Introduction to theoretical methods to describe caloric effects in ferroic materials

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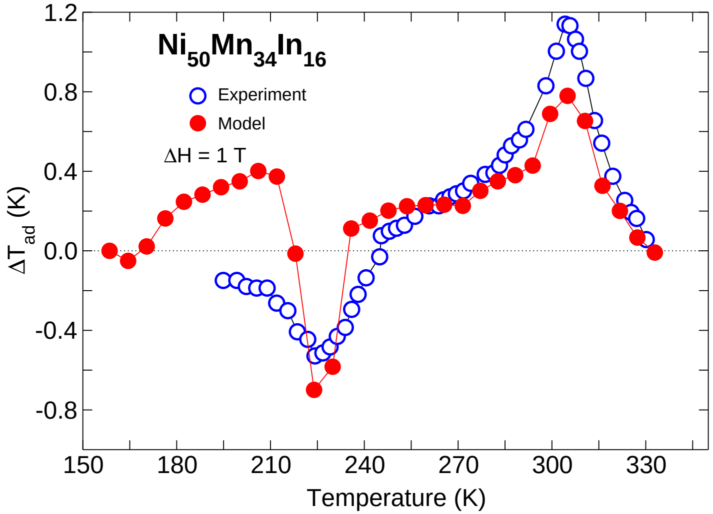

*JPD:AP **44**, 064012 (2011)*

Motivation: Functional properties of Heuslers

Interplay of magnetism and structural transformation:

– *Exchange bias (EB) effect:*
  Shift of magnetic hysteresis curve

– *Magnetocaloric effect (MCE):*
  Conventional (heating) and inverse (cooling) effect

– *Magnetic shape memory effect (MSME):*
  Huge strain effect in the martensitic phase in an external magnetic field

Origin: Competing ferro- and antiferromagnetic interactions

Introduction

Solid state refrigeration can reduce the worldwide CO_2 emission

Cooling requires to control the entropy of the refrigeration medium: (possible at phase transitions)

Solid state refrigeration requires diffusionless transformation because diffusion is too slow

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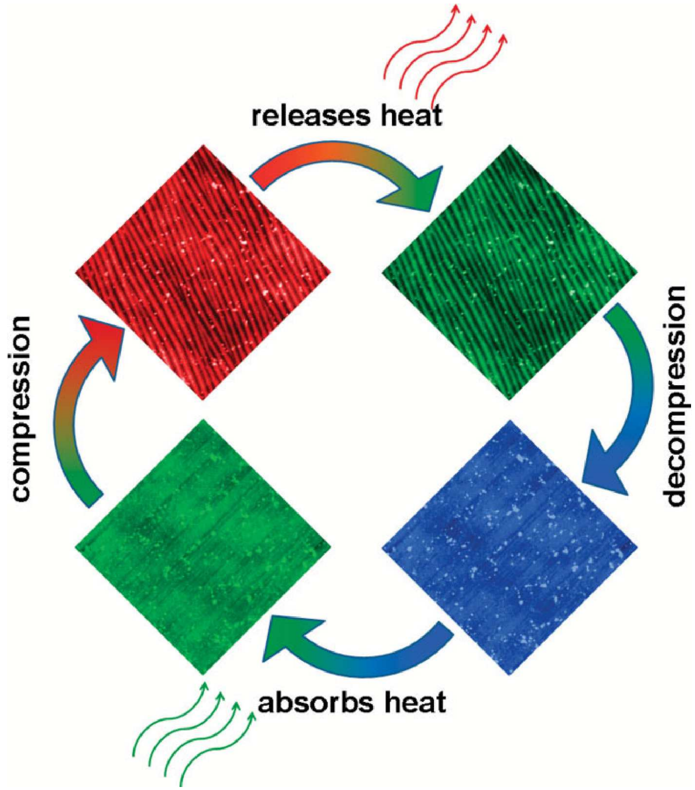

S. Fähler et al.,
*Adv. Eng. Mater. **13**, 1 (2011)*

*L. Mañosa et al., Nat, Mater. **9**, 478 (2010)*

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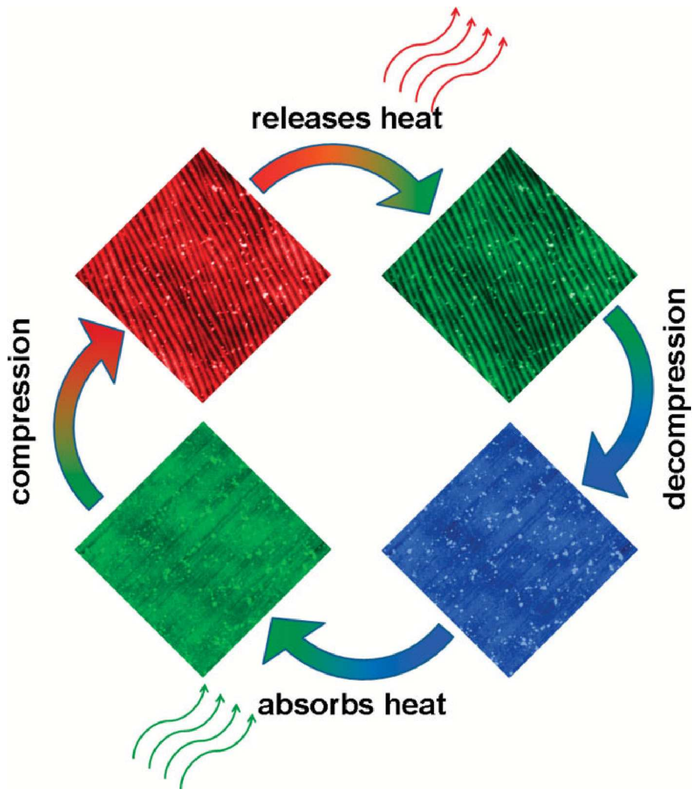

Barocaloric cooling cycle:

Adiabatic compression of austenite induces martensite / twins and increases T

Heat is releasesed to external reservoir

Adiabatic decompression induces austenite and decreases T

System is connected to cold reservoir becoming colder

S. Fähler et al.,
Adv. Eng. Mater. ***13****, 1 (2011)*

L. Mañosa et al., Nat, Mater. ***9****, 478 (2010)*

Electrocaloric effect cooling cycle

Cycle involving two constant-entropy transitions and two at constant field E

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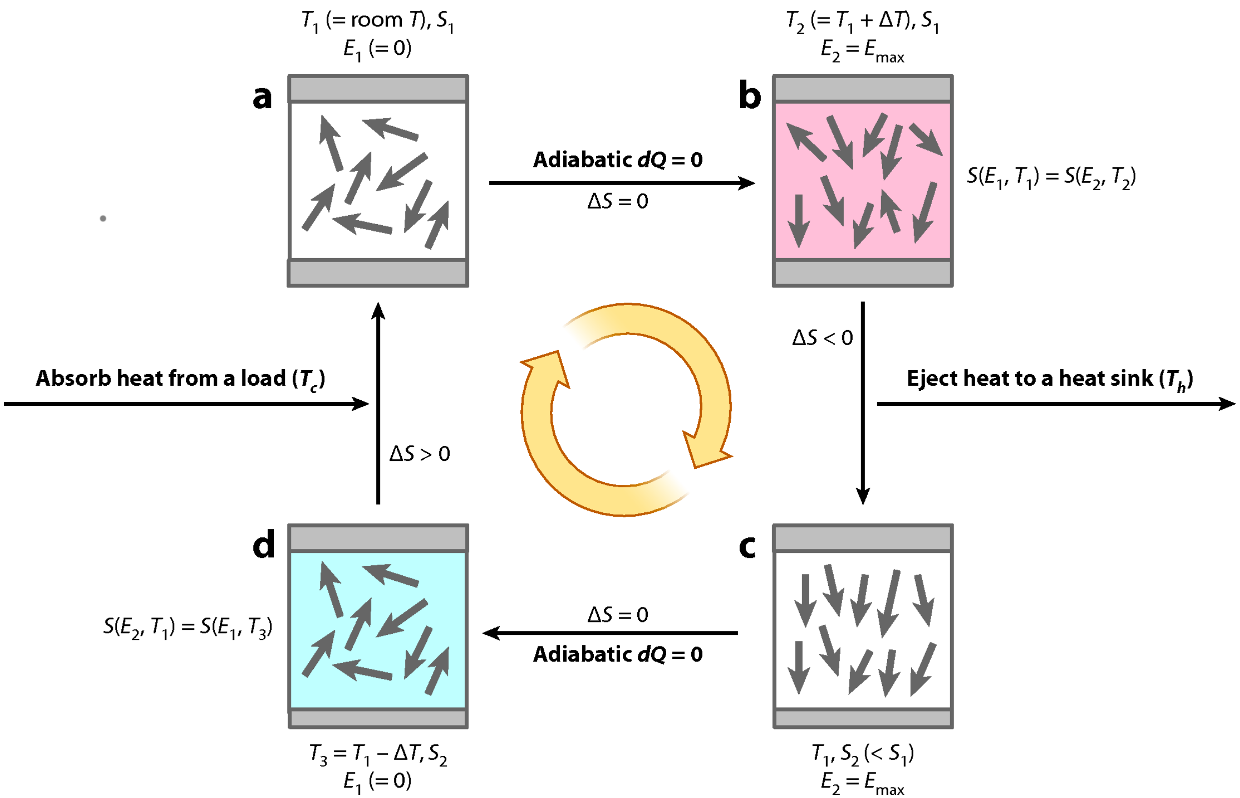

*J. F. Scott., Annu. Rev. Res. **41**, 229 (2011)*

*Z. Zhao et al., Nat, Mater. **5**, 8233 (2006)*

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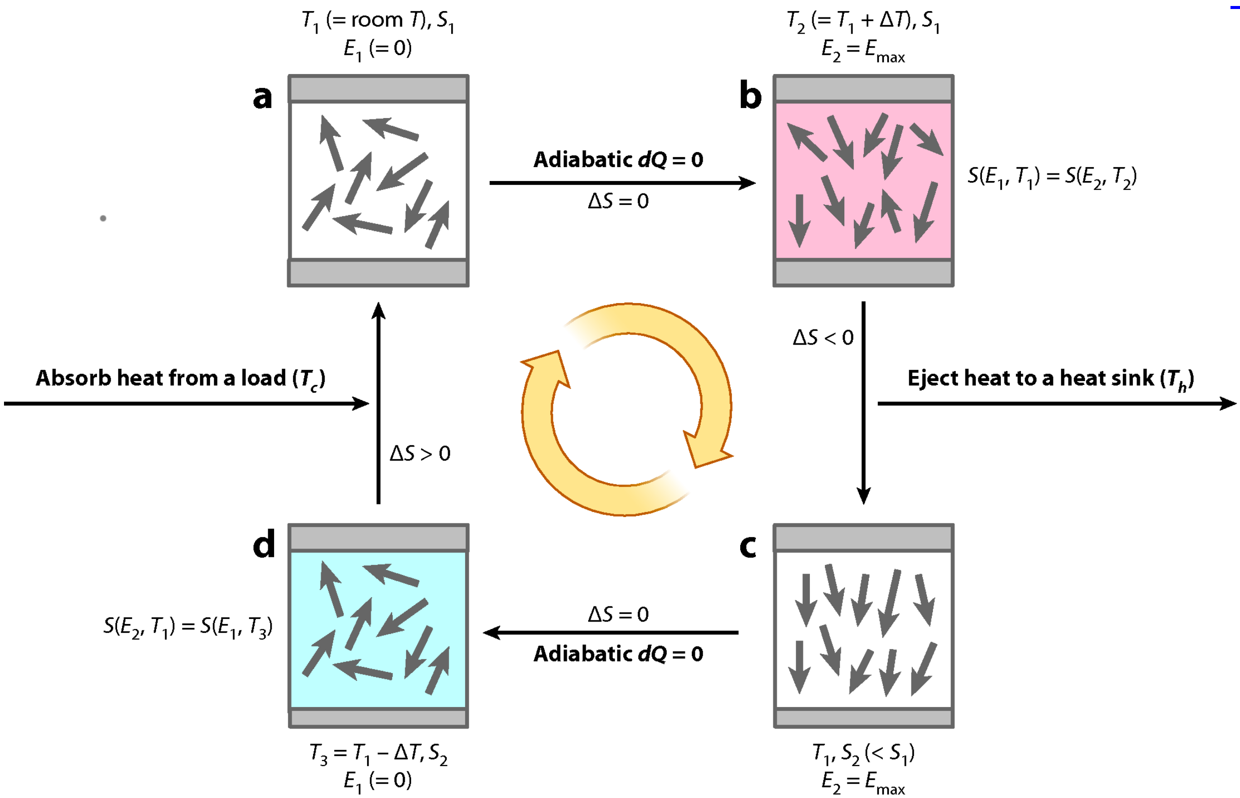

Electrocaloric cooling cycle:

(a) Initial state T - E is rapidly applied bringing the crystal to lower entropy

(b) At higher T - subsequently the crystal is allowed to cool at constant E lowering entropy to (c)

(c) E is reduced to 0 and further cooling by adiabatic depolarization

(d) System warms up to initial state absorbing heat from the local

J. F. Scott., Annu. Rev. Res. ***41****, 229 (2011)*

Z. Zhao et al., Nat, Mater. ***5****, 8233 (2006)*

Electrocaloric entropy change

Calculated entropy *S(T)* of $BaTiO_3$:

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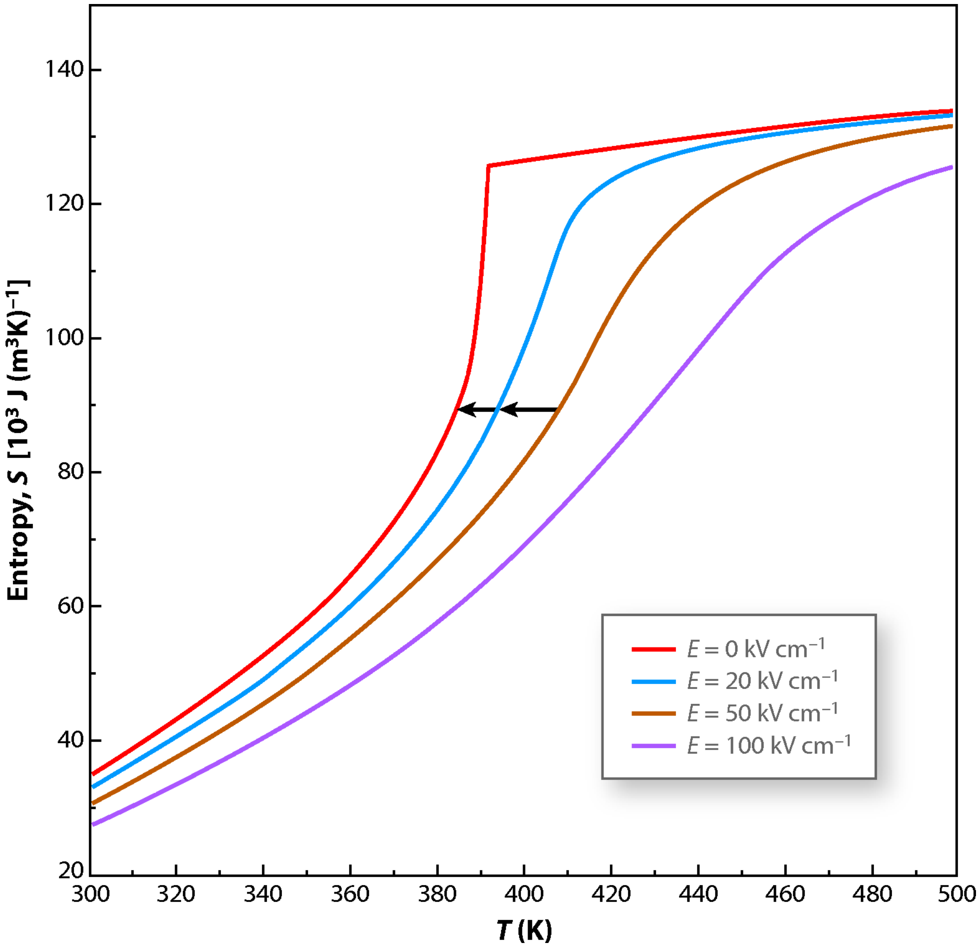

H.-X. Cao et al., J. Appl. Phys. ***106****, 094104 (2009)*

ΔT *(model calculation) is of the order of 10 K*

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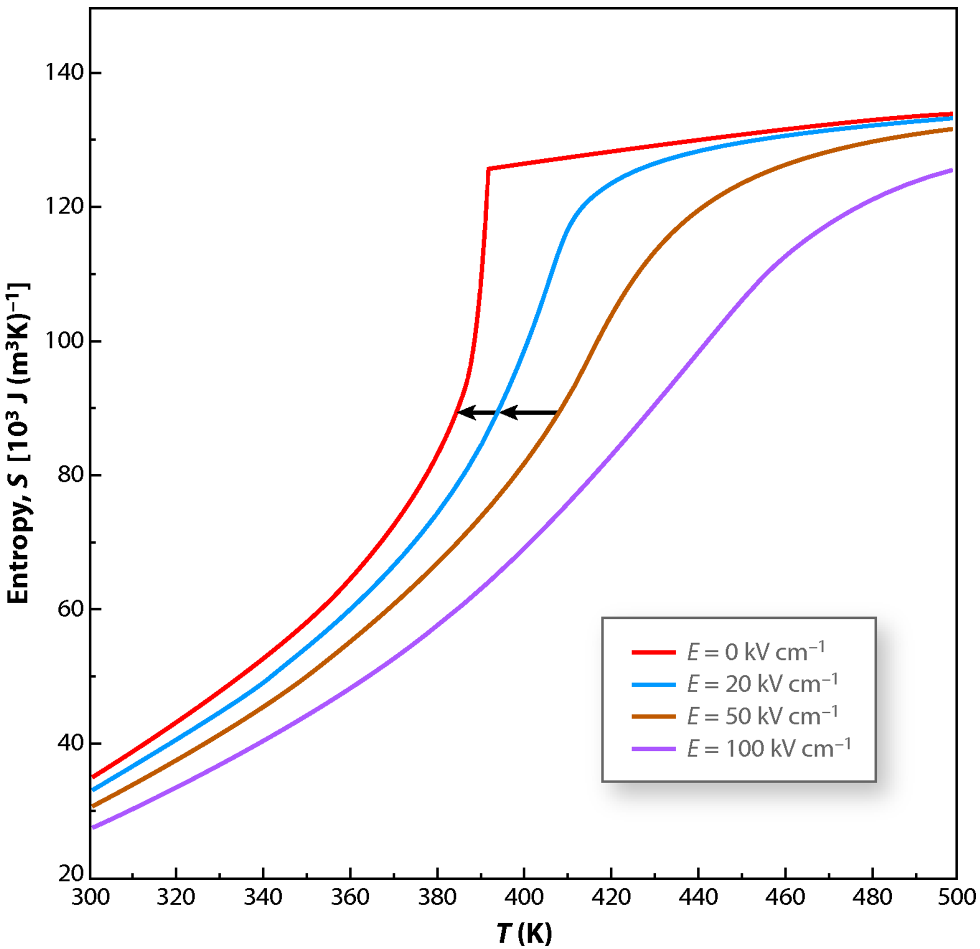

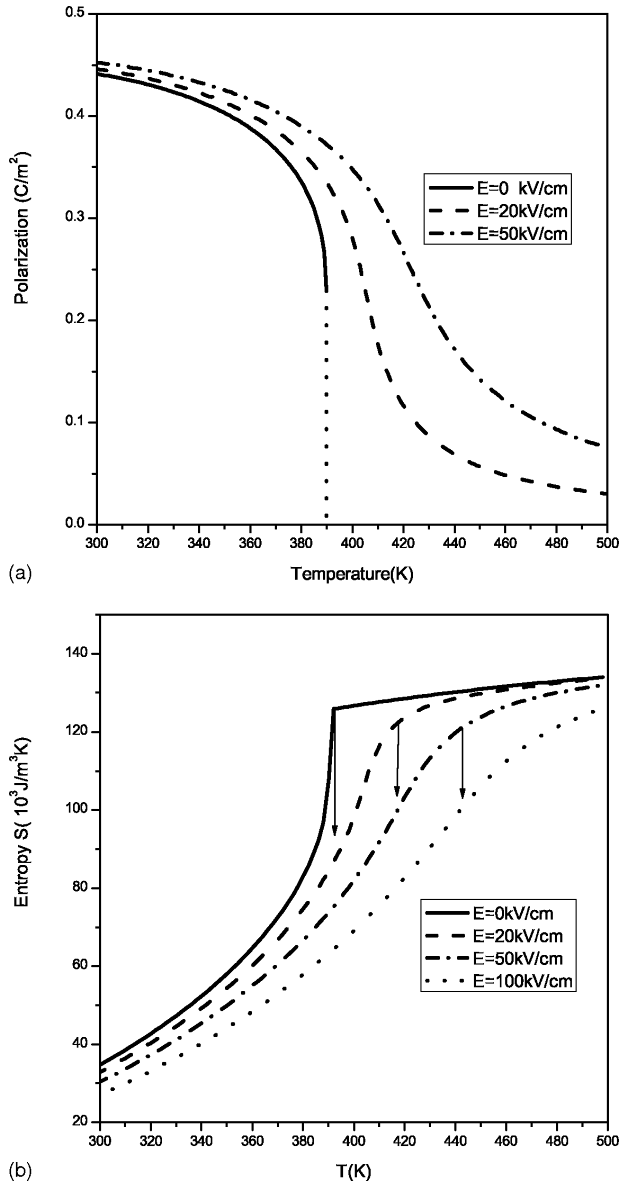

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Caloric effects in ferroic materials

Magnetocaloric effect (MCE):

- Magnetic materials change their thermodynamic properties like entropy and specific heat under the influence of a control parmeter: *S(T, V, H, x, . . .), C(T, V, H, x, . . .)*
- Effect known since 1880: *E. Warburg, Ann. Phys.* ***13****, 131 (1881)*
  Last decade: Materials which work at ambient temperature
- MCE: $\Delta S(T,H) \approx 10$ J/(kg K), $\Delta T_{ad}(T,H) \approx 1 - 10$ K
- Challenge: How can one improve "systematically" the caloric effect?
- Issue: Strong interaction of experimental and theoretical groups

Reviews:

A.M. Tishin & Y.I. Spichkin (IOP, Bristol, 2003)
The Magnetocaloric Effect and its Applications

N.A. de Oliveira & P.J. von Ranke, Phys. Rep. ***489****, 89 (2010)*
Theoretical aspects of the magnetocaloric effect

V.D. Buchelnikov & V.V. Sokolovskii, Phys. Met. Metallogr. ***112****, 633 (2011)*
Magnetocaloric effect in Ni-Mn-X (X = Ga, In, Sn, Sb) Heusler alloys

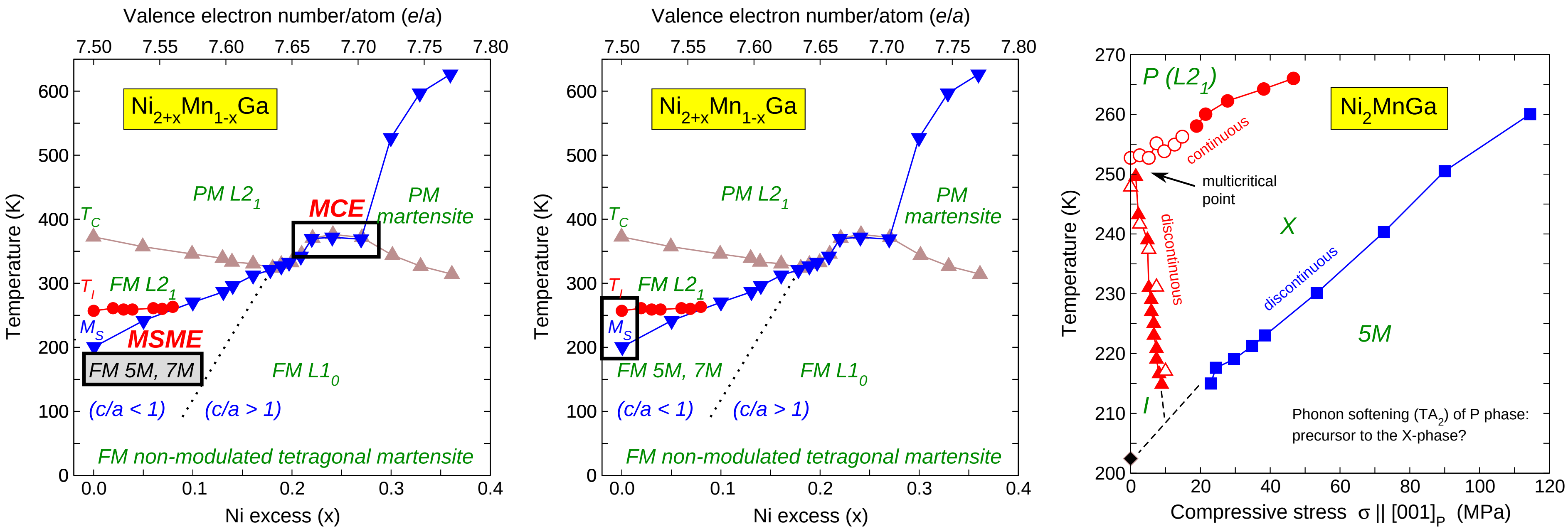
Giant MCE Materials

1990	FeRh	*Nikitin et al.*
1997	$Gd_5(Ge_{1-x}Si_x)_4$	*Pecharsky & Gschneidner*
1998	RCo_2	*Foldeaki et al.*
2000-2002	La(Fe, Si)$_{13}$	*Hu 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*
2005	$Ni_2Mn_{1+x}In_{1-x}$	*Krenke et al.*
2009	MnCoGeB	*Trung et al.*

Complex crystalline and magnetic structures

& "magnetostructural" phase transformations

Example of magnetostructural transition



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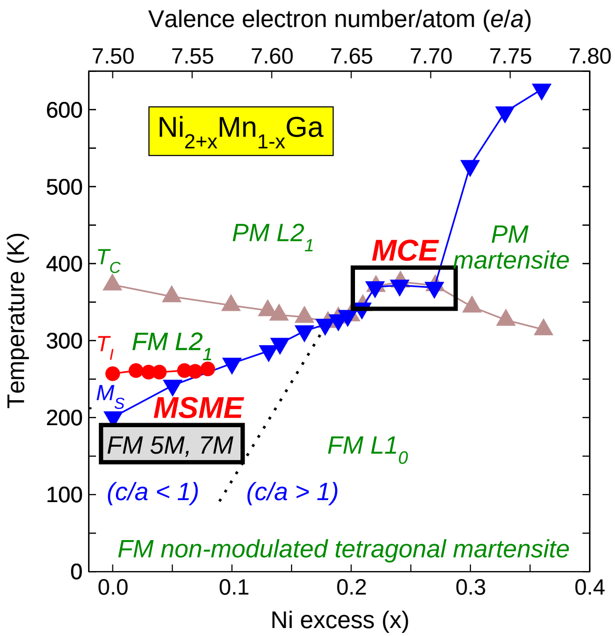

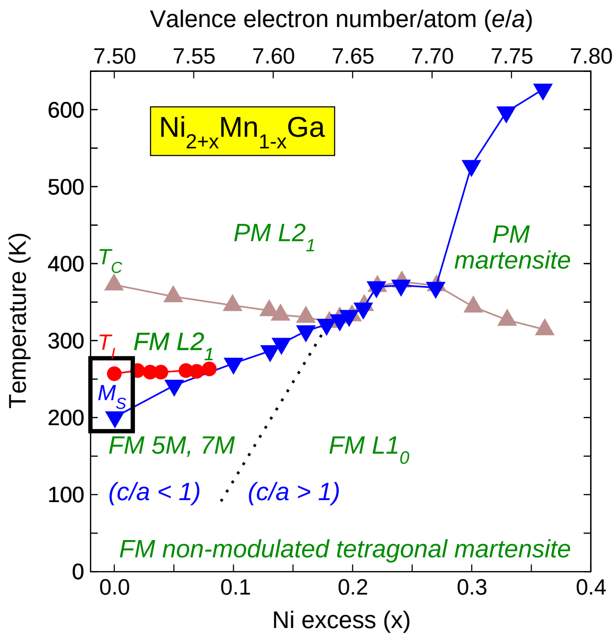

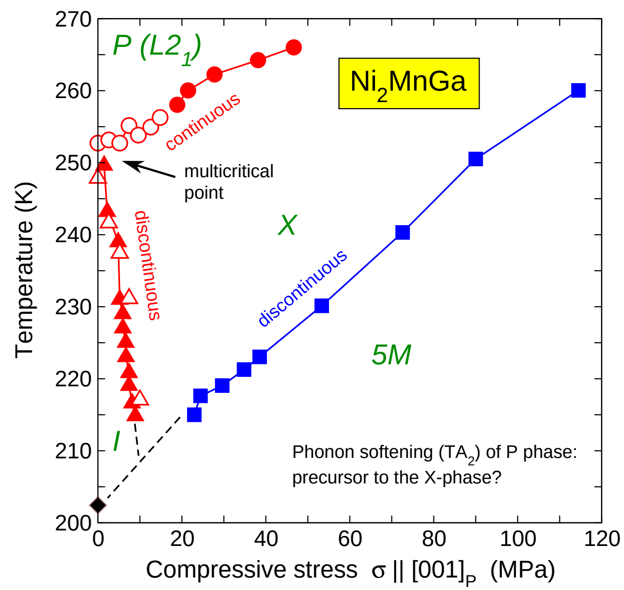

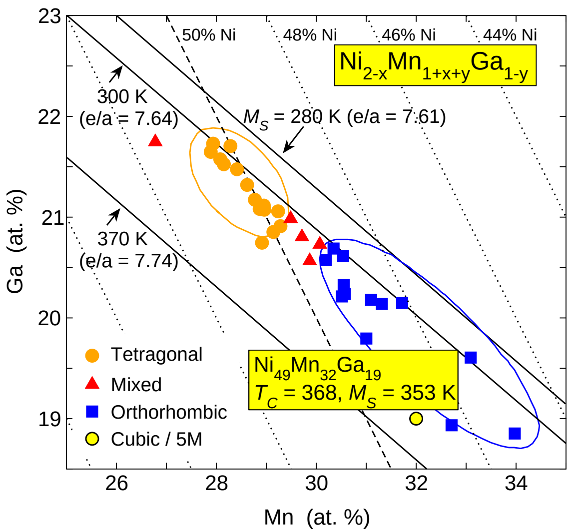

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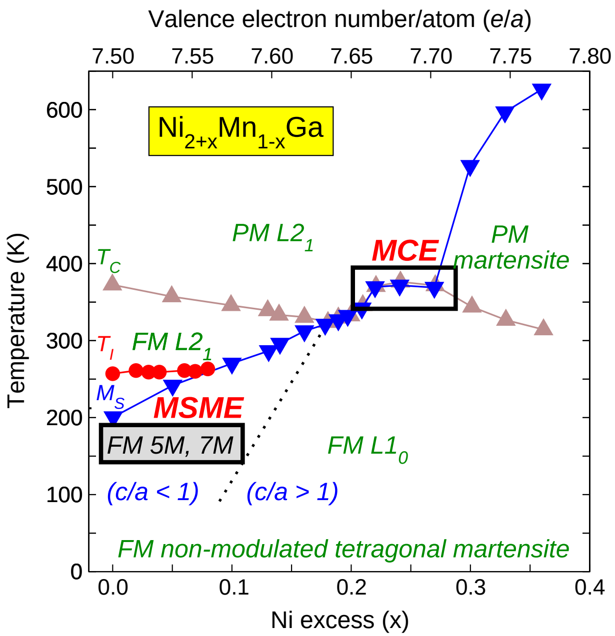
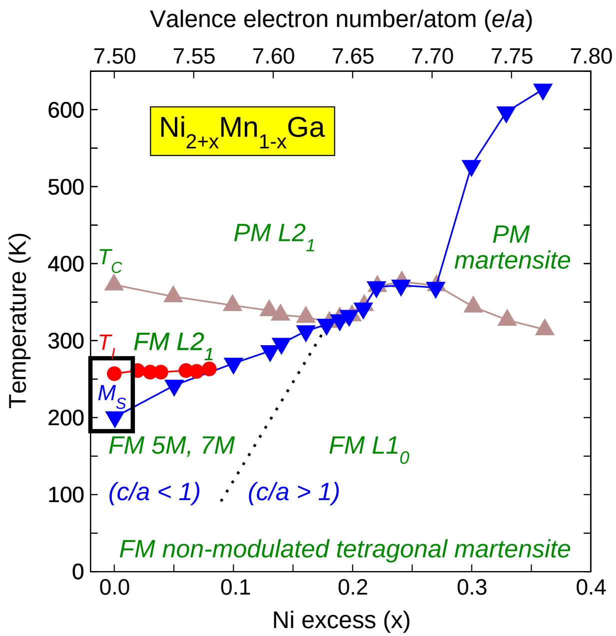
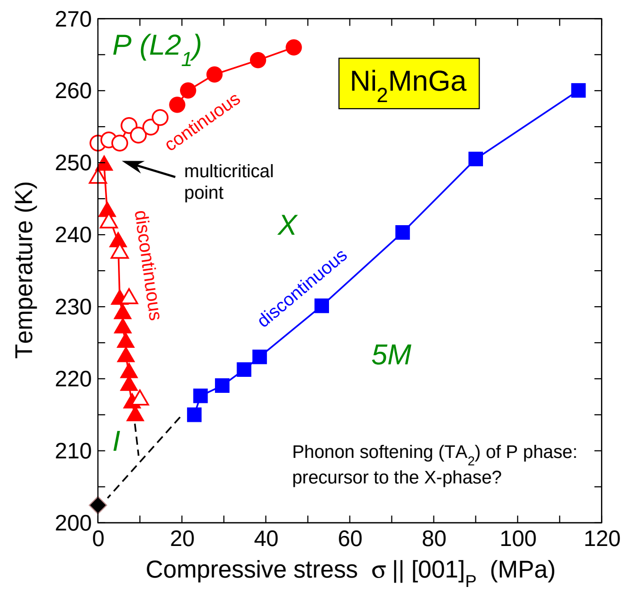
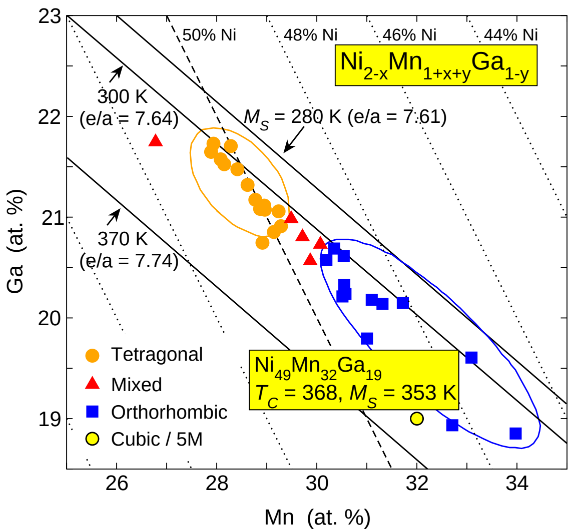








Top:

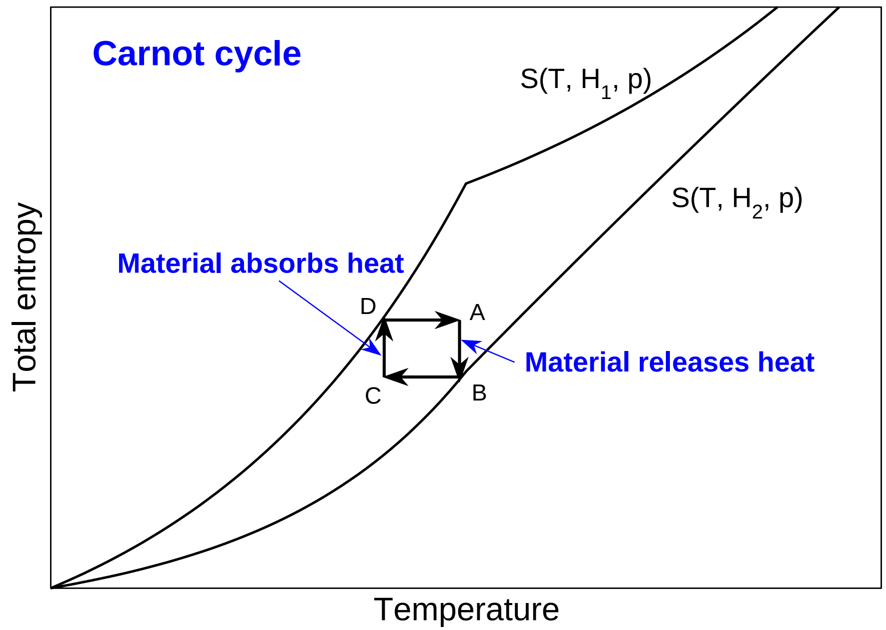
*V. V. Khovaylo et al., PRB **72**, 224408 (2005)*

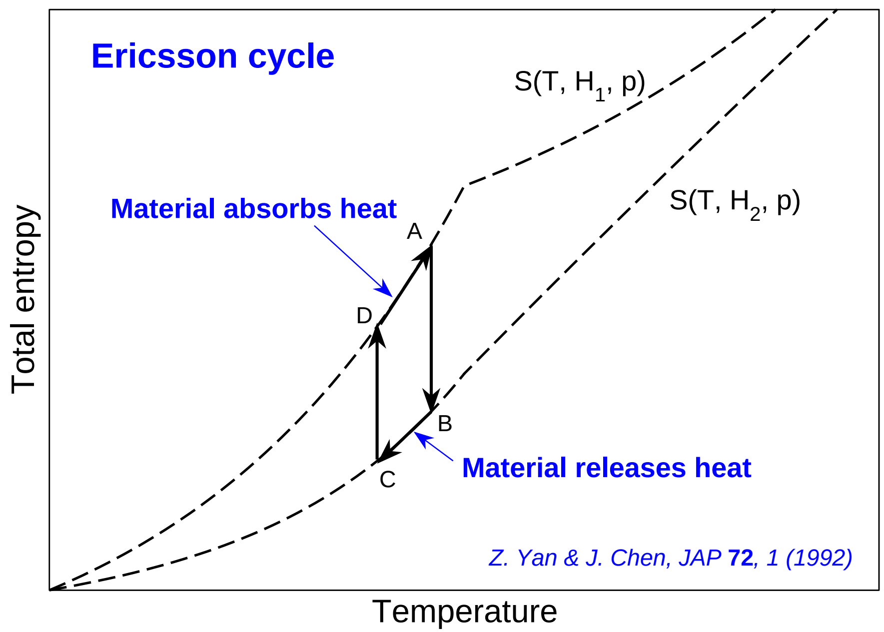
*H. Kushida et al., Scripta Mater. **60**, 96 (2009)*

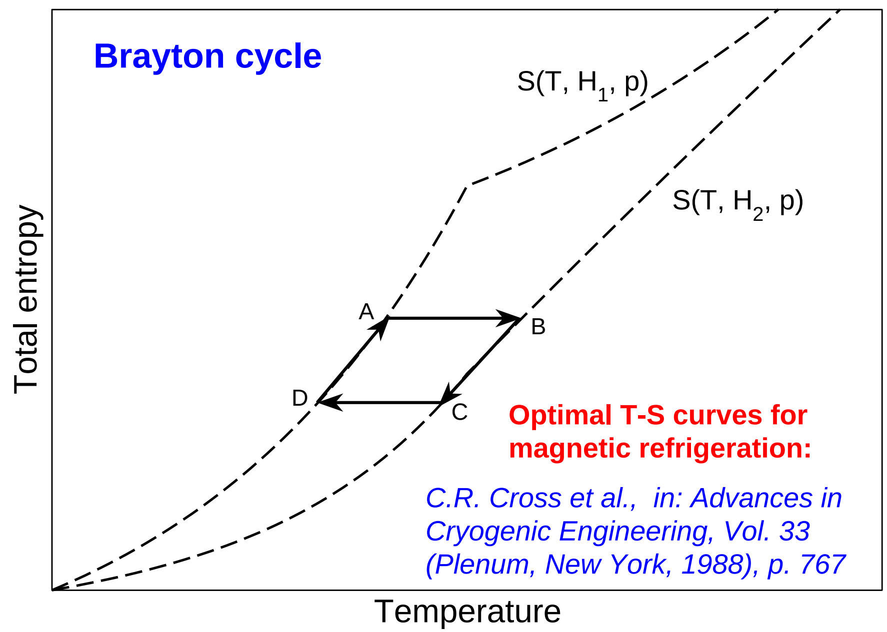
Left:

*M. Richard et al., Scripta Mater. **54**, 1797 (2006)*

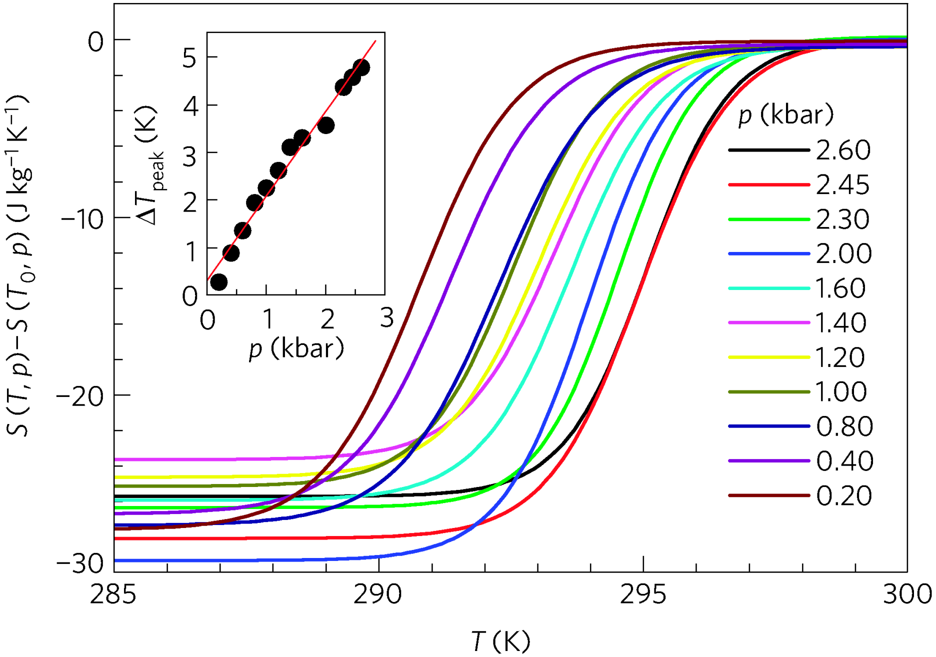
S-T diagrams: Carnot, Ericsson, Brayton cycles

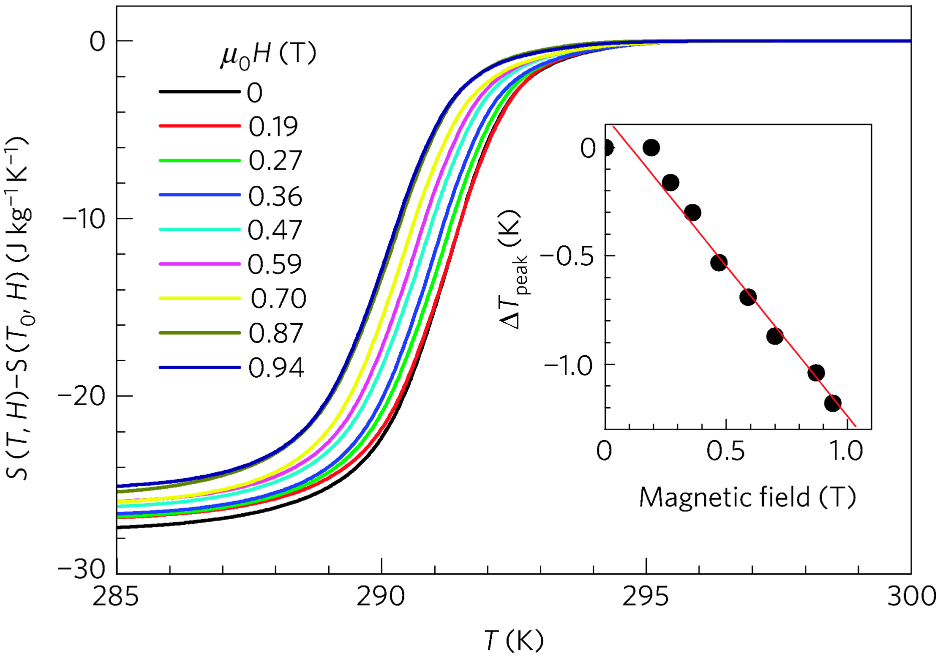






Experimental S-T curves of $Ni_{49.26}Mn_{36.08}In_{14.66}$





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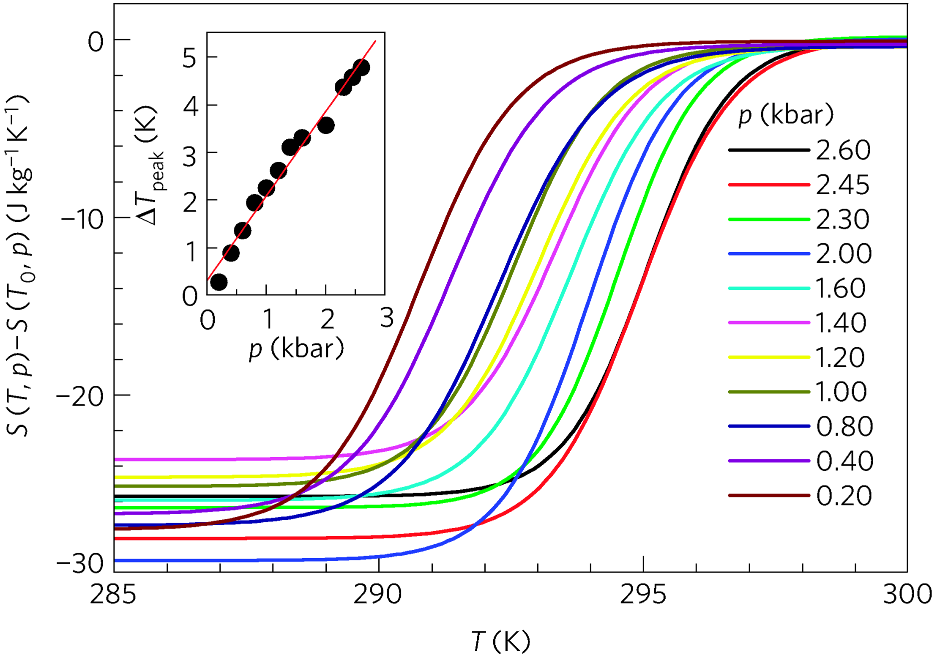

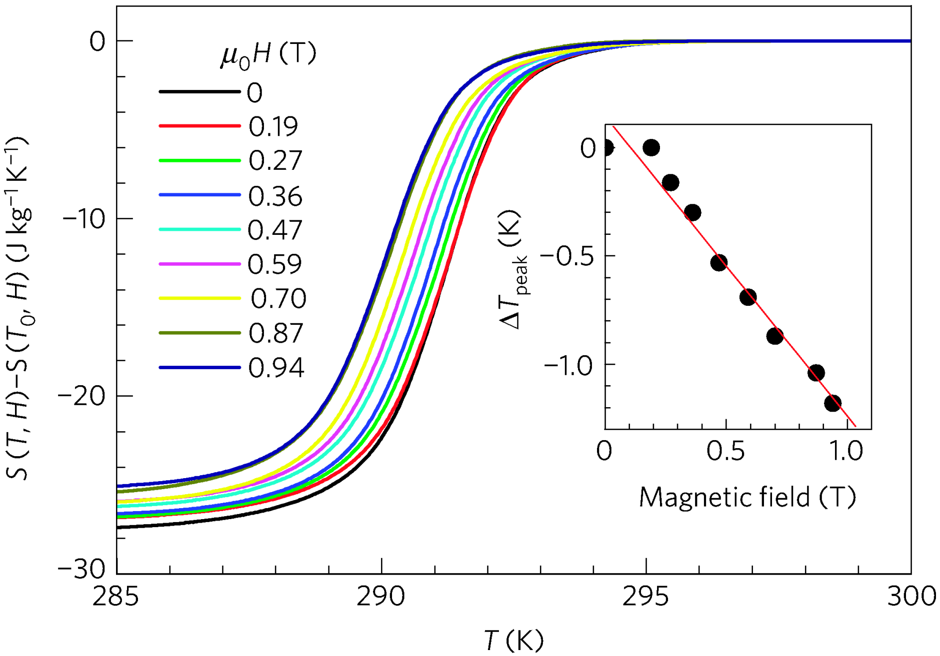

Barocaloric effect (top)

L. Mañosa et al.,

Nat. Mater. ***9****. 478 (2010)*

Inverse Barocaloric effect

L. Mañosa et al.,

Nat. Commun. ***2****. 595 (2011)*

Magnetocaloric effect (bottom)

T. Krenke et al., Nat. Mater. ***4****, 450 (2008)*

Quantities of interest: Entropy and specific heat

$$\Delta S_{mag}(T,H) = S_{mag}(T,H) - S_{mag}(T,0) \qquad (0)$$

$$\Delta T_{ad}(T,H) = -T\frac{\Delta S_{mag}(T,H)}{C(T,H)} \qquad (0)$$

$$\Delta S_{mag}(T,H) = \mu_0 \int_0^H dH' \left(\frac{\partial M}{\partial T}\right)_{H'} \qquad (0)$$

$$\Delta T_{ad}(T,H) = -\mu_0 \int_0^H dH' \frac{T}{C(T,H')} \left(\frac{\partial M}{\partial T}\right)_{H'} \qquad (0)$$

$$\boxed{\Delta C(T,H) = \frac{1}{k_b T^2}\left[\langle \mathcal{H}^2\rangle - \langle \mathcal{H}\rangle^2\right]}$$

In general,

$$\Delta S(T,Y) = \int_{\Delta Y} dY' \left(\frac{\partial X}{\partial T}\right)_{Y'} \qquad X = \{X_i\} \quad Y = \{Y_i\}$$

$X = M$, $Y = H$ (MagnetoCE) $X = V$, $Y = -p$ (BaroCE)

$X = \varepsilon$, $Y = \sigma$ (ElastoCE) $X = P$, $Y = E$ (ElectroCE)

Modelling magnetostructural coupling

$$\mathcal{H} = \mathcal{H}_m + \mathcal{H}_{lat} + \mathcal{H}_{int}$$

$$\mathcal{H}_m = -\sum_{\langle ij \rangle} J_m(i,j)\,\delta_{S_i,S_j} - g\mu_B H_{ext} \sum_i \delta_{S_i,S_g}$$

$$\mathcal{H}_{lat} = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j - K \sum_{\langle ij \rangle} (1-\sigma_i^2)(1-\sigma_j^2) - k_B T \ln(p) \sum_i (1-\sigma_i^2) - K_1 g\mu_B H_{ext} \sum_i \delta_{\sigma_i,\sigma_g} \sum_{\langle ij \rangle} \sigma_i \sigma_j$$

$$\mathcal{H}_{int} = 2U \sum_{\langle ij \rangle} \delta_{S_i,S_j} \left(\tfrac{1}{2} - \sigma_i^2\right)\left(\tfrac{1}{2} - \sigma_j^2\right) - \tfrac{1}{2} U \sum_{\langle ij \rangle} \delta_{S_i,S_j}$$

Mapping *ab initio* results onto *q*-state Potts model for Mn and Ni extended to include $\sigma = 0, \pm 1$ for cubic and tetragonal distorted structures (BEG model)

*T. Castán et al., PRB **60**, 7071 (1999)*
*V. D. Buchelnikov et al., PRB **78**, 184427 (2008)*
*V. D. Buchelnikov et al., PRB **81**, 094411 (2010)*

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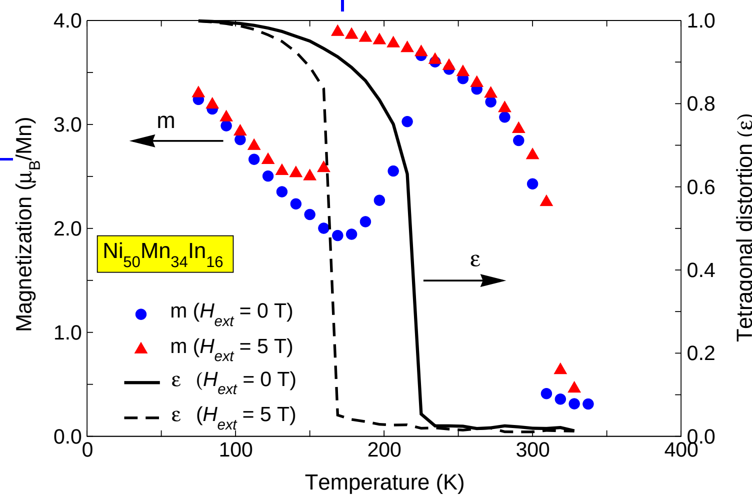
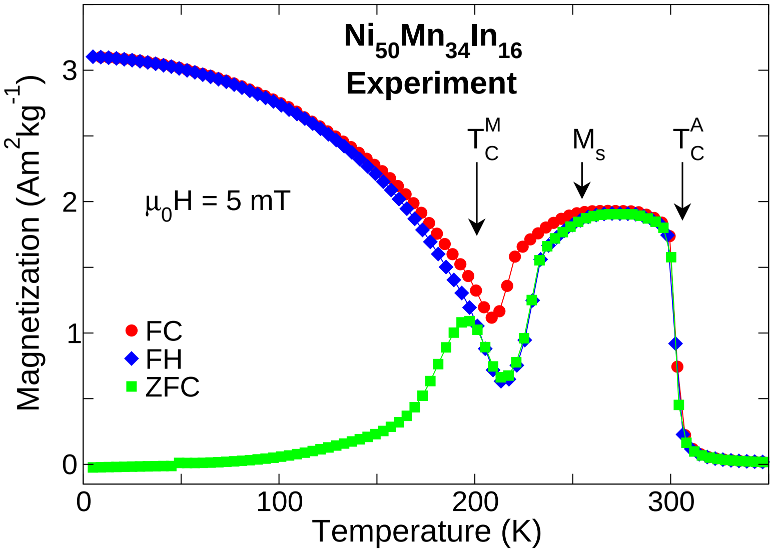
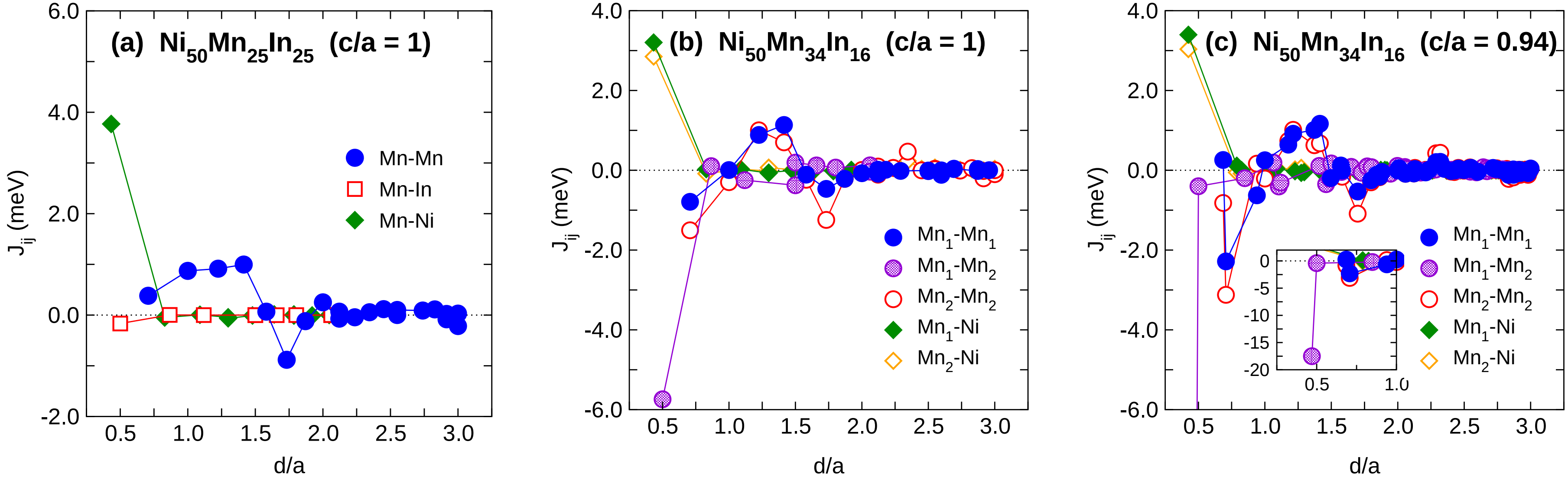


Example 1: Ni-Mn-In

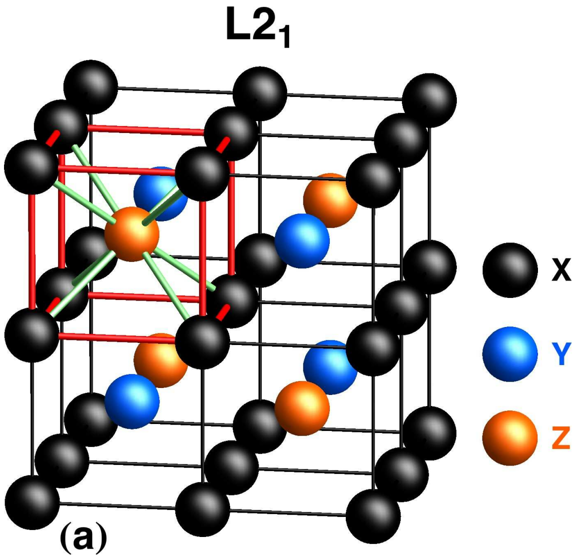


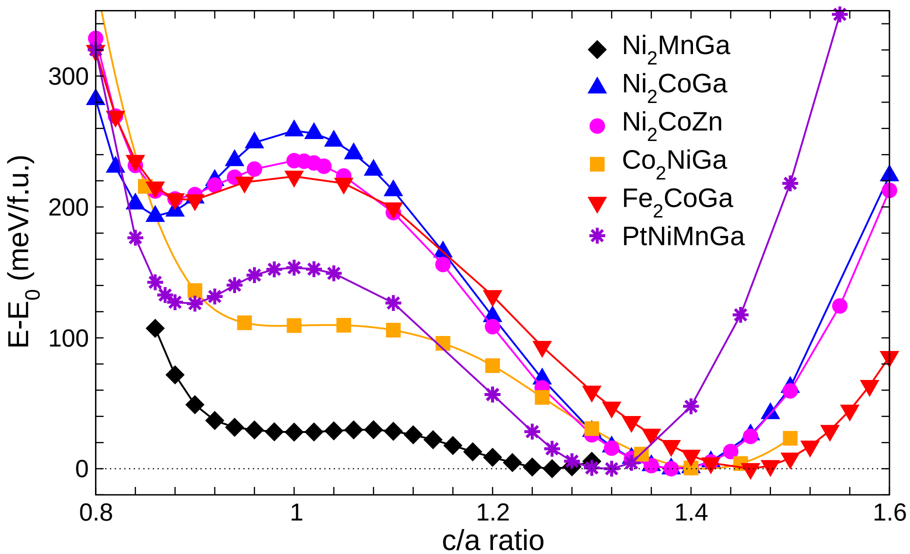


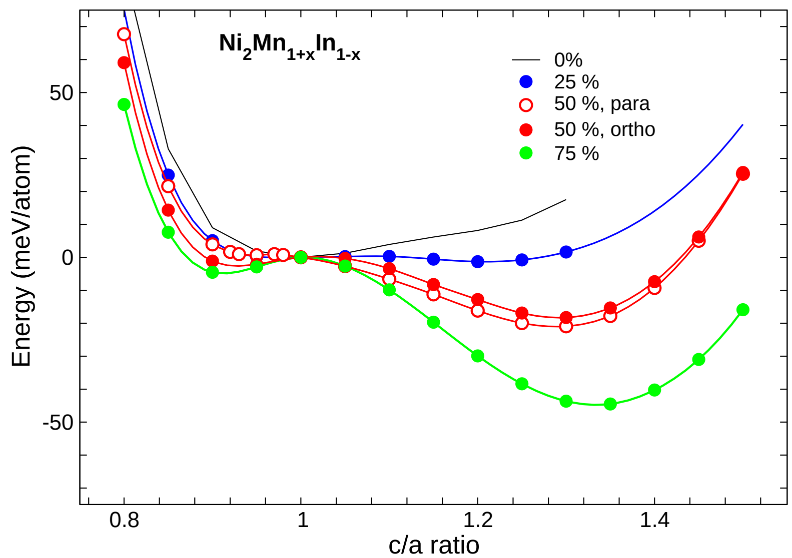
*T. Krenke et al., PRB **73**, 174413 (2006)*

*V. D. Buchelnikov et al., JPD:AP **44**, 064012 (2011)*

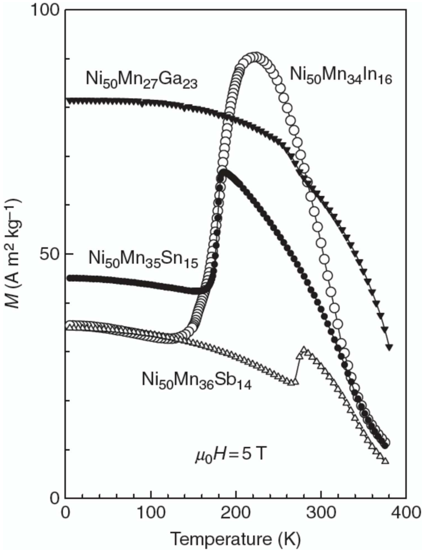
Heusler structures X_2YZ







For comparison: J_{ij} of Ni-Mn-Sn



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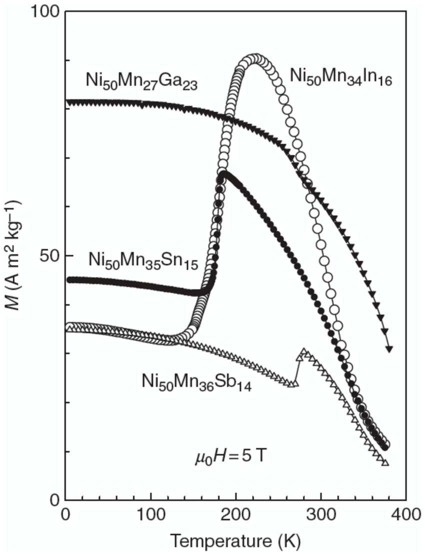

M. Acet et al., Handbook of Magnetic Materials, vol. ***19****, 231 (2011)*

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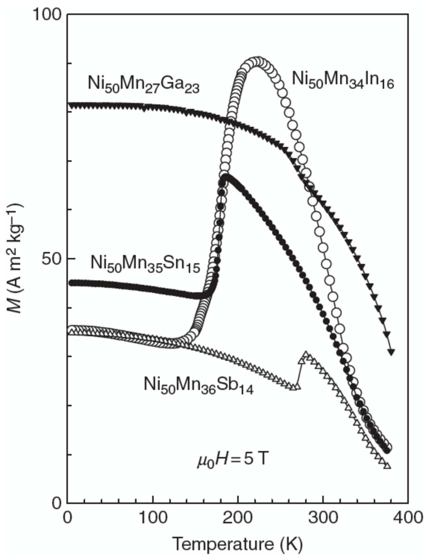
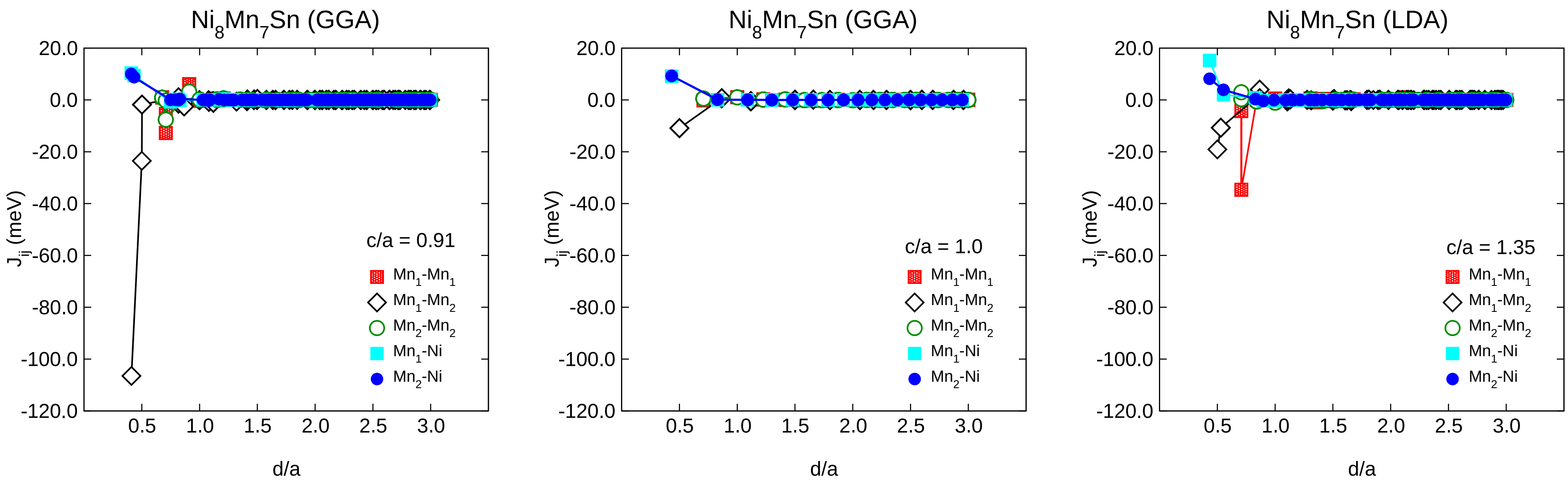
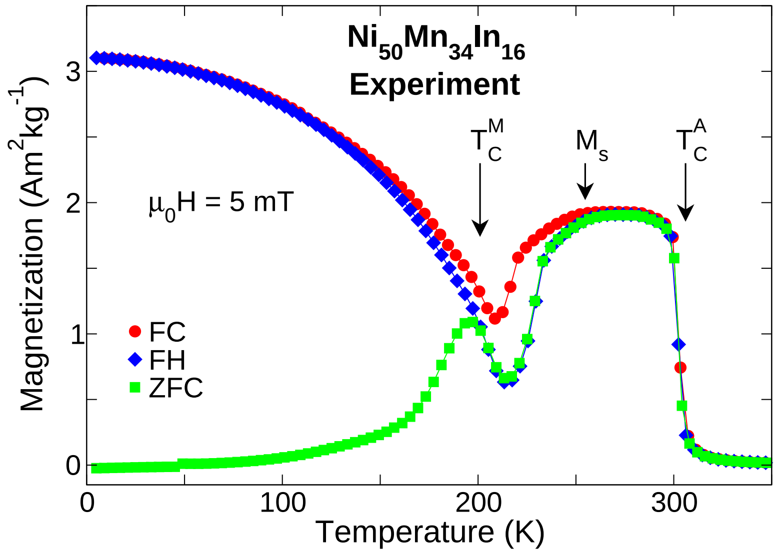


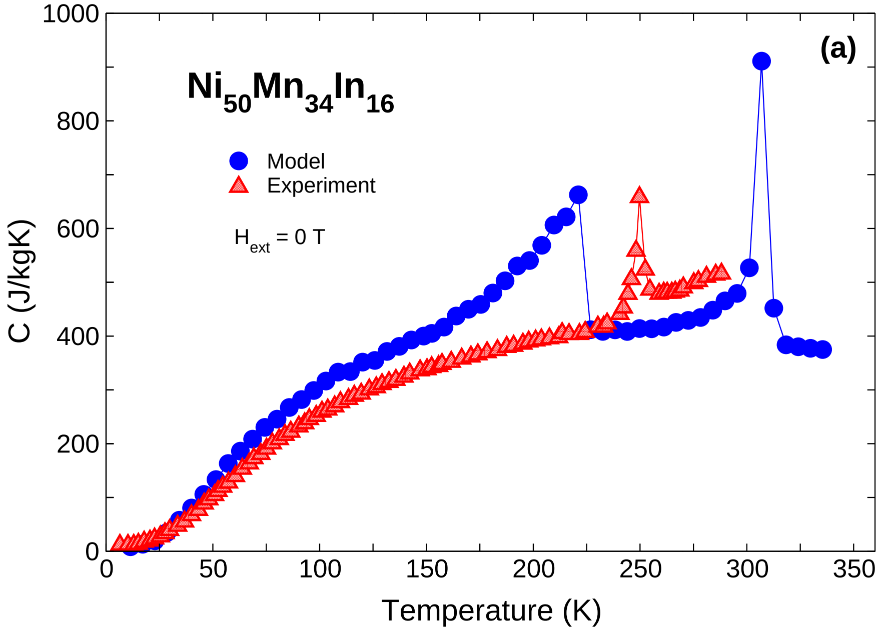
M. Acet et al., Handbook of Magnetic Materials, vol. ***19****, 231 (2011)*

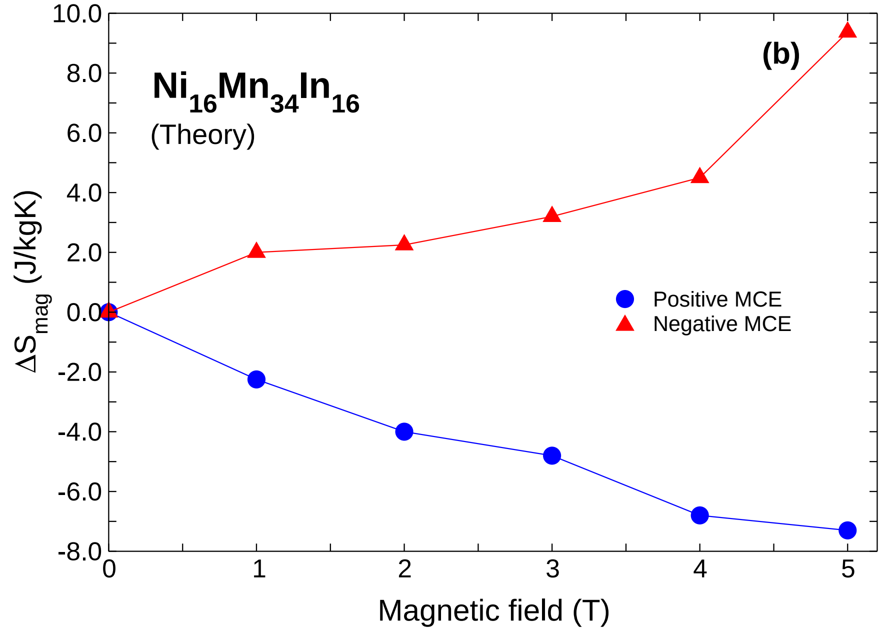


S. Sahoo et al., unpublished

Monte Carlo simulations of $Ni_{50}Mn_{34}In_{16}$

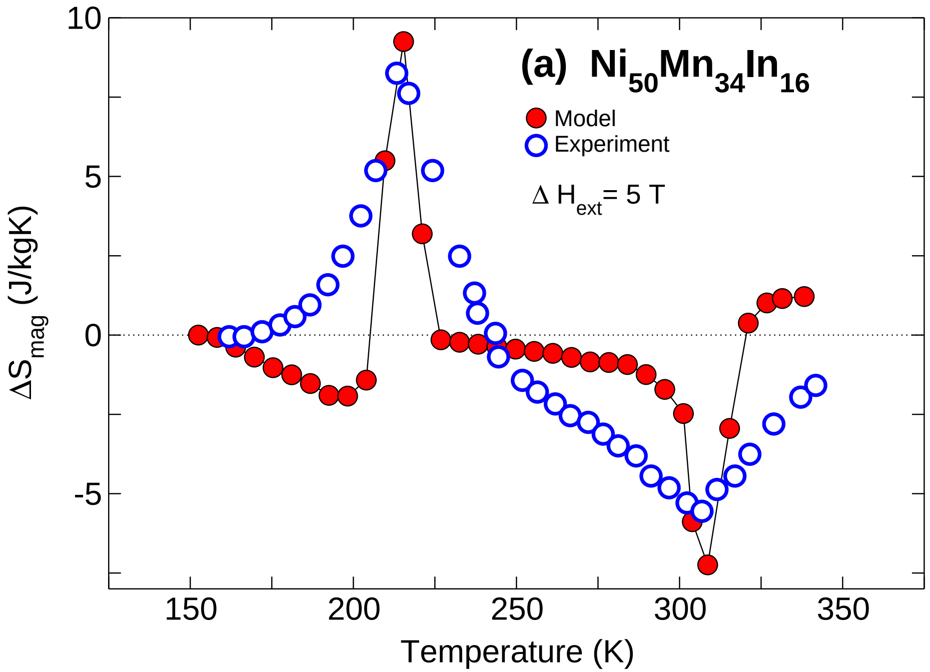


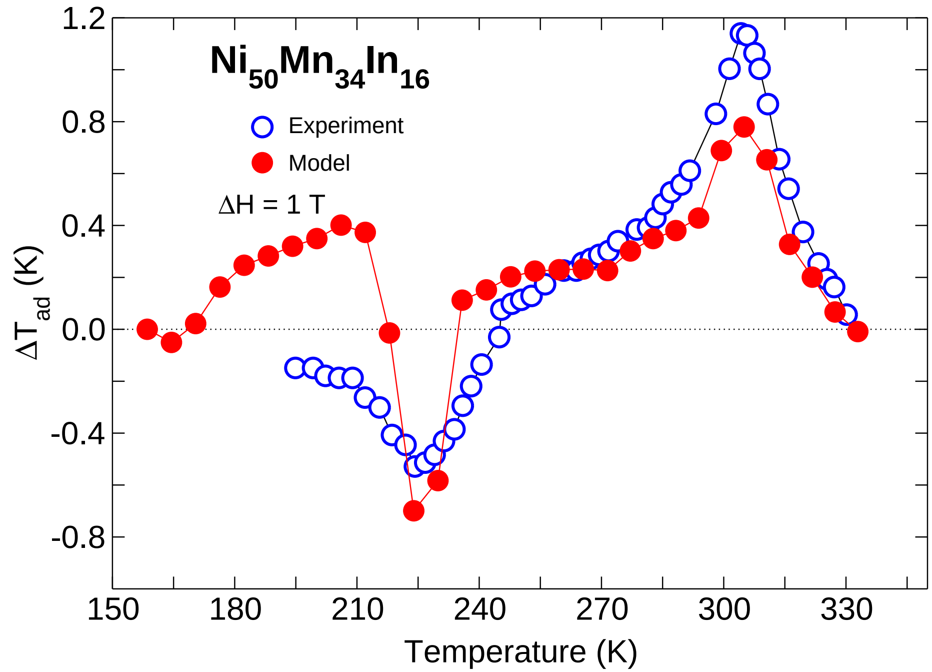




*V. D. Buchelnikov et al., JPD:AP **44**, 064012 (2011)*

Calculated $\Delta S_{mag}(T)$ and $\Delta T_{ad}(T)$ (Ni-Mn-In)

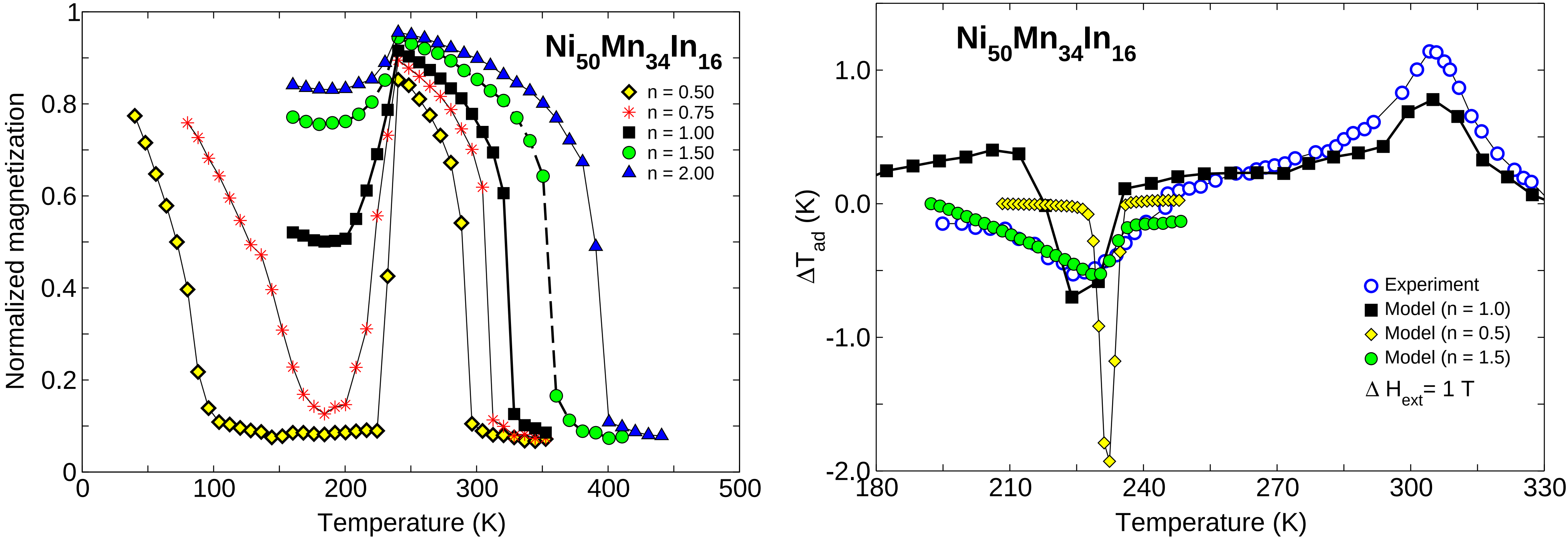




MCE: *V.D. Buchelnikov et al., JPD:AP **44**, 064012 (2011)*

BCE: *L. Mañosa et al., Nat. Mat. **9**, 478 (2010)*

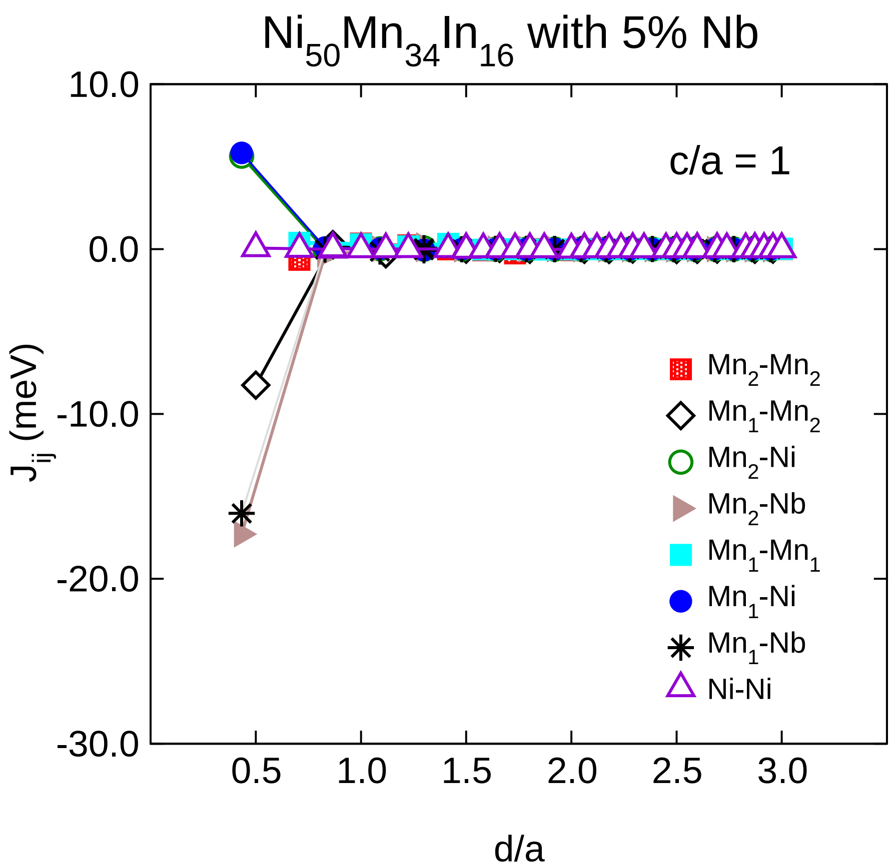
How to get a Larger MCE: Scale the J_{ij}

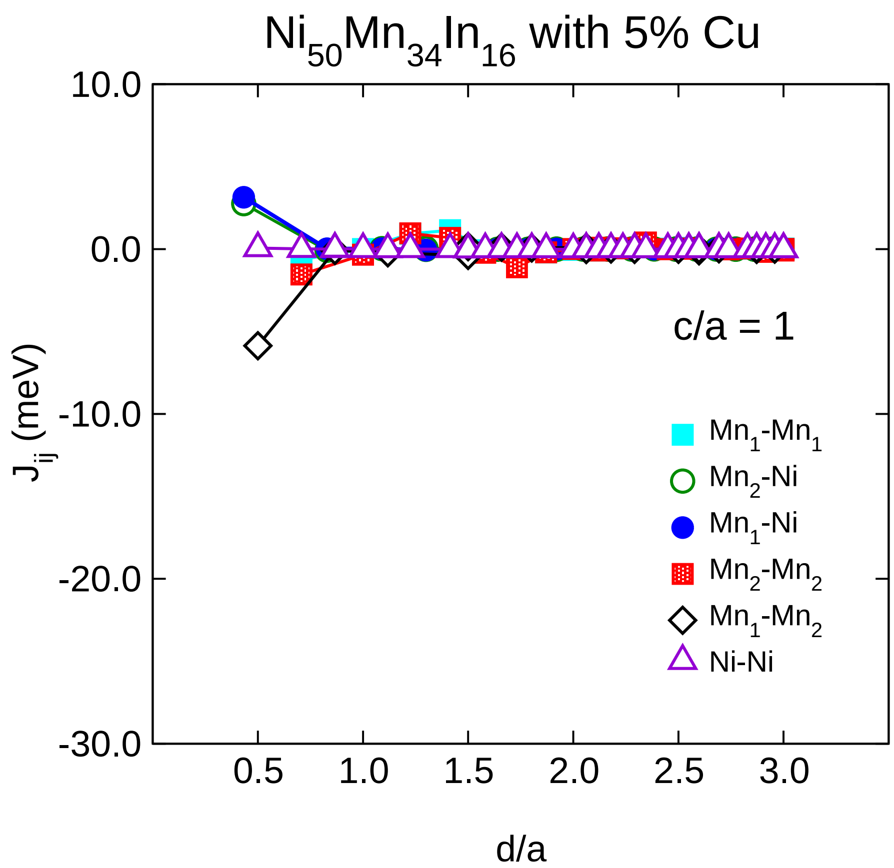


Effect of scaling on the MCE (unpublished): $n = J_{ij}^{new}/J_{ij}^{old}$

Yields a larger MCE and, simultaneously, a smaller “hysteresis”

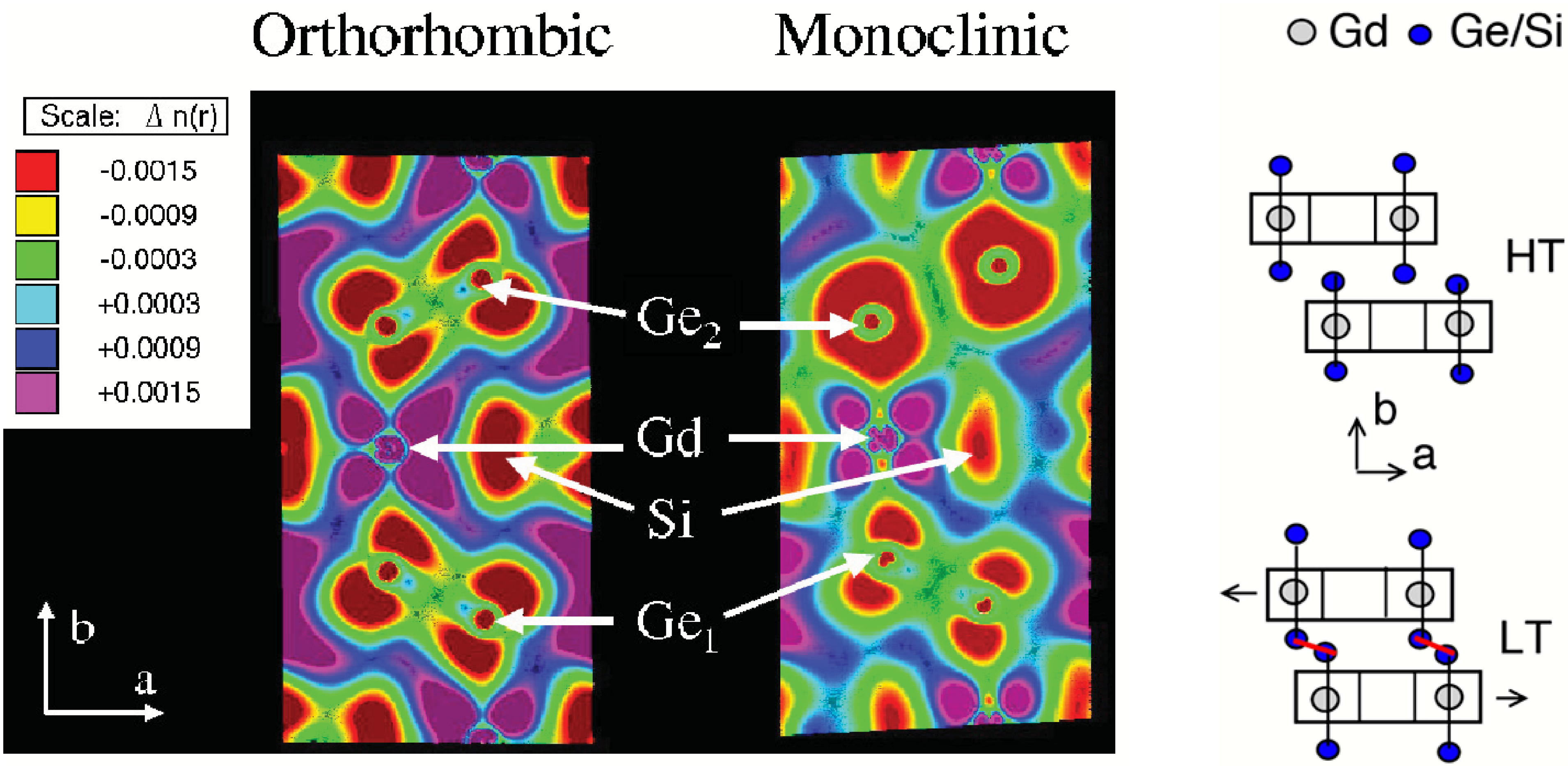
With 5 at.% transition metals





Effect of nonmagnetic TM on magnetic exchange parameters (unpublished)

Example 2: Gd-Ge-Si



First-order bond breaking magnetostructural transition responsible for the giant MCE

*W. Choe et al., PRL **84**, 4617 (2000)*

*D. Haskel et al., PRL **98**, 247205 (2007)*

Survey of theoretical methods

Landau and spin models with coupling to the lattice

- Molecular field approximation
- Monte Carlo simulations
- *Ab initio magnetic exchange parameters as input*

First-principles DFT methods, fully relativistic

- Including external magnetic field: $M(T)_H$ curves
- Finite T calculations: Phonons, magnons
- *Phase diagrams, MCE, BCE and ECE*

Theoretical tools (I)

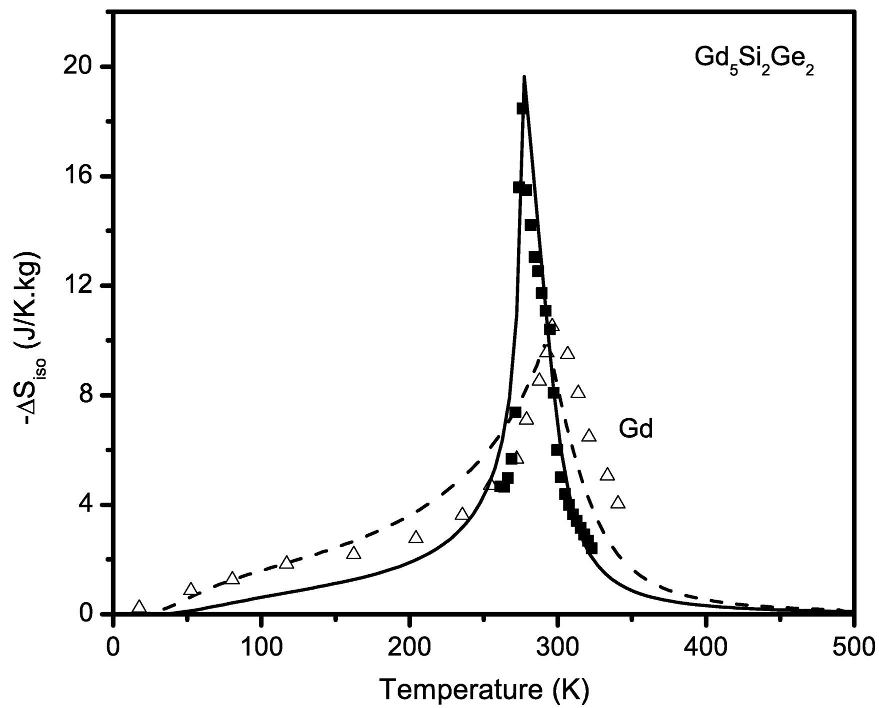
(a) MCE (RE):

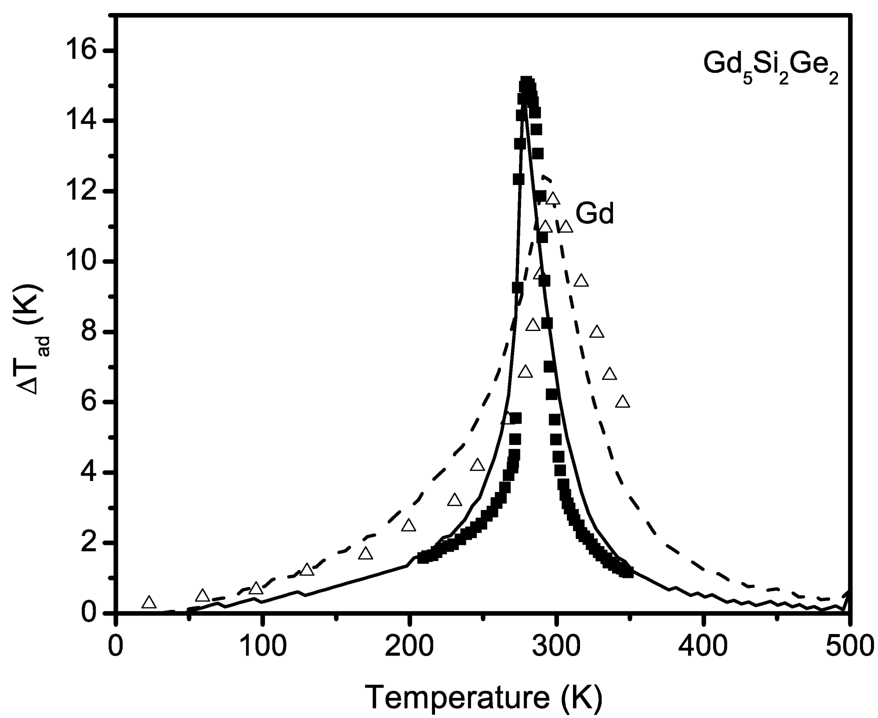
Theoretical tools (I)

(a) MCE (RE):

$$\mathcal{H} = \mathcal{H}_{el}^{spd} + \mathcal{H}_{mag}^{4f} + \mathcal{H}_{lat}$$

Complex parts: Crystal field Hamiltonian, C_{lat} and S_{lat} depend on magnetic order





$Gd_5Si_2Ge_2$ (solid lines) and Gd (dashed lines) upon magnetic field variation from 0 to 5T

*N.A. de Oliveira & P.J. von Ranke, Phys. Rep. **489**, 89 (2010)*

Theoretical tools (II)

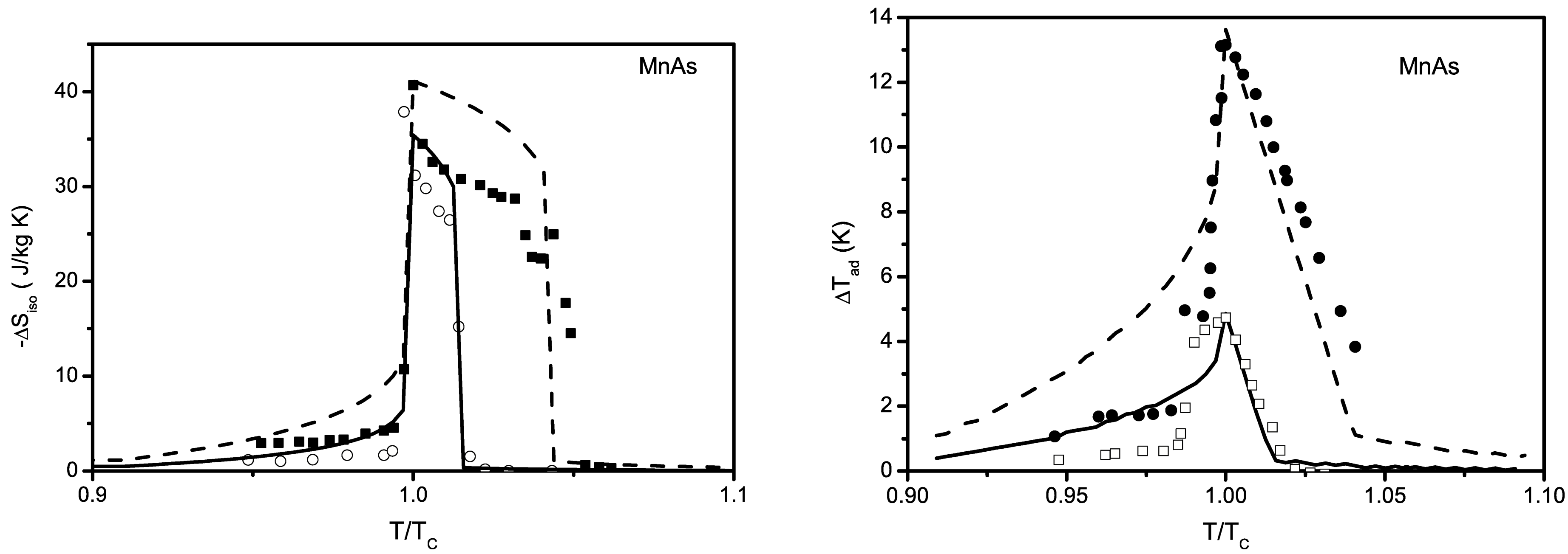
(b) MCE (TM):

Theoretical tools (II)

(b) MCE (TM):

$$\mathcal{H} = \mathcal{H}_{el}^{sp} + \mathcal{H}_{mag}^{d} + \mathcal{H}_{lat} + \mathcal{H}_{el-lat}$$

Complex parts: Hubbard Hamiltonian, elctron-phonon and phonon-magnon interactions



MnAs upon magnetic field variation from 0 to 2 T (solid lines) and from 0 to 5 T (dashed lines) compared to experiment (symbols)

N.A. de Oliveira & P.J. von Ranke, Phys. Rep. ***489****, 89 (2010)*

Theoretical tools (III)

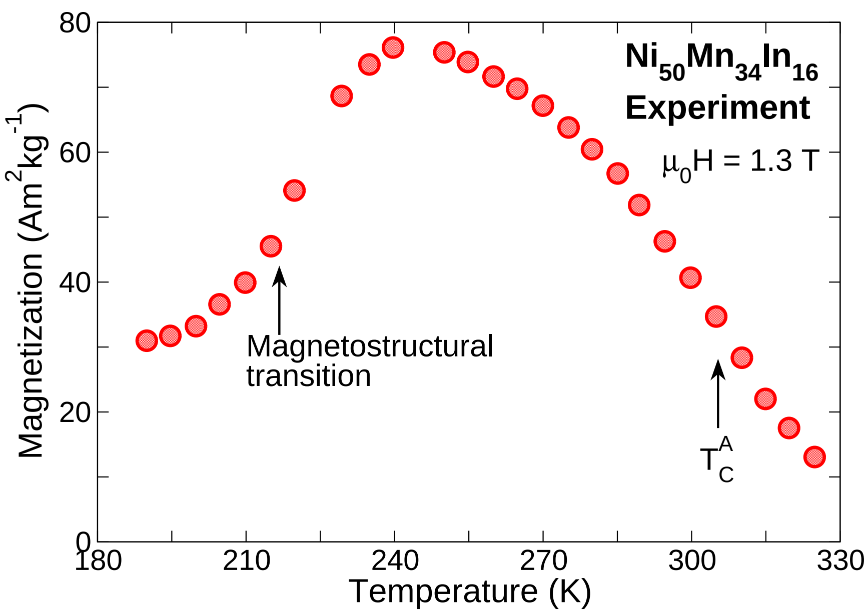
(c) MCE (Heusler alloys):

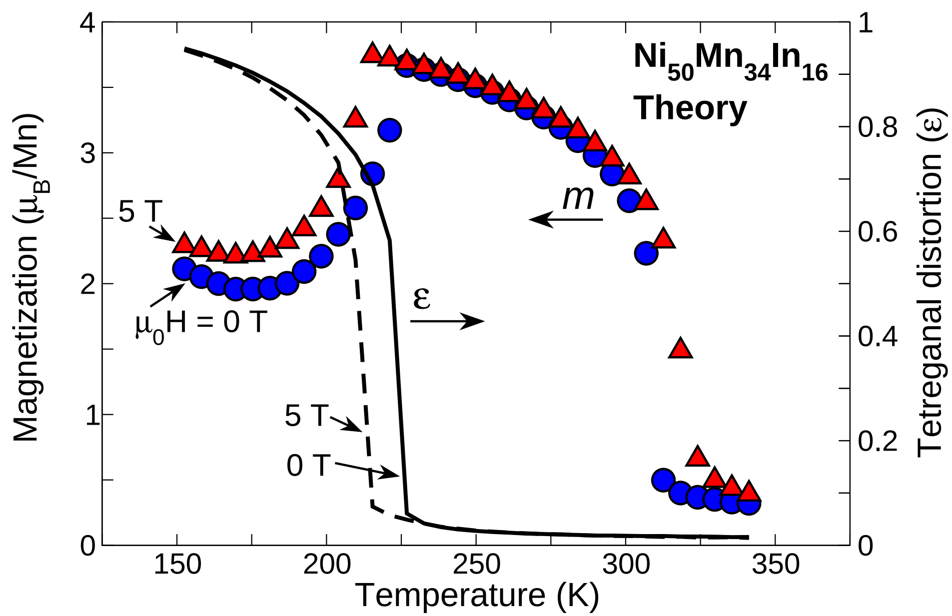
Theoretical tools (III)

(c) MCE (Heusler alloys):

$$\mathcal{H} = \mathcal{H}^{d}_{mag} + \mathcal{H}_{BEG} + \mathcal{H}_{lat}$$

Complex parts: Magnetic part coupled to the martensitic transformation





Magnetization near the magnetostructural transition in external field from Monte Carlo simulations compared to experiment

*V.D. Buchelnikov et al., JPD:AP **44**, 064012 (2011)*

Theoretical tools (IV)

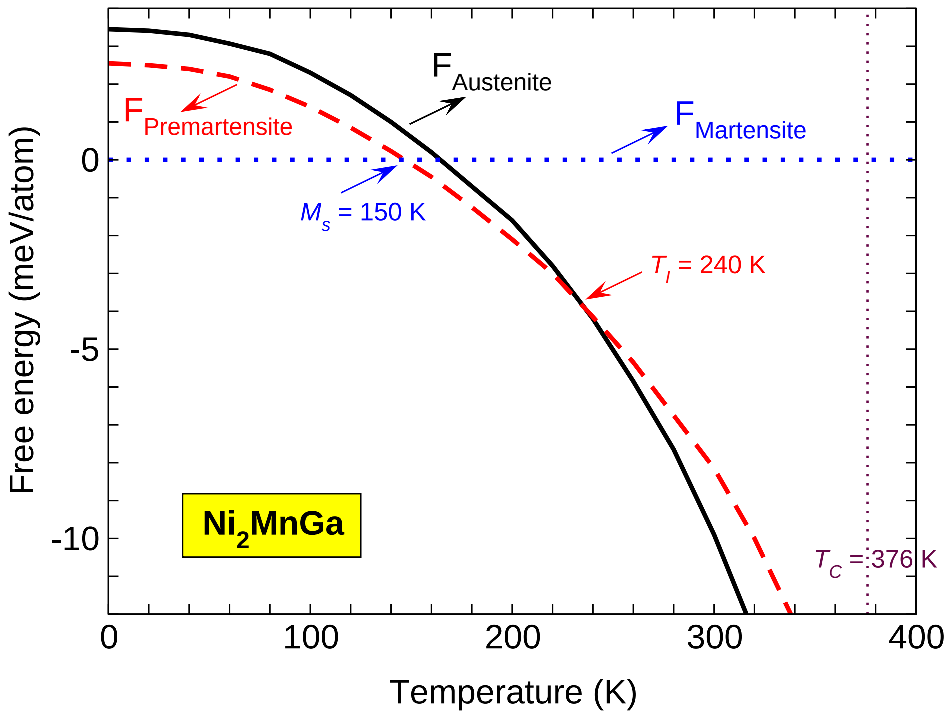
(d) MCE (Heuslers with DFT):

Theoretical tools (IV)

(d) MCE (Heuslers with DFT):

$$\mathcal{F}(V,T) = \mathcal{F}_{el}(V,T) + \mathcal{F}_{mag}(V,T) + \mathcal{F}_{ph}(V,T)$$

Complex parts: *Ab initio* evaluation of phonons and magnons and their coupling at finite *T*



Austenite-martensite transition in Ni_2MnGa

*M. A. Uijttewaal et al., PRL **102**, 035702 (2009)*

Summary

- ***Large MCE near magnetostructural transitions with competing ferro- and antiferromagnetic interactions***

$$\Delta T_{ad} = -T \frac{\Delta S_{(mag)}(T, H, p, x, \ldots)}{C(T, H, p, x, \ldots)}$$

- ***Mostly model calculations with magnetic and lattice degrees of freedom and***

  parameter fit to experiment /ab initio data

- ***First-principles DFT calculations (T = 0 K)***

  Needed: T > 0 K calculations for MCE, BCE . . .

Collaboration

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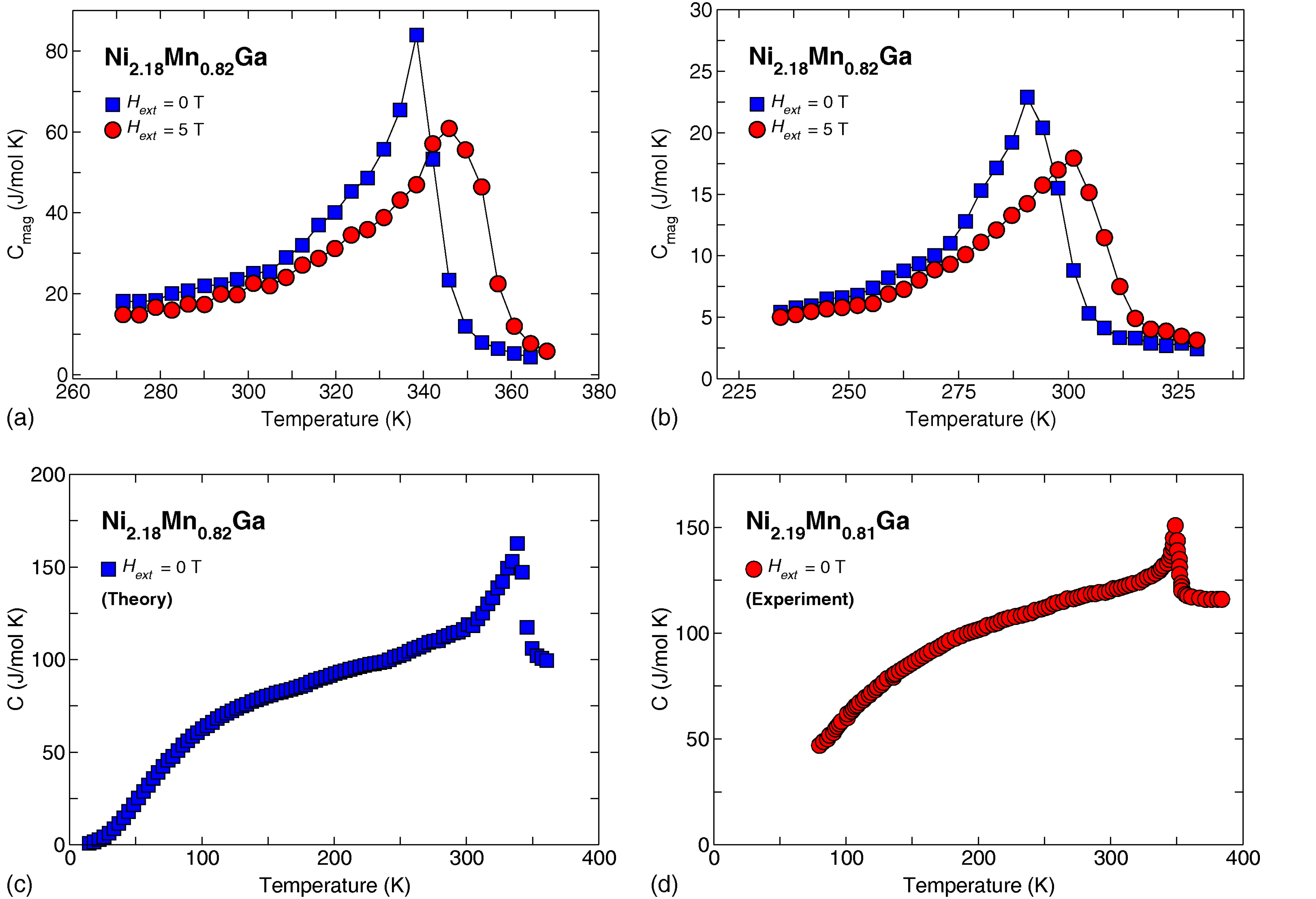
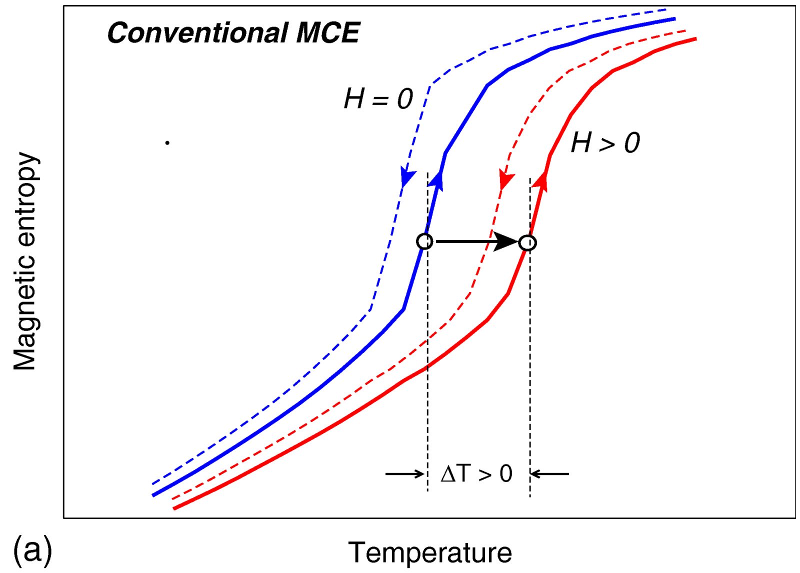
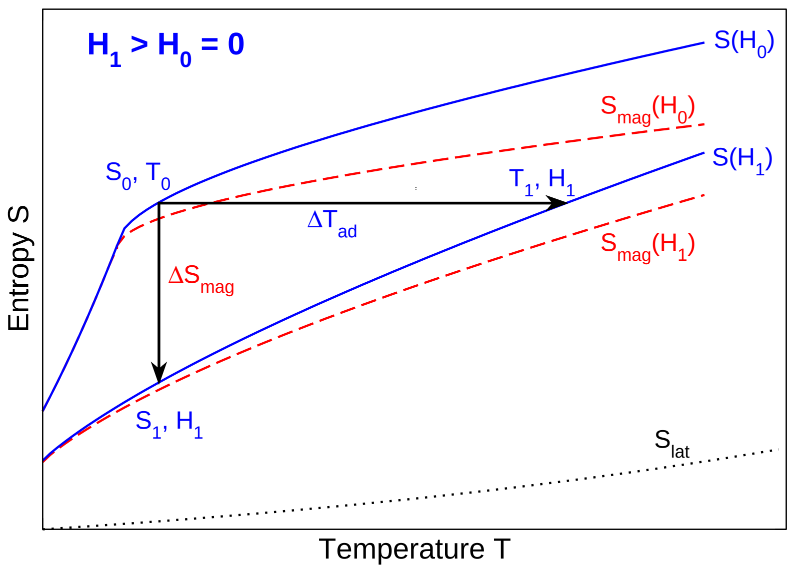
Appendix: Specific heat of $Ni_{2.18}Mn_{0.82}Ga$

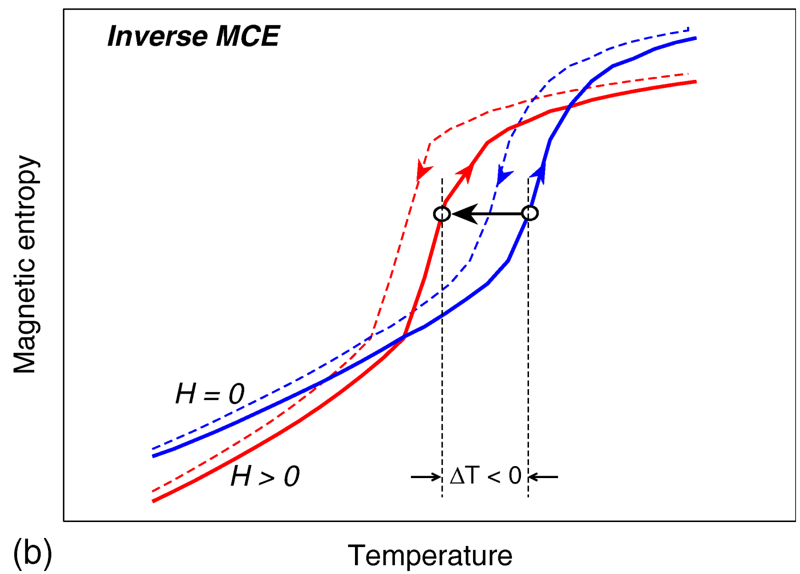
Buchelnikov et al., PRB **81**, 094411 (2010)



Appendix: Qualitative S-T diagrams







V. K. Pecharsky et al., JMMM ***200****, 44 (1999)*

V. D. Buchelnikov et al., PRB ***81****, 094411 (2010)*

Appendix: Summary of caloric effects

REFRIGERATION IN SOLID STATE

Barocaloric effect

$Y \rightarrow -p$ (pressure)
$x \rightarrow V$ (Volume)

Mechanical refrigeration

L. Mañosa et al.
Nature Mater. 9 (2010) 478

Electrocaloric effect

$Y \rightarrow E$ (Electric field)
$x \rightarrow P$ (Polarization)

Electric refrigeration

A. S. Mischenko et al.
Science 311 (2006) 1270

ΔS

ΔT

Magnetocaloric effect

$Y \rightarrow H$ (Magnetic field)
$x \rightarrow M$ (Magnetization)

Magnetic refrigeration

V. K. Pecharsky et al.
Phys. Rev. Lett. 78 (1997) 4494

Elastocaloric effect

$Y \rightarrow \sigma$ (Stress)
$x \rightarrow \varepsilon$ (Strain)

Elastic refrigeration

E. Bonnot et al.
Phys. Rev. Lett. 100 (2008) 125901