Effect of Ni doping on the Structural, Electronic and Magnetic Properties of the $Mn_{54}Al_{46}$ Alloy

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Outline

1. Introduction
2. Experimental and Computational Details
3. Results and Discussions
4. Conclusions

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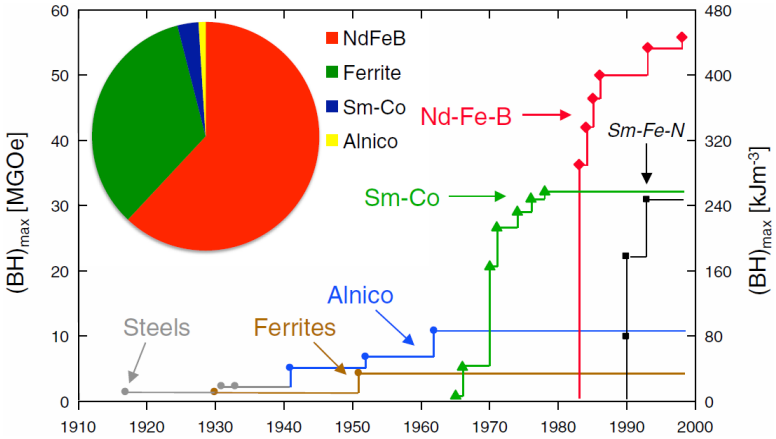
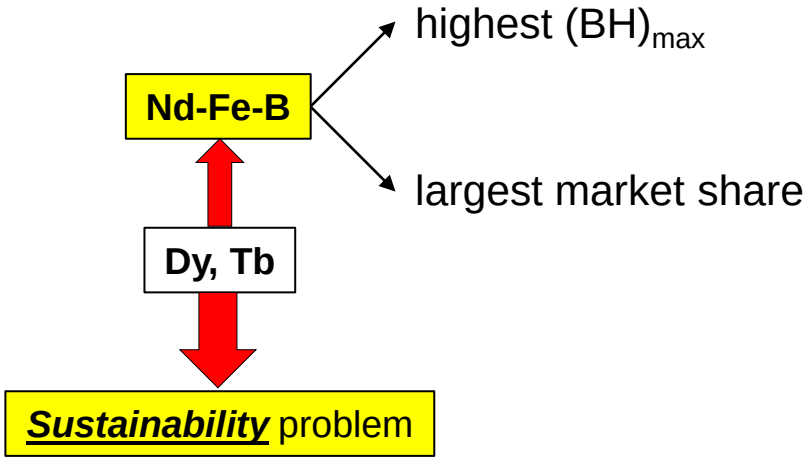


[1] O. Gutfleisch et al., *Adv. Mater.*, **23**, 821 (2011).
[2] R. Stamps et al., *J. Phys. D: Appl. Phys.*, **47**, 333001 (2014).



Rare earth (RE) price increase [3]:

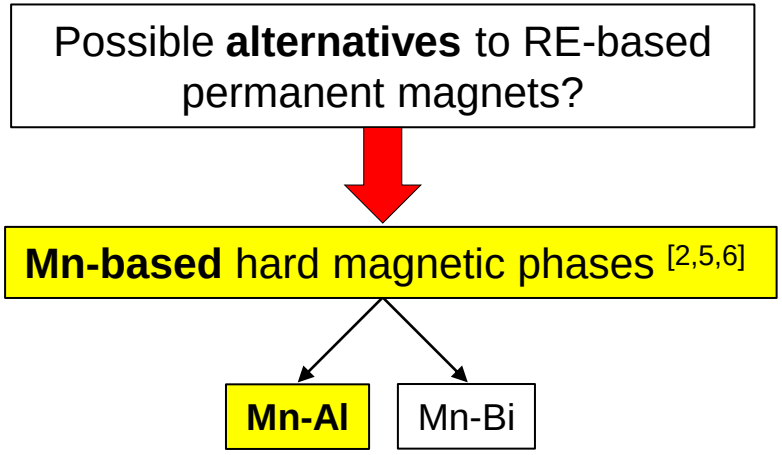
Nd: 40$/kg (2010) ➡ **500$/kg (2011)**

Dy: 260$/kg (2010) ➡ **3000$/kg (2011)**

Projected RE demand over the next 25 years [3,4]:

Nd: **700%**

Dy: **2600%**



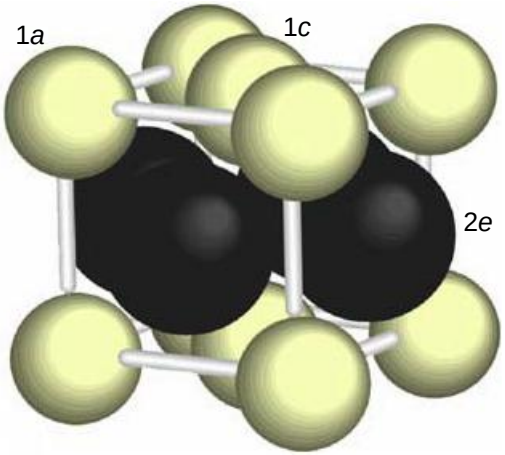
[3] L. Baldi et al., *Energy Policy*, **66**, 53 (2014)
[4] E. Alonso et al., *Environmental Science & Technology*, **46**, 3406 (2012)

[5] J. M. D. Coey, *Scripta Mater.*, **67**, 524 (2012)
[6] P. Manchanda et al., *J. Magn. Magn. Mater.*, **365**, 88 (2014)

τ-phase Mn-Al → *metastable phase* first reported by Kono in 1958 [7]
most **stable** composition: **$Mn_{54}Al_{46}$**

rapidly quenched **ε** phase + annealing around 500 ºC [7-9]

tetragonal $L1_0$ structure



[11] D.E. Laughlin et al., *Scripta Mater.*, **53**, 383 (2005)

Mn: 1*a*, 1*c*

Al: 2*e*

τ-phase $Mn_{54}Al_{46}$

T_c = 650 K [10]
M_s = 126 Am^2/kg [9]
$(BH)_{max}$ = 112 KJ/m^3 [5]
$\mu_0 H_c$ = 0.5 T [9] (ground samples)

Mn-Mn exchange interaction [12]:

FM (intralayer)
AFM (interlayer)

$Mn_{54}Al_{46}$ → **excess Mn atoms** occupy **Al** positions → magnetization decreases

Possible **solution**? → **replace** excess **Mn atoms** with **Ni** **(small magnetic moment)**

[7] H. Kono, *J. Phys. Soc. Jpn.*, **12**, 1444 (1958)
[8] J. Park et al., *J. Appl. Phys.*, **107**, 09A731 (2010)
[9] J. Wei et al., *AIP Adv.*, **4**, 127113 (2014)
[10] J. M. D. Coey, *IEEE Trans. Magn.*, **47**, 4671 (2011)
[12] A. Koch et al., *J. Appl. Phys.*, **31**, S75 (1960)

metallic systems based on Ni and Al → partial filling of the Ni 3*d* band [13]

metallic radii of Ni and Mn are close [14]

Ni: 1.246 Å
Mn: 1.264 Å
Al: 1.432 Å

Ni could occupy **both** Mn and Al positions

↓

modified magnetic properties of τ-phase Mn-Al [15,16]

← $Mn_{69.40}Al_{29.40}Ni_{0.66}C_{0.54}$ ribbons [15]
$Mn_{60-x}Al_{40}Ni_x$ thin films [16]

Aim: to investigate the **effect of Ni doping** on the structural, electronic and magnetic properties of **τ-phase $Mn_{54}Al_{46}$**

[13] V. Rednic, M. Coldea, S.K. Mendiratta, M. Valente, V. Pop, M. Neumann, L. Rednic, *J. Magn. Magn. Mater.*, **321**, 3415 (2009)
[14] A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964)
[15] Y. Sakka et al., *J. Mater. Sci.*, **24**, 4331 (1989)
[16] M. Matsumoto et al., *J. Appl. Phys.*, **69**, 5172 (1991)

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Sample Preparation

- **$Mn_{54}Al_{46}$** and **$Mn_{50}Al_{46}Ni_4$** prepared by induction melting under Ar
- **annealing** at 470-1000 ºC under Ar followed by quenching in water

Sample Characterization

Differential Thermal Analysis (DTA)

- 100-900 ºC
- ramp rate of 20 ºC/min
- Ar atmosphere

X-Ray Diffraction (XRD)

- powder samples
- Bruker D8 Advance diffractometer
- Cu Kα radiation
- FullProf software

Magnetic measurements

- Weiss balance (300-800 K)
- VSM and extraction method (4-800 K; ±10 T)

Electronic Structure Calculations

- SPR-KKR method
- Local Spin Density Approximation (LSDA)
- Coherent Potential Approximation (CPA)

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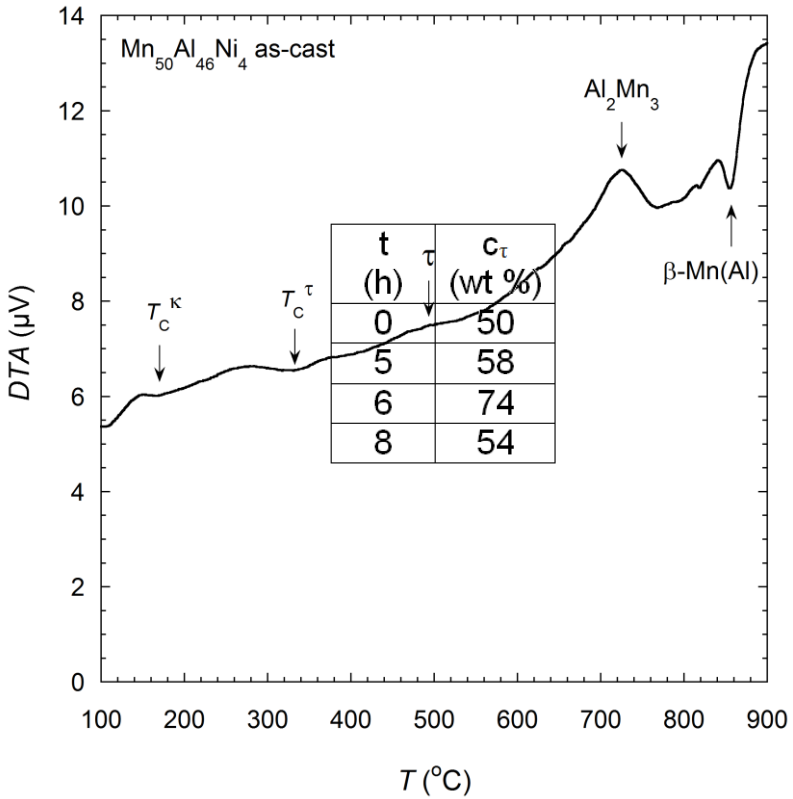
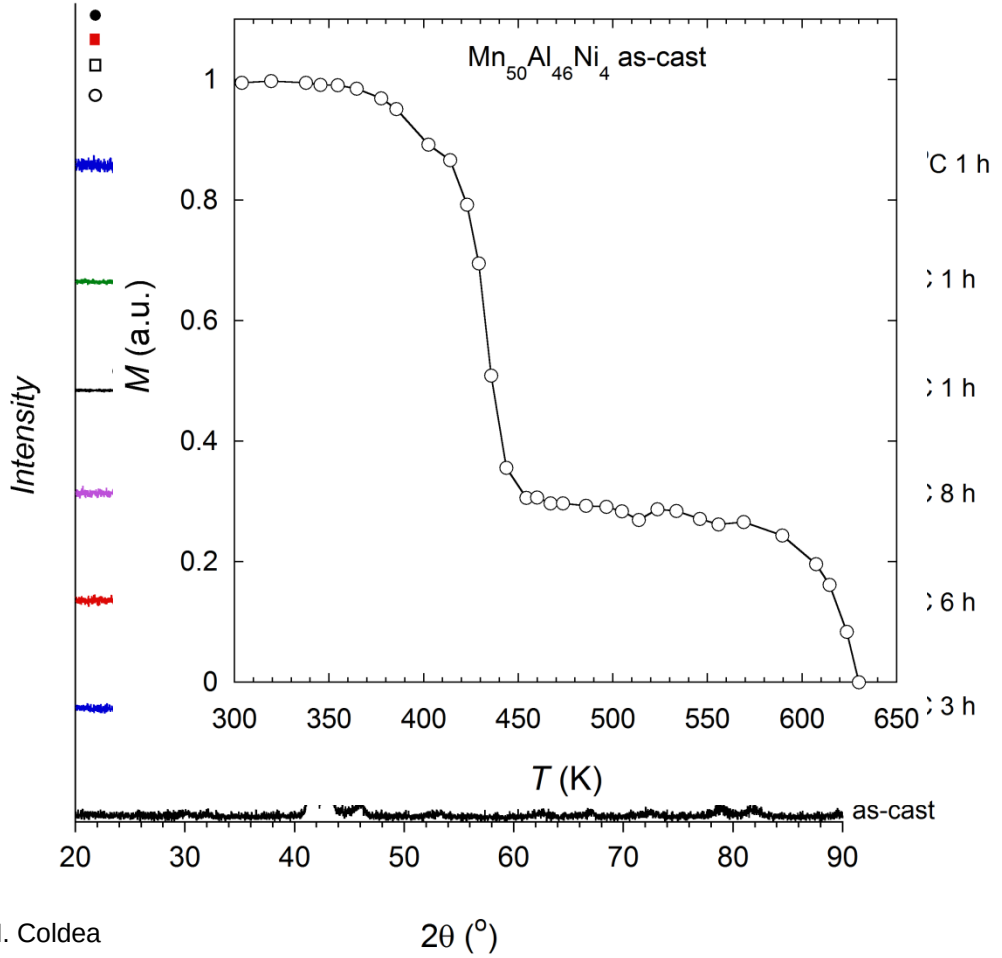
DTA and XRD Investigations

$Mn_{54}Al_{46}$ is a binary alloy

$Mn_{50}Al_{46}Ni_4$ is a **ternary** alloy → κ phase → cubic CsCl-type structure



470 °C → τ phase formation



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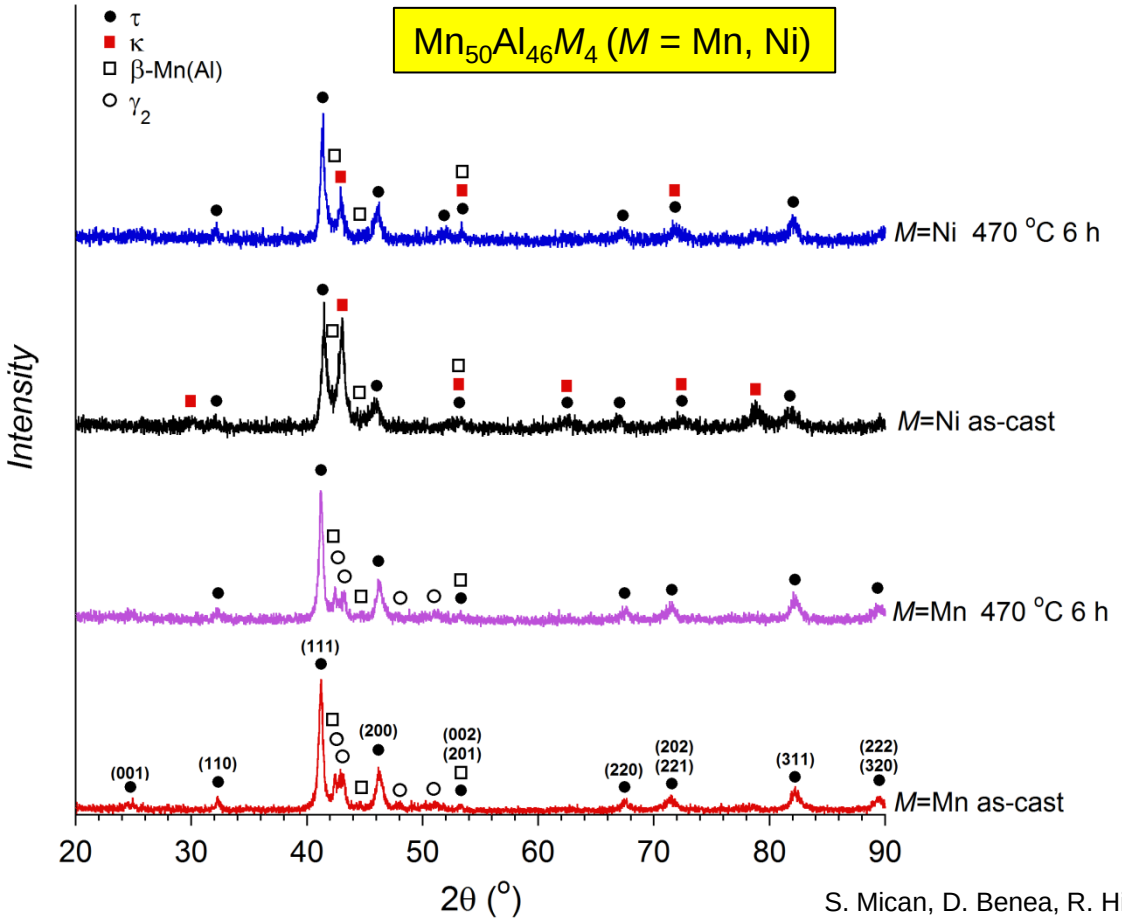

Ni addition

shrinkage of the ***c*** lattice parameter

c_τ values are comparable with previous $Mn_{54}Al_{46}$ results [8,9,17]

[8] J. Park et al., *J. Appl. Phys.*, **107**, 09A731 (2010)
[9] J. Wei et al., *AIP Adv.*, **4**, 127113 (2014)
[17] A. Chaturvedi et al., *J.Phys.: Condens. Matter*, **26**, 064201 (2014)

S. Mican, D. Benea, R. Hirian, R. Gavrea, O. Isnard, V. Pop and M. Coldea
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Sample	*a* (Å)	*c* (Å)	c_τ (wt%) ± 2%	$c_{\gamma 2}$ (wt%) ± 2%	c_β (wt%) ± 2%	c_κ (wt%) ± 2%
$Mn_{54}Al_{46}$ as-cast	3.93	3.57	68	25	7	-
$Mn_{54}Al_{46}$ + 470°C 6h	3.93	3.57	76	20	4	-
$Mn_{50}Al_{46}Ni_4$ as-cast	3.96	3.47	50	-	5	45
$Mn_{50}Al_{46}Ni_4$ + 470°C 6h	3.94	3.52	74	-	6	20

Electronic Structure Calculations

$Mn_{54}Al_{46}$	$Mn_{50}Al_{46}Ni_4$
a = 3.93 Å	a = 3.94 Å
c = 3.57 Å	c = 3.52 Å

Total energy calculations → **AFM** Mn-Mn **interlayer** coupling

Ni occupies the **Mn** ***1a*** and ***1c*** positions

Sample	Atom	m_{spin} (μ_B)	m_{orbit} (μ_B)
$Mn_{54}Al_{46}$	Al^{2e}	-0.08	0
	Mn^{2e}	-3.22	-0.01
	$Mn^{1a,1c}$	2.33	0.04
	Total (μ_B/f.u.)	**1.00**	**0.02**
$(Mn_{46}Ni_4)^{1a,1c}(Al_{46}Mn_4)^{2e}$	$Mn^{1a,1c}$	2.27	0.04
	$Ni^{1a,1c}$	-0.09	-0.01
	Al^{2e}	-0.08	0
	Mn^{2e}	-3.21	-0.02
	Total (μ_B/f.u.)	**0.88**	**0.02**

$Mn_{54}Al_{46}$
M_{Mn} = 2.20 μ_B/atom

$Mn_{50}Al_{50}$
M_{Mn} = 2.37 μ_B/atom [8]

[8] J. Park et al., *J. Appl. Phys.*, **107**, 09A731 (2010)

$Mn_{50}Al_{46}Ni_4$
M_{Mn} = 1.96 μ_B/atom

Ni moment is much **smaller** than that of **metallic Ni** (0.6 μ_B/atom)

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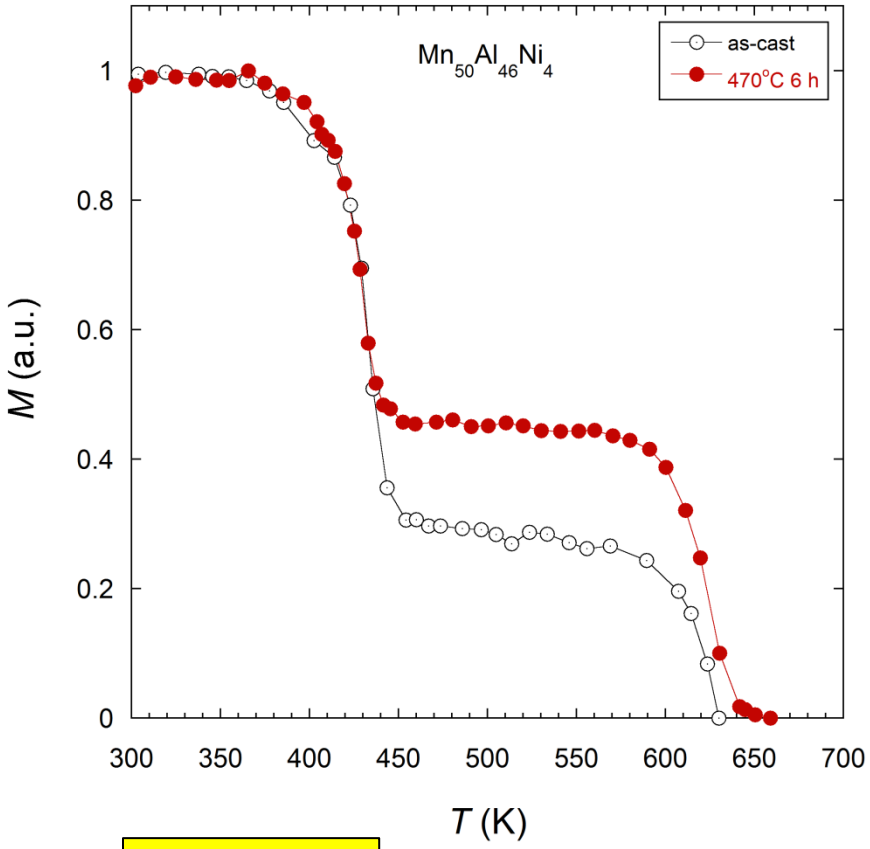
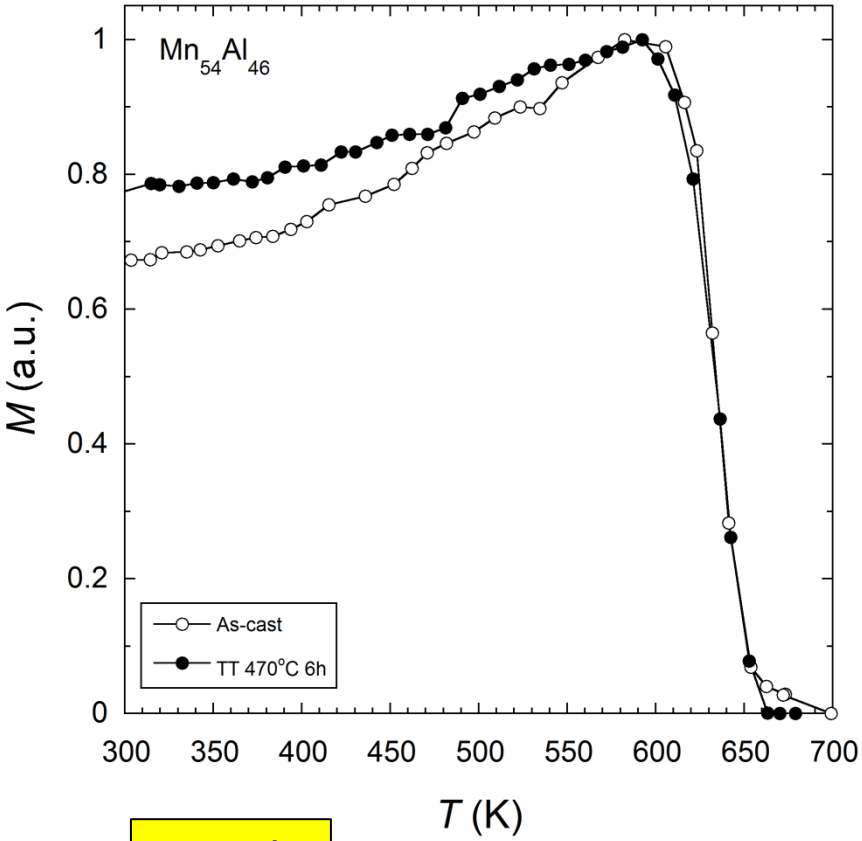
Magnetic Investigations





$Mn_{50}Al_{46}Ni_4$

→ 2 transitions

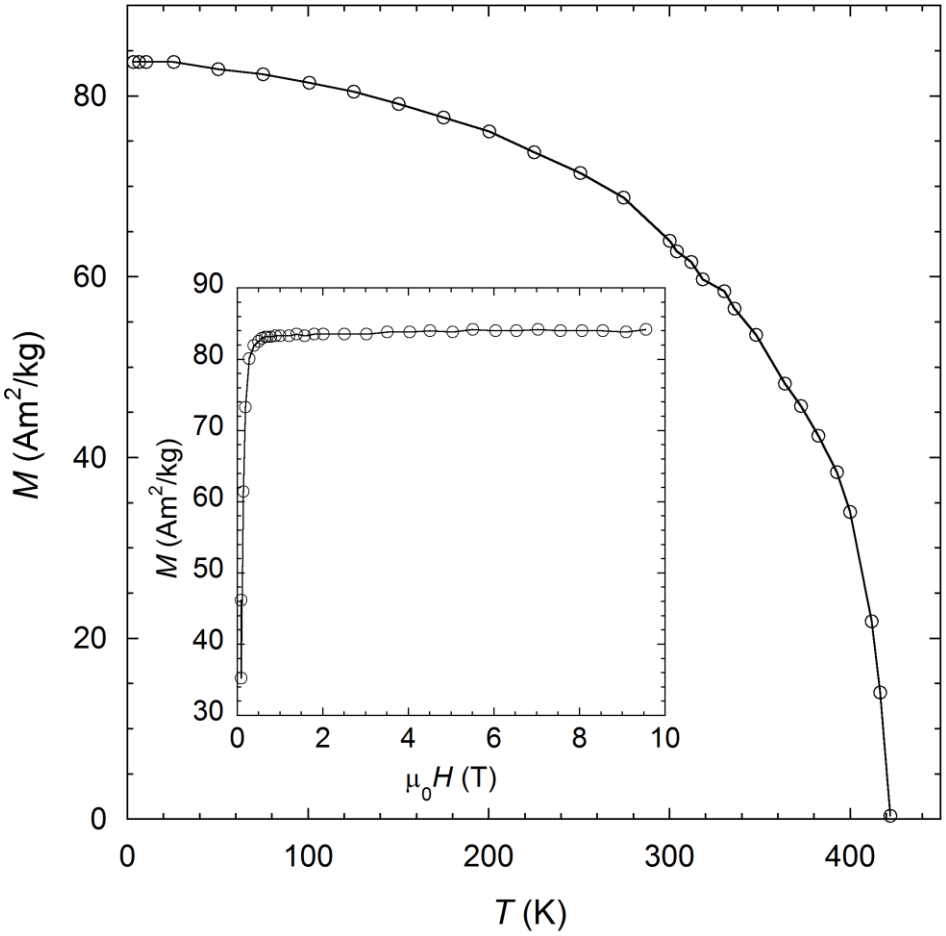
→ 437 K (κ phase)

→ 634 K (τ phase)

$Mn_{54}Al_{46}$

→ 1 transition at 645 K (τ phase)

$Mn_{40}Al_{50}Ni_{10}$ [13] → pure κ phase



T_c^{κ} = **421 K**

M_s = 84 Am^2/kg

saturation around 0.6T

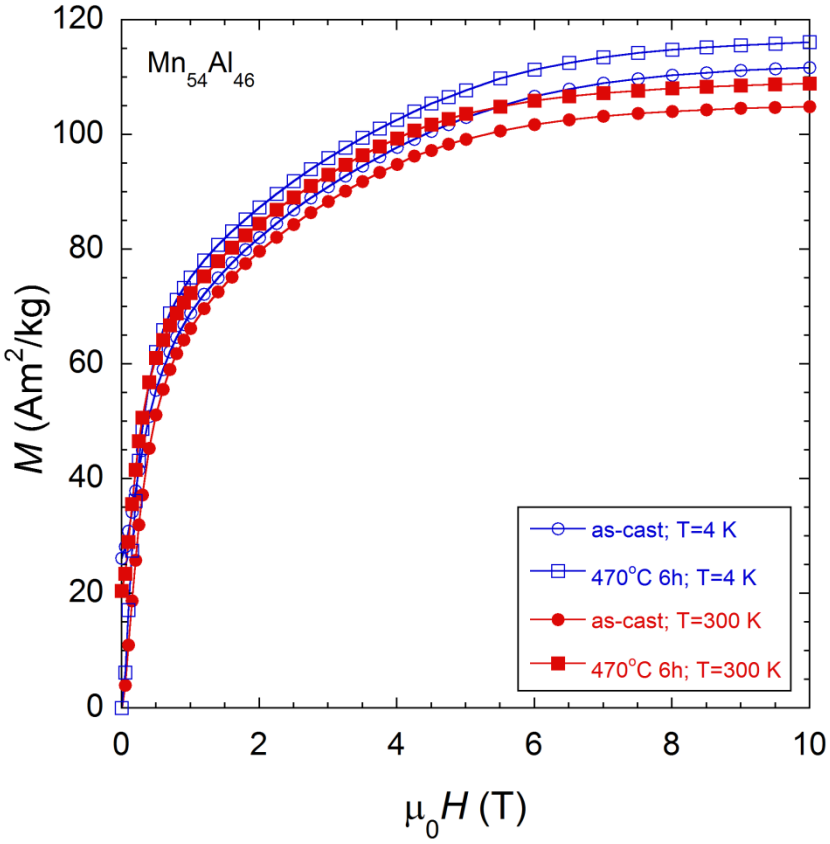
In agreement with previously reported data [18,19]

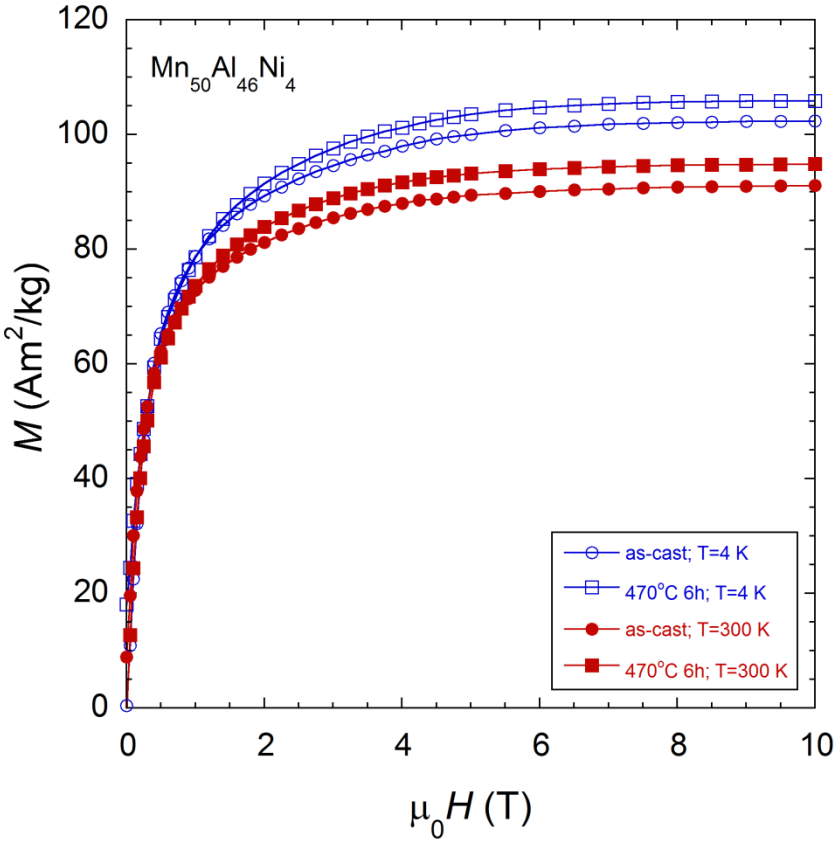
[18] I. Tsuboya et al., *J. Phys. Soc. Jpn.*, **16**, 1257 (1961)
[19] I. Tsuboya et al., *J. Phys. Soc. Jpn., Suppl. B1*, **17**, 172 (1962)

$Mn_{50}Al_{46}Ni_4$

T_c^{κ} = **437 K**

[13] V. Rednic, M. Coldea, S.K. Mendiratta, M. Valente, V. Pop, M. Neumann, L. Rednic, *J. Magn. Magn. Mater.*, **321**, 3415 (2009)





$Mn_{54}Al_{46}$

M_s (4 K) = 112 Am²/kg

pure τ phase

M_s (4 K) = **147 Am²/kg**

M_s (10 K) = 137 Am²/kg [9]

M_s (300 K) = 109 Am²/kg

$Mn_{50}Al_{46}Ni_4$

M_s (4 K) = 106 Am²/kg

pure τ phase

M_s (4 K) = **122 Am²/kg**

$M = c_\tau M_\tau + c_\kappa M_\kappa$

M_κ = 84 Am²/kg [18,19]

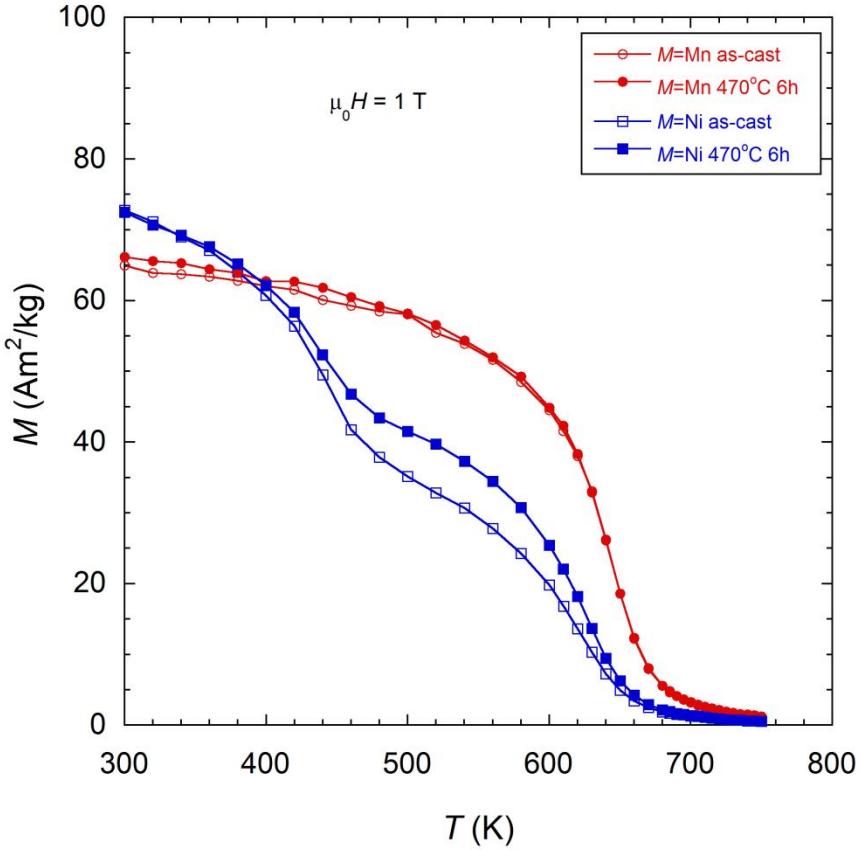
M_s (300 K) = 95 Am²/kg

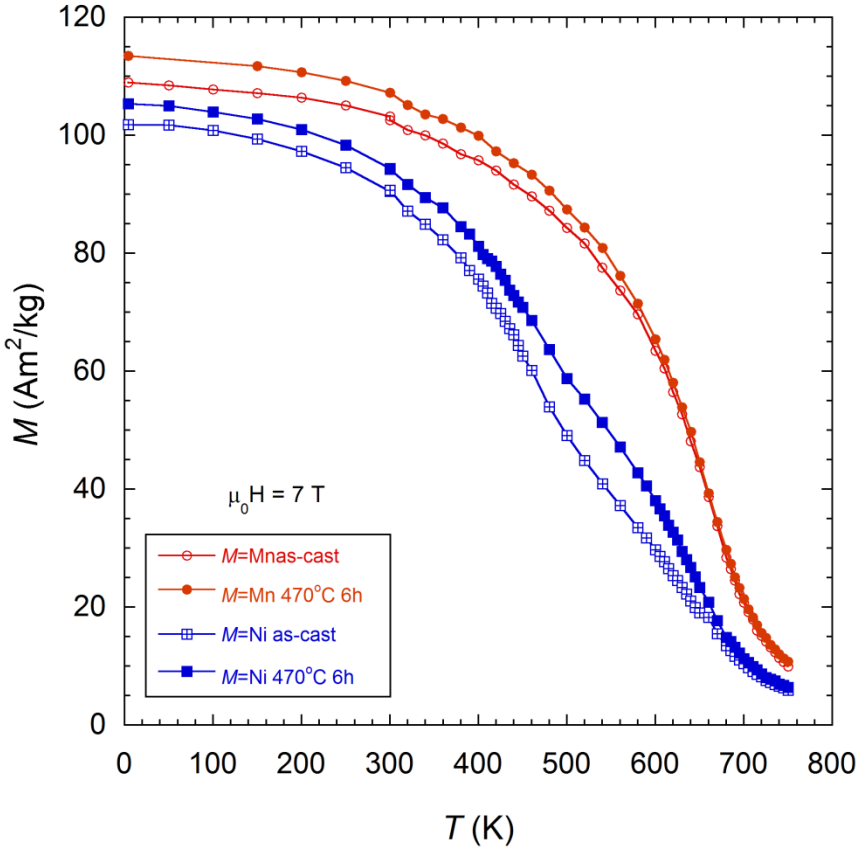
[9] J. Wei et al., *AIP Adv.*, **4**,127113 (2014)

[18] I. Tsuboya et al., *J. Phys. Soc. Jpn.*, **16**, 1257 (1961)

[19] I. Tsuboya et al., *J. Phys. Soc. Jpn., Suppl. B1*, **17**, 172 (1962)

$Mn_{50}Al_{46}M_4$ (M = Mn, Ni)

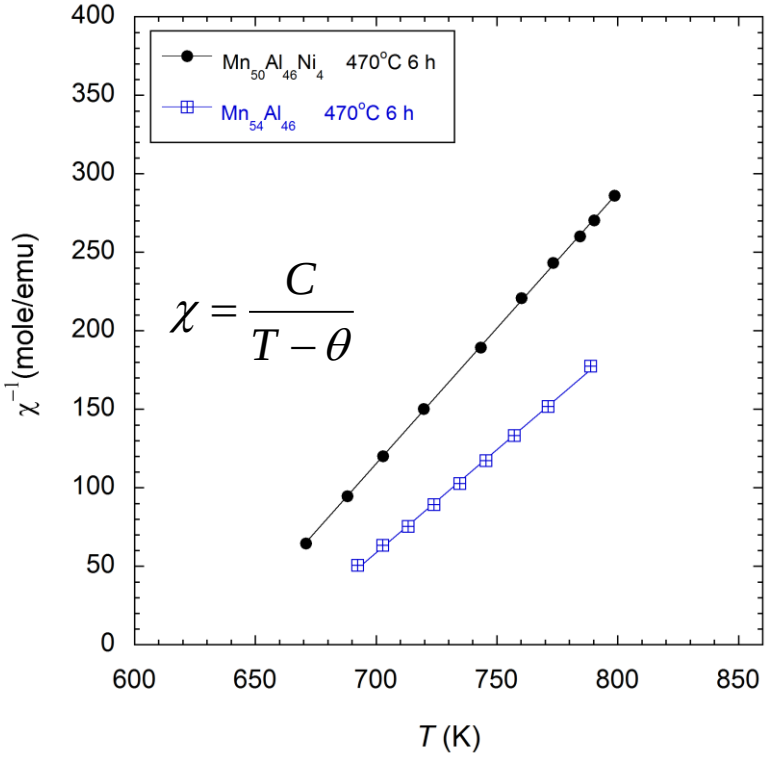




two magnetic **phases** (low fields)

$Mn_{50}Al_{46}Ni_4$

low saturation field of the κ phase



Band structure calculations →

$Mn_{54}Al_{46}$

m_{tot} = 1.00 μ_B/f.u.

m_{Mn} = 2.20 μ_B/atom

$Mn_{50}Al_{46}Ni_4$

m_{tot} = 0.88 μ_B/f.u.

m_{Mn} = 1.96 μ_B/atom

$\mu_{eff}^{\gamma 2}$ = 3.94 μ_B/atom → larger Mn-Mn distances in the γ_2 crystal structure

μ_{eff}^{κ} = 3.22 μ_B/atom [19]

[19] I. Tsuboya et al., *J. Phys. Soc. Jpn., Suppl. B1*, **17**, 172 (1962)

Sample	m_{tot} (μ_B/f.u.)	m_{Mn} (μ_B/Mn atom)	T_c (K)	μ_{eff} (μ_B/f.u)	θ (K)	μ_{eff}^{τ} (μ_B/Mn atom)	$\mu_{eff}^{\gamma 2}$ (μ_B/Mn atom)	μ_{eff}^{β} (μ_B/Mn atom) [20]	μ_{eff}^{κ} (μ_B/Mn atom)
$Mn_{54}Al_{46}$	1.11	2.41	645	2.47	655	3.26	3.94	1.70	-
$Mn_{50}Al_{46}Ni_4$	0.92	2.19	634	2.15	633	3.03	-	1.70	3.37

S (pure τ phase)

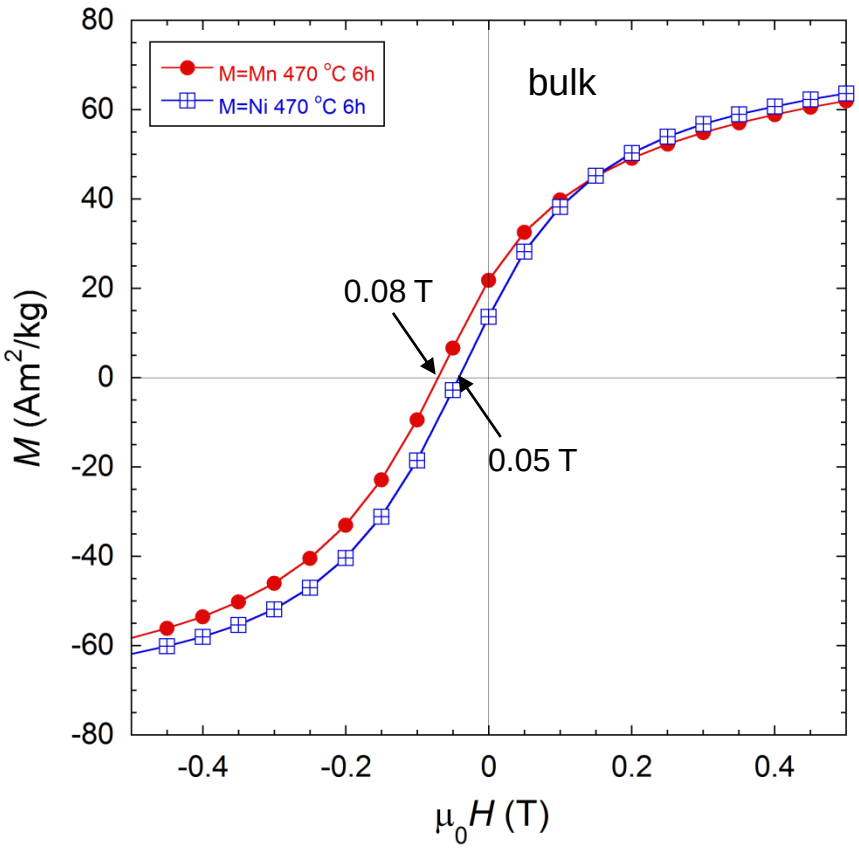
$$C = c_\tau C_\tau + c_\beta C_\beta + c_{\gamma_2} C_{\gamma_2}$$

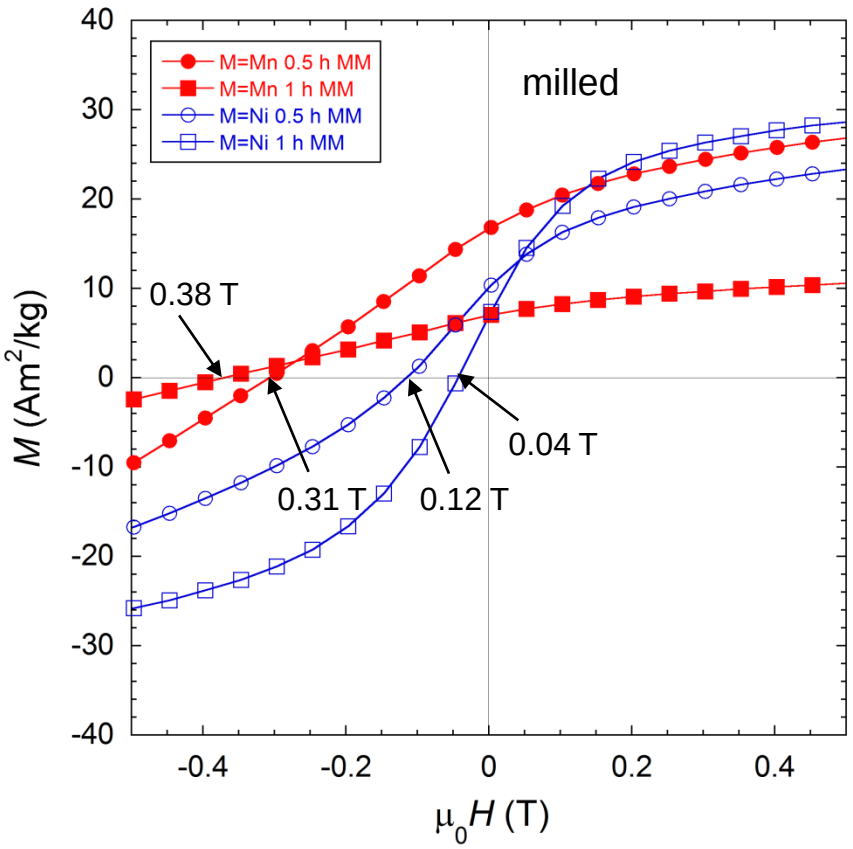
$$C = c_\tau C_\tau + c_\beta C_\beta + c_\kappa C_\kappa$$

S. Mican, D. Benea, R. Hirian, R. Gavrea, O. Isnard, V. Pop and M. Coldea *Submitted to J. Magn. Magn. Mater.*

[20] H. Nakamura et al., *J. Phys. Condens. Matter*, **9**, 4701 (1997)

$Mn_{50}Al_{46}M_4$ (M = Mn, Ni)





$Mn_{54}Al_{46}$

$\mu_0 H_c$ = 0.50 T [9] (ground samples)

$\mu_0 H_c$ = 0.36 T [17] (milled samples)

[9] J. Wei et al., *AIP Adv.*, **4**,127113 (2014)
[17] A. Chaturvedi et al., *J.Phys.: Condens. Matter*, **26**, 064201 (2014)

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Conclusions

- annealing at **470 ºC promotes τ phase formation**
- preference for **Ni** to **occupy** the **Mn 1*a*** and **1*c*** sites
- good agreement between **theory** and **experiment**
- **milling improves coercivity** (maximum **$\mu_0 H_c$ = 0.38 T for 1 h MM $Mn_{54}Al_{46}$**)

Thank you for your attention!

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