Delft days on Magnetocalorics, 2-3 november 2015, Delft

Thermodynamic models of the magnetocaloric effect at first order phase transitions

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EU - FP7 Collaboration

DRREAM
Drastically Reduced Use of Rare Earths in Applications of Magnetocalorics
K. Sandeman (coord.)

ISTITUTO NAZIONALE DI RICERCA METROLOGICA

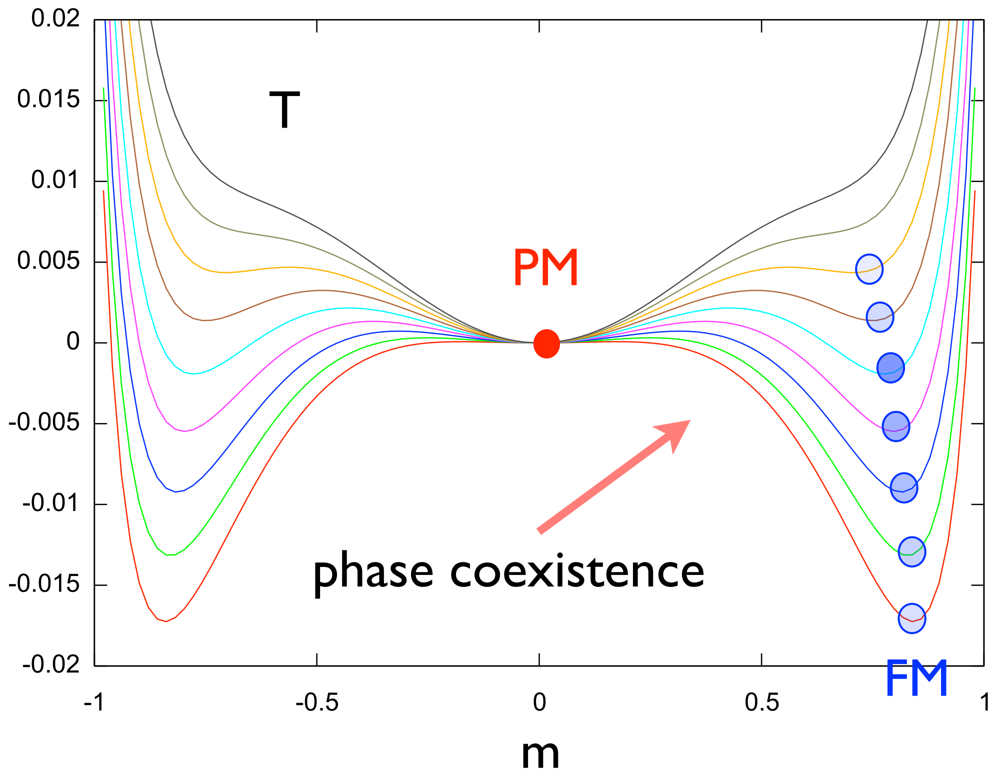
Outline

1. Thermodynamic models of MCE
2. Application to $La(Fe\text{-}Mn\text{-}Si)_{13}\text{-}H$
3. Conclusions

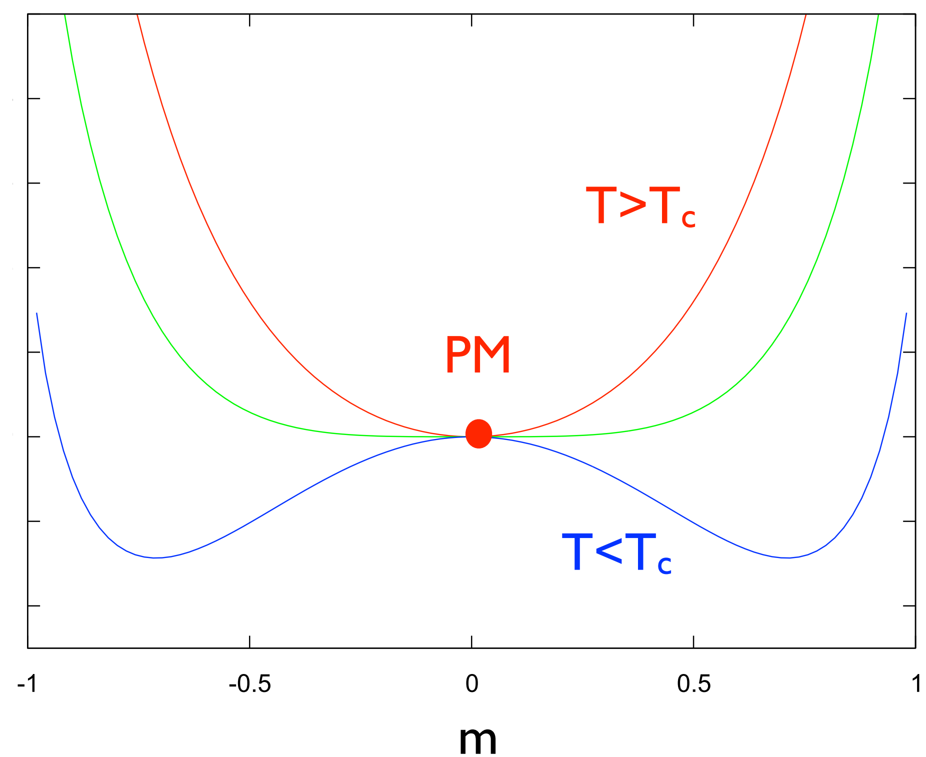
Thermodynamics

free energy f(M,T)

First order transition



Second order transition

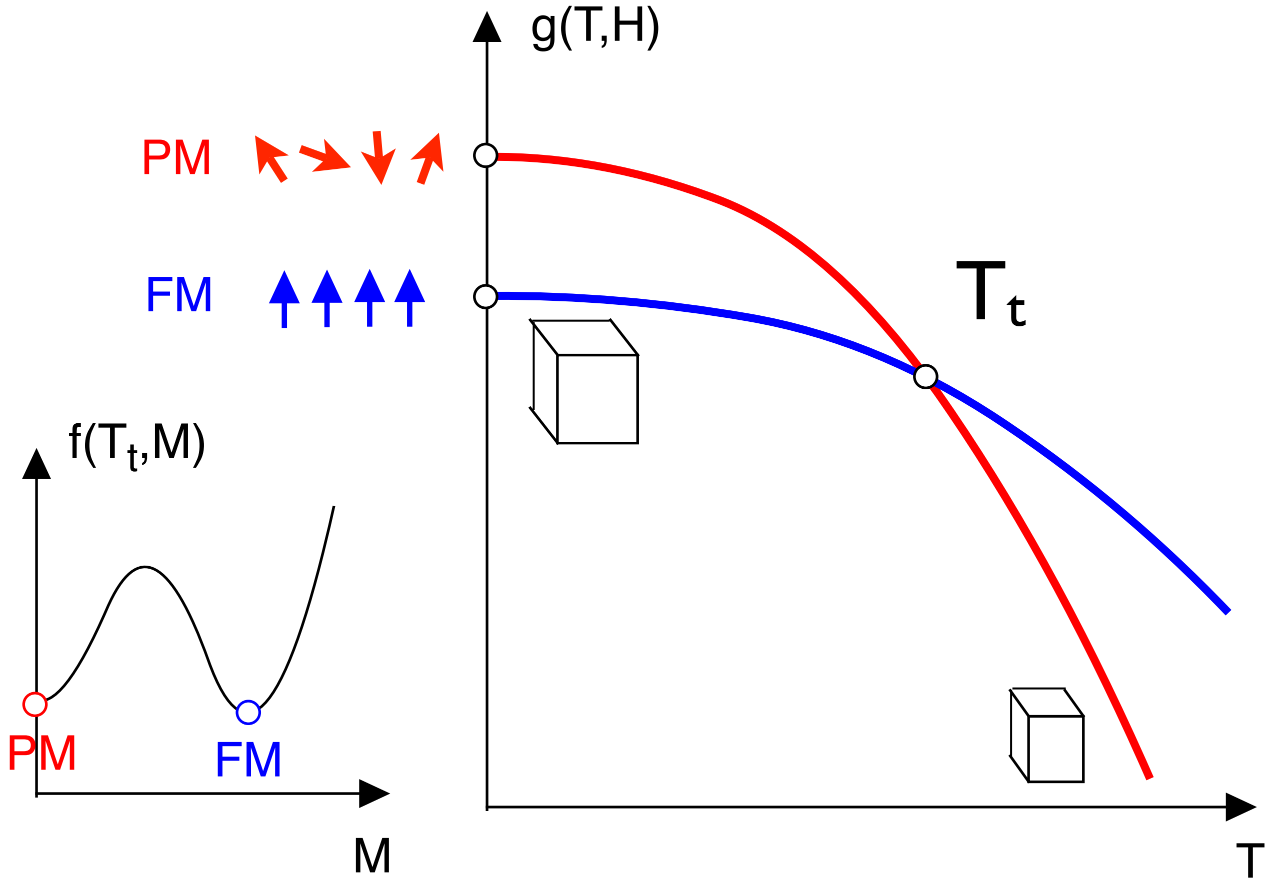


in equilibrium:
transition at $g_{PM} = g_{FM}$

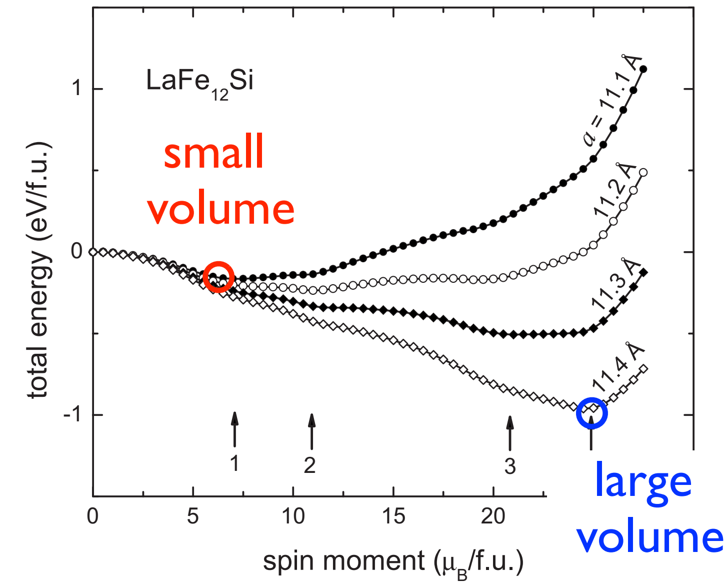
out-of-equilibrium:
hysteresis

Theory

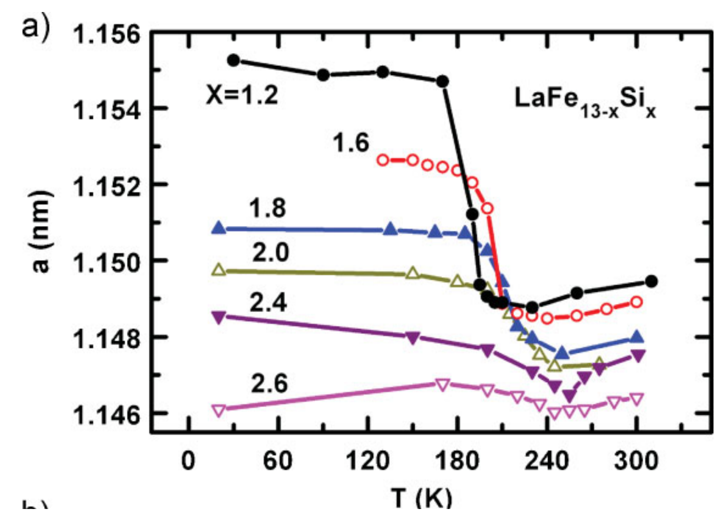
magnetism and lattice



DFT



Kuzmin et al, PRB (2007)



Shen et al, Adv. Mater. (2009)

Free energy

total free energy

$$f_L = -\frac{1}{2}W(\omega)\mu_0 M^2 - T s_M(M) + f_S(\omega, T)$$

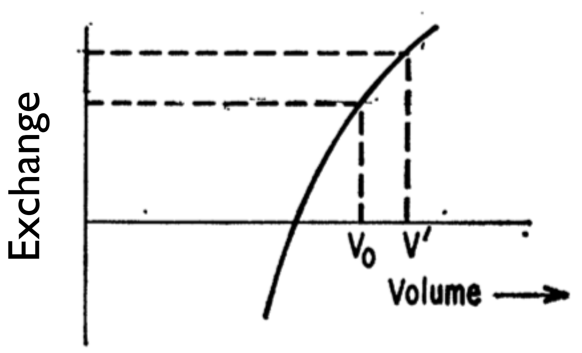
exchange

electronic spin entropy

all degrees of freedom other than magnetic

$K_B N_A \ln(2J+1)$

lattice free energy



$$\omega = \frac{v - v_0}{v_0}$$

V. Basso, J.Phys. Condens. Matter **23** (2011) 226004.

lattice free energy

$$f_S(\omega, T) = f_{ela}(\omega) + f_D(\omega, T) + f_{ele}(T)$$

elastic

phonons

electrons

- $$f_{ela}(\omega) = \frac{v_0}{2\kappa_0}\omega^2 + \mathcal{O}(\omega^3)$$

  isotropic solid

- $$f_D = f(0) + 3nk_BT\left[\ln\left[1 - \exp\left(-y\right)\right] - \frac{1}{3}\mathcal{D}\left(y\right)\right]$$

  Debye

  Debye temperature

  $$y = \frac{T_D}{T}$$

  $$T_D(\omega) = T_{D_0}(1 - \gamma\omega)$$

  Anharmonic effects

  $$\mathcal{D}(y) = \frac{3}{y^3}\int_0^y \frac{x^3}{\exp(x) - 1}dx$$

  Debye function

- $$f_{ele} = -\frac{\pi^2}{6}n(k_BT)^2\mathfrak{n}(\epsilon_F)$$

  small contribution...

P. J. von Ranke, et al. PRB 73, 014415 (2006).

lattice free energy

linear elasticity for the lattice around T_0

$$\begin{aligned} \omega &= -\kappa_T p + \alpha_p (T - T_0) \\ s_S - s_0 &= -v_0 \alpha_p p + b_p (T - T_0) \end{aligned}$$

3 free parameters

k_T - isothermal compressibility

α_p - thermal expansion coefficient

c_v - specific heat ($b_v = c_v / T_0$ - entropy coefficient)

lattice free energy around T_0

$$f_S(\omega, T) = \frac{v_0}{\kappa_T} \frac{\omega^2}{2} - \left[\frac{\alpha_p v_0}{\kappa_T} \omega + s_0 \right] (T - T_0) - b_v \frac{1}{2} (T - T_0)^2$$

term representing the Gruneisen parameter of the Debye theory

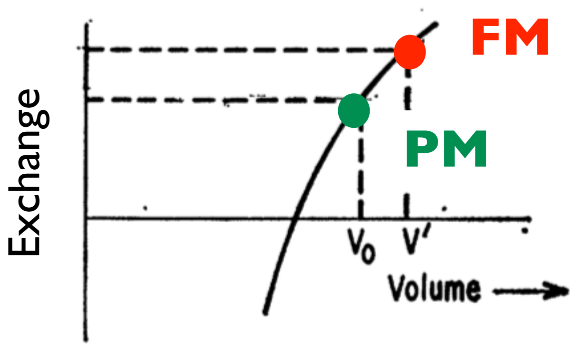
$$b_v = b_p - \alpha_p^2 v_0 / \kappa_T$$

Bean Rodbell model

magneto-volume effects

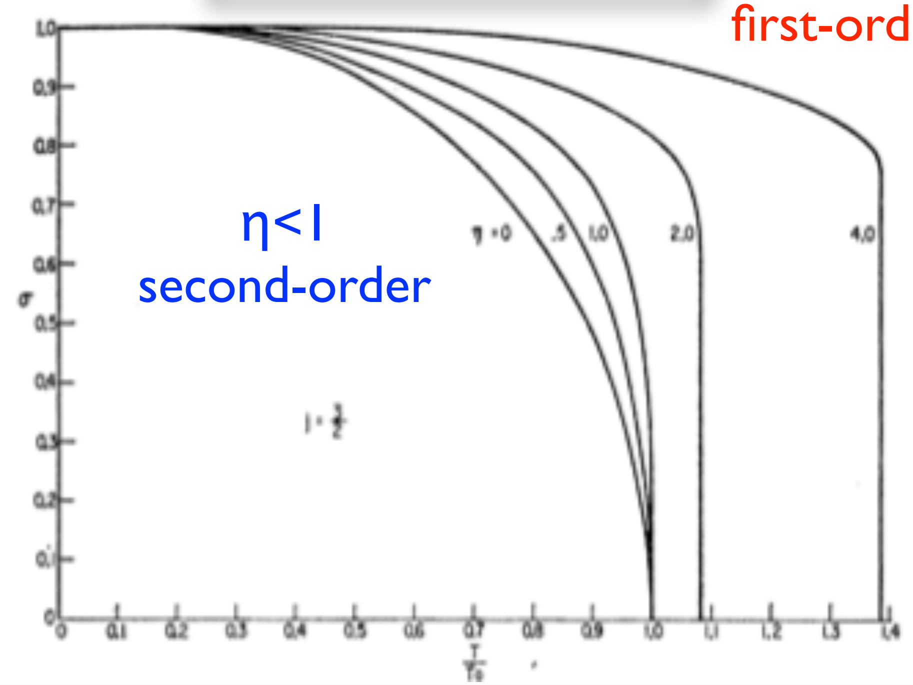
$$f_L = -\frac{1}{2}W(\omega)\mu_0 M^2 - T s_M(M) + f_S(\omega, T)$$

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



$$W(\omega) = W_0(1 + \beta\omega)$$

$$\eta = \frac{3}{2}\frac{\beta^2 \kappa_T \mu_0 M_0^2 W_0}{v_0}$$

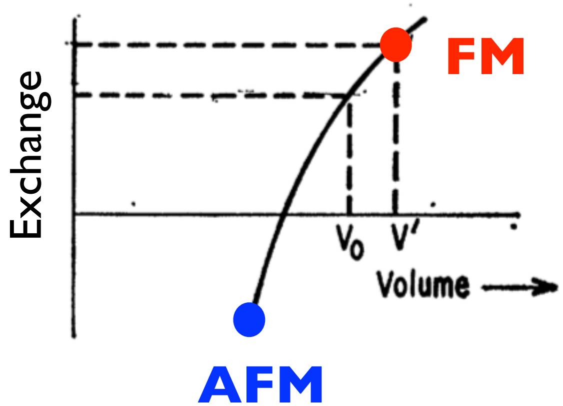


Bean and Rodbell, Phys Rev (1962)

Kittel model

exchange inversion

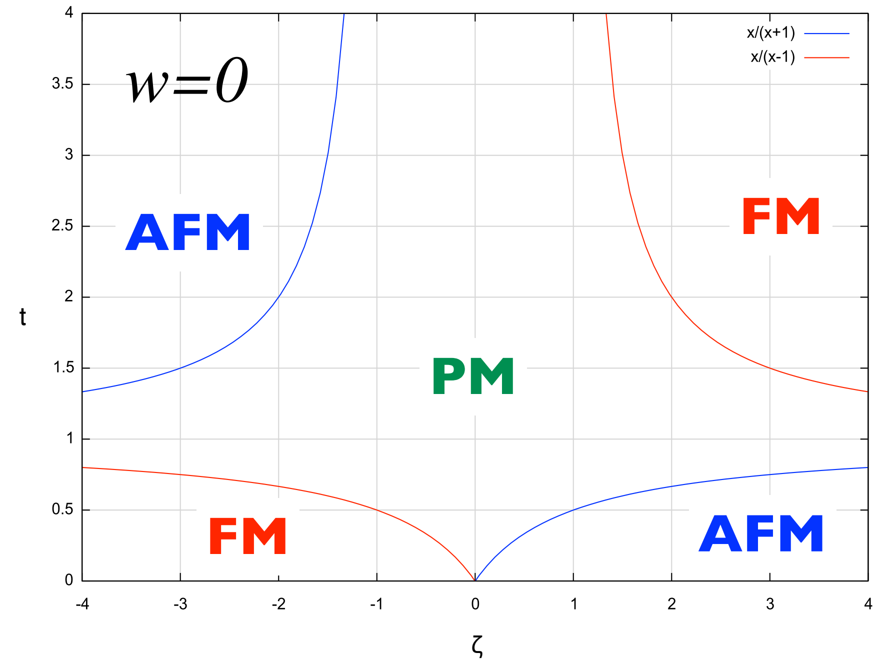
$$f_{exc} = -2W_{AB}\mu_0 M_A M_B - W\mu_0 M_A^2 - W\mu_0 M_B^2$$

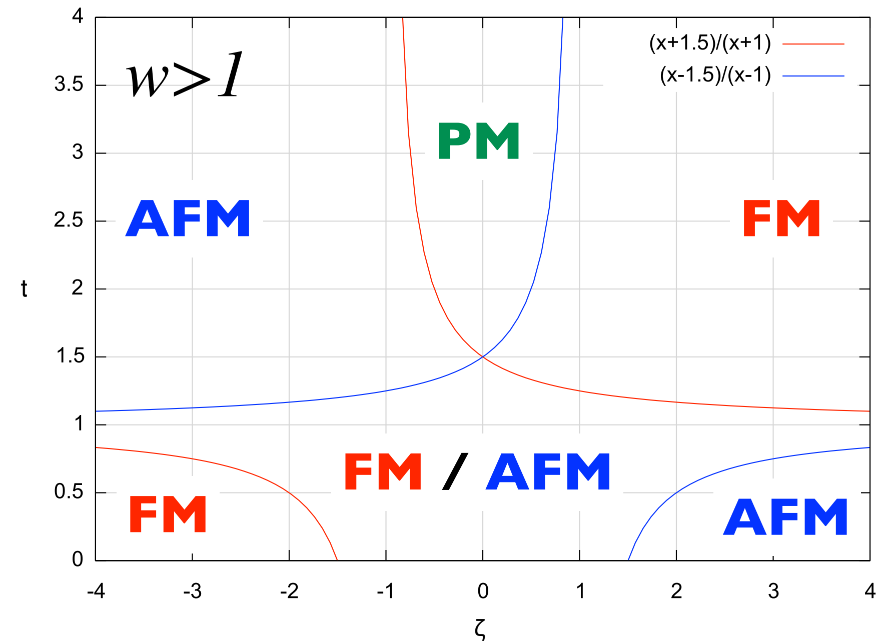


$$W_{AB}(\omega) = W_0(1+\beta\omega)$$

$$\zeta = \alpha_p \, \beta \, T_{c0}$$

Kittel, Phys. Rev. (1960)





M Piazzi et al, Physica B (2015)

entropy at the first order transition

magneto-volume effects

$$s = -\left.\frac{\partial f_L}{\partial T}\right|_{m,\omega}$$

total free energy

$$f_L = -\frac{1}{2}W(\omega)\mu_0 M^2 - T s_M(M) + f_S(\omega, T)$$

result

$$s = s_M(m) + s_W(m) + s_S(p, T)$$

magnetic only • $s_j(m) = \left[\ln(2j+1) - \frac{1}{a_j}\left(\frac{1}{2}m^2 + \frac{b_j}{4}m^4 + \mathcal{O}(m^6)\right)\right]$

magneto-elastic • $s_W(m) = \frac{nk_B}{2a_J}\zeta m^2$ of structural lattice origin

lattice only • $s_S - s_{S_0} = -v_0\alpha_p p + b_p(T - T_0)$

$$\zeta = \alpha_p \beta T_{c_0}$$

$$\hat{s} = \ln(2J+1) - \frac{1}{2a_J}\left[(1-\zeta)\,m^2 + \frac{b_J}{2}m^4 + \mathcal{O}(m^6)\right]$$

for FM to PM

GMCE only for $\zeta<0$!

values for ζ

for known MCE materials

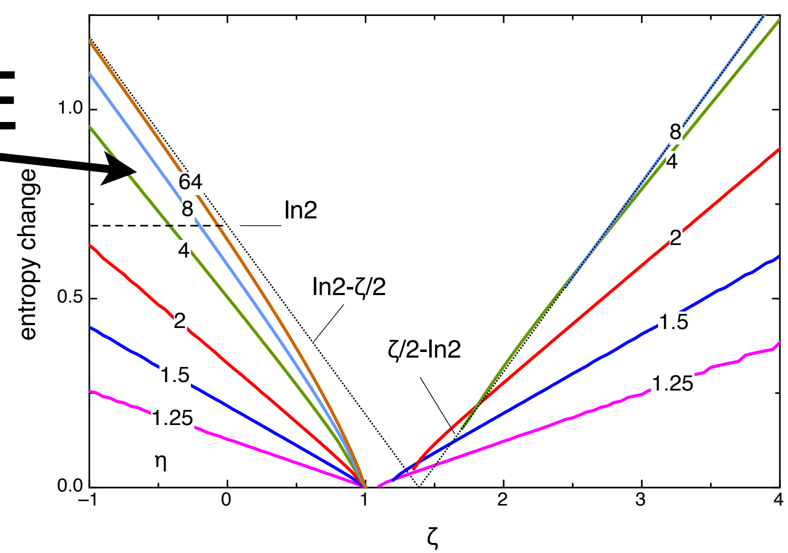
$$\zeta = \alpha_p \, \beta \, T_{c0}$$

$Gd_5Si_2Ge_2$	MnAs	Ni_2MnSn (inverse MCE)
β = -80	β >0	β >0
ζ = - 0.6	ζ = 0.25	ζ > 1
ζ<0	ζ>0	ζ>1
s_M+s_S	s_M-s_S	$-s_M+s_S$

prediction

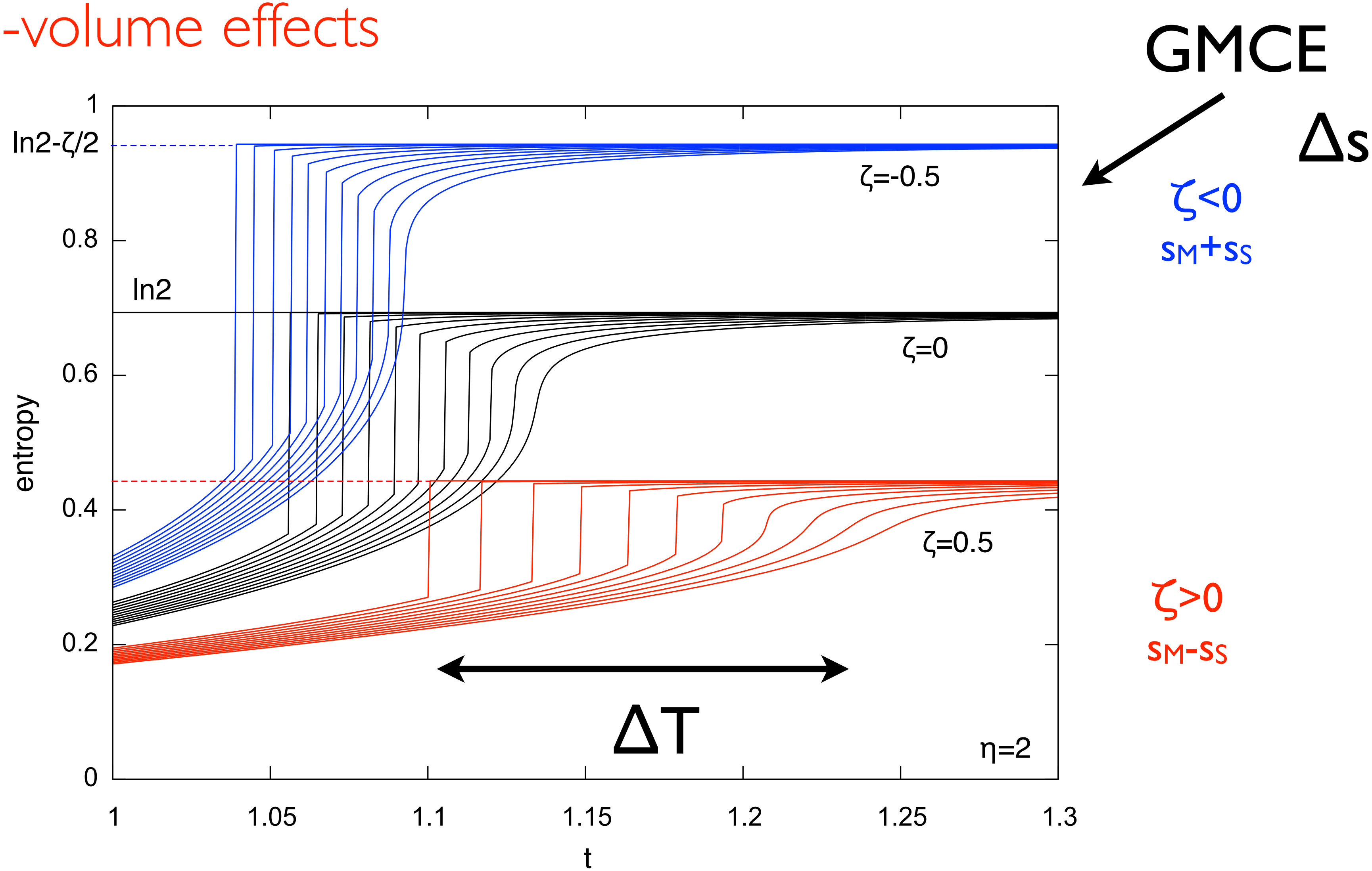
GMCE in Mn alloys (β >0) but if thermal expansion is negative

GMCE



entropy at FM-PM first-order transition

magneto-volume effects



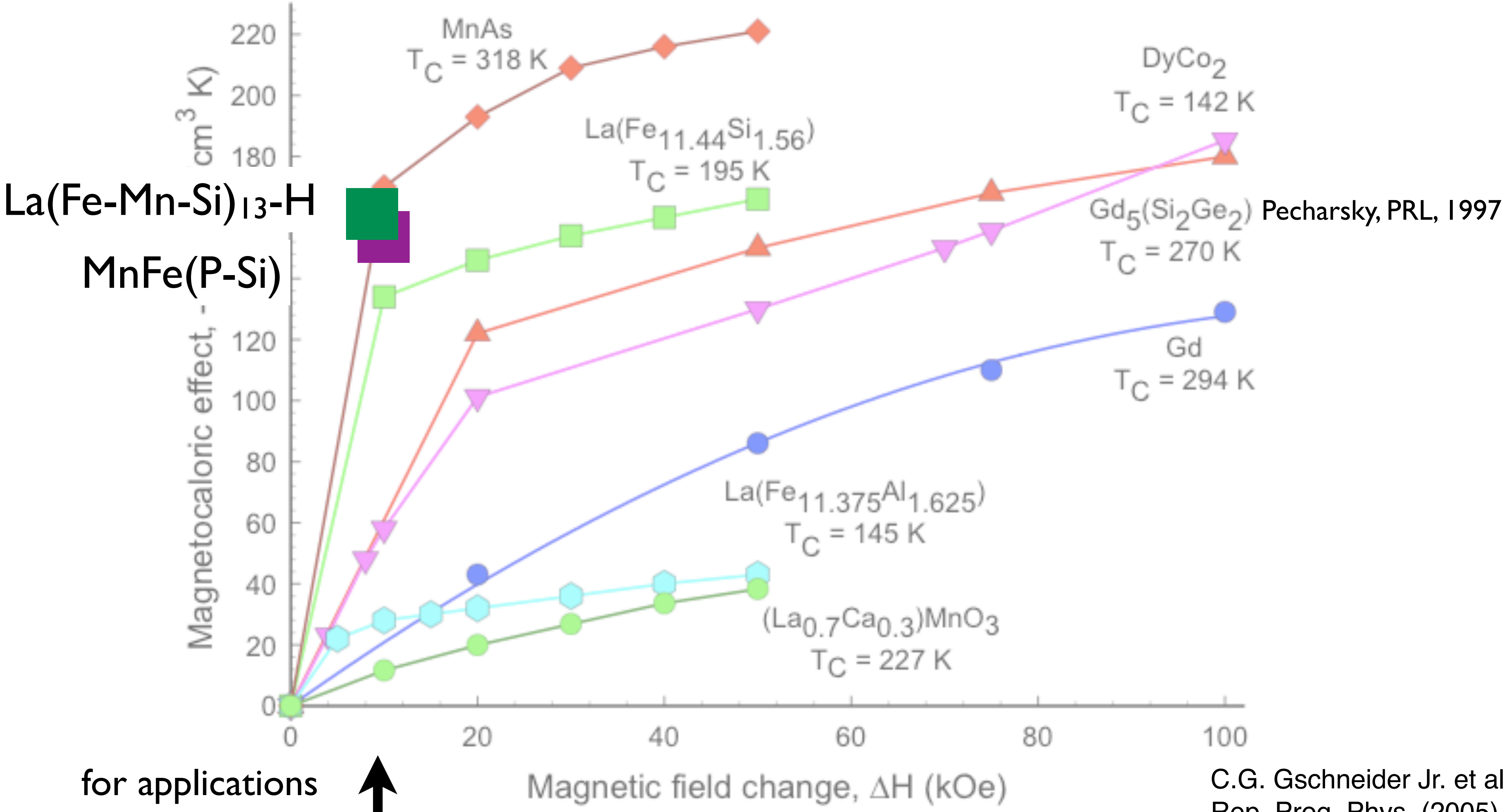
example for spin j=1/2

V. Basso, J.Phys. Condens. Matter **23** (2011) 226004.

Magnetic cooling

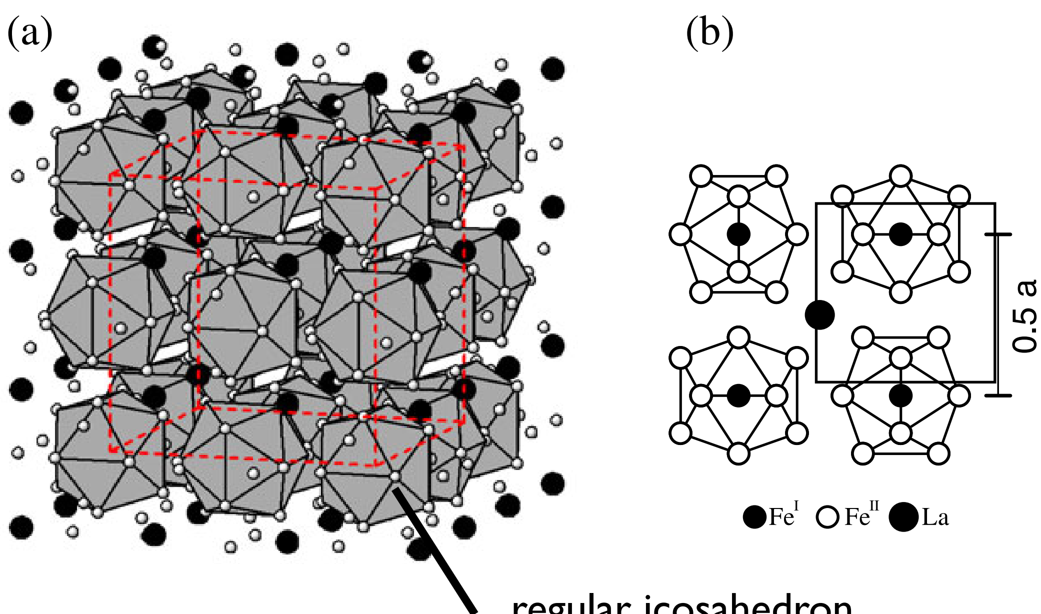
new materials

with large MCE



C.G. Gschneider Jr. et al, Rep. Prog. Phys. (2005)

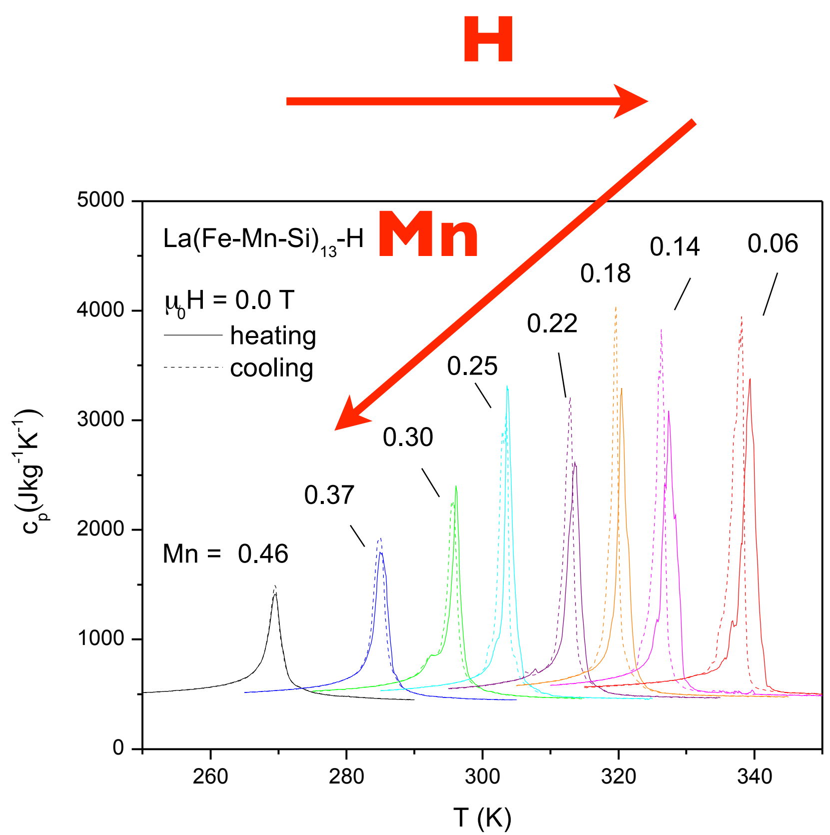
La(Fe-Mn-Si)$_{13}$H$_{1.65}$



regular icosahedron
(12 vertex)

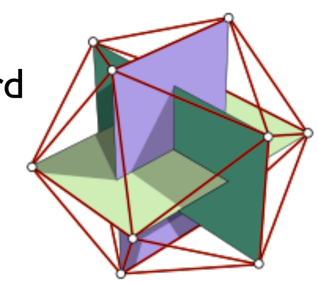
samples prepared by VAC

combine:
- substitution of Fe with Mn
- hydrogenation at saturation



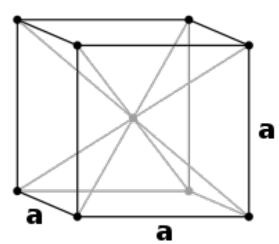
Fe (I) 1.54 μ_B
bonds:
- 12 Fe (I)

fcc-like coord



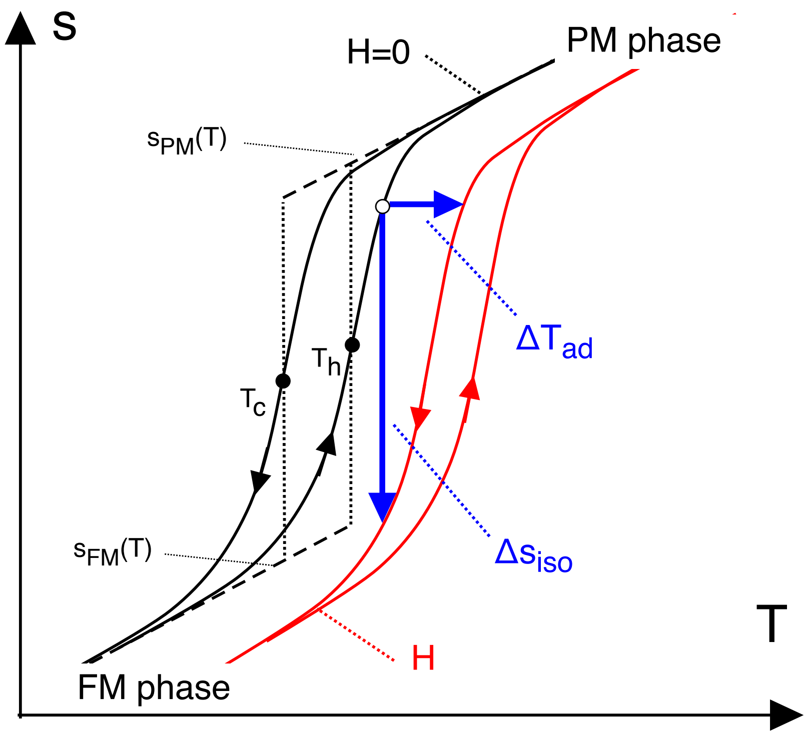
Fe (II) 2.16 μ_B
bonds:
- 1 Fe (I) short bond
- 5 inter-cluster Fe(II) short bond
- 2 intra-cluster Fe(II): long bond

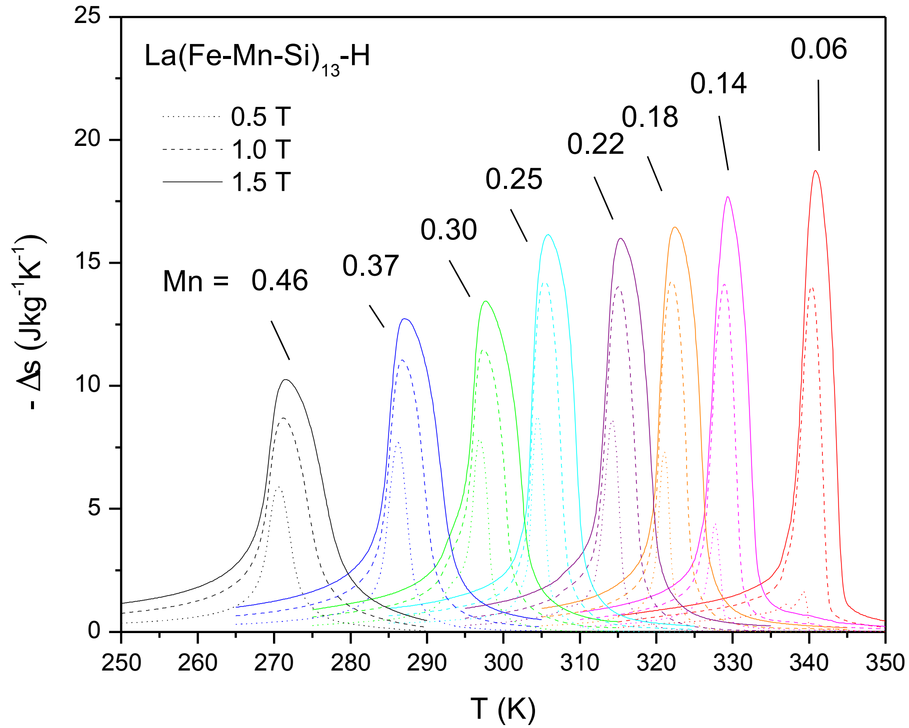
bcc-like coord

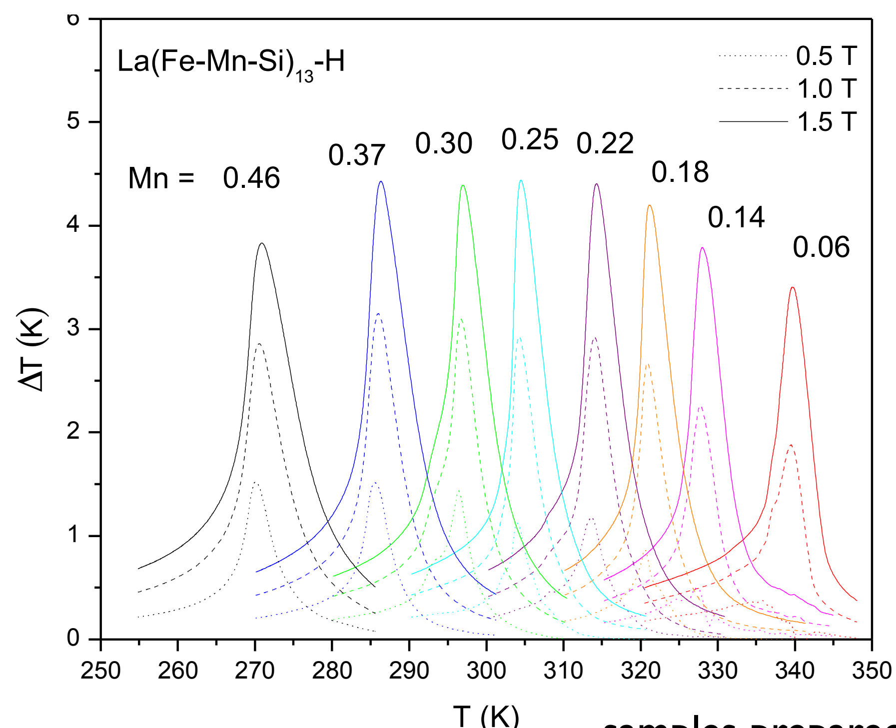


Fujita et al., PRB 2003

$La(Fe\text{-}Mn\text{-}Si)_{13}H_{1.65}$





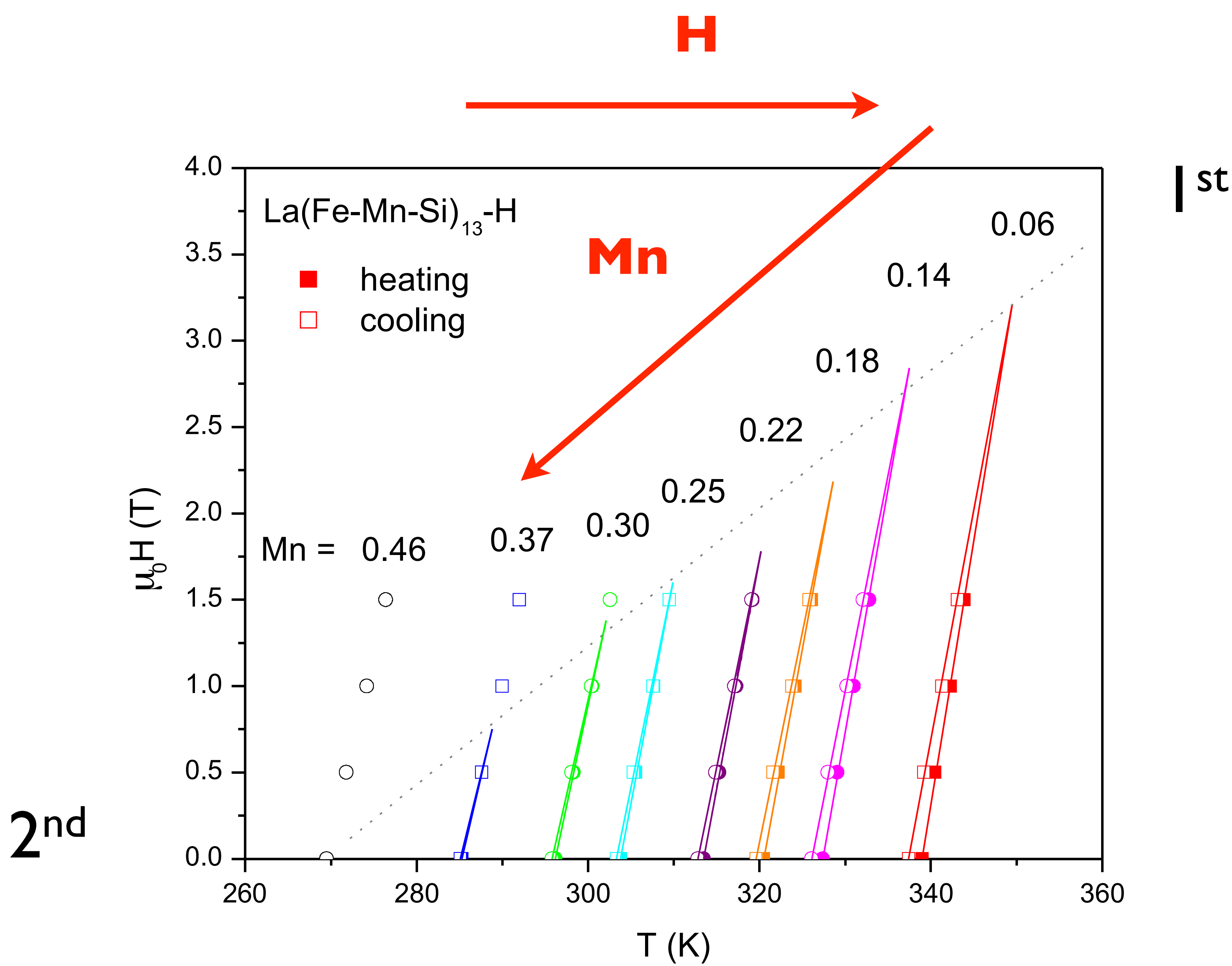


temperature hysteresis limits ΔT_{ad}

V.Basso et al., JAP (2015)

samples prepared by VAC

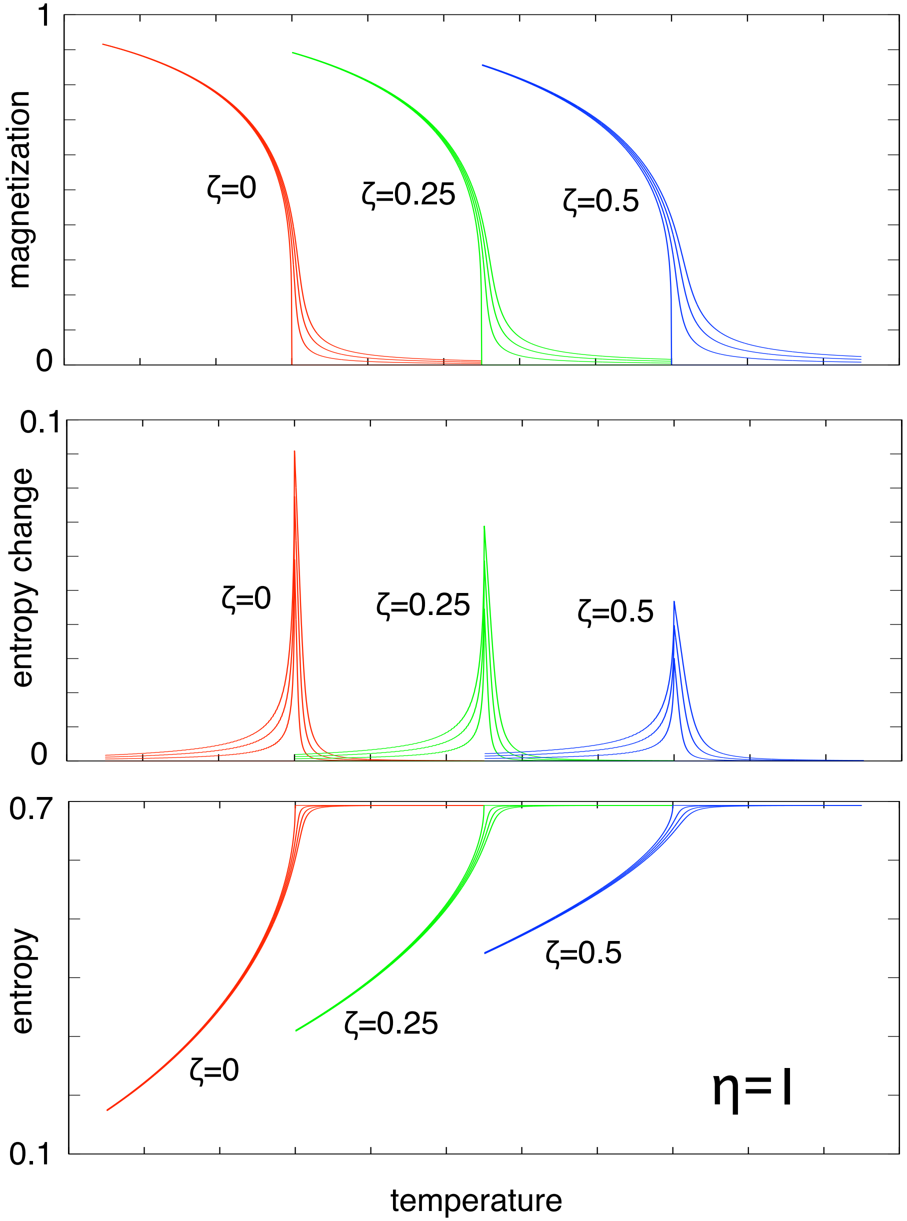
$La(Fe\text{-}Mn\text{-}Si)_{13}H_{1.65}$



V.Basso et al., JAP (2015)

samples prepared by VAC

$La(Fe\text{-}Mn\text{-}Si)_{13}H_{1.65}$ model

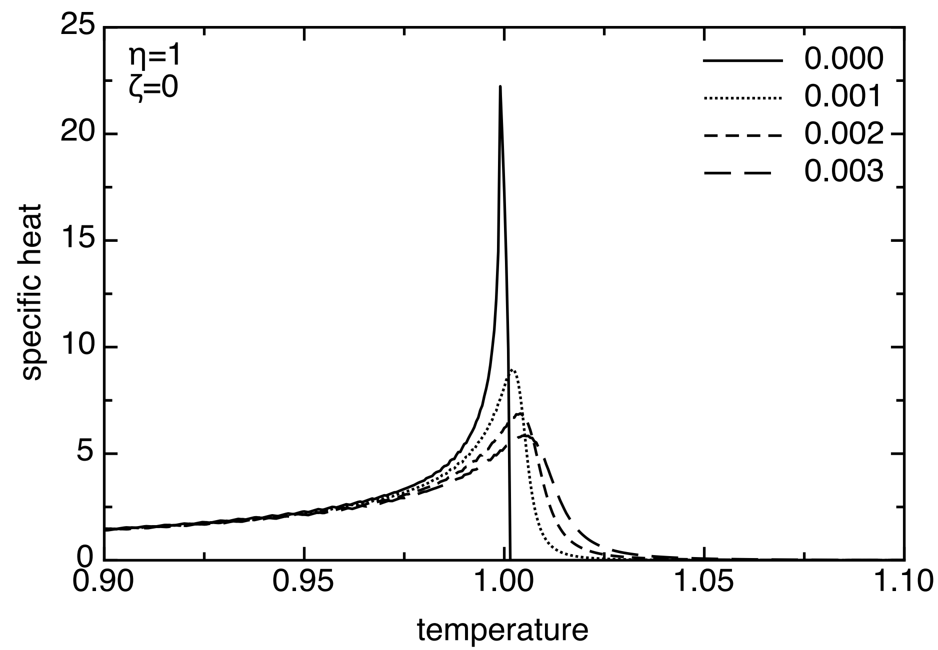


$$\zeta = \alpha_p \beta T_0$$

lattice entropy sums or subtracts

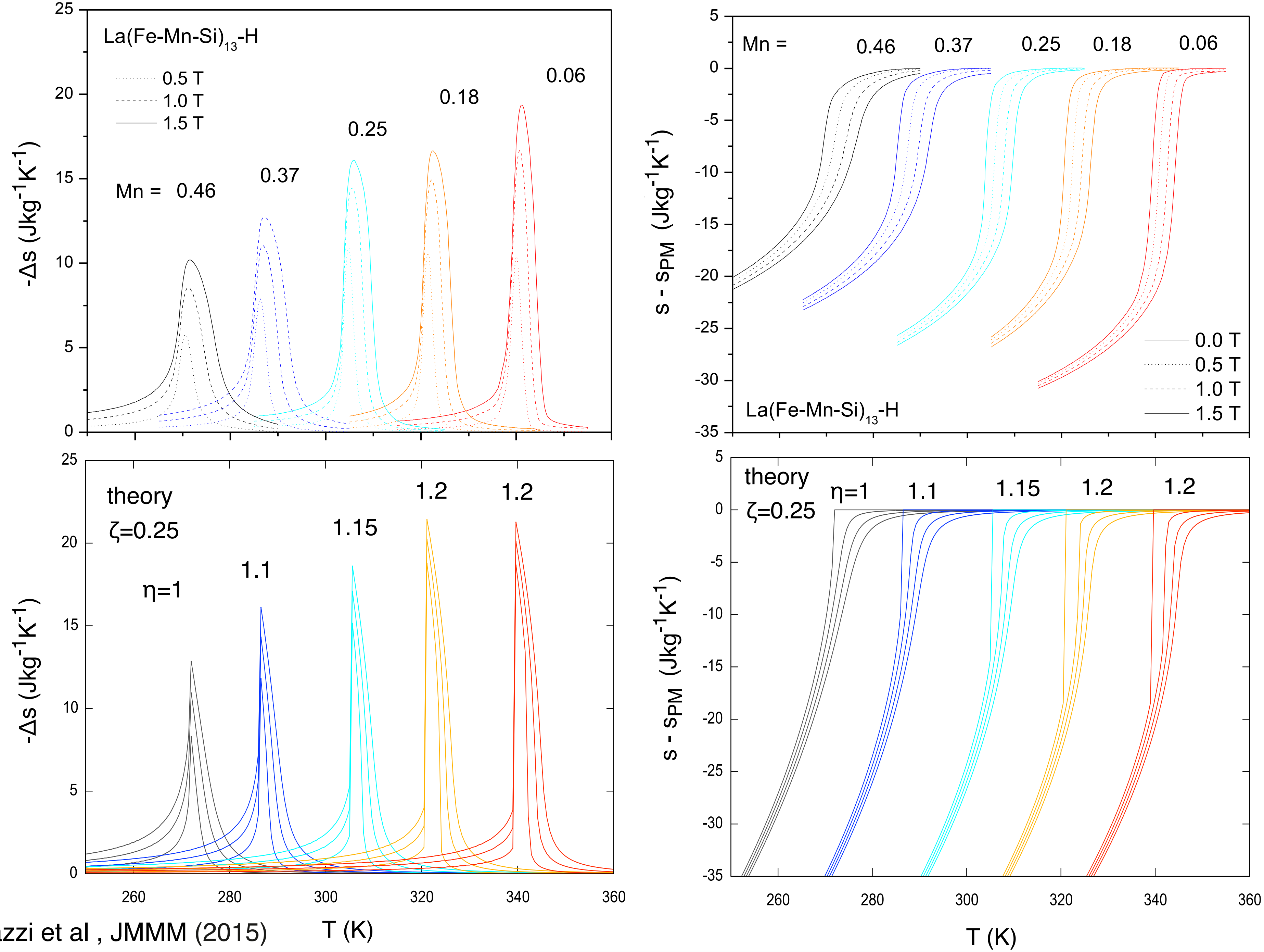
$$\eta = \frac{3}{2} \frac{\beta^2 \kappa_T n k_B}{a_J v_0} T_0$$

first order/second order



M Piazzi et al , JMMM (2015)

La(Fe-Mn-Si)$_{13}$H$_{1.65}$ model



M Piazzi et al , JMMM (2015)

Conclusions

$La(Fe\text{-}Mn\text{-}Si)_{13}H_{1.65}$ model

Fe	Mn	Si	T_0 (K)	$\mu_0 H_0$ (T)	η
11.22	0.46	1.32	272	405	1.0
11.33	0.37	1.30	286	426	1.1
11.47	0.25	1.28	305	455	1.15
11.60	0.18	1.22	320.5	478	1.2
11.76	0.06	1.18	339	505	1.2

$\zeta = 0.25$

$$\eta = \frac{3}{2}\frac{\beta^2 \kappa_T n k_B}{a_J v_0} T_0$$

first order/second order

$$\zeta = \alpha_p \beta T_0$$

lattice entropy
sums or subtracts

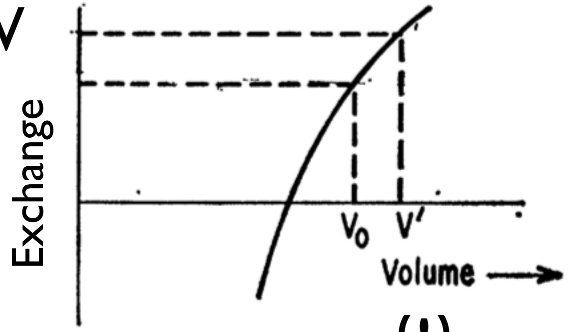
$$\kappa_T = 8.6 \cdot 10^{-12}\ \mathrm{Pa}^{-1}$$
$$\alpha_p \simeq 5 \cdot 10^{-5}\ \mathrm{K}^{-1}$$

- Mn influences the exchange W_0 (y_{Mn})
- β (magnetoelasticity) depends on the 1:13 structure

$$\beta \simeq 15$$

$$W = W_0(1 + \beta\omega)$$

W



ω

Perspectives

magnetism and lattice

- Use SDTF results to predict new transitions

f(ω,M) average magnetization vs local moment

- B. L. Gyorffy, et al. J. Phys. F: Met. Phys., 15:1337 (1985). - *Disordered Local Moment*
- J. B. Staunton et al, Phys. Rev. B, 89 :054427 (2014). - *FeRh.*

- M. Piazzi, et al Physics Procedia (ICM 2015) - *first tests*

.....

Other terms with explicit dependence on M

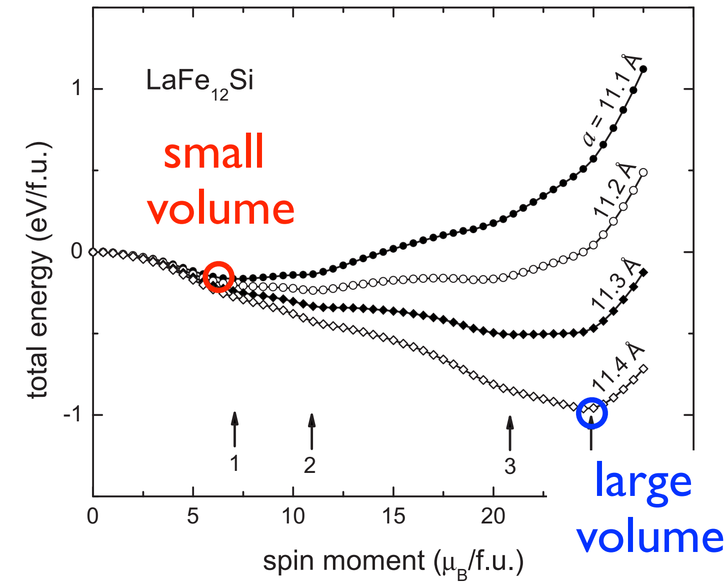
- Structural contribution (phonons)

Gruner et al. PRL 2015 where is spin entropy?

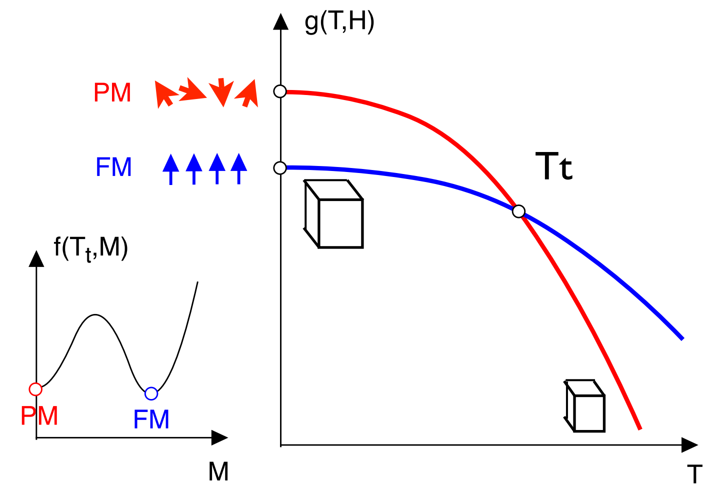
- Electronic contributions (Fermi level)

A. Fujita et al PRB (2002) - *IEM theory*

DFT



Kuzmin et al, PRB (2007)



Acknowledgements

- **EC** 7th Framework Programme
  Project **SSEEC** Solid State Energy Efficient Cooling 2008/2011

- **BASF** future business

- **EC** 7th Framework Programme
  Project **DRREAM** Drastically reduced rare earth use in applications of magnetocalorics. 2013/2015

7th International Conference on Magnetic Refrigeration at Room Temperature

Thermag VII

Torino, Italy, September 11-14, 2016

www. thermag2016.com

Conference topics:

- ***Materials:*** alloys and compound, physics, shaping and preparation
- ***Cooling systems***: design and numerical aspects, experimental tests.
- ***Novel aspects and future perspectives***: ferrocaloric materials, thermal switches, etc

Thanks for your attention