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Magnetic Phase Competition in Off-Stoichiometric Heusler Alloys: The Case of $Ni_{50-x}Co_xMn_{25+y}Sn_{25-y}$

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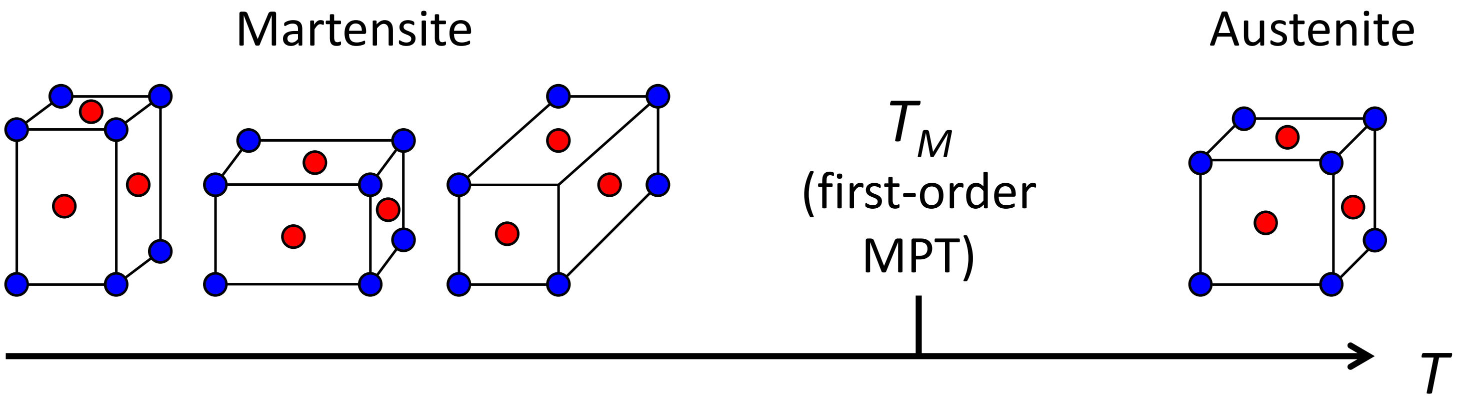
National High Magnetic Field Laboratory

U.S. DEPARTMENT OF ENERGY

Introduction: Martensitic (Magnetic) Alloys

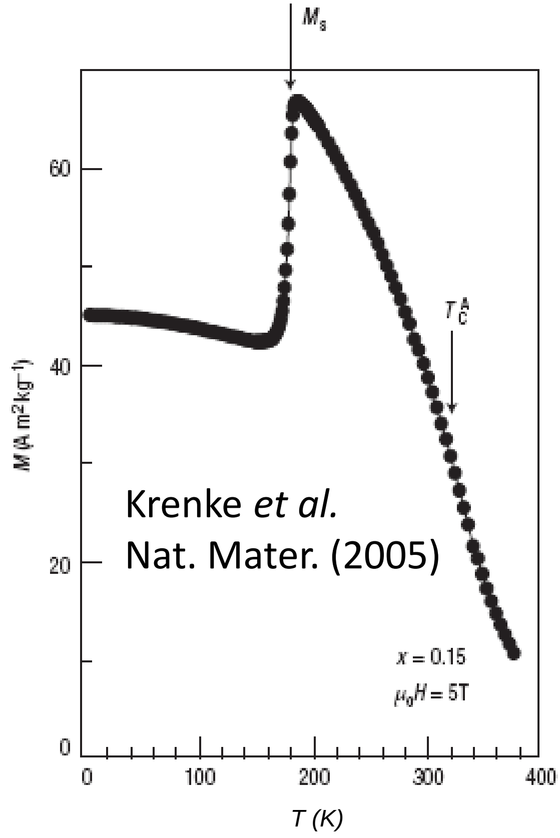


- Multiferroic alloys (ferroelastic + magnetic)

  > Magnetoelasticity, magnetic shape memory, field-induced phase transformations, magnetocaloric and barocaloric effects

  > Actuators/sensors, magnetic refrigeration, energy conversion, heat-assisted recording?

- Thermal hysteresis: Vital for applications, but fundamentals elusive….

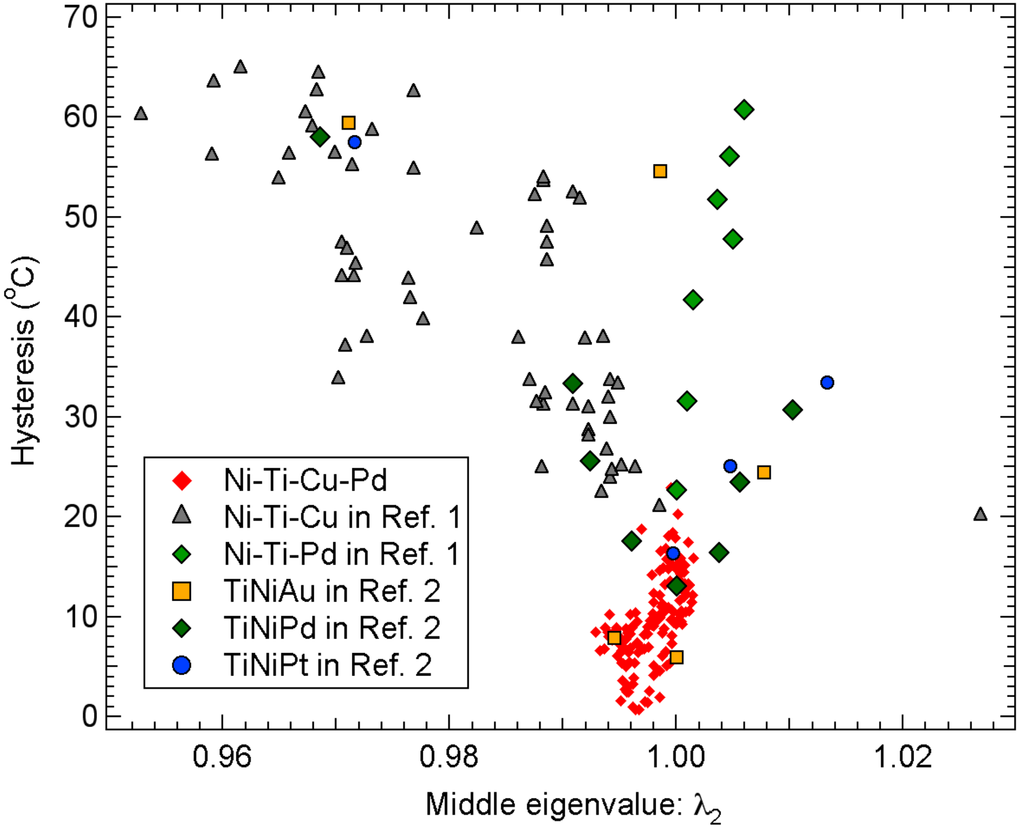


Krenke *et al.*
Nat. Mater. (2005)

Introduction: Minimization of Thermal Hysteresis

- Recent theoretical work by James *et al.*: Geometrical compatibility between austenite and martensite unit cells vital for ΔT.

- An invariant plane occurs at their interface if, $\lambda_2 = 1$, where $\lambda_{1,2,3}$ are the ordered eigenvalues of the transformation stretch matrix, $\boldsymbol{U}$.



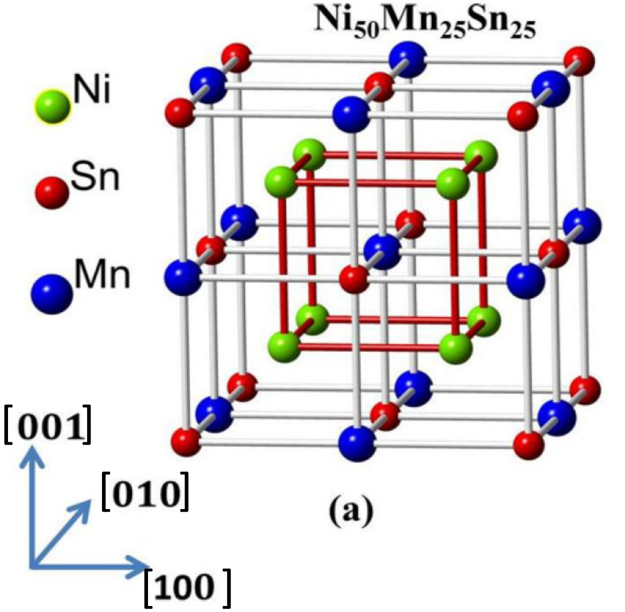
- Experiment: Remarkable correlations between ΔT and λ_2. Direct observation of "ideal" interface by HRTEM

- ΔT << 10 K !

Cui *et al.* Nat. Mater. (2006)
Zhang *et al.* Acta. Mat. (2009)

Application to Magnetic Alloys: The Route to $Ni_{50-x}Co_xMn_{40}Sn_{10}$

- Step I Full Heusler alloys Ni_2MnZ, Z = Sn, In, Ga, *etc*.
  (*e.g*. Ni_2MnSn, F, T_C = 350 K)



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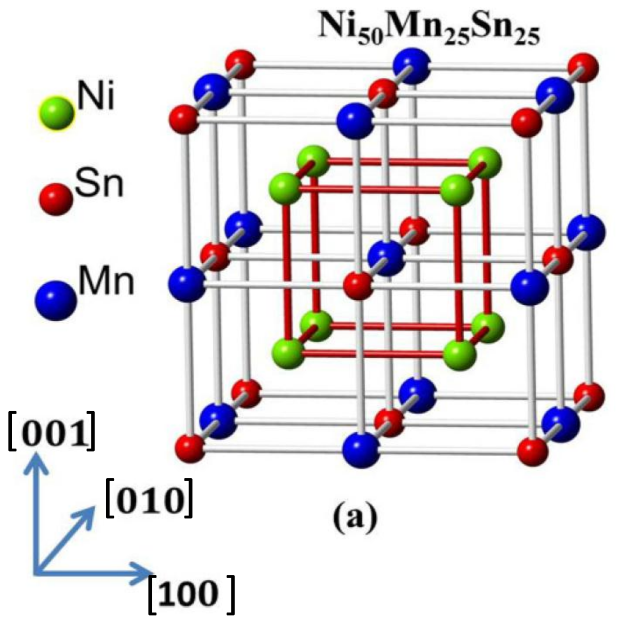
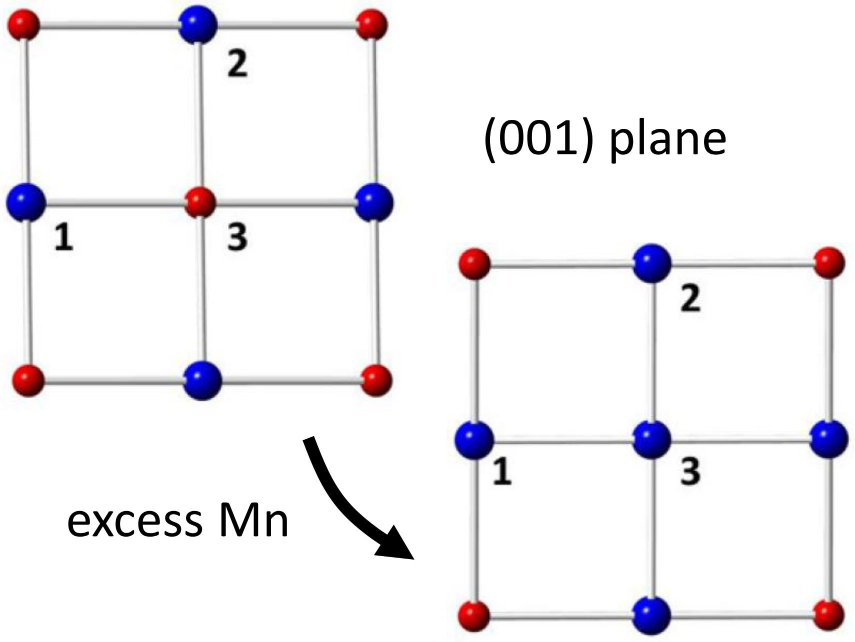
- Step II $Ni_{50}Mn_{25+y}Z_{25-y}$:
  Tunable magnetic interactions (F *vs*. AF)*
  MPT for $y > 5$
  $\lambda_2 \rightarrow 1$.





*Krenke, Acet, Wasserman, Moya, Manosa, Planes, *PRB* (2005, 2006)

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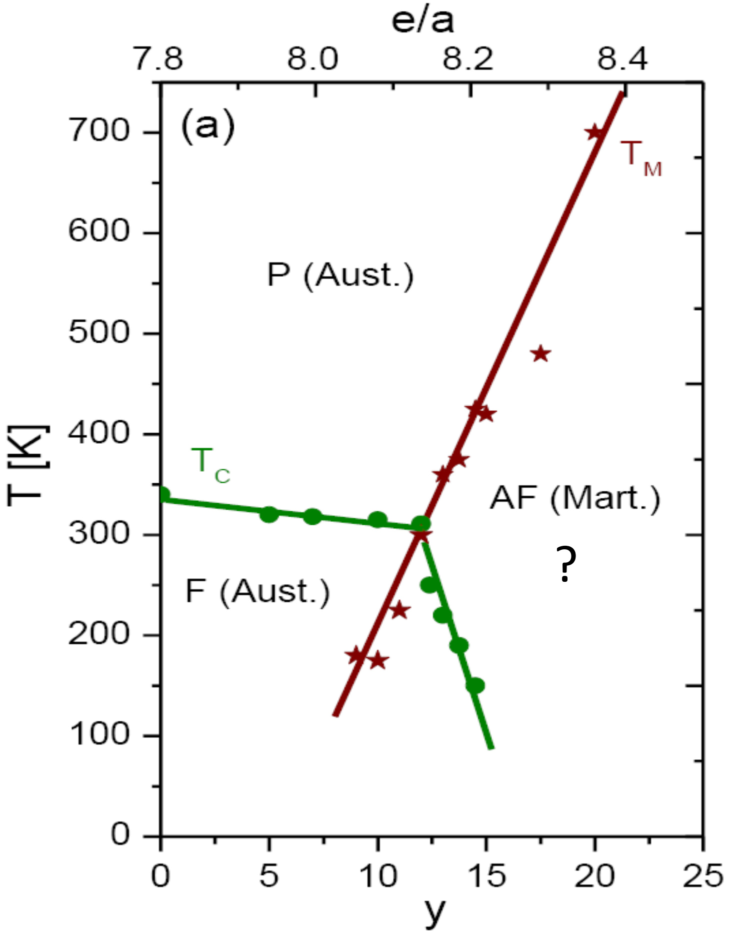
  MPT for $y > 5$
  $\lambda_2 \to 1$.

$Ni_{50}Mn_{25+y}Sn_{25-y}$



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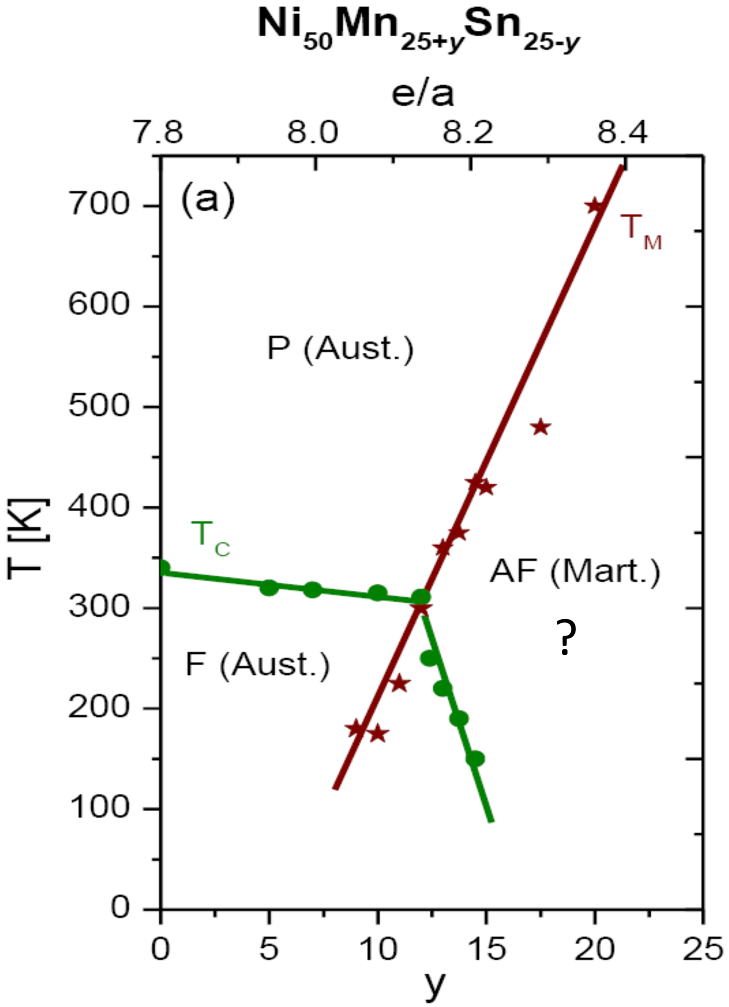
- Step III $Ni_{50-x}Co_xMn_{40}Sn_{10}$:
  Enhanced T_C, M_S
  Convenient T_M
  $\lambda_2 \approx 1$ (1.0051 @ $x = 6$)



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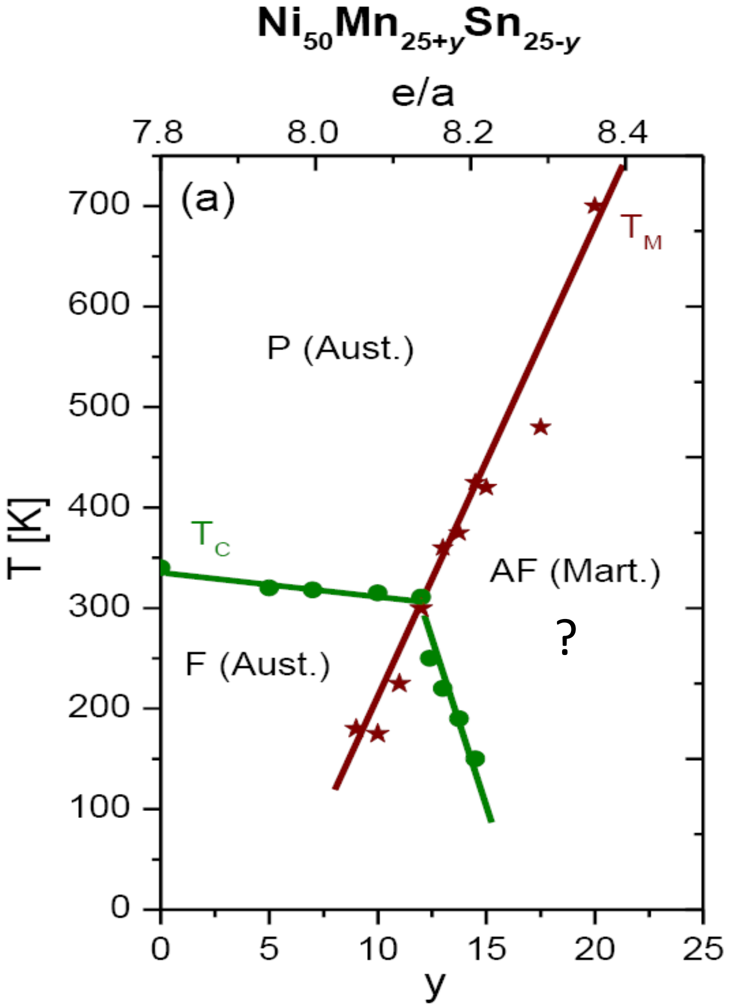
  Enhanced T_C, M_S
  Convenient T_M
  $\lambda_2 \approx 1$ (1.0051 @ $x = 6$)

- **$Ni_{46}Co_6Mn_{40}Sn_{10}$:**
  $T_C \approx 440$ K
  $T_M \approx 380$ K
  $\Delta M \approx 1000$ emu/cm^3
  $\Delta T < 10$ K



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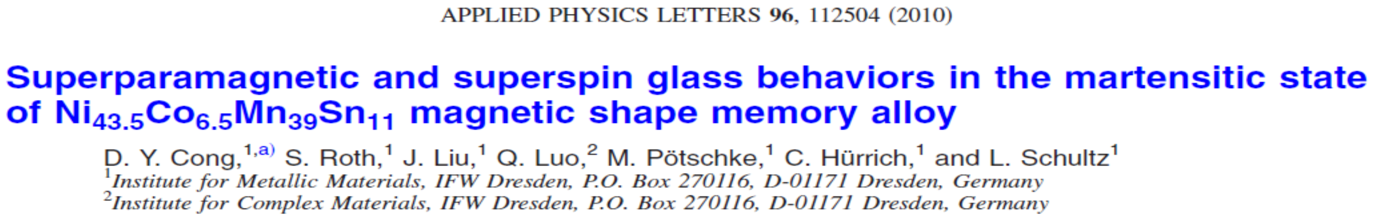
Magnetism in $Ni_{50-x}Co_xMn_{40}Sn_{10}$ (and Related Systems)

- High T_C, high ΔM, convenient T_M, low ΔT
- F austenite, non-F martensite (AF or P?)
- Nominally non-F martensite reveals some significant surprises:
  - > Superparamagnetic-like behavior at low T (in a bulk solid!)
  - > Exchange bias in blocked low T state (in a single phase)
  - > *Collective* freezing. Super-spin-glass?
  - > ZFC exchange bias

Nanoscale Magnetic Inhomogeneity?

- Acute sensitivity of magnetism to composition



APPLIED PHYSICS LETTERS **96**, 112504 (2010)

Superparamagnetic and superspin glass behaviors in the martensitic state of $Ni_{43.5}Co_{6.5}Mn_{39}Sn_{11}$ magnetic shape memory alloy

D. Y. Cong,[1,a)] S. Roth,[1] J. Liu,[1] Q. Luo,[2] M. Pötschke,[1] C. Hürrich,[1] and L. Schultz[1]
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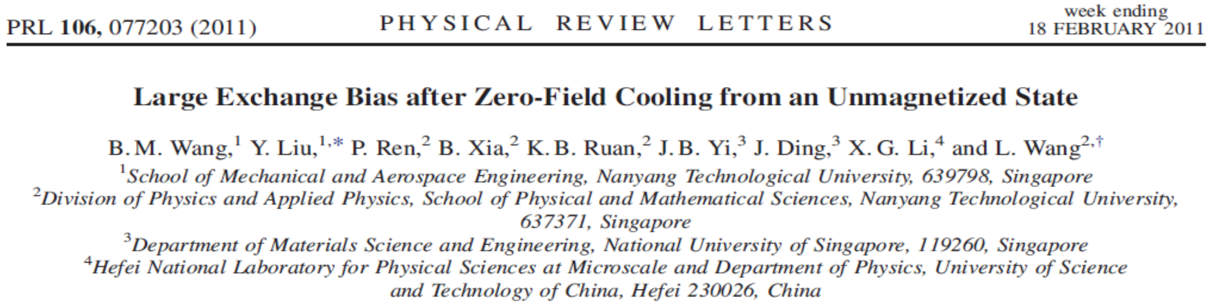


PRL **106,** 077203 (2011) PHYSICAL REVIEW LETTERS week ending 18 FEBRUARY 2011

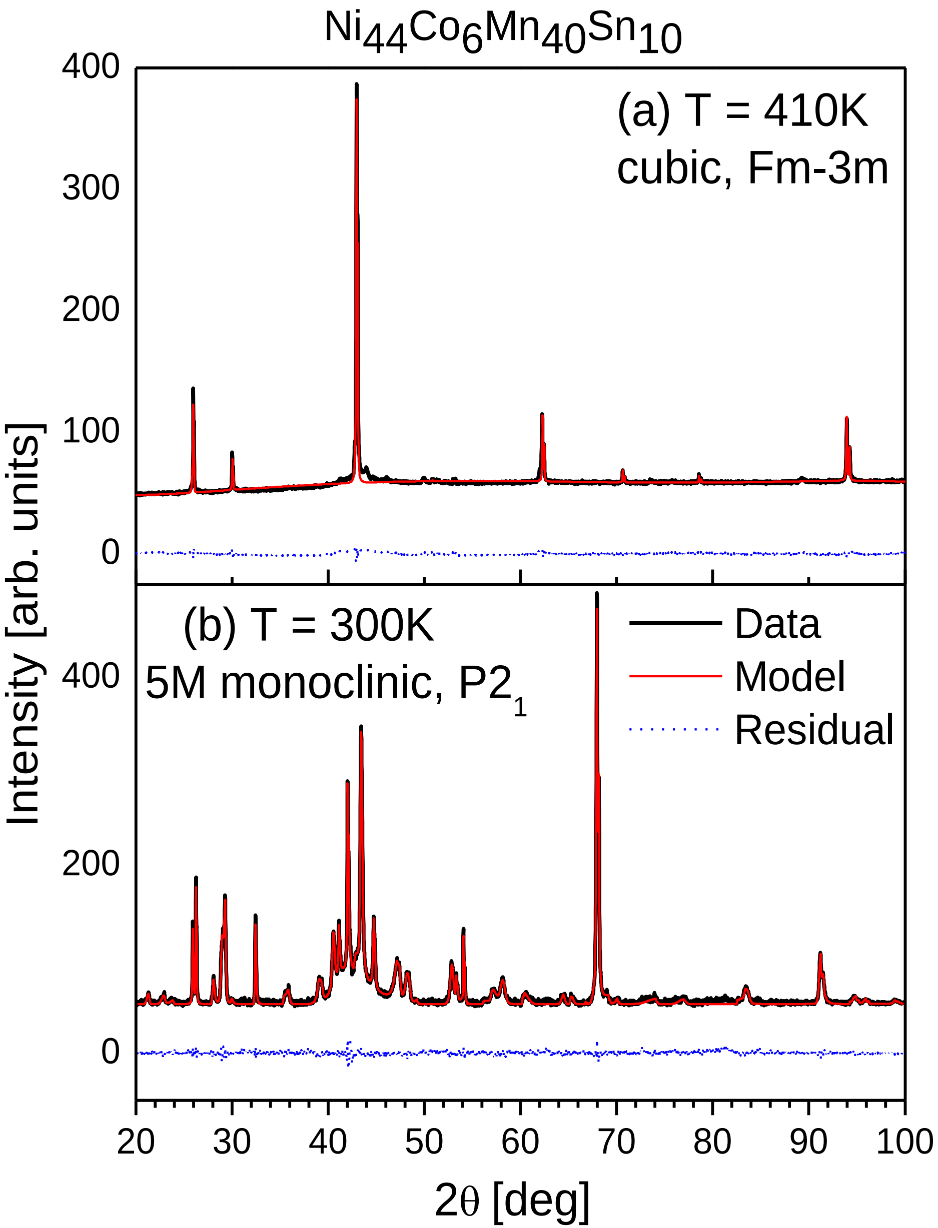
Large Exchange Bias after Zero-Field Cooling from an Unmagnetized State

B. M. Wang,[1] Y. Liu,[1,*] P. Ren,[2] B. Xia,[2] K. B. Ruan,[2] J. B. Yi,[3] J. Ding,[3] X. G. Li,[4] and L. Wang[2,†]
[1]*School of Mechanical and Aerospace Engineering, Nanyang Technological University, 639798, Singapore*
[2]*Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, 637371, Singapore*
[3]*Department of Materials Science and Engineering, National University of Singapore, 119260, Singapore*
[4]*Hefei National Laboratory for Physical Sciences at Microscale and Department of Physics, University of Science and Technology of China, Hefei 230026, China*

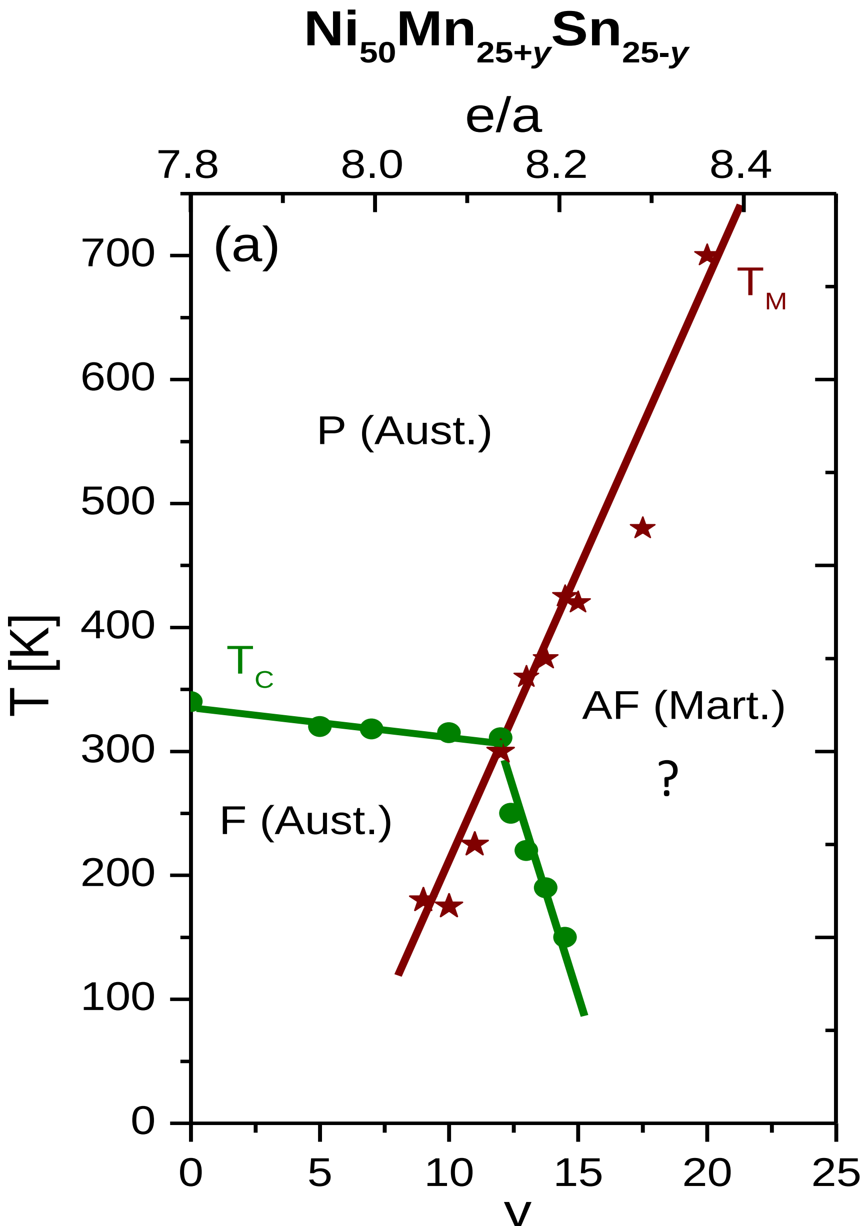
Experimental Details

- Arc-melted polycrystalline bulk ingots
  [Srivastava *et al* APL (2010);
  Bhatti *et al* PRB (2012)]

- Characterized by:
  - > DSC
  - > *T*-dependent XRD
  - > *T*-dependent Neutron Powder Diffraction (NPD)
  - > Magnetometry
  - > Small-Angle Neutron Scattering (SANS)
  - > ^{55}Mn zero-field NMR



$Ni_{50-x}Co_xMn_{40}Sn_{10}$ Phase Diagram



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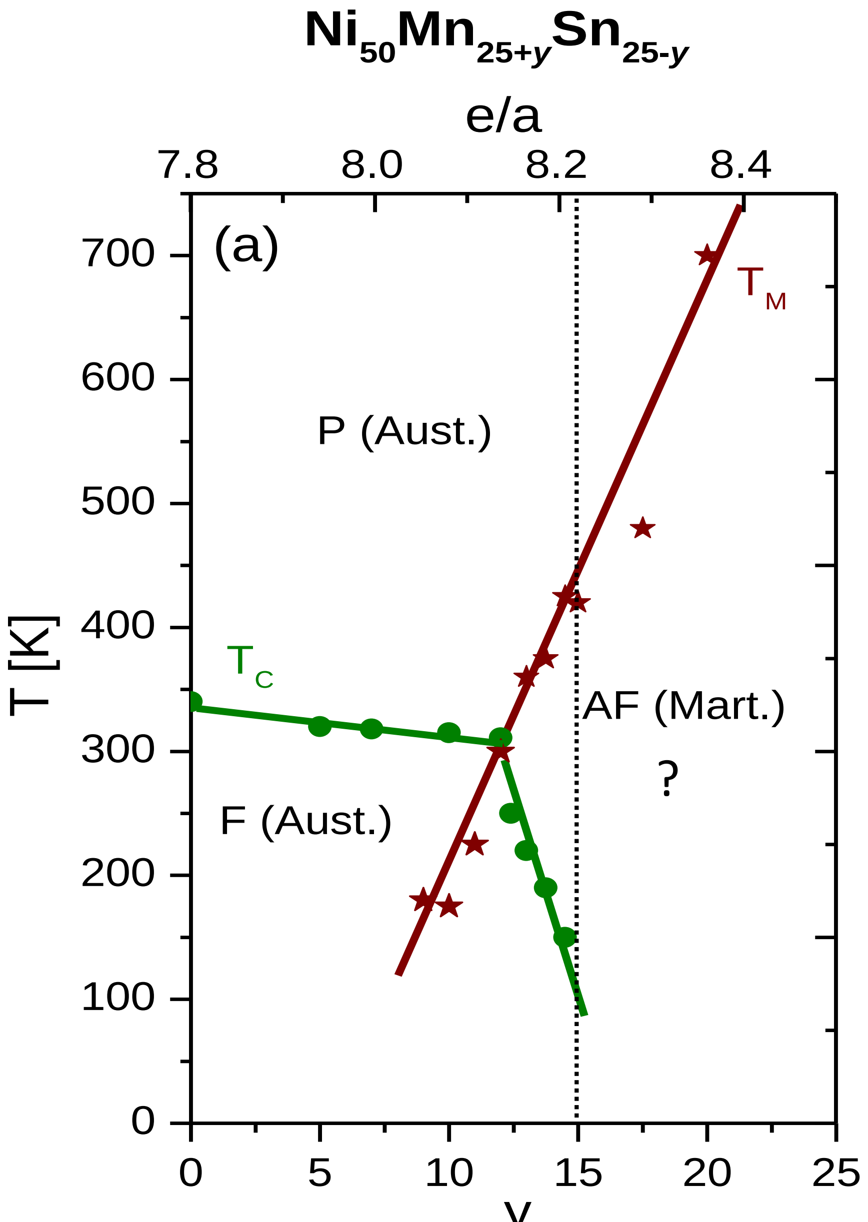

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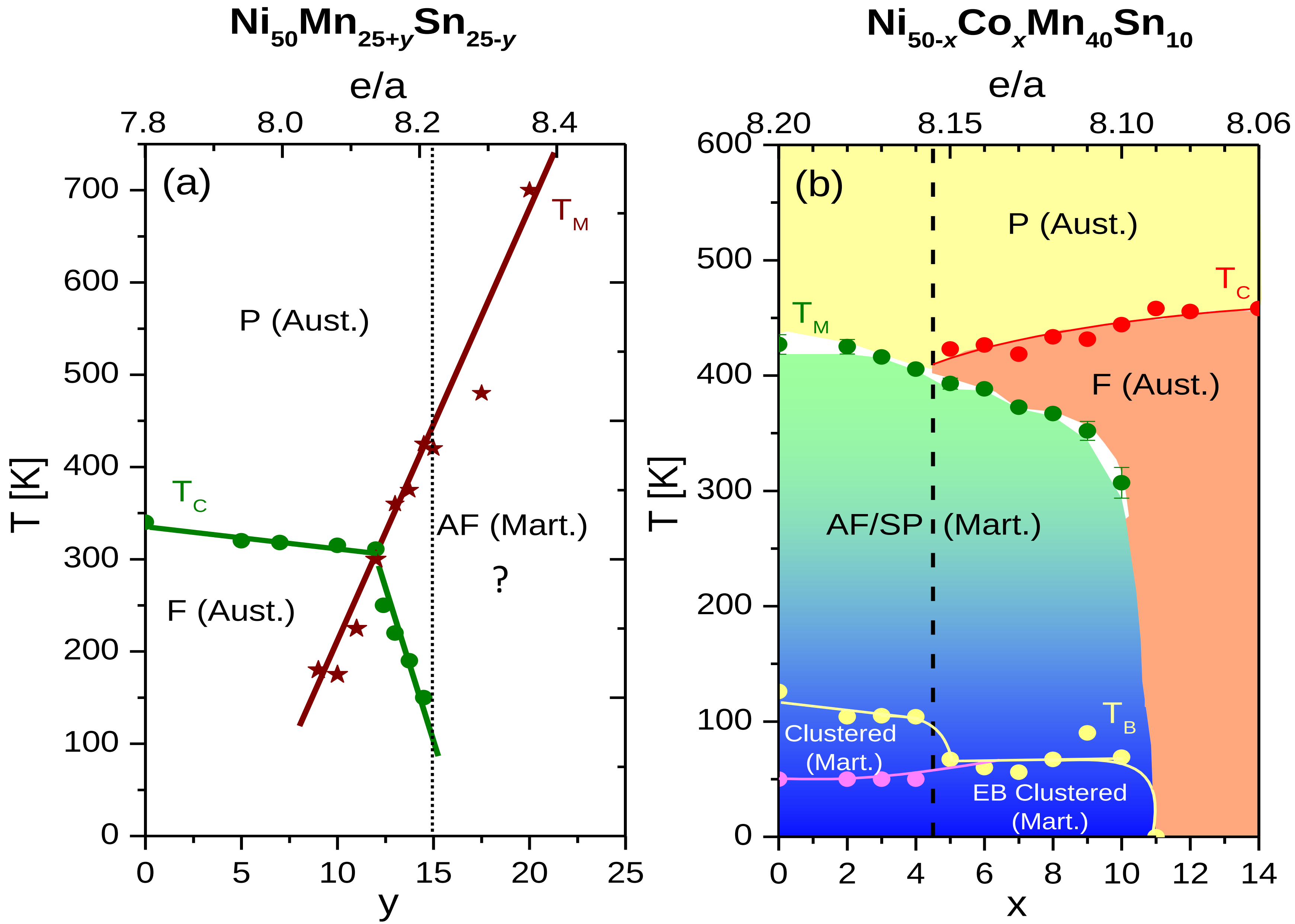
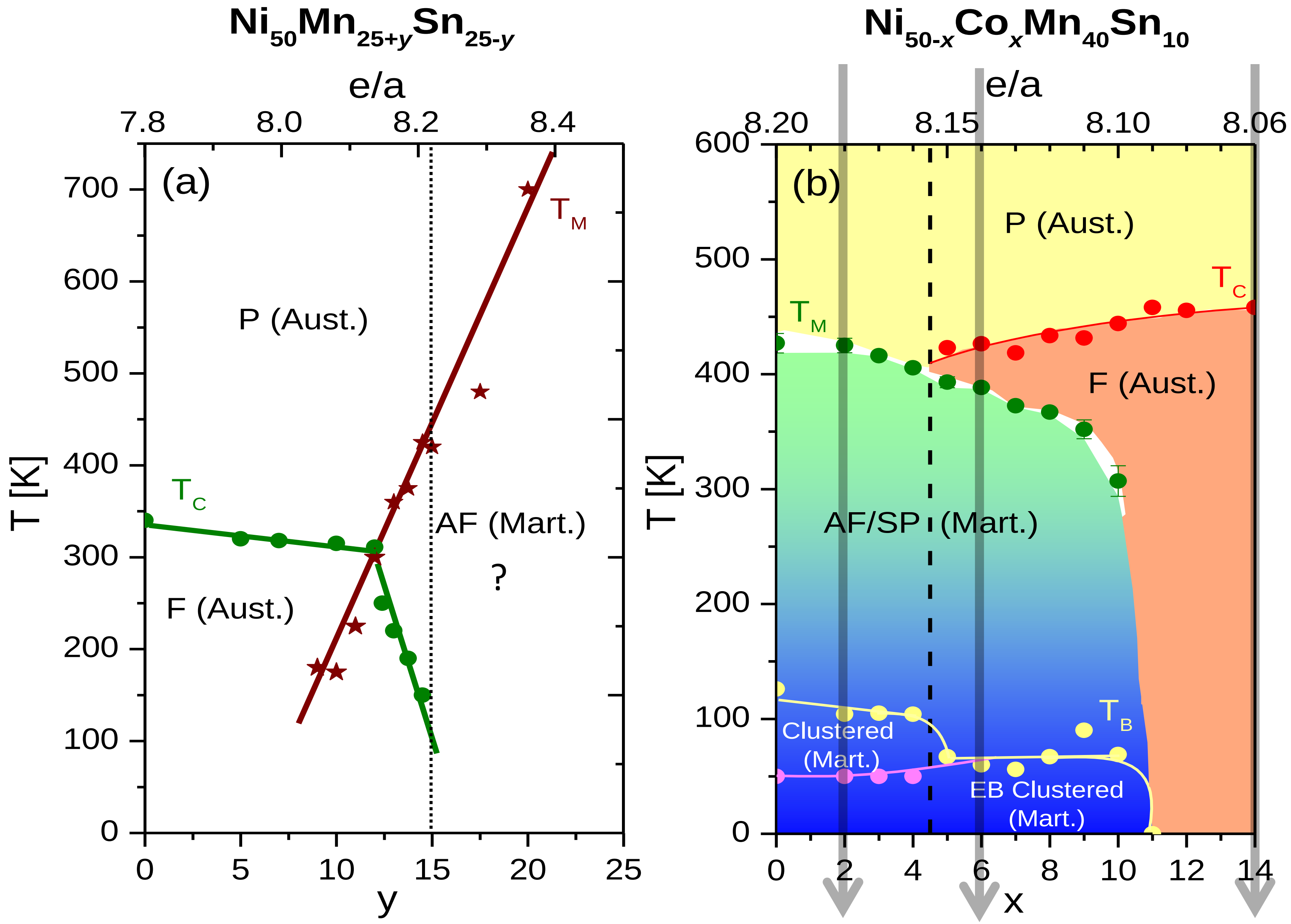


$Ni_{50-x}Co_xMn_{40}Sn_{10}$ Phase Diagram



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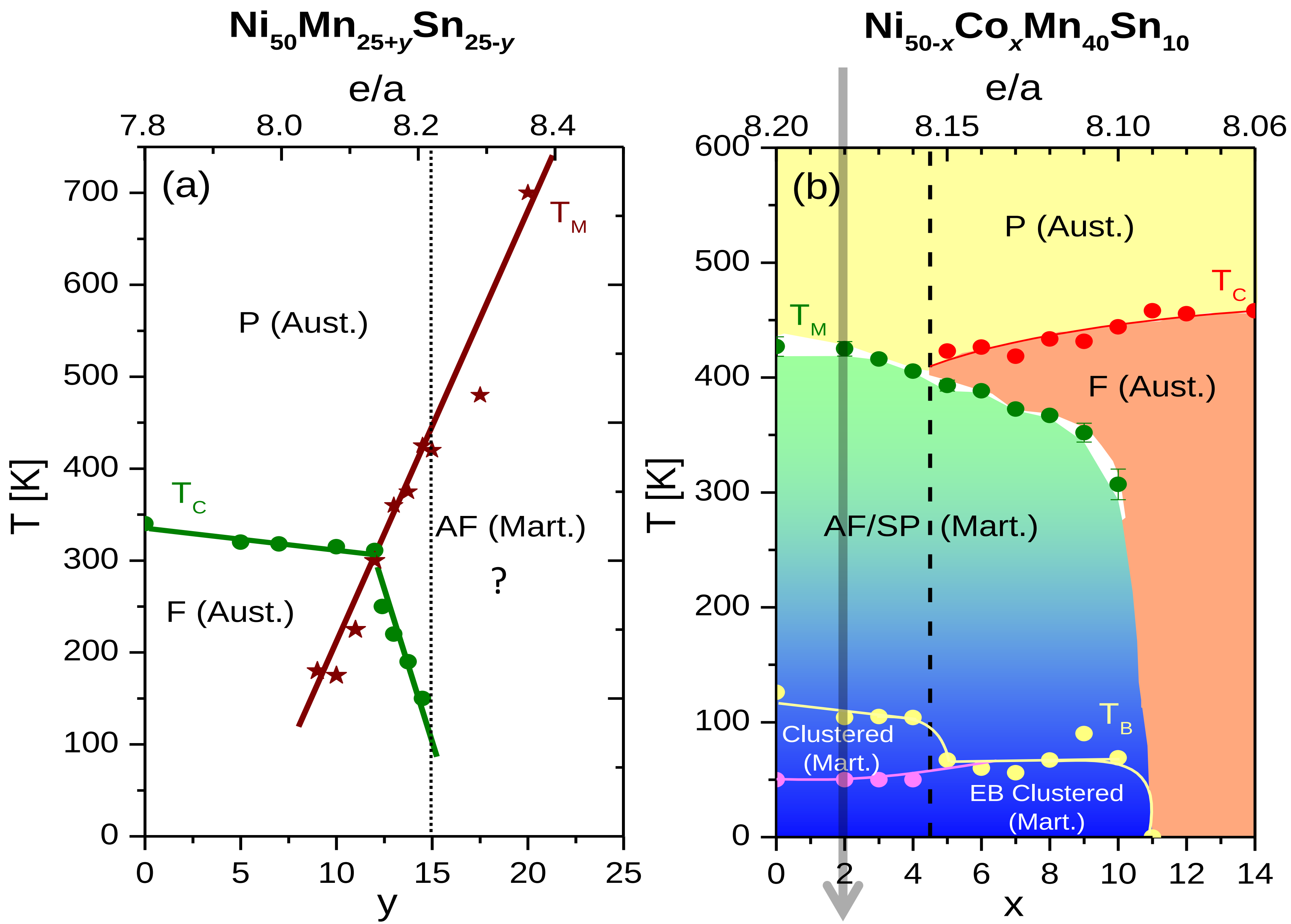
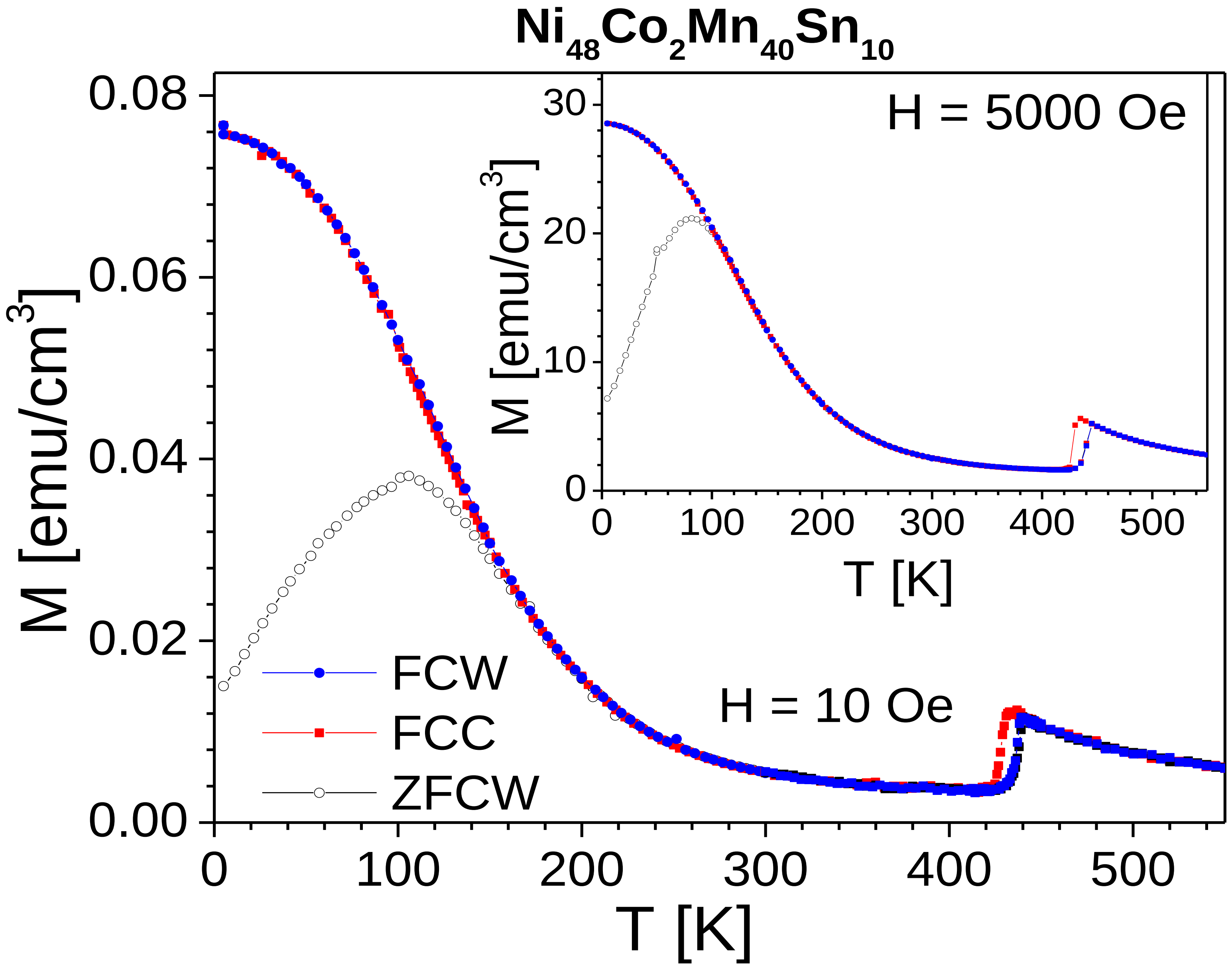
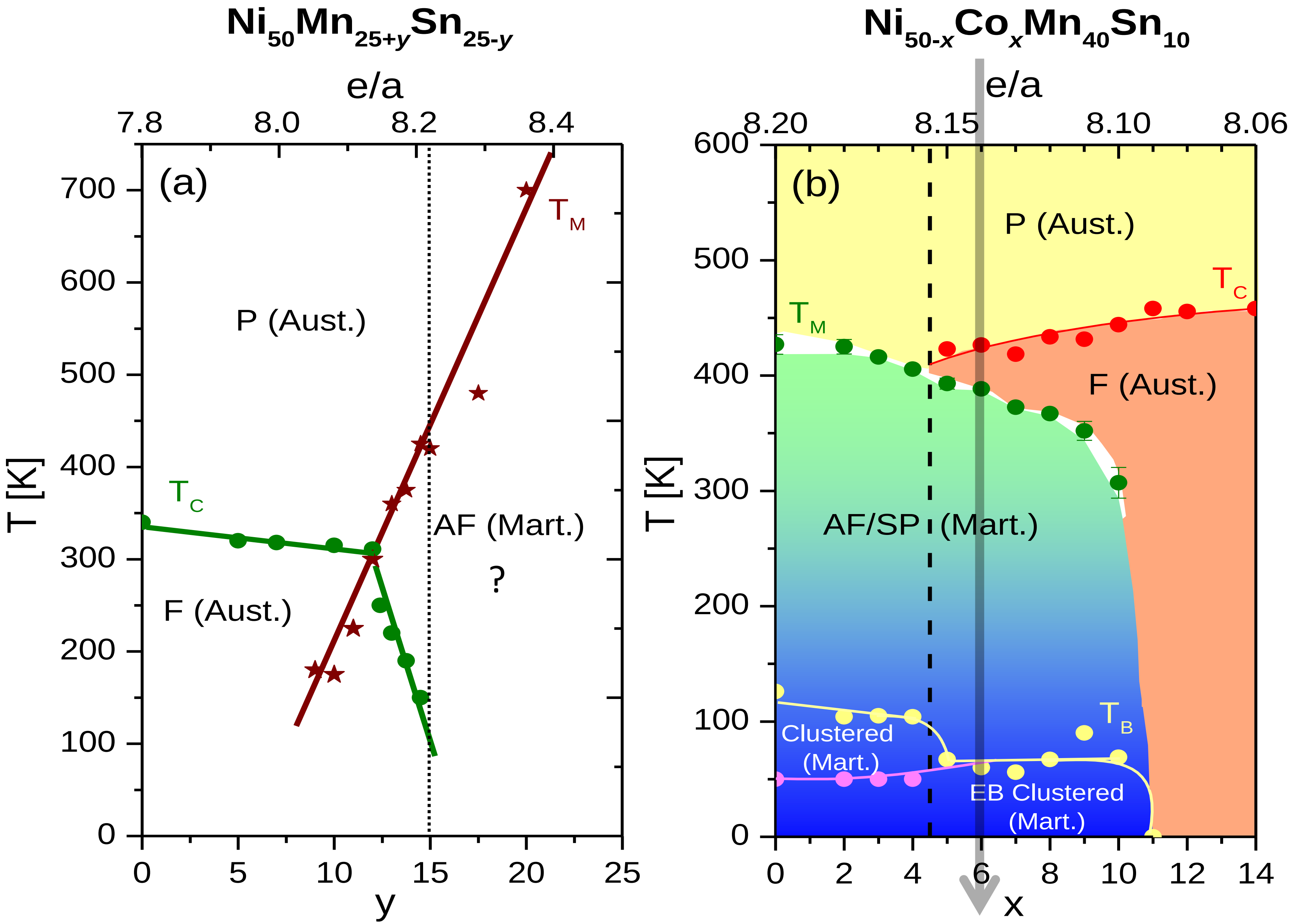


M vs. T (*x* = 2)



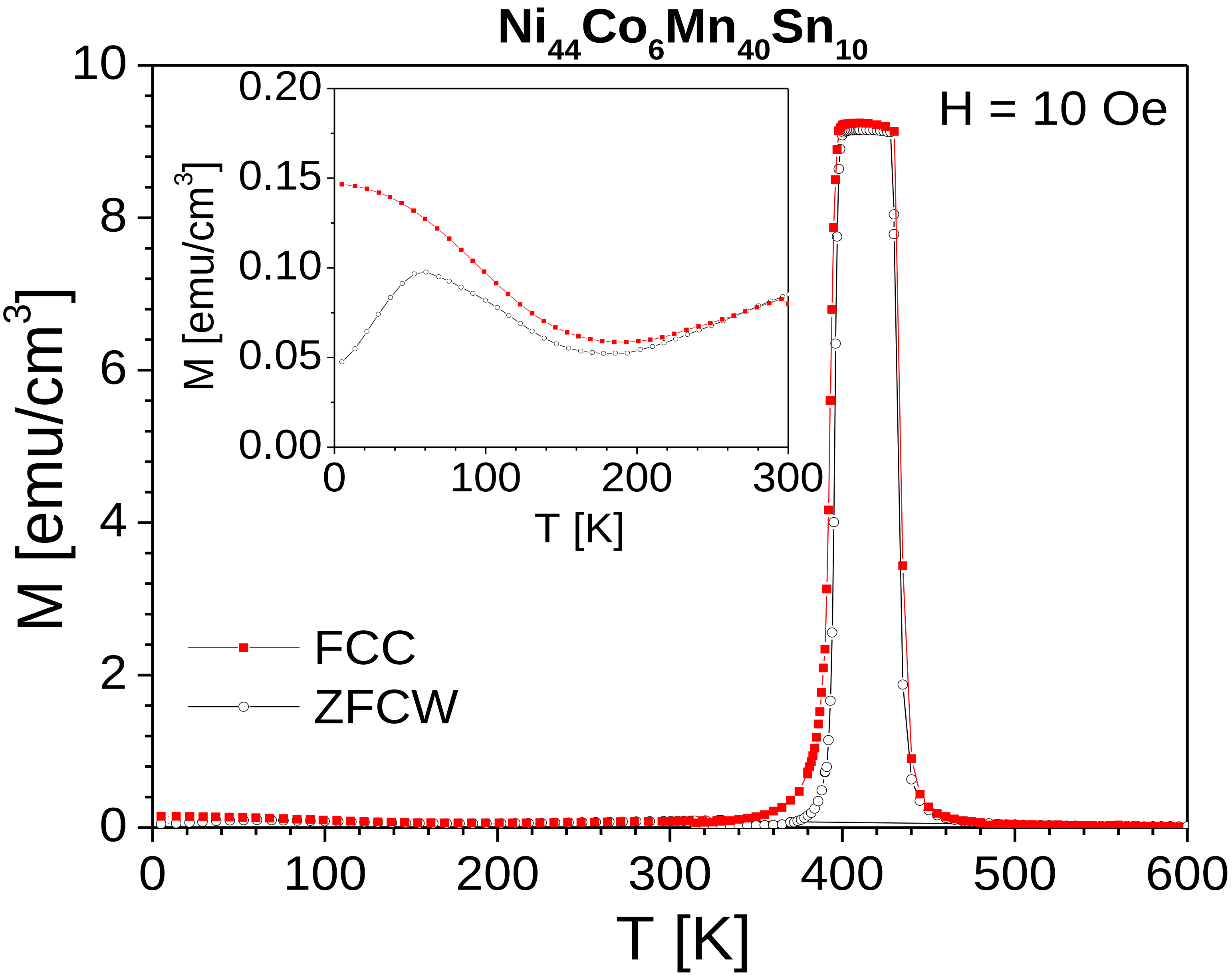
$Ni_{48}Co_2Mn_{40}Sn_{10}$
M [emu/cm^3]
0.00
0.02
0.04
0.06
0.08
T [K]
0
100
200
300
400
500
FCW
FCC
ZFCW
H = 10 Oe
H = 5000 Oe
M [emu/cm^3]
0
10
20
30
T [K]
0
100
200
300
400
500

M vs. T (*x* = 6)

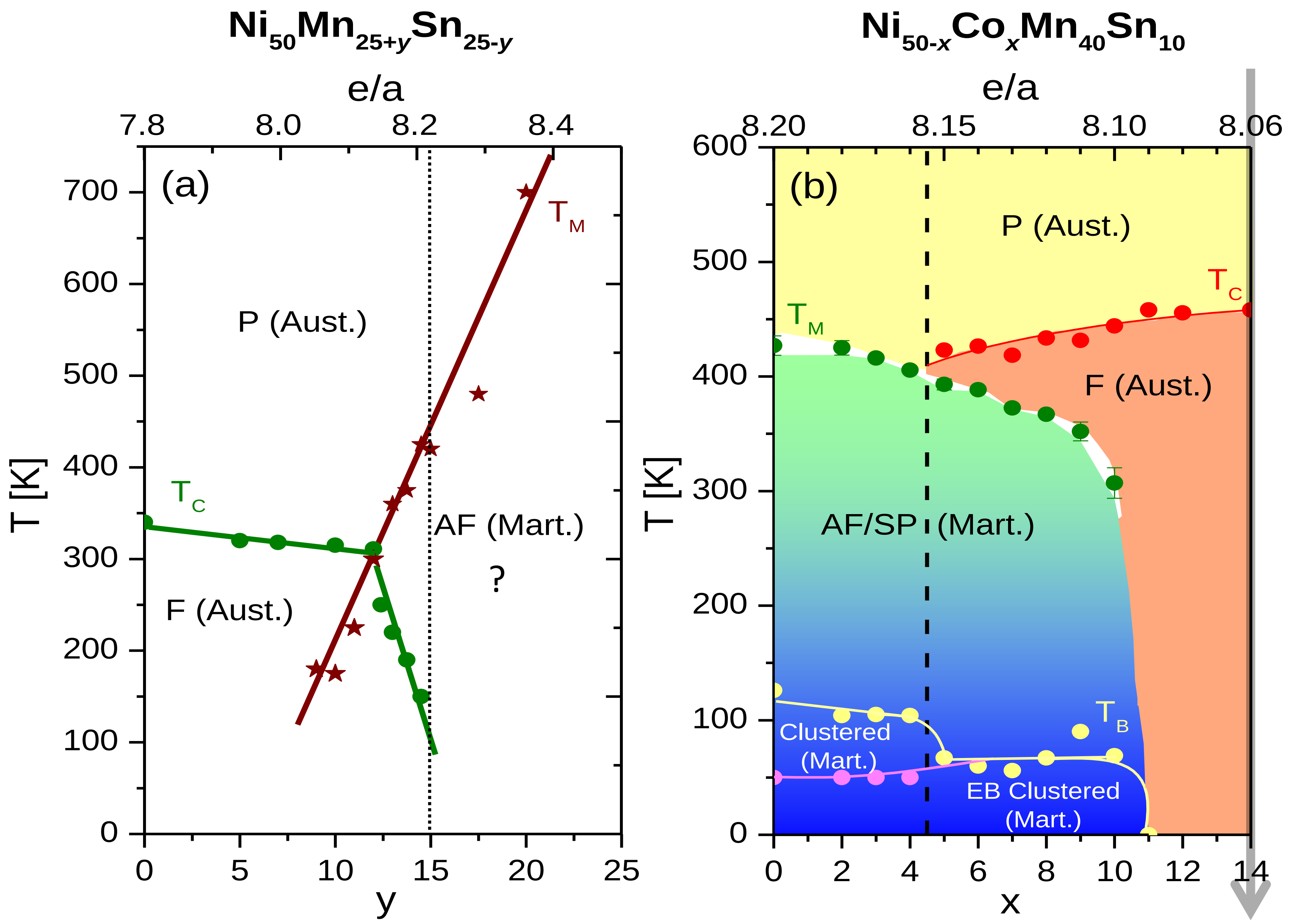


$Ni_{50}Mn_{25+y}Sn_{25-y}$
e/a
7.8
8.0
8.2
8.4
(a)
700
600
500
400
300
200
100
0
T [K]
T_M
P (Aust.)
T_C
AF (Mart.)
?
F (Aust.)
0
5
10
15
20
25
y
$Ni_{50-x}Co_xMn_{40}Sn_{10}$
e/a
8.20
8.15
8.10
8.06
600
500
400
300
200
100
0
(b)
P (Aust.)
T_C
T_M
F (Aust.)
AF/SP (Mart.)
T_B
Clustered (Mart.)
EB Clustered (Mart.)
0
2
4
6
8
10
12
14
x

M vs. T (*x* = 6)


$Ni_{44}Co_6Mn_{40}Sn_{10}$
H = 10 Oe
M [emu/cm^3]
T [K]
0
2
4
6
8
10
0
100
200
300
400
500
600
FCC
ZFCW
M [emu/cm^3]
0.00
0.05
0.10
0.15
0.20
0
100
200
300
T [K]

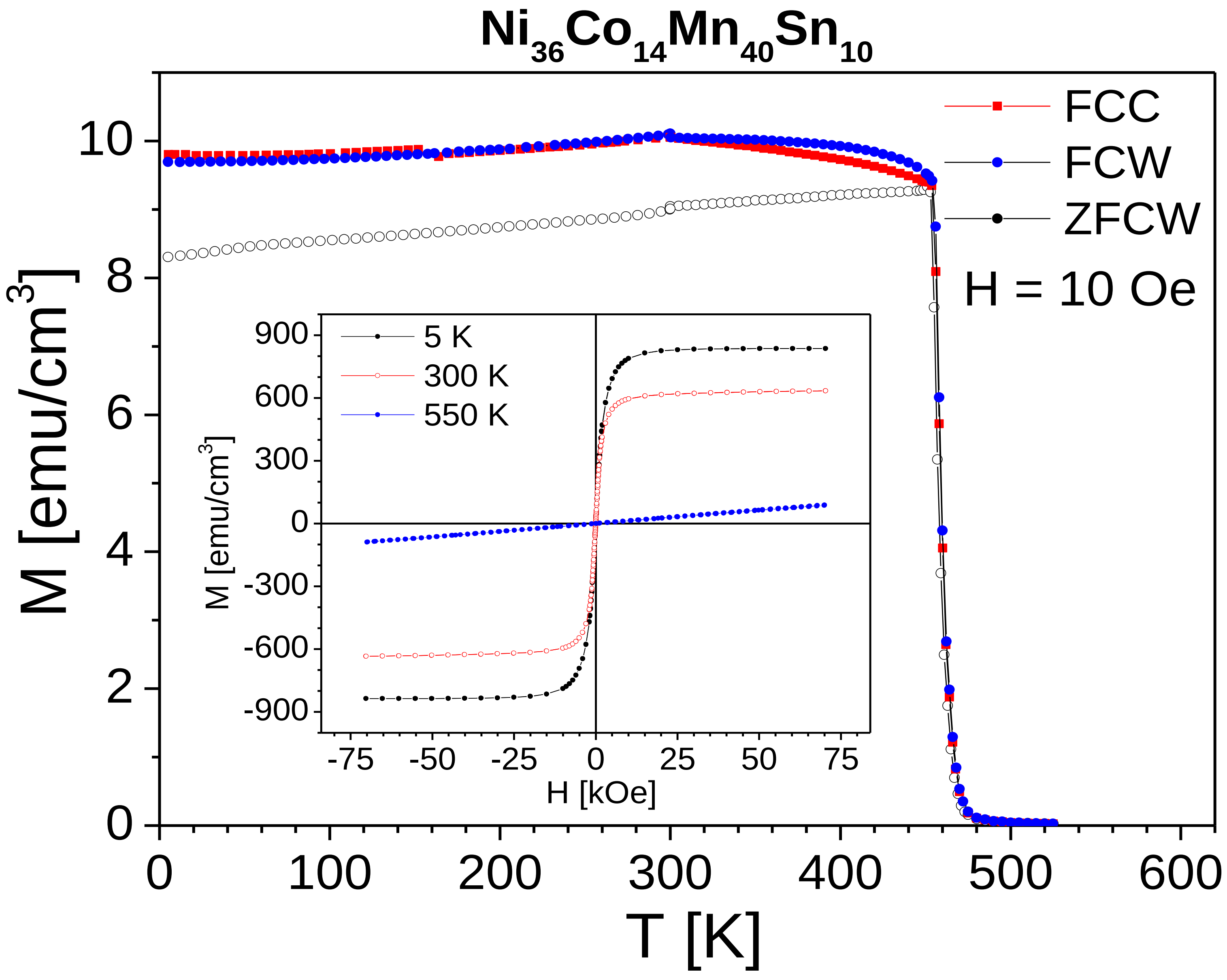
M vs. T (*x* = 14)



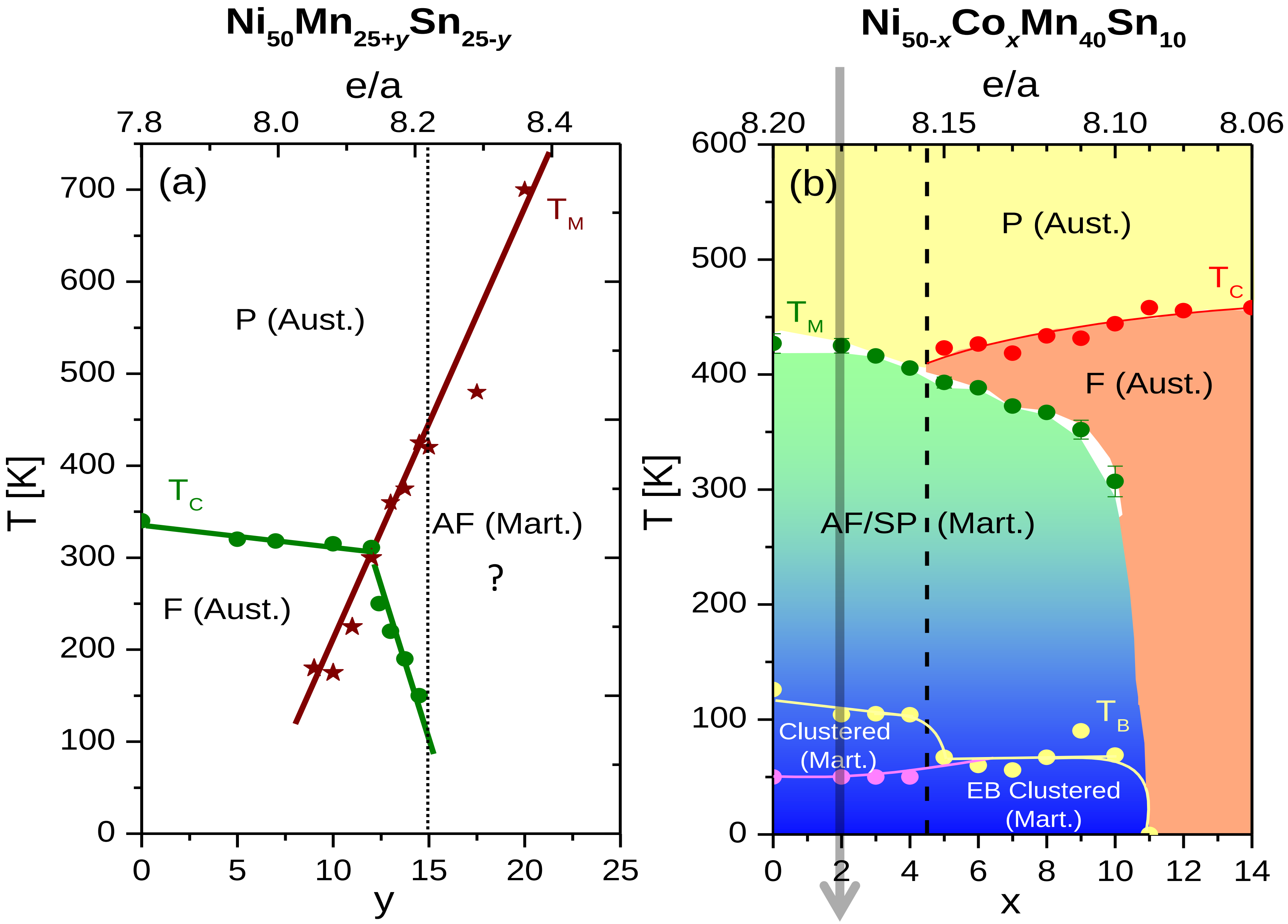
$Ni_{50}Mn_{25+y}Sn_{25-y}$

$Ni_{50-x}Co_xMn_{40}Sn_{10}$

M vs. T (*x* = 14)


$Ni_{36}Co_{14}Mn_{40}Sn_{10}$
FCC
FCW
ZFCW
H = 10 Oe
M [emu/cm^3]
0
2
4
6
8
10
T [K]
0
100
200
300
400
500
600
5 K
300 K
550 K
M [emu/cm^3]
900
600
300
0
-300
-600
-900
H [kOe]
-75
-50
-25
0
25
50
75

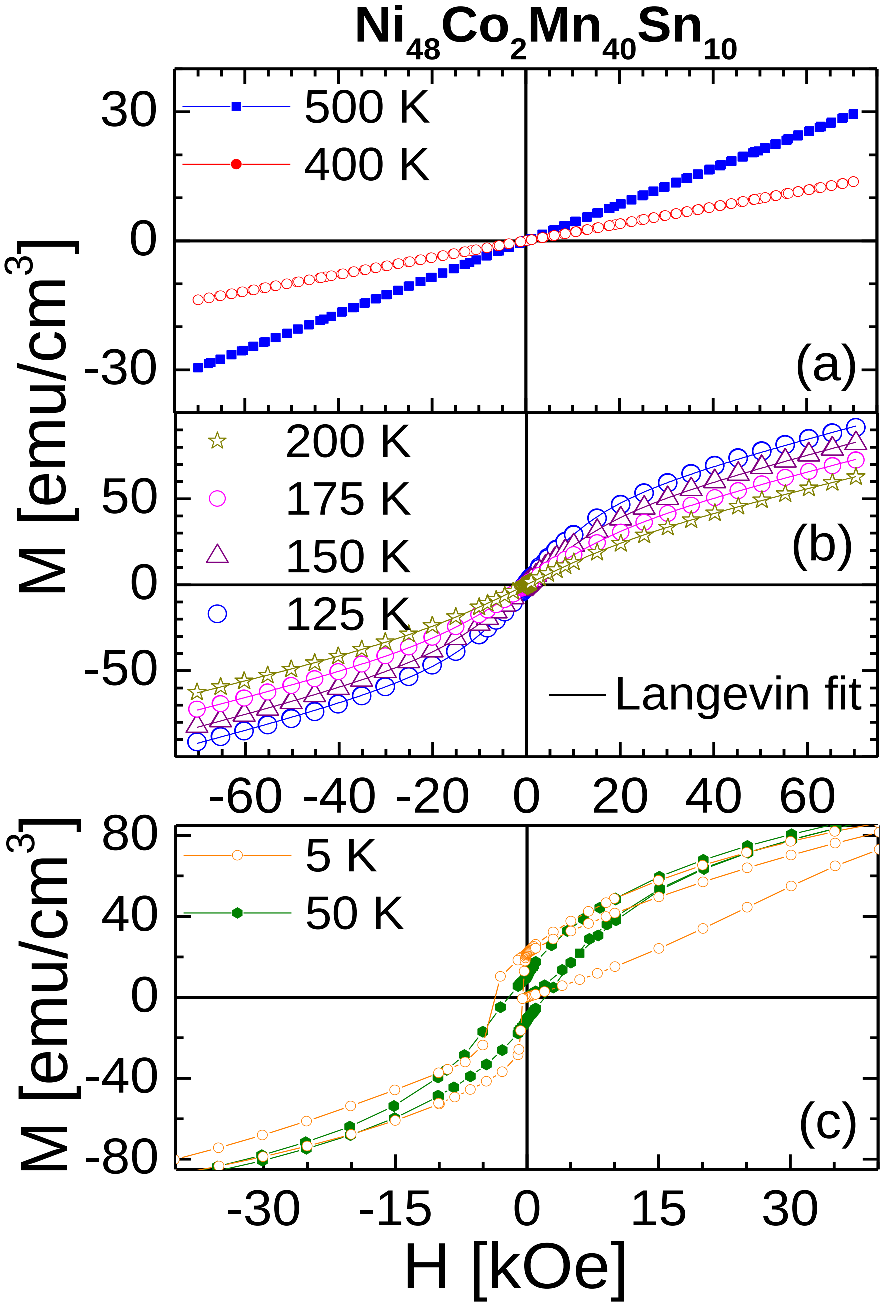
M vs. H (*x* = 2)



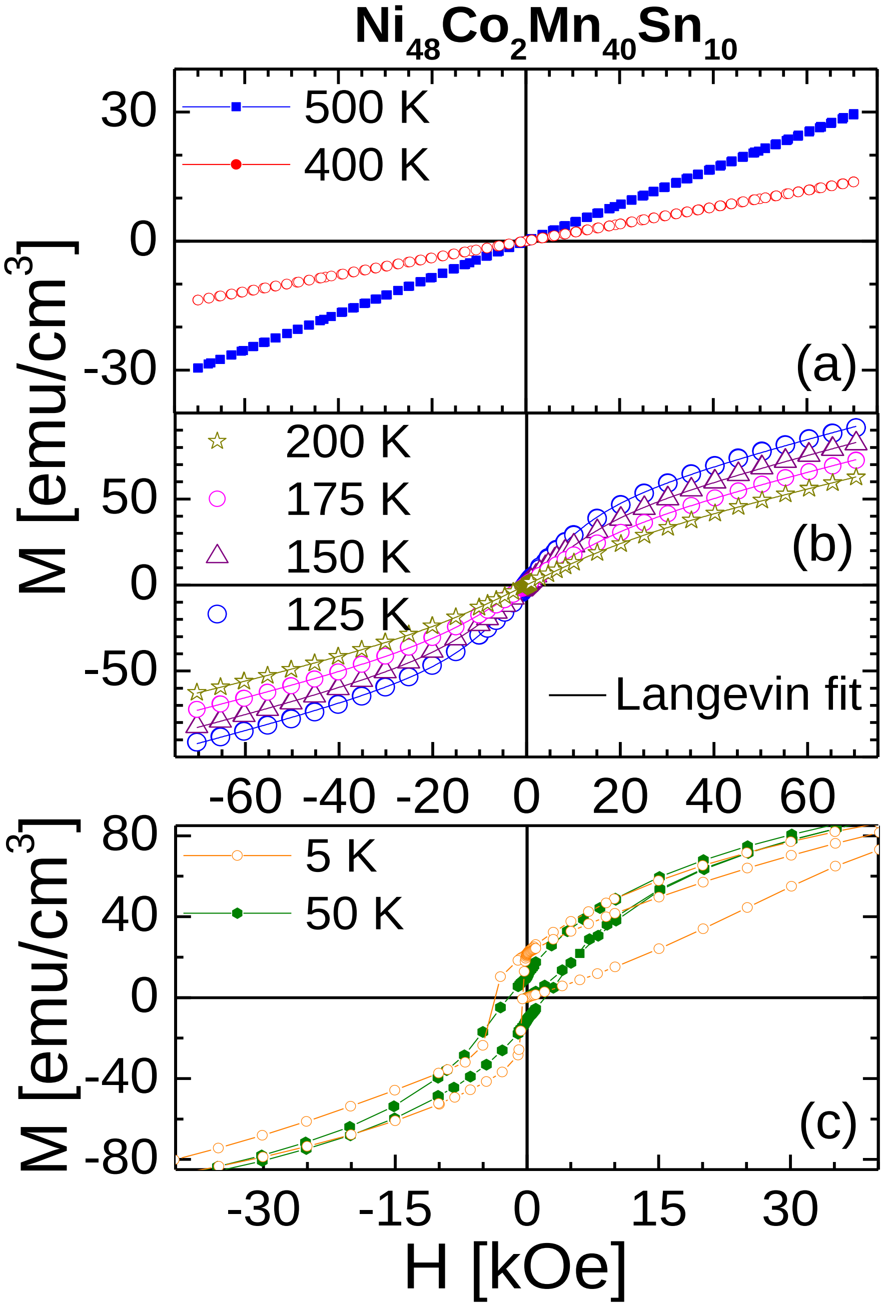
$Ni_{50}Mn_{25+y}Sn_{25-y}$

$Ni_{50-x}Co_xMn_{40}Sn_{10}$

M vs. H (*x* = 2)

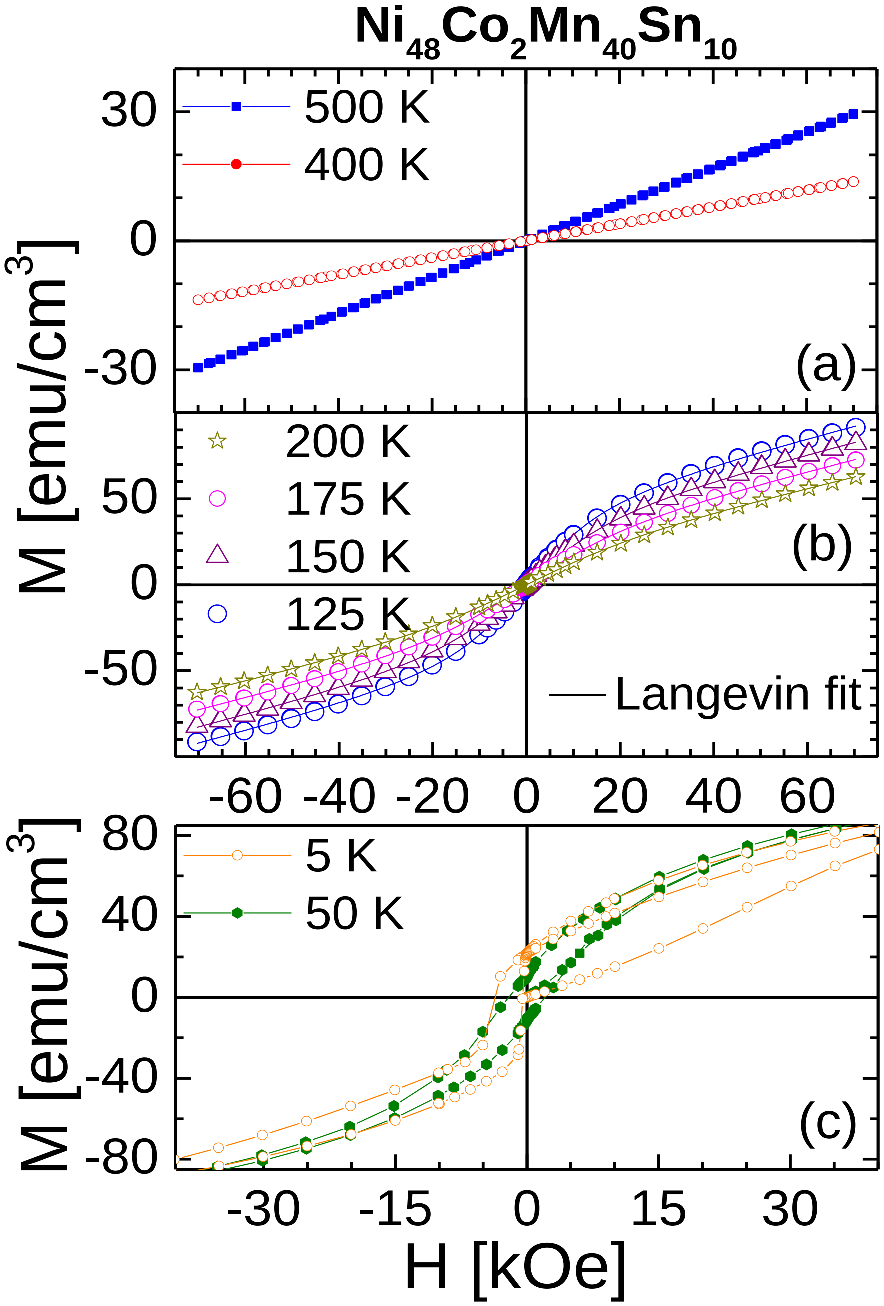

$Ni_{48}Co_2Mn_{40}Sn_{10}$
500 K
400 K
(a)
200 K
175 K
150 K
125 K
(b)
Langevin fit
5 K
50 K
(c)
M [emu/cm^3]
M [emu/cm^3]
30
0
-30
50
0
-50
-60
-40
-20
0
20
40
60
80
40
0
-40
-80
-30
-15
0
15
30
H [kOe]

M vs. H (*x* = 2)



- $T > T_M$: P
- $T < T_M$: AF/P

M vs. H (*x* = 2)

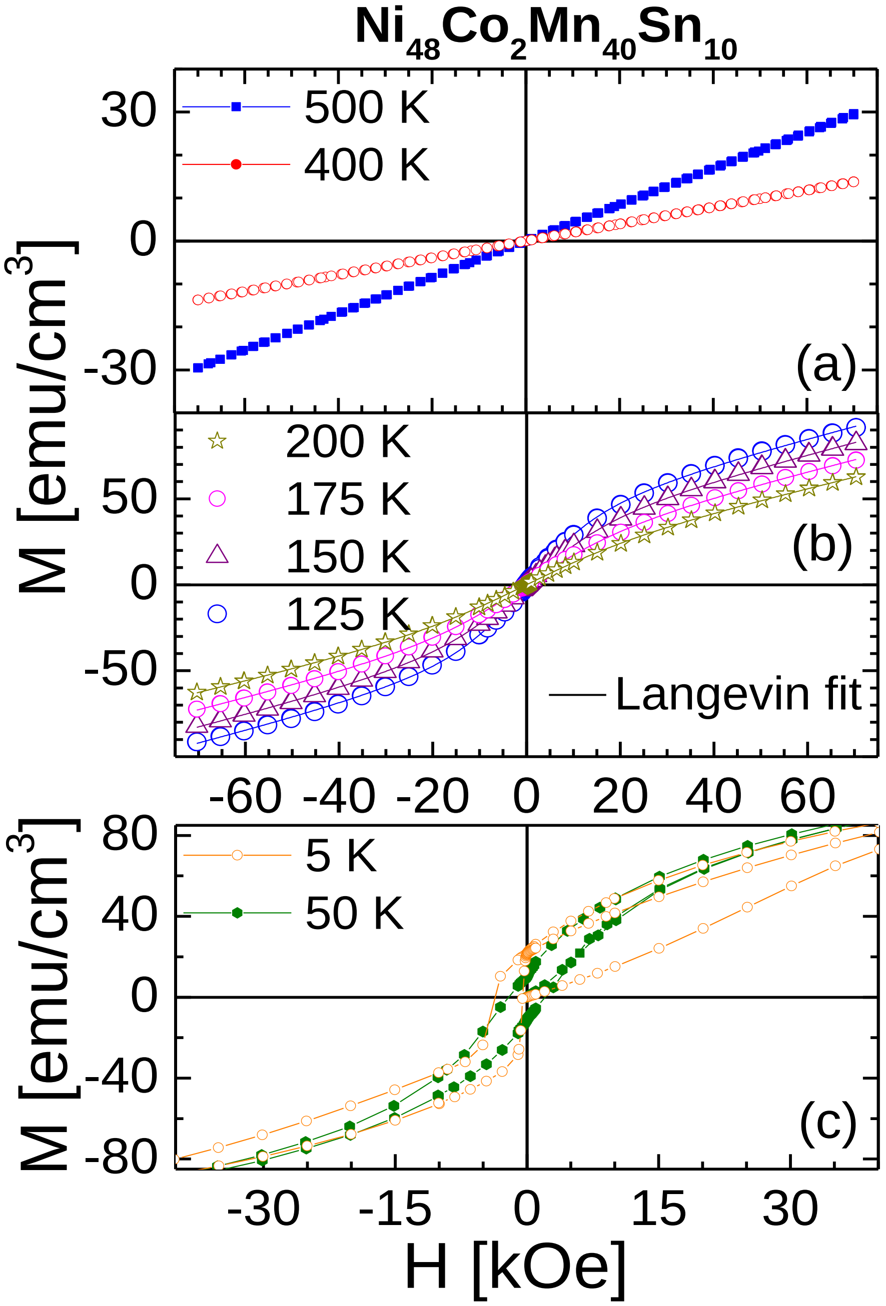


- $T > T_M$: P
- $T < T_M$: AF/P

- 300 - 100 K: Langevin-like $M(H)$

$$M(H,T) = n_C(T)\mu_C(T)\left[\coth\left(\frac{\mu_C(T)H}{k_BT}\right) - \frac{k_BT}{\mu_C(T)H}\right] + \chi_{BG}(T)H$$

M vs. *H* ($x = 2$)



- $T > T_M$: P
- $T < T_M$: AF/P
- 300 - 100 K: Langevin-like $M(H)$

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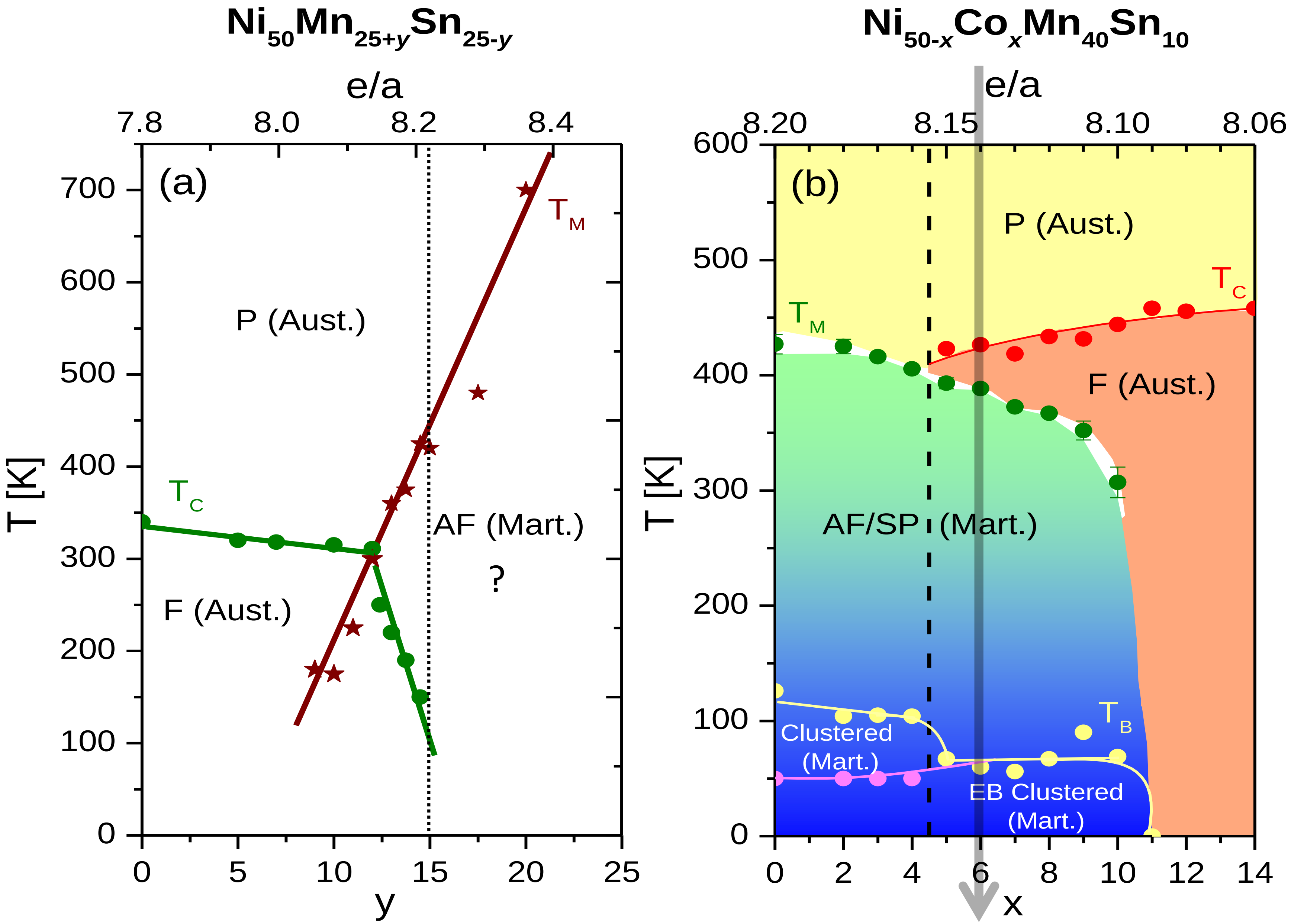
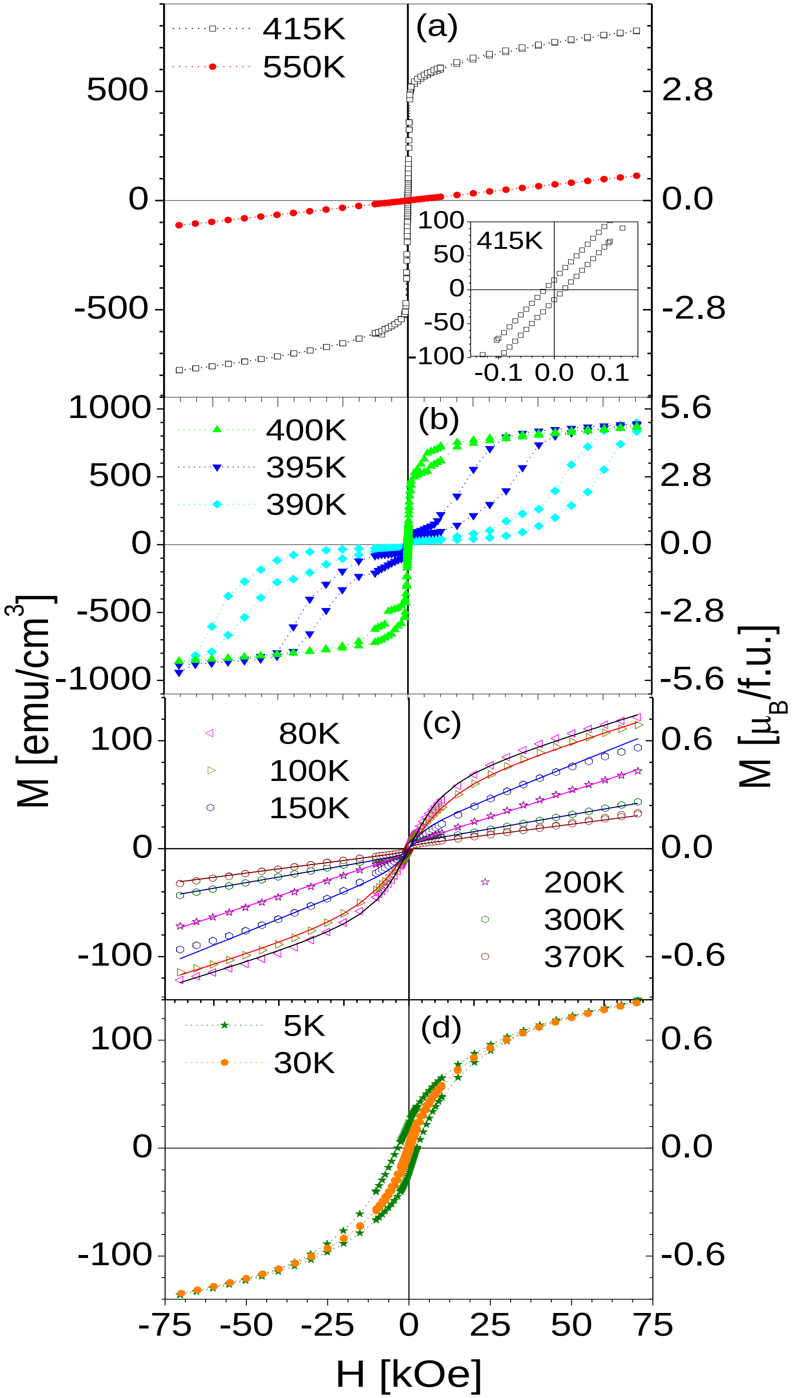
- $T < 100$ K: $M(H)$ gradually opens
  “Static” F
  ZFC exchange bias*

*Wang *et al* PRL (2011)

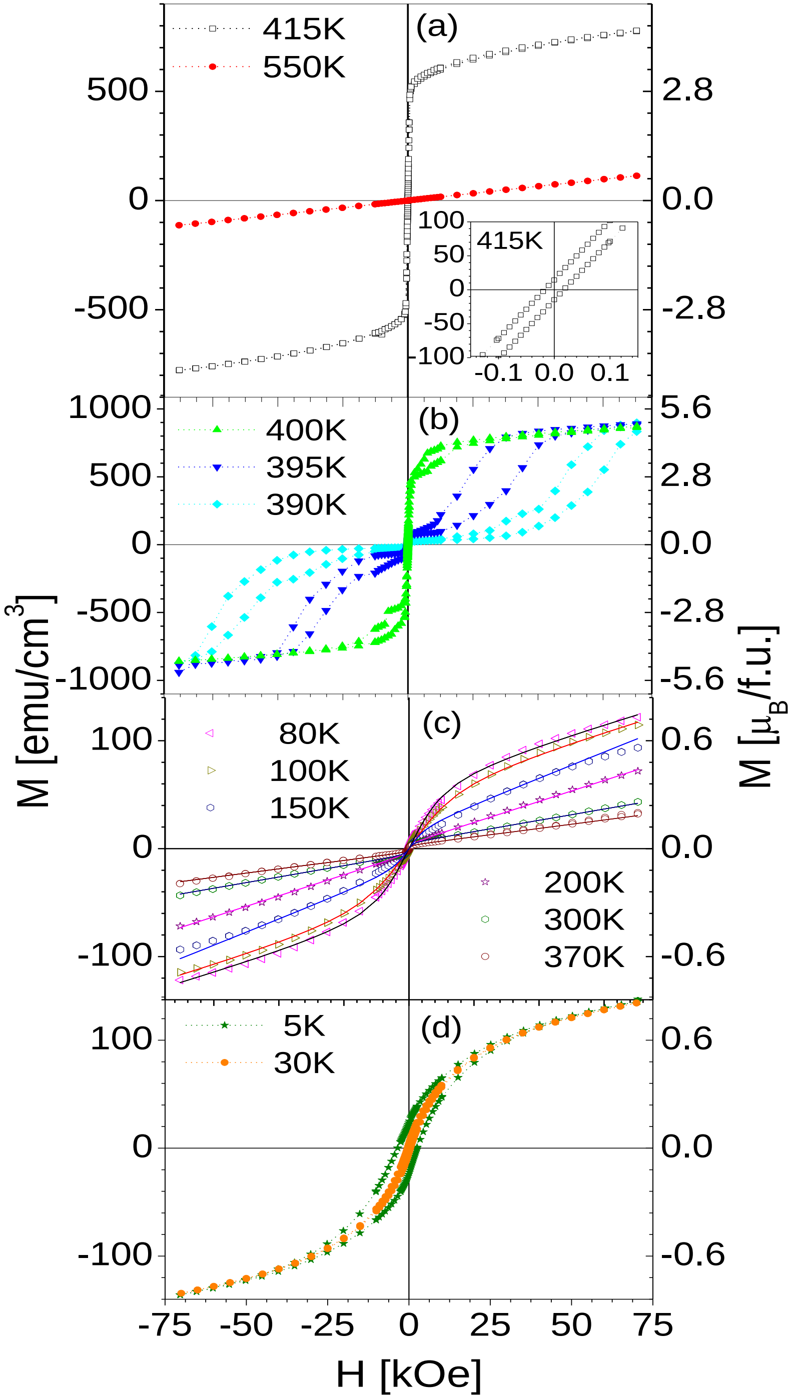
M vs. H (*x* = 6)


Ni50Mn25+ySn25-y
e/a
7.8
8.0
8.2
8.4
(a)
T_M
P (Aust.)
T_C
AF (Mart.)
?
F (Aust.)
T [K]
700
600
500
400
300
200
100
0
0
5
10
15
20
25
y
Ni50-xCoxMn40Sn10
e/a
8.20
8.15
8.10
8.06
(b)
P (Aust.)
T_C
T_M
F (Aust.)
AF/SP (Mart.)
T [K]
600
500
400
300
200
100
0
T_B
Clustered
(Mart.)
EB Clustered
(Mart.)
0
2
4
6
8
10
12
14
x

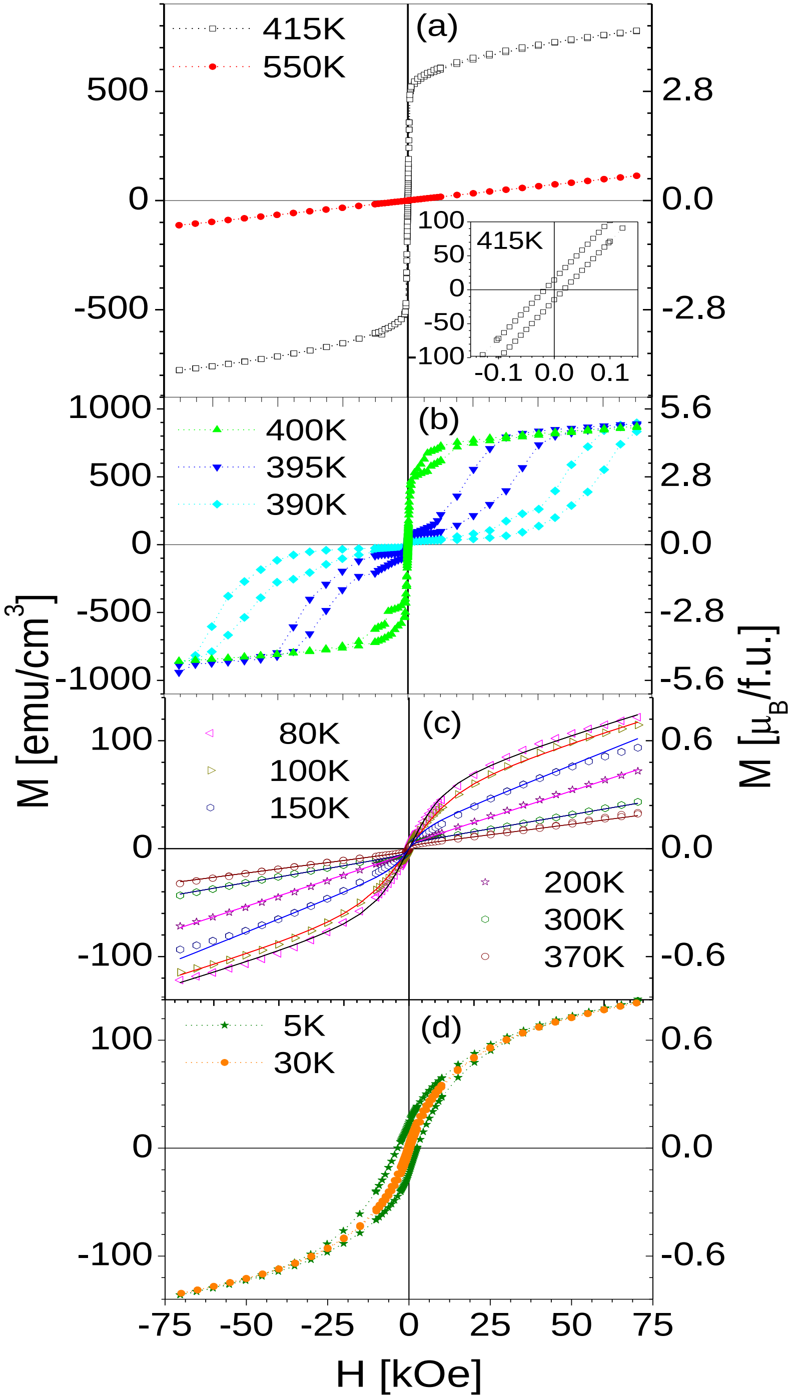
M vs. H (*x* = 6)


(a)
415K
550K
415K
(b)
400K
395K
390K
(c)
80K
100K
150K
200K
300K
370K
(d)
5K
30K
M [emu/cm³]
M [μB/f.u.]
H [kOe]
500
0
-500
2.8
0.0
-2.8
100
50
0
-50
-100
-0.1
0.0
0.1
1000
500
0
-500
-1000
5.6
2.8
0.0
-2.8
-5.6
100
0
-100
0.6
0.0
-0.6
-75
-50
-25
0
25
50
75

M vs. H (*x* = 6)



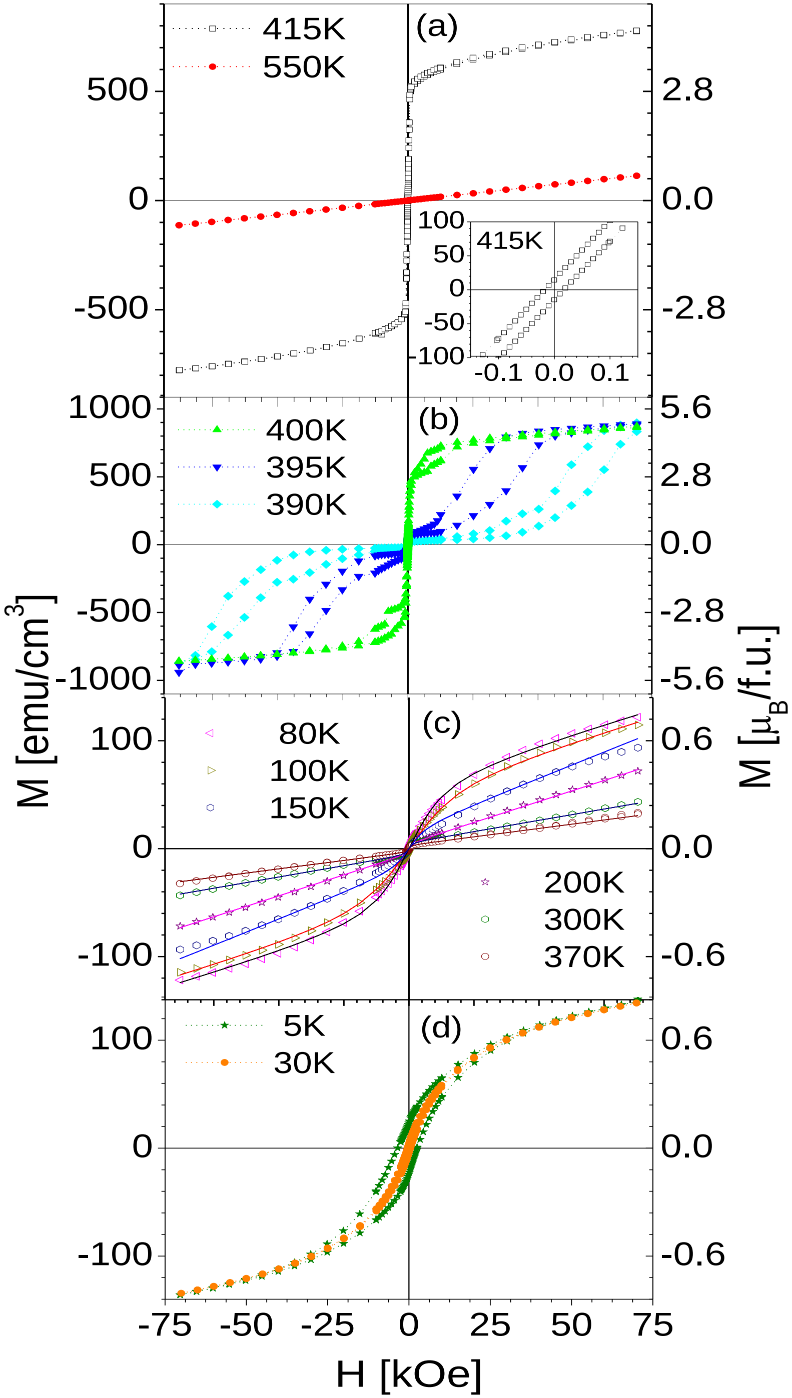
- $T > T_C$: P
- $T < T_C$: Soft F



M vs. H (*x* = 6)

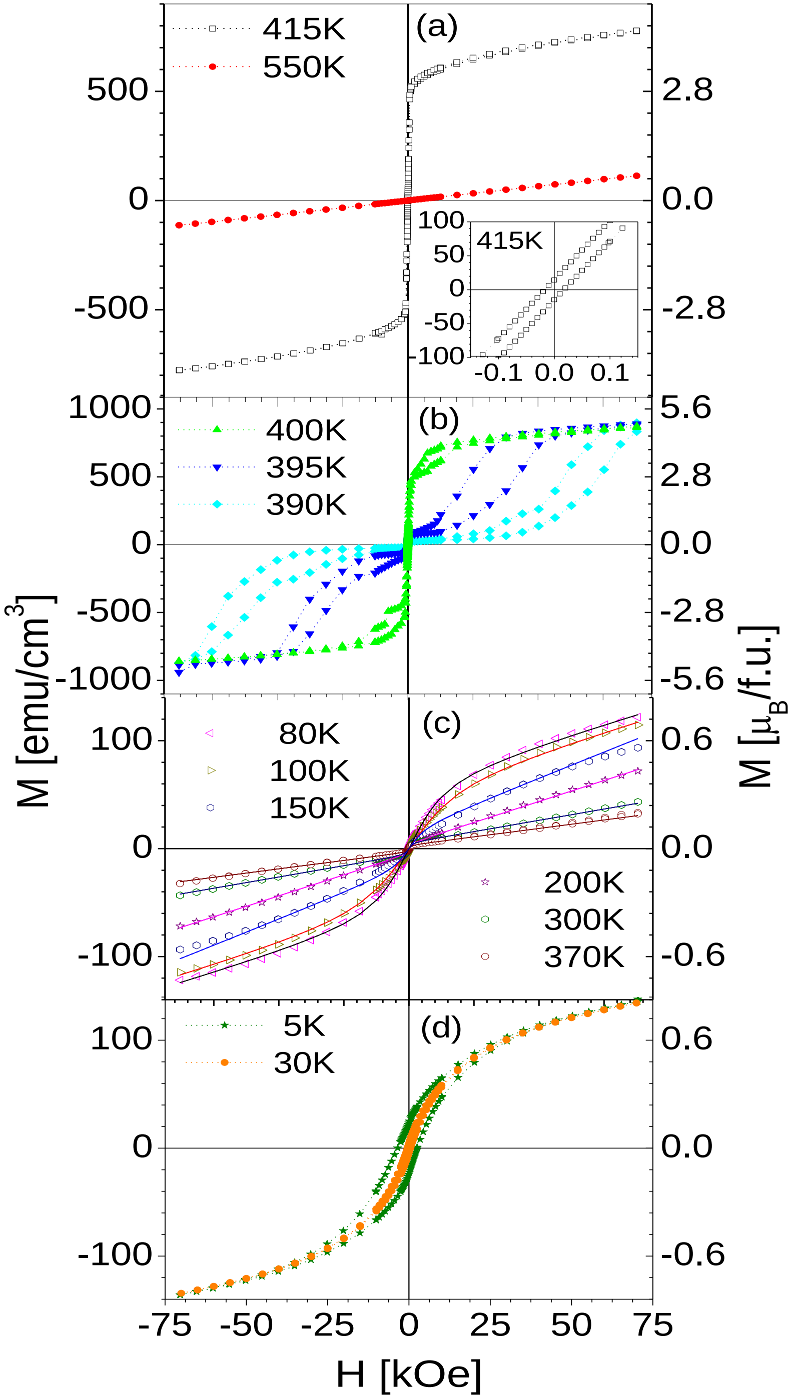
- *T* > *T*$_C$: P
- *T* < *T*$_C$: Soft F
- 400 - 380 K: Hysteresis region (*H*-induced MPT)

M vs. H (x = 6)



- *T* > *T$_C$*: P
- *T* < *T$_C$*: Soft F
- 400 - 380 K: Hysteresis region (*H*-induced MPT)
- 380 - 60 K: Langevin-like *M*(*H*)

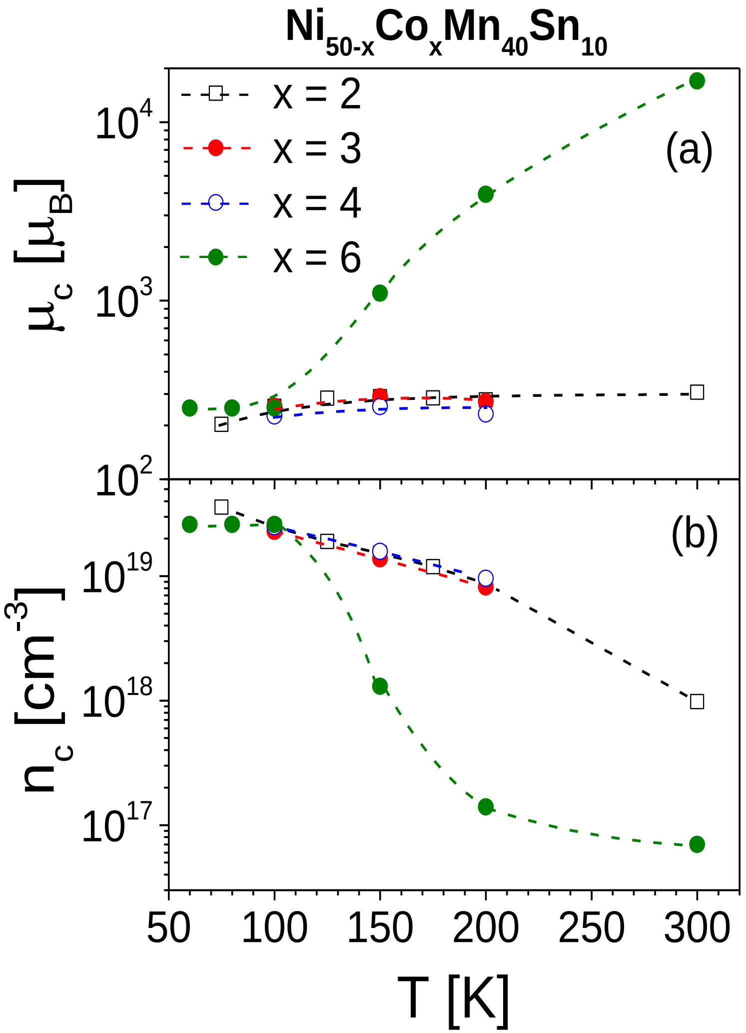
M vs. H (x = 6)



- $T > T_C$: P
- $T < T_C$: Soft F
- 400 - 380 K: Hysteresis region (*H*-induced MPT)
- 380 - 60 K: Langevin-like *M*(*H*)
- $T < 60$ K: *M*(*H*) gradually opens “Static” F

Superparamagnetic-like Behavior

$$M(H,T) = n_C(T)\,\mu_C(T)\left[\coth\left(\frac{\mu_C(T)H}{k_B T}\right) - \frac{k_B T}{\mu_C(T)H}\right] + \chi_{BG}(T)H$$



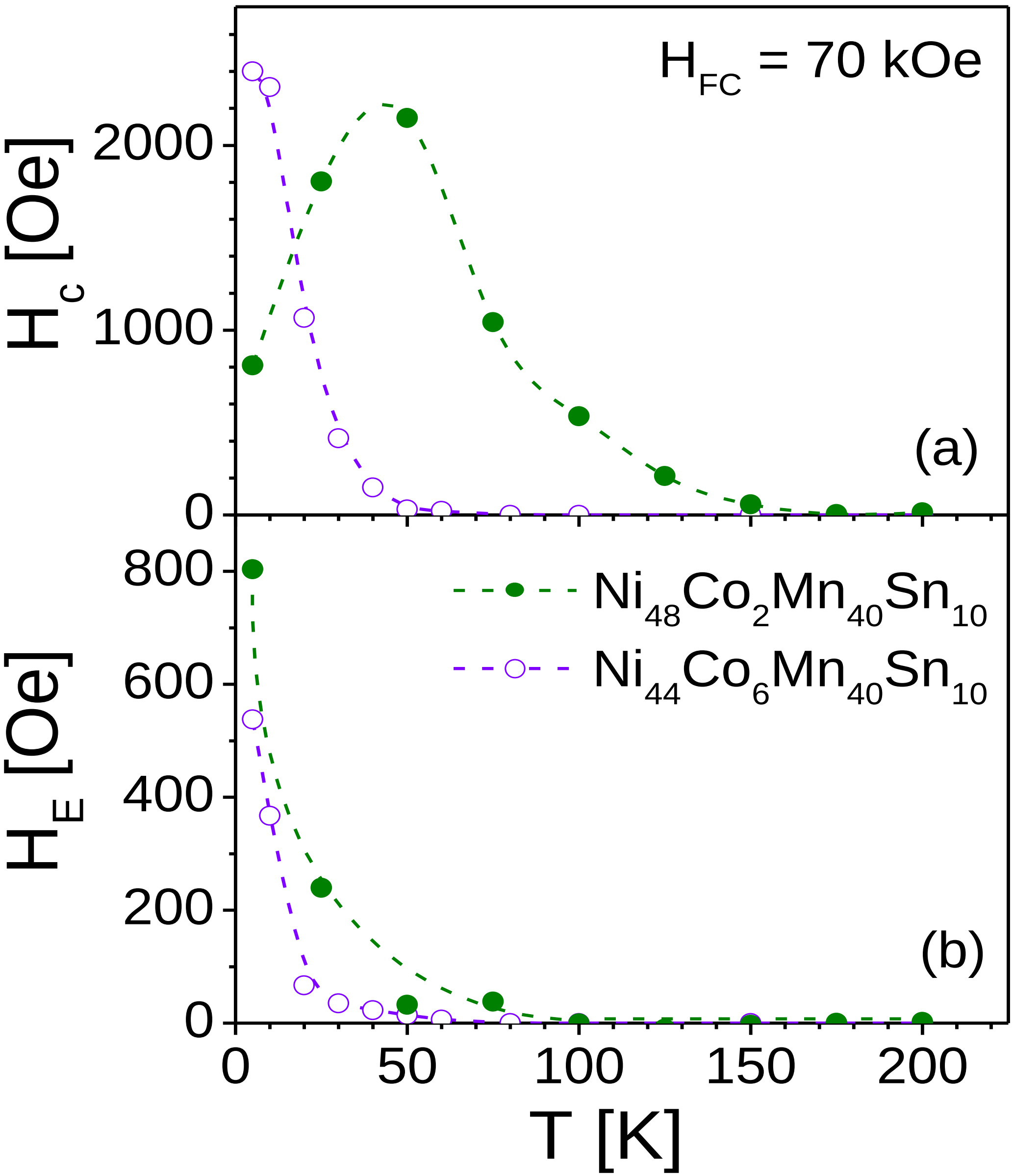
$\mu_c \approx$ 200-250 μ_B

$n_c \approx$ 2-3 x 10^{19} cm^{-3}

$d_c \approx$ 2-6 nm

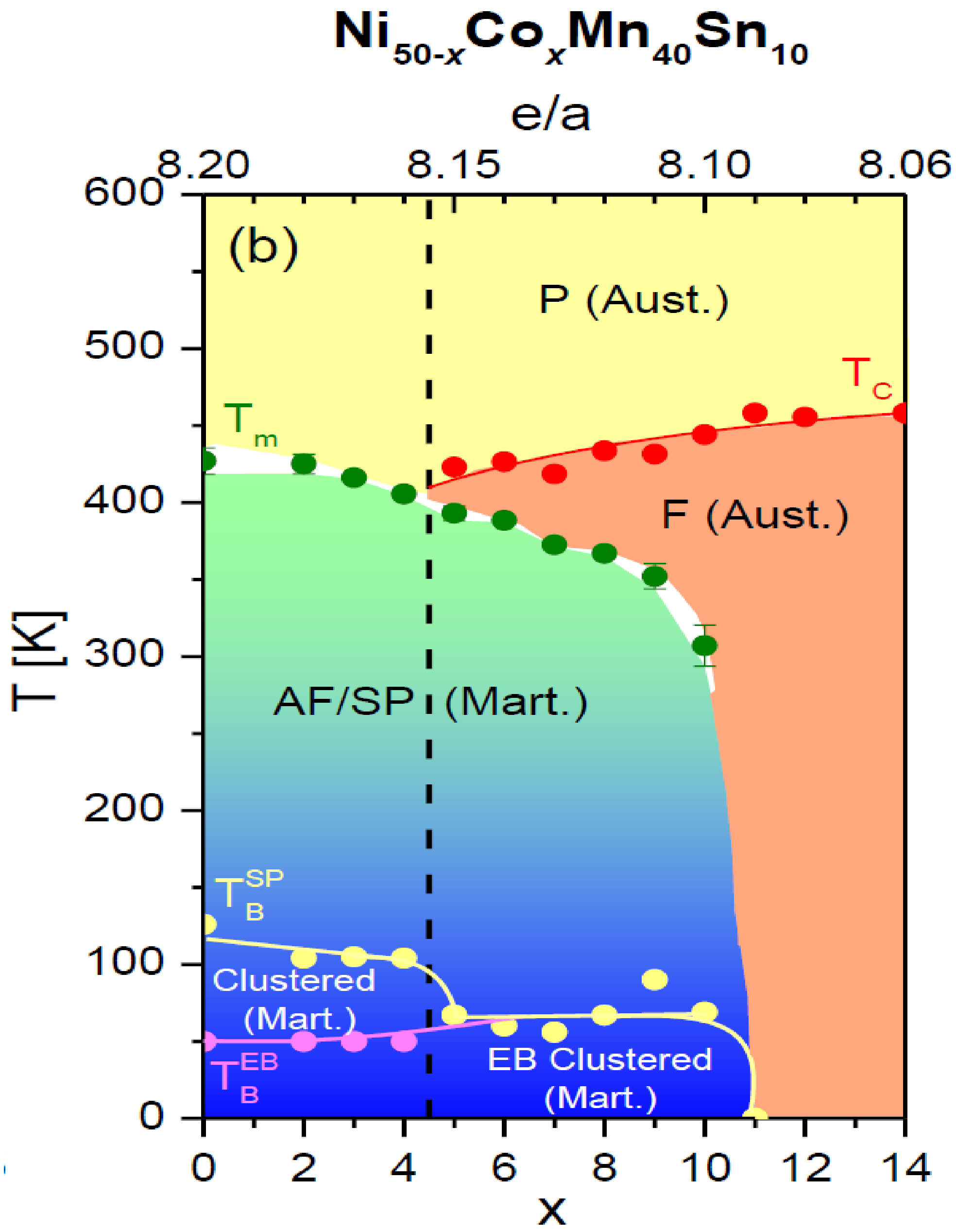
Implication: Dense ensemble of nm-scale spin clusters

Exchange Bias

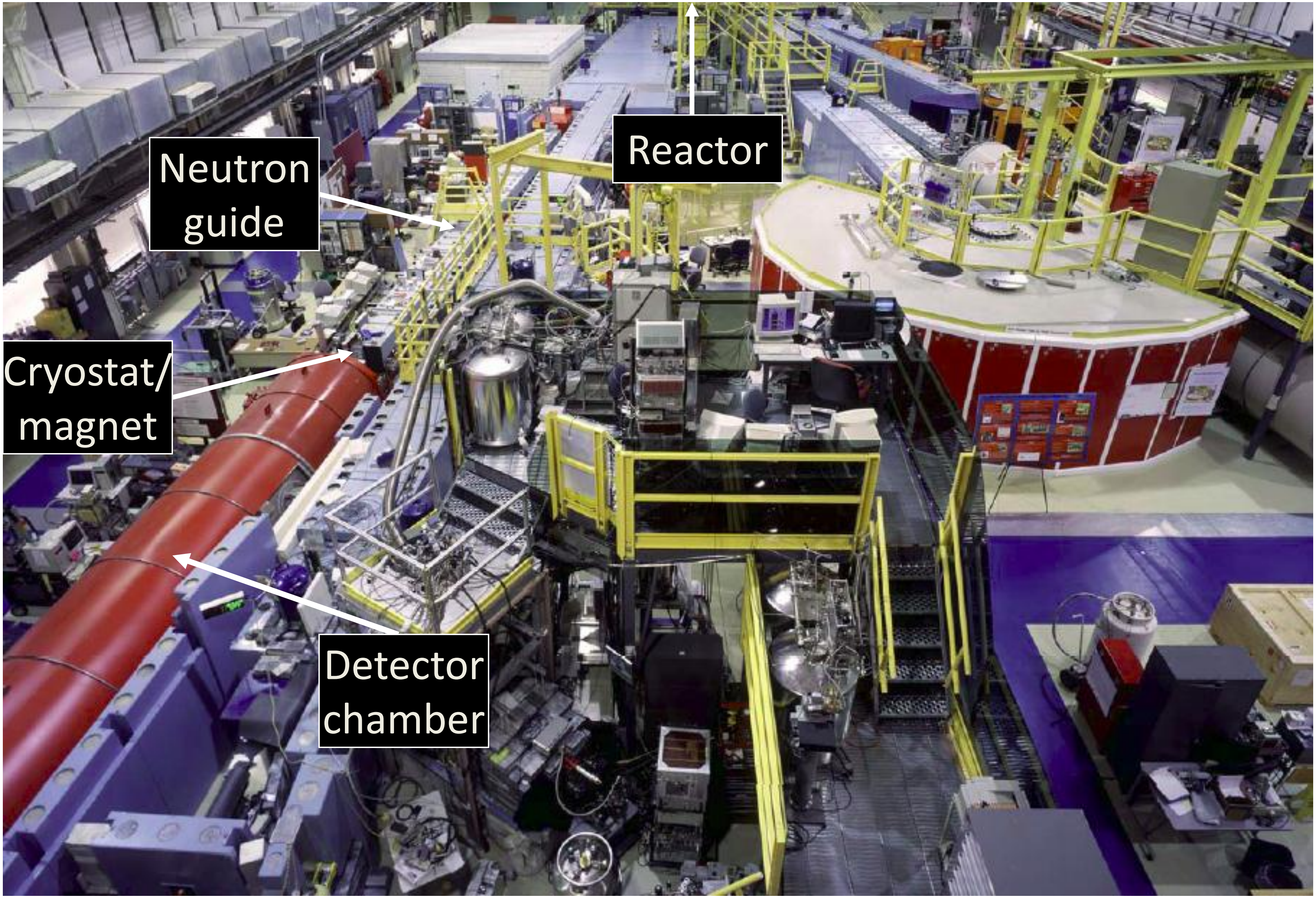


- *x* = 2:
  - > SP blocking at 100-150 K
  - > EB blocking at 60 K
  - > Large H_C peak
- *x* = 6:
  - > SP blocking at 60 K
  - > EB blocking at 60 K
  - > No H_C peak

Phase Diagram



SANS (NIST)



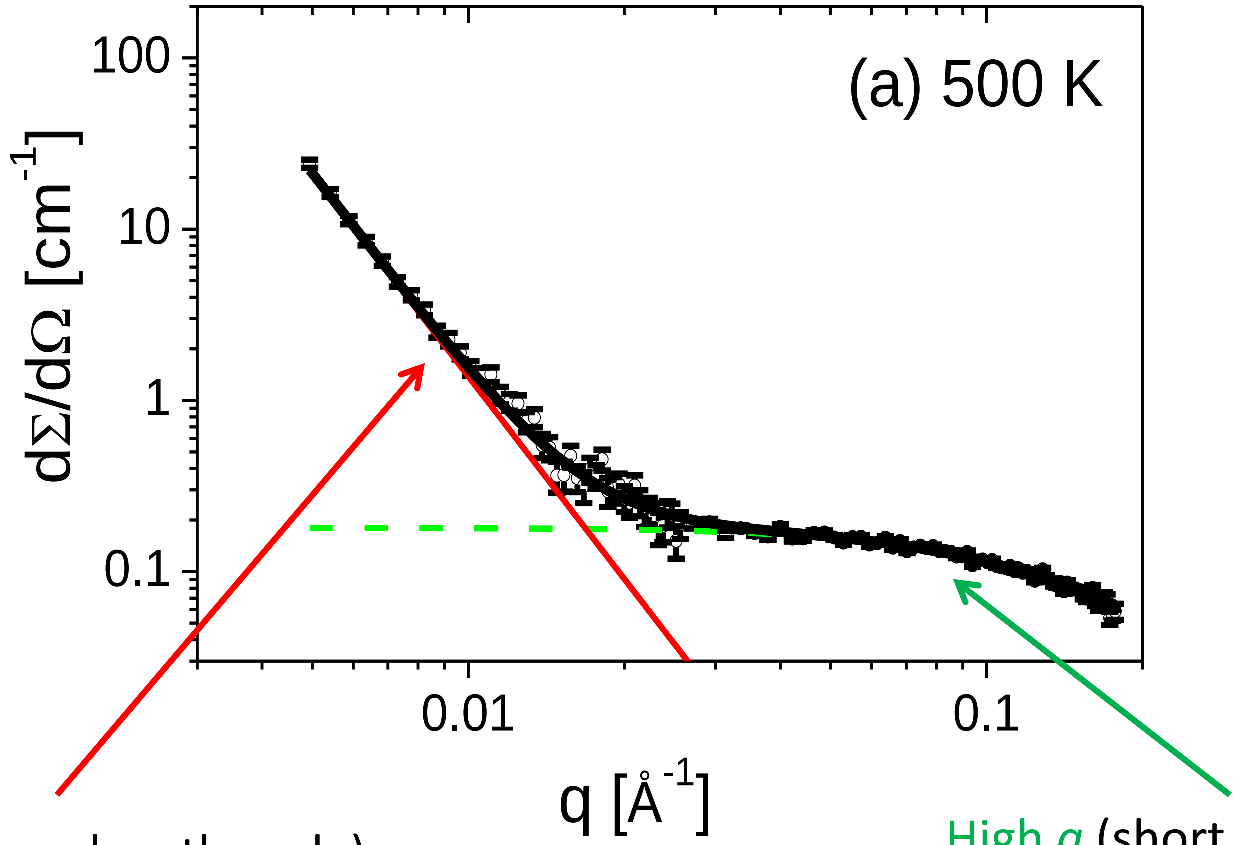
Reactor

Neutron guide

Cryostat/ magnet

Detector chamber

SANS (x = 6)



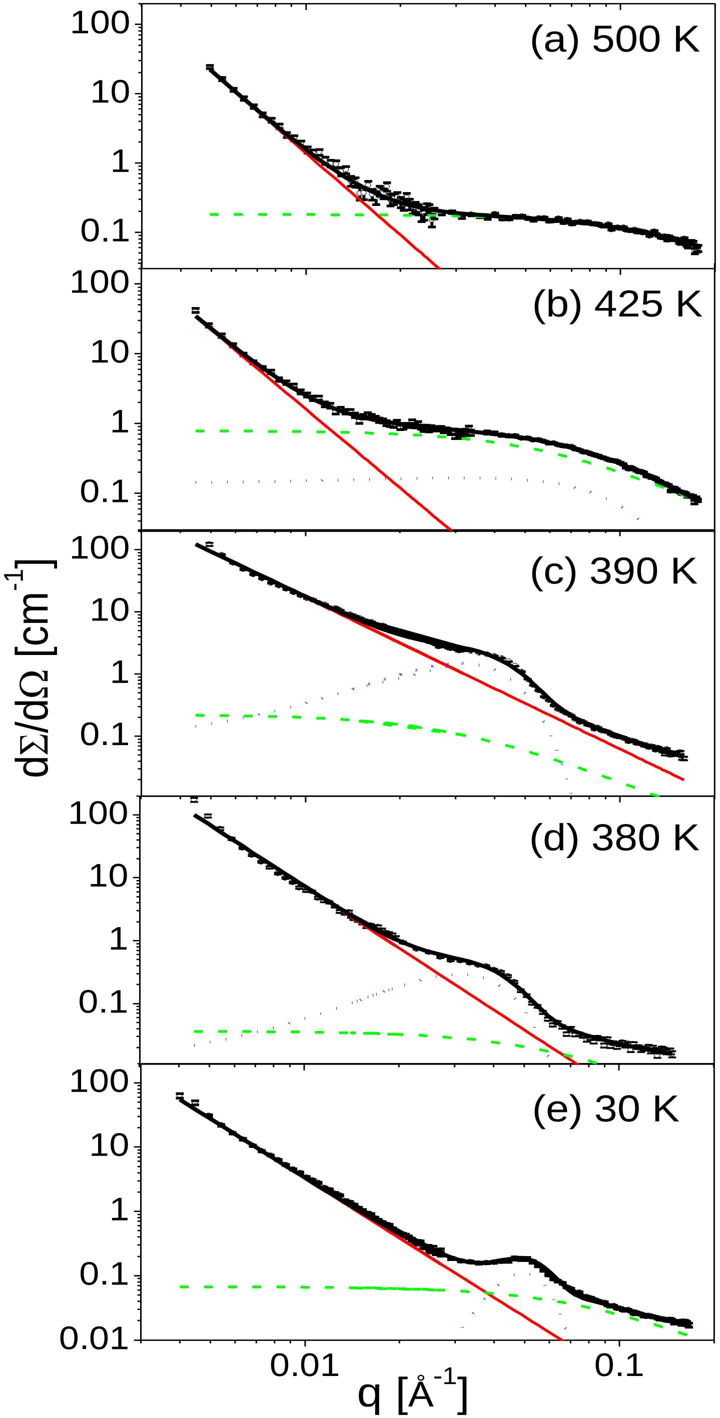
Low q (large length-scale)
Porod Scattering

$$\frac{d\Sigma}{d\Omega}(q,T)=\frac{\left(\frac{d\Sigma}{d\Omega}\right)_P(T)}{q^n}$$

High q (short length-scale)
Lorentzian Scattering

$$\frac{d\Sigma}{d\Omega}(q,T)=\frac{\left(\frac{d\Sigma}{d\Omega}\right)_L(T)}{q^2+\left(\frac{1}{\xi(T)}\right)^2}$$

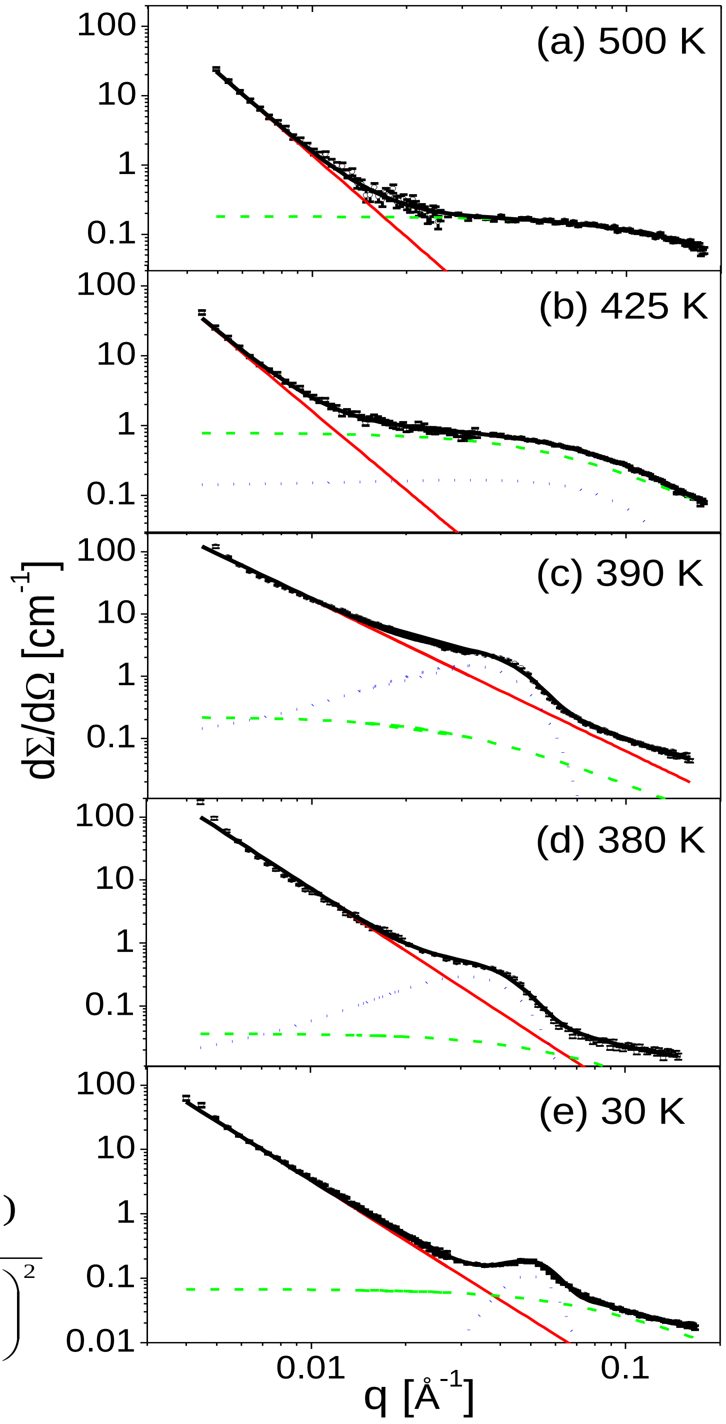
SANS: *q* Dependence



SANS: *q* Dependence

- Low *q* Porod scattering:
  - > Increases below T_C
  - > Magnetic domain scattering
  - > Proof of long-range F order (>> 100 nm)
- High *q* Lorentzian scattering:
  - > Peaks at T_C
  - > F spin correlations
- Intermediate *q* scattering:
  - > A peak develops! $2\pi/q \approx$ 120-200 Å
  - > Structure factor peak. **Liquid-like spatial distribution of magnetic clusters.**

$$\left(\frac{d\Sigma}{d\Omega}\right)_{Tot}(q,T)=\frac{\left(\frac{d\Sigma}{d\Omega}\right)_P(T)}{q^n}+\left(\frac{d\Sigma}{d\Omega}\right)_G(T)\exp\left(\frac{-(q-q_G(T))^2}{2\Delta(T)^2}\right)+\frac{\left(\frac{d\Sigma}{d\Omega}\right)_L(T)}{q^2+\left(\frac{1}{\xi(T)}\right)^2}$$



SANS: *T* Dependence

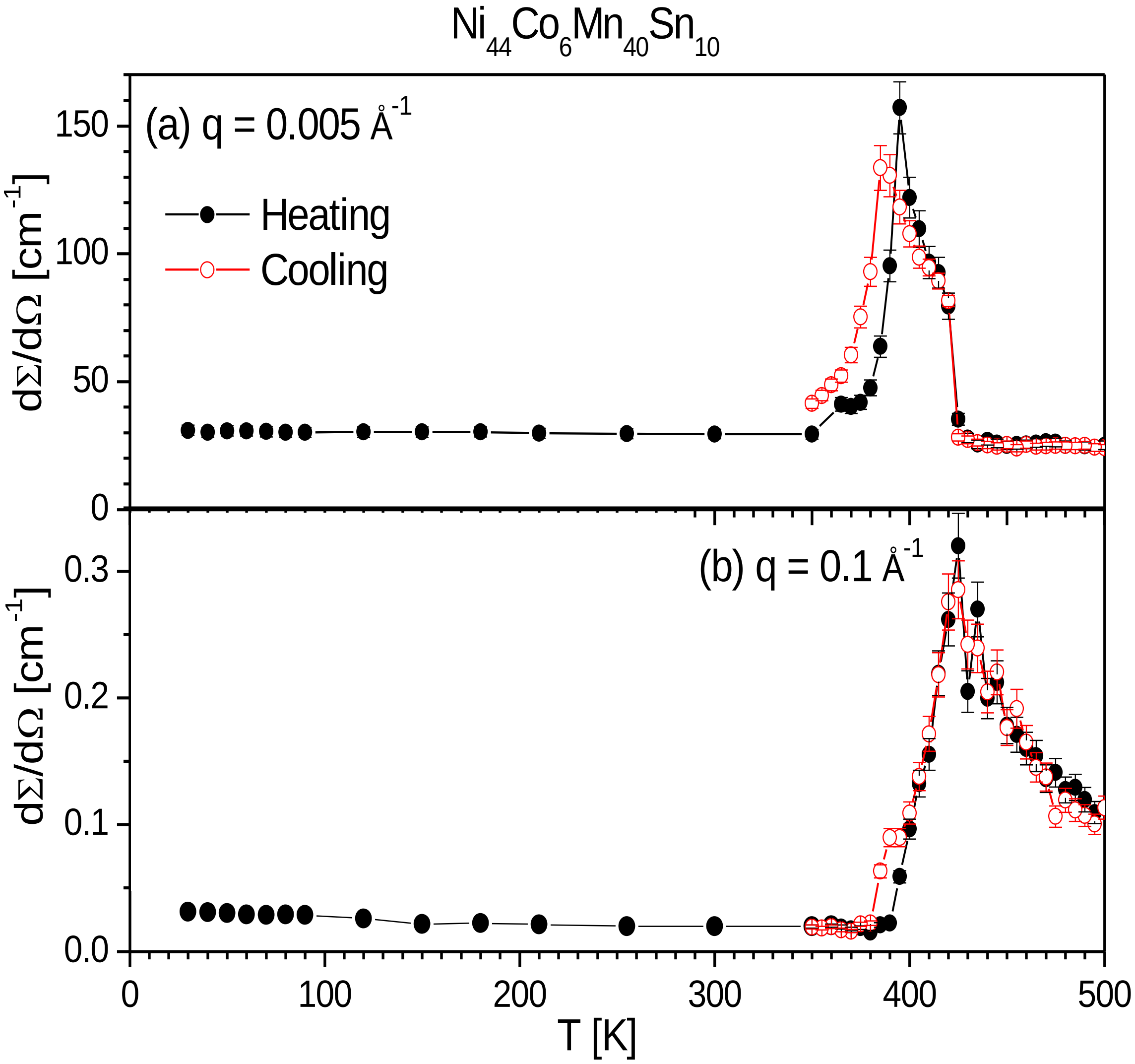
- *q* = 0.005 Å^{-1} (1200 Å):

> Sharp onset of domain scattering at T_C

> Hysteretic loss at T_M

- *q* = 0.1 Å^{-1} (60 Å):

> Critical scattering peak at T_C



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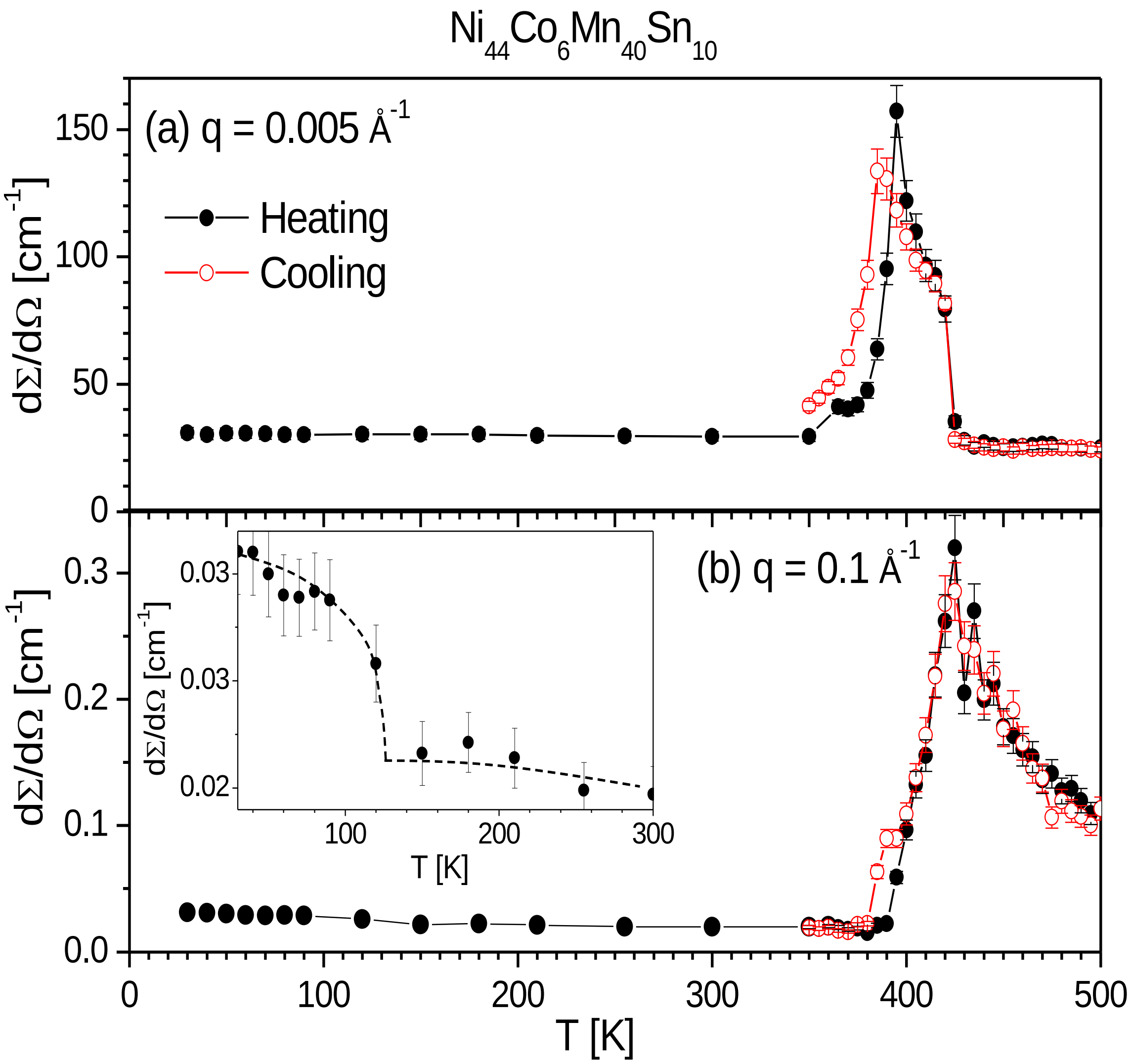
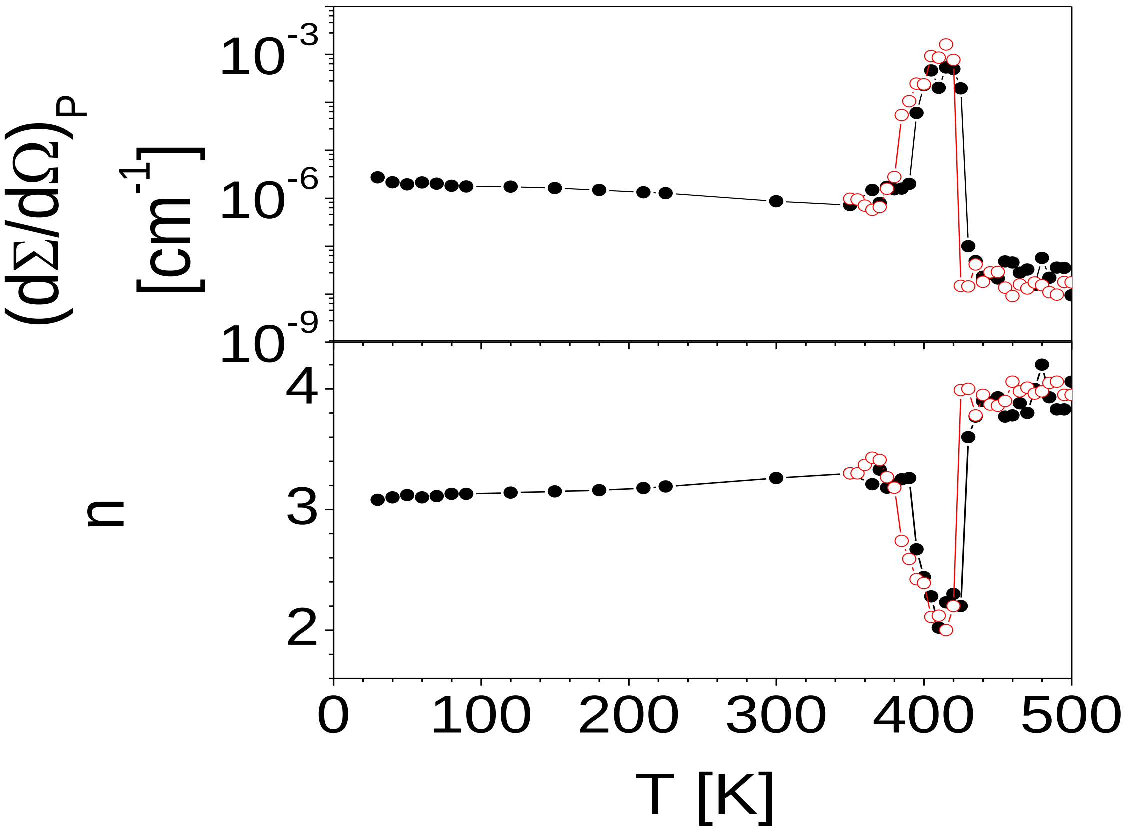
> Critical scattering peak at T_C

> 130 K transition (!), clearly associated with clusters

> Blocking at 10^{-12} s time-scales!

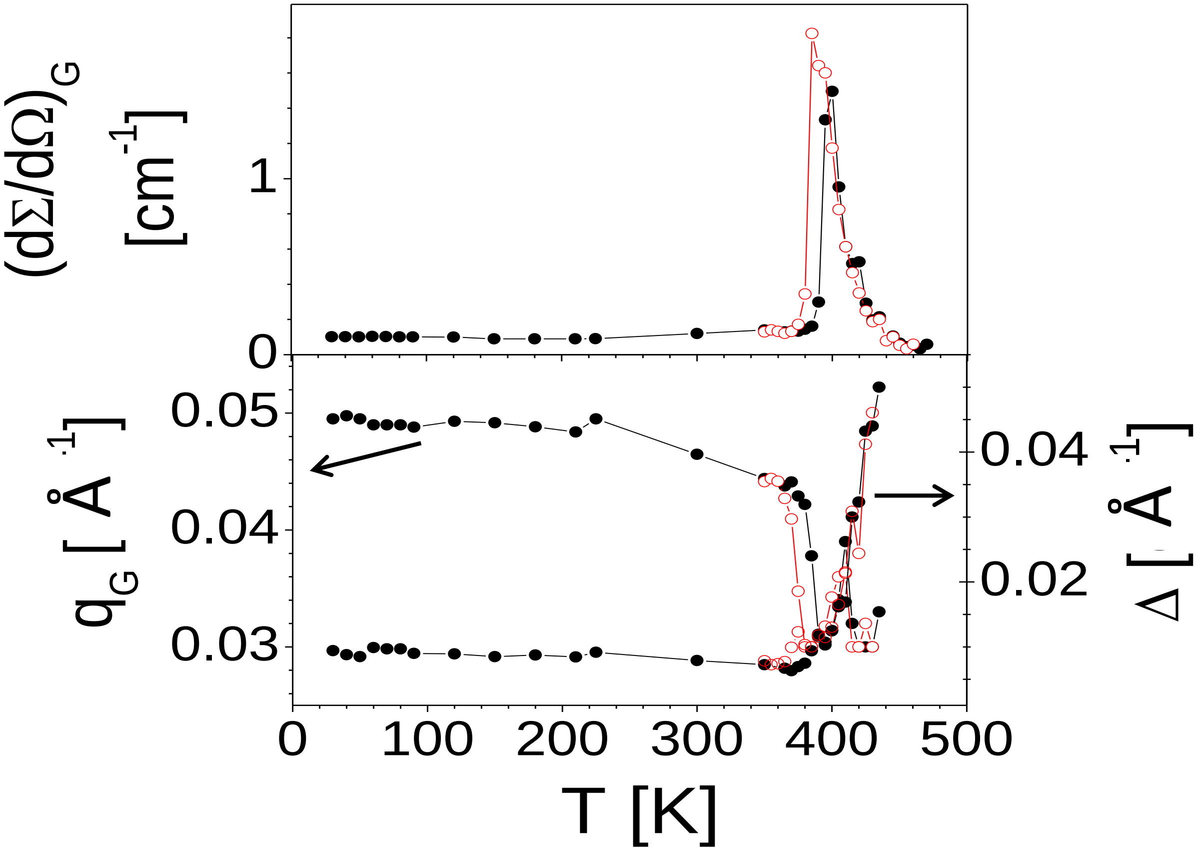


SANS *T* Dependence: Porod



- Scattering in martensite strong, *T*-dependent
- Paramagnetic, *n* = 4 (grains); Ferromagnetic, *n* = 2 (pinned domains); Martensitic, *n* = 3 (AF domains?)
- Additional (indirect) evidence for AF order in the martensite

SANS *T* Dependence: Gaussian



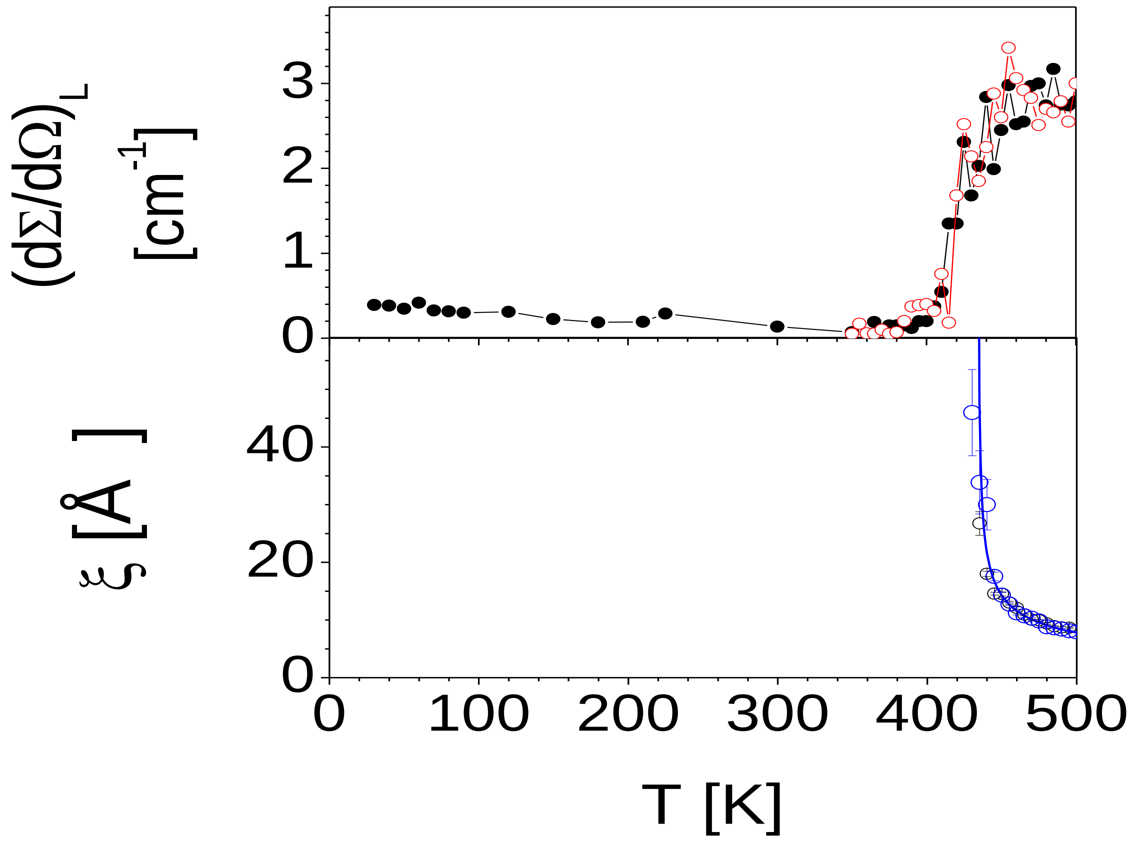
- Gaussian peak intensity actually emerges at *high T* (even *above* T_C?)

- Peak position weakly *T*-dependent. Peak width decreases on cooling

- Correlation length > 5 inter-particle spacings! Collective response*?

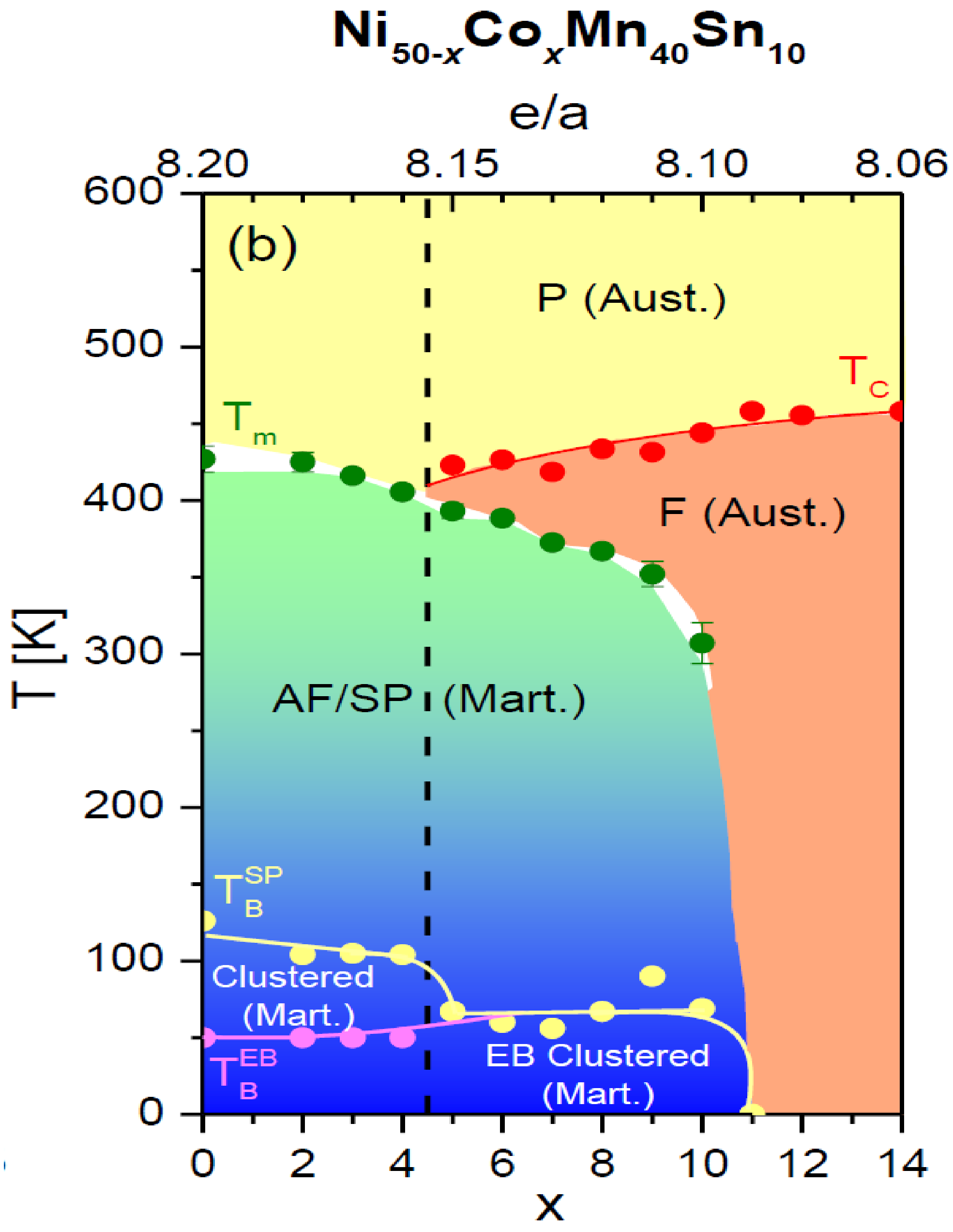
*Cong *et al* APL (2010); APL (2010) and Wang *et al* PRL (2011)

SANS *T* Dependence: Lorentzian



- Only present in significant intensities in paramagnetic phase
- Magnetic correlation length diverges as $T \to T_C^+$

Qualitative Model



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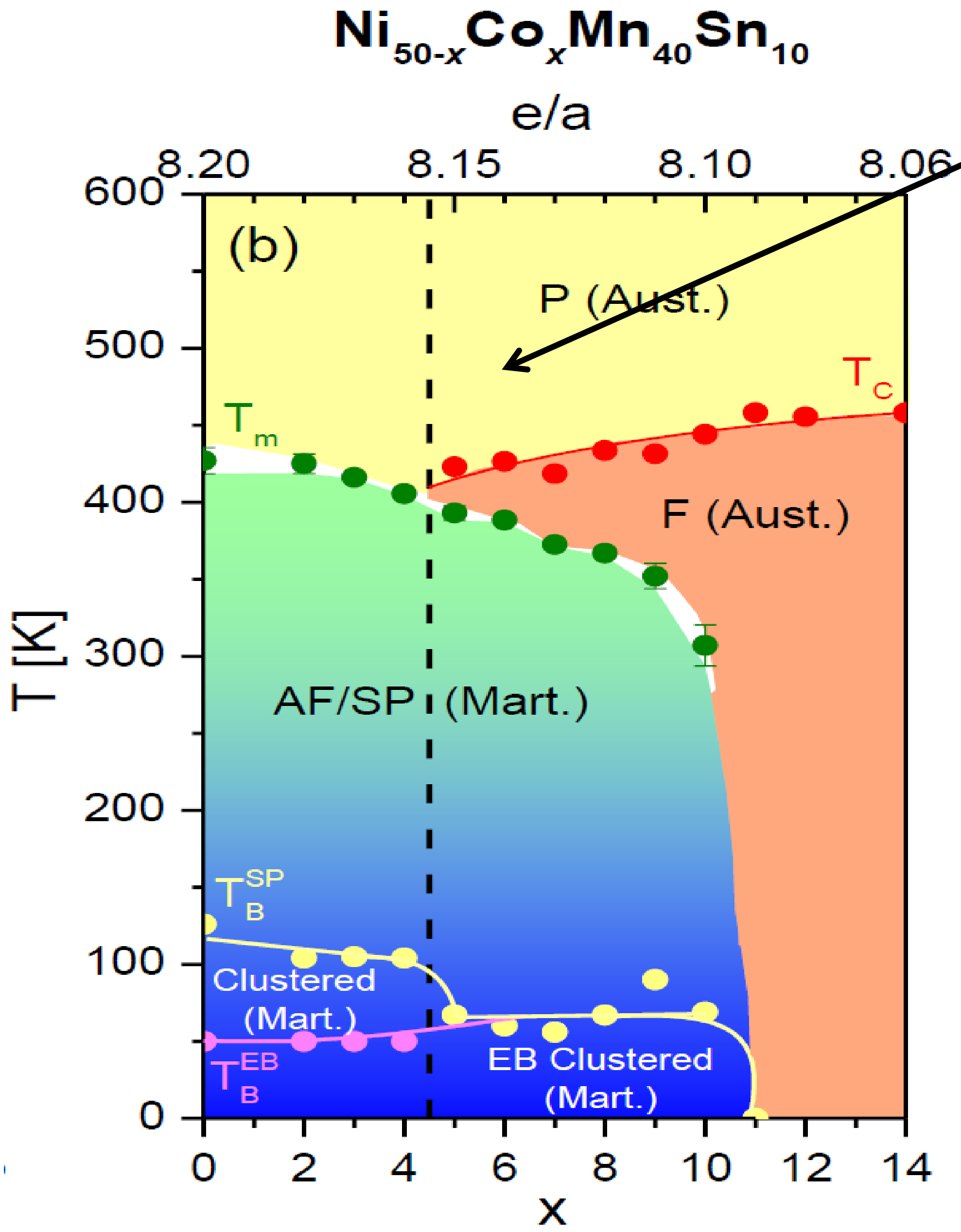

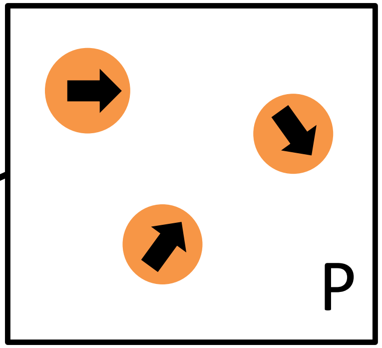

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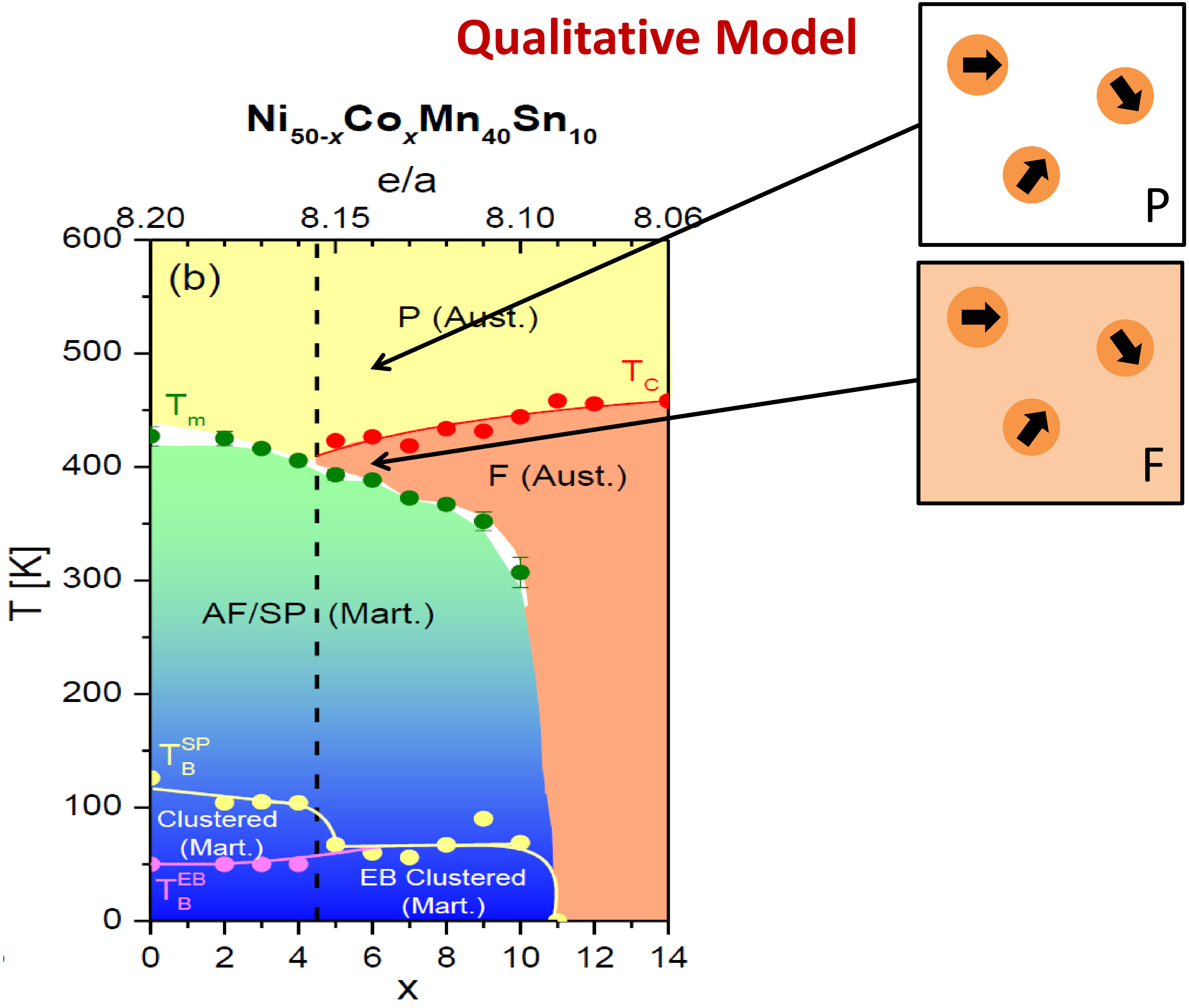

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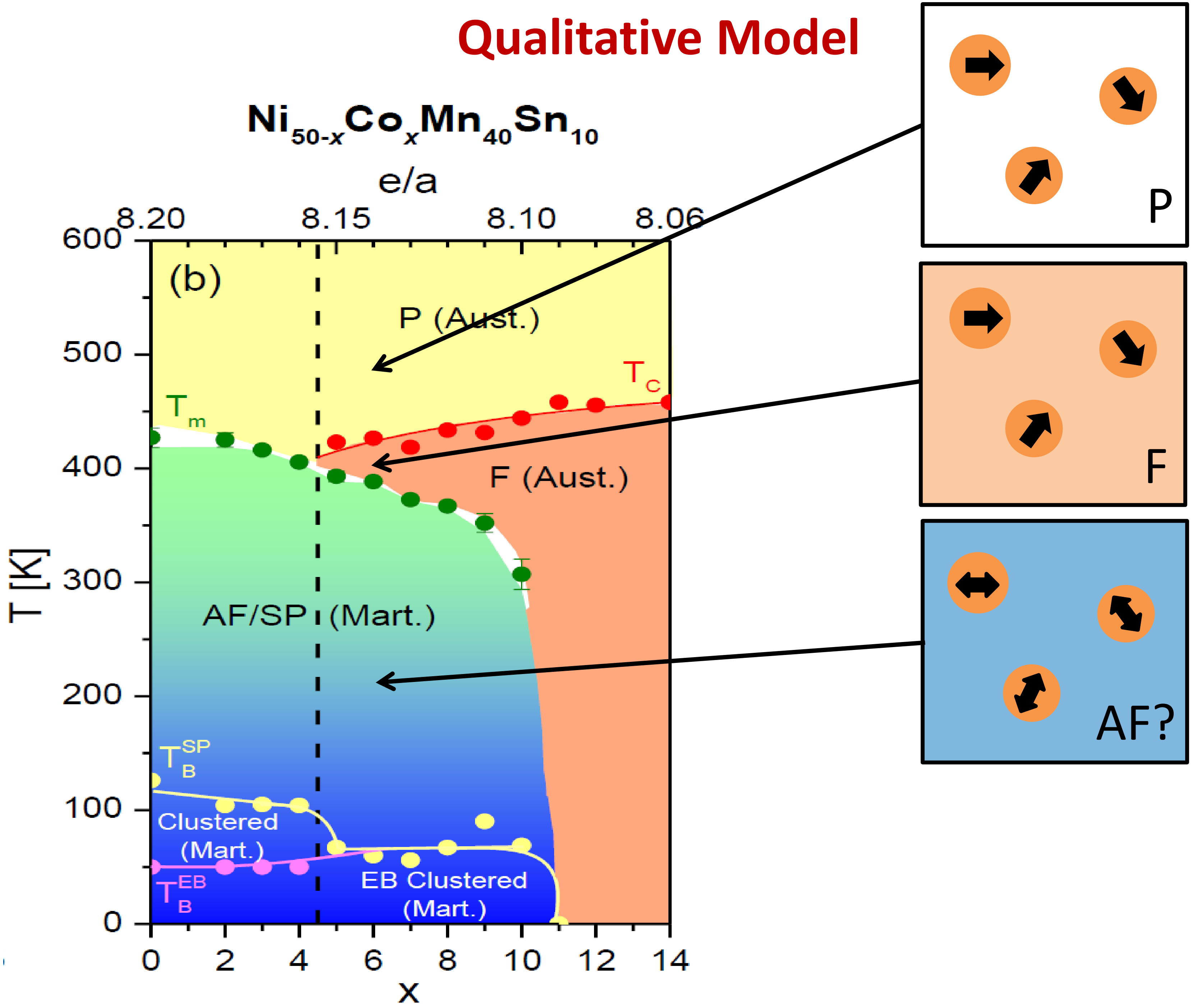
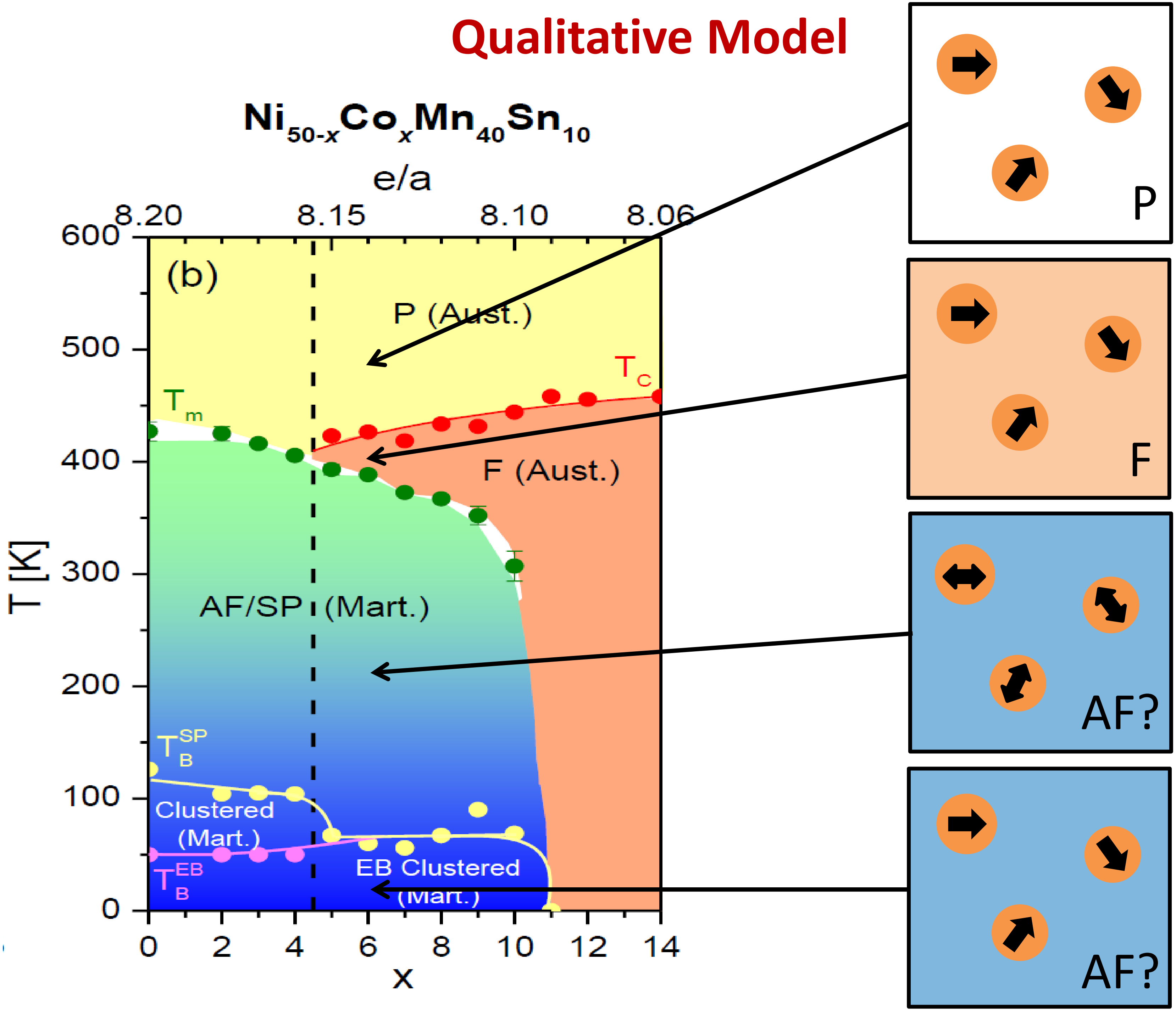


Qualitative Model



AF in the Martensite: Neutron Diffraction Problems

- AF known at $Ni_{50}Mn_{50}$, suspected *in some form* in $Ni_{50}Mn_{25+y}Sn_{25-y}$

- Indirect evidence:

  > $\chi(T)$
  > Exchange bias
  > SANS (Porod scattering)

- Why not just do neutron diffraction?

  > Texture an issue
  > Looking for the onset of AF order simultaneous with MPT to low symmetry state (*very* challenging refinement)

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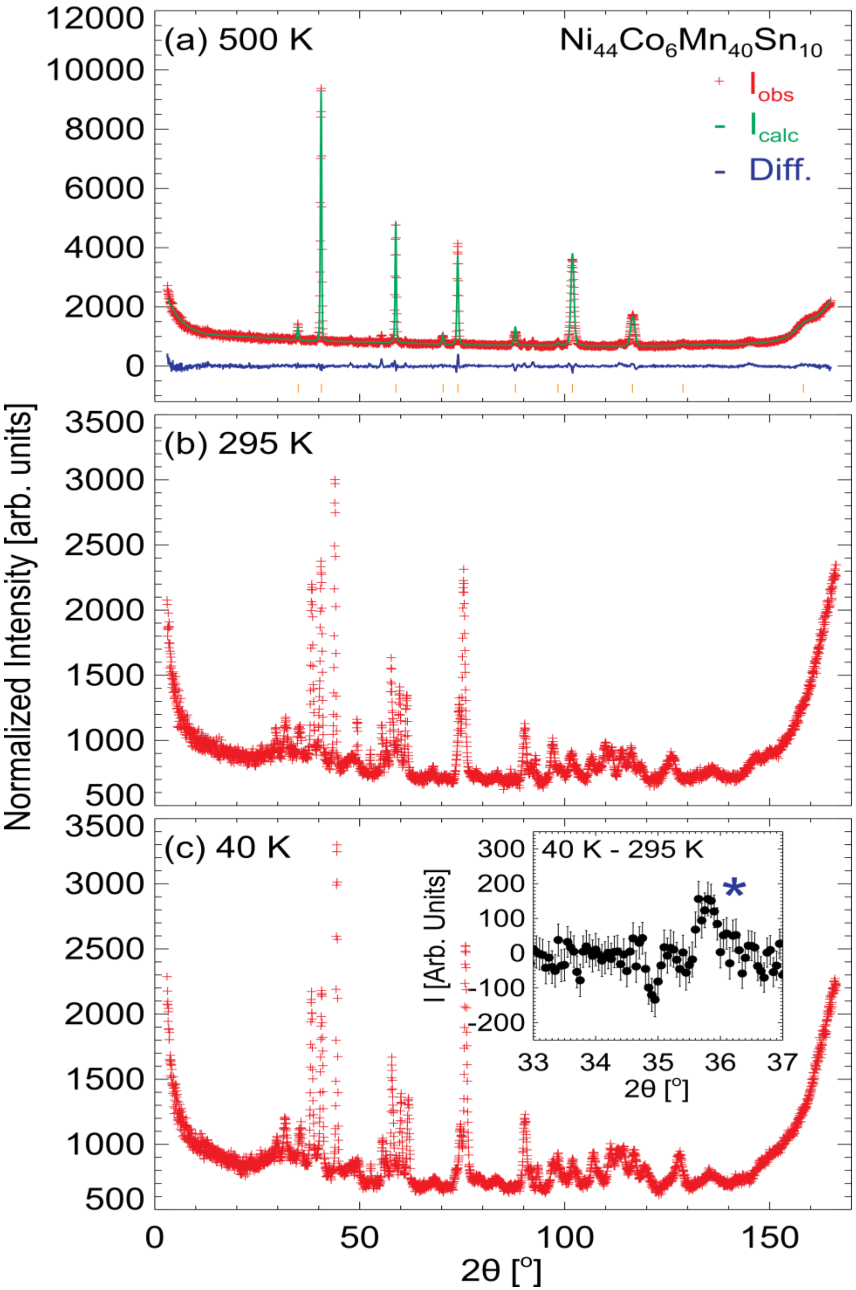

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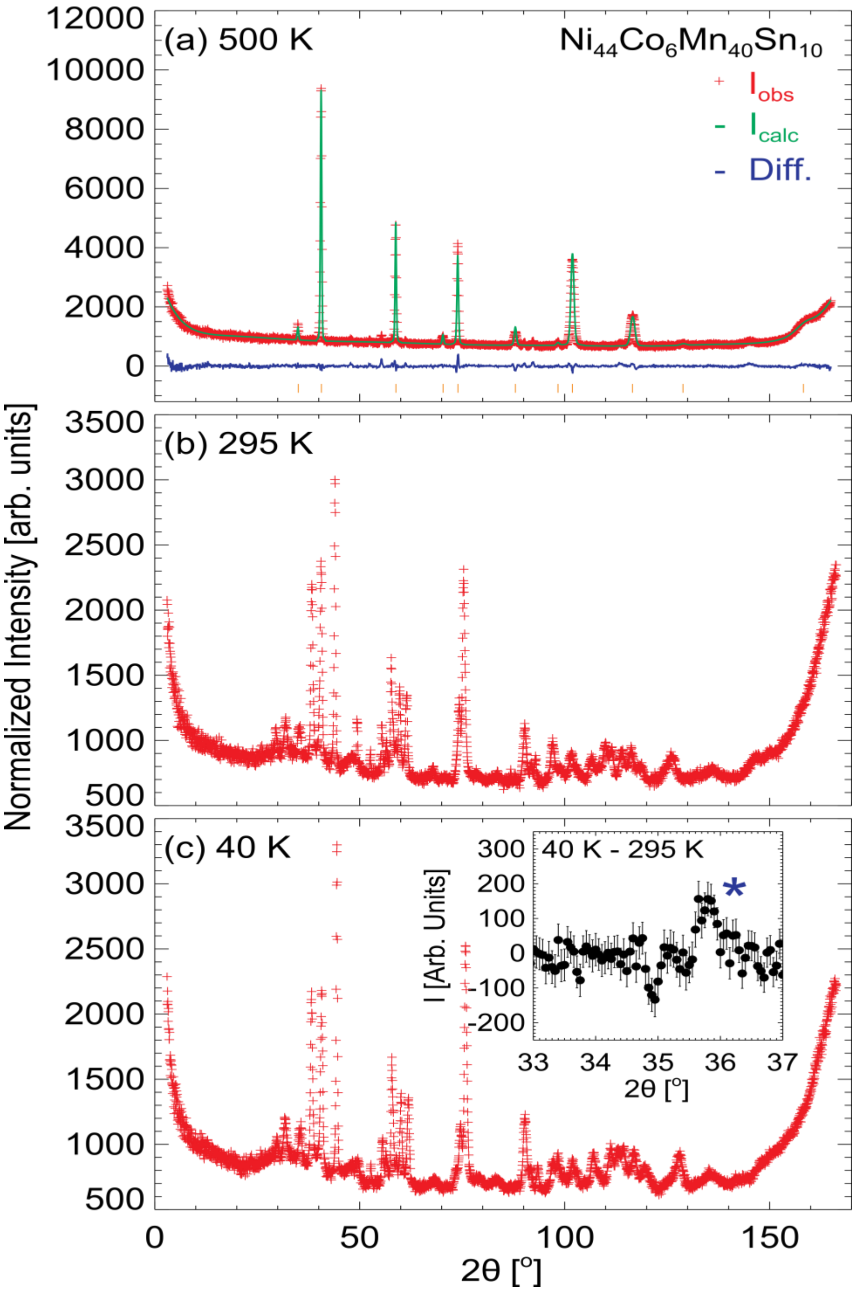
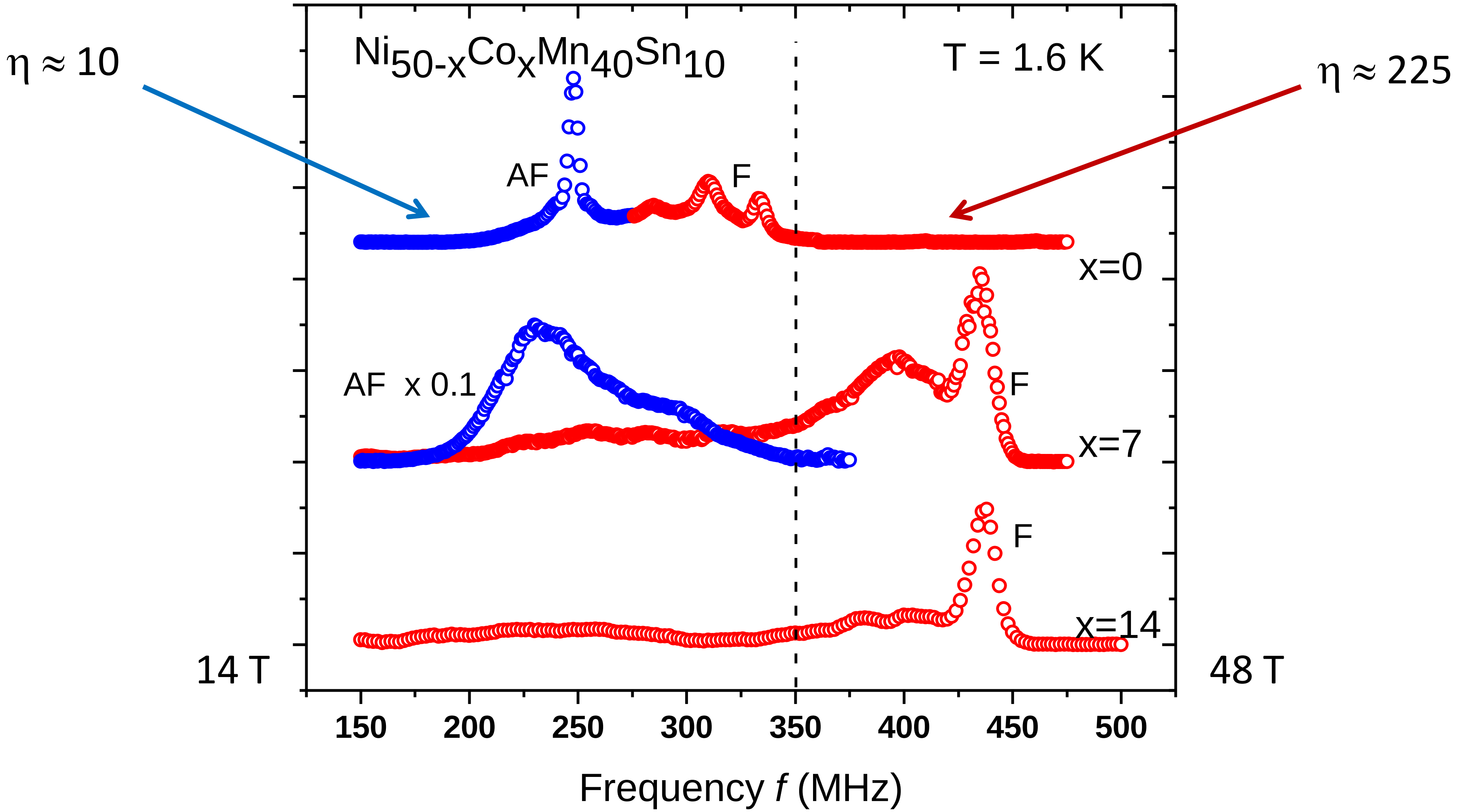
- Weak evidence for an AF order parameter?

- Polarized neutrons…….



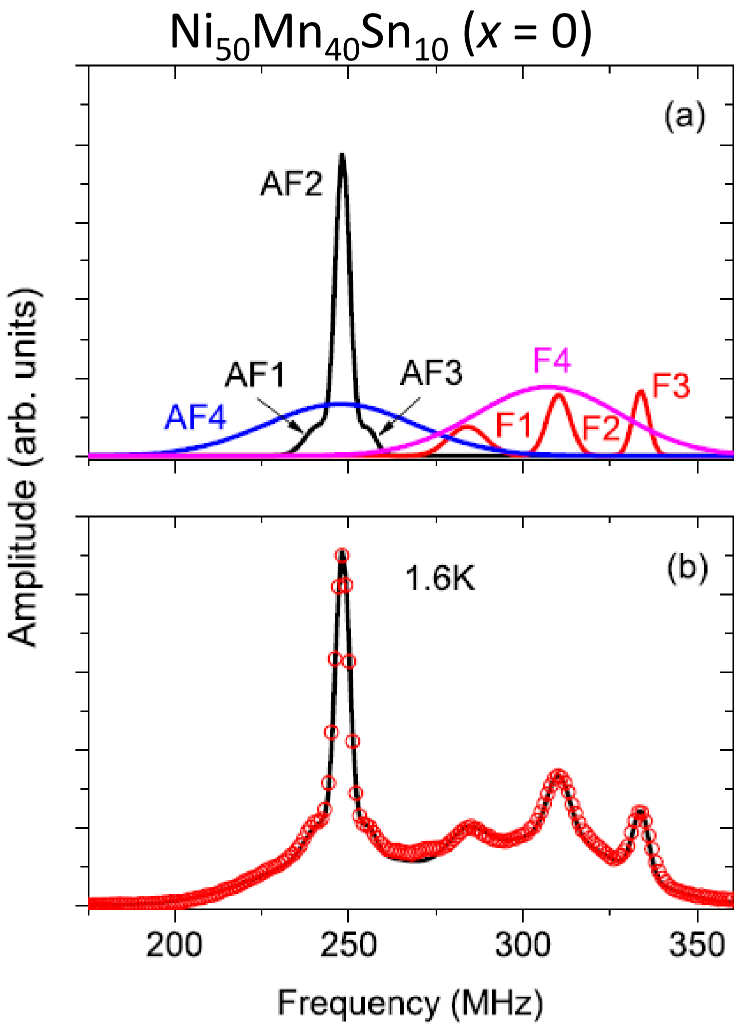
AF in the Martensite: ^{55}Mn Zero Field NMR

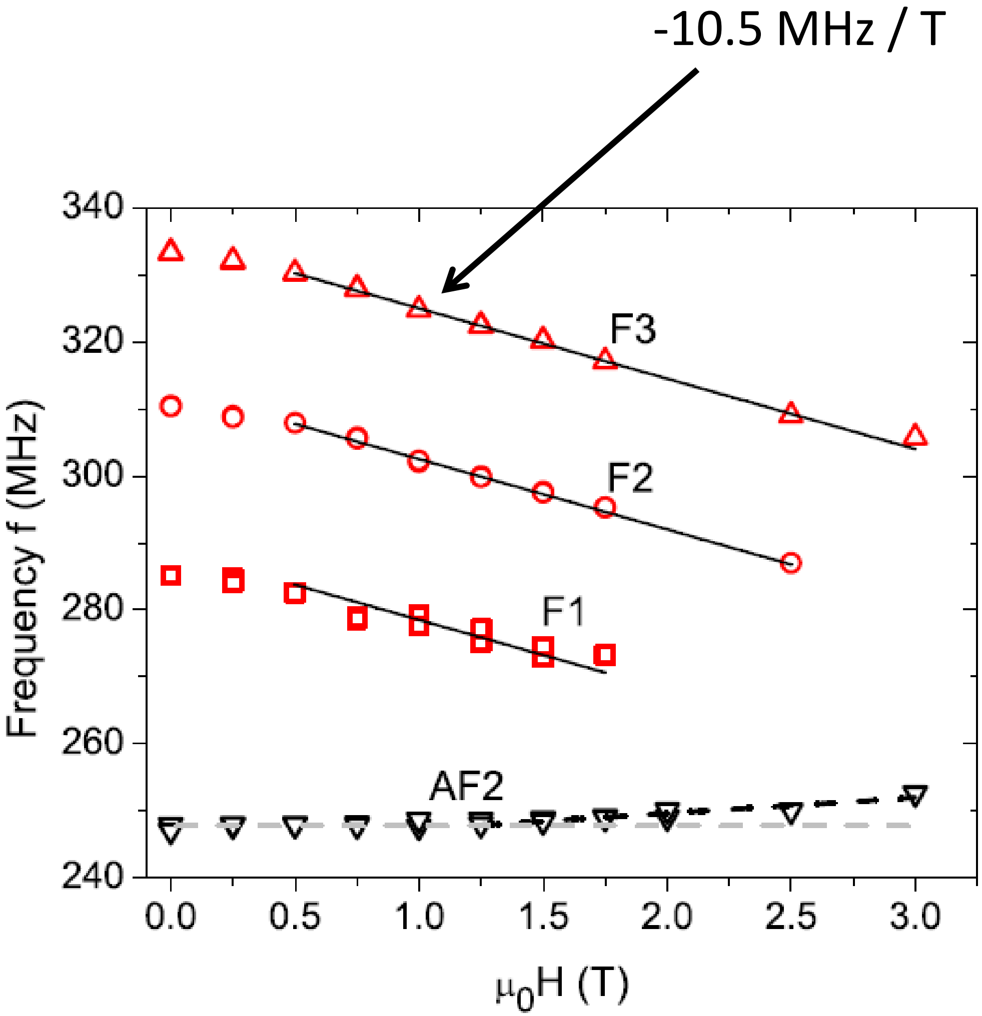
($\gamma/2\pi$ = 10.5 MHz/T)



- NMR signal enhancement factor, η, measured by calibration to ^{19}F
- Typically: High η in Fs, low η in AFs

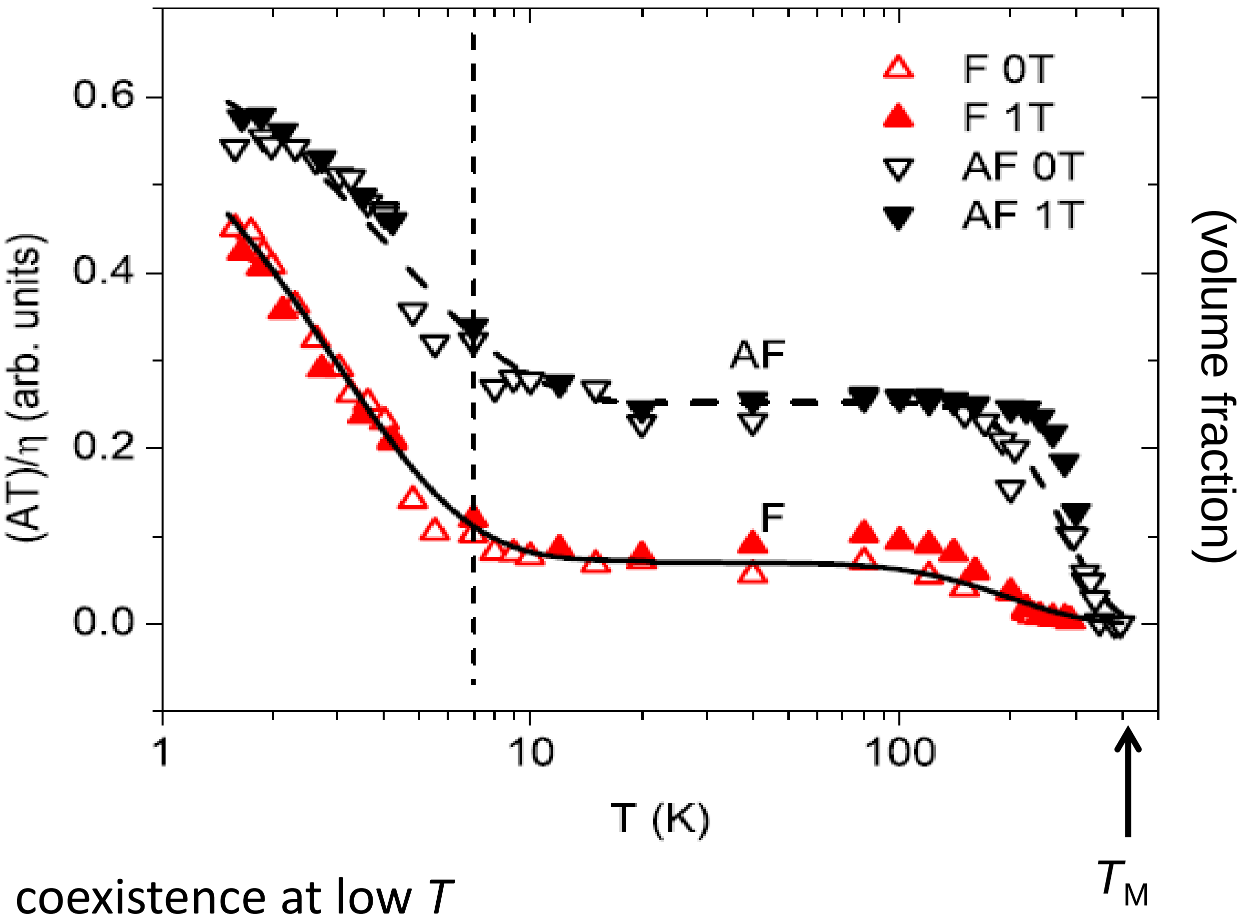
AF in the Martensite: ^{55}Mn Zero Field NMR
($\gamma/2\pi$ = 10.5 MHz/T)


$Ni_{50}Mn_{40}Sn_{10}$ (x = 0)


-10.5 MHz / T

- Unambiguous F/AF assignment
- The martensite indeed has ordered AF, decreasing with Co substitution

AF in the Martensite: ^{55}Mn Zero Field NMR



$Ni_{50}Mn_{40}Sn_{10}$
($x = 0$)

- AF/F phase coexistence at low *T*
- Volume fractions << 1 at elevated *T*. *Short-range* AF order!
- AF more thermally stable than F. Simultaneous AF/F blocking at ~ 10 K. Second F blocking at ~ 100-200 K. AF transition at ~ T_M. T_B when $T_2 \approx \tau_{NMR}$ (MHz).
- Solid lines: SP model, F cluster diameter = 8.5 ± 4.0 nm

Conclusions

- $Ni_{50-x}Co_xMn_{25+y}Sn_{25-y}$: Physically very interesting, potentially useful set of alloys

- High T_C, convenient T_M, exceptionally low ΔT, high ΔM

- Nanoscale magneto-electronic inhomogeneity:

  > SP-like freezing of nm-scale spin clusters
  > Exchange bias in a nominally single-phase system
  > First direct observation by SANS
  (liquid-like distribution, $d_c \approx$ 2-6 nm, $d_{c\text{-}c}$ = 12 nm, strong interactions)
  > First observation by zero-field ^{55}Mn NMR
  (proof of *short-range* AF order, $d_c \approx 8.5 \pm 4.0$ nm)

- New magnetic phase diagram

- Qualitative model based on (unavoidable) compositional fluctuations

Bhatti, El-Khatib, Srivastava, James, Leighton, *Phys. Rev. B.* **85**, 134450 (2012)
Bhatti, Srivastava, Phelan, James, Leighton, *Heusler Alloys*, Eds. Hirohata and Felser, Springer (2015)
Yuan, Kuhns, Reyes, Brooks, Hoch, Srivastava, James, El-Khatib, Leighton, *Phys. Rev. B.* 91, 214421 (2015)
Yuan, Kuhns, Reyes, Brooks, Hoch, Srivastava, James and Leighton, *Phys. Rev. B.*, submitted (2015)