Magnetocaloric and shape-memory properties in ferromagnetic Heusler alloys

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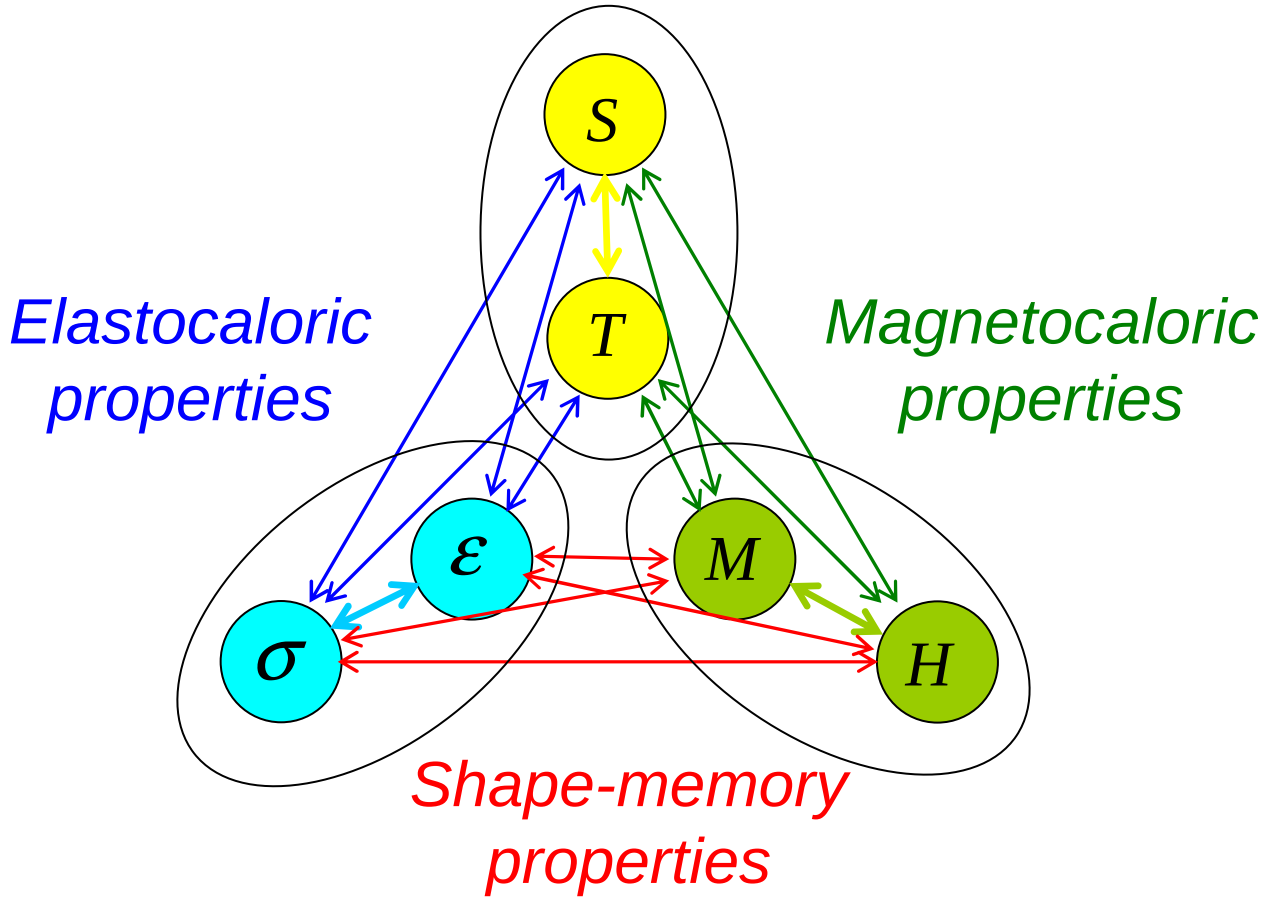
Thermodynamics

$$dU = TdS + \mu_0 \Omega H dM + \Omega \sigma d\varepsilon + \ldots\ldots$$

Coupling $\begin{cases} M = M(S,\varepsilon) \\ \varepsilon = \varepsilon(S,M) \end{cases}$



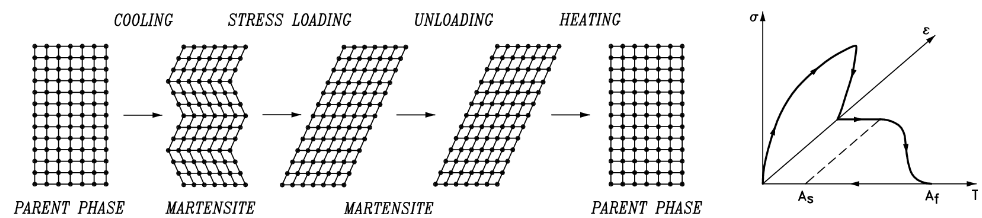
Outline

- Shape-memory properties
- Magnetic shape-memory and magnetostructural coupling
- First order transitions and magnetocaloric effect
- Results: Ni-Mn-Ga
- Other Heuler alloys
- Conclusions

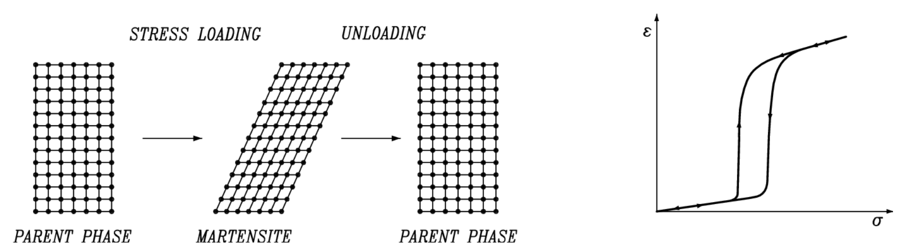
Shape-memory properties

Shape-memory properties refers to the ability of a material undergoing a martensitic transition to recover from severe deformations:

• in the martensitic phase upon heating above the transition: Shape-memory effect



• upon loading and unloading a large strain associated with the stress-induced martensitic transformation: Superelasticity



Magnetic shape-memory properties

Magnetic shape-memory: Field induced deformation caused by rearranging the martensitic variants.

Requires:

Large magnetic anisotropy

+

High twin boundary mobility

Magnetic superelasticity: Field induced deformation caused by inducing the martensitic transition.

Requires:

Significant shift of the transition with magnetic field.

Coupling

Structure ⇦ Interplay ⇨ Magnetism

⇩

Microscopic scale

⇩

Controlled by the change of *J*

⇩

Magnetic superelasticity

Mesoscopic scale

⇩

Controlled by the change of *A*

⇩

Magnetic shape-memory

Magnetocaloric effect

Magnetocaloric effect: General features

Magnetic system (T, H independent variables):

$$dS = \left(\frac{\partial S}{\partial T}\right)_{H,...} dT + \left(\frac{\partial S}{\partial H}\right)_{T,...} dH + ...$$

When magnetic field *H* is applied/removed:

Adiabatic Temperature change: $\Delta T_{adi} = -\int_{H_i}^{H_f} \frac{T}{C_H}\left(\frac{\partial S}{\partial H}\right)_T dH$

Isothermal Entropy change: $\Delta S_{iso} = \int_{H_i}^{H_f} \left(\frac{\partial S}{\partial H}\right)_T dH$

$$\Delta T_{adi} \approx -\frac{T}{C_H} \Delta S_{iso}$$

Magnetocaloric effect: Determination

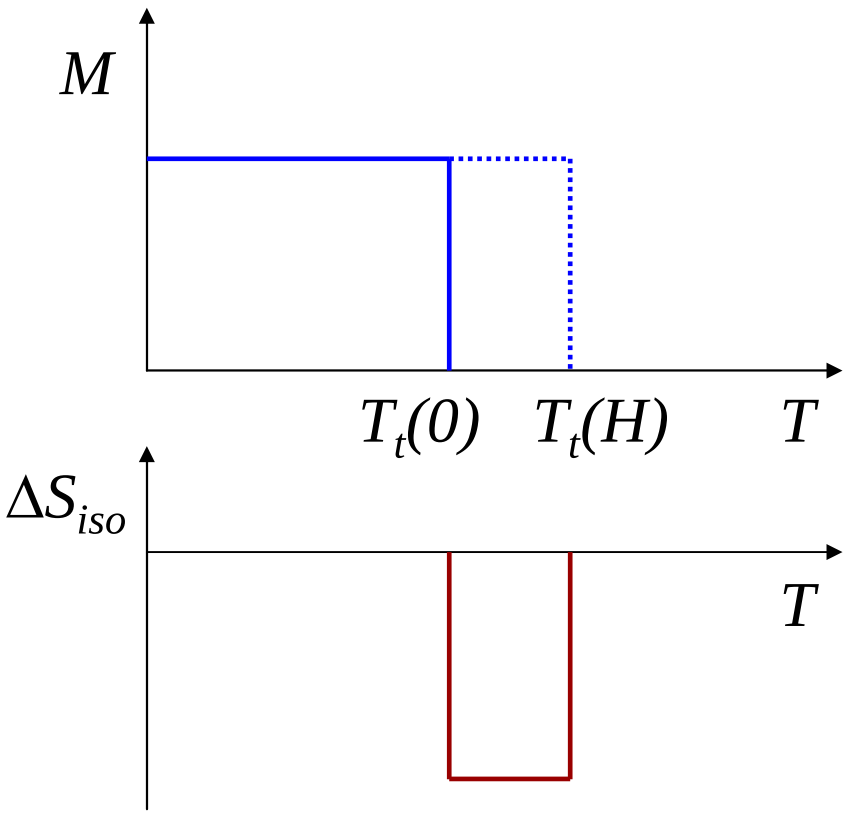
- Directly from calorimetric measurements
- Indirectly from magnetization curves

Maxwell relation $\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H \quad \Rightarrow \quad \Delta S_{iso} = \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T}\right)_H dH$

Considerations

- MCE is expected to be large in regions where M shows a fast change with $T \Rightarrow$ **vicinity of phase transitions**
- $\left(\frac{\partial M}{\partial T}\right)_H < 0 \Rightarrow \Delta S_{iso} < 0$ when $H_f - H_i > 0 \Rightarrow$ Cooling by adiabatic demagnetization
- $\left(\frac{\partial M}{\partial T}\right)_H > 0 \Rightarrow \Delta S_{iso} < 0$ when $H_f - H_i > 0 \Rightarrow$ Heating by adiabatic demagnetization

Example: Ideal first-order phase transition



$$M = \Delta M\, h[T - T_t(H)]$$

$h(x)$ is the Heaviside function

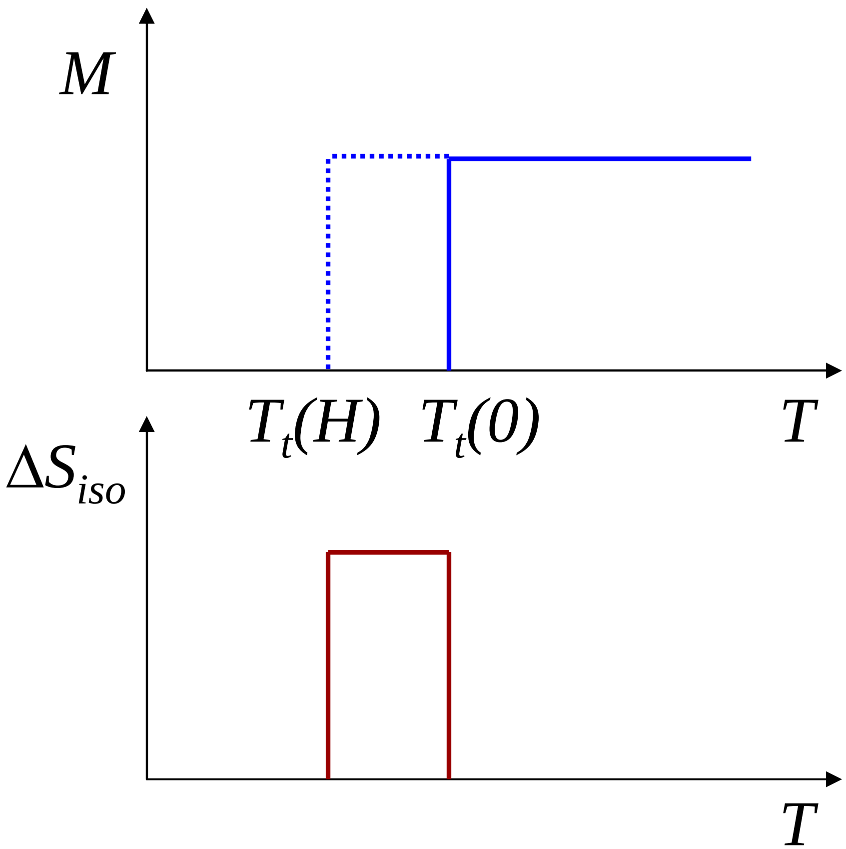
$$\Delta S_{iso} = \int_0^H \left(\frac{\partial M}{\partial T}\right) dH$$

$$= \begin{cases} -\dfrac{\Delta M}{\alpha} & for \;\; T \in [T_t(0), T_t(H)] \\ 0 & for \;\; T \notin [T_t(0), T_t(H)] \end{cases}$$

where $\alpha = |dT_t/dH|$

For $\Delta M > 0$ ($dT_t/dH > 0$) $\Rightarrow$ $\boldsymbol{\Delta S_{iso} < 0}$ (for $0 \rightarrow H$)

Example: Ideal first-order phase transition



$$M = \Delta M \, h\left[T - T_t(H)\right]$$

$h(x)$ is the Heaviside function

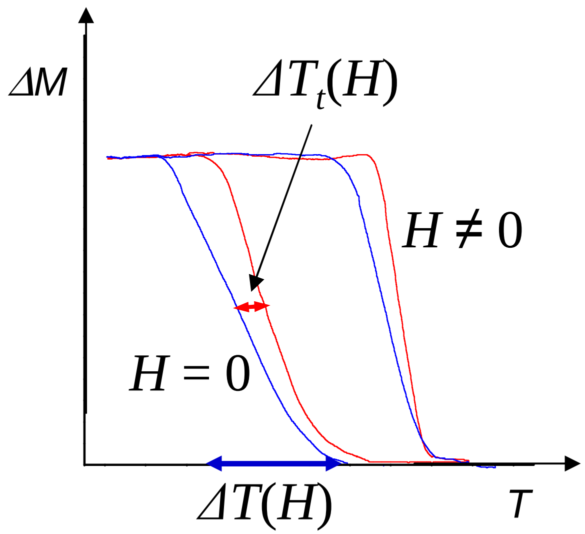
$$\Delta S_{iso} = \int_0^H \left(\frac{\partial M}{\partial T}\right) dH$$

$$= \begin{cases} -\dfrac{\Delta M}{\alpha} & for \;\; T \in \left[T_t(0), T_t(H)\right] \\ 0 & for \;\; T \notin \left[T_t(0), T_t(H)\right] \end{cases}$$

where $\alpha = |dT_t/dH|$

For $\Delta M > 0$ $(dT_t/dH > 0) \Rightarrow$ $\boldsymbol{\Delta S_{iso} < 0}$ (for $0 \rightarrow H$)

Real first-order phase transition



- The transition spreads over a range of temperatures
- It displays hysteresis

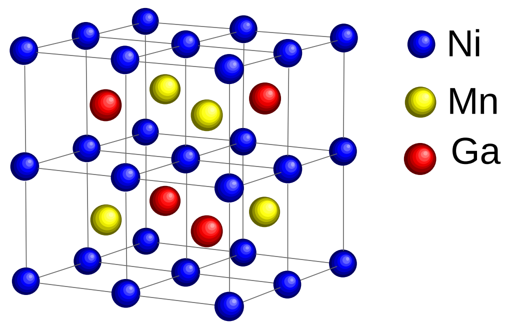
$$\langle \Delta S(H) \rangle = \frac{\mu_0}{\Delta T(H)} \int_{\Delta T} \Delta M(T,H)\, dT$$

$$\Delta T_t(H) = -\frac{\mu_0}{\Delta S_t(H)} \int_{\Delta T} \Delta M(T,H)\, dT$$

$$\Rightarrow \frac{\langle \Delta S(H) \rangle}{\Delta S_t(H)} = -\frac{\Delta T_t(H)}{\Delta T(H)}$$

Materials

Prototypical Heusler SMA: Ni_2MnGa



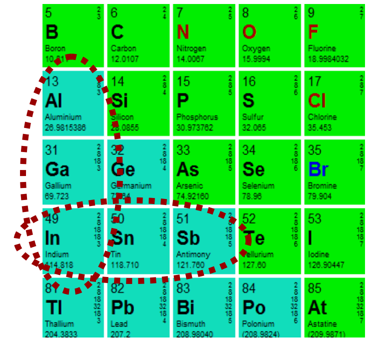
Other Heusler alloys:

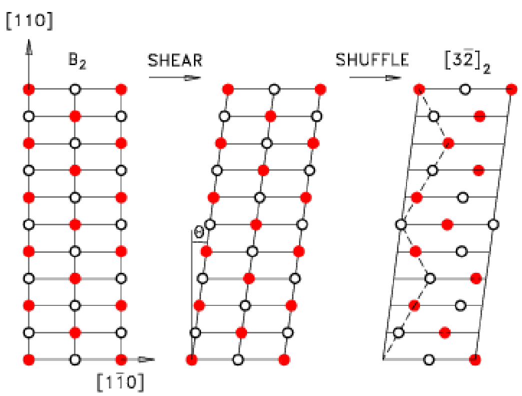
$Ni_{50}Mn_{50-x}Sn_x$

$Ni_{50}Mn_{50-x}In_x$

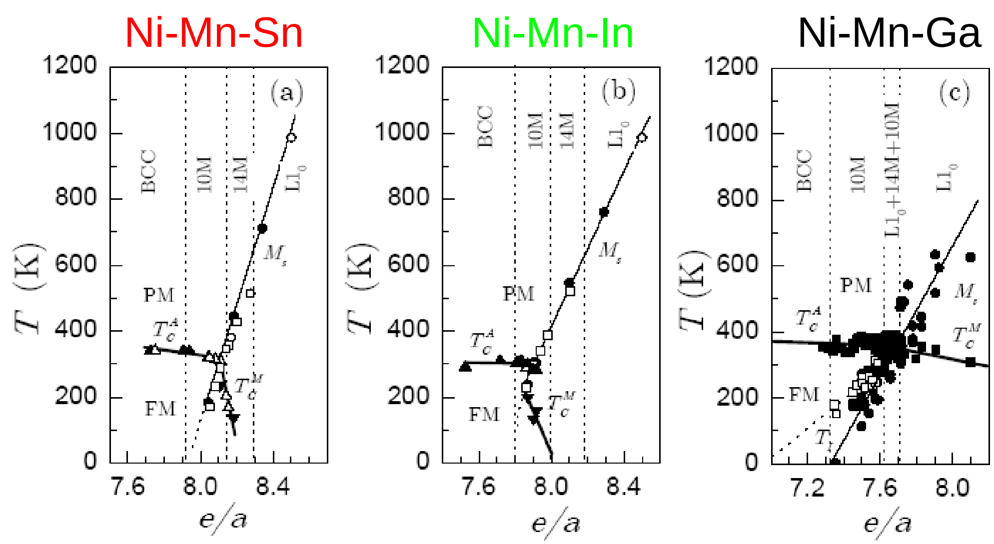
$Ni_{50}Mn_{50-x}Sb_x$

$Ni_{50}Mn_{50-x}Al_x$





Cubic ⟶ 10 *M* or 5 *M* (other 7 *M*, …)

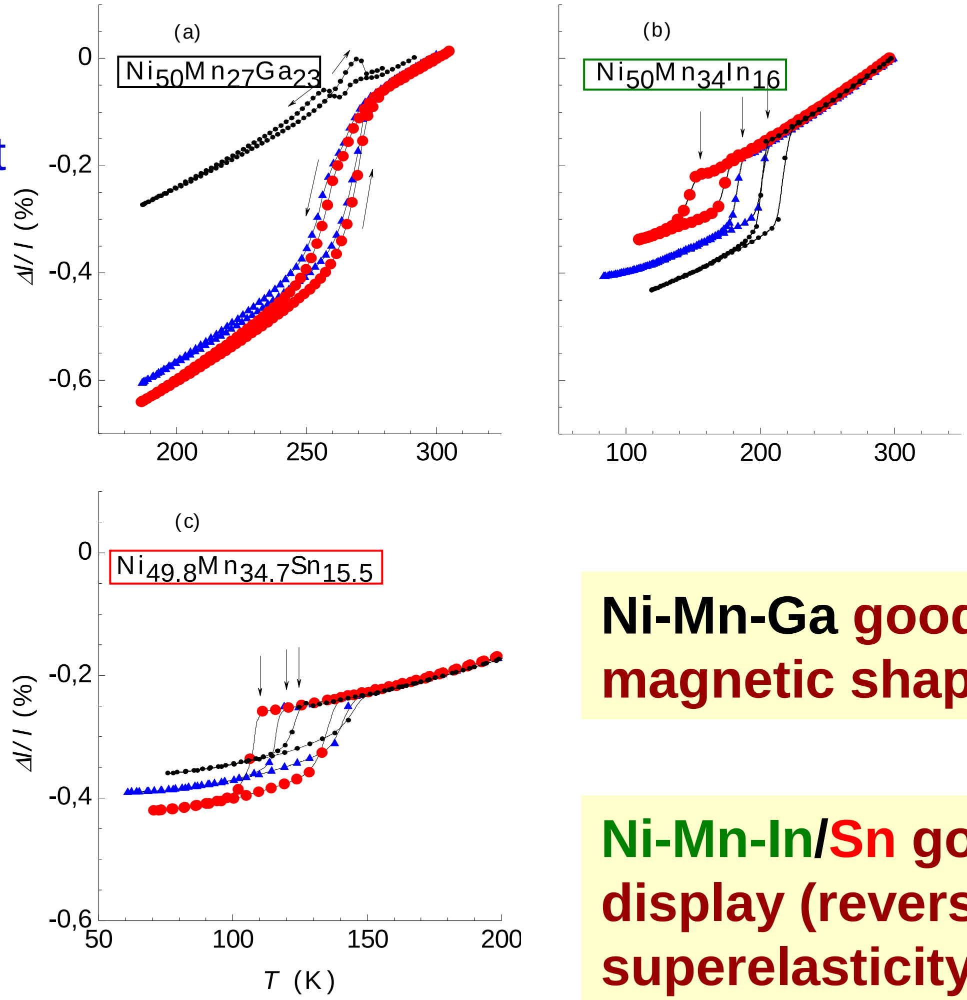


Effect of a magnetic field on the transition

Black: *H = 0*   Blue: *H* = 2 T   Red: *H* = 5 T

Ni-Mn-Ga:
- Negligeable length change at zero field
- Negligible shift of the transition
- Strong effect of the field on *Δl/l* (< *0*, easy axis: short axis)

Ni-Mn-Sn:
- Similar to Ni-Mn-In (smaller changes)



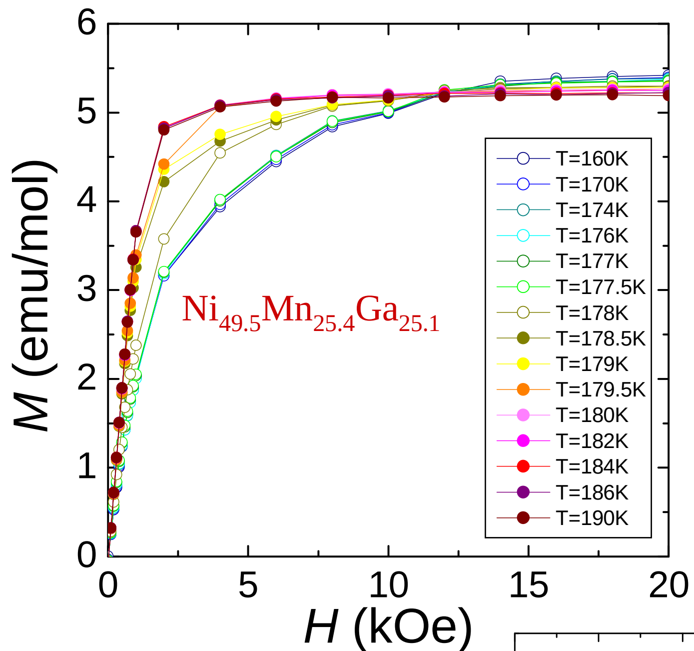
Ni-Mn-In:
- Significant shift of the transition with the field
- Noticeable length change at zero field
- *Δl/l > 0* (easy axis: long axis)

Ni-Mn-Ga good candidate for magnetic shape-memory effect

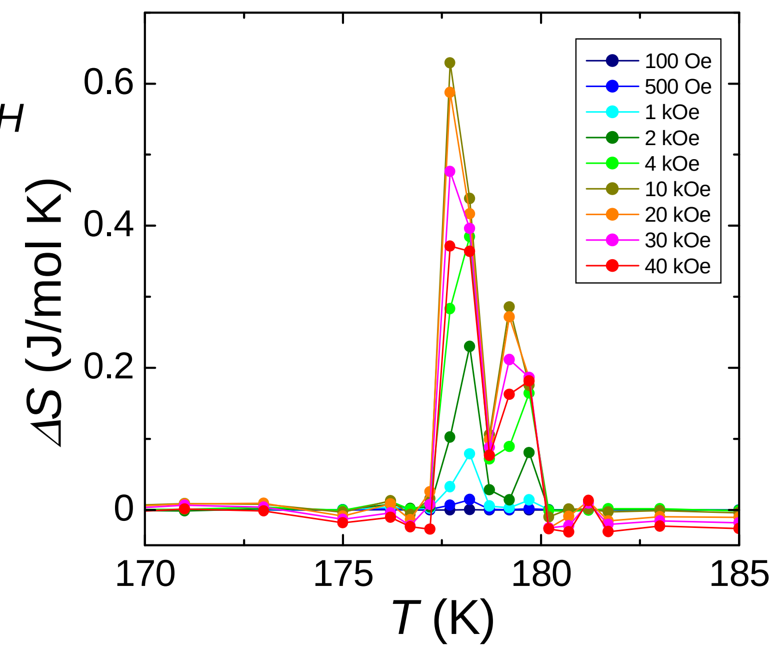
Ni-Mn-In/Sn good candidates to display (reverse) magnetic superelasticity

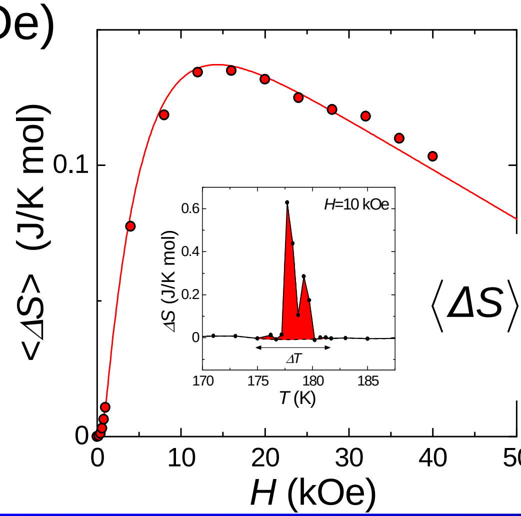
Magnetocaloric effect: Ni_2MnGa

Marcos et al., Phys. Rev. B,**66**, 224413 (2002)



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



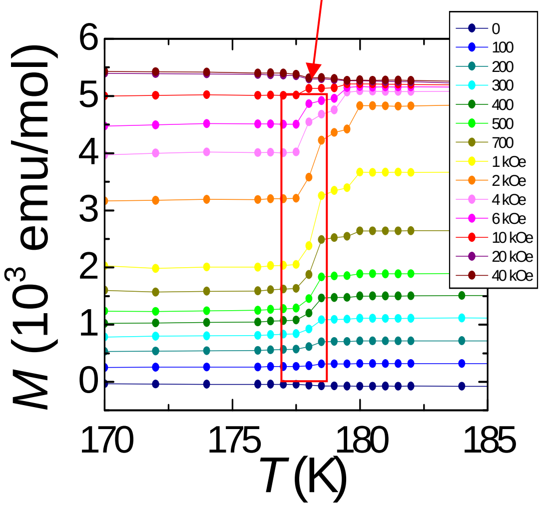


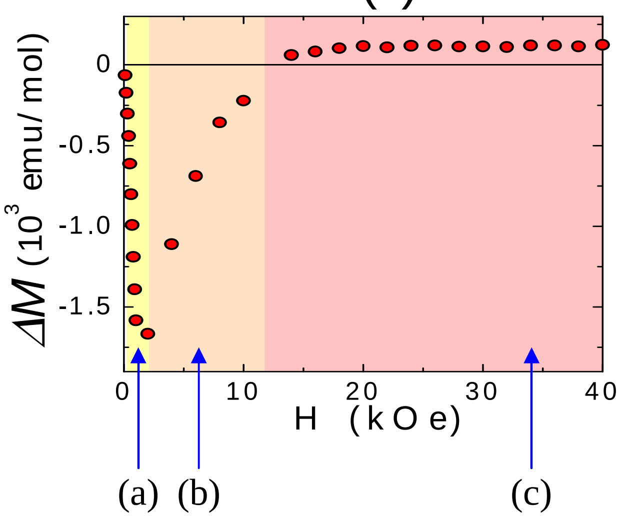
$$\langle \Delta S \rangle = \frac{1}{\Delta T} \int_{\Delta T} \Delta S(T,H)dH$$

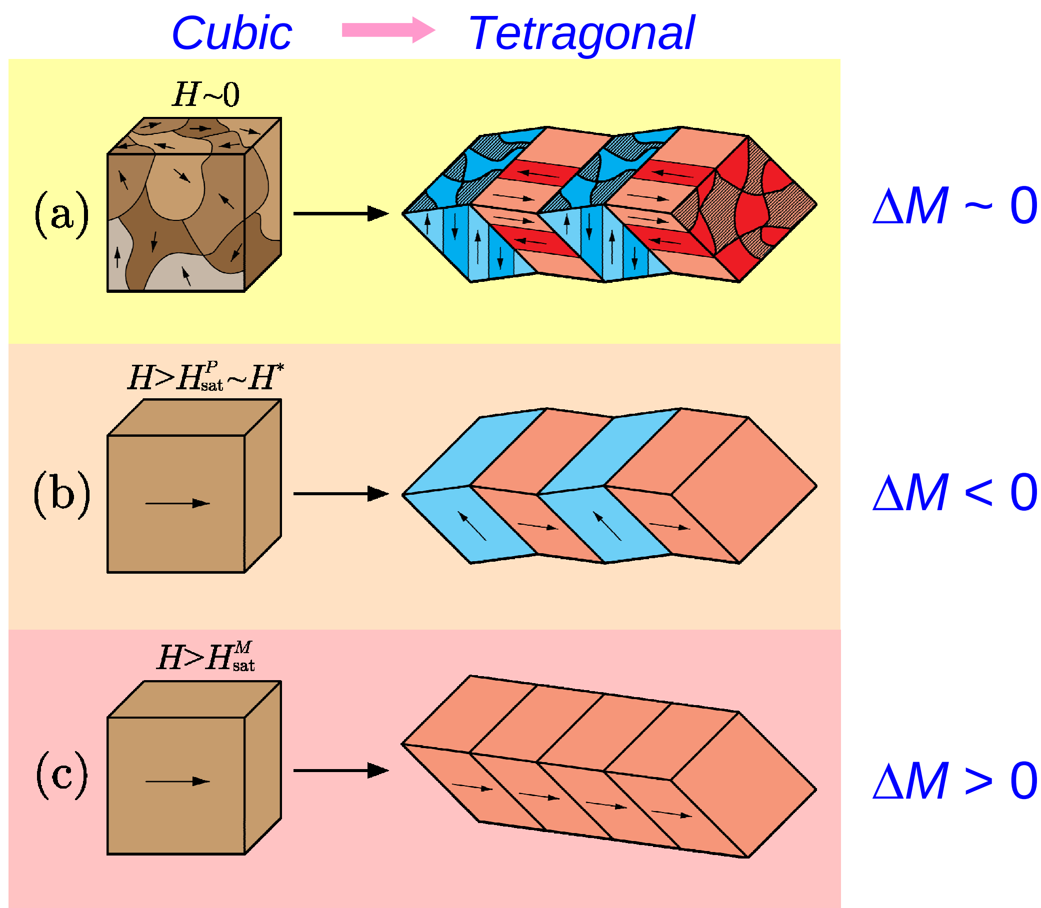
Inverse magnetocaloric effect!

Explanation

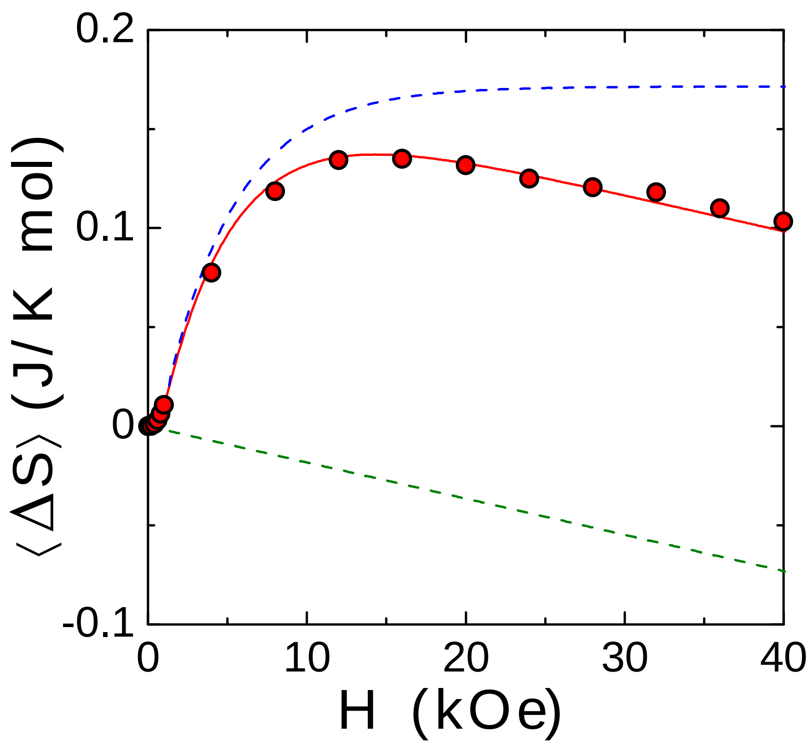
A region exists where $(\partial M/\partial T)_H > 0$







Contributions



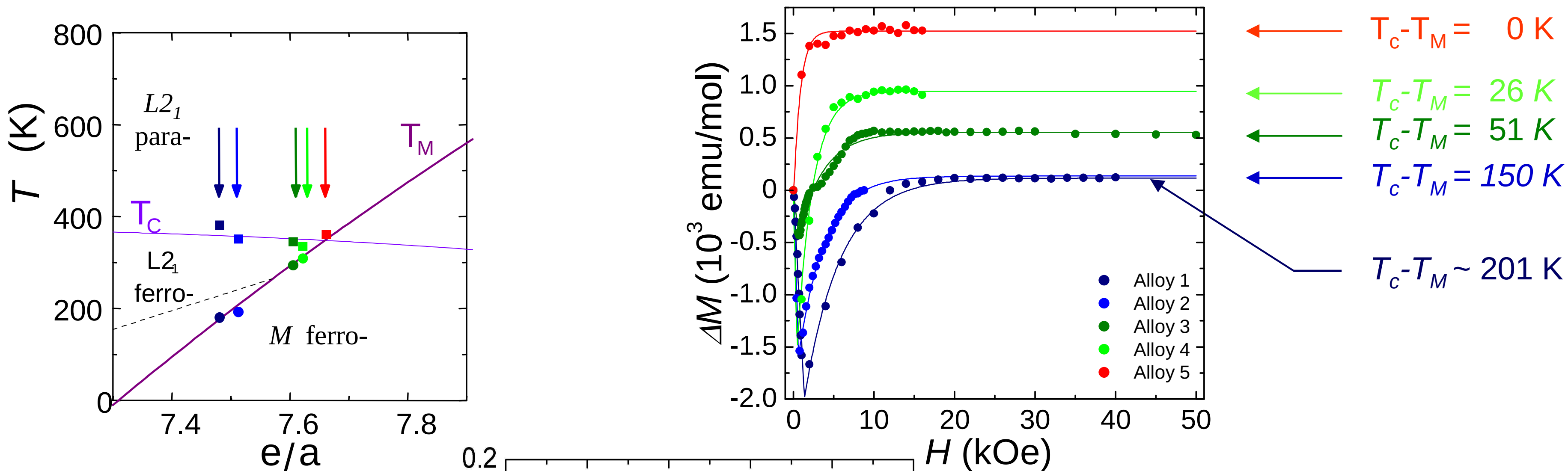
Low and intermediate fields: the dominant contribution is related to the **magnetostructural interplay at mesoscale** (magnetic anisotropy). Gives rise to an **inverse magnetocaloric effect**.

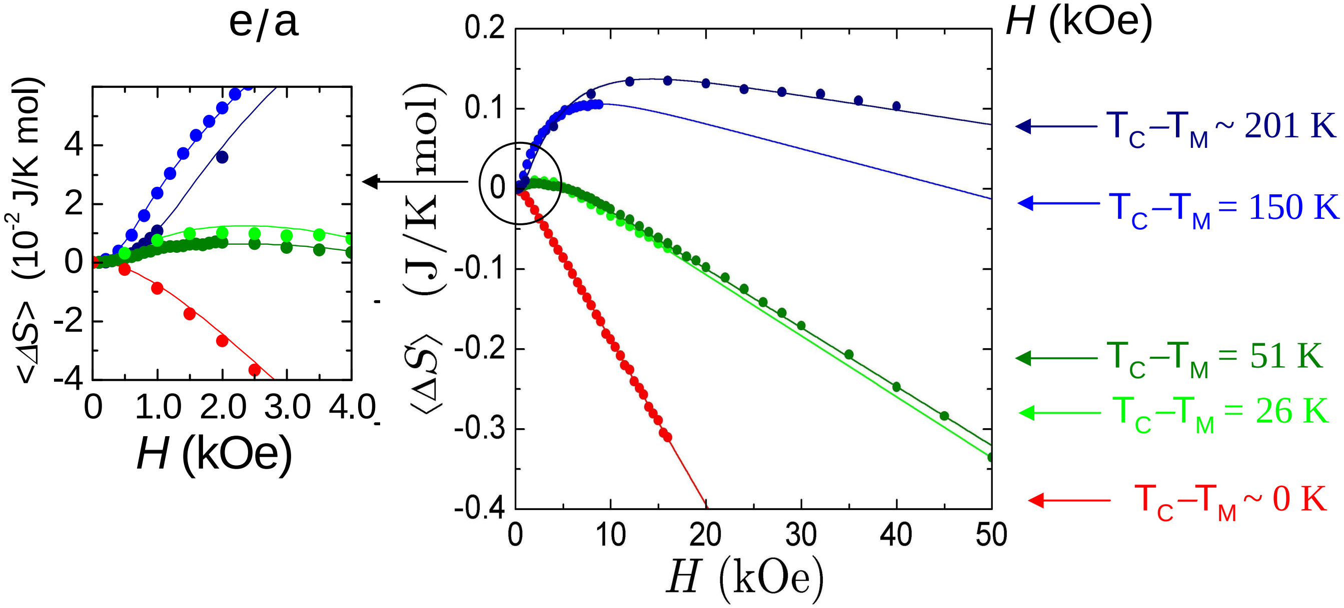
High fields: the dominant contribution is related to the **microscopic magnetostructural coupling** (change of T_M with an applied field). Gives rise to a **conventional magnetocaloric effect.**

Marcos et al., Phys. Rev. B, **68**, 094401 (2003)

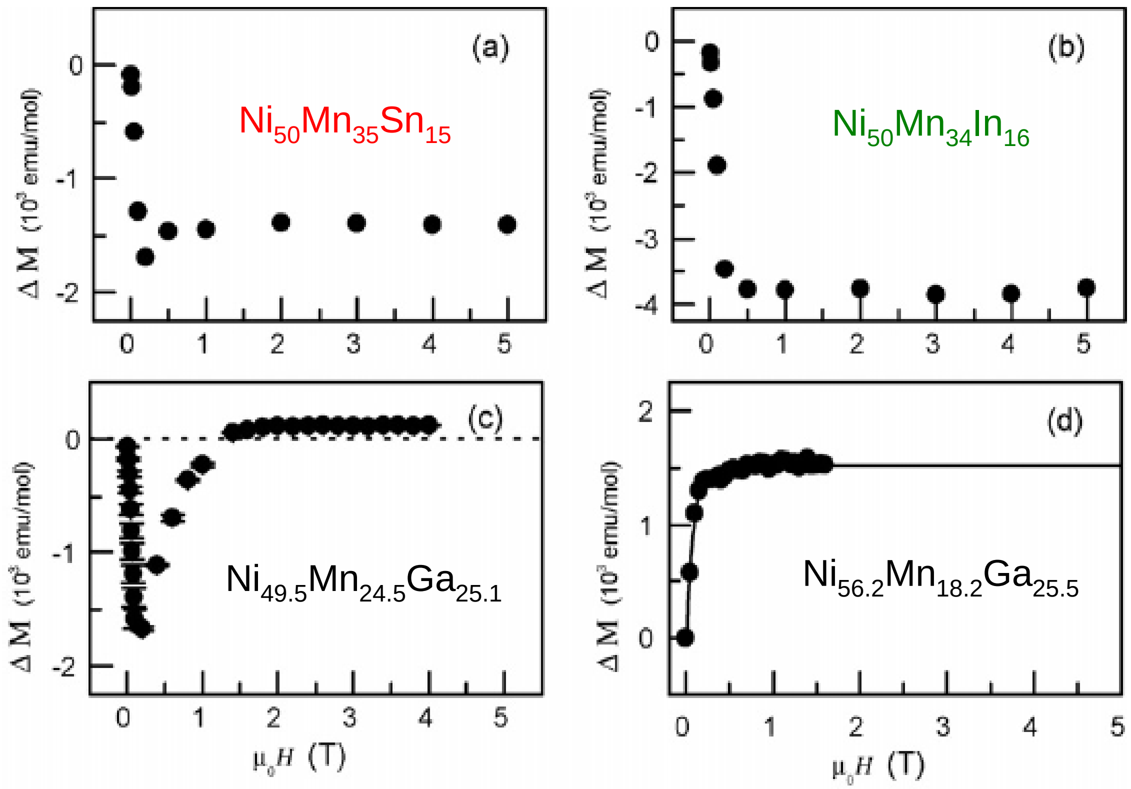
Effect of composition

Marcos et al., Phys. Rev. B, **68**, 094401 (2003)



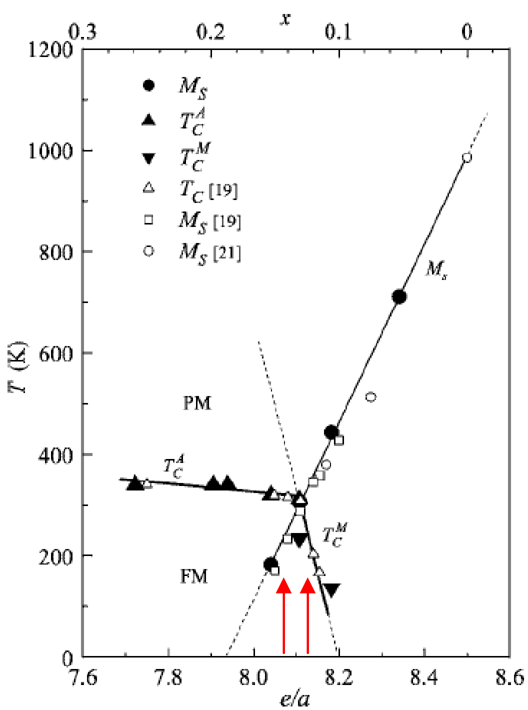


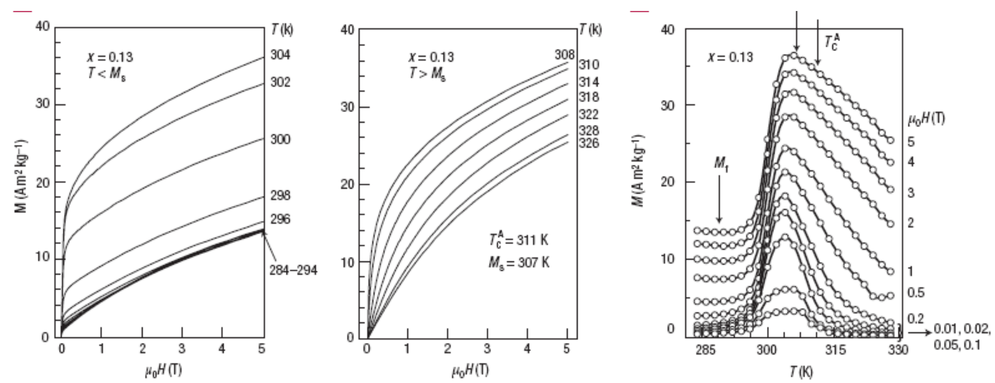
Other Heusler shape-memory alloy

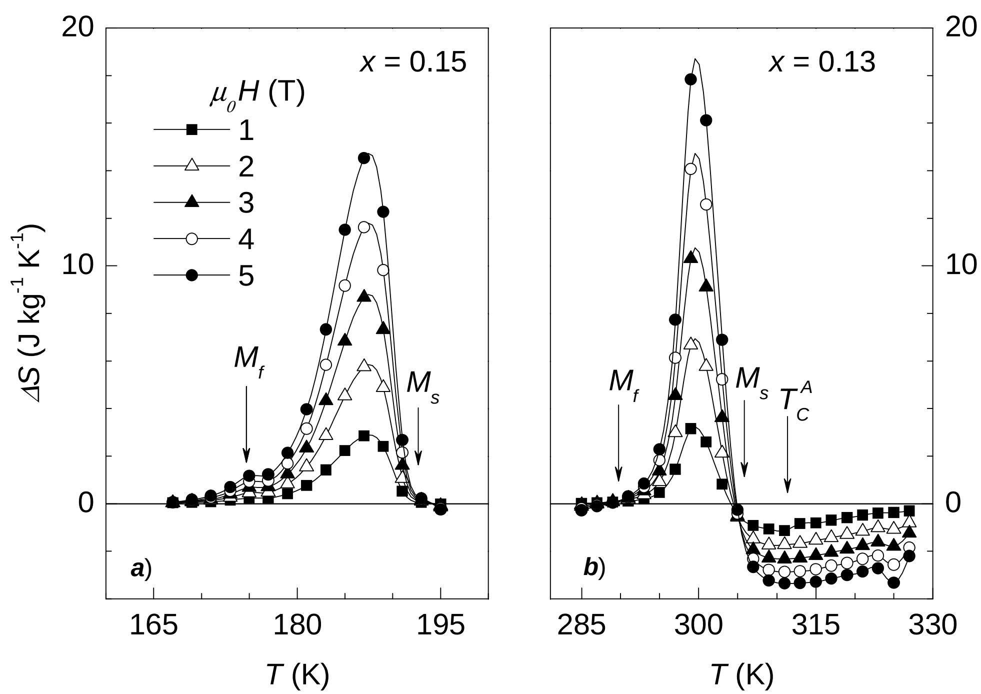


Results: Ni-Mn-Sn

Krenke et al., Nature Mater. 4, 450 (2005); Phys Rev. B, **72**, 014412 (2005)

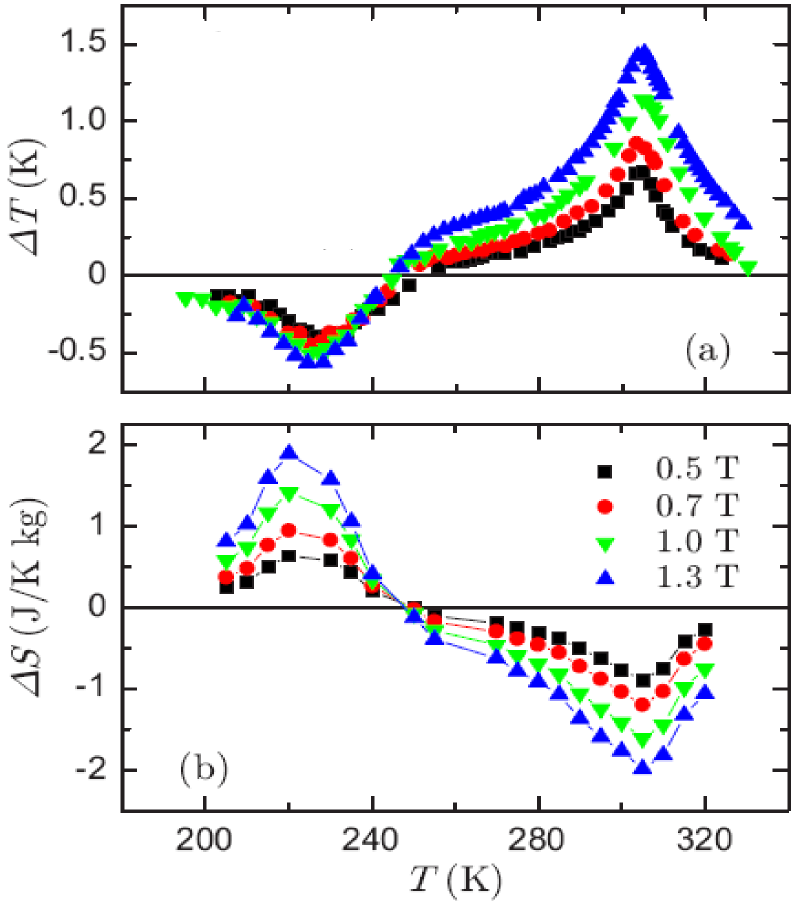






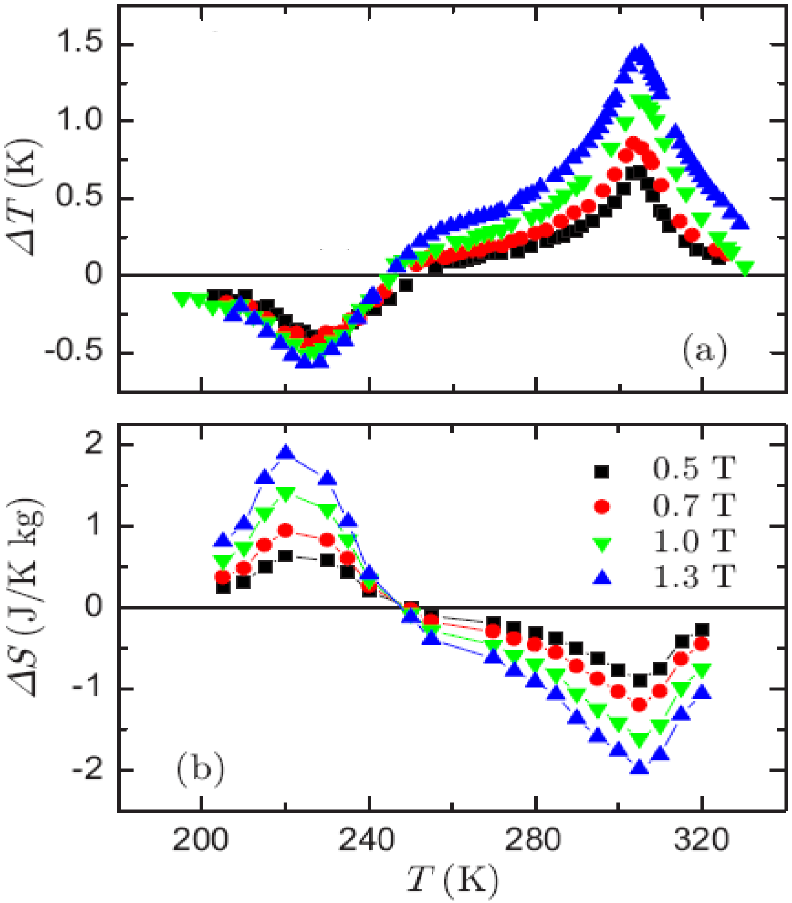
Results: Ni-Mn-In

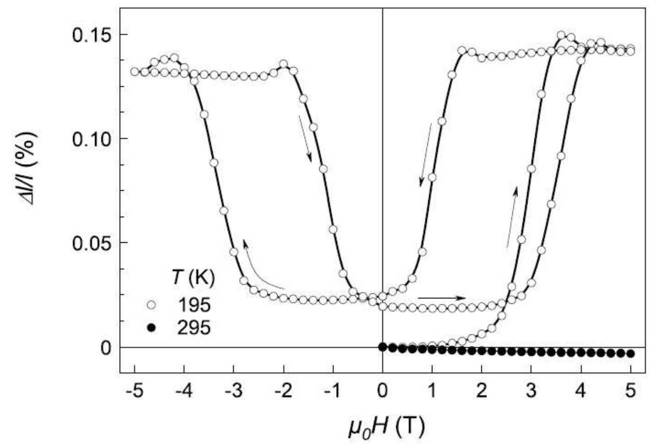
Moya et al., Phys. Rev. B, **75**, 184412 (2007); Krenke et al., Phys. Rev. B, **73**, 174413 (2006)

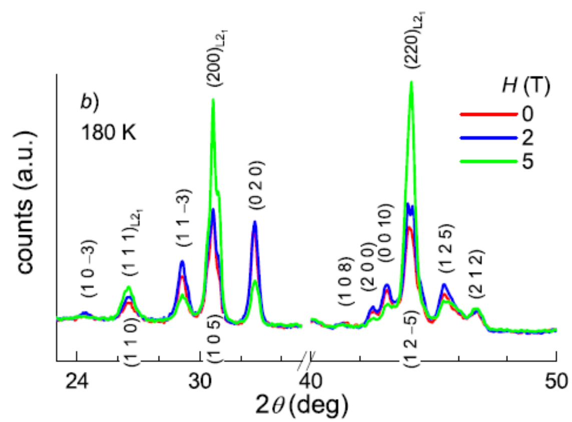


Results: Ni-Mn-In

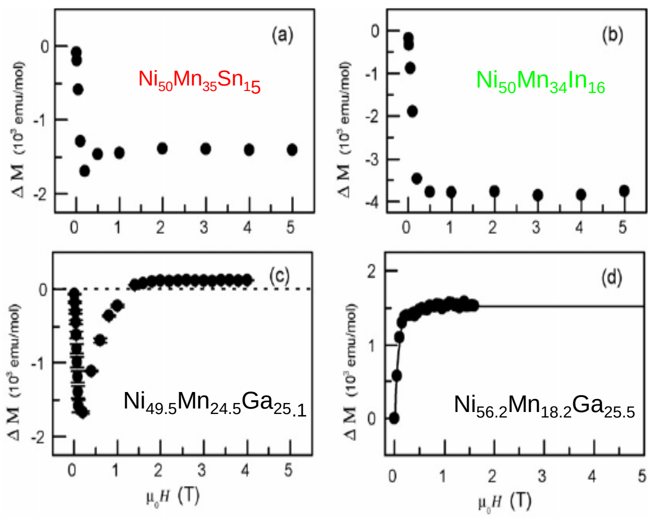
Moya et al., Phys. Rev. B, **75**, 184412 (2007); Krenke et al., Phys. Rev. B, **73**, 174413 (2006)



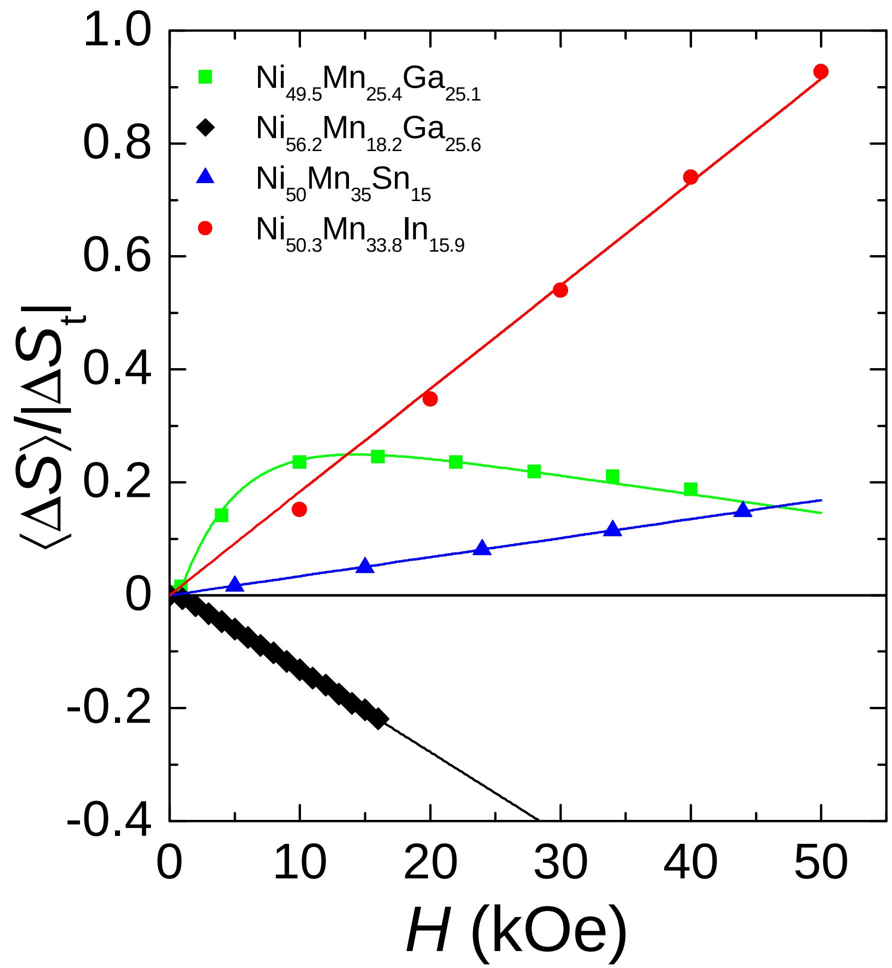




Comparison



(a)
Ni50Mn35Sn15
(b)
Ni50Mn34In16
(c)
Ni49.5Mn24.5Ga25.1
(d)
Ni56.2Mn18.2Ga25.5
Δ M (10³ emu/mol)
μ0H (T)



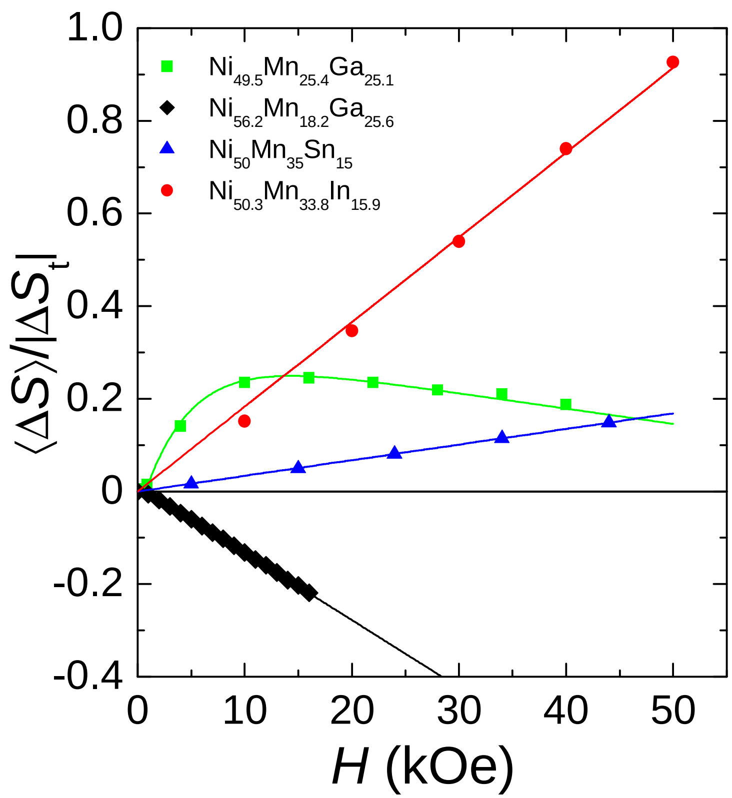
Ni49.5Mn25.4Ga25.1
Ni56.2Mn18.2Ga25.6
Ni50Mn35Sn15
Ni50.3Mn33.8In15.9
⟨ΔS⟩/|ΔSt|
H (kOe)

Magnetocaloric effect vs. Clausius-Clapeyron

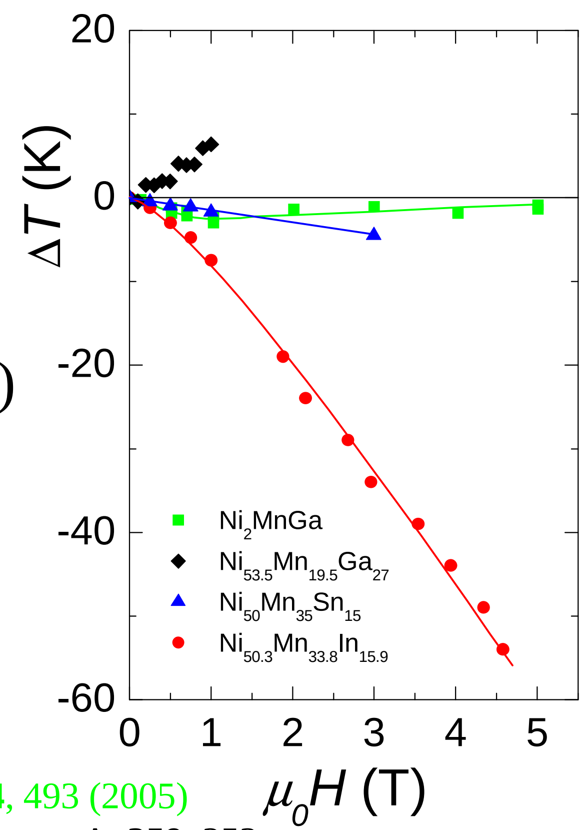
$$\langle \Delta S(H) \rangle = \frac{\mu_0}{\Delta T(H)} \int_{\Delta T} \Delta M(T,H)\, dT$$

$$\Delta T_t(H) = -\frac{\mu_0}{\Delta S_t(H)} \int_{\Delta T} \Delta M(T,H)\, dT$$

ΔS_t independent of H



$$\frac{\langle \Delta S(H) \rangle}{\Delta S_t(H)} \propto -\Delta T_t(H)$$



Kim et al., Acta Mater., **54**, 493 (2005)
Jeong et al., Mater. Sci. Engng. A, **359**, 253 (2003)

Conclusions

- Heusler alloys show large magnetocaloric effect in the vicinity of the martensitic transition.
- The physics of magnetocaloric effect is controlled by the behaviour of the magnetization change at the transition.
- In nearly stoichiometric Ni_2MnGa inverse magnetocaloric effect occurs at low applied fields due to the high magnetic anisotropy of the martensitic phase.
- In non-stoichiometric Ni-Mn-Sn and Ni-Mn-In giant inverse magnetocaloric effect is a consequence of the tendency of the excess of Mn atoms to introduce antiferromagnetic coupling.

Dissipative effects

Moya et al., Phys. Rev. B, **75**, 184412 (2007)

$$\oint \frac{\delta q}{T} \leq 0 \quad \Rightarrow \quad \frac{\delta q}{T} = dS - \delta S_i$$

$0 \rightarrow H$: Adibatic change of T

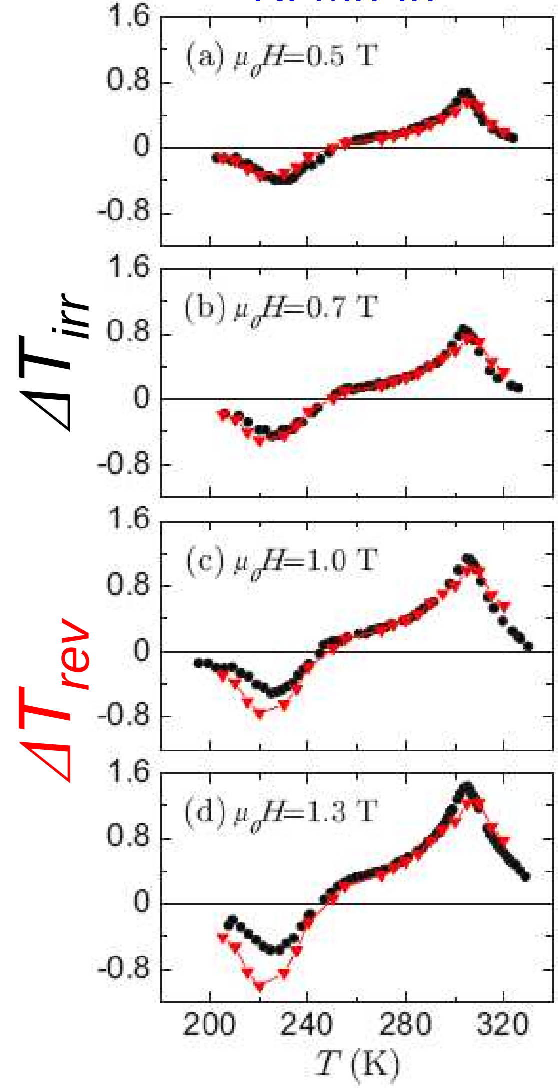
$$\Delta T_{rev} = -\frac{T}{C}\Delta S$$

$$\Delta T_{irr} = -\frac{T}{C}\Delta S + \frac{TS_i}{C}$$

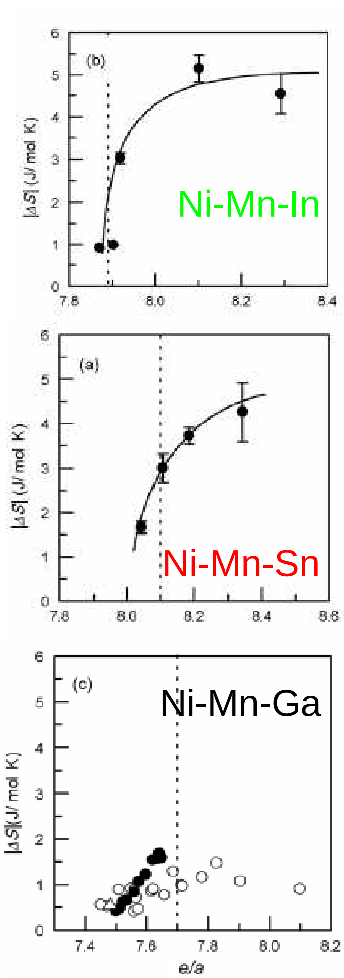
where

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

Ni-Mn-In



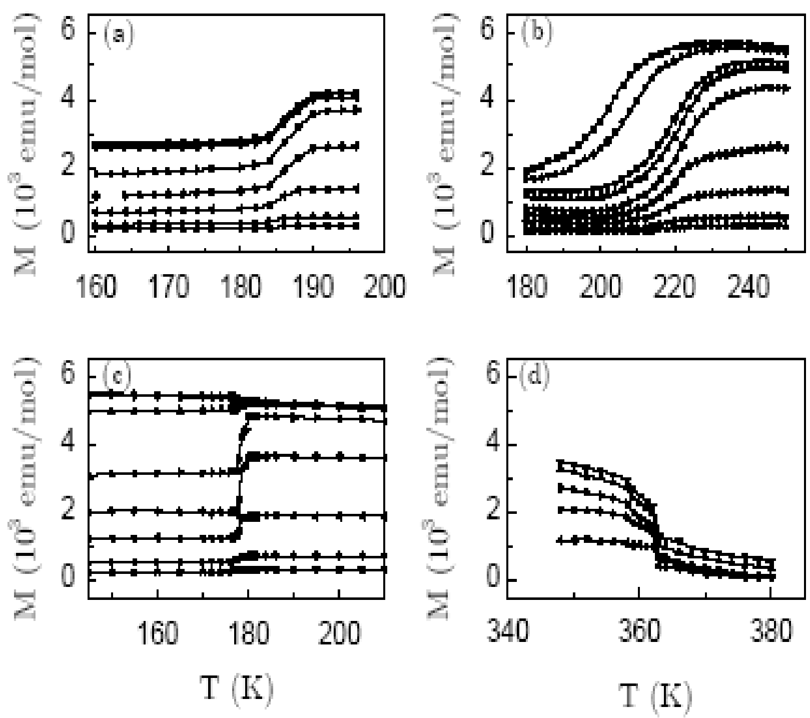
Entropy and magnetization change



Moya et al., Mat. Sci. Engn. A 438 (2006) 913

$Ni_{50}Mn_{35}Sn_{15}$
Krenke et al
Phys.Rev.B
72 (2005) 14412

$Ni_{50}Mn_{34}In_{16}$
Krenke et al
Phys. Rev B
73(2006) 174413



$Ni_{49.5}Mn_{24.5}Ga_{25.1}$
Marcos et al.,
Phys.Rev.B **66**(2002) 224413

$Ni_{56.2}Mn_{18.2}Ga_{25.5}$
L. Pareti et al.,
Eur. Phys.J B **32**(2003) 303