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Fe_2P-based magnetocaloric materials fabricated using drop synthesis method

by

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Outline

Introduction to Fe_2P-based magnetocaloric materials

Sample fabrication using drop synthesis

Characterization of $(Fe,Mn)_2(P,Si)$ compounds

Concluding remarks

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Acknowledgements

Theory

***

Olle Eriksson

Levente Vitos

Erna-Krisztina Delczeg

Petros Souvatzis

Fabrication

***

Yvonne Andersson

Viktor Höglin

Martin Sahlberg

Characterization

***

Per Nordblad

Luana Caron

Lennart Häggström

Thin films

***

Petra Jönsson

Evangelos Papaioannou

Atieh Zamani

Financial support from:

Swedish Energy Agency

Vetenskapsrådet

Victoria Sternhagen (UU, MSL) for SEM pictures

Motivation for Fe_2P

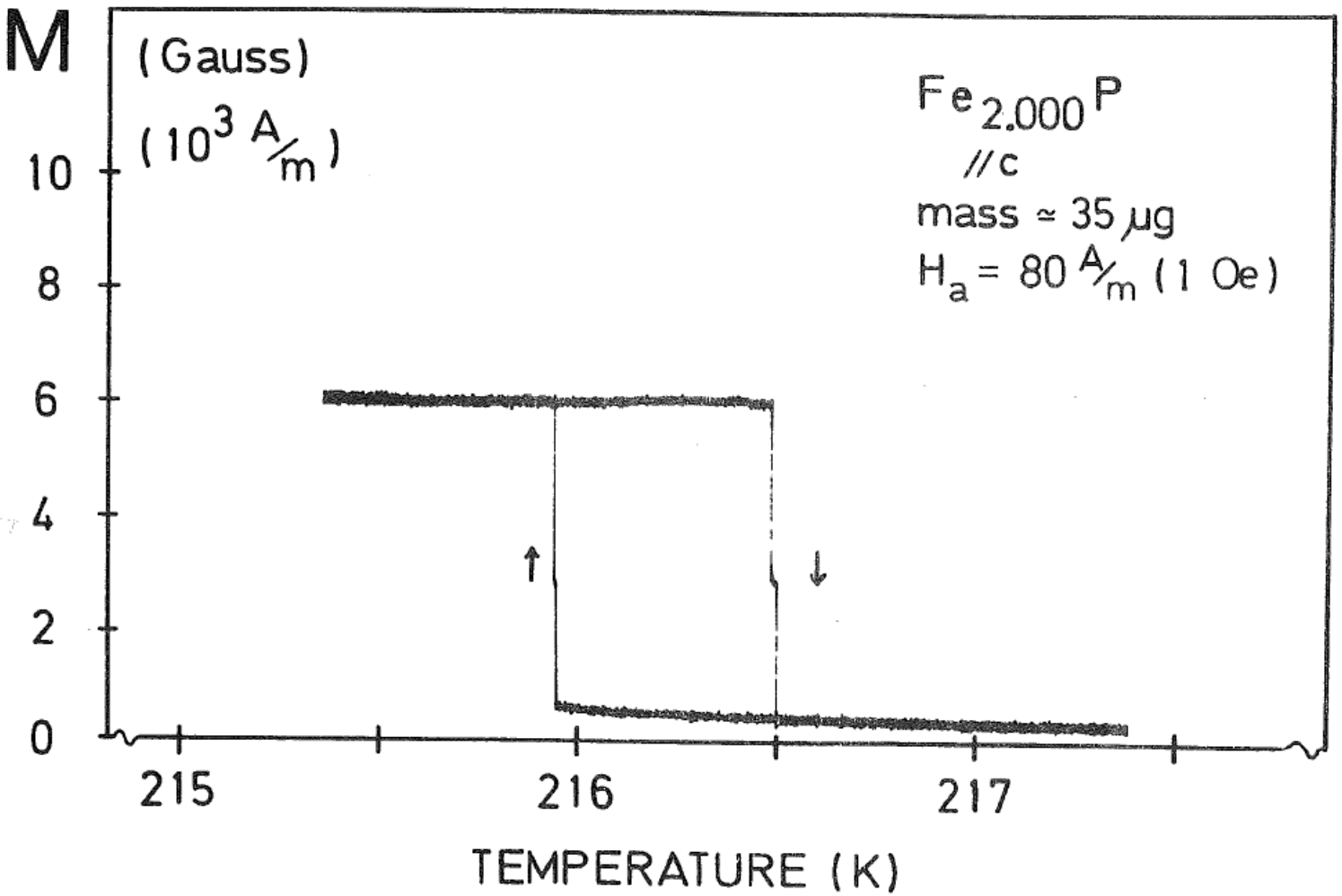

Fig. 10. An M vs T curve for a single crystal of Fe_2P showing the first order ferro- to paramagnetic phase transition. H_a = 80 A/m.

[L. Lundgren and P. Nordblad UPTEC 8025 R Mars (1980)]

Fe_2P – T dependence lattice parameter

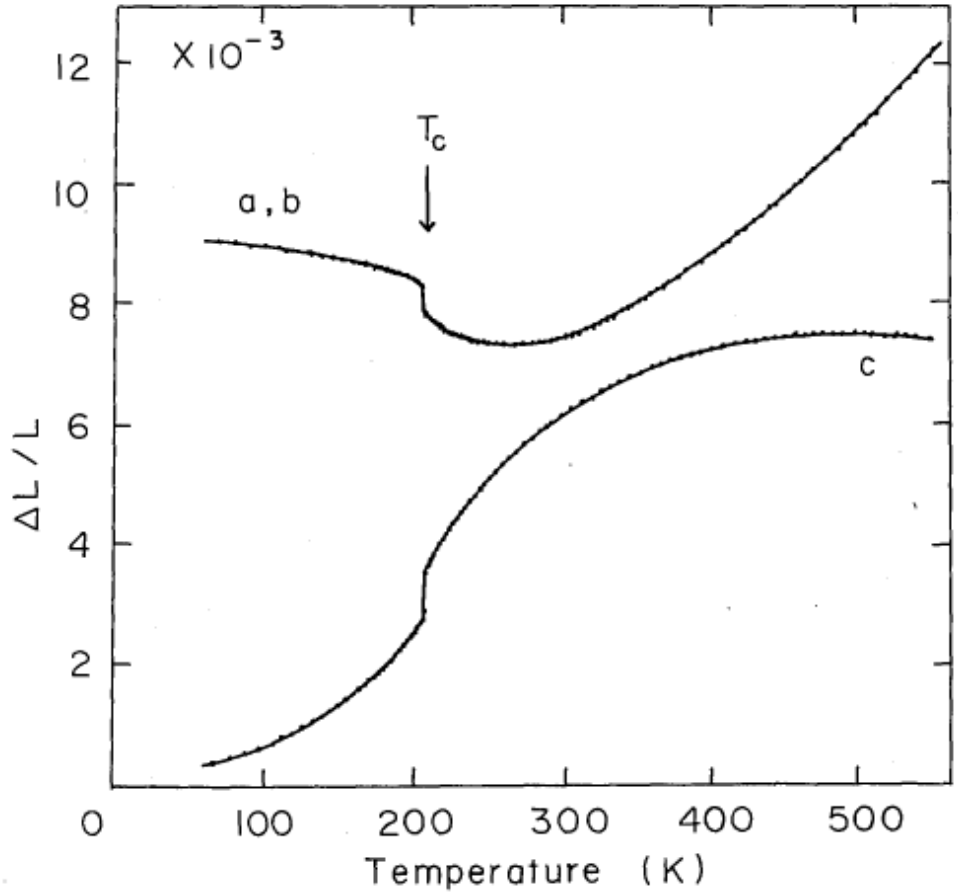

Fig. 5. Temperature dependence of the linear thermal expansion along the *a*, *b* and *c* axes.

[Fujii et al. J. Phys. Soc. Jpn., 43:1, 1977]

Di-iron phosphide - Fe_2P

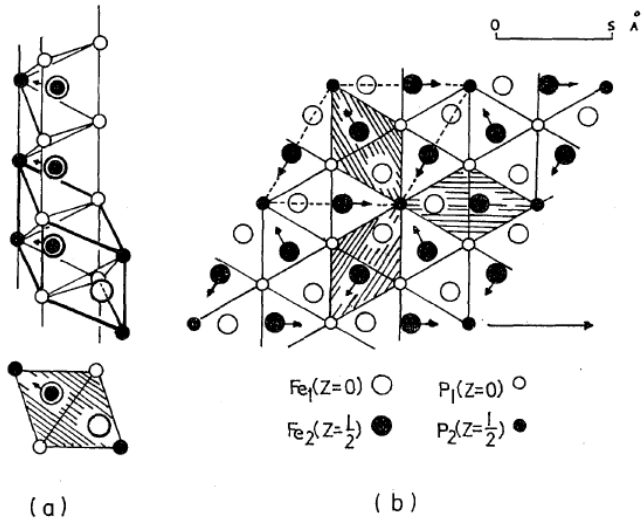

Fig. 1. Crystal structure of Fe_2P. (a) Relationship of Pyramidal-site and tetrahedral-site atoms. (b) Arrangement of rhombo-hedrall subcells.

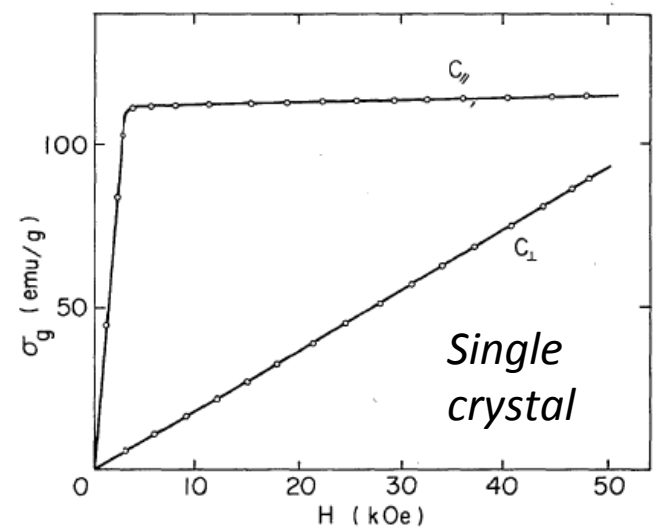

Fig. 2. Magnetization curves along the direction parallel and perpendicular to the *c* axis at 4.2 K.

- Hexagonal structure (P-62m space group)
- Para- to ferromagnetic phase transition
- $T_c \approx 216$ K
- Saturation magnetic moment ≈ 3 μ_B/f.u.
- Hyperfine fields Fe_1 and Fe_2 : 11 T and 17 T

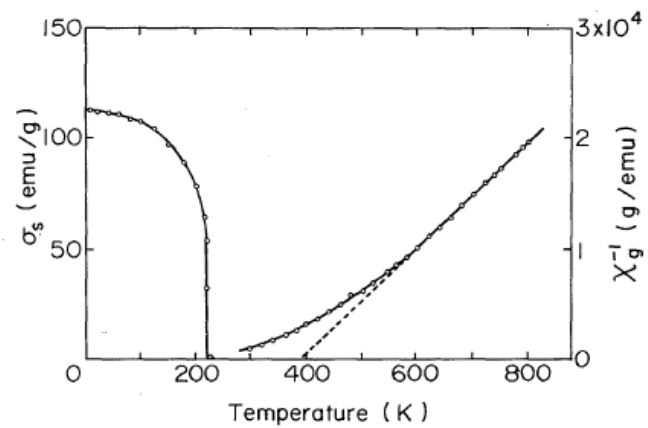

Fig. 3. Magnetic moment, σ_g, and inverse susceptibility, χ_g^{-1}, plotted against temperature.

[Fujii et al. J. Phys. Soc. Jpn., 43:1, 1977]

Mn and Si substitution in Fe_2P

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Si substitution

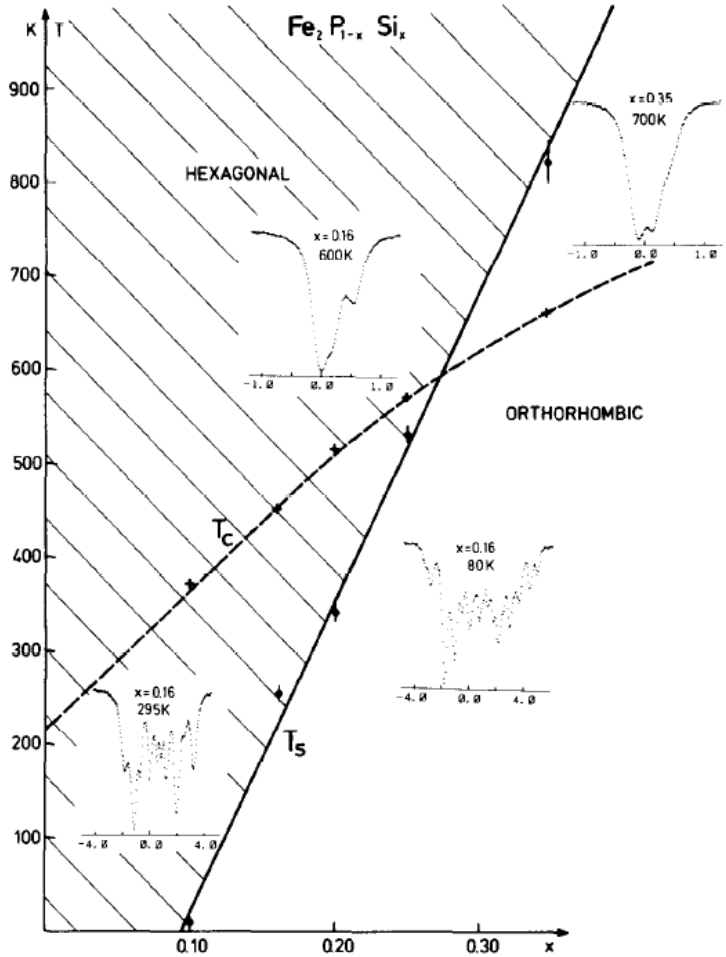

FIG. 1. The hexagonal/orthorhombic transition temperature T_s and the Curie temperature T_c function of x. Within each phase region a representative spectrum is shown.

Mn substitution

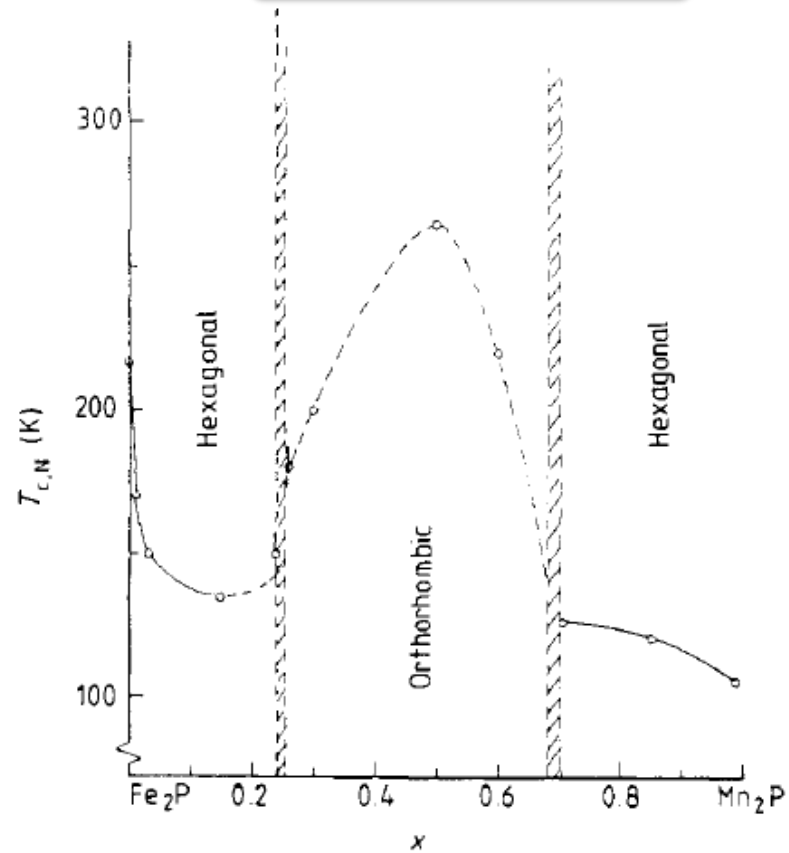

Figure 1. The magnetic transition temperature as a function of composition x in $(Fe_{1-x}Mn_x)_2P$. The value of T_N for $x = 0.5$ is taken from Häggström *et al* (1987).

Tunable magnetic and structural phase transition!

[Jernberg et al. J. Solid State Chem., 53:313, 1984]

[Srivastava et al. J. Phys. C.: Solid State Phys., 20:463, 1987]

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$(Fe,Mn)_2(P,Si)$ – Phase diagram

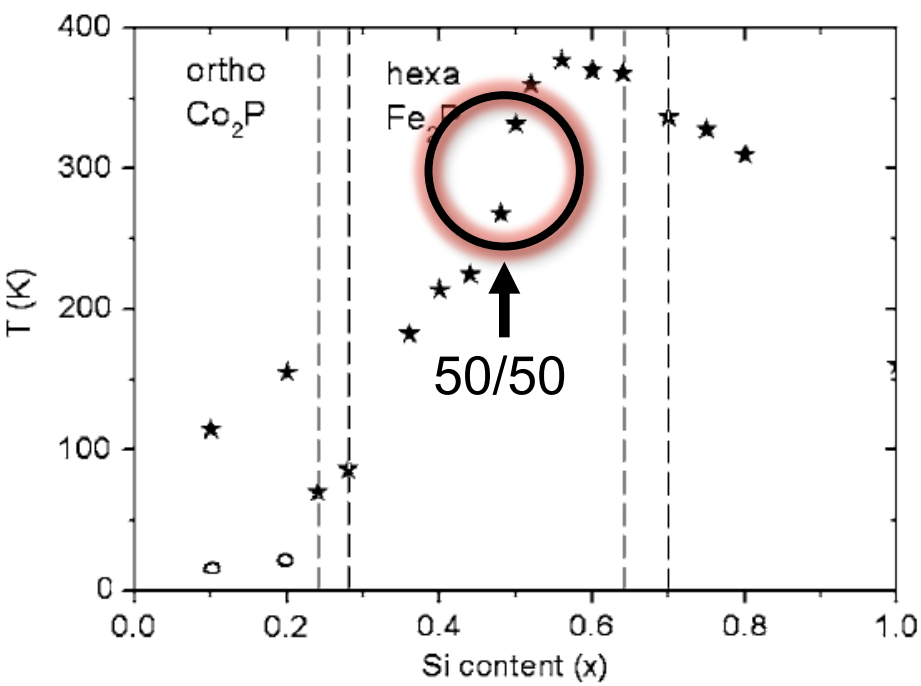
JOURNAL OF APPLIED PHYSICS **103**, 07B318 (2008)

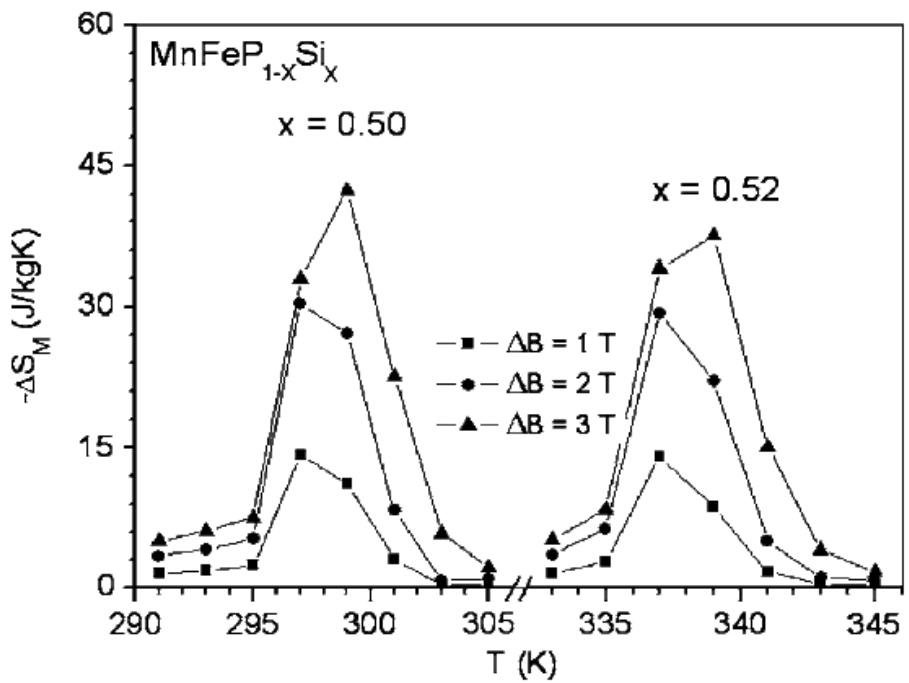
Structure, magnetism, and magnetocaloric properties of $MnFeP_{1-x}Si_x$ compounds

D. T. Cam Thanh,[a] E. Brück, N. T. Trung, J. C. P. Klaasse, and K. H. J. Buschow
Van der Waals-Zeeman Instituut, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, Netherlands

Z. Q. Ou and O. Tegus
Key Lab for Physics and Chemistry of Functional Materials, Inner Mongolia Normal University, Hohhot 010022, China

L. Caron





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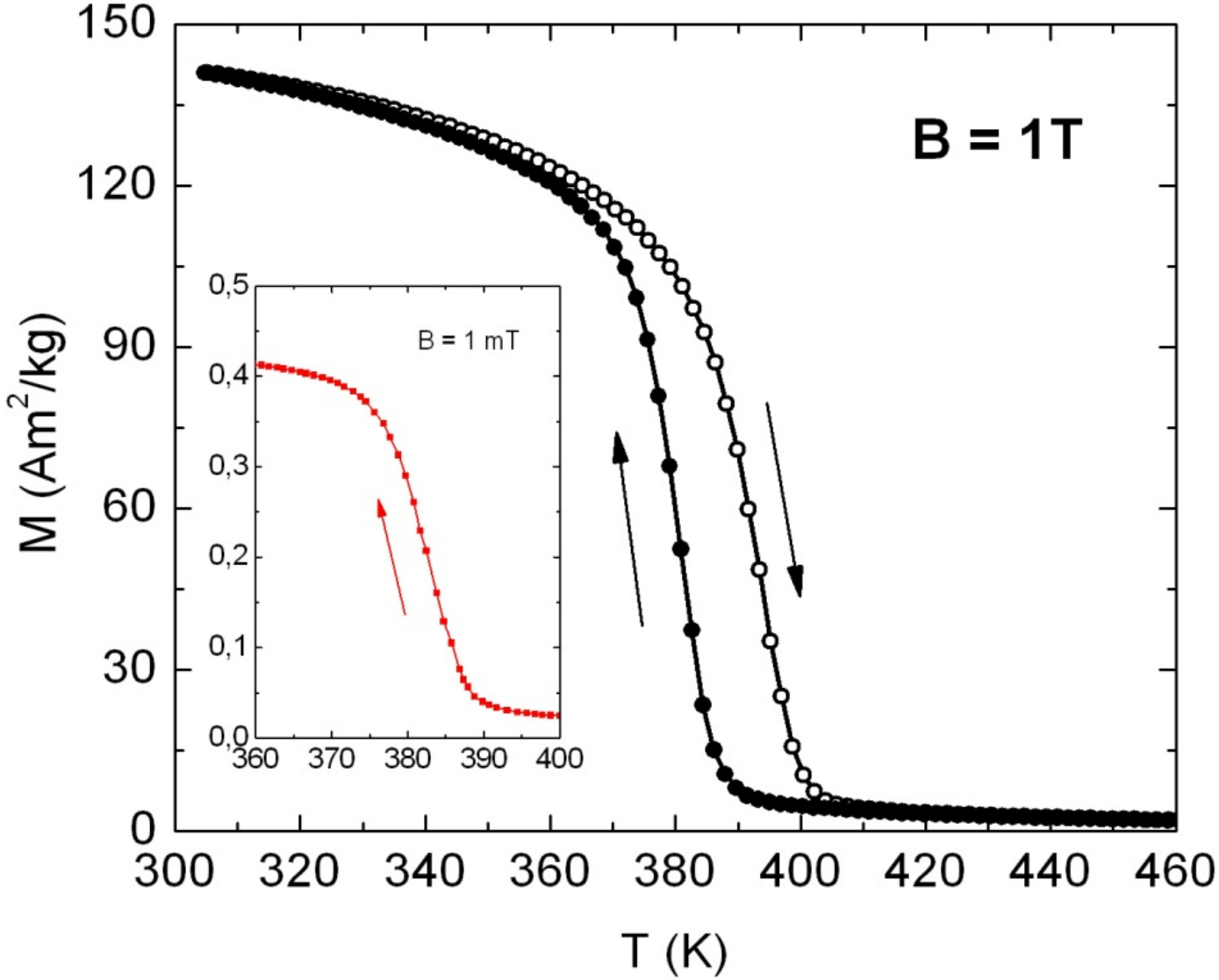
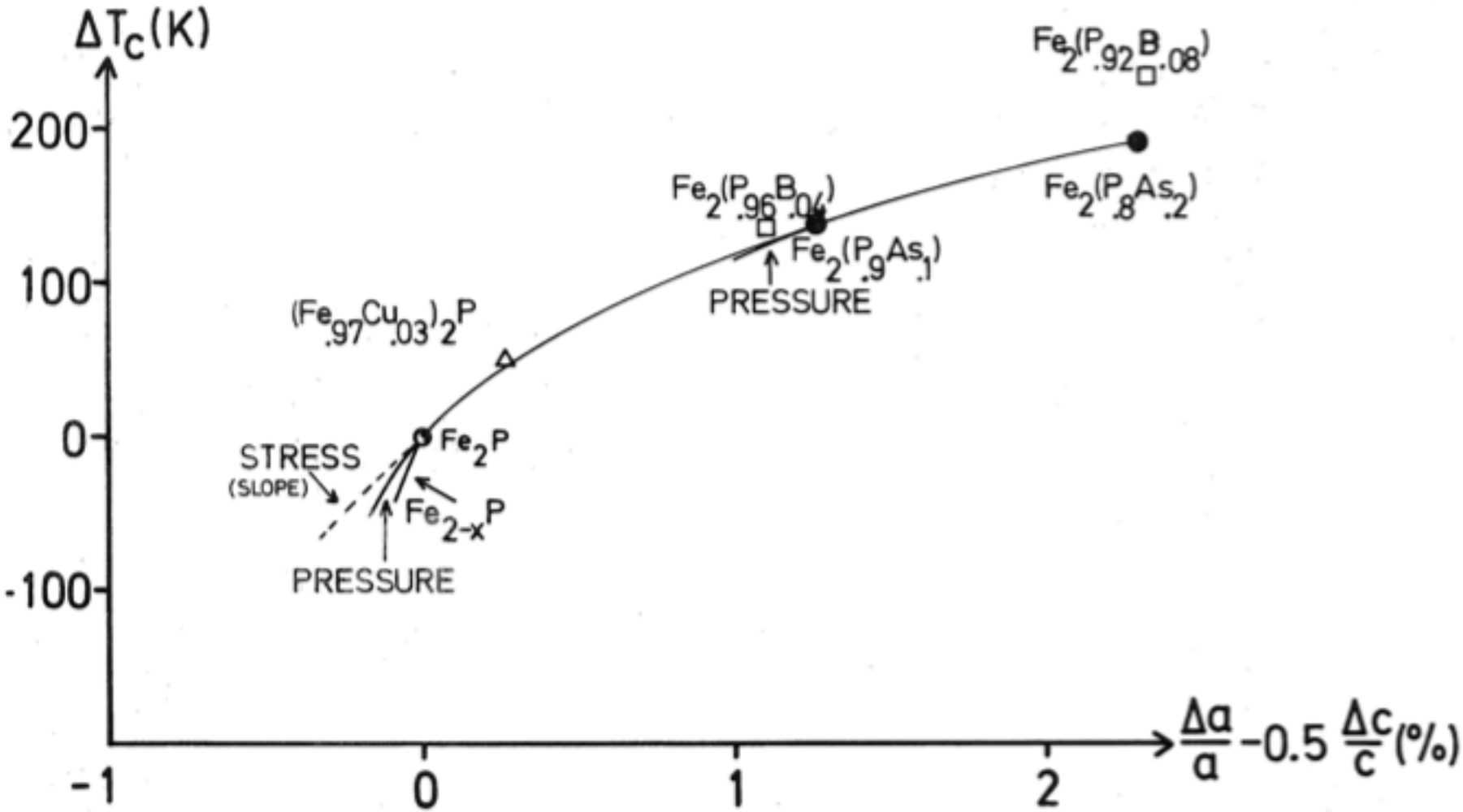
$MnFeP_{0.5}Si_{0.5}$



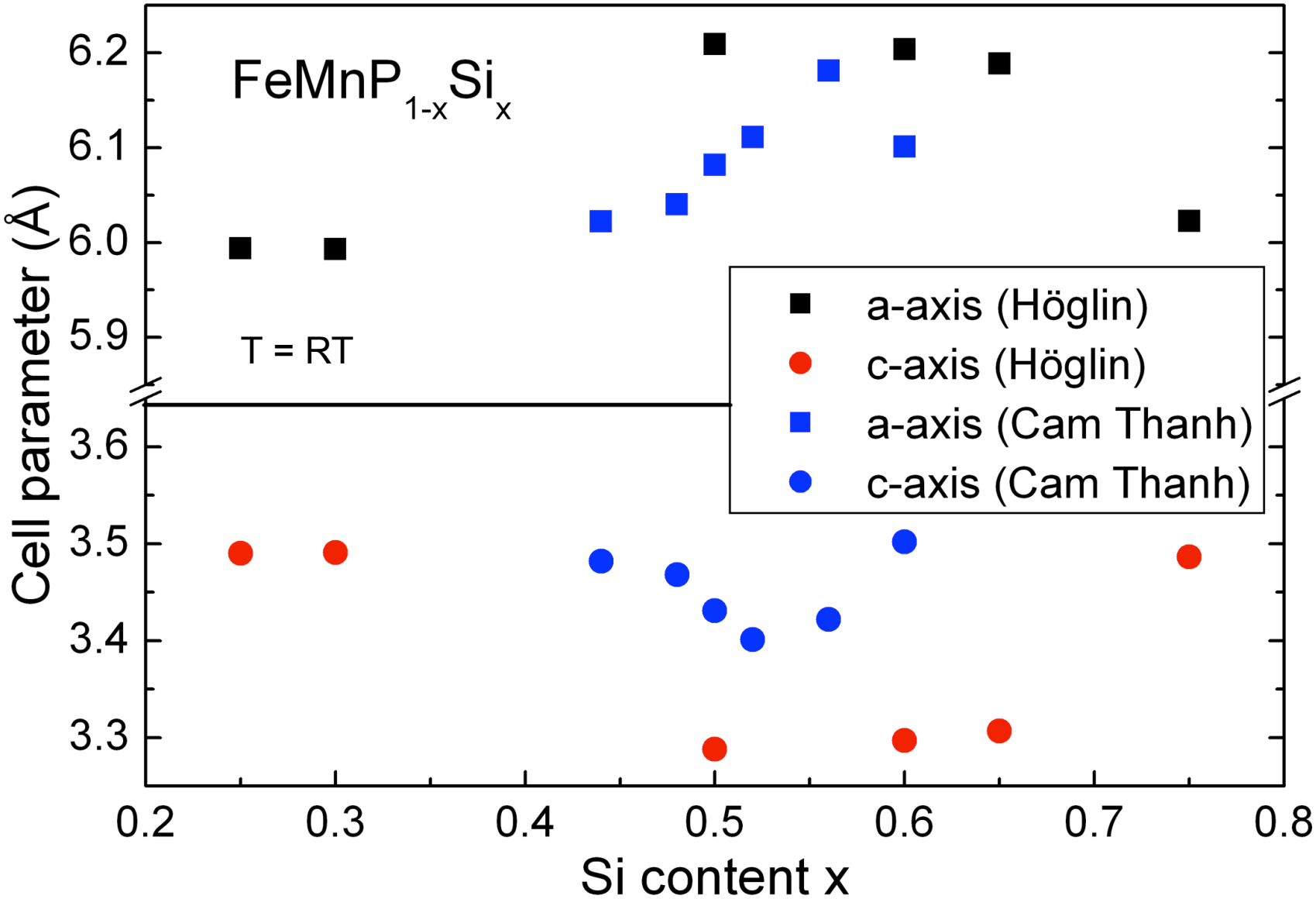
T_c ?

Correlation between T_C and lattice parameters ?



[L. Lundgren, P. Nordblad and O. Beckmann UPTEC (1980)]

Dependence of lattice parameters on Si content



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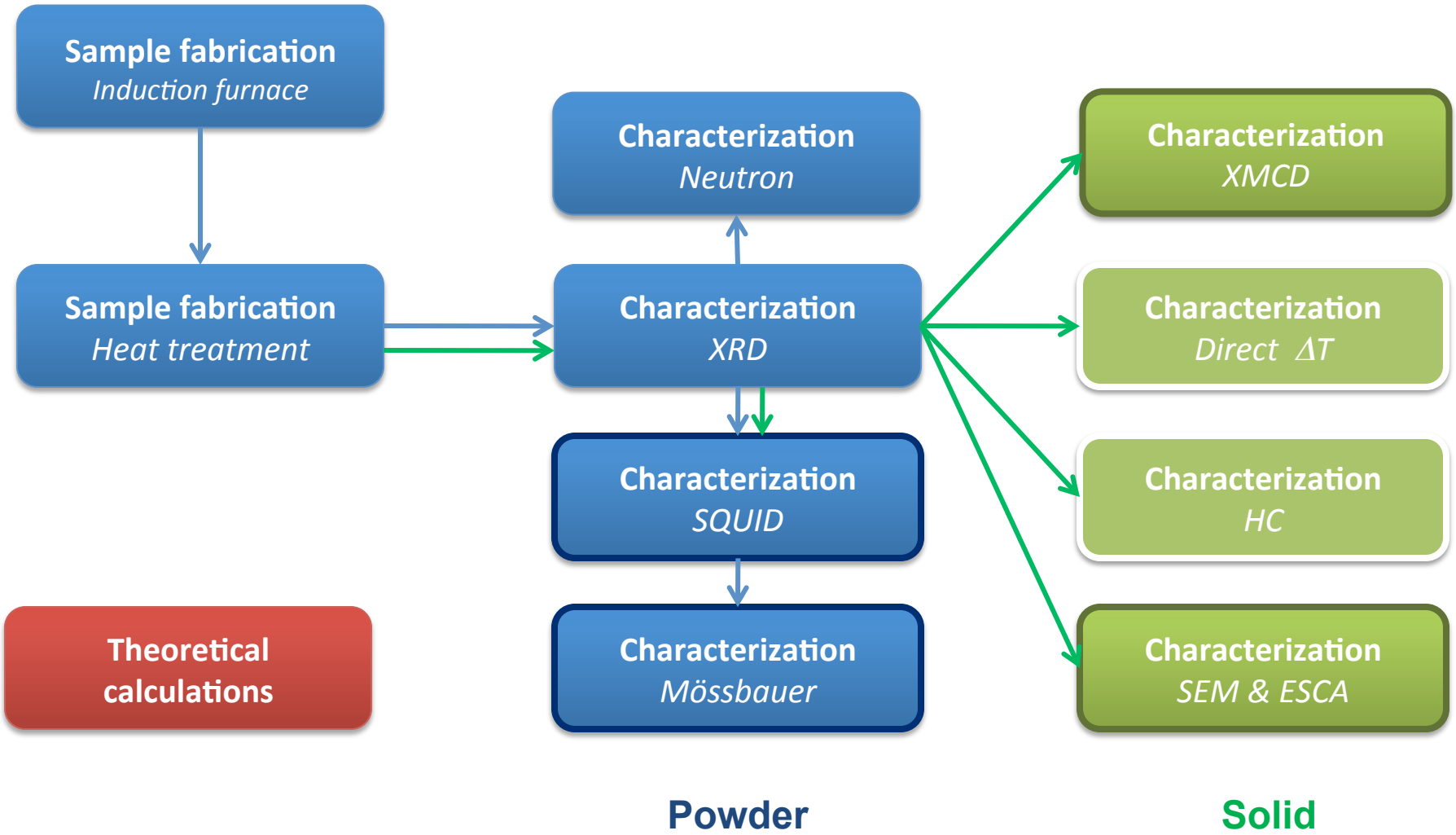
Experimental methods



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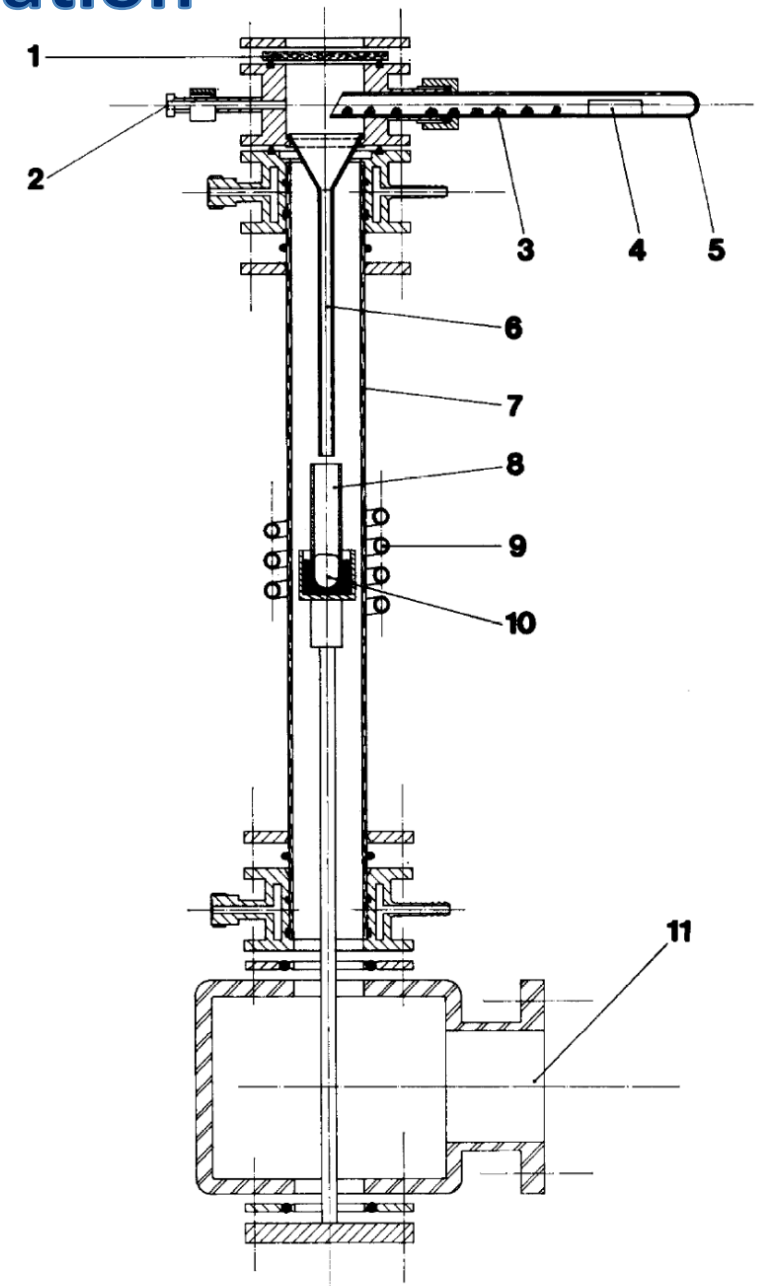
Sample fabrication

High frequency induction furnace

" Drop synthesis method"

- Argon atmosphere
- Synthesis temperature 1350 °C
- Temperature measured by pyrometer
- Steady Fe-Si melt
- Start dropping Mn and P

Sample amount: 5 – 50(+) g



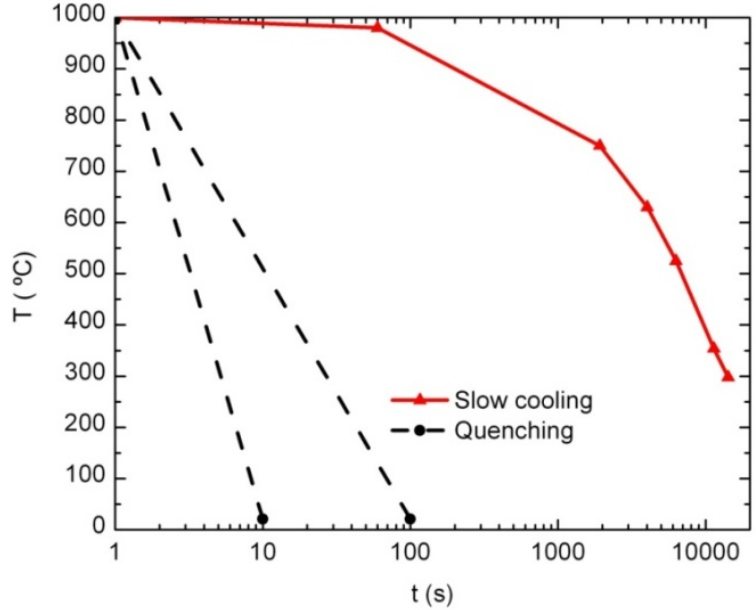
[Carlson et al. ; J. Solid State Chem. **8**,57-67 (1973)]

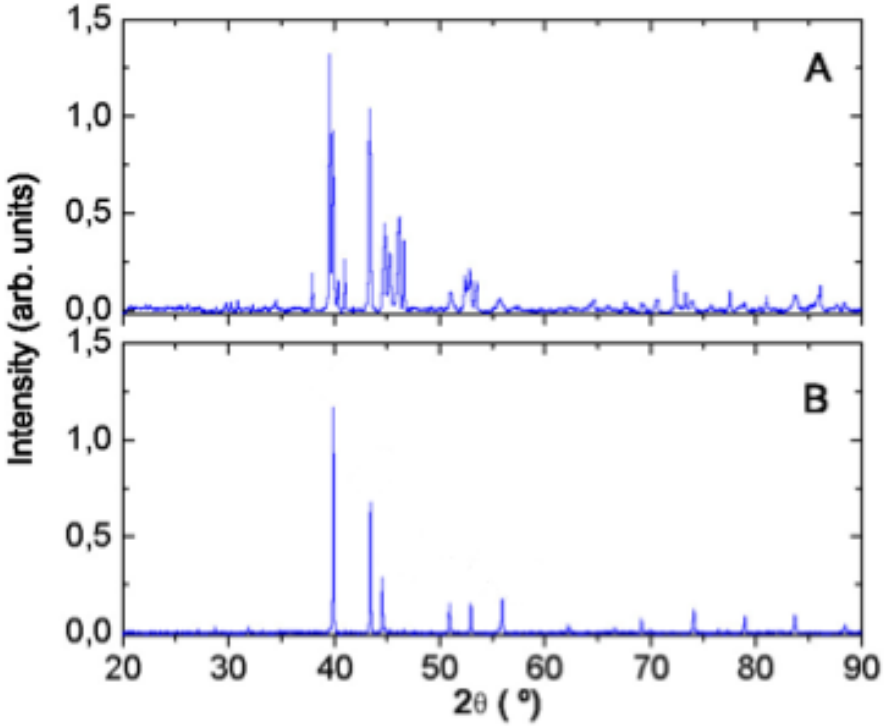
Sample heat treatment

Sintering at 1100 °C (1h)

Annealing at 800 °C (65h)

Quenching





Heat treatment + Quenching

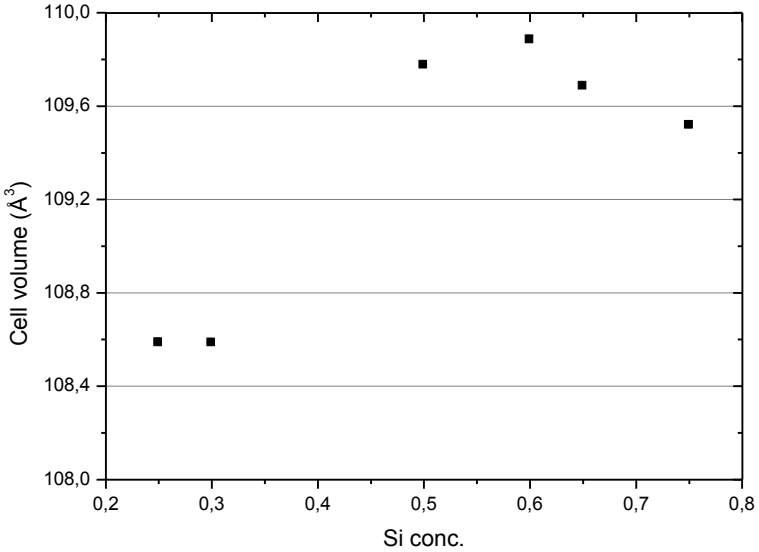
Hexagonal structure

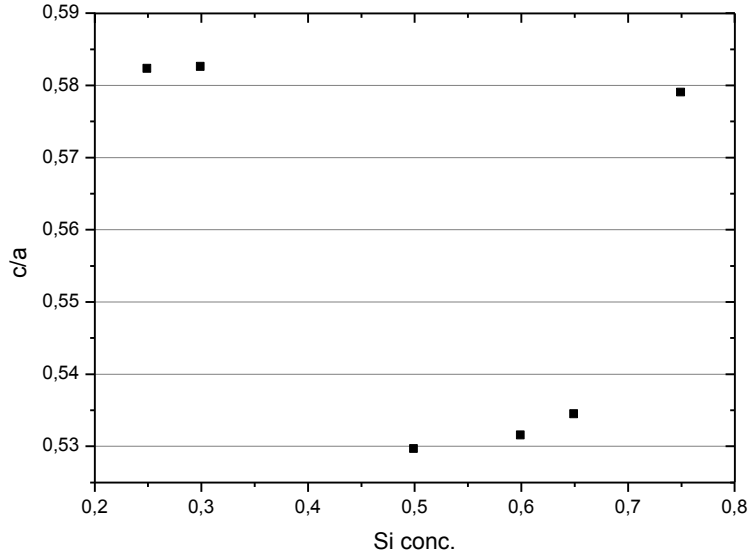
(space group: P-62m)

Dependence of lattice parameters on Si & Mn content

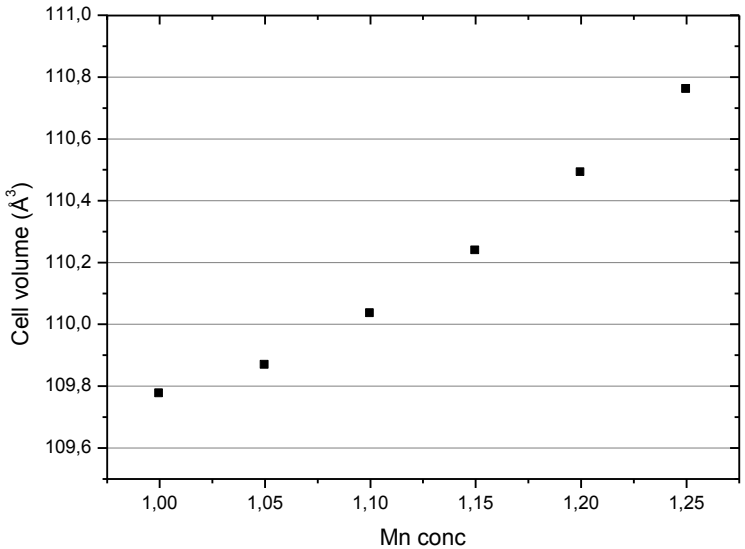
T = RT

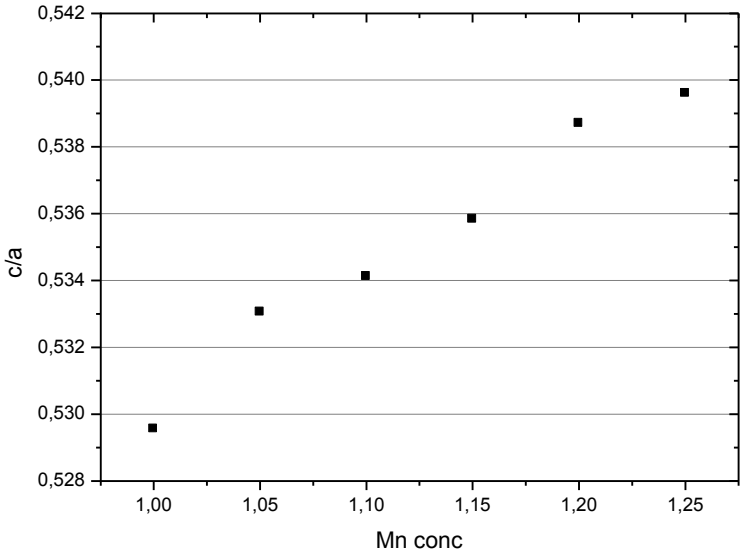
Si





Mn





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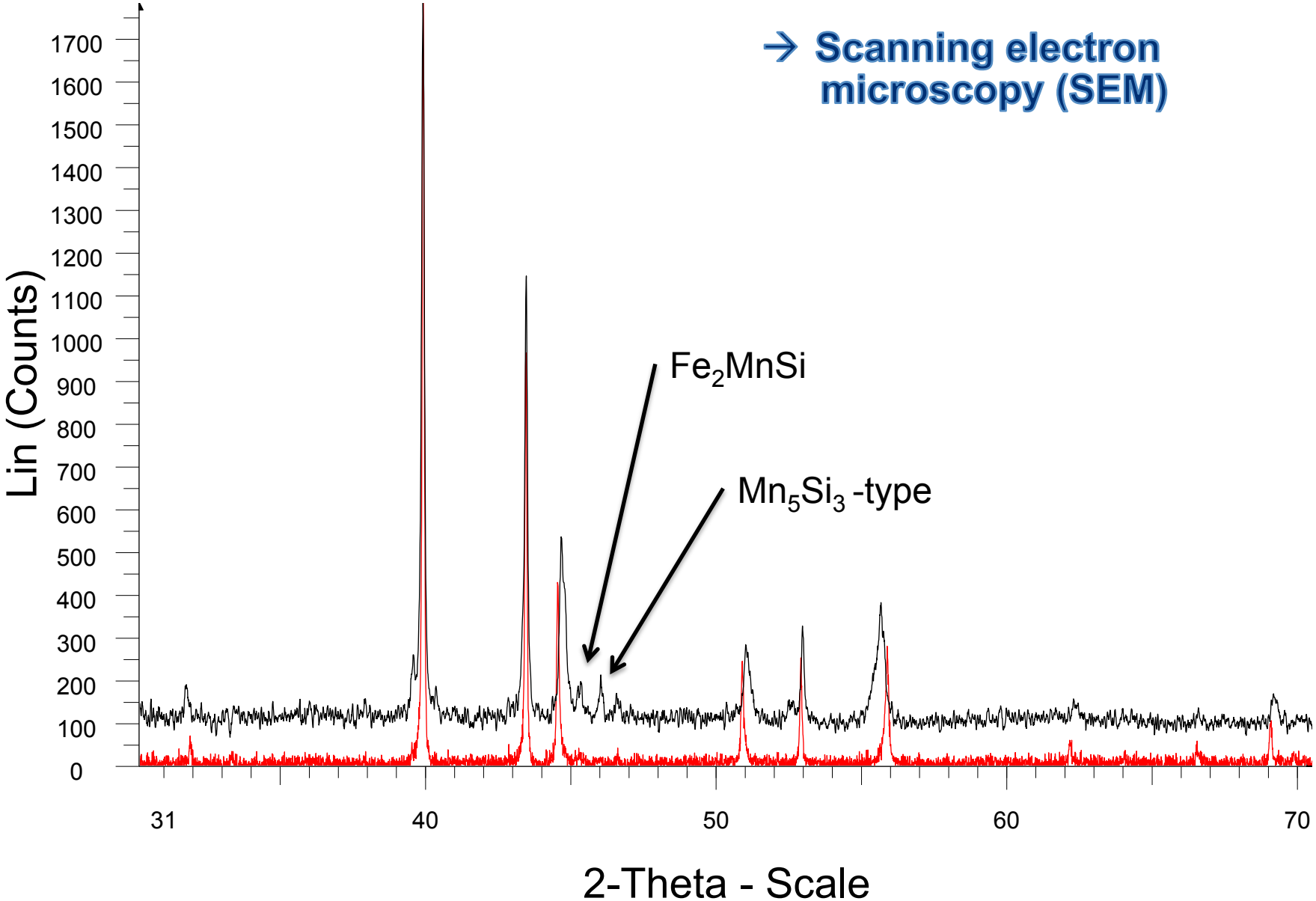
Look into the microstructure

nom. $FeMnP_{0.5}Si_{0.5}$

→ Scanning electron microscopy (SEM)



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Scanning electron microscopy (SEM)

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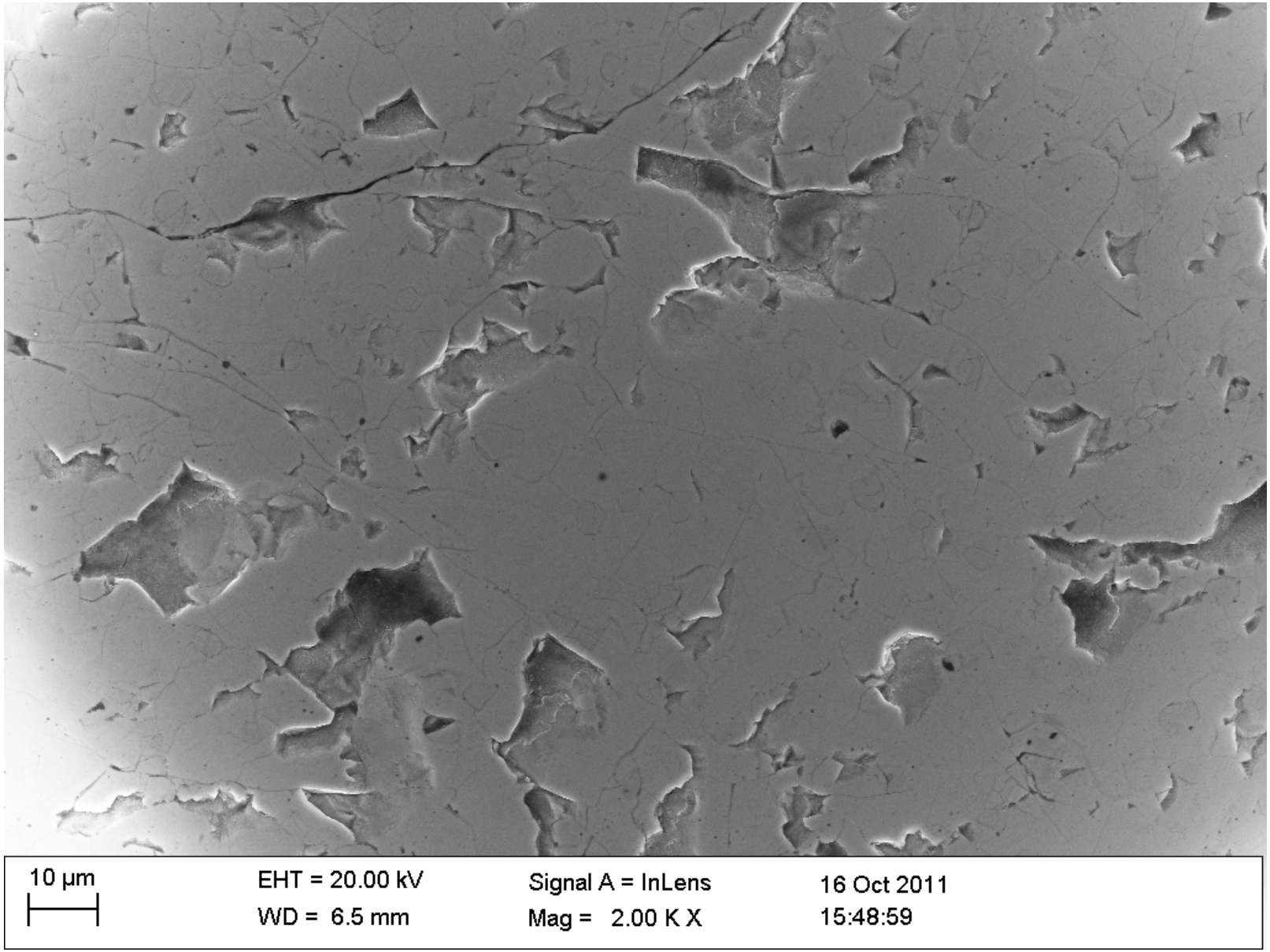

Scanning electron microscopy (SEM)

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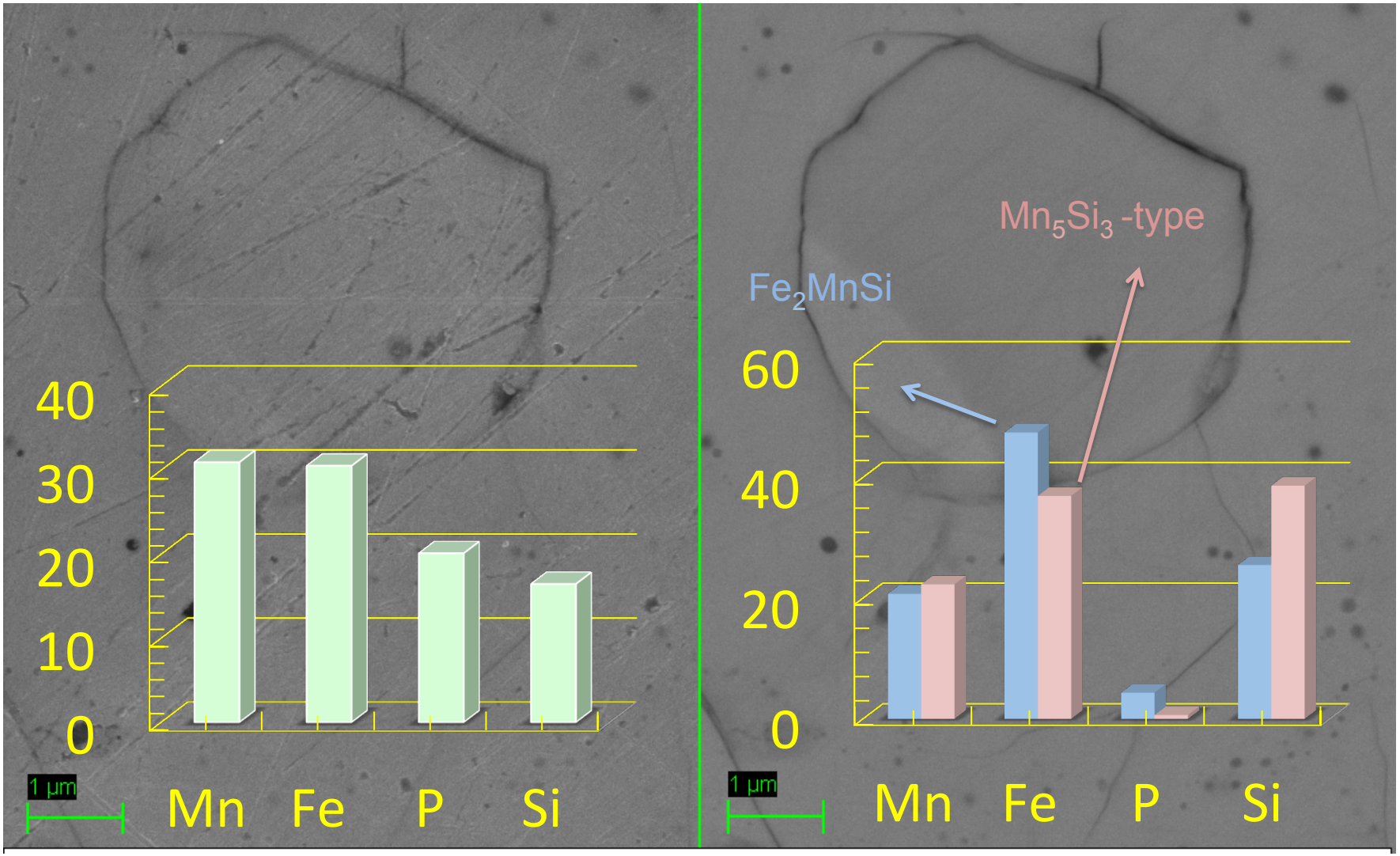

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Scanning electron microscopy (SEM)

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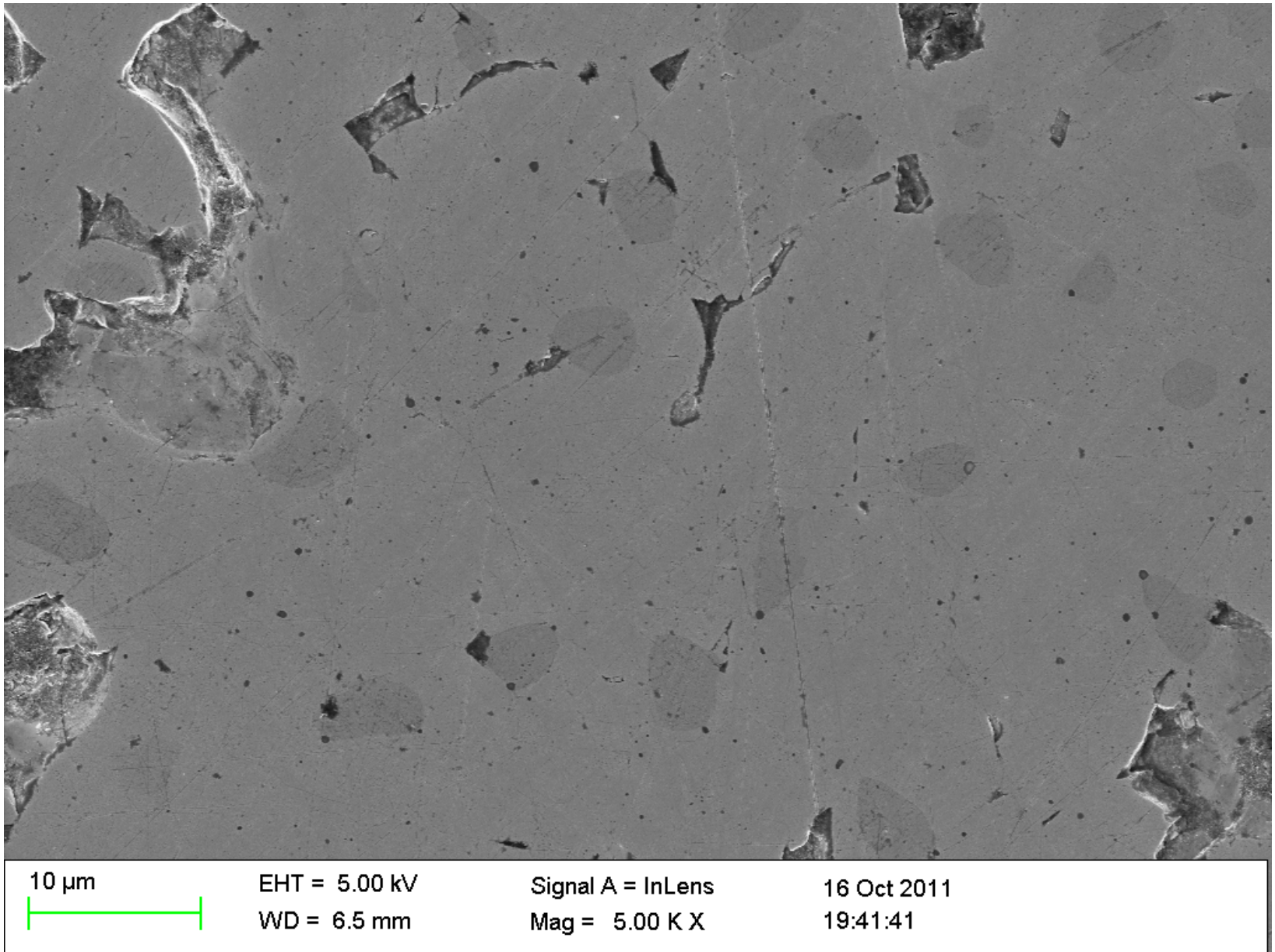

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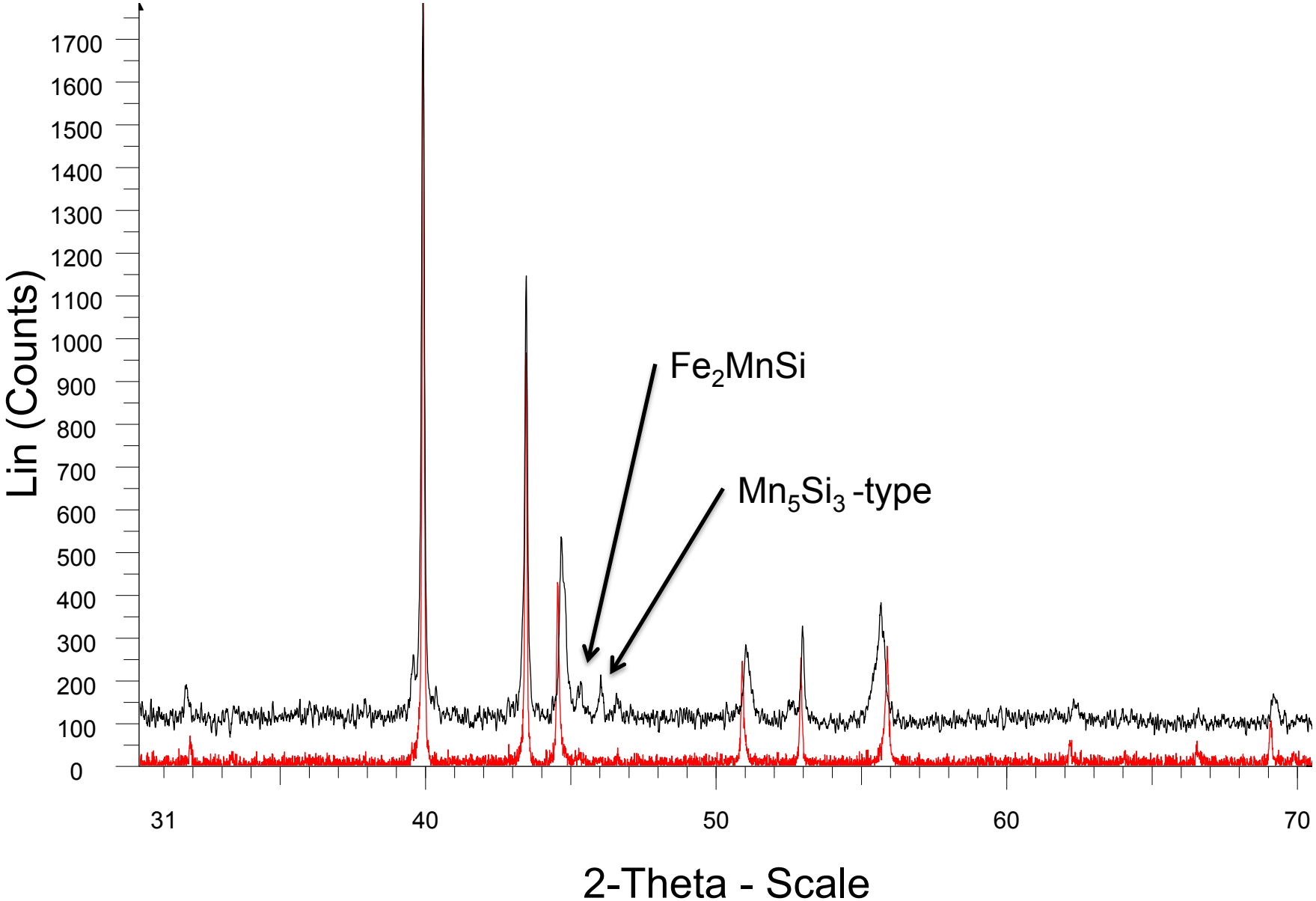
Look into the magnetocaloric properties

nom. $FeMnP_{0.5}Si_{0.5}$

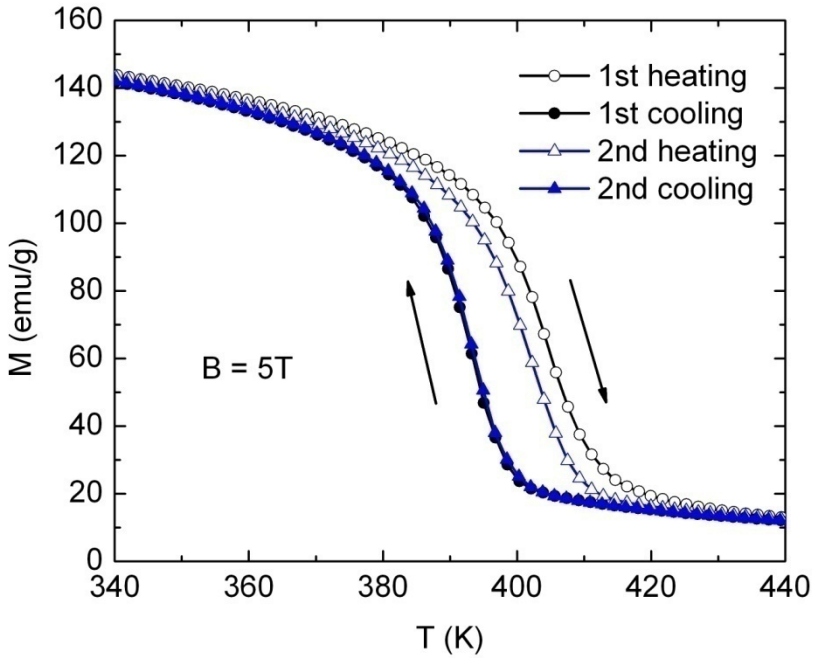


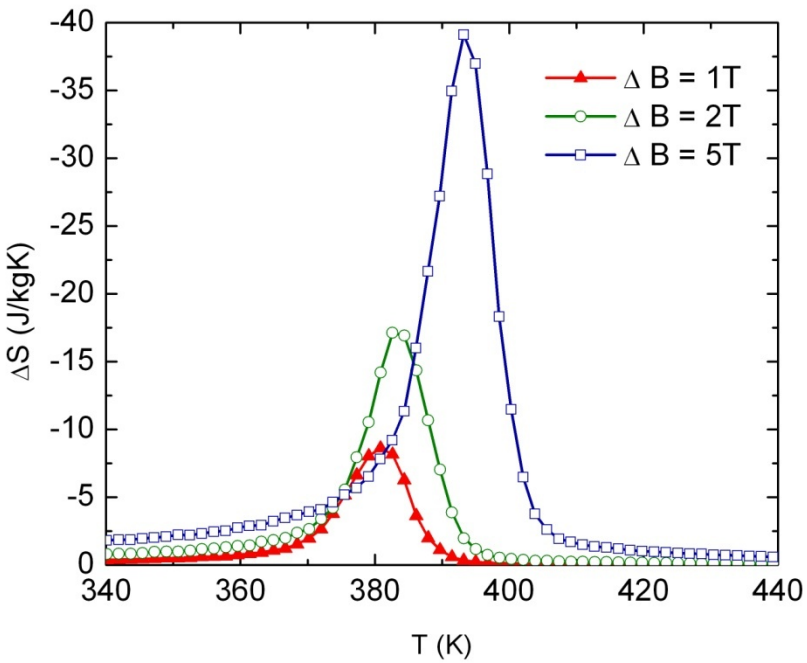
Magnetic measurements (SQUID)

- Indirect measurement of MCE
- Measure magnetisation *M(T,H)* → *Entropy change*

$$\Delta S_m \approx \frac{\mu_0}{\Delta T}\int_0^{H_f} M(T+\Delta T, H)\, dH - \int_0^{H_f} M(T,H)\, dH$$

$FeMnP_{0.5}Si_{0.5}$





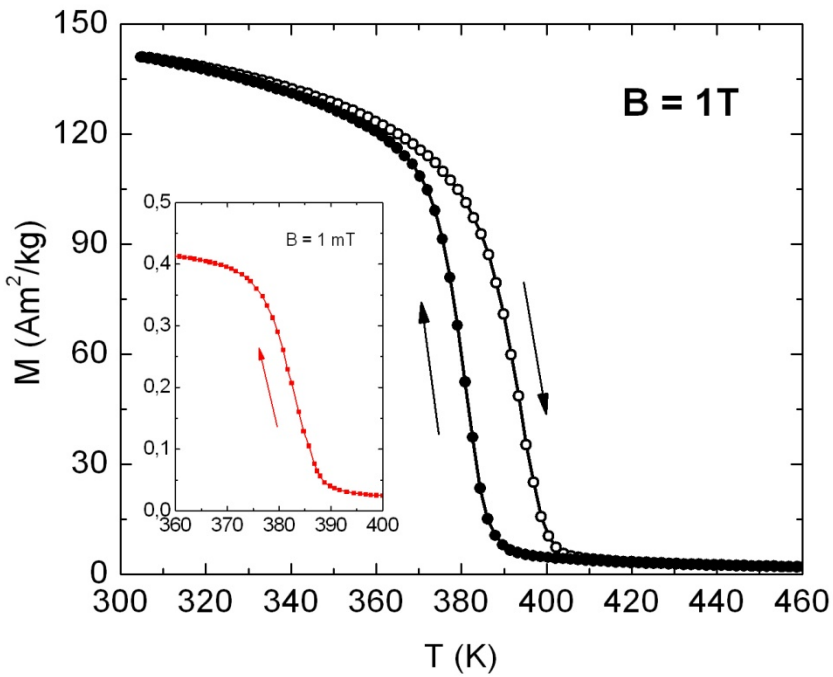
Tuning the magnetic phase transition

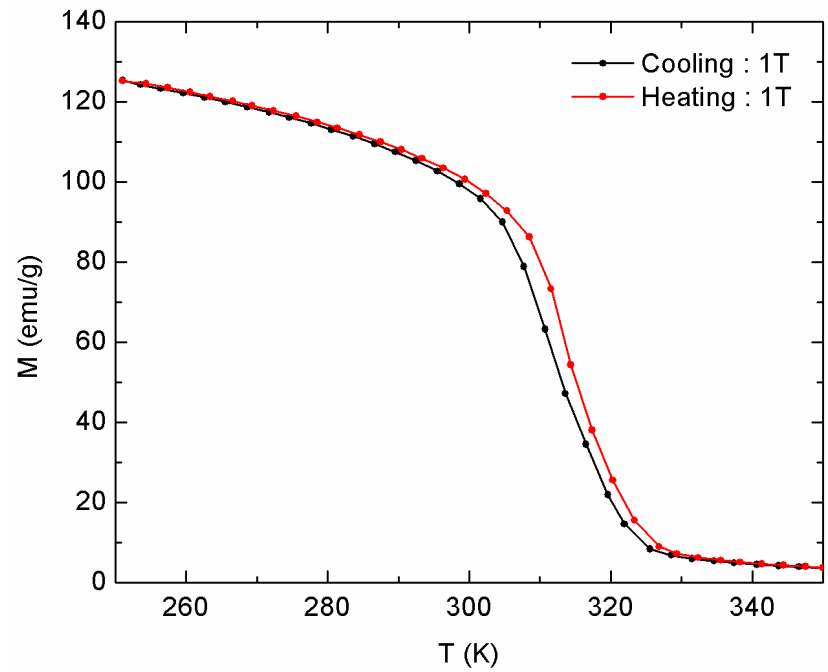
Tuning First-order magnetic phase transition to RT

$FeMnP_{0.5}Si_{0.5}$
T_c = 382 K
Thermal Hyst: 12 K

→

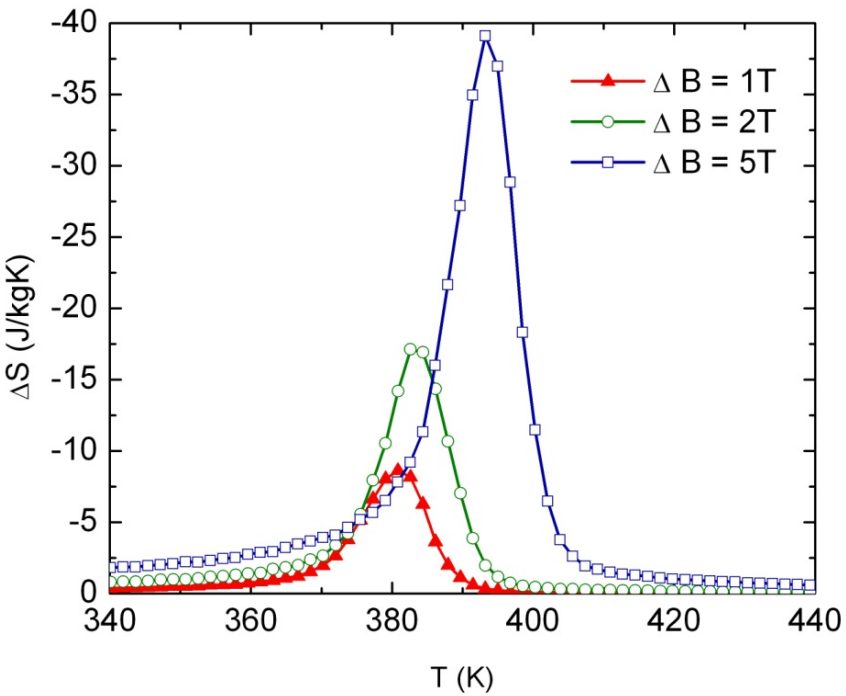
$Fe_{0.75}Mn_{1.25}P_{0.5}Si_{0.5}$
T_c = 311 K
Thermal Hyst: 3 K

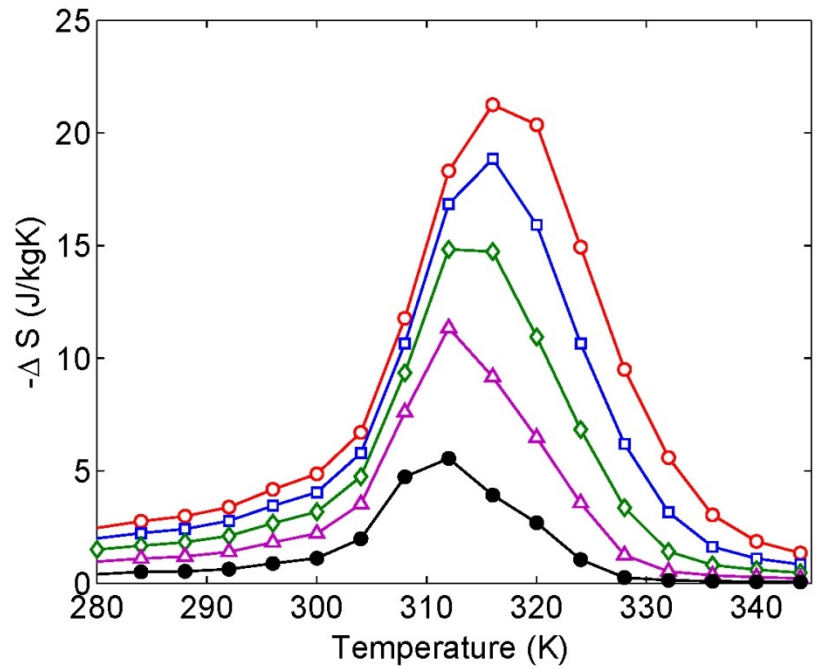




Magnetic entropy change

$FeMnP_{0.5}Si_{0.5}$ → $Fe_{0.75}Mn_{1.25}P_{0.5}Si_{0.5}$

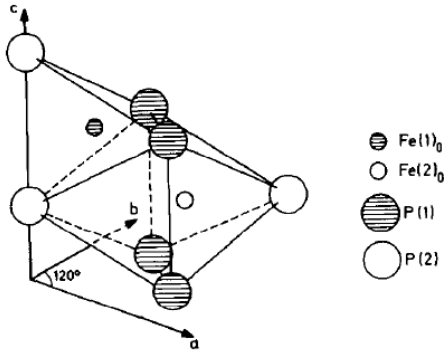


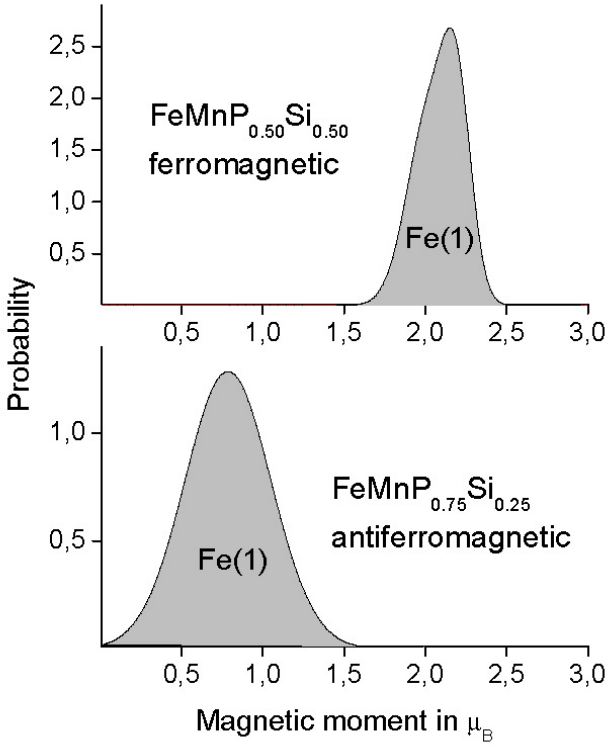


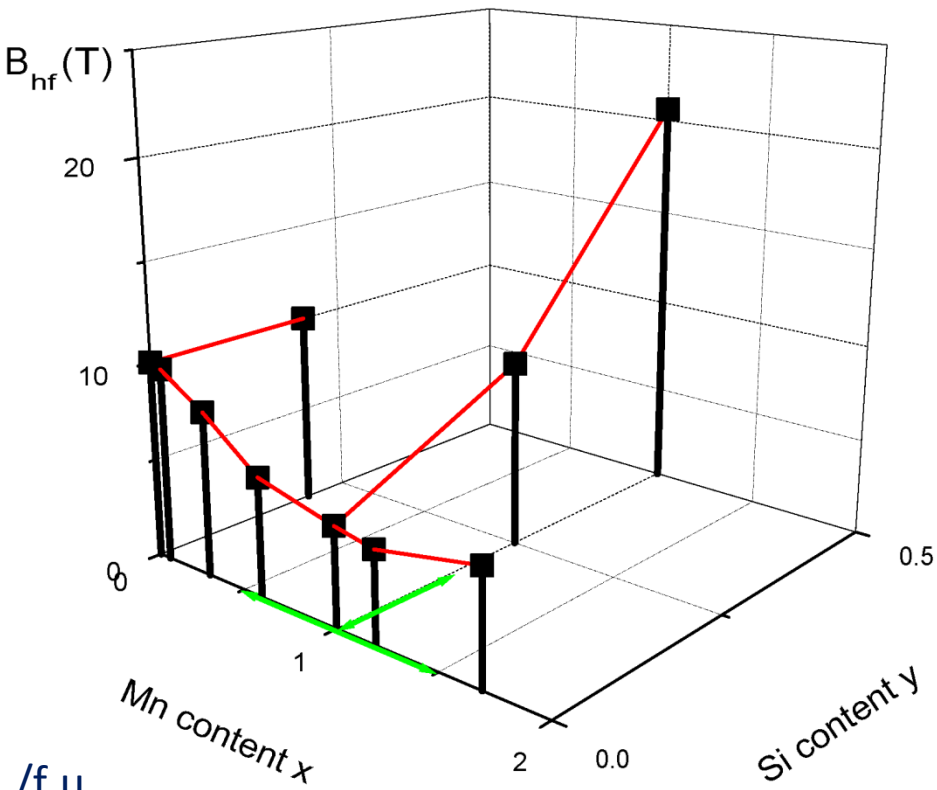
ΔS_{max} @ 5T:	39 J/kgK	21 J/kgK
FWHM @ 5T:	11 K	20 K
RC @ 5T (±25 K):	561 J/kg	500 J/kg

Mössbauer spectroscopy

- Pyramidal 3g site → Mn
- Tetrahedral 3f site → Fe

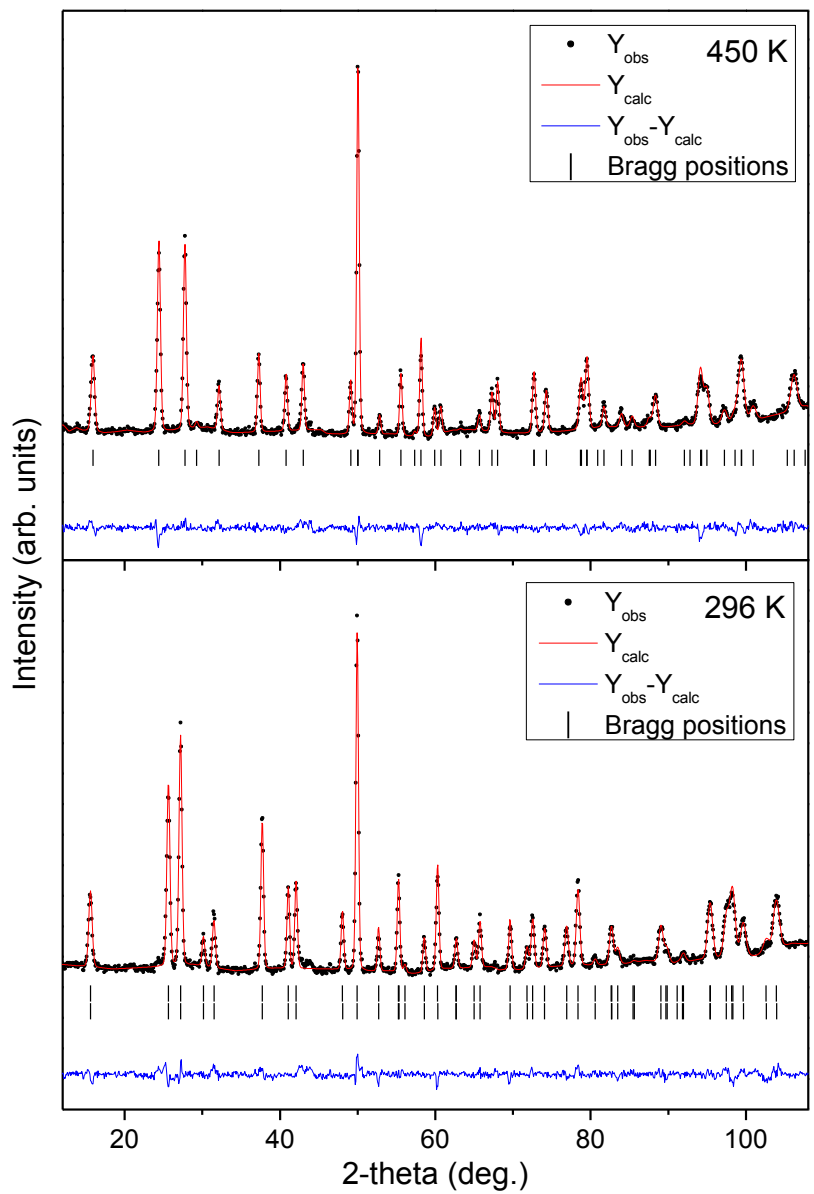


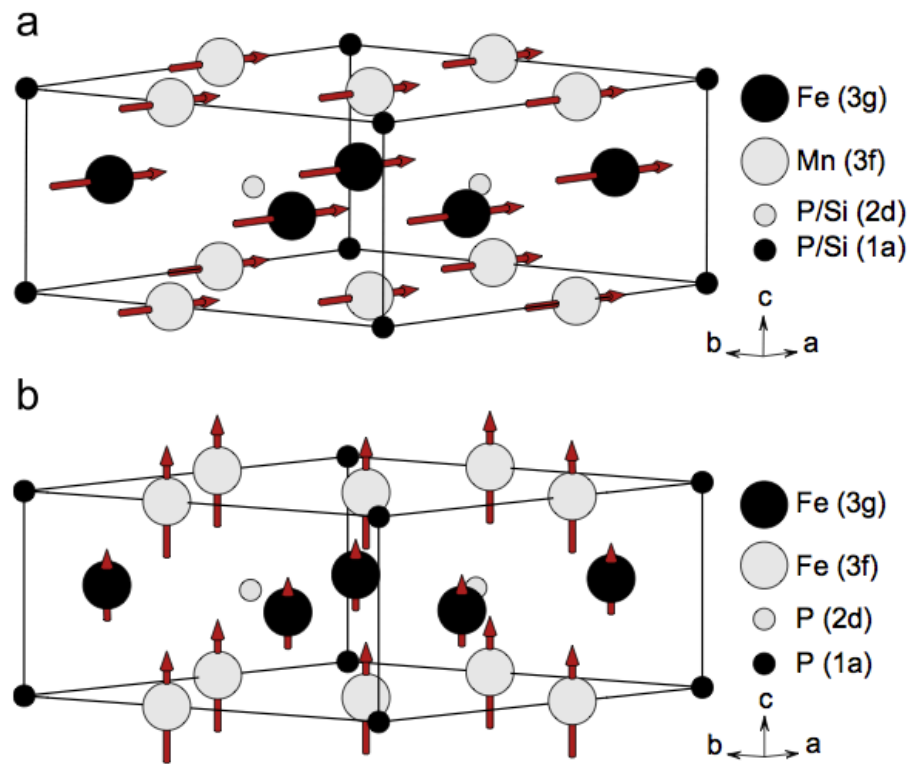




Saturation moment $FeMnP_{0.5}Si_{0.5}$ ≈ 4.4 μ_B/f.u.

Neutron measurements





Pyramidal site (gray) → Mn (2.5 μ_B)
Tetrahedral site (black) → Fe (1.9 μ_B)

→ Poster presentation Viktor Höglin

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Concluding remarks

- $(Fe,Mn)_2(P,Si)$ alloys exhibit good magnetocaloric properties which can be tuned by both Mn and Si substitution

- $FeMnP_{0.5}Si_{0.5}$ holds high saturation moment of 4.4 μ_B/f.u.

- Fe and Mn magnetic moments in $FeMnP_{0.5}Si_{0.5}$ have orientation in the *ab*-plane

- Interest in fundamental understanding of the material

Thank you for your attention!