta S_{mag} + \Delta S_{lat} = 0$$



# Electronic aspects of magnetocaloric refrigeration

$$G = G_0 + G_0 V G$$

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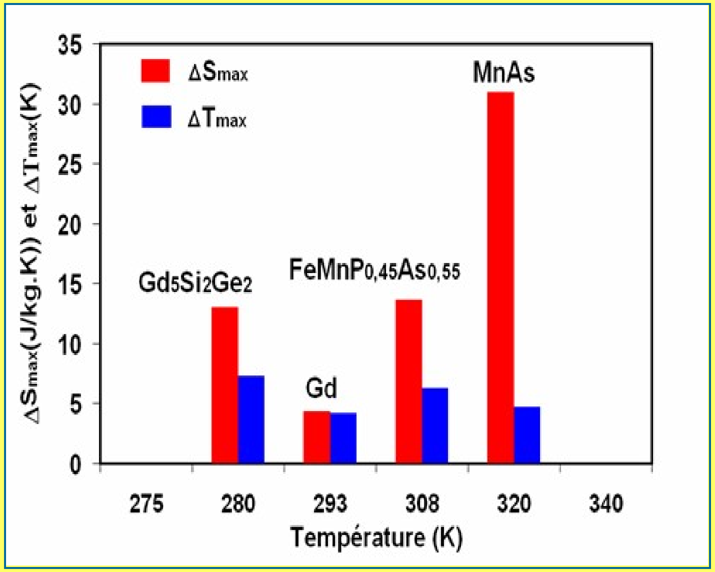
# Outline




1. Magneto-caloric effect MCE (brief history and introduction), giant MCE.

2. Entropy contributions and concept of MCE cooling – analogy to thermodynamic cycle; how to measure MCE ?

3. Illustrative examples of MC materials & experimental results
   - $Gd_5Si_2Ge_2$ - RE alloys,
   - MnAs, MnFe(As-P), $Fe_2P$, $Mn_3Sn_2$ – TM alloys.

4. Electronic structure of intermetallic MC compounds (MnAs, MnFeAs-P, …)

5. Concept of DLM (*disordered local moments*)- simulation of paramagnetic state within DFT methods.

5. Estimation of entropy jump: mean field approach for magnetic entropy.

6. Estimation of lattice entropy from phonon calculations.

7. Summary

# Brief history of MCE discovery

1881 E. Warburg, iron heats up in magnetic field ~0.5-2 K/1T, *Ann. Phys.* (1881)

1926 P. Debye (Nobel 1936, chemistry)

1927 W. Giauque (Nobel 1949, chemistry)

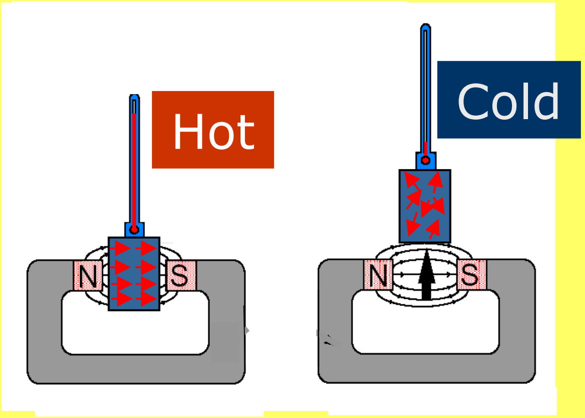
cooling via adiabatic demagnetization (order-disorder transition of magnetic moments in presence (or not) of magnetic field; for cryogenic purposes, down to 0.25 K (MacDougall, 1933).

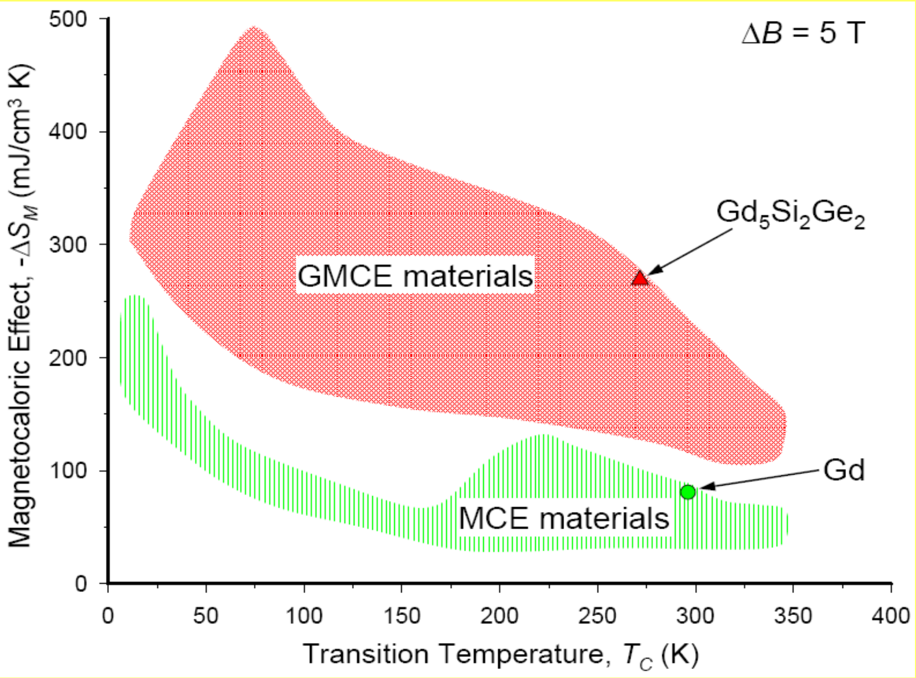
1997 K. A. Gschneider & V. Pecharsky (Ames Lab., USA), PRL (1997) - discovery of giant magnetocaloric effect :

MCE: an intrinsic property of magnetic materials;

MCE : the largest at the transition temperature, e.g. ferro-para

Adiabatic magnetization / demagnetisation



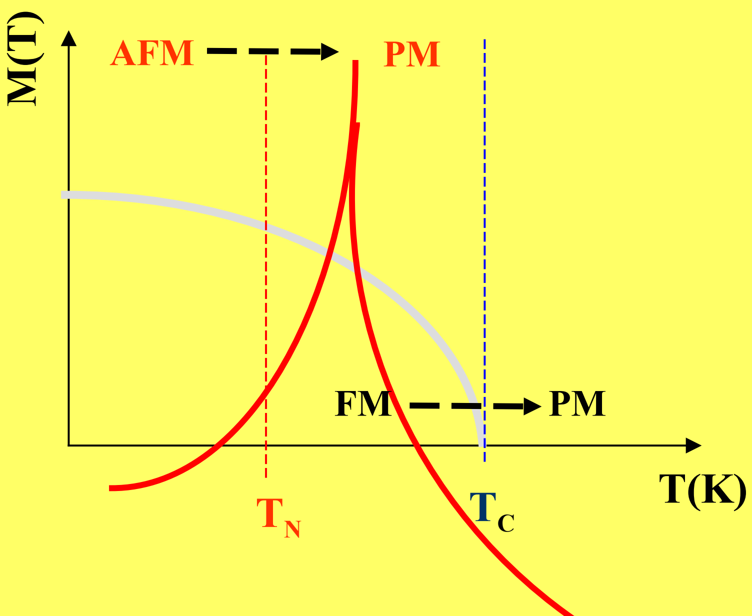
# Introduction

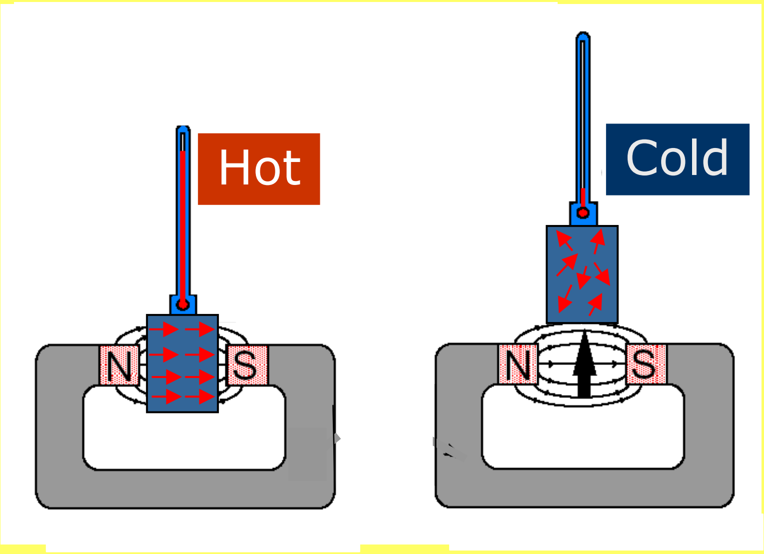
## MCE

Intrinsic property of a material

Maximal at the transition temperature

$$\Delta S_{mag} + \Delta S_{lat} = 0$$



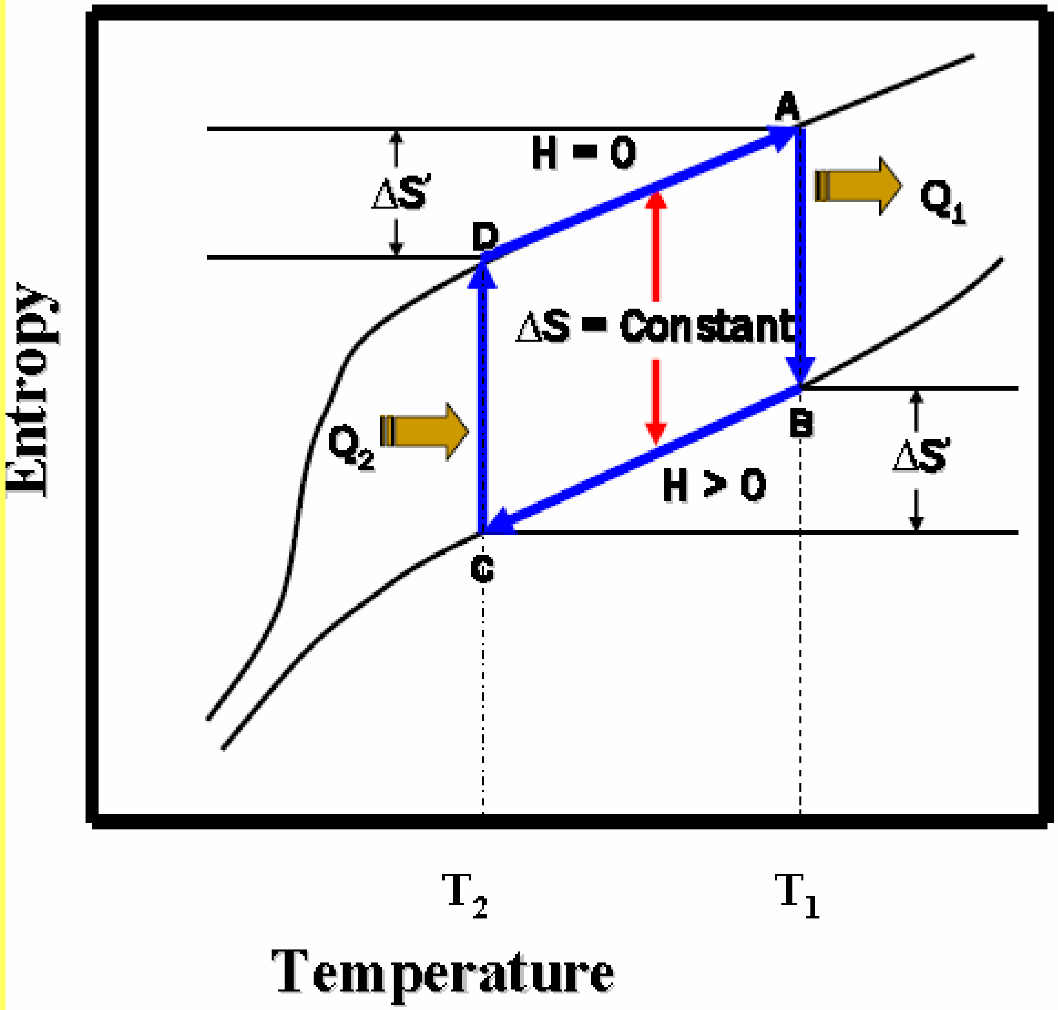




Adiabatic
Magnetisation / Demagnetisation

**Type of magnetic transitions:**
**FM-PM,**
**AFM-PM,**
**AFM-FM (but not so large)**

**Ferromagnet, Ferrimagnet, Antiferromagnet, Inhomogeneous Ferromagnet, Amorphous, Superparamagnet....**

# Analysis of Ericsson cycle




**A → B**

The magnetic refrigerant emits ΔS in the form of heat $Q_1 = \Delta S * T_1$

**B → C**

The magnetic refrigerant changes its temperature from $T_1$ to $T_2$

**C → D**

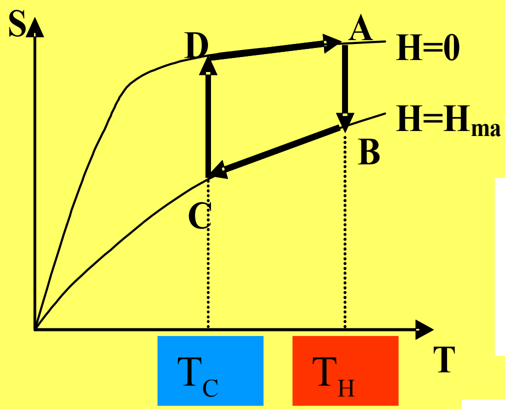
The magnetic refrigerant takes heat $Q_2 = \Delta S * T_2$ from the external heat source of temperature $T_2$

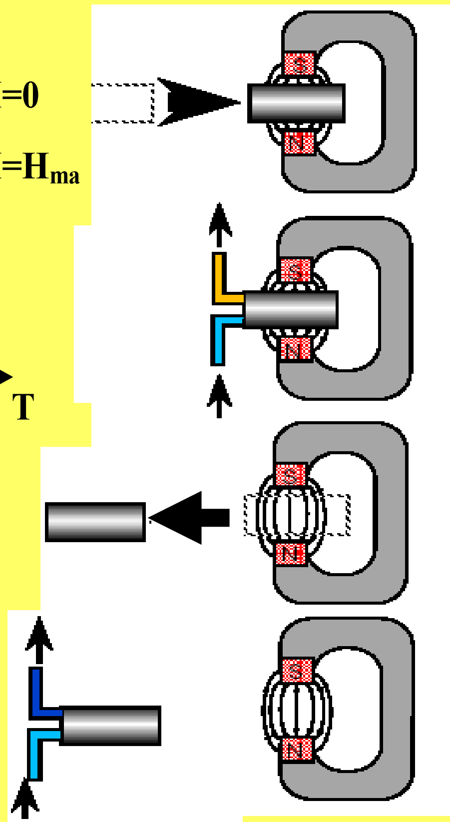
**D → A**

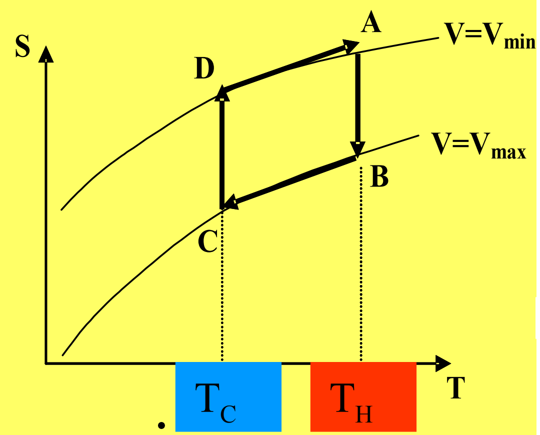
The M R takes back all the heat given to the regenerator in the second (B-C)

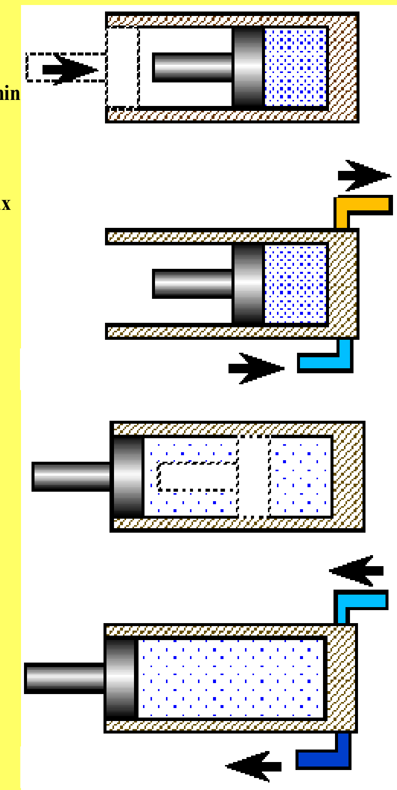
# Analogy to thermodynamic cycle

## Adiabatic magnetization/demagnetization



Ericsson cycle

pressure **P** → field **B**

volume **V** → magnetization **M**

$$B \cdot (M_1 - M_2) = \Delta S \cdot \Delta T = -\mathrm{RCP}$$

RCP – relative cooling power

Ideal Carnot cycle :

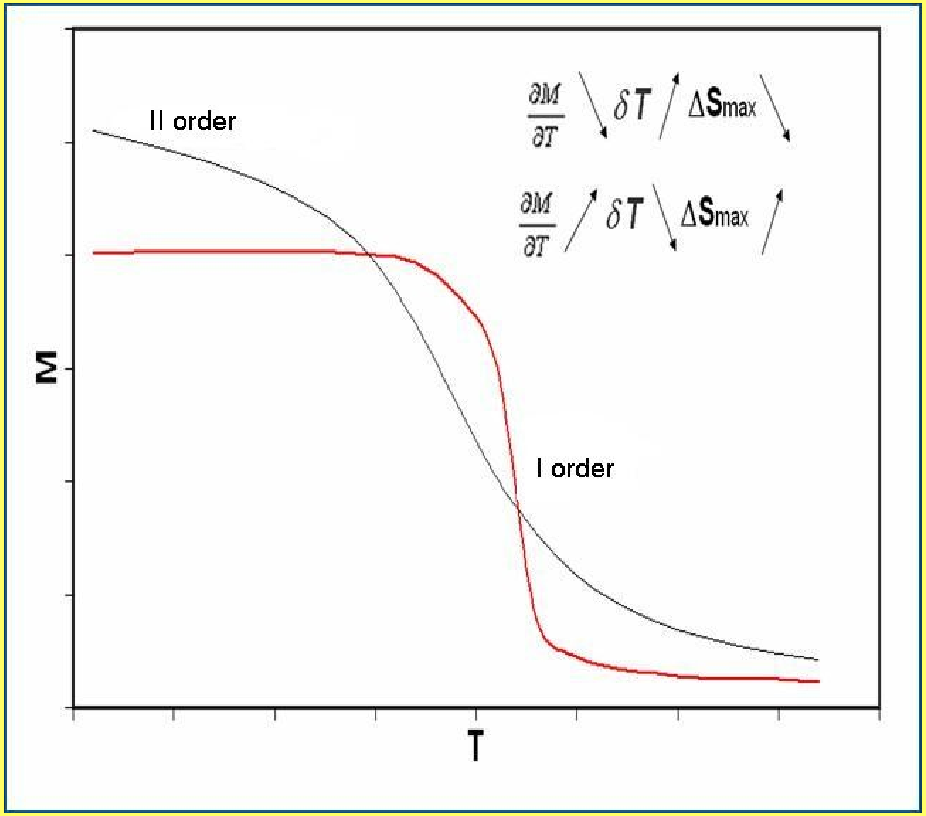
$$\eta = \frac{\Delta W}{\Delta Q_H} = 1 - \frac{T_C}{T_H} \qquad \Delta W = \oint P dV = (T_H - T_C)(S_B - S_A)$$

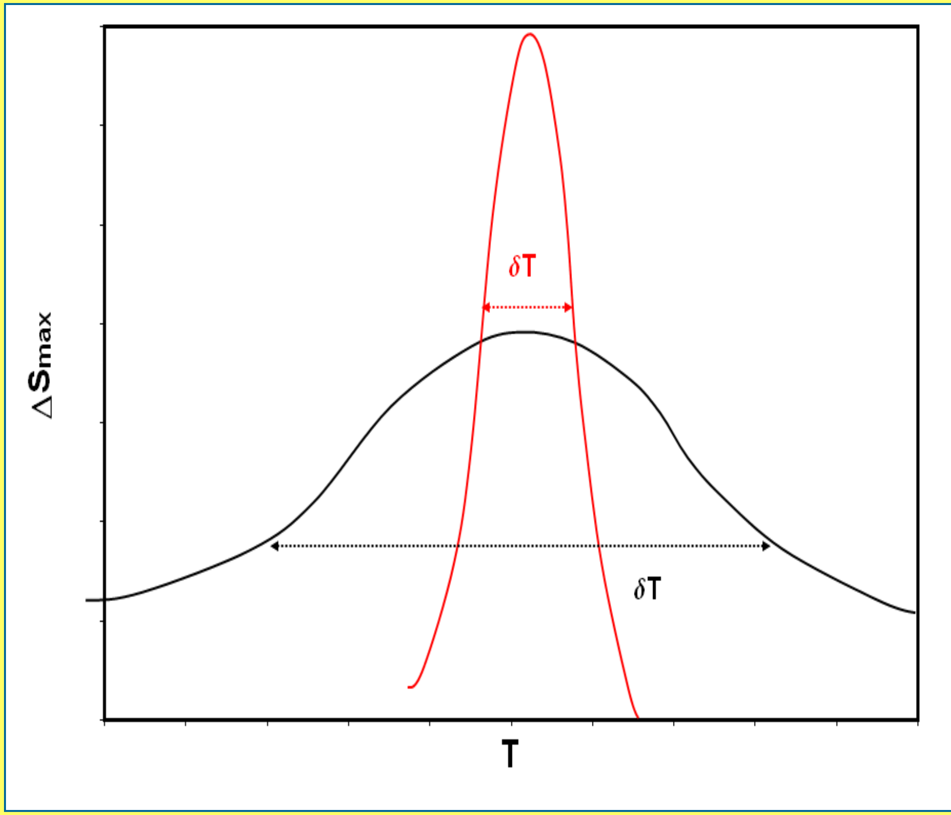
$$\Delta Q_C = T_C(S_B - S_A)$$

$$\Delta Q_H = T_H(S_B - S_A)$$

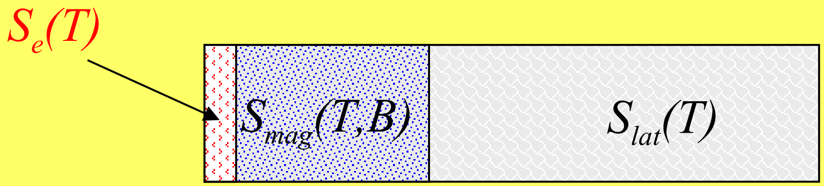
# Important conditions for giant MCE

## What model to apply for ?




**It depends first on the nature of the transition, on the type of magnetic ordering, on the nature of the material....**




$T \sim T_{room}$

# Entropy

$$S_{tot} = S_{el} + S_{mag} + S_{lat}$$

$$\Delta S_{mag} + \Delta S_{lat} = 0$$

**Adiabatic Process**

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

$$\Delta S_{lat} = C_p(B, T) \frac{\Delta T}{T}$$

$$\Delta T_{max} = \frac{-T \Delta S_{mag}}{C_p(B,T)}$$

Calorific Capacity $C_p(B,T)$

↓

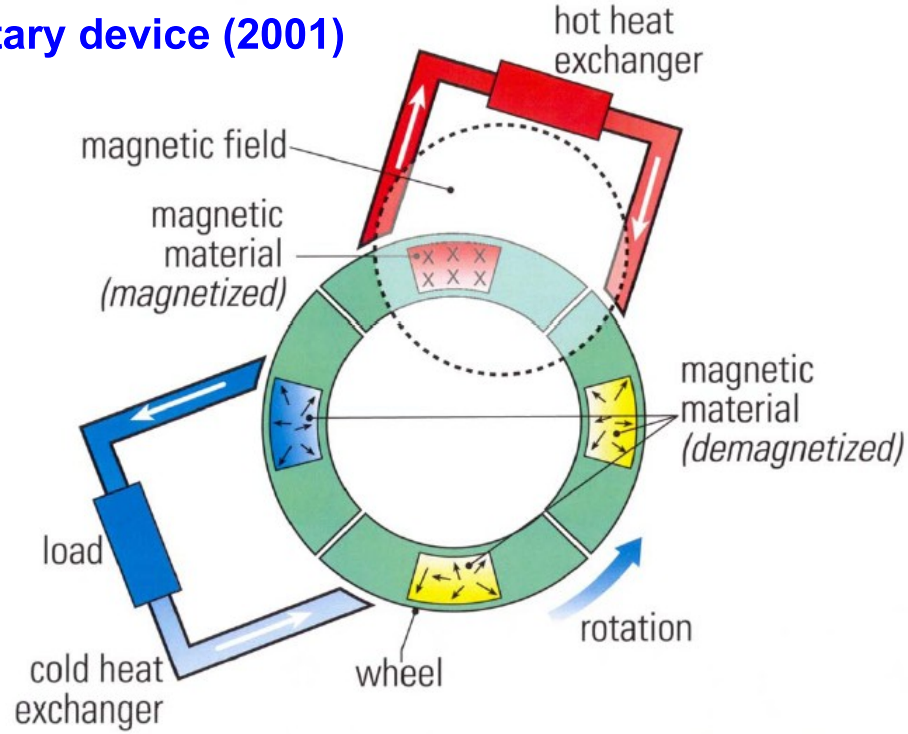
Magnetic Entropy $\Delta S_{mag}$

↓

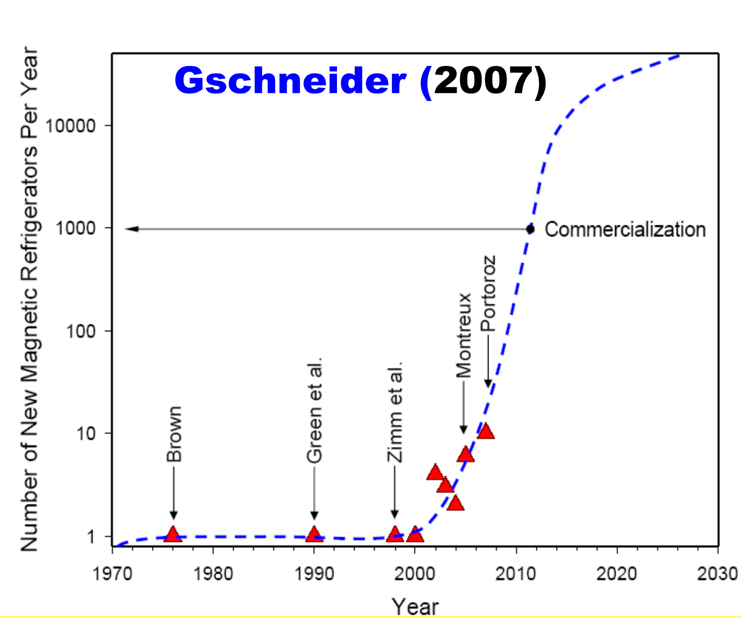
$\Delta T_{max}$

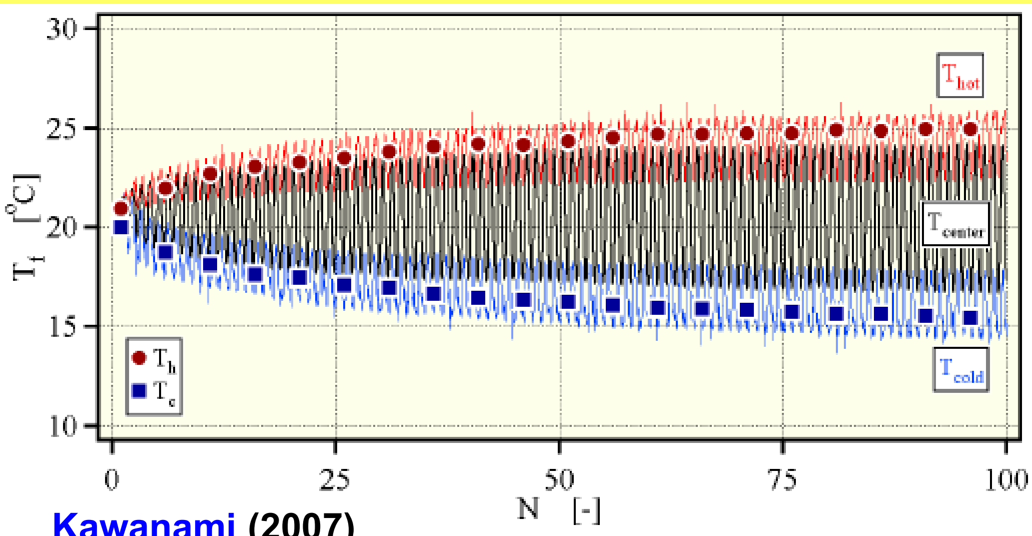
# ASTRONAUTICS

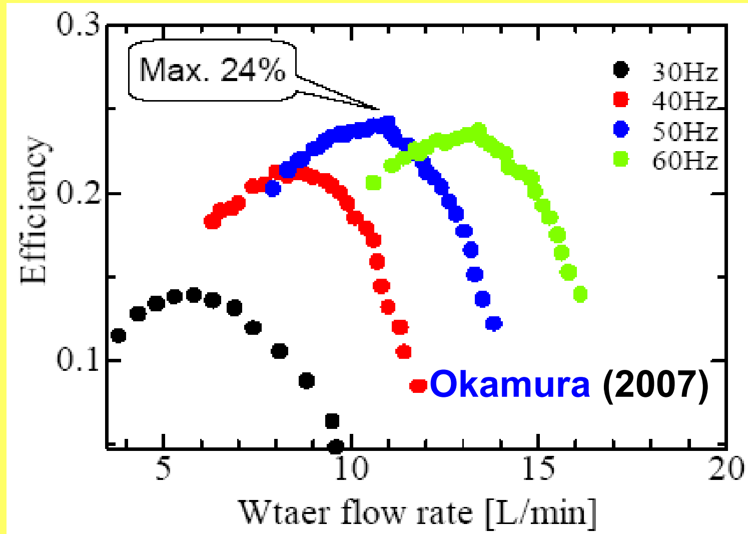
## rotary device (2001)




(S-growth curve for new technologies)




Efficiency = (Pump work) / (Power consumption)

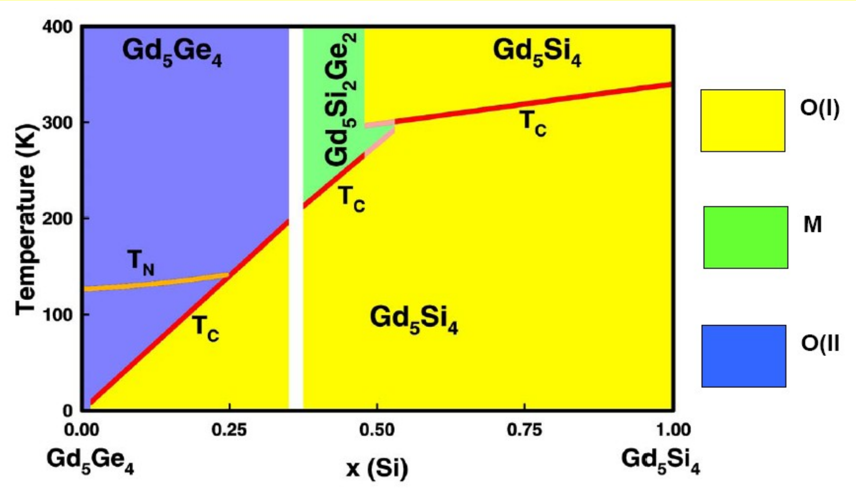
| Compound | $-\Delta S$ [J*kg$^{-1}$*K$^{-1}$] | T [K] | References |
|---|---|---|---|
| **MnAs** | **40** | **318** | **[1]** |
| **$Mn_{0.99}Cr_{0.01}As$** | **34.6** | **310** | **SCTE2006** |
| **$Mn_{0.98}V_{0.02}As$** | **30.5** | **286** | **SCTE2006** |
| **$Mn_{0.90}Ti_{0.05}V_{0.05}As$** | **24** | **274** | **SCTE2006** |
| **$Mn_{0.98}Ti_{0.02}As$** | **35.7** | **316** | **SCTE2006** |
| $MnAs_{0.9}Sb_{0.1}$ | 30 | 283 | [1-3] |
| FeMn(As,P) | 18 | 305 | [4] |
| $La(Fe_{0.88}Si_{0.12})_{13}H_1$ | 23 | 274 | [5] |
| $Gd_5Si_2Ge_2$ | 36.4 | 272 | [6] |
| Gd | 2.5 | 294 | [7] |
| $Fe_{49}Rh_{51}$ ($\Delta B$ = 2T) | 22 | 313 | [7] |
| **MnAs (under pressure)** | **267 !!** | **~280** | **[8]** |

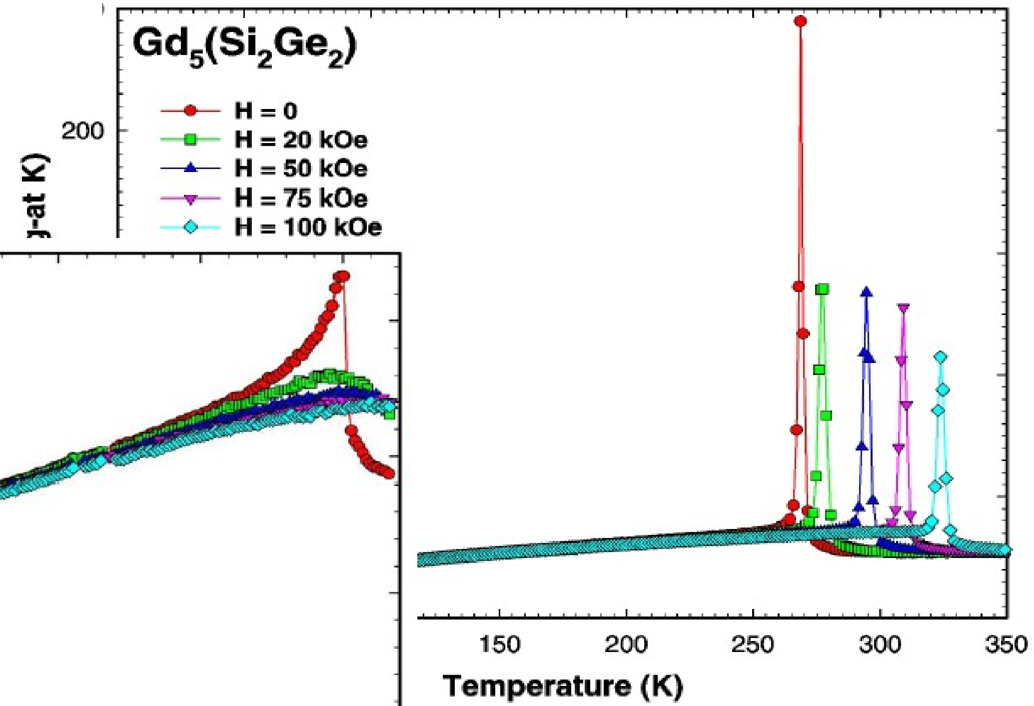
**$\Delta B$ = 5 T**

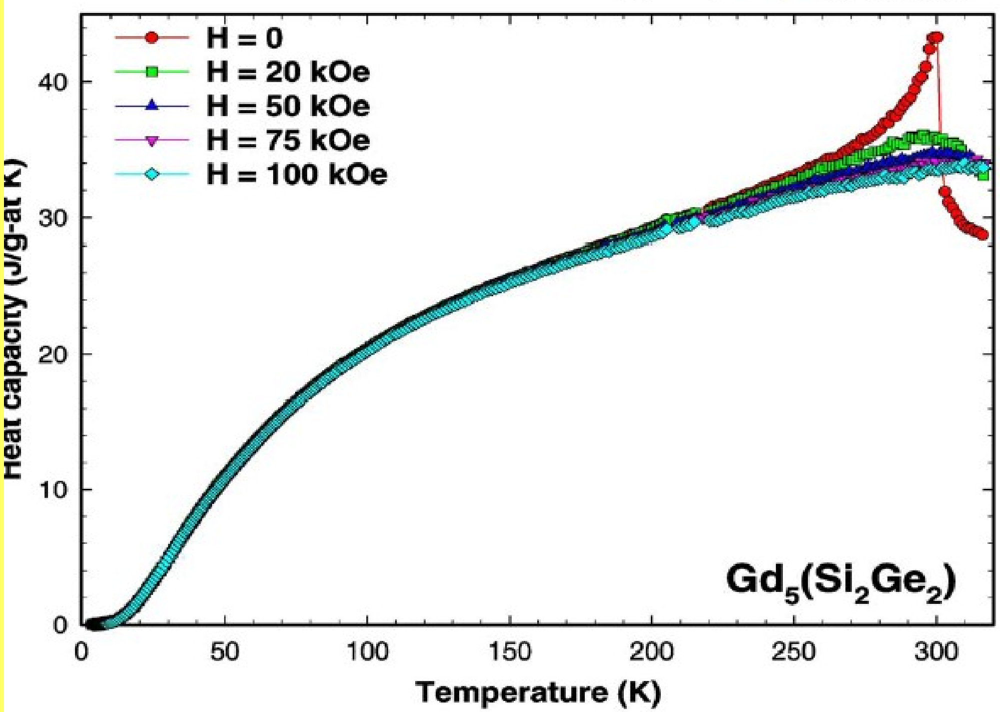

[1] H.Wada and Y. Tanabe, Appl. Phys. Lett. **79**, 3302 (2001).
[2] H.Wada, K. Taniguchi, and Y. Tanabe, Mater. Trans., JIM **43**, 73 (2002).
[3] H. Wada, T. Morikawa, K. Taniguchi, T. Shibata, Y. Yamada, and Y. Akishige, Physica B (Amsterdam) **328**, 114 (2003).
[4] O. Tegus, E. Bru¨ck, K. H. J. Buschow, and F. R. de Boer, Nature (London) **415**, 150 (2002).
[5] A. Fujita, S. Fujieda, Y. Hasegawa, and K. Fukamichi, Phys. Rev. B **67**, 104416 (2003).
[6] A.O. Pecharsky , K. A. Gschneidner, Jr.,V. K. Pecharsky, J. Appl. Phys. **93**, 4722 (2003).
[7] A.M. Tishin and Y. I. Spichkin, (Institute of Physics,Bristol and Philadelphia, 2003), 1st ed., Vol. 1, Chap. 11, p.351.
[8] S.Gama et all, Phys. Rev. Let. **93**, 237202 (2004)

# Giant MCE system

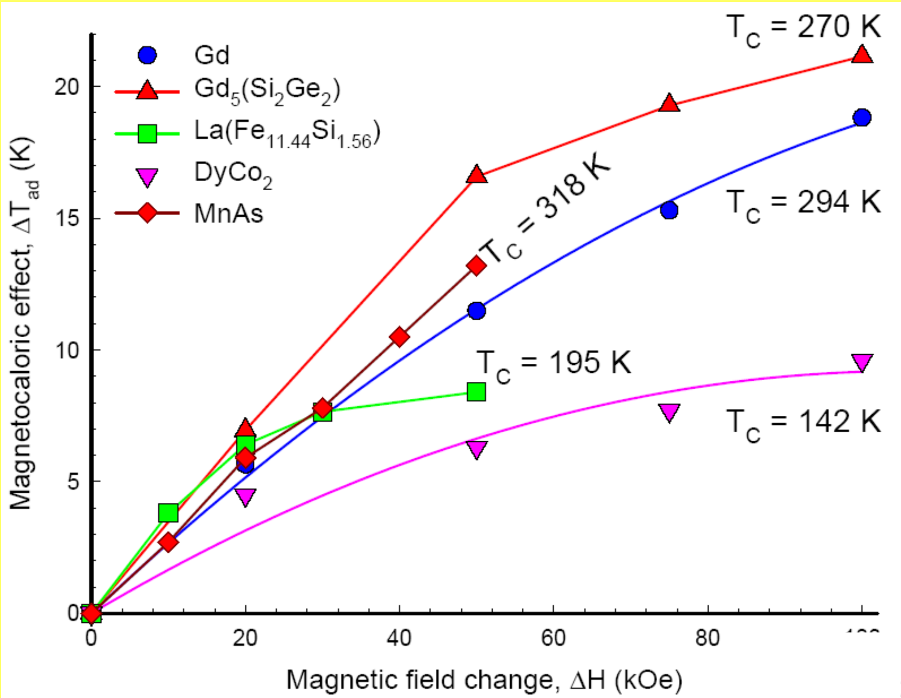
**Pecharsky & Gschneider, 1997-2007**



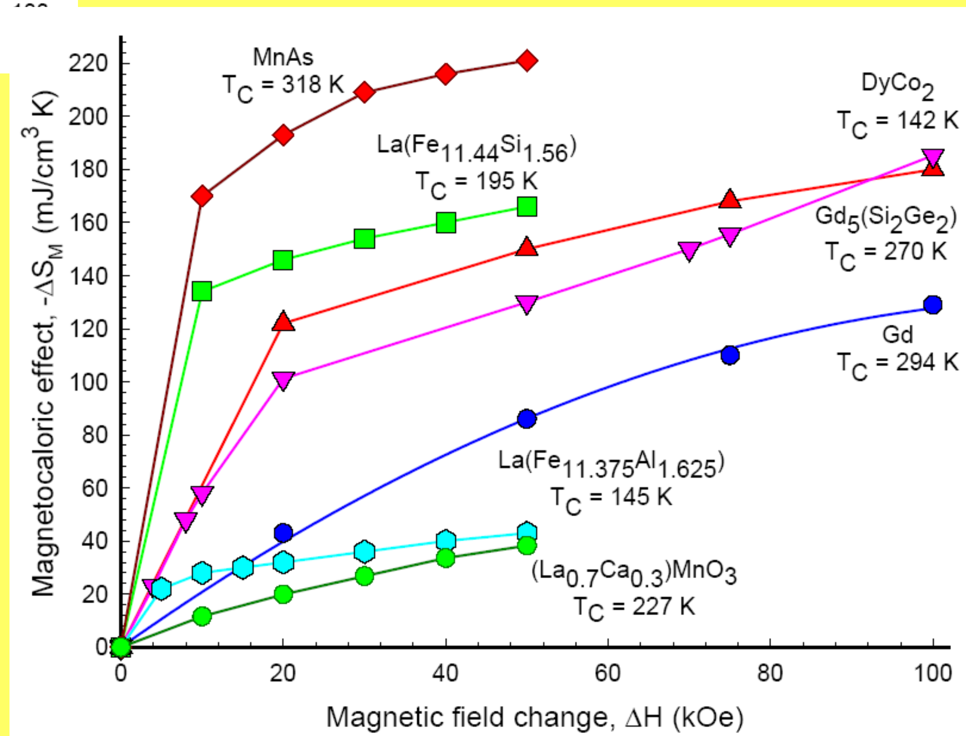



# New MCE materials



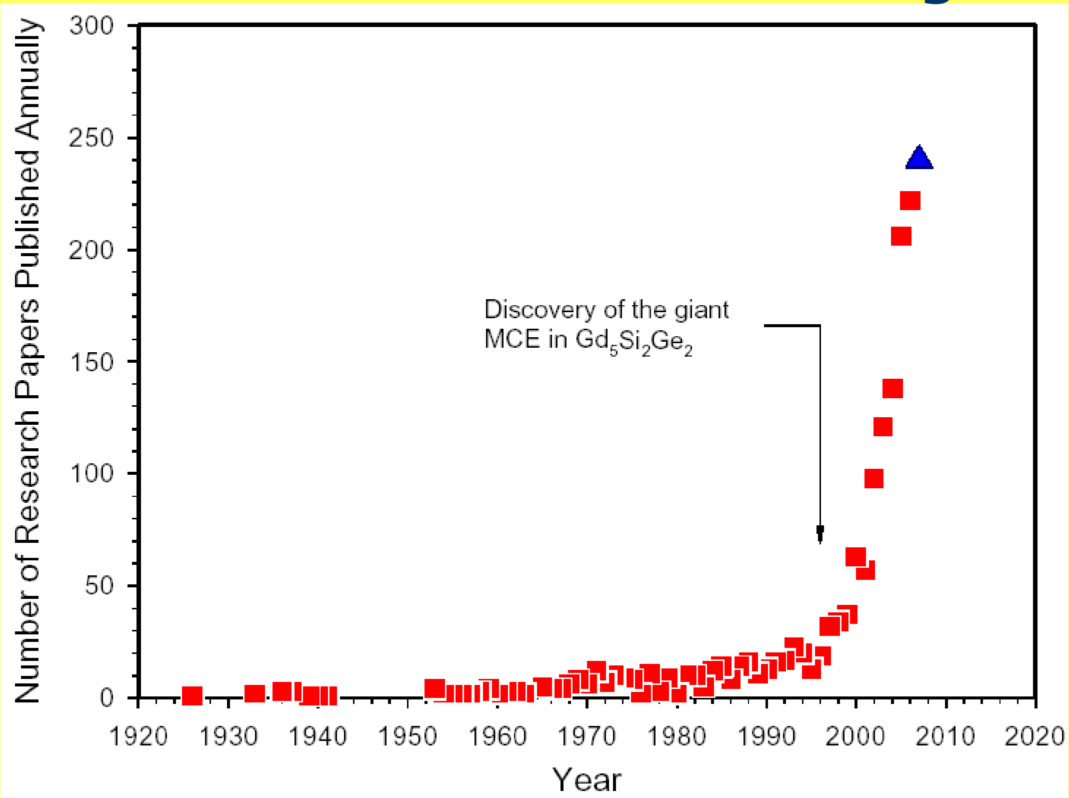

Temperature jump

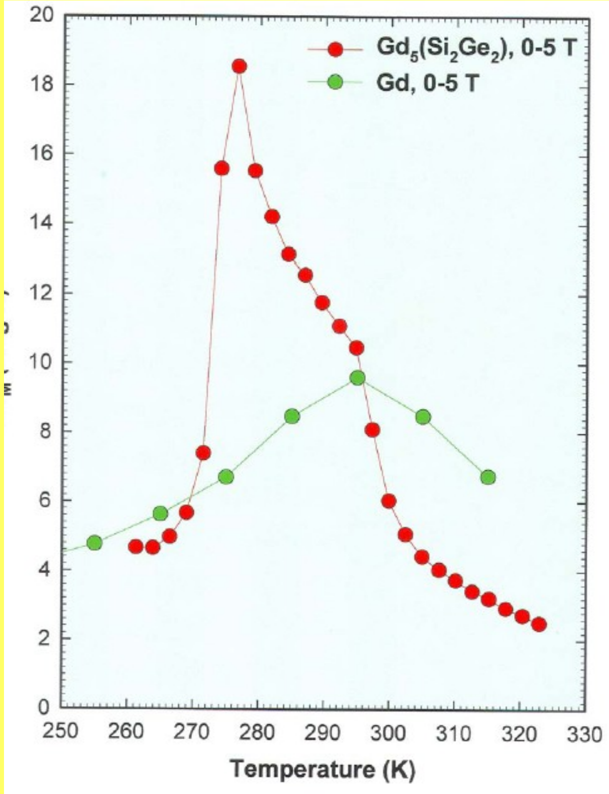
Entropy jump

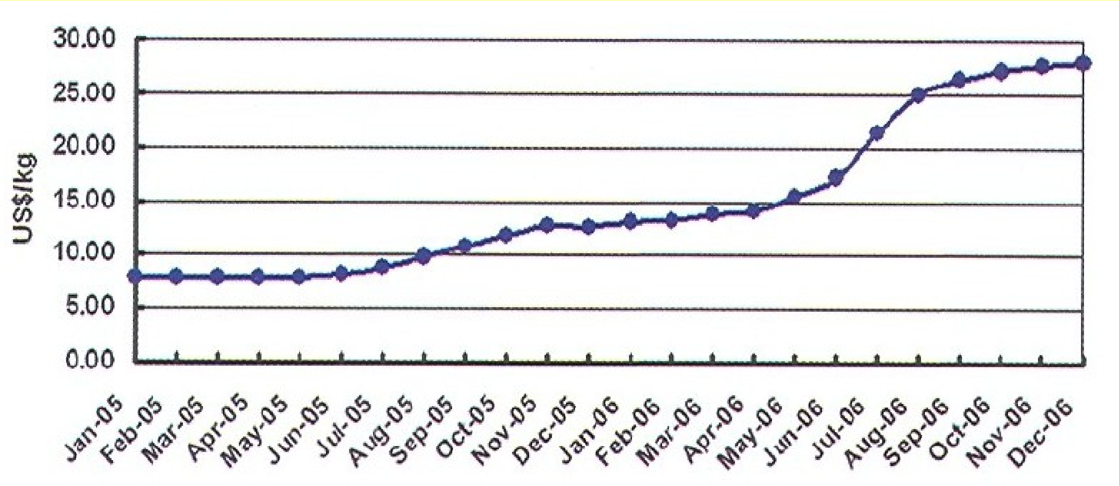



K.Gschneider, 2007

# Giant MCE – magnets demanded




Magnetic Bussiness & Technology (2007)

**Active magnetic refrigerator (AMR), e.g. Gd, La-Fe-Si**

**0.1-100 kg / AMR**

**Efficient magnets**
**Nd-Fe-B**

**0.1-100 kg / AMR**

Gschneider, 2007

# Entropy contributions and relations to *ab initio* calculations

$$S_{tot} = S_{el} + S_{mag} + S_{lat}$$

for $h^{ext} = 0$, the intergral gives $S_{el}$

$$S_{mag}(T, h^{ext}) = R\left[\sum_{\sigma}\int_{-\infty}^{\mu} \ln\left(1 + e^{-\beta(\varepsilon-\mu)}\right)\rho_{\sigma}^{el}(\varepsilon)d\varepsilon + \frac{1}{kT}\sum_{\sigma}\int_{-\infty}^{\mu}(\varepsilon-\mu)\,\rho_{\sigma}^{el}(\varepsilon)f(\varepsilon)d\varepsilon\right]$$

**de Oliveira, Eur. Phys. J. B (2004)**

$$S_{lat} = R\left[-\int \ln\left(1 - e^{-\beta\hbar\tilde{\omega}}\right)\rho^{ph}(\tilde{\omega})d\tilde{\omega} + \frac{1}{kT}\int\frac{\hbar\tilde{\omega}}{(e^{\beta\hbar\tilde{\omega}} - 1)}\rho^{ph}(\tilde{\omega})d\tilde{\omega}\right]$$

**Phonon DOS is needed to estimate lattice contribution**

**adiabatic process**

$$\Delta S_{mag} + \Delta S_{lat} = 0$$

**$S_{el} \approx \gamma T$ often sufficient**

**in MCE systems smaller than $S_{mag}$, $S_{lat}$**

$$S_{lat}(T, h^{ext}) = \left[-3R\ln\left(1 - \exp\left(-\frac{\tilde{\Theta}_D}{T}\right)\right) + 12R\left(\frac{T}{\tilde{\Theta}_D}\right)^3\int_0^{\tilde{\Theta}_D/T}\frac{x^3}{\exp(x) - 1}dx\right]$$

**BUT this can be approximatively done e.g. from Debye model**

Estimations of entropy can be made for electrons and phonons if DOS is known. Using Debye temperature, $S_{lat}$ may be roughly estimated - allowing to interpret $\Delta S$ jump in experiment.

# Reminder: magnetic susceptibility

Free energy (Helmholtz)

$$F = -k_B T \ln Z$$

$$Z = \sum_n e^{-\frac{E_n}{k_B T}}.$$

Partition function

$$Z = \sum_{J_z=-J}^{J} e^{-\eta J_z} = \frac{e^{-\eta J} - e^{\eta(J+1)}}{1 - e^{\eta}} \qquad J_z = -J, \ldots, J$$

$$= \frac{e^{-\eta(J+1/2)} - e^{\eta(J+1/2)}}{e^{-\eta/2} - e^{\eta/2}} = \frac{\sinh\left[(J+1/2)\eta\right]}{\sinh\left[\eta/2\right]}$$

Magnetisation

$$M(T) = -\frac{1}{\mu_0 V}\frac{\partial F}{\partial H} = -\frac{1}{\mu_0 V}\frac{\partial(-k_B T \ln Z)}{\partial H}$$

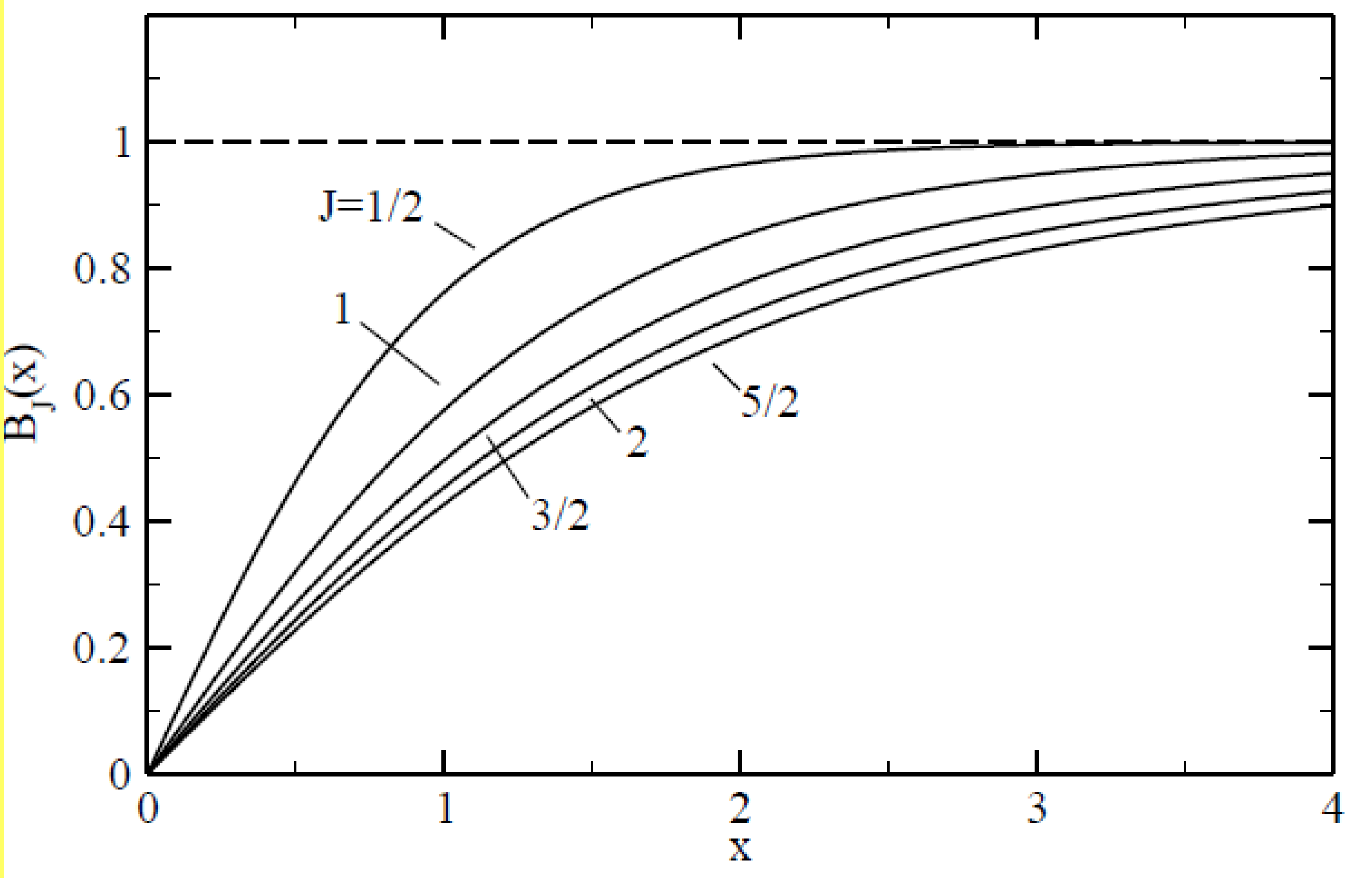
$$= \frac{k_B T}{\mu_0 V}\frac{\partial}{\partial H}\left[\ln\left(\sinh[(J+1/2)\eta]\right) - \ln\left(\sinh[\eta/2]\right)\right] = \frac{g(JLS)\mu_B J}{V} B_J(\eta).$$

$$B_J(\eta) = \frac{1}{J}\left\{(J+\frac{1}{2})\coth\left[(J+\frac{1}{2})\eta/J\right] - \frac{1}{2}\coth\left[\frac{\eta}{2J}\right]\right\}$$

# Reminder: Brillouin functions & Curie law

$$B_J(\eta) = \frac{1}{J}\left\{(J+\tfrac{1}{2})\coth\left[(J+\tfrac{1}{2})\eta/J\right] - \frac{1}{2}\coth\left[\frac{\eta}{2J}\right]\right\}$$

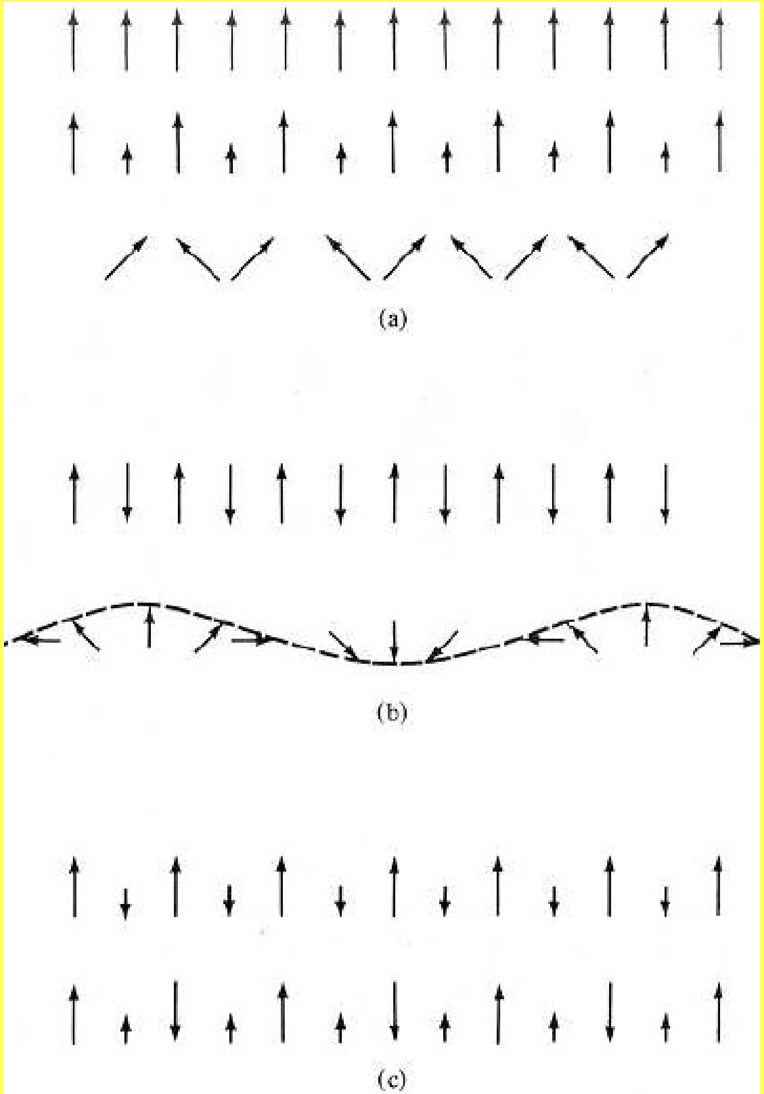
$$\eta = (g(JLS)\mu_B B)/(k_B T)$$




$$B_J(\eta \ll 1) \approx \frac{J+1}{3}\eta + O(\eta^3)$$

$$\chi^{\mathrm{mag,para}}(T) = \frac{\partial M}{\partial H} = \frac{\mu_o \mu_B^2 g(JLS)^2 J(J+1)}{3Vk_B}\frac{1}{T} = \frac{C}{T}$$

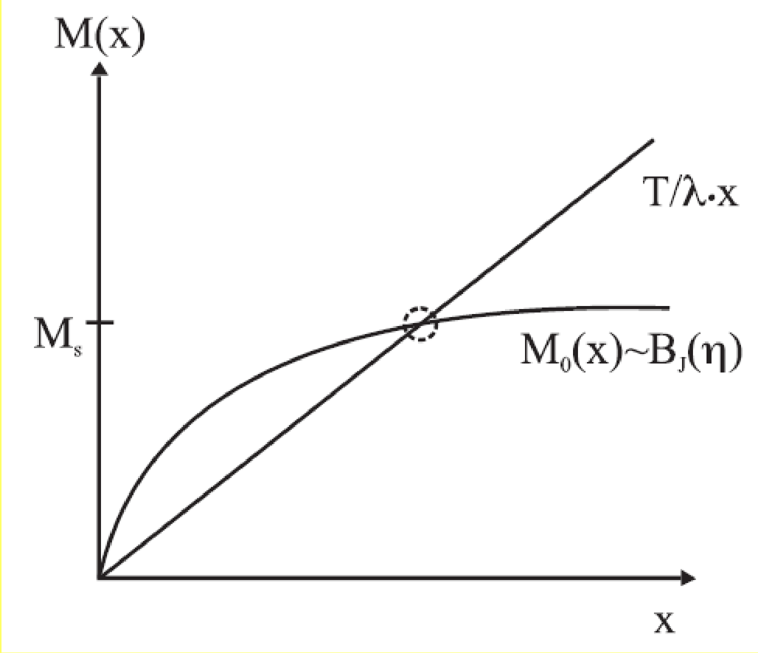
# Remider: magnetic ordering & molecular field theory (Weiss)




$$H^{\mathrm{eff}} = H + H^{\mathrm{mol}} = H + \mu_o \lambda M$$

$$M_0(T) = \frac{g(JLS)\mu_B J}{V} B_J(\eta) \quad \text{with} \eta \sim \frac{H}{T}$$

$$M(T) = M_0\left(\frac{H_{eff}}{T}\right) \rightarrow M_0\left(\frac{\lambda M}{T}\right)$$



# Reminder: Heisenberg and Ising hamiltonians

$$H_{i,j}^{\text{coupling}} = -\frac{J_{ij}}{\mu_B^2}\,\mathbf{m}_i \cdot \mathbf{m}_j$$

$J_{ij}$ exchange integral (in eV)

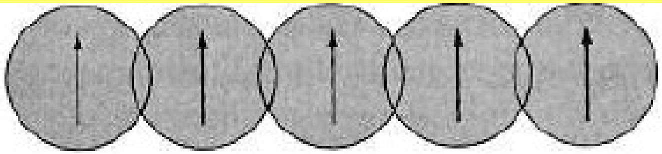
$-J_{ij} m_i m_j / \mu_B^2$ ⇨ ferro  $+J_{ij} m_i m_j / \mu_B^2$ ⇨ antiferro

$$H^{\text{Heisenberg}} = \sum_{i,j=1}^{M} H_{i,j}^{\text{coupling}} = -\sum_{i,j=1}^{M} \frac{J_{ij}}{\mu_B^2}\,\mathbf{m}_i \cdot \mathbf{m}_j$$

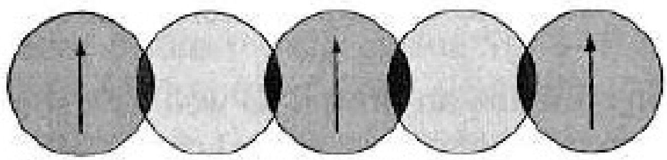
$$H^{\text{Ising}} = -\sum_{i,j=1}^{M} \frac{J_{ij}}{\mu_B^2}\,\underbrace{\mathbf{m}_{i,z} \cdot \mathbf{m}_{j,z}}_{\pm 1 \text{ only}}$$

$$H^{\text{Ising}} = -J \sum_{i=1}^{N} \sigma_i \sigma_{i+1} - h \sum_i \sigma_i$$

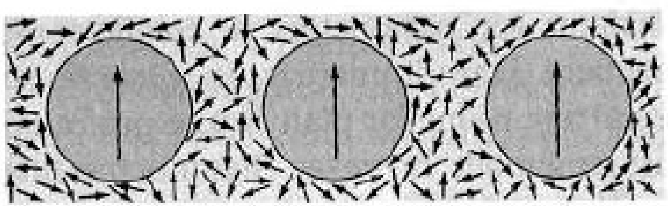
1D in magnetic field



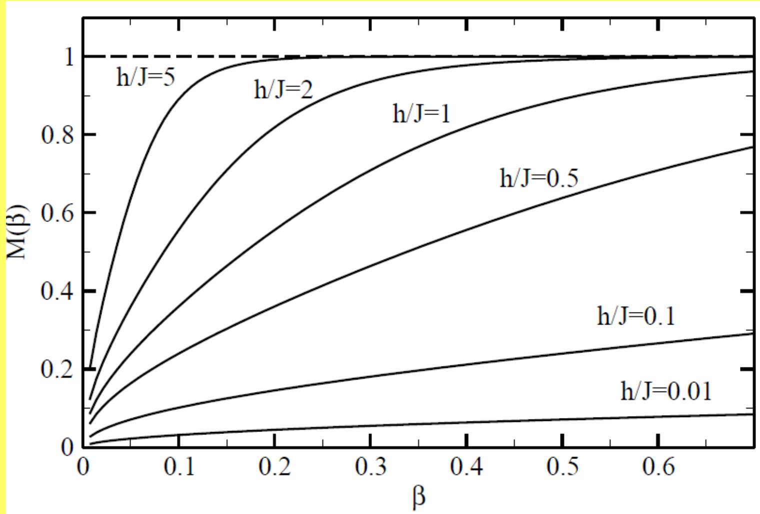
(a) Direct exchange



(b) Super-exchange via non-magnetic ions

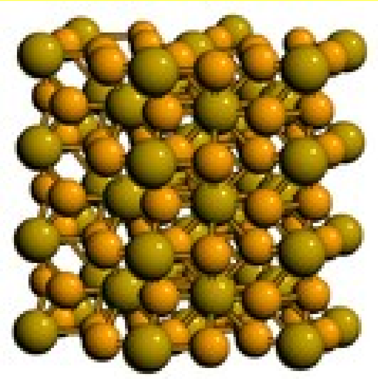


(c) Indirect exchange via conduction electrons




Magnetisation in Ising model

$\beta = (k_B T)^{-1}$

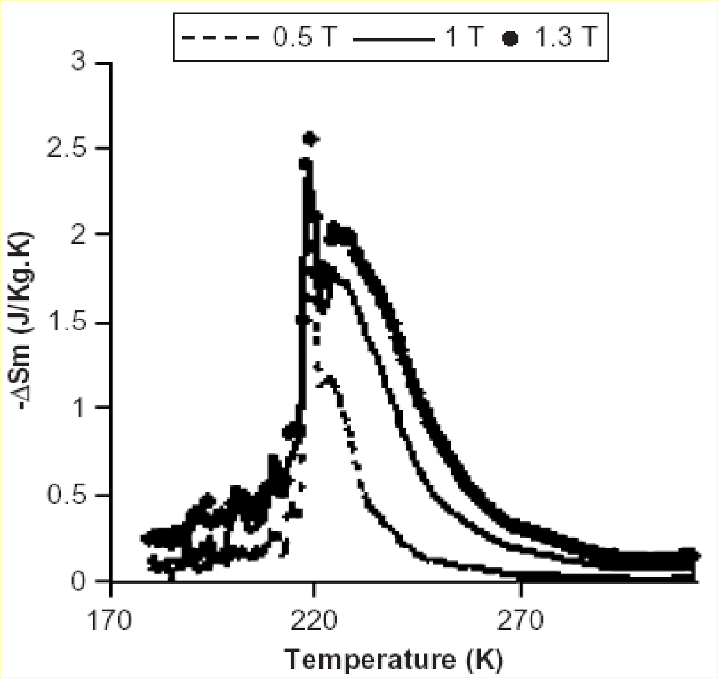


# $Fe_2P$ (magneto-elastic transition) at 217 K

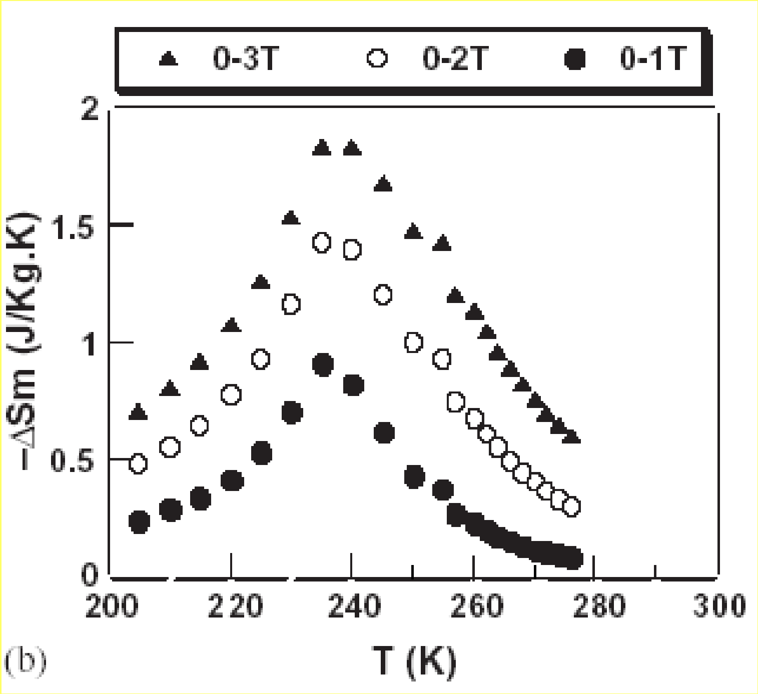
**Hexagonal** (P-62m, #189) a = 5.872 Å, c = 3.460 Å, Z=3

2 Fe sites: 3f (small magnetic moment) & 3g (large magnetic moment)

$T_C$ increases from 217 K for $Fe_2P$ to 235 K for $Fe_{1.85}Ru_{0.15}P$

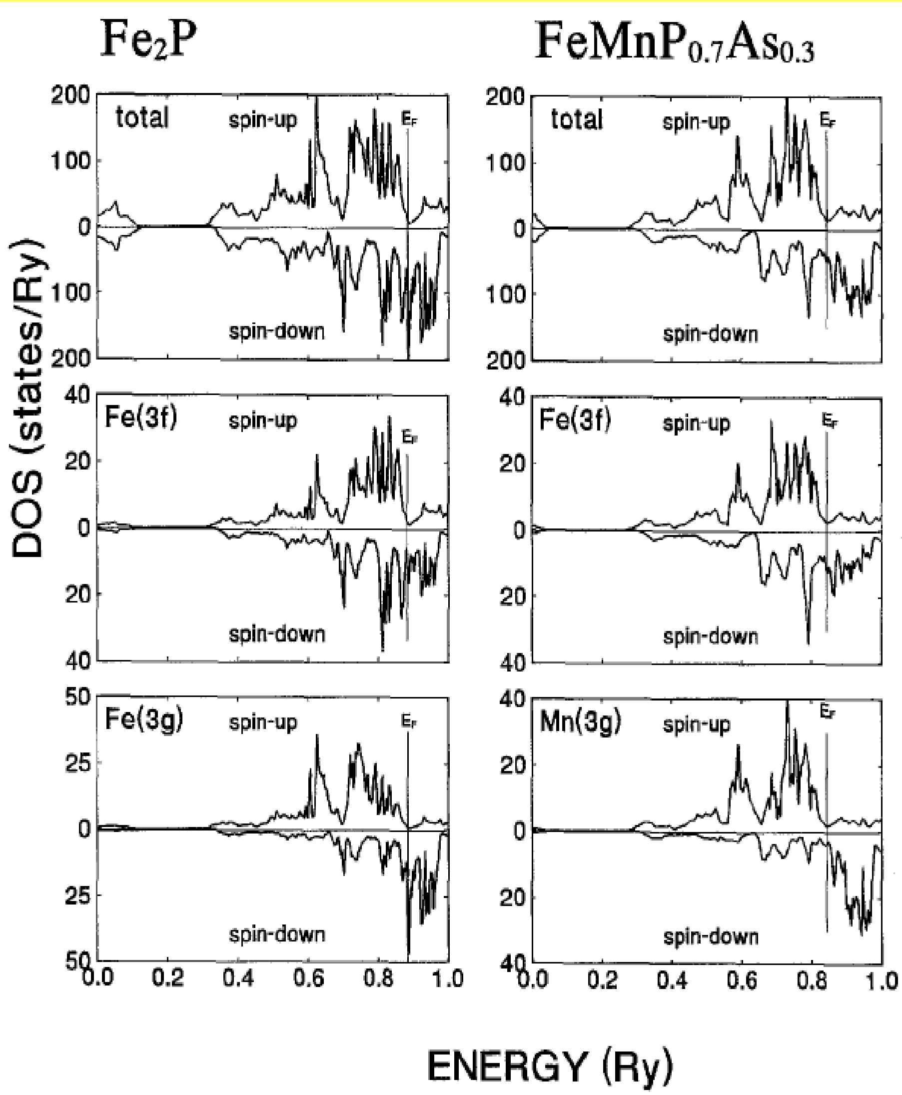



Fruchart et al., Physica A (2005)

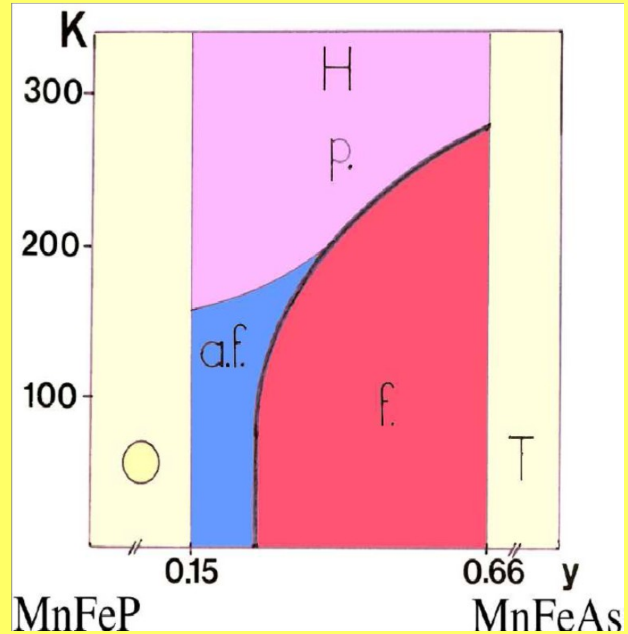



**Influence of electrons polarisation at $E_F$ in increase of $T_C$, presence of small moment 0.4 $\mu_B$/Ru, similar effect in $Fe_{2-x}Ni_xP$**

# $Fe_2P$ and MnFe(P-As)




Tobola et al., JMMM (1996)




Bacmann et al., JMMM (1994)

## MnFe(P-As)

| | Neutrons | KKR-CPA |
|---|---|---|
| Fe(3f) | 1.24 | 1.25 |
| Mn(3g) | 2.55 | 2.95 |

## $Fe_2P$

| | Neutrons | KKR-MT | KKR-FP |
|---|---|---|---|
| Fe(3f) | 0.59 | 0.80 | 0.60 |
| Fe(3g) | 2.23 | 2.33 | 2.40 |

# Calculation of entropy contributions in $Fe_{2-x}T_xP$

$$S_{el} = -R \int_{E_{min}}^{\mu_c} dE n(E)[f \ln f + (1-f)\ln(1-f)].$$

$$f = f(E, \mu_c, T) = \frac{1}{\exp[(E-\mu_c)/k_B T] + 1}$$

$$N_{val} = \int_{E_{bottom}}^{\mu_c} dE n(E) f(E, \mu_c, T),$$

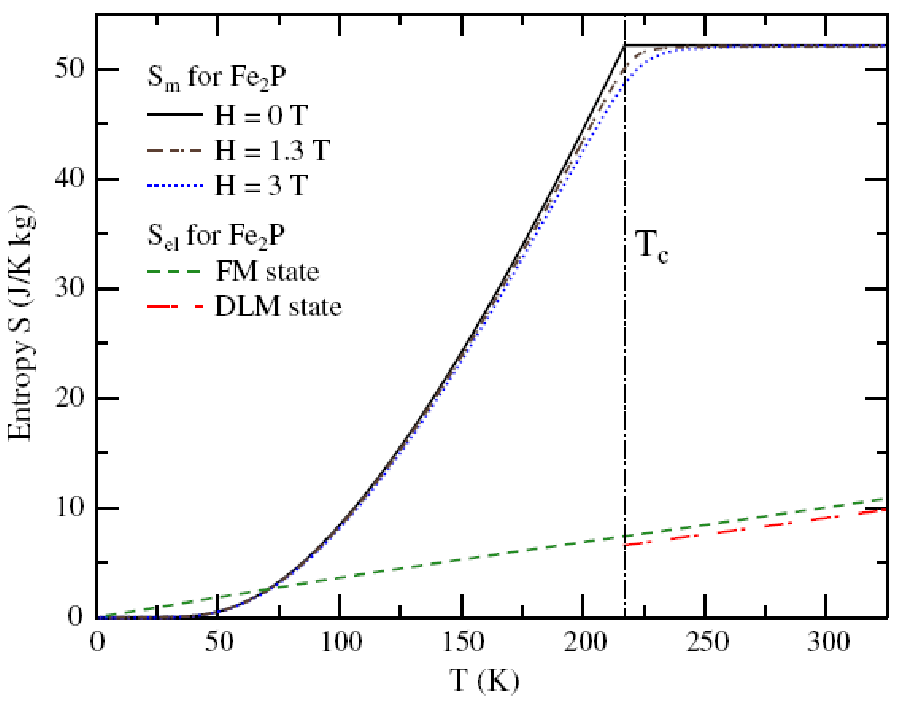
$$S_{tot} = S_{el} + S_m + S_{lat}.$$

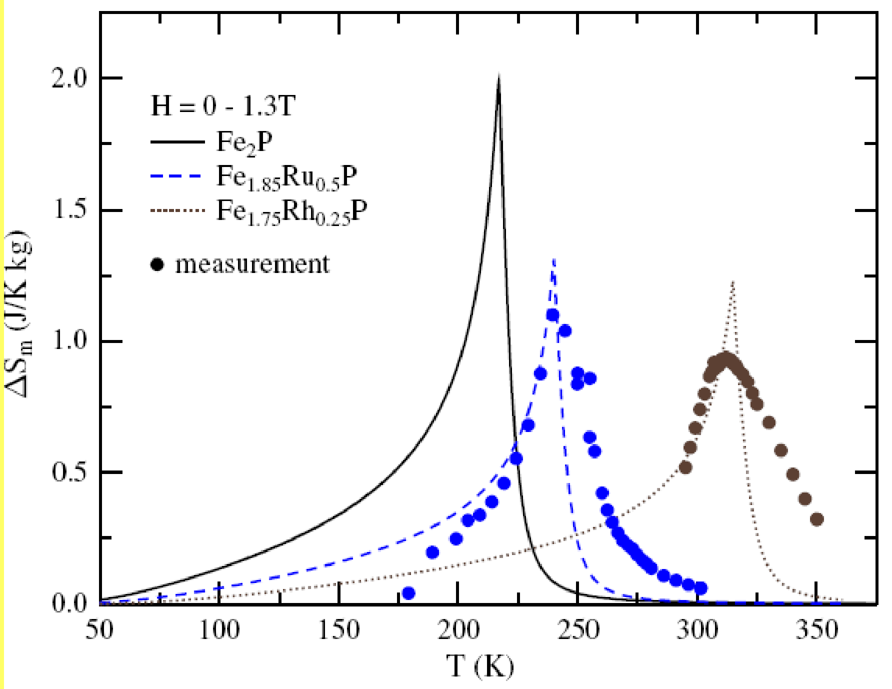
$$\Delta S(H_{max}) = \int_0^{H_{max}} \left(\frac{\partial M}{\partial T}\right)_H dH$$

$$S_m = R \left[ \ln \frac{\sinh \frac{2J+1}{2J} x}{\sinh \frac{1}{2J} x} - x B_J(x) \right]$$

$$x = \frac{g \mu_B J H}{k_b T} + 3 \frac{T_C}{T} \frac{\mu(T)}{g \mu_B (J+1)}$$

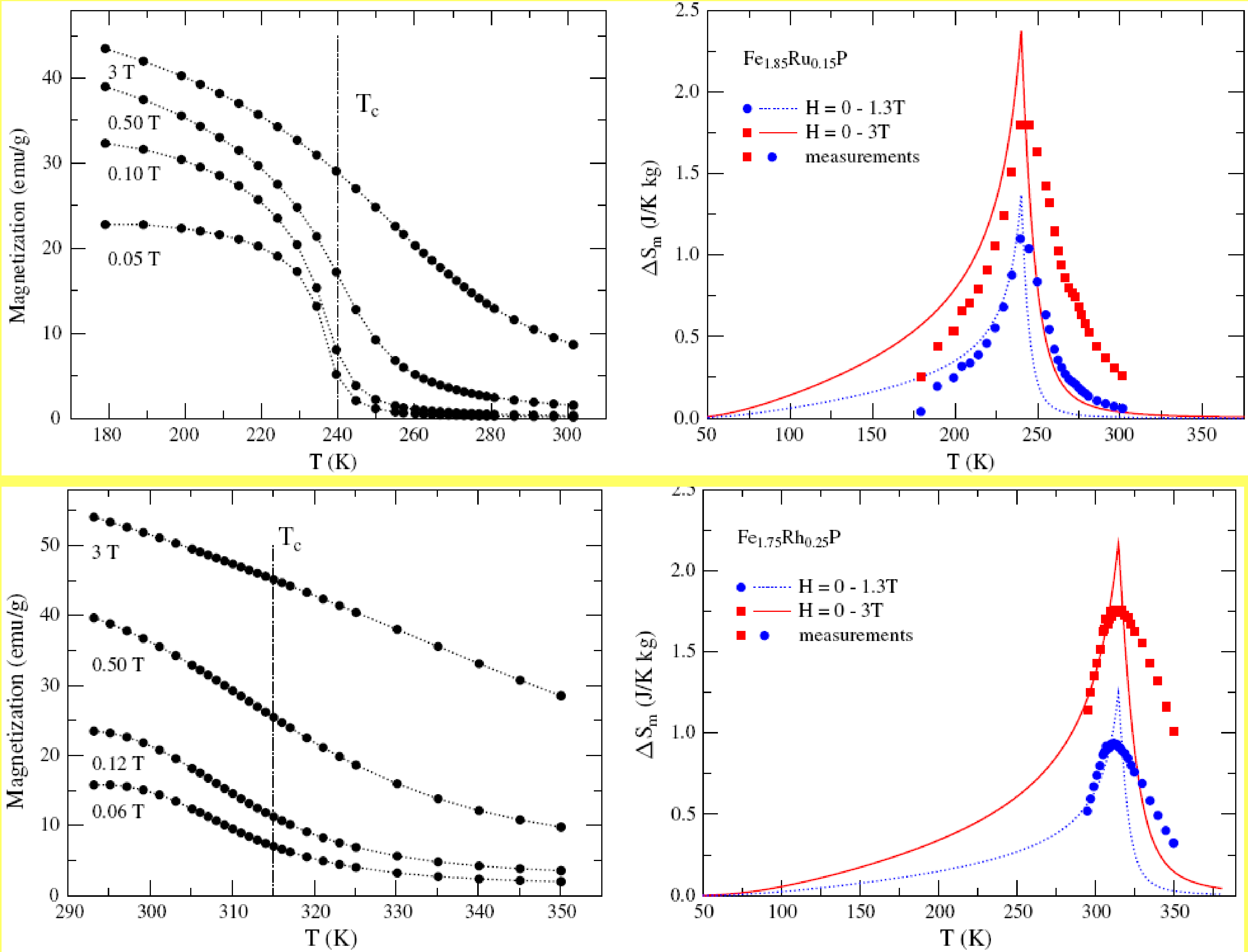
$$S_m^{max} = R \ln(2J+1)$$




B Wiendlocha, J Tobola, S Kaprzyk, R Zach, E K Hlil and D Fruchart, J. Phys. D: Appl. Phys. 41 (2008) 205007

# Entropy from electronic structure KKR-CPA & MFT




B Wiendlocha, J Tobola, S Kaprzyk, R Zach, E K Hlil and D Fruchart, J. Phys. D: Appl. Phys. 41 (2008) 205007

# Simulations of electronic structure above Curie temperature

## DLM (*disordered local moments*)

1. Analogy with chemical alloy within the coherent potential approximation) CPA **with 2 atoms on 1 site**.

2. **atom A – $Fe^{up}$** (iron with magnetic moment 'up')
   **atom B - $Fe^{down}$** (iron with magnetic moment 'down')

3. **A** and **B** atoms occupy the same crystallographic site.

4. For concentration 50% the total magnetic moment per site and unit cell is zero, but the 'local' magnetic moments may be **non-zero**.

5. CPA medium is used to **randomly distribute the magneti moments** among the sites (like in **paramagnetic state**)

| KKR+CPA | Experiment |
|---|---|
| $T_C$ =1250 K | $T_C$ =1044 K |

*Ferromagnetic phase transitions in metals*

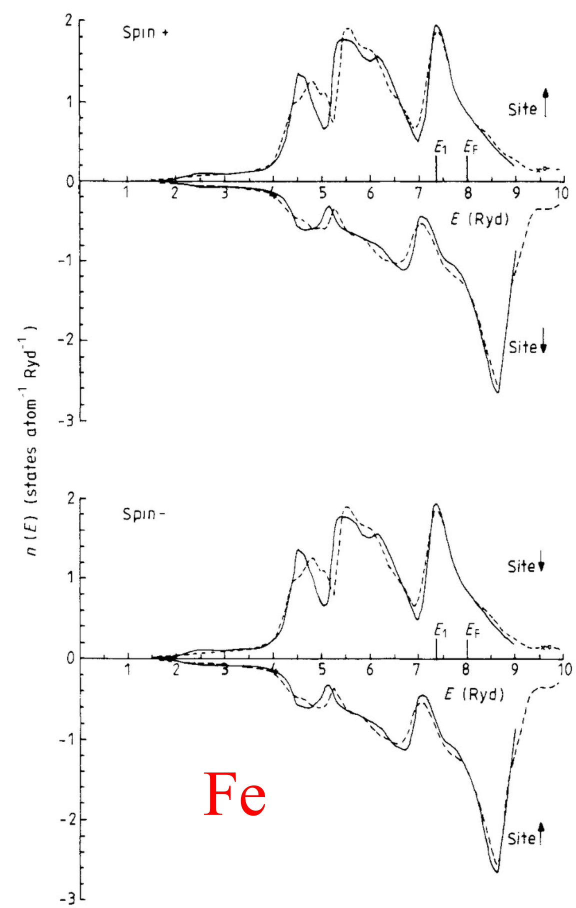



**Figure 3.** Density of states for Fe in its paramagnetic disordered local moment state.

Gyorffy et al., J. Phys. F (1985)

# Ground state properies
## KKR-CPA code

Total density of states DOS

$$N(E) = -\frac{1}{\pi}\operatorname{Im}\int_{-\infty}^{E} dE\, G(E)$$

Component, partial DOS

$$\rho_\sigma(E) = \frac{\partial}{\partial E} N_\sigma(E).$$

Total magnetic moment

$$\mu = N_+(E_F) - N_-(E_F)$$

Spin and charge densities

$$\rho_\sigma^{(k)}(\mathbf{r}) = -\frac{1}{\pi}\int_{-\infty}^{E_F} dE \langle \sigma, \mathbf{r}+\mathbf{a}_k | G(E) | \sigma, \mathbf{r}+\mathbf{a}_k \rangle$$

Local magnetic moments

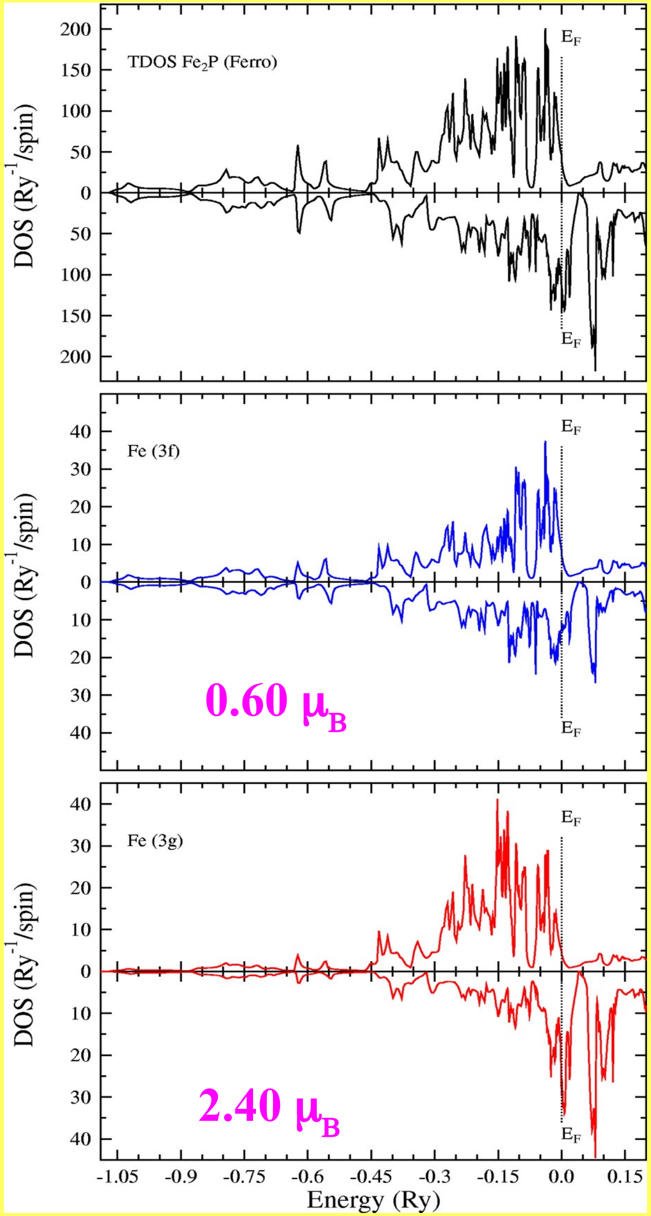
$$\mu^{(k)} = \mu_B \int_{\Omega_k} d^3 r\, s^{(k)}(\mathbf{r})$$

Fermi contact hyperfine field

$$H_{Fermi} = \frac{8}{3}\pi\mu_B[\rho_\uparrow(0) - \rho_\downarrow(0)].$$

Bands E(**k**), total energy, electron-phonon coupling, magnetic structures, transport properties, photoemission spectra, Compton profiles, …

# $Fe_2P$ (ferromagnetic vs. 'paramagnetic' DLM state)

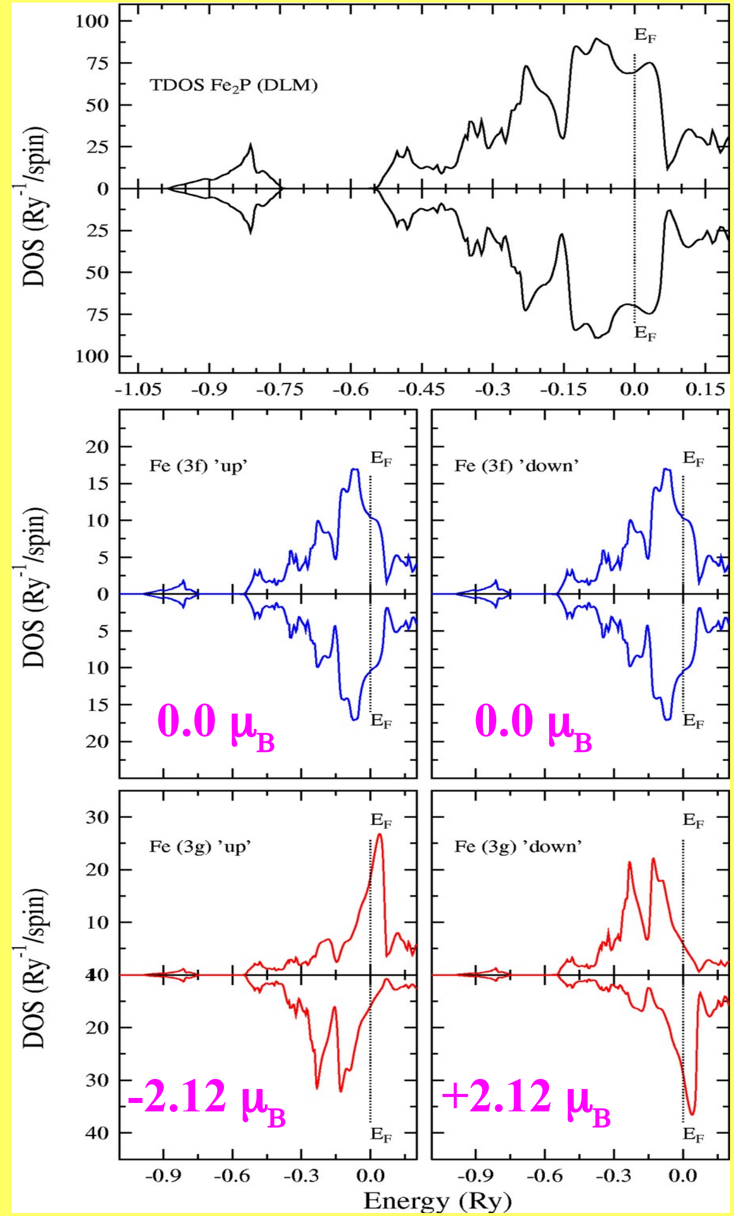



Disappearance of magnetic moment on one crystallographic site strongly modify entropy of PM state with respect to FM state:

**huge entropy jump**

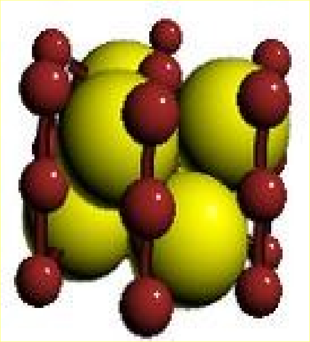
WHAT IS NEEDED to have strong MCE!!

In computations all atoms are treated independently, so to obtain zero magnetisation from non-zero magnetic moments of atoms is not authomatic, time-consuming calculations

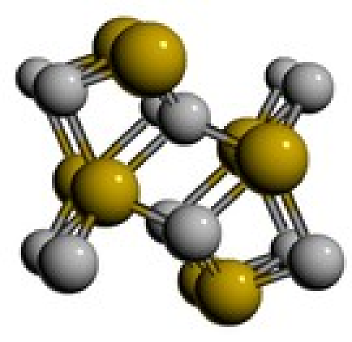



B Wiendlocha, J Tobola, S Kaprzyk, R Zach, E K Hlil and D Fruchart, J. Phys. D: Appl. Phys. 41 (2008) 205007

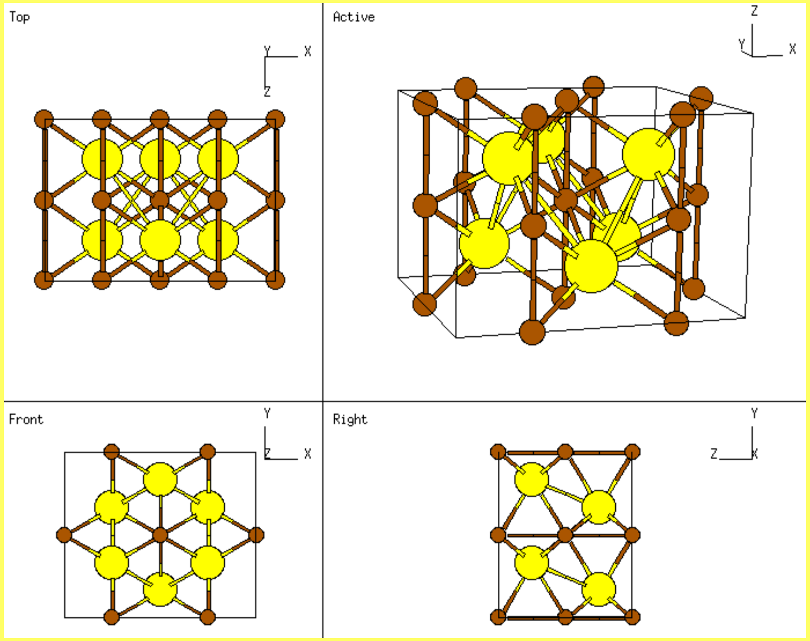
# MnAs (magneto-structural transition) at 318 K

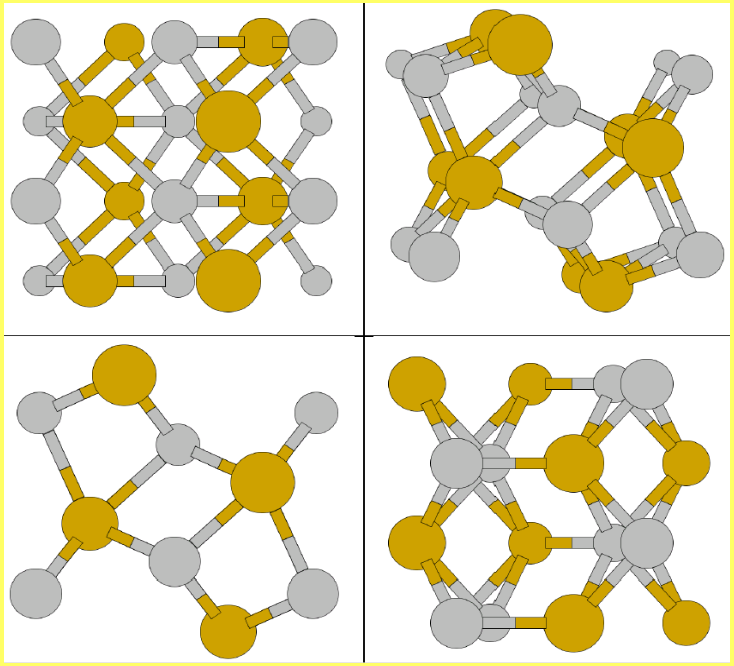


**Hexagonal** NiAs-type structure
(P63/mmc, #194)
a = 3.730 Å, c = 5.668 Å, Z=2

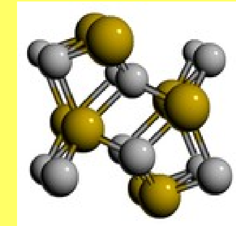


**Orthorhombic** MnP-structure
(Pnma, #62)
a = 5.72 Å, b = 3.676 Å, c = 6.379 Å, Z=4

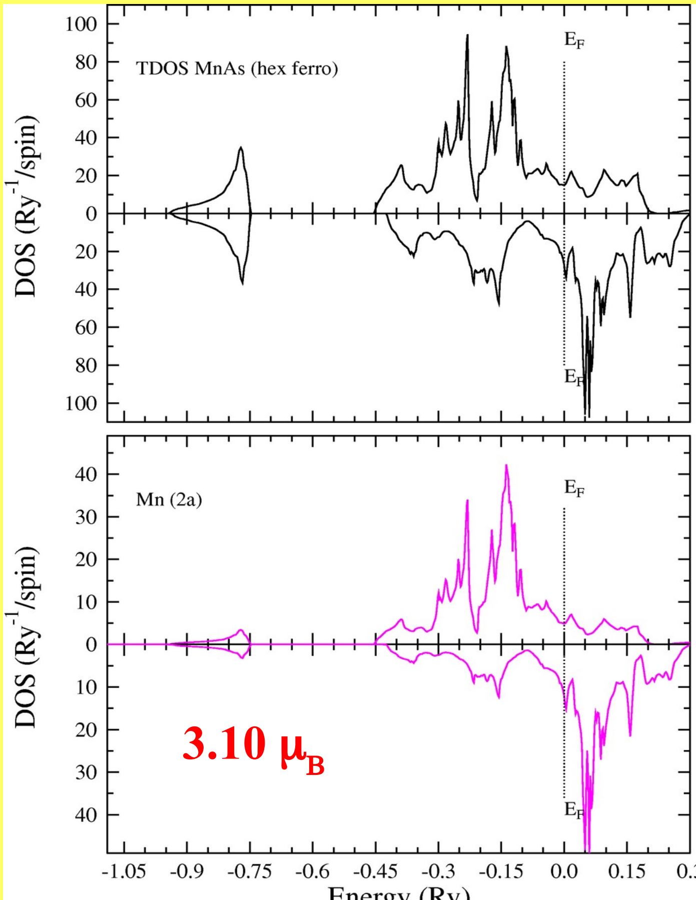


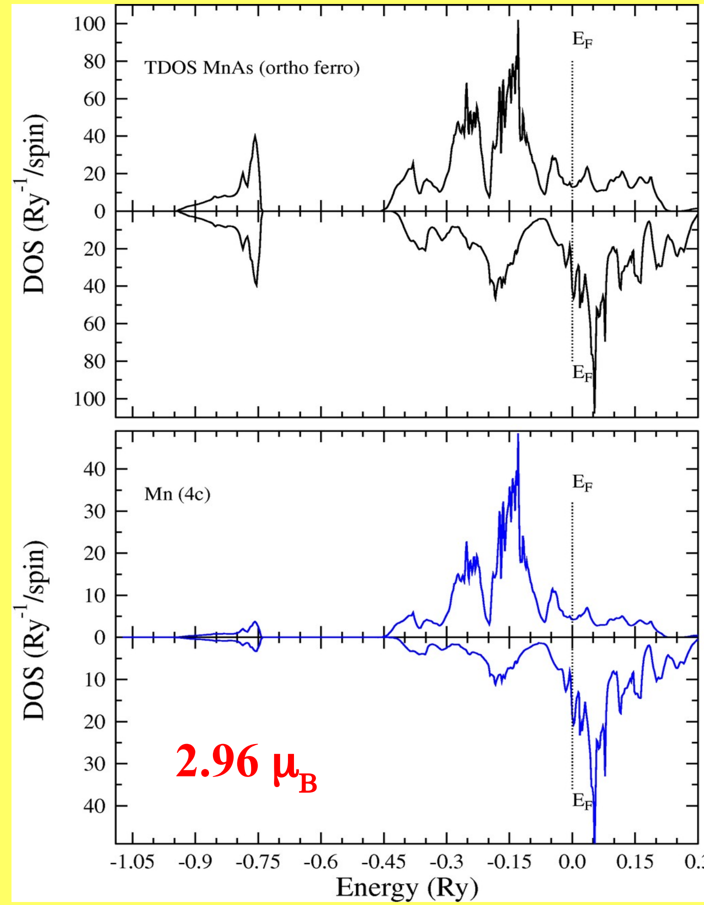
# MnAs in ferromagnetic state



## NiAs-type



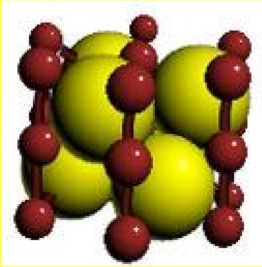

## MnP-type

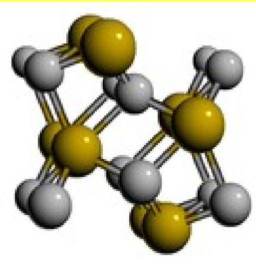



**In excellent agreement with neutron diffraction data : 3.14 $\mu_B$**

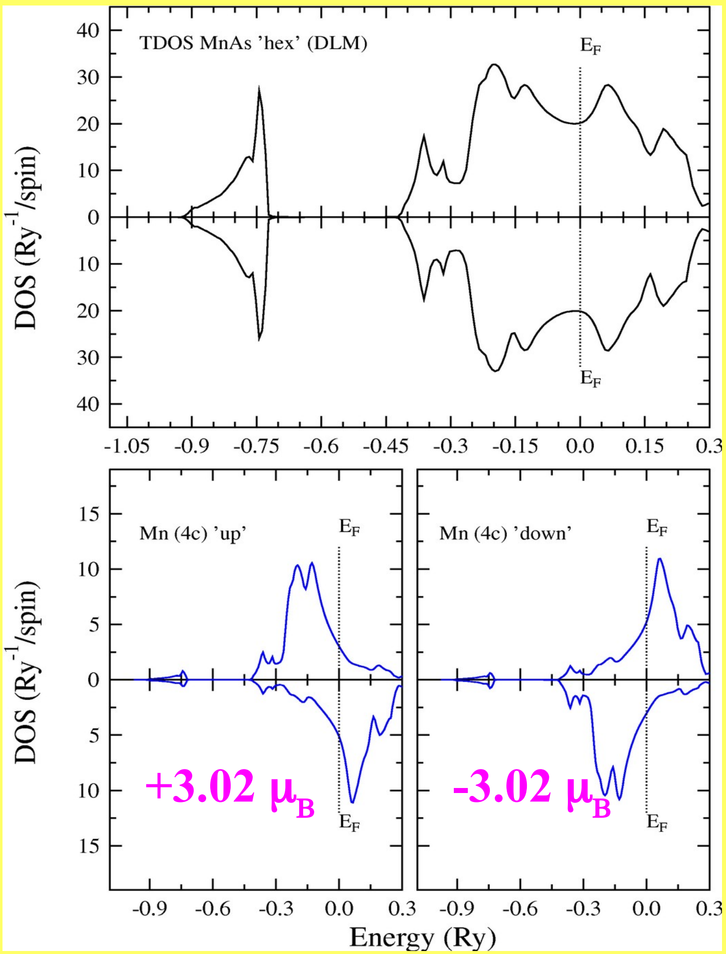
# **MnAs** in 'paramagnetic' state

DLM (*disordered local moments*)

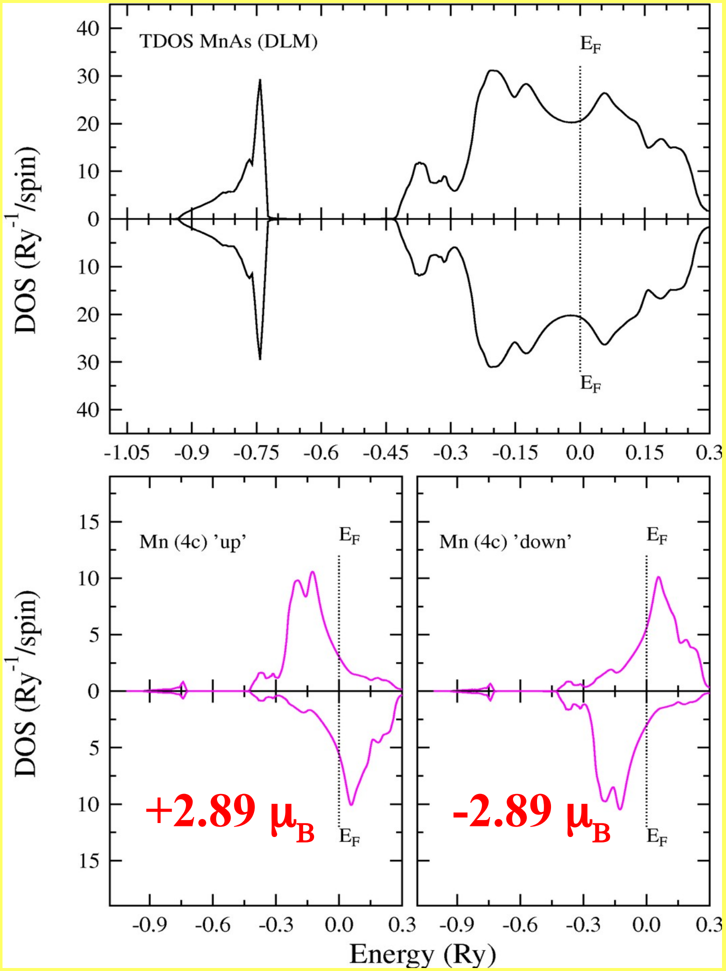




NiAs-type




MnP-type

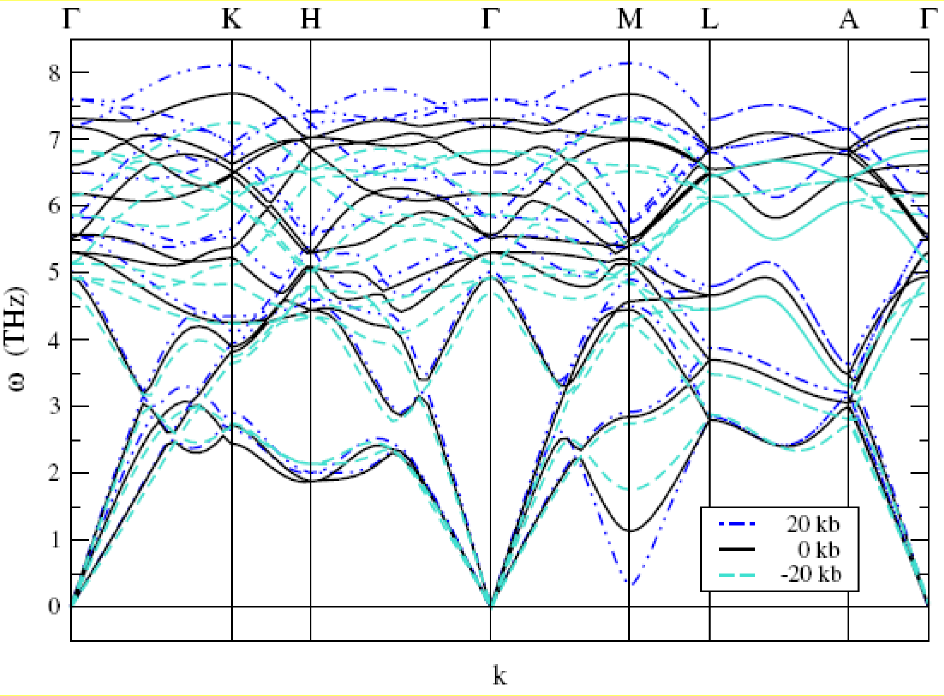


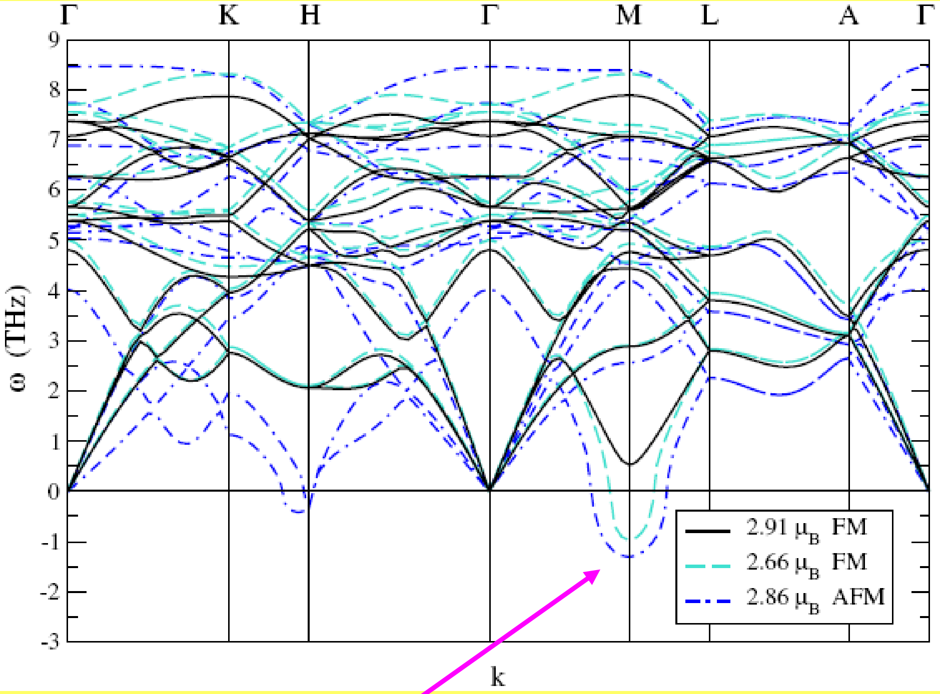
# MnAs
## phonon mechanism of magneto-structural phase transition

$$P6_3/mmc \rightarrow [M_2^+, \mathbf{k} = (0.5, 0, 0)] \rightarrow Pnma.$$

**Hexagonal** NiAs-type structure

**Orthorhombic** MnP-structure



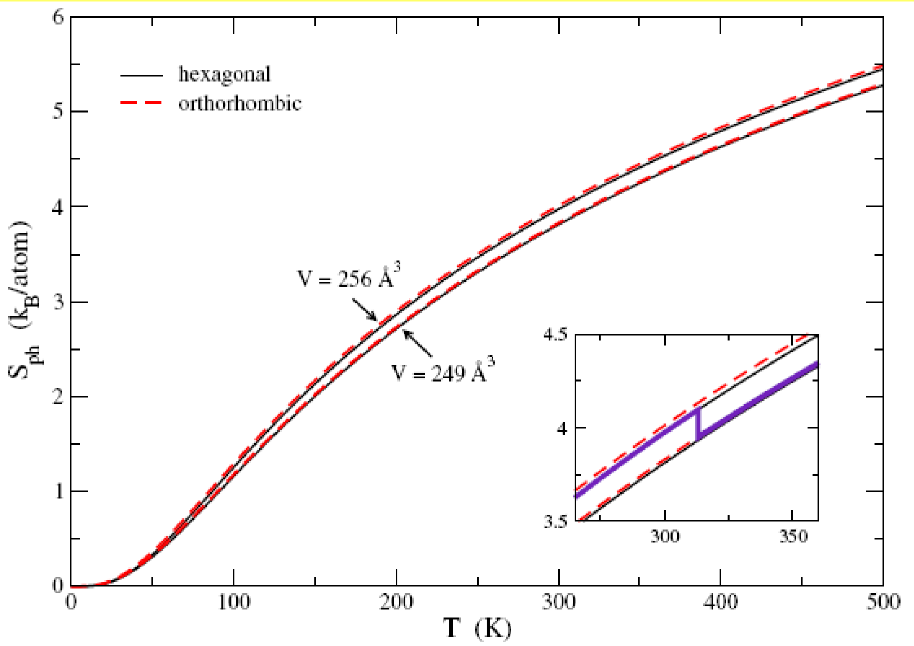

volume contration ($\Delta V/V \sim 2\%$) near Curie temperature

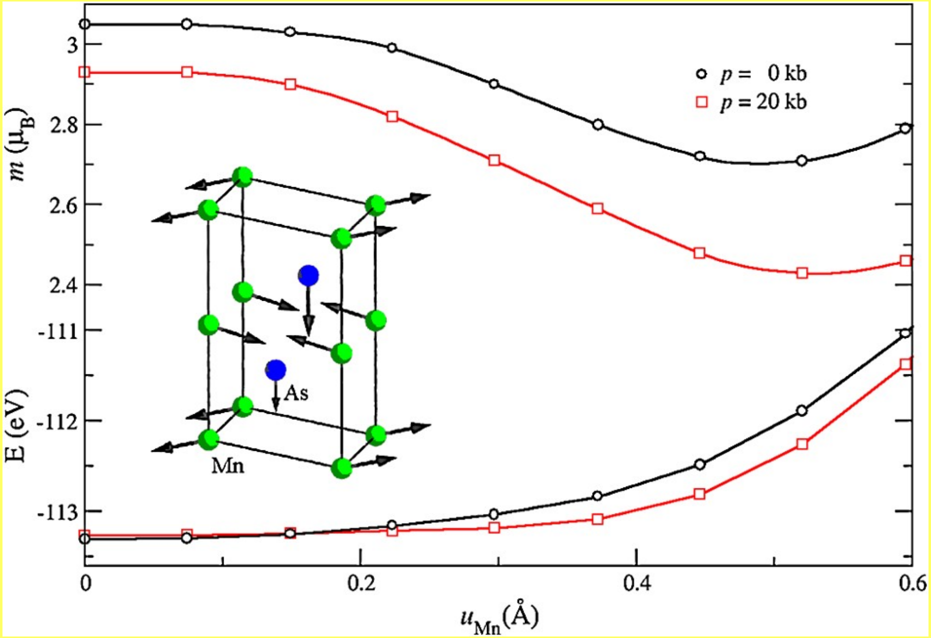
soft mode near M point (phonon calculations)

J. Lazewski, P. Piekarz, J. Tobola, B. Wiendlocha, P. T. Jochym, M. Sternik and K. Parlinski, PRL **104,** 147205 (2010)

# MnAs

## phonon mechanism of magneto-structural phase transition




$$S_{tot} = S_{el} + S_m + S_{lat}.$$

experiment $\Delta S_{tot}$= **-30** J/(K kg) for $\Delta B$ = 5 T

theory $\Delta S_{lat}$= **+9.3** J/(K kg)

<u>Entropy jump mainly related to magnetic entropy</u>

giant coupling between the soft mode and magnetic moments

$$\omega = \omega_0 + \lambda \langle \mathbf{S_i} \cdot \mathbf{S_j} \rangle$$

$$\langle \mathbf{S_i} \cdot \mathbf{S_j} \rangle = S^2 = \frac{1}{4} m^2$$

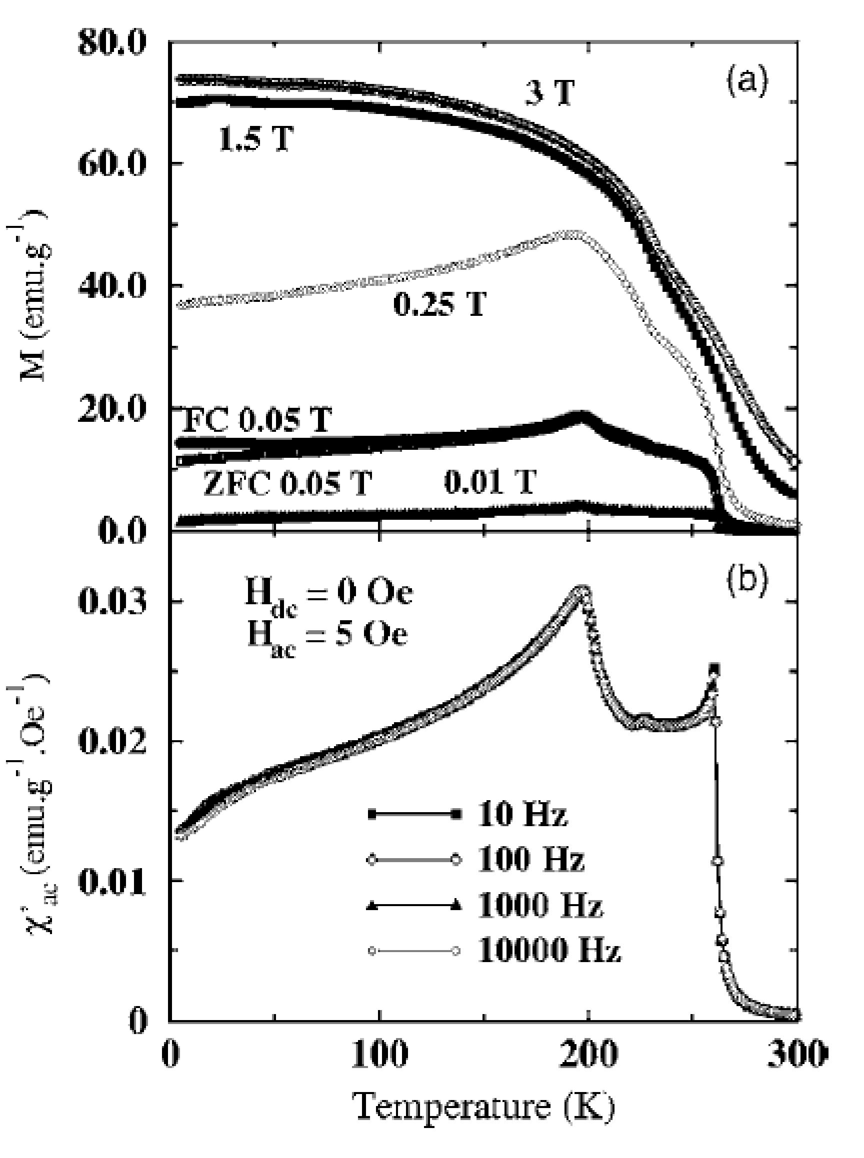
$\lambda \sim 4$ THz

J. Lazewski, P. Piekarz, J. Tobola, B. Wiendlocha, P. T. Jochym, M. Sternik and K. Parlinski, PRL **104,** 147205 (2010)

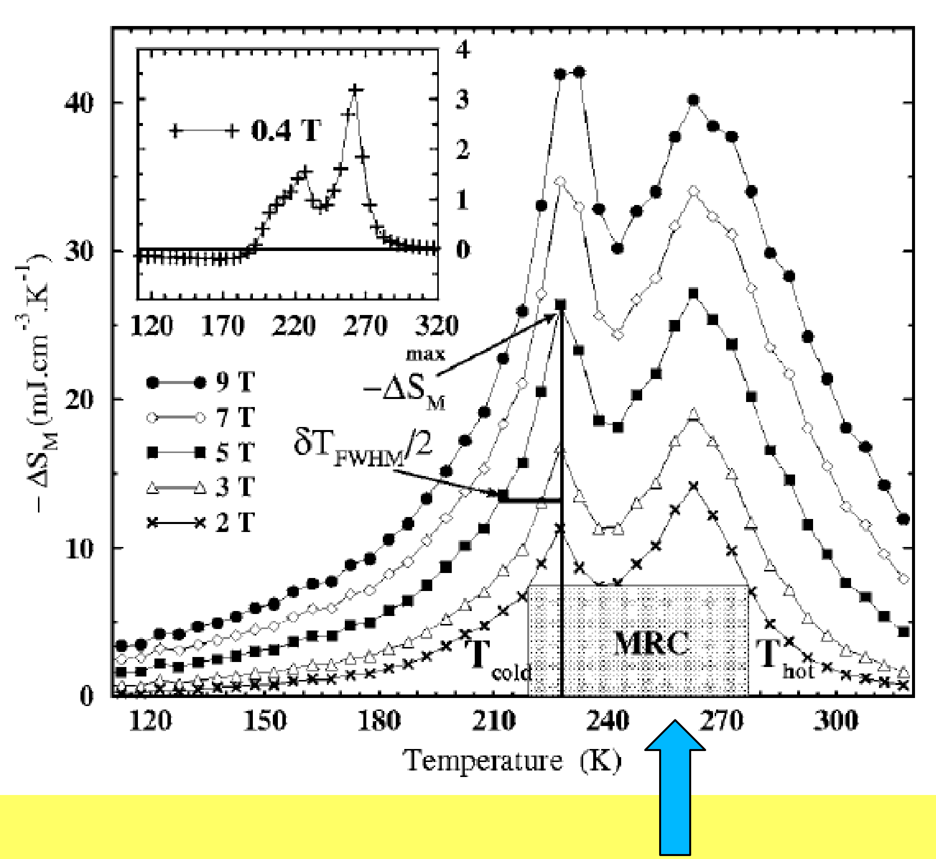
# Magnetocaloric effect in $Mn_3Sn_2$ (i)

## Magnetisation curves *M(B, T)*

Mazet, Ihou-Mouko, and Malaman, Appl. Phys. Lett. **89, 022503 (2006)**




## Magnetic entropy



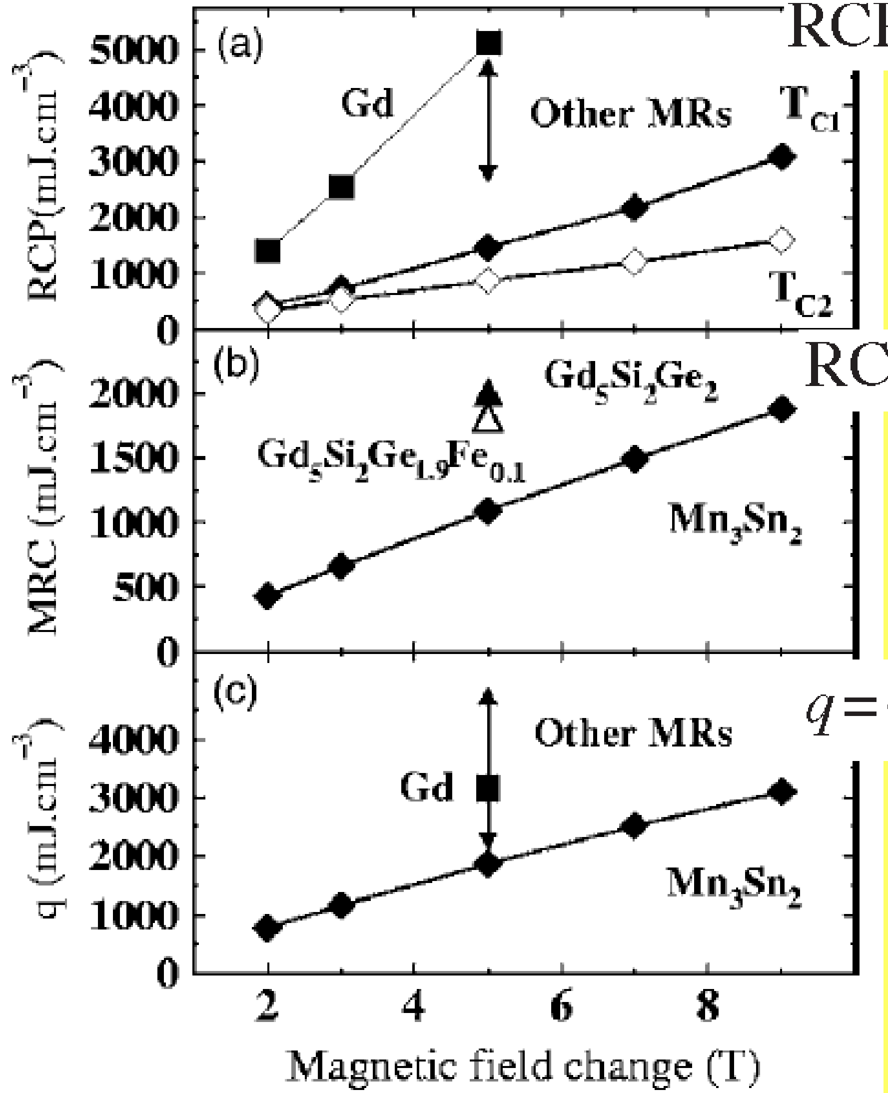

MRC - maximum refrigerant capacity

# Magnetocaloric effect in $Mn_3Sn_2$ (ii)

$RCP = -\Delta S_M^{max} \times \delta T_{FWHM}$

$RC = -\Delta S_M \Delta T_{cycl}$

$q = -\int_{T_1}^{T_2} \Delta S_M(T) dT$

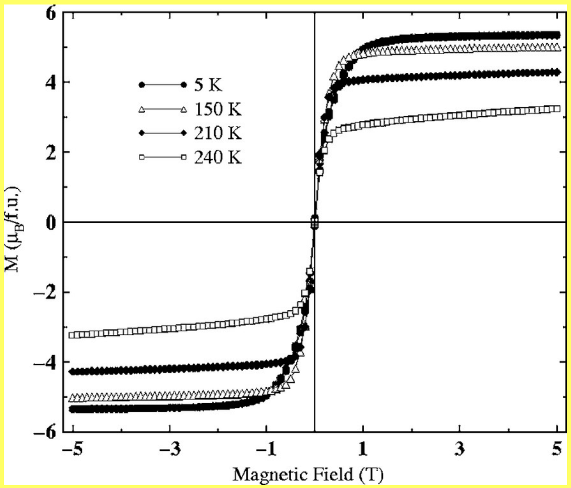



Mazet, Ihou-Mouko, and Malaman, Appl. Phys. Lett. **89, 022503 (2006)**

**MRC = max of RC**

Hystheresis loops

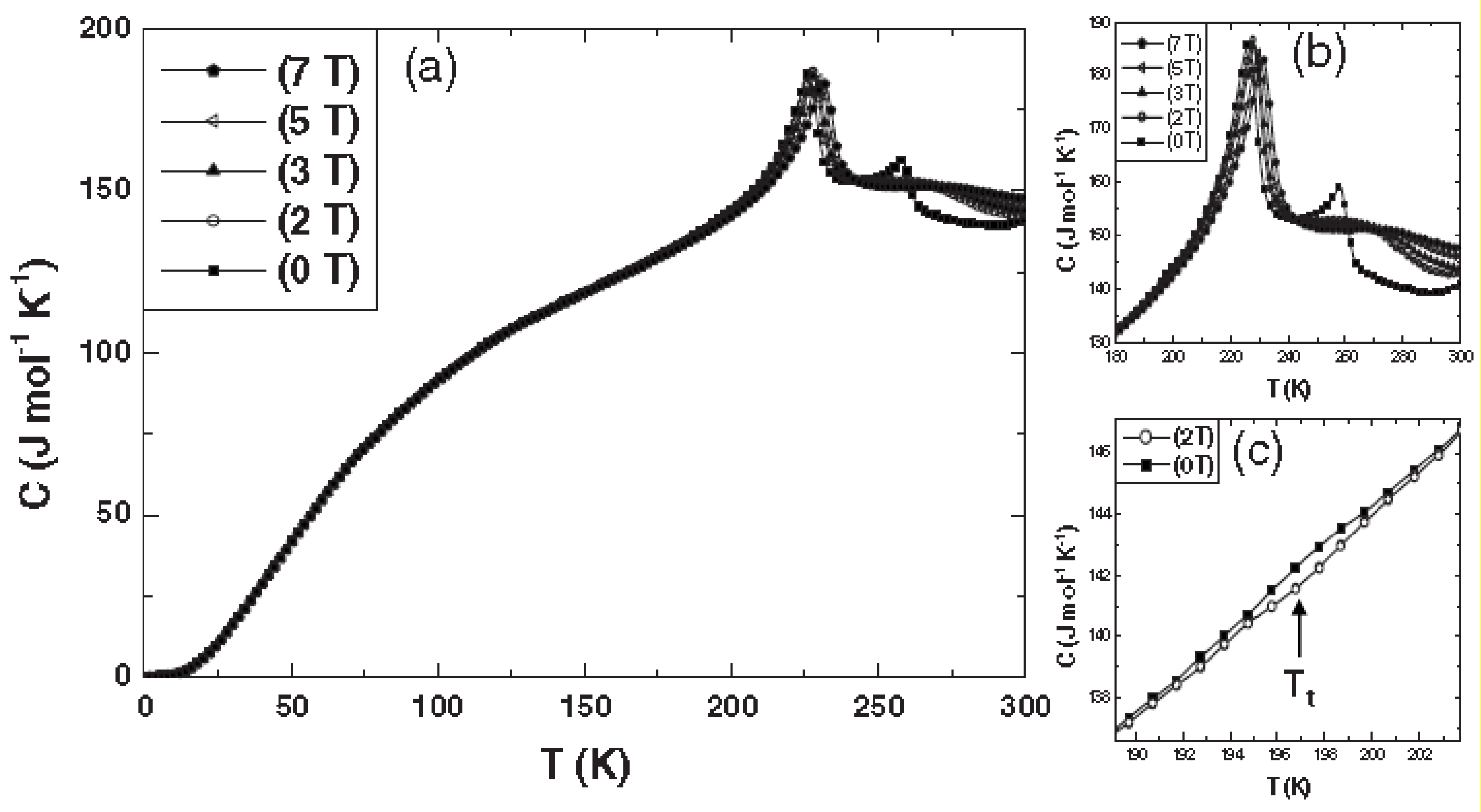
**RCP ~ 4/3 q**




MCE „figure of merit”

# Magnetocaloric effect in $Mn_3Sn_2$ (iii)

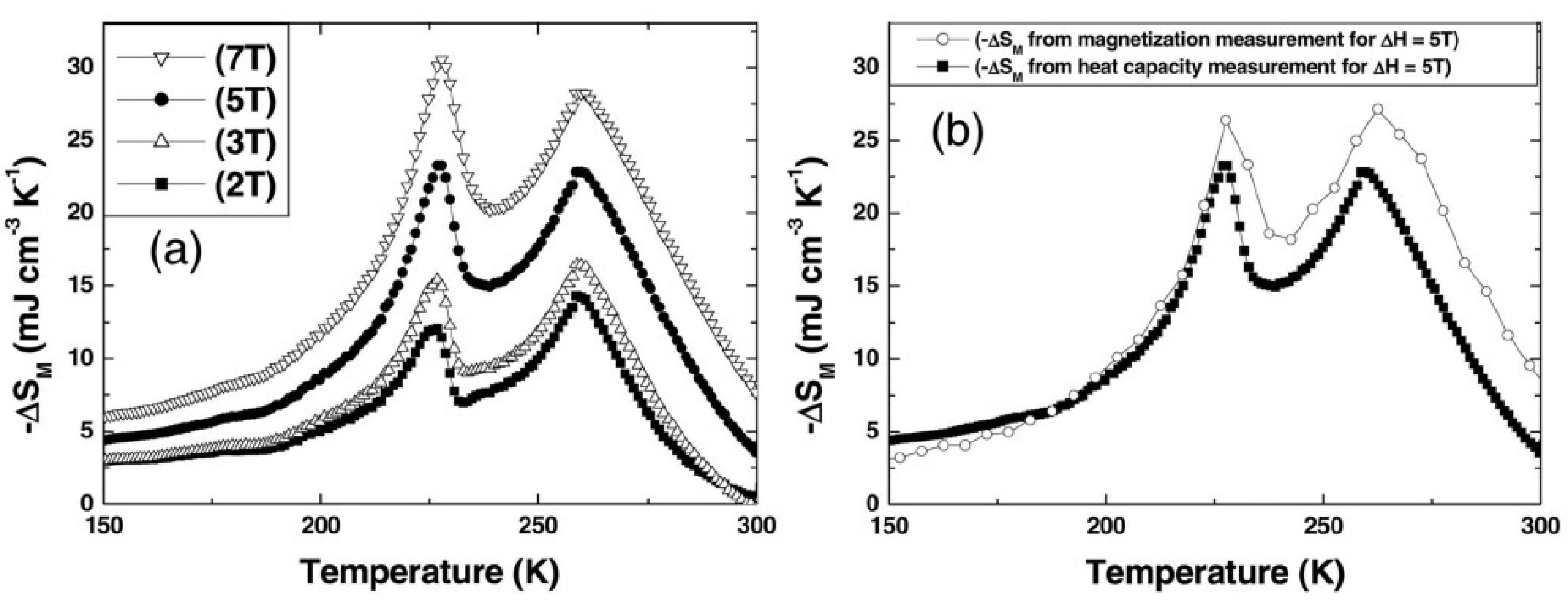
## Heat capacity *C(T, H)*

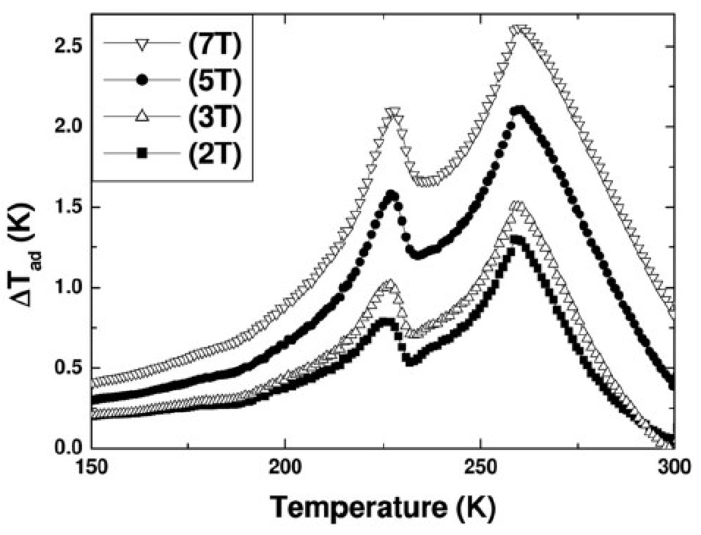



Recour, Mazet, and Malaman J. Appl. Phys. **105,** 033905 (2009)

# Magnetocaloric effect in $Mn_3Sn_2$ (iv)

## Entropy change from magnetisation & heat capacity measurements




Recour, Mazet, and Malaman,
J. Appl. Phys. **105,** 033905 (2009)

Adiabatic temperature change

## Summary

- **First principle calculations** – helpful in interpretation and description of magnetocaloric materials. Best way is to combine electronic structure and phonon calculations to enabling to estimate entropy jump near transition temperature-crucial for large MC effect.

- **The concept of DLM** were sucessfully applied to study complex MCE systems: MnAs, MnFe(As-P), $Fe_2P$ by simulating paramagnetic state from KKR-CPA .

## Illustrative examples

- **MnAs** - the calculated magnetic moment on Mn in DLM state (ortho) is comparable to FM state (hex), likely promoting large entropy jump near transition; phonon mechanism responsible for hex-ortho magneto-structural phase transition; giant spin-phonon coupling; $Mn_{1-x}T_xAs$ - remarkable variation of local magnetic moments with *T* impurity.

- **$Fe_2P$** - the magnetic moment appearing on Fe(3f) in FM state, completely vanishes in DLM state, while that one on Fe(3g) remains only slightly smaller. with respect to the FM state; MFT + KKR-CPA nicely reproduce entropy jump in disordered alloys.

- **$Mn_3Sn_2$** - with two second-order magnetic transitions very interesting compound for MCE cooling ; more difficult for calculations – noncollinear magnetism.