

# From Sensitivity to Tunability in CoMnSi-based magnetocaloric compounds

A new family of potential magnetocaloric materials

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# Outline

- 1 Introduction
  - Motivation
  - Inverse/negative magnetocaloric effect
  - Thermodynamic quantities describing the magnetocaloric effect
  - The magnetocaloric effect in metamagnets
- 2 CoMnSi-based metamagnets
  - CoMnSi
  - $\text{CoMnSi}_{1-x}\text{Ge}_x$
  - $\text{CoMn}_{1-x}\text{Ni}_x\text{Si}$
- 3 Summary and Outlook

# Why use Mn based alloys?

Mn based compounds are:

- relatively cheap
- environmentally friendly (not all of them)
- show first-order phase transitions (as well as higher order)
  - MnAs <sup>1)</sup>,  $T_C = 318 \text{ K}$ ,  $\Delta S_M = -32 \text{ J kg}^{-1} \text{ K}^{-1}$  in 5 T
  - Mn<sub>1.1</sub>Fe<sub>0.9</sub>P<sub>0.47</sub>As<sub>0.53</sub> <sup>2)</sup>:  $T_C \simeq 310 \text{ K}$ ,  $\Delta S_M = -20 \text{ J kg}^{-1} \text{ K}^{-1}$  in 5 T
  - Ni<sub>0.5</sub>Mn<sub>0.5-x</sub>Sn<sub>x</sub> <sup>3)</sup>:  $T_t \simeq 300 \text{ K}$ ,  $\Delta S_M = 18 \text{ J kg}^{-1} \text{ K}^{-1}$  in 5 T  
( $x=0.13$ )
  - Mn<sub>3</sub>GaC <sup>4)</sup>:  $T_t = 164 \text{ K}$ ,  $\Delta S_M = 12 \text{ J kg}^{-1} \text{ K}^{-1}$  in 5 T
- properties are tunable by substitution of elements
  - exchange interactions between Mn-Mn are crucial for magnetism of Mn-based compounds

<sup>1)</sup> Wada H, *Appl. Phys. Lett.* **79** 3302-3304 (2001)

<sup>2)</sup> Tegus O, *J. Magn. Magn. Mater.* **272** 2389-2390 (2004)

<sup>3)</sup> Krenke T, *Nature Mat.* **4** 450-454 (2005)

<sup>4)</sup> Tohai T, *J. Appl. Phys.* **94** 1800-1802 (2003)

# Studied inverse MCE materials

- $\text{Mn}_2\text{Sb}$  <sup>1)</sup> is ferrimagnet with  $T_C=550$  K
  - two Mn sites with different magnetic moments
  - substitution of Mn with Cr/V leads to first order antiferro- to ferrimagnetic transition
    - $\text{Mn}_{1.95}\text{Cr}_{0.05}\text{Sb}$  <sup>2)</sup>:  $\Delta S_M = 7 \text{ J kg}^{-1} \text{ K}^{-1}$  in 5 T at  $\sim 198$  K
    - $\text{Mn}_{1.82}\text{V}_{0.18}\text{Sb}$  <sup>3)</sup>:  $\Delta S_M = 5.5 \text{ J kg}^{-1} \text{ K}^{-1}$  in 5 T at  $\sim 280$  K
- $\text{Fe}_{0.49}\text{Rh}_{0.51}$  <sup>4)</sup>:
  - highest observed inverse MCE of  $20 \text{ J kg}^{-1} \text{ K}^{-1}$  at  $\Delta H = 1.95$  T
  - MCE declines when material is cycled through phase transition

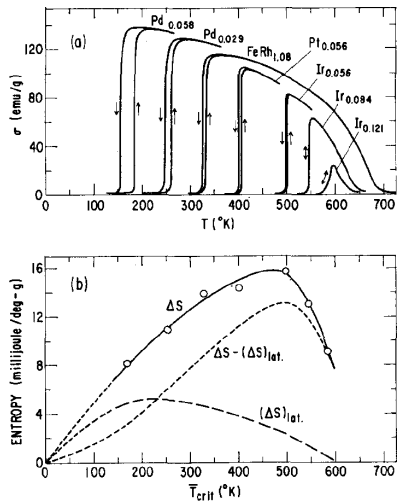
1) Wijngaard J H, *Phys. Rev. B* **45** 5395-5405 (1992) (and references therein)

2) Tegus O, *Physica B* **319** 174-192 (2002)

3) Zhang Y Q, *J. Alloys and Compounds* **365** 35-38 (2004)

4) Annaorazov et al. *J. Appl. Phys.* **79** 1689 (1996)

# Inverse MCE in FeRh



- first order magnetostructural phase transition from antiferro- to ferromagnetic state at 330 K for FeRh
- development of magnetic moment on Rh at the phase transition
- crystal volume changes at the phase transition  $\sim 0.3\%$  [2]
- spontaneous magnetostriction is a measure for lattice entropy contributions

Kouvel J S *J. Appl. Phys.* **37** 1257 (1966)  
 Annaorazov et al. *J. Appl. Phys.* **79** 1689 (1996)

## Isothermal entropy change $\Delta S_T$ and adiabatic temperature change $\Delta T_{ad}$

$$\Delta S_T = \int_{H_1}^{H_2} \left( \frac{\partial M}{\partial T} \right)_{p,H} dH$$

$$\Delta T_{ad} = \int_{H_1}^{H_2} -\frac{T}{C_{H,p}} \left( \frac{\partial M}{\partial T} \right)_{p,H} dH$$

- $\Delta T_{ad}$  and  $\Delta S_T$  are large near a phase transition,
- the sharper the phase transition the larger  $\Delta T_{ad}$  and  $\Delta S_T$ ,
- $\Delta T_{ad}$  and  $\Delta S_T$  are larger for higher magnetic fields.

For application in a room temperature magnetic refrigerator materials should have

- phase transitions around room temperature and a large MCE,
- phase transition that can be induced in small magnetic fields,
- should be environmentally friendly and cheap.

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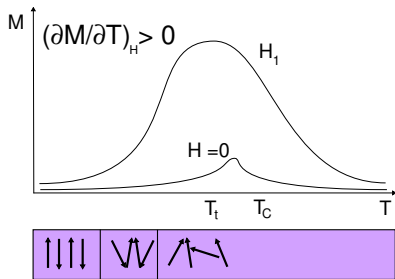
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# Metamagnets as refrigerants



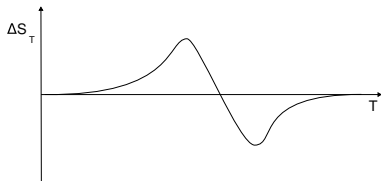
Remember:

$$\Delta T_{ad} = \int_{H_1}^{H_2} -\frac{T}{C_{H,p}} \left( \frac{\partial M}{\partial T} \right)_{p,H} dH$$

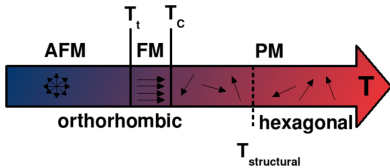
$$\Delta S_T = \int_{H_1}^{H_2} \left( \frac{\partial M}{\partial T} \right)_{p,H} dH$$

At a metamagnetic transition

- $\Delta S_T$  is positive,
- $\Delta T_{ad}$  is negative.



# The metamagnet – CoMnSi

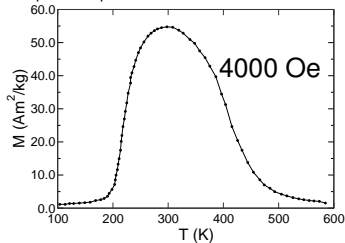


There are 3 phase transitions in CoMnSi

- antiferro- to ferromagnetic (metamagnetic) phase transition at  $T_t = 200 - 360$  K,
- ferro- to paramagnetic phase transition at  $T_c \simeq 410$  K,
- orthorhombic to hexagonal structural phase transition at  $T_{\text{structural}} = 917$  °C.

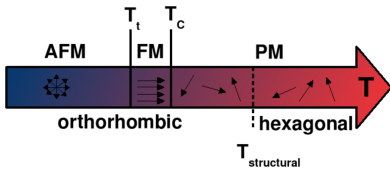
! phase transition temperatures are very sample dependent !

sample was quenched from 1000 °C



Bińczycka et al., phys. stat. sol. (a) **35** K69 (1976)  
 Johnson et al., phys. stat. sol (a) **20** 331 (1973)  
 Nizioł et al., phys. stat. sol. (a) **45** 591 (1978)

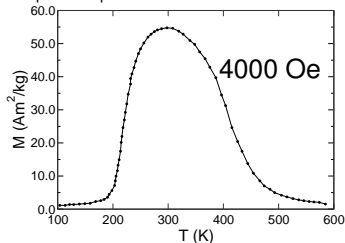
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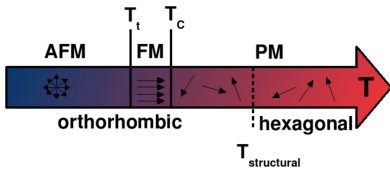
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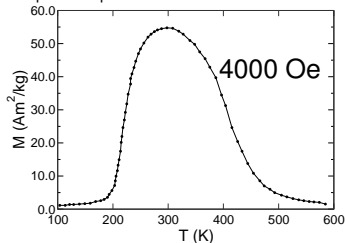


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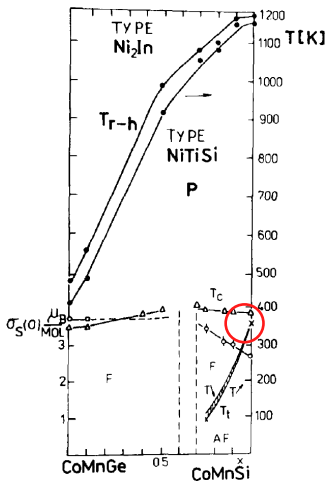
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 Johnson et al., phys. stat. sol (a) **20** 331 (1973)  
 Nizioł et al., phys. stat. sol. (a) **45** 591 (1978)

# CoMnSi<sub>1-x</sub>Ge<sub>x</sub>-system

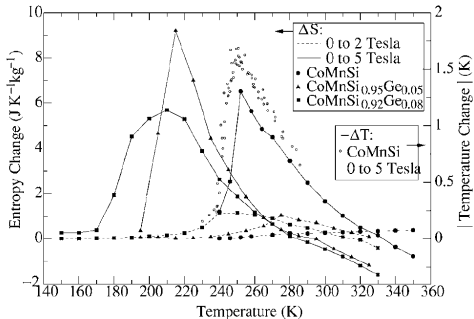
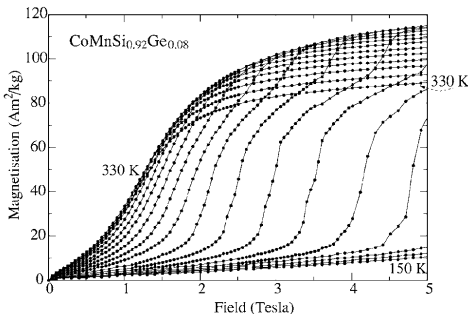


Objectives in making CoMnSi<sub>1-x</sub>Ge<sub>x</sub>:

- change sample composition and gain control over  $T_t$
- separate  $T_t$  and  $T_c$
- measure the magnetocaloric effect

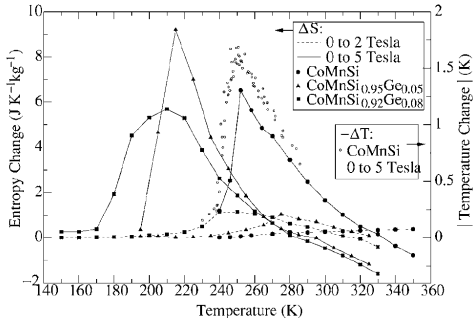
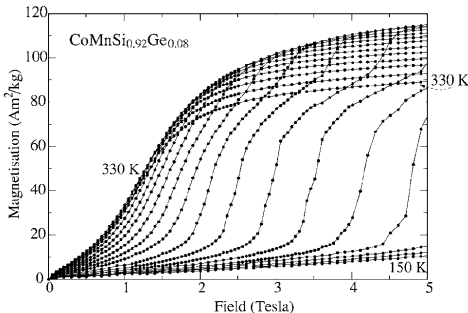
Niziol et al., J. Magn. Magn. Mat. **79** 333-337 (1989)

# Magnetization $M(H)$ and MCE of CoMnSi<sub>1-x</sub>Ge<sub>x</sub>



- Ge substitution decreases the metamagnetic transition temperature
- transition is sharpest in CoMnSi<sub>0.95</sub>Ge<sub>0.05</sub> yielding  $\Delta S_T = 9 \text{ J kg}^{-1} \text{ K}^{-1}$  at  $\Delta H = 5 \text{ T}$
- change of sign around room temperature

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interested in the microscopic magnetization? – see next talk by Kelly Morrison

# CoMn<sub>1-x</sub>Ni<sub>x</sub>Si – Aims

Objectives of making Ni substituted CoMn<sub>1-x</sub>Ni<sub>x</sub>Si are

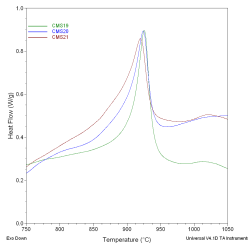
- increase  $T_C$ , far away from  $T_t$
- tune  $T_t$  near room temperature
- obtain large values for  $\Delta T_{ad}$  and  $\Delta S_T$
- get single phase material

# Synthesis and characterization of CoMn<sub>1-x</sub>Ni<sub>x</sub>Si

- quasi contact free co-melting of elements in an induction furnace,
- subsequent annealing of ingots in a box furnace at 1123 - 1373 K,
- measurement of structural transition temperatures with calorimetry,
- determination of crystal structure with X-ray powder diffraction,
- magnetic measurements with VSM and SQUID

# High temperature structural transition temperatures

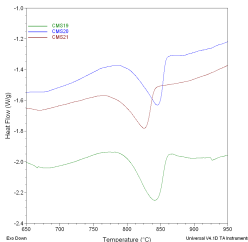
heating:



Thermal analysis (SDT) signals for heating (upper figure) and cooling (lower figure):

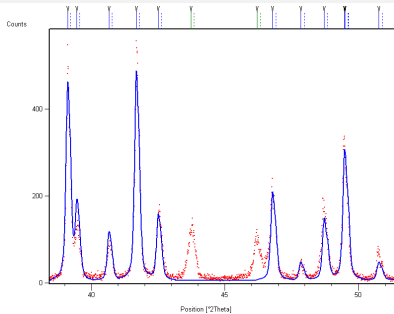
Ni (%)	$T_{\text{struc}}^{\text{heating}}$	$T_{\text{struc}}^{\text{cooling}}$	$\Delta T_{\text{struc}}$
7	926	842	84
9	924	846	78
11	920	826	94

cooling:

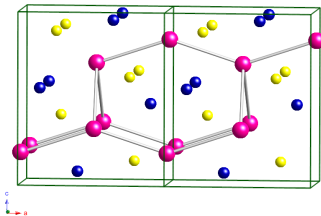


- value of  $T_{\text{struc}}$  is important to choose annealing conditions
- three different hold temperatures were chosen (850°C, 950°C, 1100°C)
- all samples were slowly cooled

# Crystal structure of CoMn<sub>1-x</sub>Ni<sub>x</sub>Si



ac-plane viewed along b-axis of the orthorhombic unit cell  
Mn (pink), Co (blue), Si (yellow)

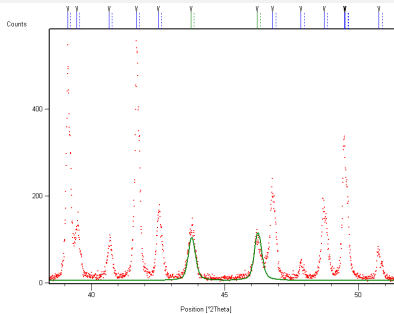


- orthorhombic Pnma phase with TiNiSi-type structure
- $a=5.83 \text{ \AA}$ ,  $b=3.68 \text{ \AA}$ ,  $c=6.86 \text{ \AA}$
- atoms in Wyckoff pos.  $4c (x, \frac{1}{4}, z)$

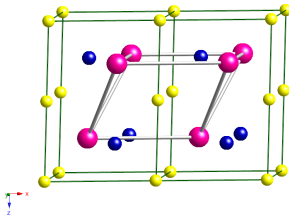
atom	x	y	z
Co	0.159(1)	0.250000	0.559(1)
Mn	0.015(2)	0.250000	0.184(1)
Ni	0.015(2)	0.250000	0.184(1)
Si	0.773(3)	0.250000	0.620(2)

not all reflections belong to the space group Pnma

# Second hexagonal crystallographic phase

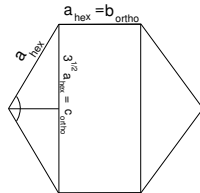


ac-plane viewed along b-axis of the orthorhombic unit cell  
 Mn in  $(\frac{1}{3}, \frac{2}{3}, \frac{3}{4})$  (pink), Co in  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$  (blue), Si in  $(0, 0, 0)$  (yellow)



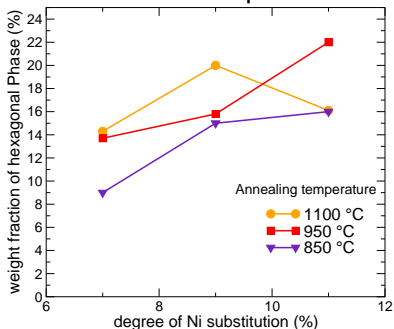
axis-transformation during orthorhombic to hexagonal unit cell transition:

- high temperature hexagonal structure is metastable at room temperature
- hexagonal P6<sub>3</sub>/mmc phase with Ni<sub>2</sub>In type
- $a=3.93 \text{ \AA}$ ,  $c=5.22 \text{ \AA}$

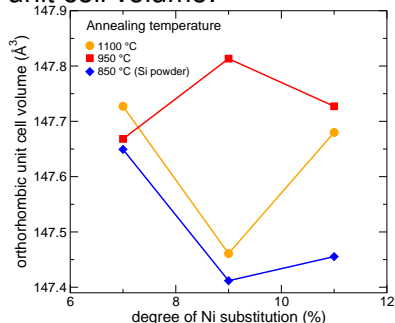


# A metastable high temperature hexagonal phase

amount of second phase:

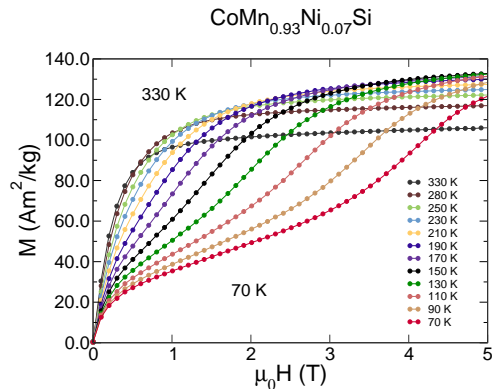


unit cell volume:



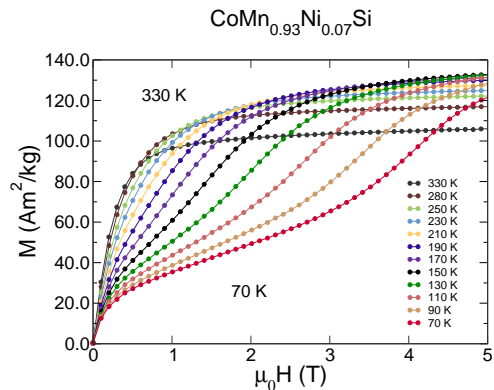
- annealing at a temperature below  $T_{\text{struc}}$  for a long time (200 h) decreases the weight fraction of second phase
- samples annealed away from  $T_{\text{struc}}$  show similar behaviour of unit cell volume versus Ni concentration

# Magnetization $M(H)$ of CoMn<sub>1-x</sub>Ni<sub>x</sub>Si at low temperatures



- sample was annealed at 950°C
- at low temperatures there are two regions where magnetization changes
- metamagnetic phase transition at  $\sim 3$  T

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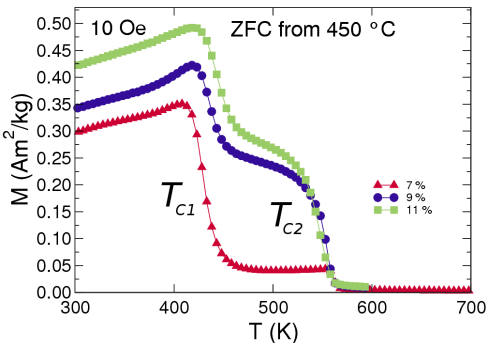


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Does the second phase have an influence on  $M(H)$ ?

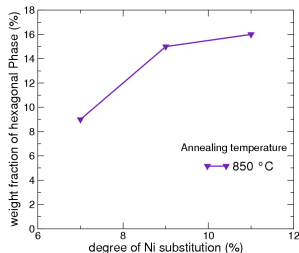
# Curie transitions above room temperature

samples annealed at 850 °C



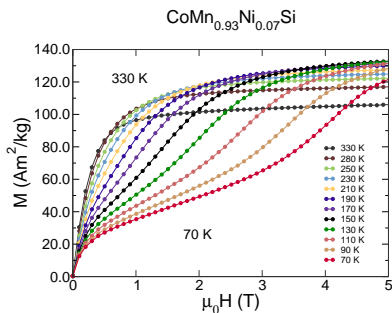
Ni (%)	$T_{C1}$ (K)
7	431
9	437
11	445

- two transitions at temperatures above room temperature
- relative drop of magnetization above  $T_{C1}$  corresponds to the amount of second phase
- $T_C$  increases with Ni content



# The magnetocaloric effect in CoMn<sub>1-x</sub>Ni<sub>x</sub>Si

magnetisation data

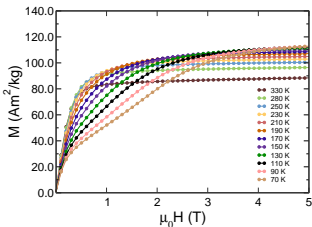
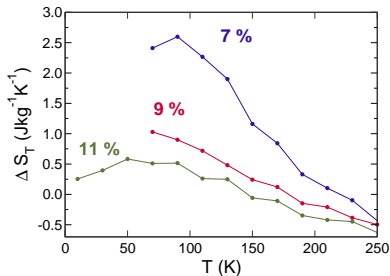
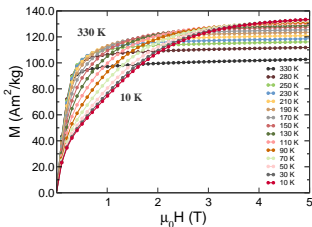


- second hexagonal phase was identified to be ferromagnetic.
- magnetic field induced metamagnetic phase transition at  $\sim 3$  T (70 K).
- from  $M$  versus  $T$  curves:  $T_t$  around 170 K in 1 T.
- $T_C$  of both phases are above 430 K

isothermal magnetisation versus magnetic field curves were used to calculate the magnetocaloric effect

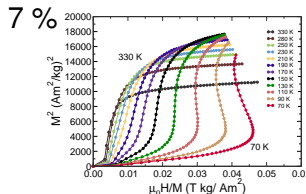
# The magnetocaloric effect in CoMn<sub>1-x</sub>Ni<sub>x</sub>Si

Temperature dependence of  $\Delta S_T$  at various Ni concentrations

CoMn<sub>0.91</sub>Ni<sub>0.09</sub>SiCoMn<sub>0.89</sub>Ni<sub>0.11</sub>Si

- maximal entropy change  $\sim 2.5$  J/kgK in a magnetic field change from 0 - 5 T at  $\sim 100$  K
- $\Delta S_T$  decreases with Ni concentration
- ferromagnetic background of second phase has negative influence

# Order of the metamagnetic phase transition



around phase transitions thermodynamic potentials can be expanded in a Taylor series with respect to the order parameter:

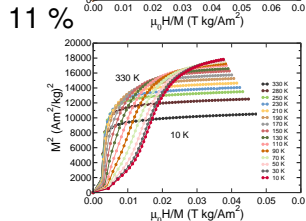
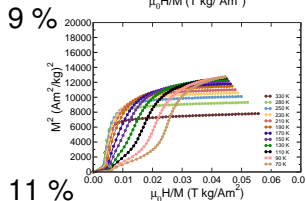
$$\Phi = \Phi_0 + aM^2 + bM^4 - MH$$

at equilibrium ( $\partial\Phi/\partial M = 0$ ):

$$\alpha M + \beta M^3 = H \longrightarrow \frac{H}{M} = \alpha + \beta M^2$$

$$\beta \begin{cases} \geq 0, & \text{higher order phase transitions} \\ < 0, & \text{first order phase transitions} \end{cases}$$

Banerjee S K, Phys. Lett. **12** 16 (1964)



# Summary

- Samples of  $\text{CoMn}_{1-x}\text{Ni}_x\text{Si}$  with  $x = 0.07, 0.09, 0.11$  were synthesised.
- A second ferromagnetic phase was identified and partial control over it was obtained.
- Maximum  $\Delta S_T$  of 2.5 J/kgK at 100 K in 5 T was calculated from isothermal  $M(H)$  curves.

# Conclusion and further work

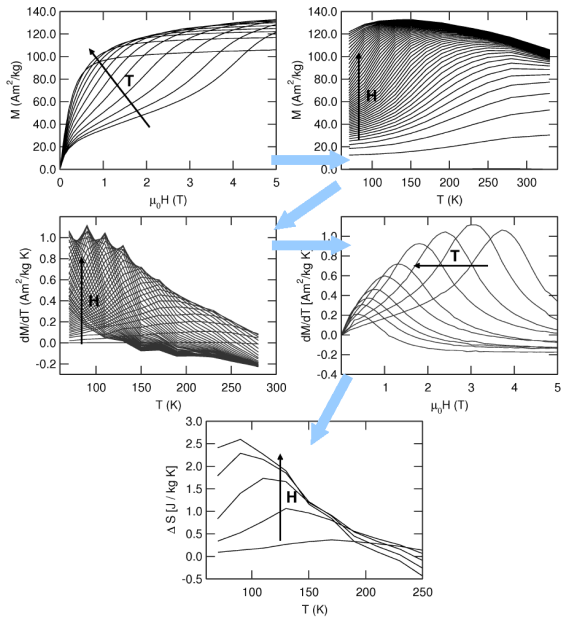
- Values for  $\Delta S_T$  are too small at a too low temperature for room temperature applications.
- Second phase broadens the metamagnetic phase transition and decreases the magnetocaloric effect.
- Further work
  - Employment of element and crystallographic phase specific experimental techniques to study the influence of the second phase (SEM with EBSD, XPEEM).
  - Try other substitutions (e.g. Ni on the Co site and Cr on the Mn site).

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# Acknowledgements

- Karl G. Sandeman for supervising me and my work.
- Sibel Özcan for sample synthesis.
- Mary E. Vickers and Andrew Moss for a lot of help with X-ray diffraction and data analysis.
- EPSRC and Camfridge Ltd. for funding.



# Peculiarities of spin and crystal structure

PHYSICAL REVIEW B 71, 174420 (2005)

## Cycloidal magnetic order in the compound IrMnSi

T. Eriksson,<sup>1</sup> L. Bergqvist,<sup>2</sup> T. Burkert,<sup>2</sup> S. Felton,<sup>3</sup> R. Tellgren,<sup>1</sup> P. Nordblad,<sup>3</sup> O. Eriksson,<sup>2</sup> and Y. Andersson<sup>1</sup>

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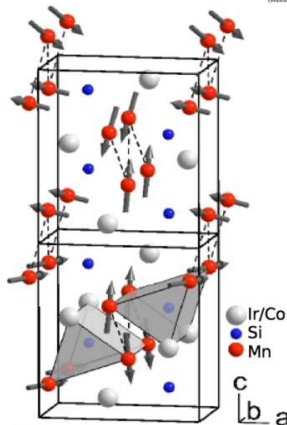
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compare...

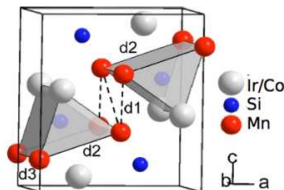
$$\mu_{\text{Mn}} \sim 2.2 - 2.6 \mu_{\text{B}}$$

$$\mu_{\text{Co}} \sim 0.2 - 0.4 \mu_{\text{B}}$$



27	Co	Cobalt	58.933200
45	Rh	Rhodium	102.90550
77	Ir	Iridium	192.222

	Vol (Å <sup>3</sup> )	T <sub>N</sub> or T <sub>i</sub> (K)	T <sub>c</sub> (K)
CoMnSi	148.2	381	420
RhMnSi	168.0	367	N/A
IrMnSi	173.0	460	N/A



In IrMnSi, Q is close to 0.45 in c-direction. For CoMnSi, Q is  $\sim 0.34$  in c

